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Synthesizing Copolymer for Reducing Pour Point of Vietnamese Diamond Crude Oil

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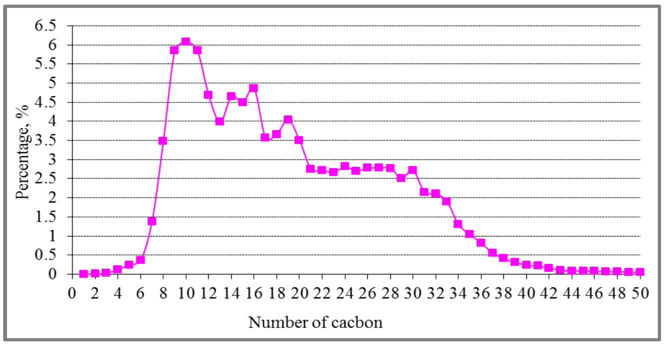
ABSTRACT

Diamond oil field is located in Block 01 and 02 Offshore Vietnam. Crude oil is evacuated from the Diamond Well Head Platform (WHP) through the subsea flexible pipeline. The lowest seabed temperature in the field is 22℃, while the pour point temperature (PPT) of Diamond crude oil is very high (36℃) due to high paraffin content (25%). There is very necessary to discover a good Pour Point Depressant (PPD) for the crude oil. The pour point of the crude oil should be reduced from 36℃ to 21℃ with the contacting with the synthesized PPD. The aim of this research is to choose appropriate monomer for copolymerization to produce copolymer based on the crude oil components (paraffin, asphaltene and resin content and distribution of n-paraffin). The reaction involves copolymerization of Behenyl acrylate, Stearyl methacrylate and Vinyl acetate under free radical forming conditions. The properties of prepared copolymer were evaluated by using viscosity, GPC, DSC and FT-IR techniques. The efficiencies of prepared copolymers were studied for their capability as PPD and flow improver for Vietnamese Diamond crude oil to solve the problem of wax deposition during transportation. The study showed that generally the prepared copolymers were efficient in the role of both pour point depressant and flow improver for the tested crude oil. Therefore, the copolymer could be considered to be used as an effective additive in transportation of crude oil.

Graphical Abstract



Distribution of n-carbon in Vietnamese Diamond Crude Oil.

Keywords: Diamond crude oil, Copolymer, Synthesis, Wax deposition.

INTRODUCTION

The term “paraffin” is used to describe oilfield wax. Waxes were solids made of long-chain (>C18), normal or branched alkane compound that were naturally present in crude oil and some condensates. Some cyclic alkanes and aromatic hydrocarbon may also be present. Waxes in crude were usually harder to control than those in condensates as they were of longer-chain alkanes [1-4].

In the reservoir, at high temperature and pressures, any wax within the oil will be in solution. As the crude oil temperature drop, wax will begin to precipitate from the crude oil, usually as needles and plates. In addition, as pressure drop during production, loss of low molecular weight hydrocarbon (light end) to the gas phase reduces the solubility of the waxes in the oil [4, 7-9].

As a result, the paraffin may begin to precipitate out and may form deposits on any cooler surface with which they come into contact. These wax deposits can cause problems, such as blockage of pipelines, valves and other process equipment. The wax may also deposit in pipelines subsequently used to transport crude oil or fractions thereof including hydrocarbon lines or multiphase transportation lines with oil, gas and/or water [4, 7].

The temperature of the pipelines from Diamond WHP to FPSO Ruby II were much cooler than the temperature of lines on Diamond platforms and were also much lower than the PPT of the oil change the flow behavior of the crude oil dramatically, below this temperature there is no any flow behavior of crude oil.

Wax deposition is a challenging problem in production, transportation and storage and cause big economic losses. The deposition of paraffin results in the impairment of the flow properties of the oil, which can result in problems during their transport and storage [1, 4, 7, 8, 10].

Wax deposition can be reduced in several ways, including keeping the lines hot, diluting the oil with solvent, or using a chemical additive which called PPD [4, 7]. The PPD were almost polymeric base that used to reduce the PPT and improve the flow ability of crude oil, respectively [1, 5-7]. This study involves the preparation and evaluation of alkyl acrylate/methacrylate and vinyl acetate copolymer as PPD by changing the feed ratios of the monomers and initiator and incorporating different alkyl side chains into the polymer backbone via polymerization for Vietnamese Diamond crude oil.

