THE INVESTIGATION ON THE DEGREE OF INHIBITION OF MAC AND DEA INHIBITORS DURING WAX DEPOSITION

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***Abstract*— Deposition of wax can cause a serious problem to the flow of the crude oil in the pipeline. Chemical methods will be applied in the crude oil industry to reduce wax deposition in transportation of crude oil through pipeline in subsea conditions. Maleic Anhydride Copolymer (MAC) and Diethanolamine (DEA) are used in this investigation to estimate the performance as an effective wax inhibitor at different temperature ranging from 5°C to 15°C and concentration ranging from 500 to 5000 ppm using cold finger apparatus equipped with an agitator. 10 mL of MAC and DEA were added into the cold finger apparatus and water bath temperature surrounding the vessel at 50 °C. The deposited wax will be scrapped and weighed. The rotation speed was fixed at 400 rpm. Based on the amount of wax deposit weight, MAC is chosen as the most effective inhibitor compared to DEA. The weight of the wax deposition are able to be reduced when using MAC.**

Keywords: Wax deposition, Wax inhibitor, cold finger, concentration of inhibitor, cold finger temperature

I. INTRODUCTION

Wax deposition in subsea pipelines is a complicated occurrence that has brought many hindrances in production, transportation and refining of crude oil in the industry of petroleum. This phenomena occurs due to the decrease in temperature and pressure during the oil production operations which caused the precipitation wax crystal to form from crude oil and deposited onto the walls of the pipeline. Wax deposit is the deposition of carbonaceous material which not dispersible or soluble by crude oil under standard state [29]. The normal conditions to maintain crude oil in its liquid state are when the pressure and temperature at the reservoir are within the range of 70-150°C and 55-103 MPa, respectively [14]. Any changes in temperature, pressure, fluid composition and flow parameters can cause wax to deposit. Furthermore, when the temperature of fluid drops below the wax appearance temperature (WAT) the long chain paraffin will agglomerates and eventually deposit in the pipelines in gel-like structure forms. Further cooling will cause the gel to harden and clog the pipelines [27].

Wax deposition can be removed or prevented chemically, mechanically or by thermal method. For this research, chemical method was chosen to reduce the rate of wax deposition. The efficiency of a particular paraffin inhibitor is different for different oil well because different oil well has variety composition of crude oil. This leads to a continuous effort, where researchers are looking for an efficient wax inhibitor for each oil well. Two different types of inhibitors were used in this study, which are maleic anhydride copolymer (MAC) and diethanolamine (DEA). MAC comprises of methyl and carbonyl group whilst DEA consists of hydroxyl groups. The methyl and carbonyl give strong van der Waals interaction between MAC and wax while for DEA, it has hydroxyl group that could not incorporate into the wax molecule. Hence, there will be more wax deposited in DEA compared to MAC. Hydroxyl group can act as a surfactant which is a good oil-in-water emulsifier that can avoid gelling problem in crude oil and act as an inhibitor. The consequence of the reaction makes the process of removing the wax deposit easier by shear forces flow streams.

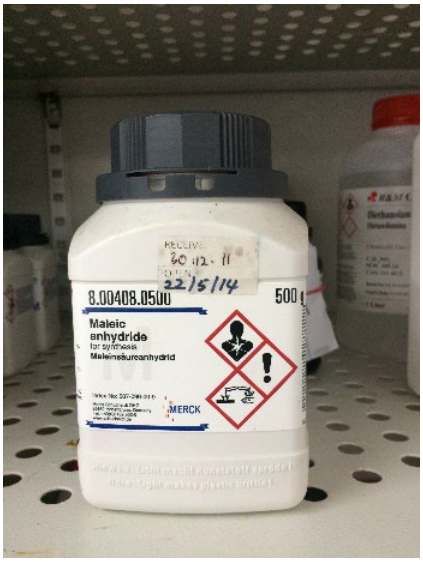
II. METHODOLOGY

A. Materials

For this research project, maleic anhydride copolymer (MAC) with melting range from 51 to 54°C and assay(GC) >99% and diethanolamine (DEA) with melt index range from 25 to 28°C, and assay(GC) >98% obtained from Merck Schuchardt and R&M Chemicals, respectively. Raw crude oil with purity of 98% was kindly supplied by PETRONAS Refinery from Kerteh, Terengganu, Malaysia. Table 1 shows the physical properties of Malaysian crude oil sample:

