CHEMICAL ENGINEERING TRANSACTIONS
VOL. 97, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš
Copyright © 2022, AIDIC Servizi S.r.l.
ISBN 978-88-95608-96-9; **ISSN** 2283-9216
DOI: 10.3303/CET2297050

Molecular Characteristics of Fatty Acid Methyl Ester (FAME) in Waxy Crude Oil as a Flow Improver

Ameer Naqiuddin Baharudin[a], Abdul Rahim Risal[a,*], Rozana Zakaria[b], Mazlin Idress[c], Farah Rosmaniza Redzuan[a]

[a]School of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM), Malaysia
[b]School of Civil Engineering, Universiti Teknologi Malaysia (UTM), Malaysia
[c]Department of Petroleum Engineering, Universiti Teknologi PETRONAS, Malaysia
abdulrahimrisal@utm.my

Mitigation of wax deposition is of major interest, especially in the oil and gas industry, to minimize the flow assurance and production problems. In view of financial savings, the currently established method still has more opportunities to improve, particularly in a green technology sector in compliance with a stringent environmental policy. Therefore, a cost-efficient and environmentally friendly alternative method is required in handling waxy crude oil. This paper describes the investigation of Fatty Acid Methyl Ester (FAME) as a waxy crude oil flow improver via changes in wax particles' growth and aggregation rate through molecular dynamics simulation using Biovia Materials Studio. The molecular dynamics simulation shows an increase in the wax molecules' interaction energy from an average of 851 kcal/mol to 972 kcal/mol. Similarly, kinetic energy increases from an average of 629 kcal/mol to 675 kcal/mol. The mean square displacement also increases from 3.195 angstrom^2 to 6.007 angstrom^2. There is also an increase in the radial distribution function by having a higher probability of finding particles in the presence of FAME. The results indicate that FAME reduces the wax particles' growth and aggregation rate, mitigating the wax depositions and improving the waxy crude oil flow.

1. Introduction

The main problem when dealing with waxy crude oil is wax deposition. Wax deposition in production tubing strings or transmission pipelines reduces the oil production rate and decreases total oil production. The wax deposition is initiated when the crude oil temperature is lower than the pour point temperature, where the paraffin content starts to solidify and then gradually deposited inside the tubing and the pipes. Severe wax deposition induces high operating costs of wax removal (White et al., 2018). The problem needs to be solved immediately to prevent a continuous decline in the oil production rate. Many mechanisms lead to wax deposition, such as molecular and thermal diffusion (Aiyejina et al., 2011), Brown diffusion (Liu et al., 2020), shear dispersion (Yang et al., 2020), and shear stripping (Olajire, 2021). The deposited wax removal includes mechanical and chemical techniques (Yao et al., 2022).

One of the common approaches to removing wax deposition is using mechanical removal techniques such as flowline pingging, rod and wireline scrappers, and free-floating piston scrappers, but the execution cost of this method is too expensive and incur longer non-productive time (NPT) (Olajire, 2021). Furthermore, in oil and gas production, mechanical removal techniques have a high risk of damaging reservoir formation (Anisuzzaman et al., 2018). The implementation of flow improvers has been applied for many years, having its first application completed to decrease pressure loss during the commencement of fluid pumping into fracture-tight formations (Almond, 1989). The flow improvers have interacting elastic macromolecules and macrostructures during turbulent flow conditions (Fink, 2016). Many flow improvers are currently used, and each brings different functions and mechanisms (Sivakumar et al., 2018), such as copolymers as flow improvers are capable of retarding the wax crystal's interaction and halting the aggregation process. However, the efficiency of copolymers depends on their content and physical and chemical properties in the solution, such as the cetane number, aromatic content and type, polymer composition, and polymer density (Sadiku-Agboola et al., 2011).