MATERIALS AND METHODS

Materials: The materials used in this study include: + Alkyl acrylate monomer: Behenyl acrylate 1822. + Alkyl methacrylate monomer: Stearyl methacrylate 1618. + Vinyl acetate monomer (VAM). + Initiator: 2,2′-azobis(isobutyronitrile) (AIBN). + Crude oil: Crude oil produced and delivered without treatment from Diamond field, Block 01 and 02 Offshore Vietnam.

A set of copolymer synthesis equipment is composed of: + Thermostat and circulation pump control unit; + Vacuum equipment; + Nitrogen gas cylinder; + Double-layer glass reaction kettle with 3 necks; + Stirring device; + Rack.

Copolymerization: The polymerization/copolymerization reaction was carried out in three-neck glass flask equipped with stirrer and thermometer (Figure 1). The reaction carried out using solvent 100 (a naphtha fraction from petroleum refinery) as solvent in which the monomers dissolved and initiated by AIBN. The polymer of this invention is prepared by polymerizing of alkyl acrylate monomer, alkyl methacrylate monomer and vinyl acetate under free radical forming condition. The polymerization is preferably conducted by heating a mixture of the monomers and free radical initiator(s) in a suitable organic solvent (Solvent 100) under constant stirring at a temperature of 80°C for 210 min of reaction time in inert atmosphere. The polymerization reaction is initiated by 2,2′-azobis(isobutyronitrile) (AIBN) [6].

Figure 1. A set of copolymer synthesis equipment.

Preparation of Behenyl acrylate/Stearyl methacrylate/Vinyl acetate polymer: Solvent 100 (45 g), Behenyl acrylate (45 g), stearylmethacrylate (6 g) and vinyl acetate (6 g) were charged to a reactor equipped with a stirrer, a heater, a thermometer. The reaction is vacuum pumped and sealed. The reactor is heated to 60°C and AIBN (0.06 g) is added. The reaction mixture is heated in the closed system at a temperature of 80°C for 210 min to provide Behenyl acrylate/Stearyl methacrylate/Vinyl acetate polymer (OP 01) having the viscosity is 148 cPs at 20°C in 40% toluene.

After the reaction had been completed, the copolymer product was diluted into a 40% solution in Solvent 100 forming a PPD. A predetermined part of the PPD was used to evaluate performance on the Vietnamese Diamond crude oil and to measure its dynamic viscosity by Viscometer - VT550. The rest of the PPD was added ethanol to precipitate the copolymer. Thereafter, the copolymer was filtered washed two times with ethanol. The obtained product was dried in an oven at 45°C for at least 12h with the final state of the copolymer being an opaque white powder. The pure copolymer then was used to determine the yield of the copolymerization reaction, average molecular weight (Mw) and the polydispersity index (PDI) by Gel Permeation Chromatography (GPC).

The performance evaluation of copolymer: The prepared copolymers were evaluated as pour point depressant and flow improver for Vietnamese Diamond crude oil. The evaluation criteria include: + Comparison of structures of paraffin crystals without and with PPD by DSC (Differential scanning calorimetry). + The pour point test based on ASTM D97. + Measure the profile of viscosity vs. temperature by Hakke Viscotester VT-550 equipment. + The gel strength test by Hakke Viscotester VT-550. + The paraffin deposition test by 6 Place Cold Finger apparatus, F5 Technologie.

Characterization: The viscosities of prepared copolymer were measured by Reverse Flow Viscometer. Other techniques including FT-IR, GPC and DSC were applied to characterize the synthetic copolymer.

RESULTS AND DISCUSSION

Characteristics of materials: Characteristics of many materials including Vietnamese Diamond crude oil, behenyl acrylate 1822, stearyl methacrylate 1618, vinyl acetate monomer (VAM) and initiator: 2,2′-azobis(isobutyronitrile) (AIBN) were listed in tables 1-5 and figure 2.