Table 1: Physical Properties of Malaysian crude oil sample

Sample Name	**Medium Light**
Viscosity At 40°C (mPa.s)	5.20
Density (abs)(g/cm^3)	0.851
SG Sample	0.851
°API	34.90
WAT (°C)	33.5
Pour Point (°C)	3.3
Wax Content At 20°C (Wt. %)	20.70



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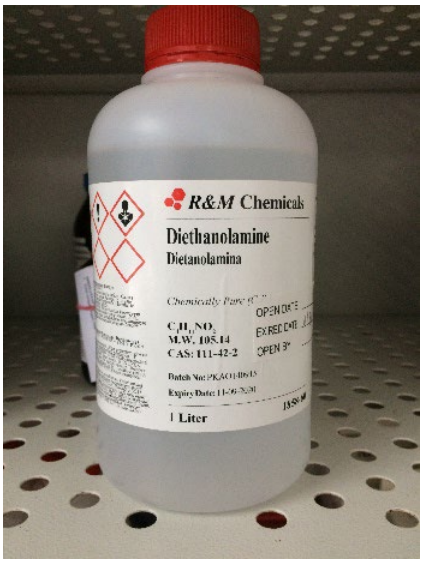

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Figure 1: Reagent bottle of (a) Maleic Anhydride Copolymer (b) Diethanolamine

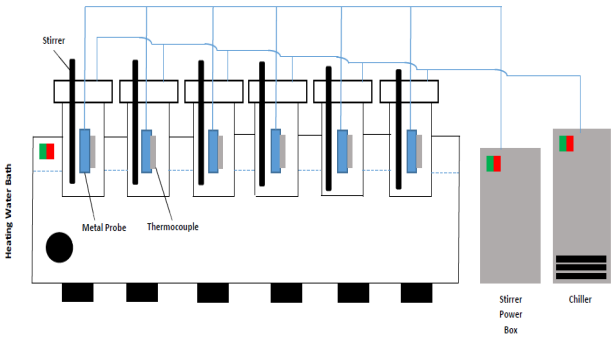
2.2. Cold Finger Experimental Set Up and Analysis

Fig. 2(a)-(b) shows a 6-panel cold finger apparatus used in this study. Firstly, 6 stainless steel panels of the cold finger apparatus were filled with 130 mL of crude oil sample. An impeller was installed in each panel in order to ensure even distribution between inhibitor and crude oil mediums and also to validate assumption that field flow would influenced heat transfer mechanism at the cold finger surfaces [23].

The cold finger and jar were placed inside a heating water bath to control the crude oil temperature. The heating bath temperature was initially fixed with a predefined temperature of 50 °C. The linking of the cold finger in the cooling bath circulation system was set up while the crude oil was heated up. Then, the valve of the cooling fluid was opened when it has reached the thermal equilibrium of the bath and jar. Crude oil with different type of inhibitors, concentration and temperature are tested in the cold finger experiment [23].

The concentration and temperature were adjusted according to the purpose of the research. The total amount inhibitor used for each experiment was approximately 10 mL with different concentration. The cold finger apparatus are run for 2 hours, 13 hours and 24 hours. Finally, visual observations were made for the physical characteristic of the deposits. The deposit are scrapped from the cold finger, and weighed.

(a)



(b)

Figure 2: (a) Set up of cold finger apparatus (b) Schematic Diagram of cold finger apparatus

III. RESULTS AND DISCUSSION

In this study, the performance of wax inhibitor was analyzed under 3 factors: inhibitor concentration, temperature effect, and the duration of deposition. Figure 3 shows the performance of blank crude oil, MAC and DEA inhibitors at 5°C and 2 hours.

