

NANOPARTICLE ASSISTED GEMINI  
SURFACTANT AS WAX DEPOSITION  
SUPPRESSANT IN MALAYSIAN CRUDE OIL  
USING EXPERIMENTAL AND MOLECULAR  
DYNAMICS SIMULATION

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Thesis submitted in fulfillment of the requirements  
for the award of the degree of  
Master of Science

Faculty of Chemical & Process Engineering Technology  
UNIVERSITI MALAYSIA PAHANG

APRIL 2022

## ACKNOWLEDGEMENTS

I would like to express my gratitude to almighty God who was always there to assured me and empowered me. I'd like to show my thankfulness to my dear God for guiding me when I was lost. Second, I'd want to thank my supervisor, Dr. Norida Ridzuan, for always being there to help me when I needed it and my co-supervisor, Mr. Junaidi Zakaria, for his vast expertise that helped make this research possible.

I'd like to express my gratitude to all my friends who were there for me when I was happy, when I was sad, and when I was lost in finishing my studies. Their friendships have added color, purpose, and fruitfulness to my journey.

Finally, I'd want to thank my parents and siblings for their moral and spiritual support as well as constant encouragement during my studies. Thank you to my entire family for always supporting of my desire to obtain my master's degree. Thank you from the bottom of my heart for all your sacrifices, support and all of your assurance.

## ABSTRAK

Pengendapan lilin boleh menyebabkan operasi menjadi perlahan atau terhenti dengan menghadkan aliran minyak mentah disebabkan lilin yang tersumbat dan mencetuskan ketidakaturan tekanan. Perencat kimia berinteraksi dengan molekul lilin dalam minyak mentah dan mencegah molekul lilin yang besar daripada melekat bersama. Penggunaan Gemini surfactant dan nanopartikel untuk mengelakkan pemendapan lilin masih tidak menyeluruh. Dalam tesis ini, kecekapan Gemini surfactant 2,5,8,11 Tetramethyl 6 dodecyn-5,8 Diol Ethoxylate (GS), tiga nanopartikel yang berbeza: silikon dioksida (NP1), timah oksida (NP2) dan nikel (III) oksida (NP3) dan campuran antara keduanya dinilai pada keadaan operasi yang berbeza bagi mengkaji pengaruh terhadap kelikatan minyak mentah menggunakan DV-III Brookfield viskometer dan perencatan lilin menggunakan analisis jari sejuk. Sebagai tambahan, simulasi model dinamik (MD) digunakan untuk menganalisa interaksi intermolekular diantara molekul lilin (n-icosane) dengan perencat menggunakan Accelrys Material Studio 8. Interaksi molekul lilin dengan perencat dianalisis menggunakan nilai fungsi taburan jejarian (*rdf*). Penggunaan GS dan nanopartikel secara berasingan dapat mengurangkan kelikatan minyak mentah dan pengendapan lilin dengan ketara. Walau bagaimanapun, prestasi yang lebih baik dapat dilihat dengan menggabungkan GS dan nanopartikel berbanding dengan penggunaan secara penggunaan tunggal untuk kelikatan dan analisis jari sejuk. Secara keseluruhannya, kelikatan minyak mentah berkurang sebanyak 85-92% pada suhu 10°C dengan penambahan GS dan nanopartikel. Pengurangan kelikatan tertinggi yang diperolehi adalah sebanyak 92.8% menggunakan campuran GS dan NP1. Penambahan nanopartikel kepada GS meningkatkan kecekapan perencatan dengan meningkatkan kadar penyebaran. Namun begitu, penggunaan GS dan nanopartikel secara tunggal mencapai kecekapan perencatan paraffin (PIE) sebanyak 45-48%. PIE tertinggi iaitu 61.63% telah dicapai bagi campuran GS/NP3 manakala yang terendah adalah 45.3% dengan menggunakan NP1 secara tunggal. Bagi keputusan MD, campuran GS/NP3 menunjukkan interaksi intermolekular yang paling lemah bersama n-icosane dengan nilai *rdf* tertinggi iaitu 5.25Å. Campuran GS/NP3 mempunyai interaksi van der Waals (vdW) yang kuat bersama atom hidrogen didalam n-icosane berbanding dengan sistem penggunaan tunggal GS dan NP3 yang berasingan. Ini disebabkan oleh kehadiran kumpulan O karbonyl didalam GS dan NP3, yang mana ia memperkukuhkan bilangan ikatan hidrogen yang lebih banyak. Oleh itu, perencatan lilin dalam n-icosane adalah lebih tinggi dalam campuran GS/NP3 berbanding dengan sistem penggunaan tunggal GS dan NP3. Ujikaji melalui analisis jari sejuk mengesahkan keputusan simulasi yang membuktikan bahawa gabungan GS/NP3 dapat mengurangkan pembentukan lilin dengan ketara sebanyak 61.6%. Sebagai perbandingan, penggunaan GS dan NP3 secara tunggal dapat mengurangkan pembentukan lilin masing-masing sebanyak 46.5% dan 47.7%. Secara keseluruhan, gabungan GS dan NP3 menunjukkan kecekapan tertinggi dalam perencatan lilin melalui analisis jari sejuk dan kebolehlarutan lilin tertinggi melalui analisis *rdf*. Oleh itu, campuran GS/NP3 adalah perencat terbaik berbanding dengan kombinasi perencat yang lain bagi menghalang perencatan lilin dalam minyak mentah Malaysia.