Table 1. The physicochemical characteristic and composition of Vietnamese

Diamond crude oil (extracted gas)

Characteristics	Method	Unit	Value
Density at 21°C	ASTM D1298-99	g mL^{-1}	0.8634
Density at 60°C	ASTM D1298-99	g mL^{-1}	0.8698
Pour point	ASTM D97/ D5853	^oC	36
Kinematic viscosity at 40°C	ASTM D445-09	cSt	18.23
Kinematic viscosity at 70°C	ASTM D445-09	cSt	6.54
n-paraffin content	UOP-46	% wt	25.31
Resin content	GC, LC	% wt	3.26
Asphaltene content	IP 143-90	% wt	1.35
Wax appearance Temperature (WAT)	DSC	^oC	55
Wax disappearance Temperature (WdisAT)	DSC	^oC	70

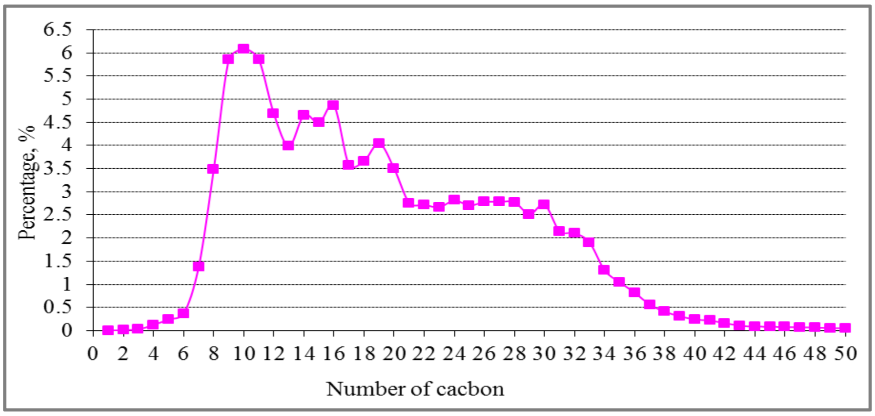


Figure 2. Distribution of n-carbon in Vietnamese Diamond Crude Oil

Table 2. The properties of Behenyl acrylate monomer

Characteristics	Value
Assay (Gas chromatography)	min. 91 %
Physical form	solid
≤ C16 ester, (GC)	max. 1.5 %
C18 ester, (GC)	42 ± 2 %
C20 ester, (GC)	11 ± 2 %
C22 ester, (GC)	44 ± 2 %
≥ C24 ester, wt. %	max. 2 %
Density at 60°C (ISO 6883)	0.8 g/cm3
Melting point	43 – 45°C
Boiling point	410°C

Table 3. The properties of Stearyl methacrylate monomer

Characteristics	Value
Assay (Gas chromatography)	min. 97 %
Appearance	pale yellow
Physical form	liquid or solid
Odor	characteristic
≤ C14 ester, (GC)	max. 5 %
C16 ester, (GC)	27.5 ± 2.5 %
C18 ester, (GC)	67.5 ± 2.5 %
≥ C20 ester, (GC)	max. 3 %
Density at 20 °C	0.86 g/cm^3
Viscosity (dynamic, 25 °C)	11 mPa · s
Melting point	19°C
Flash point	196°C
Boiling range	190 – 210°C at 64 hPa

Table 4. The properties of Vinyl acetate monomer (VAM)

Characteristics	Value
Appearance	Colorless
Physical form	liquid
Odor	characteristic
Melting point	- 93°C
Boiling range	72 °C
Specific Gravity (Water = 1)	0.9
Solubility in water, g/100 mL at 20°C	2.5
Solubility in Organic Solvents at 25°C (Acetone, Benzene, Ethyl Ether Heptane, Methanol, Carbon Tetrachloride)	Complete
Vapor Pressure, kPa at 20°C	11.7
Vapor Density (Air = 1)	3.0
Flash Point	-8°C c.c.
Auto-Ignition Temperature	402 °C
Flammable Limits	LOWER: 2.6%; UPPER: 13.4%
Partition coefficient: n-octanol/water	log Pow 0.73

Table 5. The properties of 2,2′-azobis (isobutyronitrile) (AIBN)

Characteristics	Value
Appearance	White
Physical form	Liquid
Solubility	soluble in alcohols and normal organic solvents, not soluble in water.

