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Constituents of Pour Point Depressant(PPDS) and their effect on flow properties of Neem crude oil

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ABSTRACT

Five commercial pour point depressant (A, B, C, D, and E) have been tested for their structure and effectiveness in remediating paraffin (wax) depositions from neem crude oil. All PPDS were characterized by FTIR. The results showed that all sample contain aromatic compound, aliphatic compound but some of them contain ester and olfien .
The samples were also surveyed by GC. The results showed that all PPDS contain mainly different type of solvents such as ethyl benzene ,O-xylene ,p-xylene ,toluene in high concentration naphthalene ,cyclopentylcyclopentene,1,2,3,4 tetramethyl benzene,1,2,3 trimethyl benzene and eicosadiene in small concentration .PPDS evaluated as pour point depressant and flow improver on Neem crude oil . The pour point and viscosity at different temperatures for different doses (500, 750, 1000, 1250ppm) were studied by measuring viscosity and pour point,result showed that the best reduction in viscosity was appeared when adding E at doses1250 ppm then D then A but B did not have any effect in these type of crude oil,also the results of pour point showed that the best results E PPDS the reduction of pour point 9 C^0 Then D PPDS then A and finally B did not have any effect

المستخلص

تم اختبار خمسة انواع من المواد الكيميائية التجارية المستخدمه لتخفيض درجه حرارة الانسكاب للخامات البترولية من ناحية التركيب و من ناحية فعاليتها فى علاج ترسيب البرافين المتكون في النفط الخام . و لقد تم دراسة التركيب بواسطة جهاز الاف تي اى ار و اظهرت النتائج ان هذه المواد الكيميائية تحتوي على مركبات اروماتية و مركبات اليفاتية و لكن بعض منها يحتوي ايضا على استرات و اليفينات . و ايضا تم دراسة التركيب لهذه المواد بواسطة جهاز الغاز كروماتوغرافي و النتائج اوضحت ان كل هذه الانواع تحتوي بصورة رئيسية على انواع مختلفة من المذيبات مثال لها الايثايل بنزين و الاورثو زايلين و التولوين بنسب عالية و ايضا تحتوي على النافثينات و السيكلوبنتايل و السايكلوبنتين و ايكوسارين بنسب بسيطه . و ايضا تم تقييم فعاليتها في علاج البرافين المترسب على خطوط الانابيب في خام حقل نيم حيث تم قياس نقطة الانسكاب و قياس اللزوجة و تم اضافتها بنسب مختلفه هي١٠٠٠,٧٥٠,٥٠٠، ١٢٥٠ واظهرت النتائج ان افضل هذه الانواع هوE عند اضافته بنسبة ١٢٥٠و يليه D و يليه A و لكن B ليس له اي تاثير على هذا النوع من الخامات . و اوضحت نتائج نقطة الانسكاب ان افضل نوع هو ايضاE حيث خفض نقطة الانسكاب بحوالي تسع درجات ثم يليه في الترتيب D ثم يليه A و اخيرا B حيث لم يحدث اي تغير في درجة الانسكاب

***Keywords*:** wax treatment chemicals, wax deposition , viscosity, and pour point

INTRODUCTION

Wax deposition is a common problem in the oil industry, when the oil temperature is lower to its trouble point, paraffin crystals begin to precipitate, this deposit took place at any level of the production facilities (tubing, production lines, separators, storage tank, pipeline). Wax deposition on the pipe walls limits the pumping of waxy crude oil. The deposits may vary from soft to hard, from yellow to black and consist of a mixture of wax, oil, asphaltenes and inorganic material.(1) The petroleum wax is long hydrocarbon chains found naturally in crude oils and condensate and contains at least 15 or more carbon atoms. There are different methods applied for preventing and removing wax deposition such as mechanical removing, heating application, solvent techniques, and wax treatment chemicals. In this study we concentrate on wax treatment technique and it is divided into two types:

Wax Removing Chemicals: There are many different types of chemicals that can be used to remove wax depositions, and several methods on how to apply them. The most common chemical methods used in the oil and gas industry as a removal technique are hot oiling and wax solvents. The application of thermo chemical packages is a more controversial wax removal technique.(1)

Hot Oiling: The hot oiling is a technique that has been used a lot in the early days in the oil and gas industry removing wax depositions down hole and in the flow lines. In the process hot oil is heated to a temperature above the melting point for wax and then pumped into the well(1-3) .

Wax Solvent: The different solvents have different abilities to dissolve wax deposits, which depends on the wax, the location in the system and the temperature.(4) Thermochemical Packages: Thermochemical packages are wax removal methods that utilizes the heat of an exothermic reaction to melt the wax deposits down hole or in flow lines(1).