Paper Received: 29 June 2022; Revised: 11 September 2022; Accepted: 12 September 2022
Please cite this article as: Baharudin A.N., Risal A.R., Zakaria R., Idress M., Redzuan F.R., 2022, Molecular Characteristics of Fatty Acid Methyl Ester (FAME) in Waxy Crude as Flow Improver, Chemical Engineering Transactions, 97, 295-300 DOI:10.3303/CET2297050

The bio-based pour-point depressants are also suitable improvers due to having both hydrophobic and hydrophilic natures, reducing the interfacial and surface tension when dealing with fluids with different polarities (El-Sheshtawy and Khidr, 2016). Lastly, nano-hybrid pour-point depressants can also be considered one of the flow improvers capable of reducing the solidifying point of crude oil and having long-term stability compared to other surfactants' pour-point depressants (He et al., 2016). Worthy to note that the application of pour point depressant is still limited to the type of crude oil and depressant as well as the concentration of depressants (Yao et al., 2022).

One of the potential elucidations is the utilization of Fatty Acid Methyl Ester (FAME), biodiesel derived from renewable sources as wax deposition inhibitors and flow improvers. FAME productions commonly used catalyzed transesterification of waste cooking, animal fats or tallows, soya oil, rapeseed oil, sunflower oil, and palm oil (Vyas et al., 2010). FAME is one of the types of fatty acid esters that have recently been considered an alternative energy source in the form of biodiesel. In this study, palm oil-based FAME is chosen because of its resource abundance, as Malaysia is one of the largest palm oil-producing countries. This study observes the changes in the waxy crude oil before and after FAME is added and validates the implementation of FAME as a wax retarder and flow improver using molecular dynamic simulations.

2. Methodology

The experiment methodology includes identifying the materials, sample preparation, molecular dynamic simulation, and comparing the results.

2.1 Identification of materials

The medium used for testing would be waxy Dulang Crude Oil due to its high wax content (22% w/w) and relatively high pour point of 34 °C (Hassan and Ismail, 1988). As for the FAME, the fatty acid component is extracted from palm oil. The catalyst for FAME production is sodium hydroxide.

2.2 Sample preparation

FAME was prepared using homogeneous alkali-catalyzed transesterification with sodium hydroxide as the catalyst. Later, FAME is mixed with the crude oil using a magnetic mixer. Before the molecular dynamics simulations, the crude oil components were analyzed using Gas Chromatography-Mass Spectrometry (GSMS) to identify the average carbon compound inside the paraffin. The average carbon compound was calculated using Eq (1) based on the weighted average method.

$$Average\ Carbon\ Compound\ = \frac{Sum\ of\ N(Abundance)}{Sum\ of\ Abundance} \quad (1)$$

2.3 Molecular dynamics simulation

The molecular dynamics were simulated using the Biovia Materials Studio. This software predicts and comprehends the materials' atomic and molecular structure connections and their properties and behavior based on comprehensive modeling and simulation environment after the average carbon compound was determined. Initially, the simulator built the molecules based on the 80:20 concentration ratio of Dulang Crude Oil and FAME paraffin content. Then, the molecules were quantified by converting the produced molecules into amorphous stages.

2.4 Making comparison

Lastly, the interaction energy sum of potential and kinetic energy, Mean Square Displacement (MSD), and Radial Distribution Function (RDF) were simulated using the build-in forcite tools in Biovia Materials Studio for the solvent-free paraffin was compared with the paraffin and FAME mixture.

3. Results and discussion

3.1 Gas chromatography results

The gas chromatography method identified the composition of each component of the sample. The gas chromatography results of waxy Dulang crude oil is as in Table 1. The average carbon compound was calculated using Eq(1) and then benchmarked to the reported relative retention time in the literature. Table 1 shows that the average carbon composition in the paraffin content of Dulang Crude Oil is C-22. The calculated average carbon composition was later applied in the molecular dynamics simulation to build the paraffin molecule model.

