PERFORMANCE EVALUATION OF WAX INHIBITOR WITH SODIUM CLOISITE THROUGH EXPERIMENTAL AND MOLECULAR DYNAMICS SIMULATION (MD)

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MASTER OF SCIENCE

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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Thesis submitted in fulfillment of the requirements
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Master of Science

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Dedicated to my beloved parents:
Subramanie A/L Ramasamy and Letchimy A/P Ramiah.
My siblings and my best friends
Those who has influenced my life on the right path,
Thank you from the bottom of my heart.

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ABSTRAK

Pengendapan lilin adalah pembentukan dan pertumbuhan lapisan fasa pepejal yang berlaku semasa pengeluaran minyak mentah. Lilin ini dikenali sebagai parafin dan terbentuk di saluran paip dan peralatan pengeluaran. Kehadiran lilin parafin dalam minyak mentah menyebabkan banyak masalah dan komplikasi dalam industri minyak dan gas. Di Malaysia, pengendapan lilin parafin di dalam dan di permukaan peralatan pengeluaran dan pengangkutan saluran paip dikenal pasti sebagai cabaran utama semasa pengeluaran minyak mentah. Sekiranya lilin parafin tidak dikeluarkan dari masa ke semasa, ia boleh menyebabkan saluran paip tersumbat dan akhirnya aliran minyak mentah akan terhenti. Objektif kajian ini adalah untuk menilai prestasi perencat lilin melalui ekperimen jari sejuk dan untuk menjelaskan interaksi molekul lilin dengan molekul perencat lilin melalui simulasi dinamik molekul (MD). Empat faktor telah dipertimbangkan iaitu tempoh masa ekperimen, kesan suhu jari sejuk, putaran pendesak dan kepekatan nanopartikel bagi mengesahkan keberkesanan perencat lilin campuran antara poli(etilena-bersama-vinil asetat) (EVA) dan nanopartikel (NP). Mendakan lilin di jari sejuk dikikis dan ditimbang bagi mengira peratus kecekapan perencatan (PIE). Tingkah laku molekul perencat lilin bersama dan tanpa penggabungan nanopartikel dan molekul lilin telah disimulasikan untuk mengkaji interaksi intermolekul melalui nilai fungsi taburan jejarian (rdf) yang memacu pembentukan dan pencacatan bentuk lilin menggunakan simulasi MD. Campuran antara EVA dan NP menunjukkan prestasi yang terbaik bagi mengurangkan kadar pengendapan lilin berdasarkan nilai PIE dan nilai kelikatan. Campuran antara EVA dan NP ini telah berjaya mengurangkan pengendapan lilin dan kelikatan masing-masing sebanyak 80.91% dan 94%. Jumlah lilin yang paling minimum telah diperoleh pada suhu 25 ° C, ini membuktikan bahawa suhu jari sejuk memainkan peranan paling penting dalam mengubah kadar pengendapan lilin. Molekul n-icosane di dalam minyak mentah terikat bersama bagi membentuk pepejal hablur lilin dengan interaksi van der Waals (vdW) antara hidrogen 59, H59 dan hidrogen 60, H60. Nilai rdf beralih dari 2.75 Å ke 3.25 Å apabila campuran EVA dan NP digunakan sebagai perencat kerana ia menawarkan lebih banyak ikatan berfungsi bagi molekul lilin untuk berinteraksi berbanding dengan EVA secara sendirian, dengan itu interaksi antara lilin-lilin menjadi berkurangan. EVA memperlihatkan interaksi vdW yang kuat melalui atom oksigen di dalam vinil asetat (VA) dan ikatan ini diperkuatkan lagi dengan penambahan nanopartikel dengan kehadiran tiga ikatan berfungsi oksigen di dalam natrium cloisit (Na +) yang boleh membentuk ikatan hidrogen dengan molekul lilin. Kajian ini memperlihatkan penggabungan nanopartikel dengan perencat lilin sebagai kaedah yang berkesan bagi mengurangkan isu pengendapan lilin dalam industri minyak dan gas.