Chemical Prevention Technique: There are mainly three different preventive chemicals used against wax depositions as follows:

Wax dispersants are surface active chemicals which prevent wax deposition by reducing their tendency to adhere to pipeline walls.(5)

Wax inhibitors are chemicals referred to as wax crystals modifiers and will affect the wax appearance temperature (WAT) for the crude oil.(5)

PPDs are chemicals that affect the pour point which reduce the gelling of the crude oil as temperature decreases, and thereby, improve the flow.(6)

The chemicals used as wax inhibitors and PPDs are normally polymers with long alkyl chains, which are intended to interfere with the wax crystallization and growth process. However the mechanisms for the wax inhibitors and PPDs are not fully understood and different mechanisms have been proposed. The general mechanism is that wax inhibitor polymers contain a structure similar to the wax structure, which will allow the polymer to be incorporated into the wax crystal growth. Beside the similar structure the polymer can also contain a structural part, which will cover the wax site, and thereby prevent new wax molecules to attach to the wax and continuing further growth(7). The effect of this alternation causes a reduction in the three dimensional network the wax deposition can form, and promote the formation of smaller wax aggregates. The overall effect will give a lower

pour-point and a reduction in the viscosity of the crude oil, which makes it easier to transport the crude oil. [5]

The wax inhibitor chemicals are often waxy materials and solid at room temperature, and therefore must be dissolved before they are applied in the field [8].The wax inhibitors are usually dissolved in aromatic solvents when they are applied in cold deepwater fields. The use of a good solvent in cold climates can also avoid gelling of the wax inhibitor, such as toluene, xylene and cyclopentane.

In general good wax inhibitors, with concentration of 50-200 ppm, have shown to prevent wax deposition at temperatures from 10-15 °C below the WAT. While the PPDs, with relatively high dosage, have shown to reduce the pour point temperature with up to 30°C[5]

The objective of this research is to study the characterization of pour point depressant by GC and FTIR To investigate the effectiveness of adding pour point depressant on the flow properties of neem crude oil.

MATERIALS AND METHODS

Five different types of commercial pour point depressant, Sudanese crude oil from neem field were used for evaluating the performance of the additives

Pour point: The tested crude oil were heated up to 60C^{o} and PPD additives were added at different concentration, the solution was transferred to bottle test tube in water bath cooled at 48C^{o}. The tube was transferred to another cooling bath cooled down to 24C ^{o}. The tube was transferred to cooling bath cooled down to 0C^{o}, then the pour point temperature was measured at temperature 48C^{o} (ASTM D97-93).

Rheological measurements: Haake Rheometer model Haake Rheoscope 1(C25p)was utilized to measure the dynamic viscosity for untreated and treated crude oil with five commercial pour point depressant at different concentrations (from 500 to 1250ppm) and at different temperatures above and below pour point of crude oils ranging from 75-28C^{o}. Apparent viscosity values was determined

Whole-Oil Gas Chromatography Analysis: Five commercial pour point depressants, were subjected to whole oil- Gas chromatographic analysis. This was achieved by using Varian CP 3800 Gas Chromatograph, equipped with Flame Ionization Detector; 50mm × 0.2 mm film thickness 0.5µm fused silica capillary columns, coated with methyl silicone (PONA). The sample (1µL) was injected. Detector (FID) and injector temperatures were kept at 280°C. The oven temperature was programmed as listed in table (1)

Table (1): oven temperature programme

Temperature(C^{o})	Rate(C^{o}/min)	Hold(min)	Total time(min)
60	-	5	5
150	10	0	14
300	20	60	81
310	20	15	97

Helium was used as carrier gas. The data were collected from retention time: 0-97minutes FTIR measurements : Sample was loaded directly in the KBr Windows, introduced into the FTIR and scanned at 4000-400 cm^{-1}at resolution intervals of 4.000cm-1using NICOLET(370 DTGS).A description of the spectrum is attached.

RESULTS and DISCUSSION

In this wor five commercial pour point depressants have been tested for their

structure and effectiveness in remediating paraffin (wax) depositions from Neem crude oil. All PPDS were characterized by FTIR and Gas chromatograph.

The chemical structure of PPDS was studied by FTIR SPECTROSCOPY in this respect, FTIR spectra of all types of PPDS are represented in Table (2).

Figures (1, 2, 3, 4, and 5) shows increasing in the peak intensity at 3100 $cm^{-1}$and decreasing of peak intensity at3000cm-1which represent C-H stretching of alkene ,aromatic, furthermore the appearance of strong peak at 1500 and 1600 cm^{-1}(indicating the presence of aromatic ring) and also be confirmed from the pattern of the weak overtone and combination tone bands found from 2000 to 1600 cm^{-1}, also show a strong absorption band between 3000cm^{-1} and 2850cm^{-1}which is attributed to the presence of aliphatic hydrocarbon.