Table 1: Calculation of the average carbon composition in the paraffin content of Dulang Crude Oil

Retention Time (m)	Stoppage Time(m)	Relative RT (Calculated)	Relative RT (Literature Review)	N-Carbon	Abundance	Ratio	N (Abundance)
62.988	65	0.97	0.96	34	0.113	0.362	3.842
60.599	65	0.93	0.93	33	0.118	0.378	3.894
58.625	65	0.90	0.91	32	0.356	1.140	11.392
56.92	65	0.88	0.89	31	0.480	1.537	14.880
55.428	65	0.85	0.86	30	0.855	2.738	25.650
53.978	65	0.83	0.84	29	0.935	2.994	27.115
52.478	65	0.81	0.81	28	1.583	5.069	44.324
50.884	65	0.78	0.78	27	1.465	4.691	39.555
49.263	65	0.76	0.75	26	1.928	6.173	50.128
47.548	65	0.73	0.73	25	2.058	6.590	51.450
45.777	65	0.70	0.70	24	2.202	7.051	52.848
43.904	65	0.68	0.66	23	2.134	6.833	49.082
41.955	65	0.65	0.63	22	2.325	7.445	51.150
39.89	65	0.61	0.60	21	2.345	7.509	49.245
37.694	65	0.58	0.57	20	2.538	8.127	50.760
35.325	65	0.54	0.53	19	2.286	7.320	43.434
32.743	65	0.50	0.49	18	2.306	7.384	41.508
29.854	65	0.46	0.45	17	2.357	7.547	40.069
26.498	65	0.41	0.40	16	2.166	6.935	34.656
22.406	65	0.35	0.36	15	0.681	2.180	10.215
Sum of Abundance							31.231
Sum of N(Abundance)							695.197
Average Carbon Compound							22

3.2 Molecular structure design, geometrical optimization, and dynamic interaction energy

After the molecular structures of FAME and Paraffin C-22 were built as per Figures 1a and 1b, the molecules were quantified by making them into amorphous stages with frames. Figures 2a and 2b show the amorphous stages of Paraffin C-22 and a mixture of Paraffin C-22 and FAME, while interaction energy between molecules is shown in Table 2.

(a) (b)

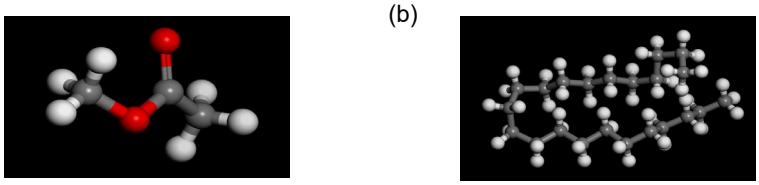

Figure 1: Molecular structure of a) Fatty Acid Methyl Ester (FAME) and b) Paraffin C-22

(a) (b)

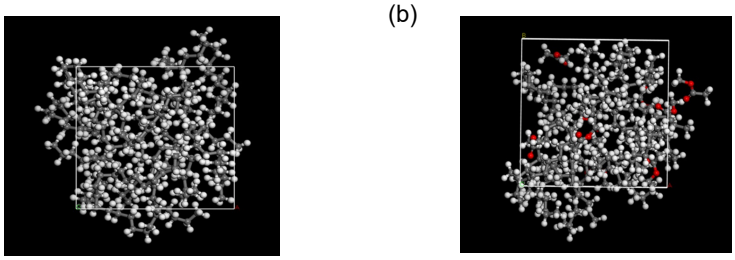

Figure 2: The amorphous stages of a) Paraffin C-22 only and b) Paraffin C-22 and FAME

Table 2: The calculated interaction energy for Paraffin C-22

	Paraffin C-22				Paraffin C-22 + FAME			
Frames	Total Energy (kcal/mol)	Non-bond Energy (kcal/mol)	Van Der Waals (kcal/mol)	Electrostatic (kcal/mol)	Total Energy (kcal/mol)	Non-bond Energy (kcal/mol)	Van Der Waals (kcal/mol)	Electrostatic (kcal/mol)
1	-815.7	-335.8	-212.4	-116.2	-844.9	-563.9	-91.4	-464.9
2	-868.3	-373.2	-222.1	-143.9	-946.2	-665.5	-128.4	-529.6
3	-866.7	-368.5	-230.8	-130.5	-1026.4	-681.4	-123.6	-550.1
4	-859.0	-360.0	-214.5	-138.3	-924.6	-635.1	-102.9	-524.6
5	-850.2	-345.3	-225.0	-113.2	-912.9	-643.9	-106.3	-530.1
6	-853.7	-363.6	-218.4	-138.1	-1,002.5	-668.3	-119.3	-541.4
7	-879.7	-386.0	-226.3	-152.6	-833.2	-556.6	-46.1	-502.9
8	-821.3	-344.1	-208.6	-128.5	-878.4	-651.9	-126.9	-517.5
9	-851.5	-378.9	-211.1	-160.6	-982.7	-673.3	-128.2	-537.5
Avg	-851.8	-361.7	-218.8	-135.8	-928.0	-637.8	-108.1	-522.1

