SYNTHESIS OF POLYMERIC ADDITIVES FROM NATURAL OILS AND ITS EFFECT AS VISCOSITY REDUCER

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ABSTRACT

From the naturally occurring polymer, four polymeric compounds are created. A waxy crude oil was tested as a pour point depressant (PPD) using vegetable oils fatty acid. A FTIR and GPC analysis was used to characterize the chemical additives developed. Reduction in substantial amounts comparing PPD treated crude oils with virgin crude oils, we observed differences in pour point and apparent viscosity. That showed that the crude oil flowed better at low temperatures, polymeric pour point depressants have a very important practical application in of waxy crude oil pipeline transportation.

Keyword: Pour Point Depressant, Waxy crude oil, Viscosity reducer, Wax Inhibitors

1. INTRODUCTION

A wax crystal precipitates on the surface overlapping and interlocking thin plates and needles create a network that has three dimensions. Depression is caused by these drugs as a result of their existence, they obstruct the growth of lateral crystals precipitation of wax leads to adsorption. When the oil temperature drops below the wax appearance temperature (WAT), wax begins to precipitate pipelines perform negatively during oil phase, which leads to a number of issues. In recent decades, polymeric pour point depressants have played an important role in decreasing pour point and improving fluidity under severe conditions an oil that is wax. As the length of the alkyl chain in PPD increases, its efficiency improves,

which may be due to the effect of molecular weight. This finding verifies that molecular weight affects the effective radius of polymers, and, thus, the viscosity.

It's getting harder and harder to find waxy crude oil across the globe. Temperature and pressure in the reservoir are as high as it needs to be to keep wax crystals soluble, as it travels through surface facilities. By lowering the temperature in the subsea flowlines, report a tendency for paraffins to precipitate. The point of pour It is not possible to move crude oil due to its non-Newtonian behavior and its high viscosity this paraffin molecules are also precipitated more readily when the wall of the pipeline (or the ambient temperature) is at a certain temperature crude oil at this temperature falls below the wax appearance temperature (WAT) is mostly observed in the deep sea. As a result of wax crystallization of petroleum under water temperature and impairs the production process of crude oil looked at crude oil movement. Wax molecules are the Contains normal paraffin in crude oil cycloalkane, branched chain alkane (Golden), and alkane. At the time of use, paraffin wax caused problems there is a direct relationship between crude oil's quantity and its production and transportation the composition of the present and the present itself. It tends to form a cage-like network of wax crystals during temperature decline, liquid fuel is trapped. The movement of crude oil completely ceases at the pour point, resulting in a blockage in the pipelines as a result.

Below the surface, there's paraffin deposition due to the evaporation of lighter components, the crude oil composition changes. Aside from these issues, there is also a huge investment in capital that needs to be made waxy crude oils must also be transported and stored safely it occurs during restart or after pipeline shutdown. Developing difficulties in separating the sol from the gel. Flow through pipeline. Various solvents, dispersants, and other chemicals are used in chemical methods describes the use of surfactants and wax crystal modifiers. Chemicals are used in a variety of industries with the added additives, wax crystals are inhibited from growing and the crystals are not formed smaller crystals occur, where volume to surface ratio is high. During the result is a reduction in wax crystal interlocking, which then lead to a reduction in wax crystals as an example, Chanda (1998) used the point method. It prevents crystallization of wax in polymeric additive beneficiated crude oil, the reactions may be delayed by nucleation, co-crystallization, or adsorption. Mechanism of operation in order for PPDs to work, they have to satisfy at least one of the following steps: nucleation, co-crystallization, adsorption, and enhanced wax dispersion.