Also from figures (2, 3, 4, and5) FTIR Spectrums shows increasing of peak intensity at1735cm^{-1} and decreasing of peak intensity at 1700cm^{-1}, this strong band indicates either carboxylic acid, ester, aldehyde and amide, also the appearance of strong peak at 1150 cm^{-1} and 1240 cm^{-1} co-vibration indicating formation of ester group.

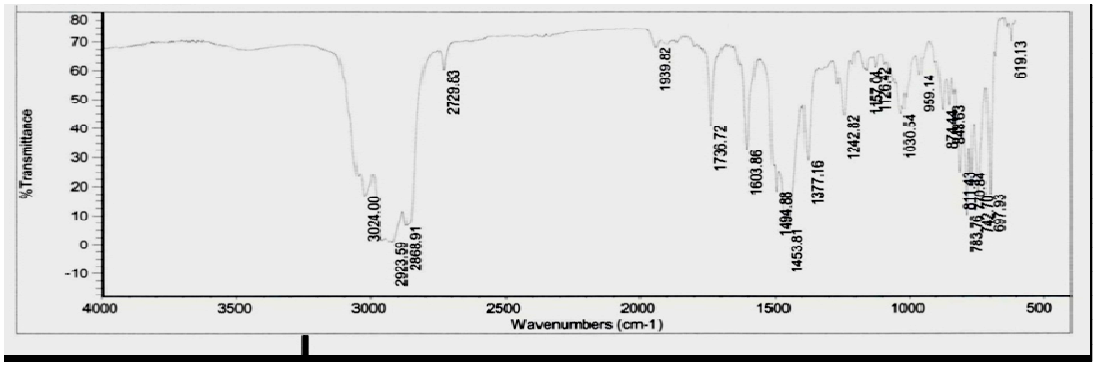

Figure (1): FTIR spectrum of)A) PPD

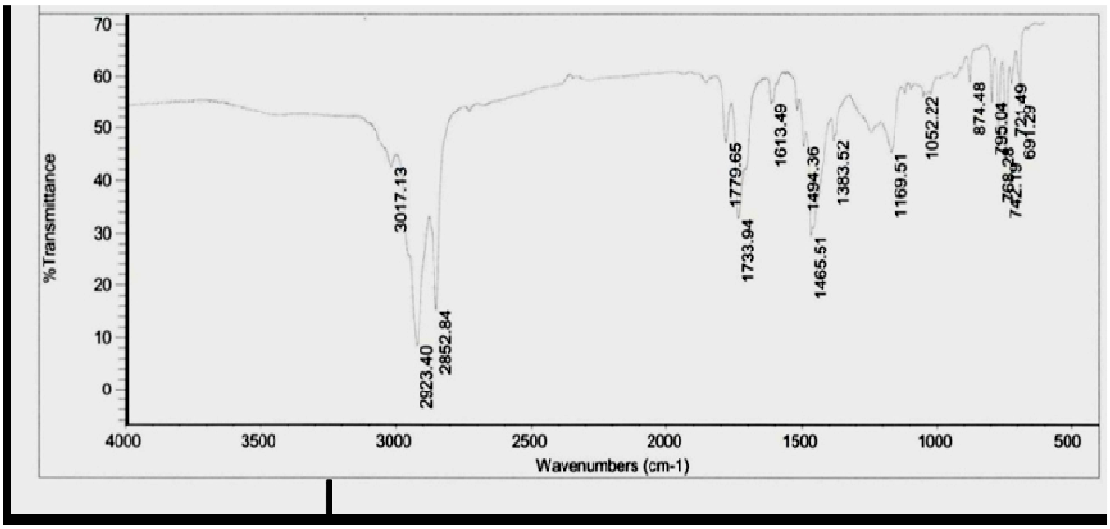

Figure (2): FTIR spectrum of (B) PPD

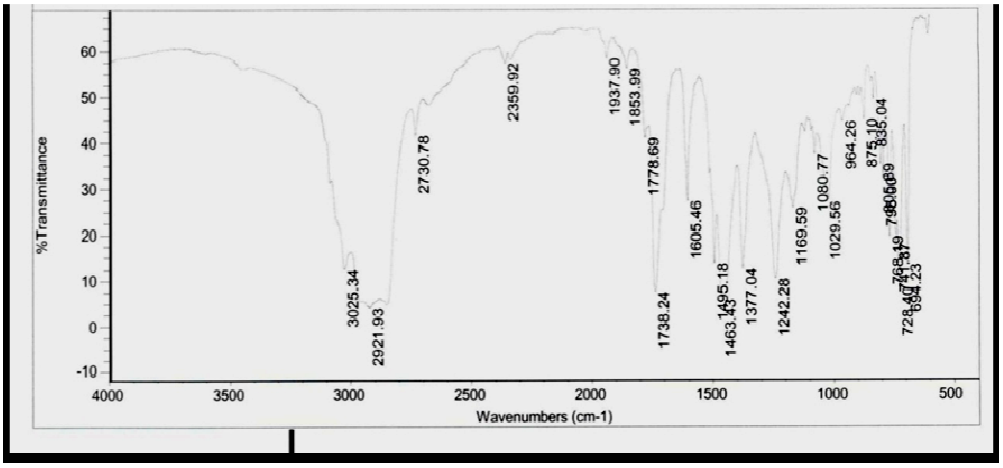

Figure (3): FTIR spectrum of (C) PPD

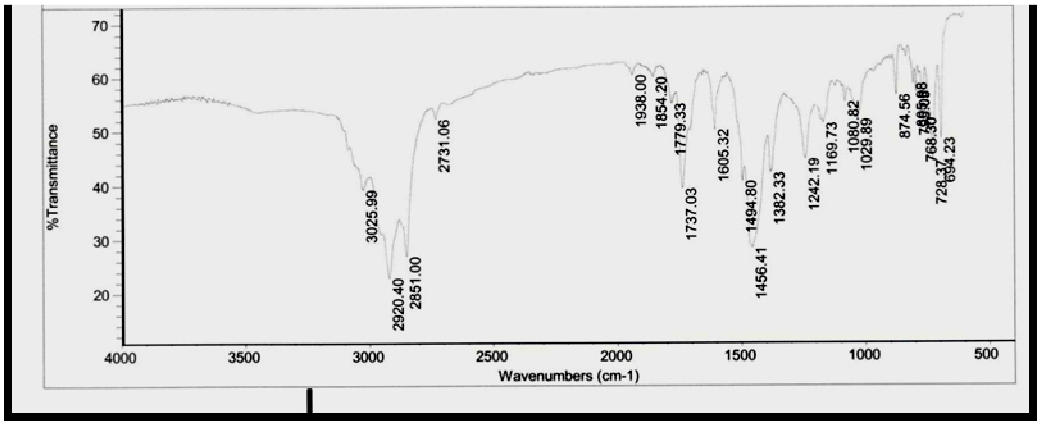

Figure (4): FTIR spectrum of (D) PPD

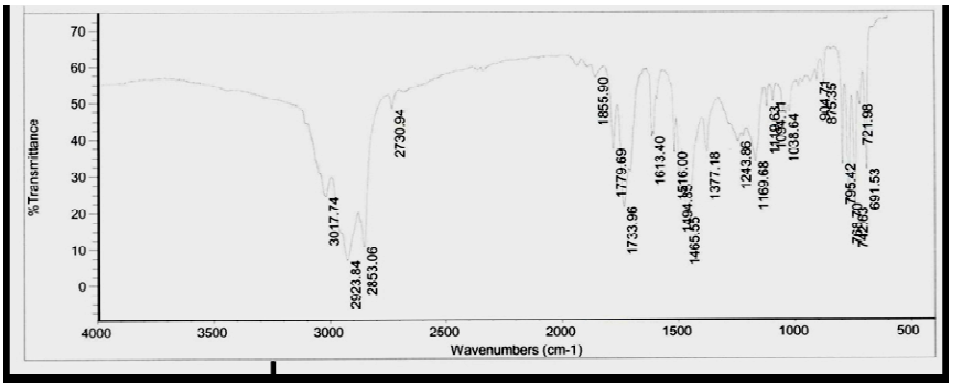

Figure (5): FTIR spectra of (E) PPD

Table (2): FTIR Spectral interpretation

(A) PPD	(B) PPD	(C)PPD	(D) PPD	(E) PPD
• Mono substituted aromatic hydrocarbons • Aliphatic hydrocarbons	• Meta substituted aromatic hydrocarbons • Ester (general) • Aliphatic hydrocarbons	• Meta substituted aromatic hydrocarbons • Ester (general) • Aliphatic hydrocarbons	• Mono substituted aromatic hydrocarbons • Aliphatic hydrocarbons • Ester (general) • Trans olefins	• Mono substituted aromatic hydrocarbons • Aliphatic hydrocarbons • Ester (general)

Characterization of pour point depressants by GC. Its observed from Tables (3, 4, 5, 6 and 7) that most of PPDs contain mixtures of aromatic solvents and other compounds such as polymer, ester, olefins, etc. while some of PPDs mainly contain strong solvents (A PPD) (Table 3) and this means that the presence of solvents is very important. From tables (6)(7) it is observed that the PPDS contain mainly different types of benzene compounds such as ethyl benzene, toluene, O-xylene ,m-xylene ,p-xylene in high concentration 1,2,4 trimethyl benzene,1,2,3 trimethyl benzene, and other in small concentration. From Table (3) it can be seen that the presence of other solvent such as 1-cyclopentylcyclopentene,1-methyl-naphthalene. Wax deposition not only contains wax, but also contains other compound such as resin, asphaltenes these need dissolve by solvent. From Tables (4 and 5) it can be seen that the presence of long olefins such as1,19eicosadiene, 9-nonadecene, 5-eicosadiene is due to the fact that(the general mechanism is the wax inhibitor polymer contains a structure similar to the wax structure , which will allow the polymer to be in corporate into the wax crystal growth ,beside the similar structure the polymer can also contain a structural part , which will cover the wax site , and thereby prevent new wax molecules to attach to the wax and continuing further growth.