The negative value indicates that the molecule is experiencing attractive forces mainly because of opposite charges (Kumar and Manik, 2016). The result also shows the increase in total attraction forces when FAME is added, indicating that FAME acts as a wax crystal modifier instead of a dispersant, and this proves that FAME reacts and modifies the growth of wax. Despite increasing the attraction energy, the total Van Der Waals interaction energy decreases due to the retarded growth of wax particles hence, higher effective surface area. Table 3 shows the analysis and calculation of total energy, enthalpy, temperature, and pressure for Paraffin C-22 before and after FAME is added.

Table 3: Total energy, enthalpy, temperature, and pressure of Paraffin C-22

	Paraffin C-22			Paraffin C-22 + FAME		
	Initial	Final	Average	Initial	Final	Average
Potential Energy (kcal/mol)	-151.543	-201.795	-204.064	-452.986	-443.122	-391.995
Kinetic Energy (kcal/mol)	576.494	627.022	629.585	606.695	730.581	675.210
Total Enthalpy (kcal/mol)	1,219.671	1,624.341	1,432.801	1,654.178	1,609.543	1,466.966
Temperature (K)	298.000	324.119	325.444	298.000	358.851	331.653
Pressure (GPA)	1.121	1.692	1.421	1.882	1.658	1.485

Based on Table 3, an increase in every calculated parameter proves that adding FAME increases the crude oil fluidity and decreases its viscosity, making it easier to flow. According to Lennard-Jones' theory, the negative potential energy suggests that the particles are experiencing the attractive force, and the potential energy decreases as the molecules are attracted closer. Typically, the displacement between two particles in a liquid is infinite. Anything less than infinity is considered to have negative potential energy. For example, the interactions between two distanced particles, no matter how weak, still correspond to negative potential energy. So, the total potential energy for the interaction of given particles is negative for liquid.

3.3 Mean square displacement and radial distribution function

Mean Square Displacement (MSD) is a method implemented to describe the random movement of particles in a specific amount of time according to Eq (2) (Masiren et al., 2016).

$$\mathrm{MSD} = |\mathrm{x}(\mathrm{t}) - \mathrm{x}(0)|^2 \quad (2)$$

where x(t)=current position,x(0)=initial position.

From the MSD results, the distance of the particles' motion and the conditions of the particles can be determined. Table 5 compares the mean square displacement of Paraffin C-22 and the mixture of Paraffin C-22 and FAME in angstrom2, while Figure 3 shows the MSD versus time.

Figure 3a and 3b show a linear trend of MSD with time, indicating a pure diffusion between particles. Table 4 shows that the distance increases in every direction when FAME is added, demonstrating that the particles inside the crude oil move faster for the mixture of paraffin and FAME, indicating that FAME lessens the Dulang crude oil viscosity and enhances the fluidity.