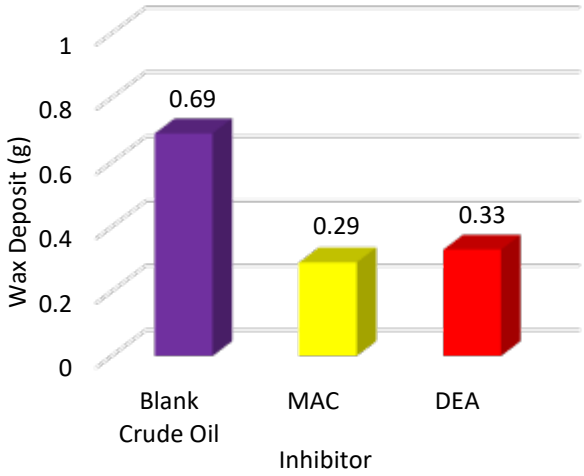
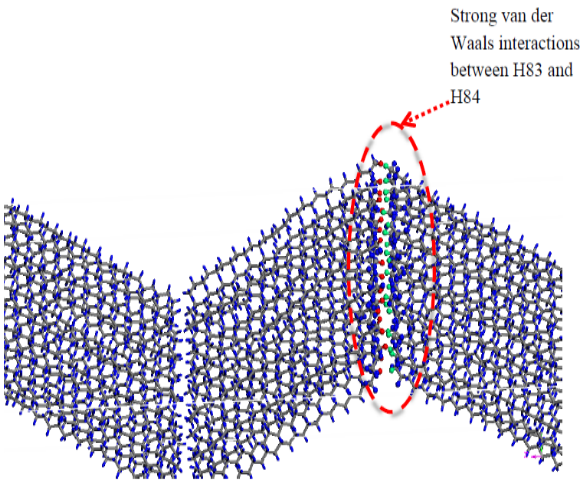


Figure 3: Comparison of amount of wax deposit for different types of inhibitors

According to Figure 3, the weight of wax deposited in the presence of 500 ppm MAC inhibitor is 0.29 g while the weight deposited is 0.33 g when 500 ppm DEA was added. When no inhibitor was added, the wax for blank crude oil sample deposited is 0.69 g. MAC showed the least wax which means that MAC weakens the solid deposit through strong van der Waals bonding between the molecules of MAC and the wax molecules. This can be proven with N-Octacosane molecule. N-Octacosane molecule is a non-polar compound in which H38 and H84 have been identified as the active hydrogen atoms in the wax formation. Based on Figure 4(a)-(b), there is strong van der Waals forces between the molecules of N-Octacosane but by adding MAC inhibitor it decrease the ability of the molecule to coalesce and prevents the solid wax deposition. The results obtained have proven that chemical inhibitor has the ability to control the amount of wax deposit by altering the crystal structure itself.



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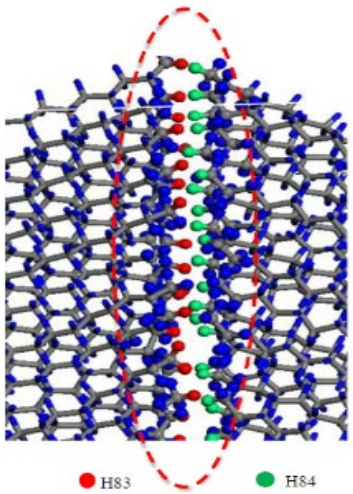
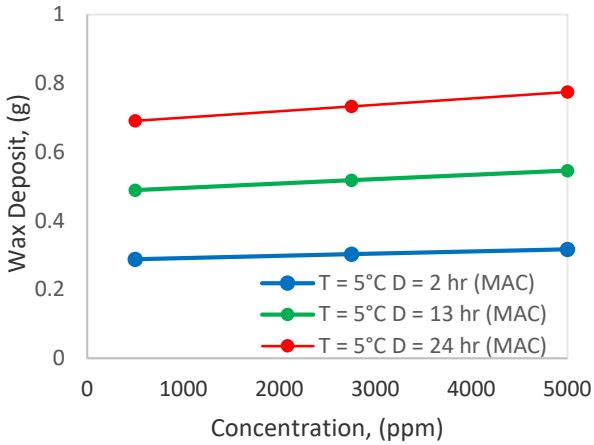


(b)

Figure 4: Crystal lattice of N-Octacosane (a) N-Octacosane crystal supercell and (b) enlarged image of H83 and H84 atoms, showing strong van der Waals interactions [23].