From FTIR and GC Results it was observed the presence of ester in the instullation of some of them such (B),(C), (D),(E) the structure and composition of flow improvers should posses high polar functional groups such as amide , ester,amine and hydroxyl groups, when additives contains both long chain hydrocarbon and polar moieties it may be efficient as was wax dispersants and flow improver become this polar functional groups increase the solubility of PPDS in crude oil.

Table (3): Characterization of (A) PPD by GC

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Benzene	C6H6	3.08	78	96060	0.4797
2	Toluene	C7H8	5.36	92	120699	0.6027
3	Ethylbenzene	C8H10	8.63	106	10390000	51.88
4	m-Xylene	C8H10	8.98	106	943754	4.713
5	p-Xylene	C8H10	9.01	106	468515	2.340
6	o-Xylene	C8H10	9.88	106	437930	2.187
7	propyl-Benzene	C9H12	12.33	120	74328	0.3712
8	1-ethyl-4-methyl-Benzene	C9H12	12.65	120	365282	1.824
9	1-methyl-3-(1-methylethyl)- Benzene	C10H14	16.96	134	42608	0.2128
10	1-Cyclopentylcyclopentene	C10H16	18.01	136	405671	2.026
11	(1,1-dimethylpropyl)- Benzene	C11H16	20.21	148	1700000	8.489
12	Naphthalene	C10H8	21.68	128	2077000	10.37
13	1,2-diethyl-5-methyl-Benzene	C11H16	21.84	148	369260	1.844
14	1,3-diethyl-5-methyl-Benzene	C11H16	21.89	148	499237	2.493
15	1,4-diethyl-5-methyl-Benzene	C11H16	22.24	148	147063	0.7344
16	pentamethyl-Benzene	C11H16	24.83	148	240383	1.200
17	1-methyl-Naphthalene	C11H10	25.63	142	1321000	6.597
18	2-methyl-Naphthalene	C11H10	26.16	142	248699	1.242
19	2,6-dimethyl-Naphthalene	C12H12	29.69	156	77799	0.3885

Table (4): Characterization of (B) PPD by GC

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Ethylbenzene	C8H10		106	21790000	13.46
2	(p+m)-Xylene	C8H10		106	95440000	58.96
3	o-Xylene	C8H10		106	44420000	27.44
4	1-ethyl-2-methyl-Benzene	C9H12	11.10	120	18349	0.0113
5	1,2,4-trimethyl-Benzene	C9H12	14.04	120	27129	0.0168
6	1-ethyl-3-methyl-Benzene	C9H12	15.15	120	9114	0.0056
7	Isobutylbenzene	C10H14	16.31	134	7845	0.0048
8	2-ethyl-1,4-dimethyl-Benzene	C10H14	16.55	134	18968	0.0117
9	1-methyl-2-(1-methylethyl)-Benzene	C10H14	17.64	134	4308	0.0027
10	1-methyl-3-(1-methylethyl)-Benzene	C10H14	18.88	134	7942	0.0049
11	1,2,3,4-tetramethyl- Benzene	C10H14	19.01	134	13850	0.0086
12	9-Nonadecene	C19H38	47.45	266	53408	0.0330
13	1,19-Eicosadiene	C20H38	51.34	278	43015	0.0266
14	5-Eicosene	C20H40	55.18	280	21375	0.0132

Table (5): Characterization of (C) PPD by GC

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Ethylbenzene	C8H10	8.62	106	15520000	13.36
2	(p+m)-Xylene	C8H10	9.04	106	67660000	58.23
3	o-Xylene	C8H10	9.92	106	32800000	28.23
4	1-ethyl-2-methyl-Benzene	C9H12	11.11	120	20549	0.0177
5	1,2,3,4-tetramethyl- Benzene	C10H14	16.57	134	9354	0.0081
6	9-Nonadecene	C19H38	19.03	266	9043	0.0078
7	1,19-Eicosadiene	C20H38	47.75	278	89753	0.0772
8	5-Eicosene	C20H40	51.73	280	83455	0.0718