Free-radical polymerization: Free-radical polymerization is a method of polymerization by which a polymer forms by the successive addition of free-radical building blocks. Free radicals can be formed by a number of different mechanisms, usually involving separate initiator molecules. Following its generation, the initiating free radical adds (non-radical) monomer units, thereby growing the polymer chain. Free-radical polymerization is a key synthesis route for obtaining a wide variety of different polymers and material composites. One drawback of free radical polymerization is uncontrolled structure of produced polymer. In this study, the reaction conditions such as temperature and time were fixed and change monomers and initiator ratio in order to obtain a copolymer which can use PPD for Vietnamese Diamond crude oil. The viscosity of synthetic copolymer 40% in toluene solvent will be measured at different temperatures. The results were summarized below in table 6.

Table 6. The viscosity of Copolymers at different temperatures

Copolymer	Viscosity, cP					
	25°C	20°C	15°C	10°C	5°C	0°C
OP 01	115	148	153	156	160	170

FT-IR characterization of the OP 01 copolymer: FT-IR spectrum of the OP 01 was described in figure 3. There were some strong absorption peaks appeared at wave numbers of 2924 cm^{-1} and 2853 cm^{-1} assigned for covalence stretching of $–CH_3$ and $–CH_2$-, respectively; another strong peak occurred at wave number of 1726.94 cm^{-1} corresponding to the stretching of the C=O in ester groups; a peak at wave number of 1464.67 cm^{-1} was assigned for the bending of the $–CH_3$ and -CH_2- groups; and peak at wave number of 1194.69 cm^{-1} was caused by the C-O-C groups. They were all peaks specializing the synthetic copolymer.

GPC characterization of the OP 01 copolymer: GPC spectrum of the OP 01 was described in figure 4. The GPC reflected average molecular mass (M_{ave}) and polydispersity index (PDI) of the synthetic copolymer. Results revealed that the M_{ave} ranged from 25,390 to 53,300 Daltons, and the PDI ranged from 1.10 to 1.73. In optimized synthetic conditions, copolymer had M_{ave} of 40,238 Dalton and PDI of 1.597. These reasonable values effectively contributed to its ability in decreasing pour point of the Vietnamese Diamond crude oil.