A. The effects of Inhibitors Concentration

Based on figure 5(a)-(b), the weight of the wax deposit increases linearly as the concentration increases but the weight of the wax deposit using MAC inhibitor is still less than the weight of wax deposit using DEA. This is because of the methyl and carbonyl functional groups contain in the MAC. Methyl and carbonyl functional group are the polar part of the co-polymer. They are different to wax crystals and prevent the growth of wax matrices because the polar part will control the wax compound homologs viscosity and solubility. Besides that, DEA could not give strong van der Waals interaction because this inhibitor contains a hydroxyl group (OH) that could not incorporate into the wax molecule



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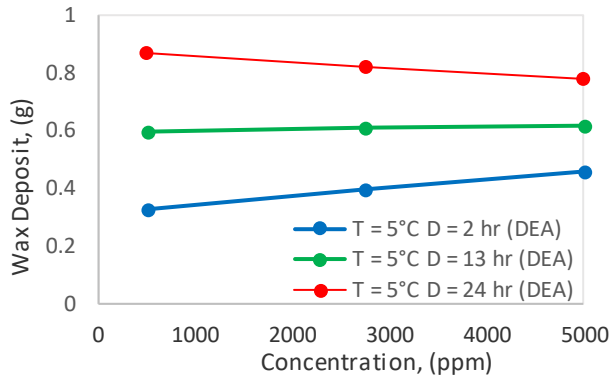

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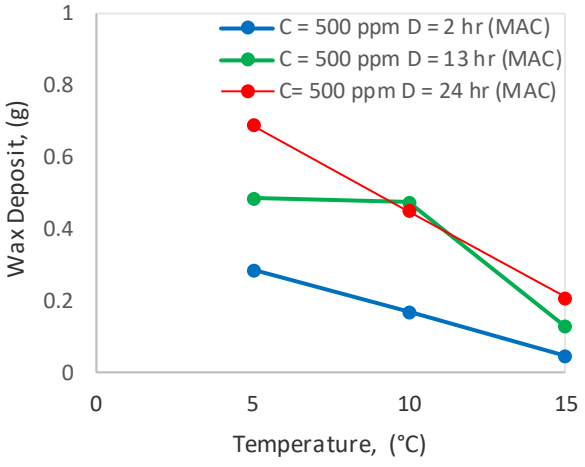
Figure 5: The effect of concentration (ppm): (a) MAC, (b) DEA on the amount of wax deposited, m (g)

B. The effects of Temperature on Wax Deposition

Temperature plays a vital role in the weight of the wax deposit from the cold finger. Wax will produced if the temperature of crude oil is below WAT. Surface which has the highest temperature difference will produce more deposit. In this study, temperature of 5°C is used to simulate the temperature deep sea water temperature. When the temperature is 5°C, the wax produced is thicker and darker while at 15 °C the wax produced is very light, thin and wet. Based on Figure 6(a), the weight of wax deposition at 5°C is the highest compared to 10°C and 15°C which is 0.29 g. The reason is because of crude oil sample solidify when the temperature differential between the bulk crude oil temperature and cold finger surface existed. When the temperature difference is increases, there will be an increase of thermodynamic driving force to execute the wax deposition [18]. The wax appearance temperature (WAT) of the crude oil which is 33.5°C and at 5°C, it has the highest temperature difference compared to 10°C and 15°C. The crude oil will tend to be thicker at 5°C and it will change phase from liquid to amorphous solid. If the temperature beyond 20°C there will be rapid movements of the wax molecules and it will reduced their tendency to interact compared to temperature below 20°C. Thus, the rate of wax formation is low at this temperature and crude oil can be transferred more easily.