Table (6): Characterization of (D) by GC

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Toluene	C7H8	5.36	92	19820000	41.78
2	Ethylbenzene	C8H10	8.61	106	3176000	6.69
3	m-Xylene	C8H10	8.97	106	9898000	20.86
4	p-Xylene	C8H10	9.01	106	6308000	13.30
5	o-Xylene	C8H10	9.87	106	3786000	7.981
6	propyl-Benzene	C9H12	12.35	120	51965	0.1095
7	1-ethyl-4-methyl-Benzene	C9H12	12.66	120	1085000	2.287
8	1-ethyl-3-methyl-Benzene	C9H12	12.78	120	295781	0.6235
9	1,2,3-trimethyl-Benzene	C9H12	13.01	120	195350	0.4118
10	1-ethyl-2-methyl-Benzene	C9H12	13.37	120	73129	0.1542
11	1,2,4-trimethyl-Benzene	C9H12	14.03	120	2628000	5.540
12	1,4-diethyl- Benzene	C10H14	15.13	134	54064	0.1140
13	1-methyl-3-(1-methylethyl)- Benzene	C10H14	16.54	134	67460	0.1422

Table (7): Characterization of (E)by GC

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Toluene	C7H8	5.35	92	16047758	42.77
2	Ethylbenzene	C8H10	8.60	106	2354000	6.274
3	m-Xylene	C8H10	8.97	106	7976000	21.26
4	p-Xylene	C8H10	9.01	106	5145000	13.71
5	o-Xylene	C8H10	9.87	106	2726000	7.265
6	propyl-Benzene	C9H12	12.35	120	38582	0.1028
7	1-ethyl-4-methyl-Benzene	C9H12	12.65	120	723730	1.929
8	1-ethyl-3-methyl-Benzene	C9H12	12.78	120	220078	0.5865
9	1,2,3-trimethyl-Benzene	C9H12	13.01	120	172415	0.4595
10	1-ethyl-2-methyl-Benzene	C9H12	13.36	120	65106	0.1735
11	1,2,4-trimethyl-Benzene	C9H12	14.02	120	1995000	5.3170
12	1-methyl-3-(1-methylethyl)- Benzene	C10H14	16.53	134	57162	0.1523

The effect of PPDS on pour point reduction of Neem crude oil: The effectively of any PPDS depends upon its ability to keep the paraffin wax compound in solution or dispersed. It is observed that crude oil responses differently with the same additives at different doses these responses may be interms of change in pour point or change in rheological properties or both. The high wax crude oils are characterized by high pour point, high viscosity, high gel strength, and abundant wax deposits. It is well known that, as the paraffin wax content increases in crude oil, this leads to difficult solubility of wax in oil, in some cases forming a separate solid phase.

The relation between Δp and additive concentration for crude oils without and with additives are shown in figure (6). The pour point reduction was calculated by the following equation

Pour point reduction (Δp) = PPpure-PPadd

Where, PPpure is the pour point of the pure crude oil and PPadd is the pour point of the crude oil containing additives .

From fig(6) it was shown that the Δp value of all concentration for (B) PPD is zero. This means that there is no effect of PPDS in the reduction of pour point ,as for(A) PPD note also the Δp value is equal to zero for all concentrations except 1250 ppm the value is 3, but for (D) PPD the value is 3 for all concentration except 1250 ppm is 6 and for (E) the Δp value for concentration 500, 750ppm is 3 and 1000,1250ppm is 9,this means that the best PPDS of all types is(E) and most suitable one with this type of crude oil.

Table (8): Eeffect of different type of PPDS on pour point reduction of neem crude oil doses

doses	(A) ppds reduction	(B) reduction	(C) reduction	(E) redution
500 ppm	0	0	3	3
750 ppm	0	0	3	3
1000 ppm	0	0	3	9
1250 ppm	3	0	6	9

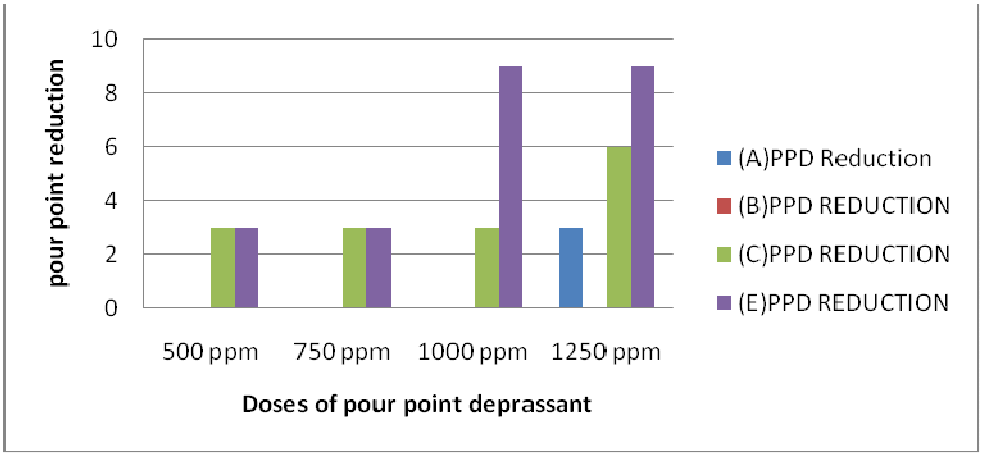

Figure (6): The effect of PPDS at different concentrations on pour point reduction of Neem crude oil.