Alternatively, it has been suggested that polymeric additive improves flowability surface modification phenomena combined with this is based on the solubility of the compound according to thermodynamics. Polyacrylate is used in the manufacture of a number of products pour point depressants were developed

with comb polymers. analyzed clay nanoparticles made of inorganic clay a nanocomposite is formed when the nanoparticles are introduced into a polymer matrix beneficial effect have been the focus of recent research polymerized nanoparticles. As Yao pointed out, resin stabilized asphaltene and chemical flow improvers work synergistically crude oil/model oil has a decreased pour point, gelation point, and apparent viscosity. In the course of this research, to obtain wax solubility in crude oil, asphaltene is employed. Over the last several decades, many additives have been developed to prevent wax precipitation in order to achieve this goal, a number of sources have been uncovered and synthesized. There has been a recent growth in the number of laboratories a few researchers are working on vegetable oil based chemical additives. In crude oil, naturally derived products reduce the pour point to prevent contamination. A number of additives are being developed by them to produce a better product oils and fatty acids derived from seeds to improve the efficiency of these chemicals, they can be combined with other chemicals. According to using natural products as components is motivated by the following reasons: This reaction occurs when the components react with the appropriate base chemicals as a result, crude oil flow properties can be improved to a higher degree. As a result of free radical polymerization of fatty acids extracted from coconut oil, two new polymeric additives have been prepared in this research article evaluation of maleic anhydride in vegetable oils. Temperature at which wax appears, gelation point, and storage of wax this research involved the determination of modulus, loss modulus, viscosity, microscopic analysis, and wax deposition.

It is believed that the formation of wax crystal is the primary reason for the poor liquidity of crude oil at low temperatures. The course of wax crystallization involves three main processes: nucleation, crystal growth, and agglomeration of wax crystal particles. To form crystal nuclei, supersaturated waxes precipitate from oil phase. When the wax nucleus grows, a lot of them aggregate to make wax crystals. In the wax molecules in the crude oil, the adjacent atoms rotate around the C-C single bond to maintain the constant thermal motion. PPD reduces the interacting forces between wax molecules and reduces the motion order of wax molecules, molecular structures. Polymer pour point depressants interact with wax in several ways through nucleation, adsorption, co-crystallization and dissolution, all of which have a significant influence on the morphology of the wax.

The spin structure of wax molecules is based on wax crystal growth rule this boosts both molecular arrangement and potential energy. Molecules are restricted by each other. During cold weather, the attraction is stronger wax molecules start interacting with each other if the difference between them is greater than the difference between them and oil molecules. As a result of the oil phase precipitating.

At temperatures below WAT, higher-molecular-weight polymeric PPD molecules precipitate and are more readily crystalline than lower-molecular-weight wax molecules assist in the formation of crystals. Due to the fact that polymeric PPDs generally have self-assemble ability which causes aggregates that resemble micelles. Self-assembled structures are more complicated than that of the molecules with a low molecular weight. This process is called polynucleation. Then the bigger sub-critical crystalline nucleus is formed, which is similarly known. Besides inhibiting wax crystal growth, partial shielded crystalline nucleus also reduces super saturation. The flowability of crude oil is improved by a decrease in wax crystal size.

More spherulitic-like crystals appear in crude oil with higher concentrations than long-stick-like crystals or plates-like crystals. With precipitated wax crystals, the solid particles serve as dispersal phase and the liquid serves as continuous phase. The energy of the system is very high, leading to instability of the system in the absence of polymeric PPDs, there is a large interface between the wax crystal and liquid phase, resulting in a large solid-liquid interface.

As a result of this, wax crystals would coalesce and grow into a solid. There is a tendency for wax crystals to form large solid crystals, and then to form three-dimensional networks as a result of the formation of those large solid crystals. It is possible to ensure the high dispersion of wax crystals by adding polymeric PPDs. Polymeric additive molecules and wax crystals form the polar groups on the surface of the eutectic. Substances with low molecular polarity in crude oil are preferentially absorbable onto the eutectic's surface. According to secondary layer which is also called solvation layer is induced by the adjacent first layer, it exists at the top.

2. EXPERIMENTAL WORK

2.1 Materials

Castor oil and sunflower oil, collected for the extraction of ricinoleic acid and linoleic acid, respectively came from the local market.

2.1.1 Castor Oil

Ricinus communis, a member of the spurge family (Euphorbiaceae), is the plant that produces castor beans, which are used to make castor oil, also known as ricinus oil. It is employed in the production of synthetic resins, plastics, textiles, paints, varnishes, and wide range of other substances, including plasticizers and drying oils.

2.1.2 Sunflower Oil

Sunflower oil is the non-volatile oil is extracted from the sunflower seed. Both as a frying oil and an emollient in cosmetic applications, sunflower oil is frequently utilized the food. The bulk of the lipids in sunflower oil are oleic acid and the monounsaturated fatty acid linoleic acid.