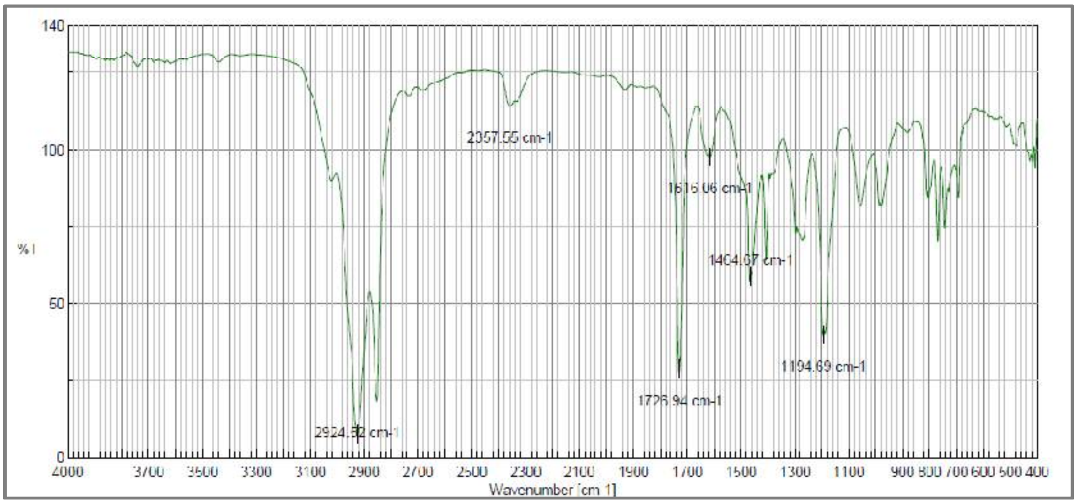
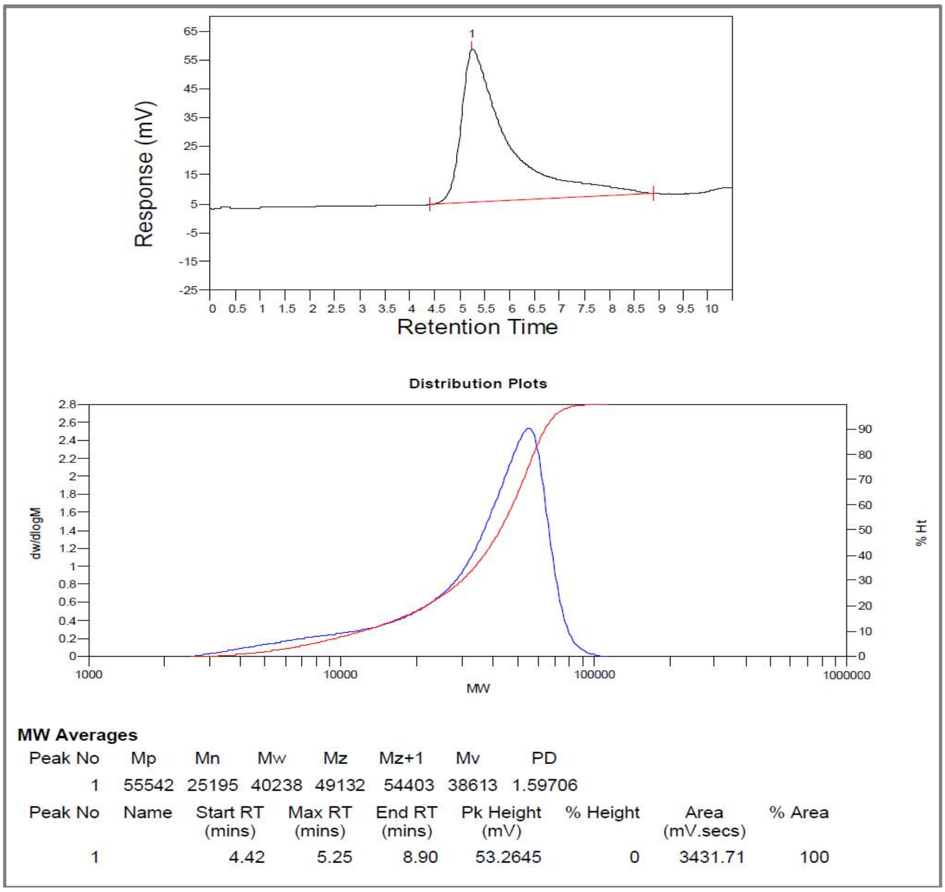


Figure 3. FT-IR spectrum of the OP 01 copolymer



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	55542	25195	40238	49132	54403	38613	1.59706

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		4.42	5.25	8.90	53.2645	0	3431.71	100

Figure 4. GPC spectrum of the OP 01 copolymer.

DSC characterization of the OP 01 copolymer: GPC spectrum of the OP 01 was described in figure 5 for determining physical properties and stability of the synthetic copolymer. Results showed that the copolymer had freezing point of 85°C, melting point of 110°C, stability of 210°C and structure changing point of above 300°C. Hence, the copolymer could be pumped to the oil well without any precaution of its structure change.