Impact of PPDS on viscosity of NEEM crude oil at different temperature: The viscosity is used to evaluate the crude oil flow ability in the absence and presence of the pour point depressant additives the viscosity at different temperatures (75-28°C) for untreated

and treated crude oil with different doses (500-1250ppm) were determined . It was observed that the viscosity of crude oil was increased with cooling.

The high wax content leads to the formation of gelled crude oil at low temperatures due to crystallization of wax which in turn affects the viscosity of crude oil.

The apparent viscosities (CP) of the untreated and treated crude oils with five commercial pour point depressant were determined at different temperatures to evaluate the effect of PPD on viscosity and what is the best one

The value of the viscosity (cp) decreased by addition (A) PPD(Figure 7) at high concentration (1250ppm) but in other concentrations (500,750,1000ppm) no decrease in viscosity .either in (B)(Figure 8) does not have any decrease in viscosity at all concentrations, on the other hand it was observed that the viscosity of crude oils was decrease with adding (D) (Figure 9) at all concentration (500, 750, 1000, 1250 ppm) but the largest decrease in viscosity appear when adding (E) (Figure 10) at all concentrations, especially in the 1250ppm where the viscosity reduce from 3572.571cp to303.2686 at 28°C this means (E)is the best one and suitable with this type of crude oil.