2.1.3 Ricinoleic Acid

A fatty acid, Ricinoleic acids is also known as 12-hydroxy-9-cis-octadecenoic acid. It is a hydroxy acid and an unsaturated omega-9 fatty acid. It is a key ingredient in the seed oil made from the seeds of the castor plant and is also present in the sclerotium of ergot.

Formula: $C_{18}H_{34}O_3$

Molar mass: 298.46 g/mol

Classification: Fatty acid

Density: 0.945 g/cm^3

2.1.4 Linoleic Acid

Linoleic acid is an organic compound with the formula COOH(CH2)7CH=CHCH2CH=CH(CH2)4CH3. Both alkene groups are cis. It is a fatty acid sometimes denoted 18:2 (n-6) or 18:2 cis-9,12. A linoleate is a salt or ester of this acid.

There is a high consumption of PUFAs in humans, especially linoleic acid. The fate of linoleic acid depends on consumption. Energy can be derived from fatty acids. You can convert it to triacylglycerols, phospholipids, and cholesterol esters by esterification. In order to maintain a certain level of waterproofing in other words, a certain level of fluidity in the membrane is maintained by linoleic acid as part of membrane phospholipids Skin (epidermis). The product can also be enzymatically oxidized by enzymes after it has been released from membrane phospholipids 13-hydroxy or 13-hydroperoxy octadecadienoic acid derivatives involved in cell signaling. In addition to a number of bioactive v6 PUFAs, linoleic acid can be elongated and desaturated into g-linolenic acid and other bioactive v6 PUFAs that are particularly useful as anti-inflammatory agents' Arachidonic acid is subsequently released into the body. As a result of its conversion into a myriad of bioactive compounds particularly prostaglandins and leukotrienes, it is called an eicosanoid.

When persistently produced in excess, these eicosanoids contribute to a number of diseases, from heart disease to diabetes. Inflammatory diseases and cancer are common chronic diseases. This is what it is Linoleic acid has received the most attention due to its conversion to arachidonic acid.

Enterocytes absorb the nutrients after consumption. A chylomicron is formed from linoleic acid in the small intestine, which is packaged into phospholipids, triacylglycerols, or cholesterol esters, and this enters the subclavian vein (the subclavian vein carries the thoracic duct). A combination of hepatic and pancreatic cells receives linoleic acid. A chylomicron as a part of its transition to much smaller remnant particles is delipidated in extrahepatic tissues as chylomicrons are delipidated enroute to and cleared by the liver. Uptake occurs in cells as a result of the requirements of the tissue, linoleic acid decides where it shall live. Desaturation and elongation of membrane phospholipids are some examples of these processes. The 12th and 9th carbons of linoleic acid contain double bonds, making it an essential (indispensable) nutrient Carbonyl groups are formed by adding oxygen to carbonyl groups. In order to prevent human error, The ninth carbon of a fatty acid is the carbon after which a double bond can be incorporated Fat, not synthesized, must be acquired. As a result. Linoleic acid is ceramide component transdermal water is maintained by acid.

2.2 Apparatus

The reaction was carried out in a three-necked round bottom flask equipped with a Dean-Stark collection apparatus the water from the reaction. The reaction was carried out in presence of toluene solution and sulfuric acid catalyst. The reaction was carried out at reflux temperature. the water released from the reaction was collected in a Dean-Stark apparatus.

2.3 Synthesis of Pour Point Depressant

Experimental Setup was prepared to synthesize ester from Linoleic acid and Behenyl Alcohol which was taken into 3 necks round bottom flask with the addition of Toluene, the round bottom flask was equipped with condenser. The reaction was heated to 110°C with continuous stirring for 8-9 hours. The reaction mixture was separated and washed with warm deionised water. Then dry the product and then was reacted with Natural oil (sunflower and castor oil) to synthesize the Pour Point depressant. The second step was carried out at 90^0C under Nitrogen with prepared ester, sunflower oil or castor oil and 100ml toluene. The Synthesized PPD was then characterized by GPC and IR.