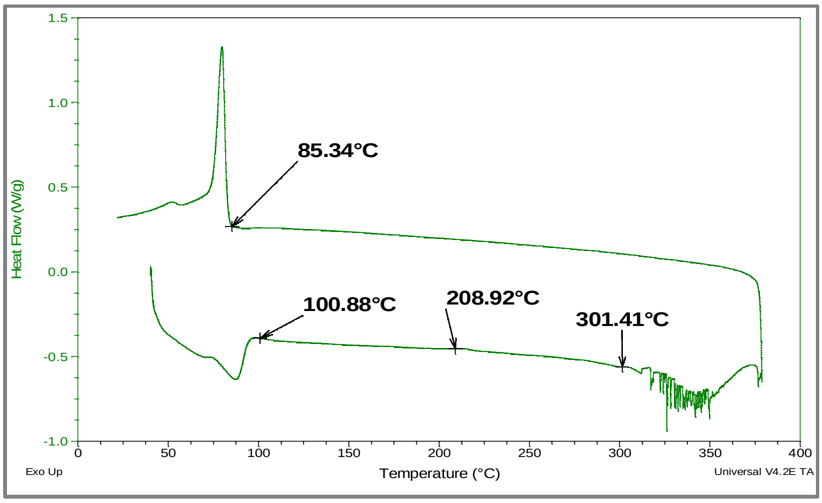


Figure 5. DSC spectrum of the OP 01 copolymer.

Additive used with Vietnamese Diamond crude oil in the study was the PPD, namely the synthetic copolymer in solution with Solvent 100. Although mechanism for depression of the crude oil under the contact with the PPD was still unclear, the PPD was known for its ability of changing shape and size of wax molecules through contacting with paraffin composition in the wax [1, 4, 7]. Therefore, formation of 3-D network of the wax molecules was inhibited followed by improvement of the flow properties of the crude oil. Many investigations relating to the flow properties of the Vietnamese Diamond crude oil under contacting with the PPD additive were studied below.

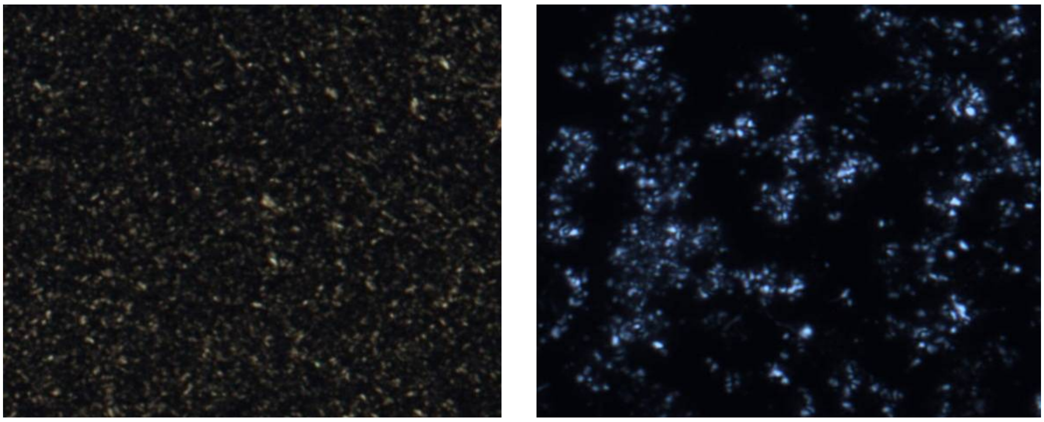
The influence of copolymer on Pour Point of crude oil: Evaluate the performance of synthetic copolymer on pour point depression capacity for Vietnamese Diamond crude oil base on ASTM D-97 standard. The results were presented below in table 7.

Table 7. The pour point temperature of treated Vietnamese Diamond crude oil with PPDs at different dosage

Dosage, ppm	The pour point temperature (°C) of OP 01
0 (Blank)	36
500	33
750	30
1000	27
1250	24
1500	24
1750	21
2000	21

Above results proved that the synthetic copolymer has capability to reduce pour point temperature of said crude oil. The combination contained both Behenyl acrylate and Vinyl acetate was more effective than the other in reducing the pour point temperature of the crude oil. The research also presented that the copolymer prepared from Behenyl acrylate 1822 which contain 44% C18; Stearyl methacrylate which contain 67.5% C18 and Vinyl acetate polymer can reduce the pour point temperature of the Vietnamese Diamond crude oil from 36°C to 21°C at 1750 ppm of dosing rate. The effects of the copolymer OP 01 on the properties (structure of paraffin crystals; rheology and paraffin deposition) of the oil were further researched as below.

The influence of copolymer on structure of paraffin crystals of crude oil: Use cross-polarized microscopy to study the structures of paraffin crystals in crude oil. The structures of paraffin crystals in the Vietnamese Diamond crude oil untreated and treated with a copolymer OP 01 by microscopy were shown in figure 6 (a) and (b).