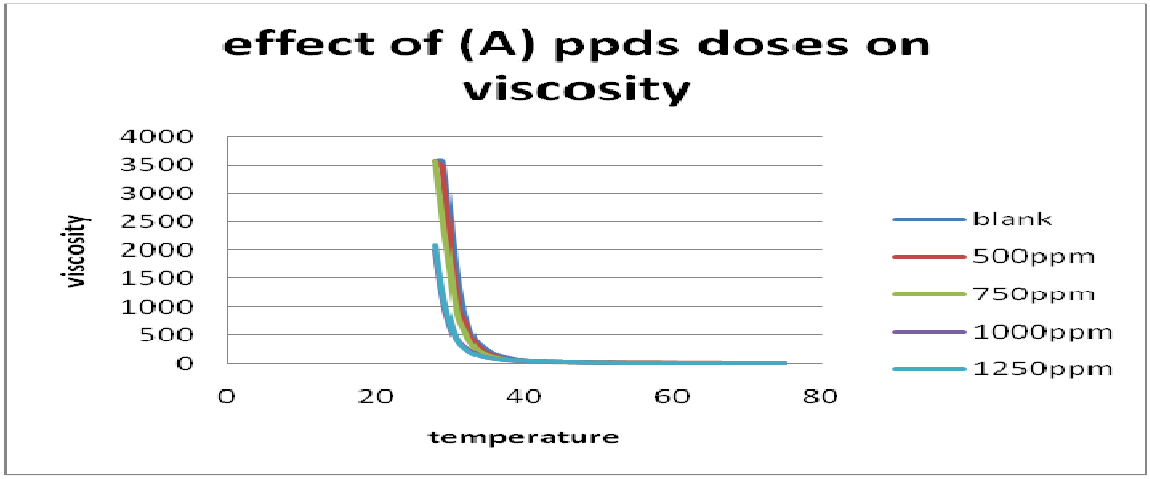

Figure (7): Effect of(A)PPD at different concentrations on viscosity

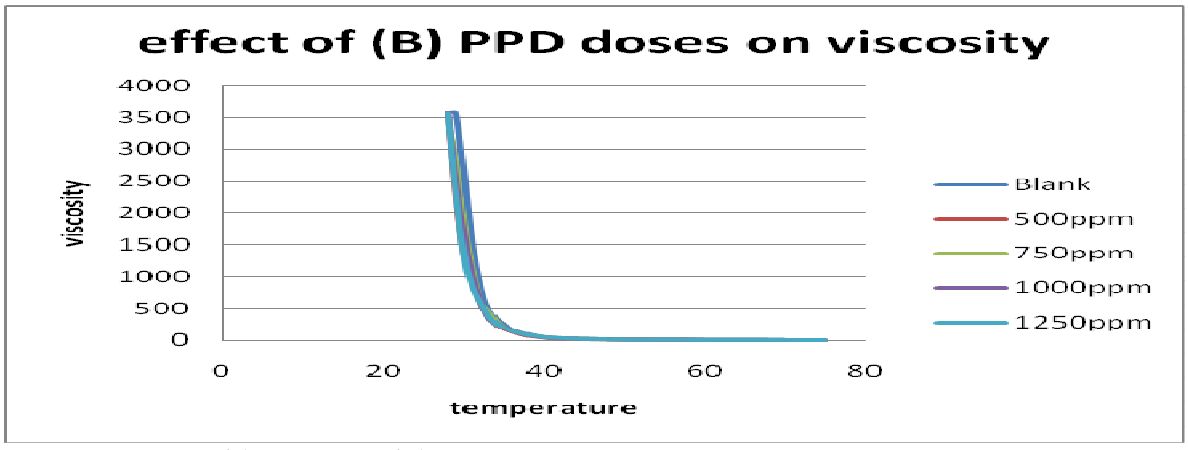

Figure (8): Effect of(B)PPD at different concentration on viscosity

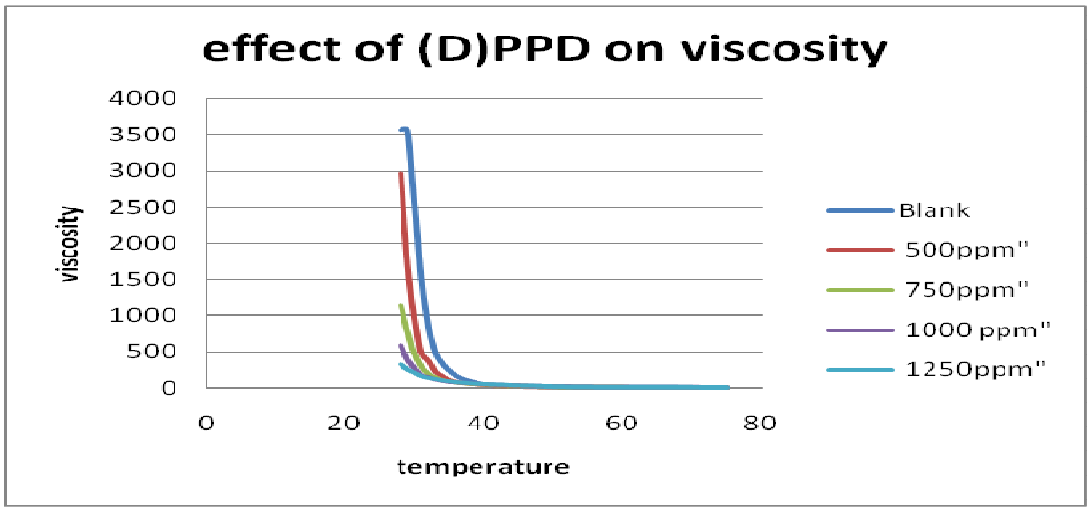

Figure (9): Effect of(D) PPD at different concentration on viscosity

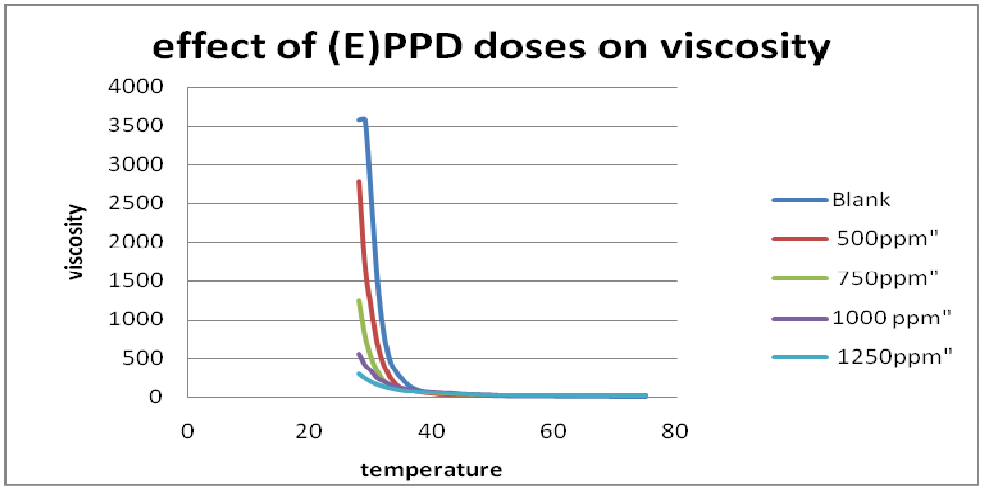

Figure (10): Effect of (E) PPD at different concentration on viscosity

CONCLUSIONS

In this work that largeted the effective pour point depressant for improving the flow properaties of neem crude oil , five pour point depressants were characterized and evaluated in labrotary ,it was found that the best PPDS was (E) and the effective concentration 1250 ppm. And also it was found that all PPDS contain aromatic compound, aliphatic compound and contain mainly different type of solvents such as ethyl benzene ,O-xylene, p-xylene,toluene in high concentration

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