Fig 1: Esterification Process

3. RESULT AND DISCUSSION

We synthesized two different Pour Point Depressants (PPDs) with linoleic acid and natural oils. The pour point depressants (PPDs) we synthesized are to be experimented on the crude oil which reduces the Pour Point of the crude oil. Synthesized products are able to improve the flow characteristics of crude at low temperature by substantially reducing Pour Point and viscosity of crude oil.

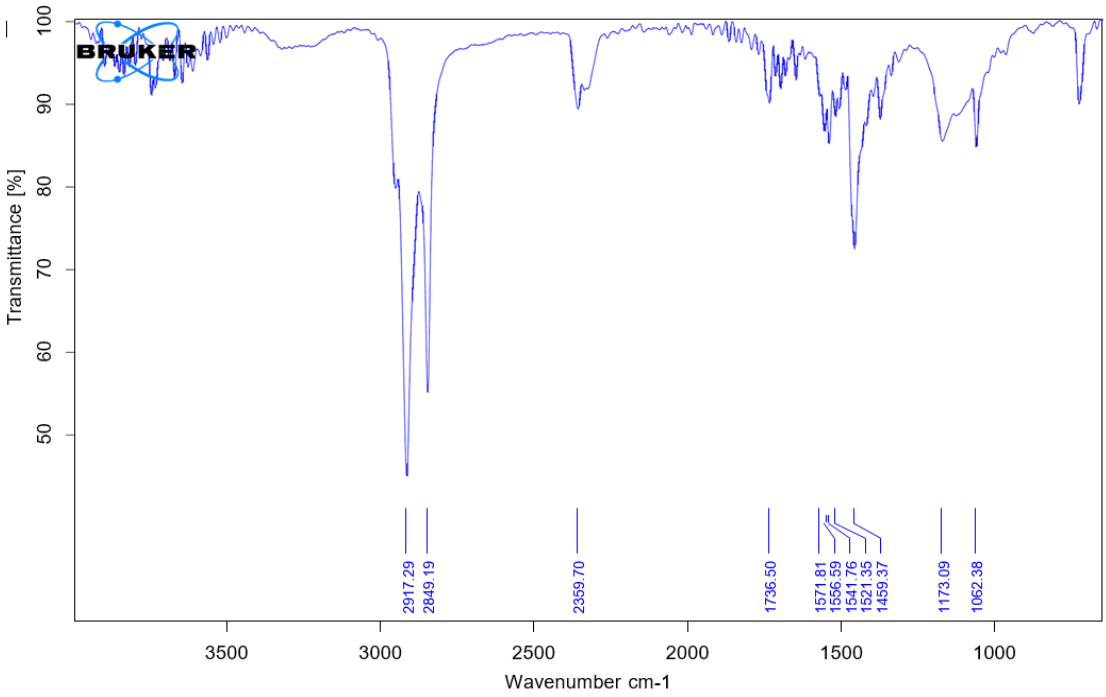

Fig 2: FTIR spectra of ester

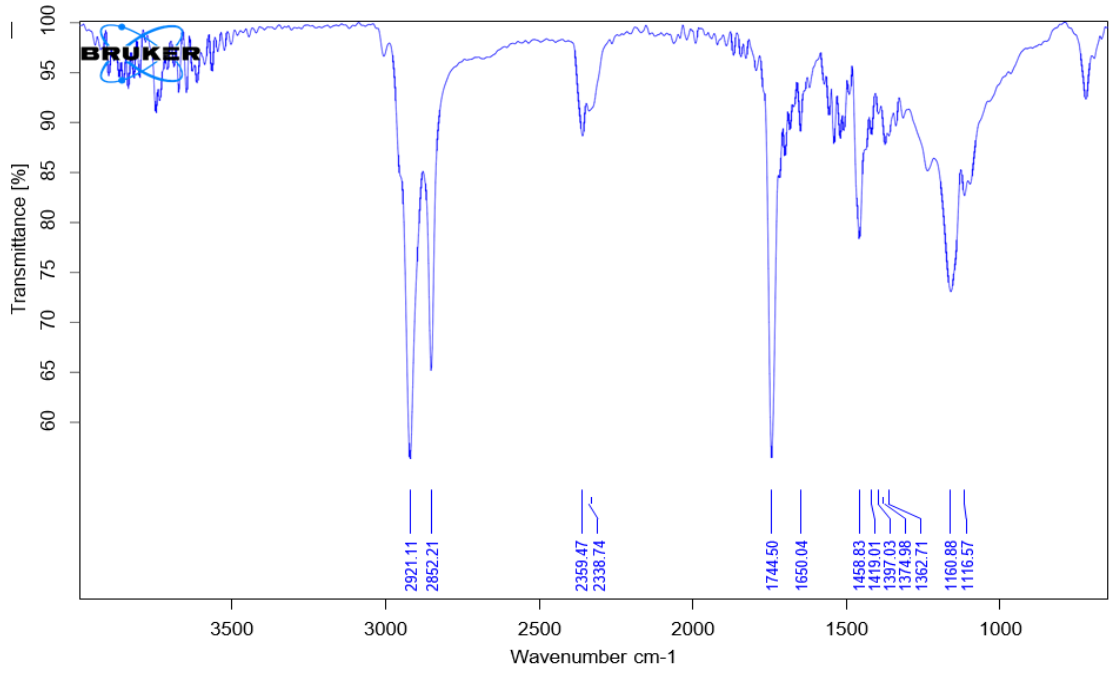

FIG 3: FTIR spectra of castor oil

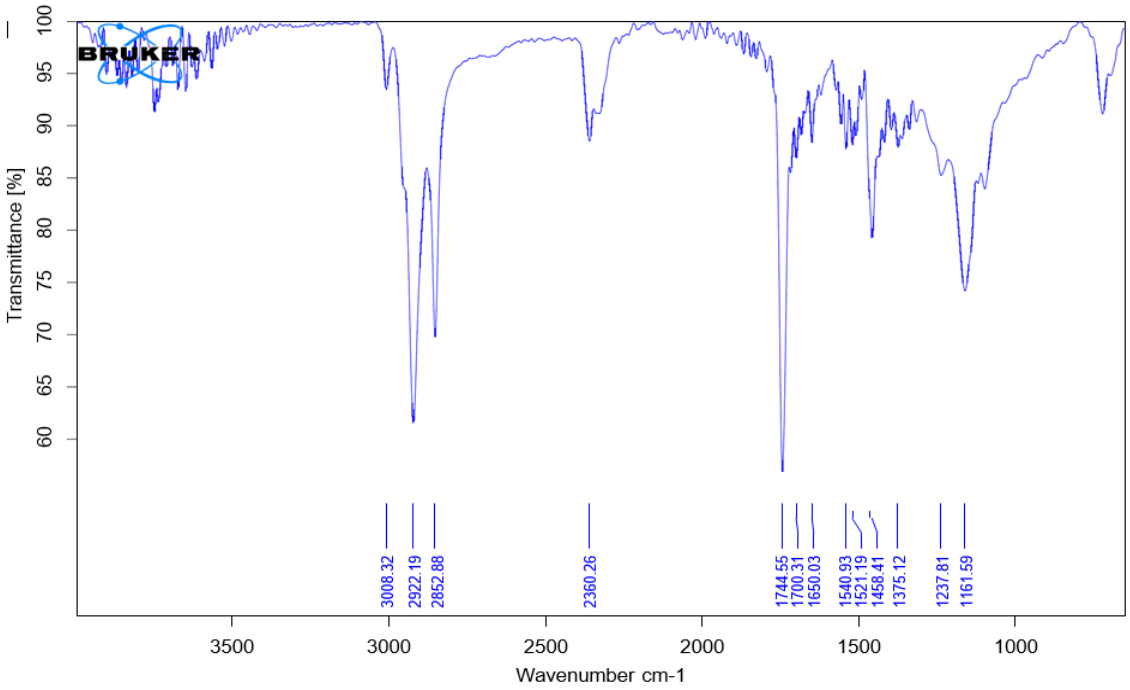

Fig 4: FTIR spectra of sunflower

Analysis of the Wax Crystal Structures in Waxy Crude Oil Beneficiated With and Without a PPD

A micrograph of wax crystals in fresh raw Limbadara shows the wax crystal aggregates in oil enriched with a concentration of 500 ppm U-22 PPD at room temperature. The wax crystals have a corresponding homogeneous size distribution and a high degree of particle dispersity. This imposes a high surface energy on fresh crude oil and therefore wax crystals tend to easily combine into a three-dimensional lattice structure under intense cooling or high shear stress, which affects the behaviour of flow of waxy crude oil. Individual wax crystals grow larger and tend to cluster together, increasing the area unoccupied by particles. In addition, the formation of a three-dimensional network structure requiring more precipitated paraffin, the low temperature fluidity of the treated oil is improved.