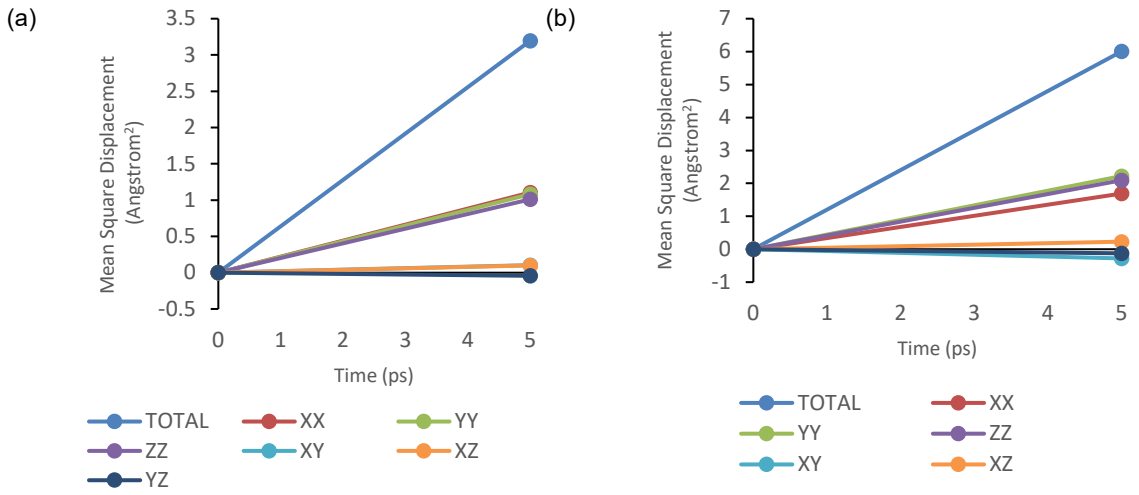

Figure 3: Mean Square Displacement a) without FAME b) with FAME

Table 4: Comparison of Mean Square Displacement (MSD) between only paraffin and the paraffin and FAME mixture

	XX	YY	ZZ	XY	XZ	YZ	Total
Paraffin C-22	1.104	1.081	1.010	0.104	0.100	-0.043*	3.195
Paraffin C-22 and FAME	1.691	2.221	2.094	-0.279*	0.229	-0.125*	6.007

Negative values indicate negative displacement

Radial Distribution Function (RDF), which measures the probability of finding any particle at a certain distance from a reference particle based on RDF = $4\pi r^2$ (p(r) – p (0)) where p(r) is particle concentration radius and p(0) is bulk particle concentration., further confirms the effect of FAME as an oil flow improver (Dimitroulis et al., 2015). Based on Figure 4a and 4b, as distances increase, the number of peaks increases, and the peak intensity decrease. It is shown that the peaks in the paraffin and FAME mixture have a higher probability of finding particles at shorter distances than the solvent-free paraffin, while at a longer radius, the presence of particles is lesser, proving that FAME acts as an effective wax crystal modifier. FAME increases the bonding between compressed particles and forms a lattice structure to restrict the growth of wax. If FAME acts as a dispersant, the peaks at the further distance should have a higher probability, but that does not show in this case.

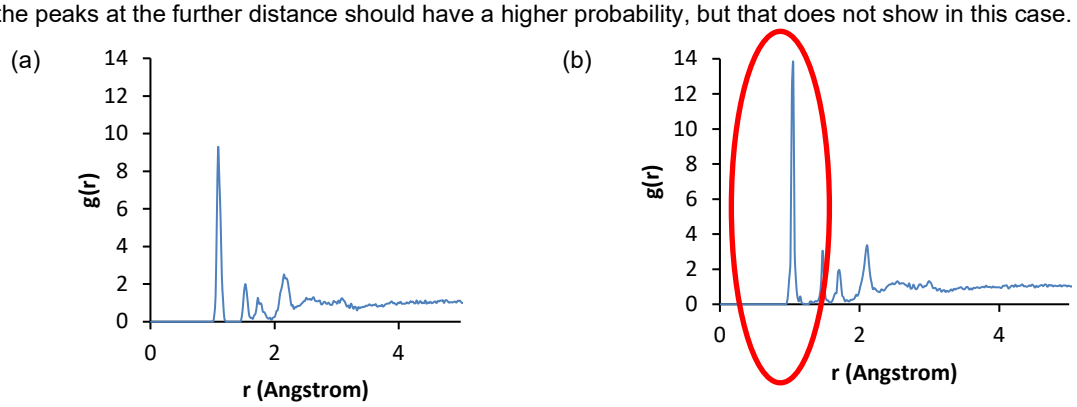

Figure 4: Radiation Distribution Function a) without FAME b) with FAME

4. Conclusion

This study has corroborated the implementation of FAME as a solvent to mitigate and prevent wax deposition. The results obtained from the tests and simulations confirm that FAME can act as a wax crystal modifier that reduces crude oil viscosity indicated by increased interaction and kinetic energy, which correspond to more crude oil mobility and less viscosity. The MSD increments and higher RDF in the presence of FAME prove that the crude oil particles move faster. In conclusion, FAME is an excellent wax crystal modifier and effective flow improver.