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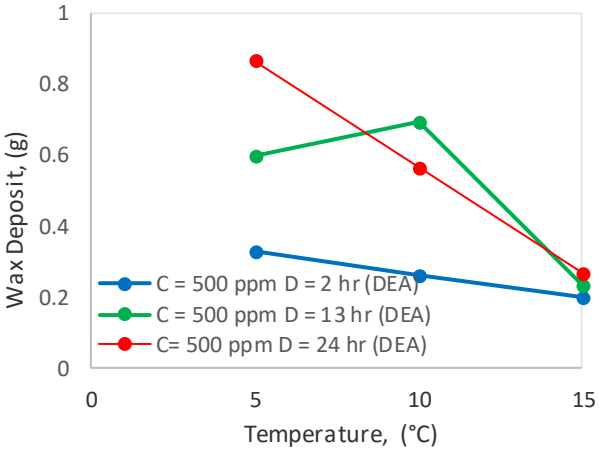

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Figure 6: The effect of temperature: (a) MAC, (b) DEA on the amount of wax deposited, m (g)

Based on Figure 7, the amount of wax deposited at increasing temperature is decreasing. Similar trend is shown by [30] where the amount of wax decreasing linearly when the temperature increases. When using MAC as inhibitor, the trend shows that it decreases linearly at the gradient of 0.024 g/°C while when using DEA, the trend shows that it decreases linearly at the gradient of 0.013 g/°C.

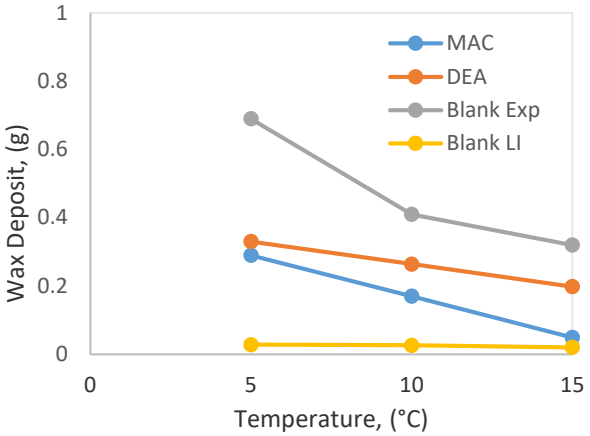


Fig. 7: Comparison of amount of wax deposited using different inhibitors

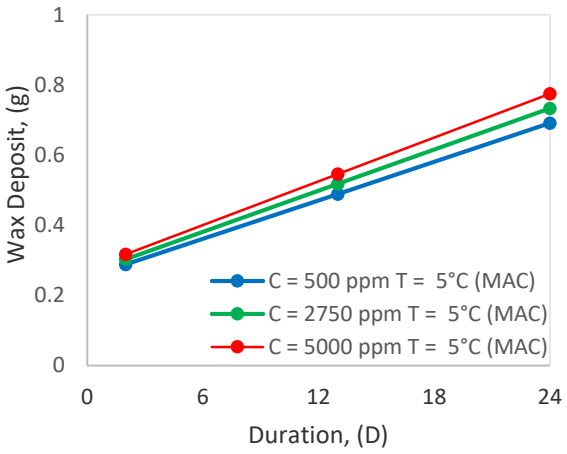
(a)

(b)

Figure 8: Changes of wax deposit surface and thickness with increasing temperature using MAC inhibitor at (a) 15°C (b) 5°C

C. The effects of Deposit Duration on Wax Deposition

Figure 9(a)-(b) shows that as the duration increases, the weight of the wax formed will increases. Weight of wax formed using MAC inhibitor is lesser than using DEA. When the time increases, the intermolecular forces of the inhibitor molecules become weaker and the molecules of the wax tend to repel the inhibitor molecules. This will cause the wax to formed more layer of wax on the surface of the cold finger instead of the inhibitor and increase the degree of crystallization of wax. When the waxes at different time are analysed Figure 10(a)-(b) using the optical microscope, the surface of wax deposited at 2 hours appeared to be wet and smooth while the surface of wax deposited at 24 hours appeared to be dry, rough and yellowish. At 2 hours, the inhibitor molecules has stronger intermolecular forces causes the molecules of the wax to be separated. Hence, the wax produced at 2 hours appears to be thinner than at 24 hours.