(a) (b)

Figure 6. Images of paraffin crystals in untreated crude oil (a) and treated with PPD (b).

The paraffin crystal in untreated crude oil (Figure 6a) distribute regularly, has small size and link to strongly network. The paraffin crystals in treated crude oil (Figure 6b) become bigger and aggregate as clusters, increase the space between clusters, so that the property of treated crude flow at low temperature is improved.

The influence of copolymer on rheology of crude oil: The viscosity and gel strength of Vietnamese Diamond crude oil treated by the copolymer OP 01 at different dosage were presented in figure 7 and figure 8, respectively.

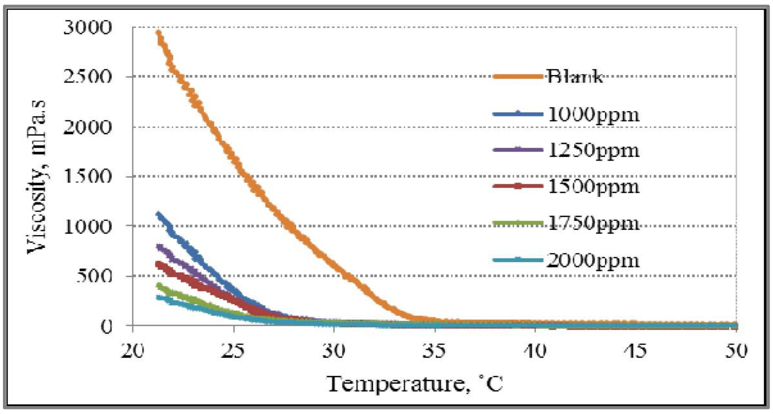


Figure 7. The profile of viscosity vs. temperature of Vietnamese Diamond crude treated with OP 01 at different dosages.

The results showed that at high temperatures (above pour point temperature of the crude oil) the viscosities of the crude oil were not much different between the crude oil treated and untreated by PPD. As the temperature drops, the effectiveness of the PPD was clearly shown. The viscosity of the crude oil reduced significantly; from 452.5 mPa.s of the blank to 20.9 mPa.s when treated by 1750 ppm of the copolymer OP 01 at 31°C; and from 2952 mPa.s of the blank to 413.2 mPa.s at the same dosing rate of the PPD at 21°C. This means that the crude oil can be transported with less energy loss.

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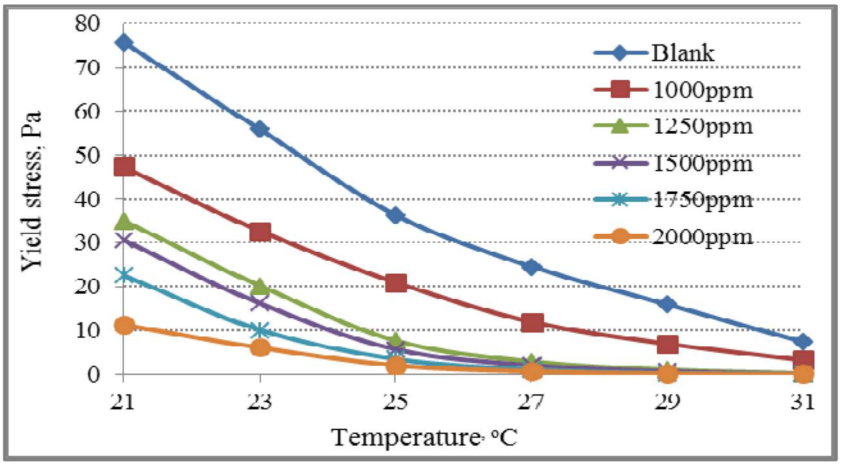

Figure 8. The Gel strength of Vietnamese Diamond treated with OP 01 at different dosages.