## ABSTRACT

Wax deposition can cause a slowdown or halt in operation by restricting crude oil flow in the pipeline due to the wax blockage and triggering pressure irregularities. Chemical inhibitors interact with the wax molecule in crude oil and prevent large wax molecules from attach. The use of Gemini surfactant and nanoparticles to prevent wax deposition is still in its infancy. In this thesis, the efficiency of Gemini surfactant 2,5,8,11 Tetramethyl 6 dodecyn-5,8 Diol Ethoxylate (GS), three different nanoparticles: silicon dioxide (NP1), tin oxide (NP2) and nickel (III) oxide (NP3) and their blends at different operating conditions are assessed to study their influence on the crude oil viscosity using Brookfield DV-III viscometer and wax inhibition using cold finger analysis. In addition, molecular dynamics modeling (MD) is used to analyze the intermolecular interaction between a wax molecule (n-icosane) with inhibitors using Accelrys Material Studio 8. The interaction of wax molecules with inhibitors were analysed through radial distribution function (rdf) value. The separate use of GS and nanoparticles significantly reduced crude oil viscosity and wax deposition. However, combining the GS and nanoparticles showed better performance than their corresponding individual use in viscosity and cold finger analysis. Overall, the viscosity of crude oil was reduced by about 85-92% at 10°C with the addition of GS and nanoparticles. The highest viscosity reduction obtained was 92.8% using the blend of GS and NP1. The addition of nanoparticles to GS improved their inhibition efficiency by providing dispersion. Nevertheless, the use of GS and nanoparticles individually achieved a paraffin inhibition efficiency (PIE) of 45-48%. The highest PIE of 61.6% was achieved by GS/NP3 blend while the lowest was 45.3% with NP1 individual used. For the MD results, GS/NP3 blend shows the weakest wax-wax intermolecular interaction with n-icosane, indicating higher wax solubility with the highest radial distribution function (rdf) value of 5.25 Å. Also, the GS/NP3 blend has the stronger van der Waals (vdW) interaction with a hydrogen atom in n-icosane compared to the individual systems of GS and NP3 separately. This can be due to the presence of the O carbonyl group in both GS and NP3, which can establish a higher number of bonds. Therefore, wax inhibition in n-icosane is higher in GS/NP3 blend compared to the individual system of GS and NP3. An experimental study through cold finger analysis validated simulation result which proved that the GS/NP3 blend significantly reduced the wax formation by 61.6%. In comparison, the individuals of GS and NP3 reduced wax formation by 46.5% and 47.7% respectively. Overall, the combination of GS and NP3 has shown highest efficiency in wax inhibition through cold finger analysis and highest wax solubility in rdf analysis. Thus, GS/NP3 blend is the best inhibitor among tested inhibitor combinations in inhibiting wax in Malaysian crude oil.

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