The evaluating test of pour point

The physicochemical properties of these pour point depressors. It was determined that there were certain characteristics. Prepare a flask with a capacity of 250 mL an oil sample of 100 mL of crude oil was heated using a condenser and an electric stirrer. There is a significant impact of the previous thermal and shear history. For 15 minutes, immerse in warm water at 50 degrees Celsius, water was removed from the flask**.**

A temperature of 35 degrees Celsius was reached in the bath and its contents. A pour point tube was then loaded with additive-treated crude oil.

4. CONCLUSION

Wax precipitation is responsible for crude oil characterization the crude oil studied has a significant flow assurance issue. It was evaluated that polymeric additives were effective pour point depressants, which reduced oil thickness, freezing time, and viscosity. Flow was also improved by the PPDs. In this way, wax is greatly reduced from being deposited on the crude oil lines through tubing. A dispersion of wax crystals was also achieved after the two PPDs were applied. The crude oil is thus prevented from precipitating from the microscopic analysis and thus can be used as flow improvers.

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REFERENCES

[1] M.G. Botros (1997). U.S. Patent 5,681,359, October 28, 1997.

[2] C. Chang, D. Ngyuen, H.P.J. Rønningsen, J. Non-Newtonian Fluid Mech. 87 (1999) 2, 127–2, 154.

[3] J.C. Chen, (1985). U.S. Patent 4,512,775, April 23, 1985.

[4] L.-M. Dong, S.-W. Xie, Acta Petroeli Sinica Chinese (Petroleum Processing Section) 12 (4) (1996) 66.

[5] I.E. El-Gamal, A.M. Atta, A.M. Al-Sabbagh, Fuel 76 (14/15) (1997) 1471–1478.

[6] I.M. El-Gamal, T.T. Khidr, F.M. Ghuiha, Fuel 77 (5) (1998) 375–385.

[7] Emanuele Vignati, Roberto Piazza, Ruben F.G. Visintin, Romano Lapasin, Paolo D'Antona, Thomas P Lockhart, J. Phys.: Condens. Matter 17 (2005) S3651–S3660.

[8] N. Feldman (1980). U.S. Patent 4,184,851, January 22, 1980.

[9] N. Feldman, J.J. Habeeb (1992). U.S. Patent 5,094,666, March 10, 1992.

[10] G. Gavlin, E.A. Swire, S. Jones Jr., Indian Eng. Chem. 45 (1953) 2327.

[11] G.A. Holder, J. Winkler, J. Inst. Pet. 51 (1965) 228.

[12] S. IInyckyj, B. Charles (1962). U.S. Patent 3,048,479, August 7, 1962.

[13] S. IInyckyj, C.O. Cole (1976). U.S. Patent 3,961,916, June 8, 1976.

[14] S. IInyckyj (1979). U.S. Patent 4,147,520, April 3, 1979

[15] Karen S. Pedersen, Hans P. Rønningsen, Energy & Fuel 14 (2000) 43–51.

[16] N.A. Kidd (1982). U.S. Patent 4,362,533, December 7, 1982.

[17] L.I. Rossemyr, Indian Eng. Chem. Prod. Res. Dev. 18 (1979) 227–230.

[18] E.F. Lorensen, W.A. Hewitt, ACS Div. Pet. Chem. 7 (4) (1962) 61.

[19] K. Liao, Y. Zhai Pet, Sci. Technol. 17 (1&2) (1999) 51.

[20] H. Pieter, H. Rodolf (1973). U.S. Patent 3,726,653, April 10, 1973.

[21] H.P.J. Rønningsen, Pet. Sci. Eng. 7 (1992) 177–213.