The results showed that PPD OP 01 was significantly effective in reducing the gel strength of the Vietnamese Diamond crude oil. The yield stress of the crude oil descended considerably; from 7.44 Pa of the blank to 0.18 Pa when treated by 1750 ppm of the optimal PPD at 31°C; and from 75.84 Pa of the blank to 22.6 Pa at the same dosing rate of the PPD at 21°C. In other words, the gel strength of the Vietnamese Diamond crude oil treated by the PPD at 1750 ppm of dosing rate was 41.3 and 3.4 times lower than the untreated crude oil at 31°C and 21°C respectively. The above results from figure 7 and 8 showed that the viscosity and gel strength of the crude oil have reduced significantly when treated by copolymer OP 01.

The influence of copolymer on paraffin deposition of crude oil: The paraffin deposition testing was presented in table 8. The results from Table 8 showed that the copolymer OP 01 could reduce paraffin/ wax deposition significantly-more than 70%.

Table 8. The paraffin deposition rate of Vietnamese Diamond crude treated with copolymer OP 01 at different dosages

Temperature °C		Duration time, h	Wax deposition rate, $g/m^2/d$					
Water bath	Cold finger		0	750 ppm	1000 ppm	1200 ppm	1500 ppm	2000 ppm
60	21	2	293.7	46.8	20.9	19.6	21.3	22.1
50	21	2	575.1	107.1	50.3	25.6	29.8	28.4
40	21	2	1006.8	197.3	115.4	70.9	89.6	90.5
30	21	2	-	324.5	245.2	203.1	213.5	238.2
Total weight of Wax, $g/m^2/d$			1875.6	675.5	431.8	319.2	354.2	379.2

APPLICATION

The synthetic copolymer could be used in drilling, transporting crude oil as an effective additive in decreasing its melting point.

CONCLUSION

In this study, four copolymers with different combination of monomers were synthesized and evaluated as pour point depressants and flow improver (rheology properties, paraffin deposition) for Vietnamese Diamond crude oil. The copolymer named OP 01 had optimum dosage of around 1750 ppm for the crude oil treatment. The pour point of the Vietnamese Diamond crude oil decreased from

36°C to 21°C when using the PPD additive proving the high quality of the synthetic copolymer. Other flow properties of the crude oil were also improved after adding the PPD including structure of paraffin crystal, the rheology and the paraffin deposition.

REFERENCES

[1]. Ayman M. Atta, Rasha A. El-Ghazawy, Fatma A. Morsy, Ali Mohamed Salah Ali, Abdullah Elmorsy, Synthesis and characterization of polymeric additives and their effective on flow improver of waxy Egyptian crude oil, King Sand University, Riyadh, **2013**.

[2]. Karen S. Pedersen Calsep, G. Lundtoftevej, Influence of wax inhibitors on wax appearance temperature, pour point, and viscosity of waxy crude oils, *Energy Fuels*, **2003**, 17 (2), 321–328.

[3]. Layla M. Alghanduri, Mohamed M. Elgarni, Joao a. P. Coutinho, Characterization of Libyan waxy crude oils, *Engery Fuels*, **2010**, 24 (5), 3101–3107.

[4]. Malcom A. Kelland, Production chemicals for the oil and gas industry, CRC Press, Tay Lor & Francis Group, New York, **2014**.

[5]. Olga Shmakova-Lindeman, Paraffin inhibitors, Patent No US20050215437 A1, **2004**.

[6]. Pavel Kriz, Simon I. Andersen, Effect of asphaltenes on crude oil wax crystallization, *Energy Fuels*, **2005**, 19 (3), 948–953.

[7]. Simon Neil Duncum, Bracknell, Philip Kenneth Gordon Hodgson, Inhibitors and their uses in oils, US Patent No. WO1998021446 A1, **2001**.

[8]. Wuhua Chen, Zhongchang Zhao, Caoyong Yin, The interaction of waxes with pour point depressants, *Fuel*, **2010**, 89(5), 1127-1132.

[9]. Qasim Y. Mohammed, Wali M. Hamad, Desalting of crude oil and some products at Kurdistan region – Iraq, *J. Applicable Chem*., **2013**, 2(2), 197-201.

[10]. Nguyen Khanh Dieu Hong, Hoang Thi Phuong, Dinh Thi Ngo, Research Paper: Synthesis of Nanosilica by Condensation Method For Crude Oil Adsorption, *J. Applicable Chem.*, **2017**, 6(2), 322-332.