ABSTRACT

Wax deposition is the formation and growth of solid phase layer that occurs during crude oil production. These wax precipitates regularly known as paraffin and builds up in pipelines and other production equipment. The presence of paraffin wax in crude oil cause many problems and complications in oil and gas industry. In Malaysia, depositions of paraffin wax in the inner and on the surface of production equipment and transportation pipelines have been identified as the utmost challenge during crude oil production. If the paraffin wax is not being removed time to time it can wholly cause a block in the pipeline and eventually stops the flow of the crude oil. The objective of this study is to evaluate the performances of wax inhibitors through cold finger experiment and to elucidate the interaction of wax molecules with wax inhibitor molecules through molecular dynamic (MD) simulation. Four parameters have been considered as follows, effect of cold finger temperature, experimental duration, impeller rotation and amount of nanoparticle loading to confirm the effectiveness of the poly (ethylene-co-vinyl acetate) (EVA) and nanoparticle (NP) blend wax inhibitor. Wax deposited in cold finger was scraped and weighed to calculate the percentage inhibition efficiency (PIE). The behaviour of wax inhibitor molecule with and without incorporation of nanoparticles and wax molecules was simulated in order to investigate the intermolecular interaction through radial distribution analysis (rdf) which drives the formation and deformation of wax using MD simulation. EVA and NP blend shows the best performance to reduce the wax deposition rate based on percentage of inhibition efficiency, PIE and viscosity value. EVA and NP blend successfully reduced wax deposition and viscosity about 80.91 % and 94 % respectively. The minimum amount of wax obtained was at 25 °C proving that cold finger temperature plays important role in altering the wax deposition rate. The n-icosane molecules in crude oil are bonded together to form wax crystals with van der Waals (vdW) interaction between hydrogen 59, H59 and hydrogen 60, H60. The rdf value is shifted from 2.75 Å to 3.25 Å when EVA and NP blend is used as the inhibitor as it offers more functional bonds for wax molecules to interact compared to EVA alone thus reducing the wax-wax interaction. EVA exhibit strong vdW interaction via the oxygen atom in vinyl acetate (VA) compound and this bond is further strengthen by addition of nanoparticle whereby the presence of three functional oxygen bonds in sodium cloisite (Na^+) that can form hydrogen bonds with wax molecules. This study presents the incorporation of nanoparticle with wax inhibitors as an efficient mitigation method to overcome wax deposition issue in oil and gas industry.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Å	Amstrong Meter
ρ_{sample}	Density of Crude Oil Sample
ρ_{water}	Density of Water
T_o	Temperature of Crude Oil
T_c	Temperature of Cold Finger
ΔT	Temperature different between of Crude Oil and Cold Finger
mPa.s	Millipascal Seconds
D	Impeller Diameter
N	Rotational Speed of Impeller
μ	Viscosity of Crude Oil
ρ	Density of Crude Oil
$g_{xy}(r)$	Probability
r	Spherical Radius
ρ_y	Density of Y Atom
N_y	Number of Y Atom
y	Atoms in A Shell of Width Δr at Distance R
x	Reference Atom
w_f	Reference Amount of Wax Deposition without Chemical Treatment
w_t	Amount of Wax Deposited after Treatment
m	Meter
cm	Centimetre

LIST OF ABBREVIATIONS

3D	three dimensional
ANOVA	Analysis of variance
COMPASS	condensed-phase optimized molecular potentials for atomistic simulation studies
DSC	differential scanning calorimeter
EVA	Poly(ethylene-co-vinyl-acetate)
EOR	Enhanced oil recovery
g(r)	probability
hr	hour
GC-FID	Gas chromatography flame ionization detector
GC-MS	Gas chromatography mass spectrometry
MA	Poly- (maleic anhydride-alt-1-octadecene)
MD	molecular dynamics
NP	nanoparticle
N_{Re}	Reynolds number
ppm	part per million
PPD	pour point depressant
rdf	radial distribution function
rpm	rotation per minute
SARA	saturates, aromatics, resins, asphalthenes
SG	specific gravity
UOP	universal oil product
vdW	van der Waals interaction
VA	vinyl acetate
WAT	wax appearance temperature
XRD	x-ray power diffraction

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