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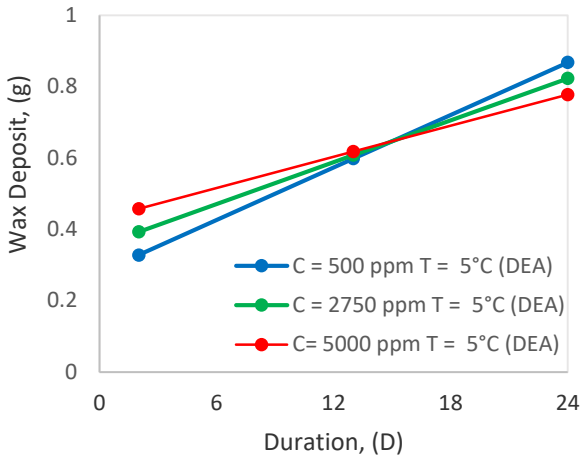

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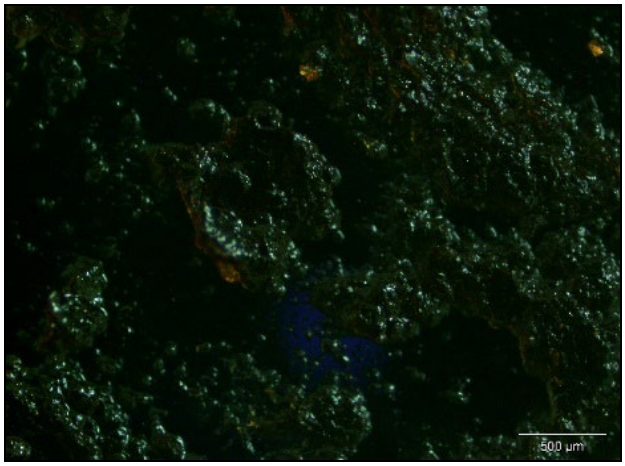
Figure 9: Comparison of weight of wax deposit at different duration: (a) MAC (b) DEA



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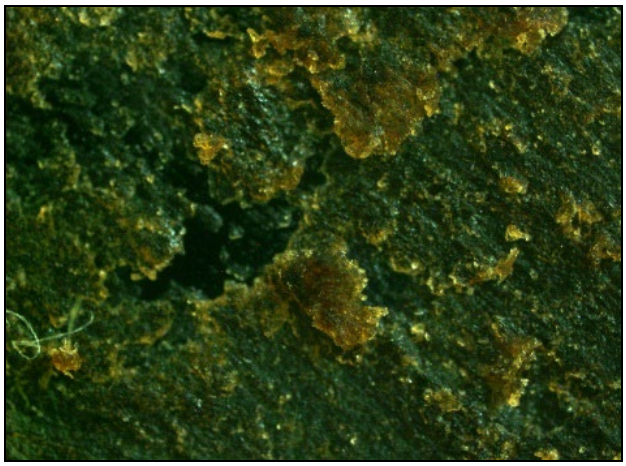

(b)

Figure 10: Comparison image of the surface of the wax deposited at different time using optical microscope: (a) 2 hr (b) 24 hr

IV. CONCLUSION

MAC inhibitor is selected as the most efficient inhibitor to reduce the deposition of wax based on the amount of wax deposit weight. This study discovered that as the concentration and temperature increases, the amount of wax deposit was found to be decreased in the presence of inhibitors.

ACKNOWLEDGMENT

I am deeply grateful that I have these individuals to help me in completing my research project. First and foremost, I would like to thank my supervisor, Dr Hazlina Husin for spending some time in giving guidance and advices although she is busy. Thank you for the support and patience in assisting me. I also want to take this opportunity to thank Master student, Azwan for providing me the knowledge, assistance and facilities. Then, I would like to thank my family and all of my friends for their moral support, help and ideas throughout the period. With all the support and love, I am able to complete my research successfully. Last but not least, I would like to thank Universiti Teknologi Mara for giving me the opportunities to conduct my research and providing the materials and apparatus that I need to use.

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