[22] R. Venkatesana, N.R. Nagarajanb, K. Pasoa, Y.-B. Yic, A.M. Sastryc, H.S. Foglera, Chem. Eng. Sci. 60 (2005) 3587–3598.

[23] Elsharkawy AM, Al-Sahhaf TA, Fahim MA. Wax deposition from Middle East crudes. Fuel 2000;79:1047–55.

[24] Hunt A. Uncertainties remain in predicting paraffin deposition. Oil Gas J 1996;7:96–103.

[25] Bernadiner MG, Advanced asphaltene and paraffin control technology, SPE paper no. 25192 presented at the Int. Symp on oilfield Chem New Orleans LA 1993; 2–5.

[26] Marie E, Chevalier Y, Eydoux F, Germanaud L, Flores P. Control of n-alkanes crystallization by ethylene-vinyl acetate copolymers. J.Colloid Interf Sci 2005;290:406–18.

[27] Pedersen KS, Ronningsen HP. Influence of wax inhibitors on wax appearance temperature, pour point, and viscosity of waxy crude oils. Energy Fuels 2003;17:321–8.

[28] Srivastava SP, Tandon RS, Verma PS, Saxena AK, Joshi GC, Phatak SD. Crystallization behavior of n-paraffins in Bombay-High middle-distribution wax/gel. Fuel 1992;71:533–7.

[29] Zhang FS, Wang B. Studies on the mechanisms involved in pour point depressant and viscosity deduction by some pour point depressants/viscosity reducers. Oilfield Chem 1995;12:347–52.

[30] Holder GA, Winkler J. Crystal-growth poisoning of n-paraffin wax by polymeric additives and its relevance to polymer crystallization. Nature 1965;207: 719–21.

[31] Randolph AD, Larson MA. Theory of particulate processes. analysis and technique of continuous crystallization. New York: Academic Press; 1988. pp. 129–32.

[32] Rubin IDM, Munmaya PRD, Pour point and flow improvements in lubes. The interaction of waxes with methacrylate polymers. SAE Technical paper series, 1991; 1–10.

[33] Qian JW, Qi GR, Ding XZ, Yang SL. Assessment of polymer flow improvers for crude oil by viscometry. Fuel 1996;75:307–12.

[34] Qian JW, Qi GR, Han DL, Yang SL. Influence of incipient chain dimension of EVA flow improver on the rheological behavior of crude oil. Fuel 1996;75:161–3.

[35] Hu J, Zhang LG, Dai YC. New pour point depressants-molecule design, synthesis and performance mechanism. Acta Pet Sinica 1996;12:73–9.

[36] Wang B, Zhang HB, Zhang FS. A study on a new type pour point depressant used for crudes. Acta Pet Sinica 1998;19:97–102.

[37] Ding XZ, Qi GR, Yang SL. Thermodynamic analysis for the interaction of polyacrylate with wax in heptane. Polymer 1999;40:4139–42.

[38] Zhang JL, Wu CJ, Li W, Wang YP, Han ZT. Study on performance mechanism of pour point depressants with differential scanning calorimeter and X-ray diffraction methods. Fuel 2003;82:1419–26.

[39] Ashbaugh HS, Guo XH, Schwahn D, Prudhomme RK, Richter D, Fetters LJ. Interaction of paraffin wax gels with Ethylene vinyl acetate copolymers. Energy Fuels 2005;19:138–44.

[40] Aboul Gheit AK, Abd-el-Moghny T, Al-Eseimi MM. Characterization of oils by differential scanning calorimetry. Thermochim Acta 1997;306:127–30.

[41] Meihua Bi, Development and Application of CE Crude Pour-Point Depressant. Oilfield Surface Eng. 1992; 11: 44–46.

[42] Feng Ou. Handbook of petroleum products application technology. Publishing House of Oil Industry, 1984.

[43] Pauly J, Dauphin C, Daridon JL. Liquid-solid equilibria in a decane+multiparaffins system. Fluid Phase Equilib 1998;149:191–207.

[44] Chevallier V, Petitjean D, Bouroukba M, Dirand M. Mixtures of numerous different n-alkanes: 2. Studies by X-ray diffraction and differential thermal analysis with increasing temperature. Polymer 1999;40:2129–30.