EXPERIMENTAL INVESTIGATION AND MODELLING OF WAX DEPOSITION INHIBITION IN PIPELINE TRANSPORTATION OF CRUDE OIL

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DOCTOR OF PHILOSOPHY

UNIVERSITI MALAYSIA PAHANG

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NORIDA BINTI RIDZUAN

Thesis submitted in fulfilment of the requirements
for the award of the degree of
Doctor of Philosophy

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

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LIST OF SYMBOLS

$g_{xy}(r)$	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	the reference atom
w_f	the reference amount of wax deposition without chemical treatment
m	meter
cm	centimeter
ns	nanosecond
fs	femtosecond
V	volume
P	pressure
T	temperature
N	number of molecules
ρ_{sample}	density of crude oil sample
ρ_{water}	density of water
w_t	the amount of paraffin deposition with chemical treatment
Å	amstrong meter
b_o	regression coefficients for intercept terms
b_i	regression coefficients for linear terms
b_{ii}	regression coefficients for quadratic terms
b_{ij}	regression coefficients for interaction terms
T_{oil}	temperature of crude oil
T_{wall}	pipe wall temperature
T_{diff}	temperature different between temperature of crude oil and wall
T_{WAT}	wax appearance temperature
ΔT	temperature different between temperature of crude oil and cold finger
mPa. s	milliPascal seconds

LIST OF ABBREVIATIONS

EVA	Poly(ethylene-co-vinyl-acetate)
MA	Poly- (maleic anhydride-alt-1-octadecene)
DEA	Diethanolamine
C-DEA	Diethanolamine cocoamide
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatography–mass spectrometry
rdf	Radial distribution function
MD	Molecular dynamics
DOE	Design of experiment
RSM	Response surface methodology
CCD	Central composite design
FFD	Full factorial design
h	Hour
ppm	Part per million
rpm	Rotation per minute
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
CPM	Cross polarised microscopic
I.D	Inner diameter
g(r)	Probability
UOP	Universal oil products
WAT	Wax appearance temperature
OFAT	One factor at time
EXP	Exponential
SG	Specific gravity
PPDs	Pour point depressants
COMPASS	Condensed-phase optimized molecular potentials for atomistic simulation studies

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ABSTRACT

Wax deposition causes serious problems in crude oil flow assurance due to the long chain n-paraffin. The application of wax inhibitors is an effective method to prevent wax formation and deposition. In this thesis, seven commercial groups of wax inhibitors were introduced and their performances were evaluated through cold finger and rheological methods. From both methods, poly(ethylene-co-vinyl acetate) (EVA) showed the highest inhibition performance based on the reduction of the wax deposit amount and the decrement of the crude oil viscosity value. To substantiate even further in the wax inhibitor selected, molecular dynamics (MD) simulation was introduced to understand the interaction between wax crystals and wax inhibitor at the molecular level. The interaction of wax crystals with inhibitors were analysed through radial distribution function (rdf) value which described the structure of inhibitor in wax crystals. MD simulations confirmed the increased percentage of inhibition efficiency (PIE) of the experimental study using EVA. Thus, EVA had inhibited the formation of n-octacosane wax solid of crude oil better than poly(maleic anhydride-alt-1-octadecene) (MA). N-octacosane wax crystal is a long chain molecule of crude oil and it has a strong van der Waals (vdW) interaction between the carbonyl group in EVA and hydrogen atoms in the n-octacosane. This increases its solubility. In addition, EVA has strong vdW interaction via the oxygen atom in the vinyl acetate functional group with the hydrogen atom in n-octacosane, resulting in a higher probability value of inhibition ($g_{xy}(r)$). Design of experiment (DOE) was used to screen four possible factors that contribute to the n-paraffin wax formation. The factor of cold finger temperature (B) was identified as the most significant factor of wax problem, followed by experimental duration (C), rotational speed (A) and inhibitor concentration (D). The combination effect between factors B and C showed the highest percentage of contribution of wax deposit formation. The optimisation of wax deposit formation was achieved using response surface methodology (RSM). The optimised conditions were obtained at 1.5 h and 25°C. The minimum value of wax crystal formation achieved after the optimisation and transformation was 0.0042 g. This value shows over 150-fold decrement of wax formation expression compared to prior the optimisation process. Therefore, the model obtained from RSM is useful to provide an insight for engineers or researchers to estimate wax formation at other conditions.

ABSTRAK

Pengendapan lilin menyebabkan masalah yang serius dalam aliran minyak mentah disebabkan oleh n-parafin berantai panjang. Penggunaan perencat lilin adalah satu kaedah berkesan bagi mencegah pembentukan dan pengendapan lilin. Dalam tesis ini, tujuh kumpulan perencat lilin komersial diperkenalkan dan prestasinya dinilai melalui kaedah jari sejuk dan kaedah reologi. Dari kedua-dua kaedah tersebut, poli(etilena-bersama-vinil asetat) (EVA) menunjukkan prestasi perencatan tertinggi berdasarkan pengurangan jumlah pengendapan lilin serta penyusutan nilai kelikatan minyak. Simulasi dinamik molekul (*molecular dynamics*, MD) diperkenalkan bagi memahami dengan lebih lanjut interaksi antara hablur lilin dengan perencat lilin pada tahap molekul. Interaksi hablur lilin dengan perencat dianalisis menggunakan nilai fungsi taburan jejarian (*radial distribution function*, rdf) bagi menggambarkan struktur perencat dalam hablur lilin. Simulasi MD mengesahkan peningkatan peratus kecekapan perencatan (*percentage of inhibition efficiency*, PIE) dalam kajian eksperimen menggunakan EVA. Ini bermakna, EVA berjaya menghalang pembentukan pepejal lilin n-oktakosana dalam minyak mentah lebih baik berbanding poli(maleik anhidrida-berselang-1-oktadekena) (MA). Hablur lilin n-oktakosana adalah molekul rantai panjang minyak mentah dan ia mempunyai interaksi van der Waals (vdW) yang kuat antara kumpulan karbonilnya di dalam EVA dan atom hidrogen daripada n-oktakosana. Ini bertindak meningkatkan keterlarutan. Sebagai tambahan, EVA memiliki interaksi vdW yang kuat melalui atom oksigen dalam kumpulan berfungsi vinil asetat dengan atom hidrogen dalam n-oktakosana yang menyebabkan peningkatan nilai kebarangkalian perencatan ($g_{xy}(r)$). Reka bentuk eksperimen (*design of experiment*, DOE) juga digunakan bagi menyaring empat faktor yang mungkin menyumbang kepada pembentukan lilin n-parafin. Faktor suhu jari sejuk (B) dikenal pasti sebagai faktor utama bagi permasalahan lilin, diikuti oleh tempoh eksperimen (C), kelajuan putaran (A) dan kepekatan perencat (D). Kesan gabungan antara faktor B dan C menunjukkan peratusan tertinggi menyumbang kepada pembentukan deposit lilin. Pengoptimuman bagi pembentukan deposit lilin dicapai menggunakan kaedah gerak balas permukaan (*response surface methodology*, RSM), Keadaan optimum yang diperoleh adalah pada 1.5 jam dan 25 °C. Nilai minimum yang diperoleh bagi pembentukan hablur lilin selepas pengoptimuman dan transformasi adalah 0.0042 g. Nilai ini menunjukkan penyusutan pembentukan lilin sebanyak lebih 150 kali ganda berbanding sebelum proses pengoptimuman. Jadi, model yang diperoleh daripada RSM ini berguna untuk meningkatkan pemahaman jurutera atau penyelidik ketika menganggar pembentukan lilin pada keadaan yang berbeza.

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