Acknowledgments

The authors hereby extend their appreciation to the Malaysia Ministry of Higher Education and Universiti Teknologi Malaysia (UTM) for financing this research under UTM Encouragement Grant (Ref: QJ130000.2651.18J65). Sincere appreciation to the authors and researcher from Universiti Teknologi Malaysia (UTM) and extended thanks to Universiti Teknologi PETRONAS (UTP), co-authors, and everyone who has been involved directly or indirectly for assisting and supporting this study.

References

Aiyejina A., Chakrabarti D.P., Pilgrim A., Sastry M., 2011, Wax formation in oil pipelines: A critical review International Journal of Multiphase Flow, 37(7), 671-694.

Almond N.E, 1989, Pipeline flow improvers. API Pipeline Conference, Dallas, TX, U.S.A, 307-311.

Anisuzzaman S., Fong Y. W., Madsah M., 2018, A review on various techniques and recent advances in polymeric additives to mitigate wax problems in crude oil, Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 48(1), 53-64.

Dimitroulis C., Raptis T., Raptis V., 2015, POLYANA—A tool for the calculation of molecular radial distribution functions based on Molecular Dynamics trajectories, Computer Physics Communications, 197, 220-226.

El-Sheshtawy H., Khidr T., 2016, Some biosurfactants used as pour point depressants for waxy Egyptian crude oil, Petroleum Science and Technology, 34(16), 1475-1482.

Fink J.K., 2016, Guide to the practical use of chemicals in refineries and pipelines: Gulf Professional Publishing, Montanuniversitaet Leoben, Austria.

Hassan M.N., Ismail M.Y., 1988, Environmental impact Assessment of the Dulang Oilfield Development Project. 7th Offshore South East Asia Conference, 784-796.

He C., Ding Y., Chen J., Wang F., Gao C., Zhang S., Yang M., 2016, Influence of the nano-hybrid pour point depressant on flow properties of waxy crude oil, Fuel, 167, 40-48.

Kumar, N., Manik G., 2016, Molecular dynamics simulations of polyvinyl acetate-perfluorooctane based anti-stain coatings, Polymer, 100, 194-205.

Liu Z., Li Y., Wang W., Song G., Lu Z., Ning Y., 2020, Wax and Wax–Hydrate Deposition Characteristics in Single-, Two-, and Three-Phase Pipelines: A Review, Energy & Fuels, 34(11), 13350-13368.

Masiren E., Harun N., Ibrahim W., Adam F., 2016, Effect of temperature on diffusivity of monoethanolamine (MEA) on absorption process for CO_2 capture, International Journal of Engineering, Science and Technology, 5(1), 43-51.

Olajire A.A., 2021, Review of wax deposition in subsea oil pipeline systems and mitigation technologies in the petroleum industry, Chemical Engineering Journal Advances, 6, 100104.

Sadiku-Agboola O., Sadiku R.E., Adegbola A.T., Biotidara O., F. 2011, Rheological properties of polymers: structure and morphology of molten polymer blends, Materials Sciences and Applications, 2, 30-41.

Sivakumar P., Sircar A., Deka B., Anumegalai A.S., Moorthi P.S., Yasvanthrajan N., 2018, Flow improvers for assured flow of crude oil in midstream pipeline-A review, Journal of Petroleum Science and Engineering, 164, 24-30.

Vyas A.P., Verma J.L., Subrahmanyam N., 2010, A review on FAME production processes, Fuel, 89(1), 1-9.

White M., Pierce K., Acharya T., 2018, A review of wax-formation/mitigation technologies in the petroleum industry. SPE Production & Operations, 33(03), 476-485.

Yang J., Lu Y., Daraboina N., Sarica C., 2020, Wax deposition mechanisms: Is the current description sufficient?, Fuel, 275, 117937.

Yao Z., Zhang Y., Zheng Y., Xing C., Hu Y., 2022, Enhance flows of waxy crude oil in offshore petroleum pipeline: A review, Journal of Petroleum Science and Engineering, Part C(208),109530