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Synthesis of Poly-Hydrazide from Canola Oil and Use as Flow Improver for Crude Oil

Qiang DENG[1], Yun BAI[1], Xue-Fan GU[1,a], Gang CHEN[1, b *], Zhi-Fang ZHANG[2]

[1]College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an 710065, China

[2]School of Chemistry and Chemical Engineering, Yulin University, Yulin 719000, China

[a]xuefangu@xsyu.edu.cn, [b]gangchen@xsyu.edu.cn

*Corresponding author

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Abstract. In this work, poly-hydrazide (PH) is designed and prepared from vegetable oil, hydrazine hydrate and dichloroethane. Nitrogen atoms are fixed in the main chain of the polymers to modify the polarity. The effectiveness of the PHs on four crude oil was tested as pour point depressants as well as paraffin inhibiters. The results showed that the highest pour point reduction depression was achieved as 10.6℃. The paraffin crystal morphology studies were conducted on simulated crude oil to elucidate the mechanism of pour point reduction.

Introduction

Petroleum containing n-paraffin waxes tends to be separated from the oil in low temperature. The waxes generally crystallize as an interlocking network of fine sheets, thereby entrapping the remaining fuel in cage-like structures. The lowest temperature at which crude oil can still flow is generally known as the pour point. Crude oil contains a wide range of hydrocarbon components with extremely differing physical properties, in which the flow properties play the most important role in its production, storage, transport and refining [1, 2]. Especially under deep water or in cold weather, crude oil production will encounter severe operational problems, in which the main one is a wax blockage with serious economical consequences due to possible obstruction of flow pipes or production lines [3, 4]. Waxes are mixtures of hydrocarbons constituted of linear/normal chains, comprising mainly from 20 to 40 carbon atoms, in addition to alkanes with branched and cyclic chains[5,6]. The lowest temperature at which crude oil can still flow is generally known as the pour point. Therefore, it is very important to minimize the adverse effects of wax on the flow properties of crude oil[7].

Several options are available in practice, which include blending with lighter oil, stream heating, mechanical scraping and use of chemical additives [8]. Among these methods, pretreatment of the crude oil with flow improver (FI), pour point depressants (PPD) and paraffin inhibitors (PI) are the most acceptable due to their convenience and economy [6,9,10]. FIs can modify the size and shape of paraffin crystals and inhibit the formation of large crystal lattices [11]. They typically have a wax-like paraffinic part inclining to co-crystallize with paraffin and a polar part limiting the degree of co-crystallization [9,12]. Polyethylene derivatives with these characteristic structures are the most popular flow improvers and pour point depressants, such as homo and copolymers of alpha olefins, ethylene-vinyl acetate, alkyl acrylates and methacrylates, alkyl esters of styrene, maleic anhydride and alkyl fumarate-vinyl acetate [6, 9,10,12]. Although these polymers display perfect performance for many crud oil samples from global, flow improvers are very selective, in other word, no additives are sufficiently effective for every crude oil [13], besides, the long molecular chain, large molecular weight and high thermo stability is a serious problem in oil refines process [14,15].

In this work, we will report the design, preparation and evaluation of new flow improver (poly-hydrazide, PH) beginning with vegetable oil and hydrazine hydrate (as shown in Scheme 1), and the performance as crude oil pour point depressants and paraffin modifier were investigated.

Experimental

Materials

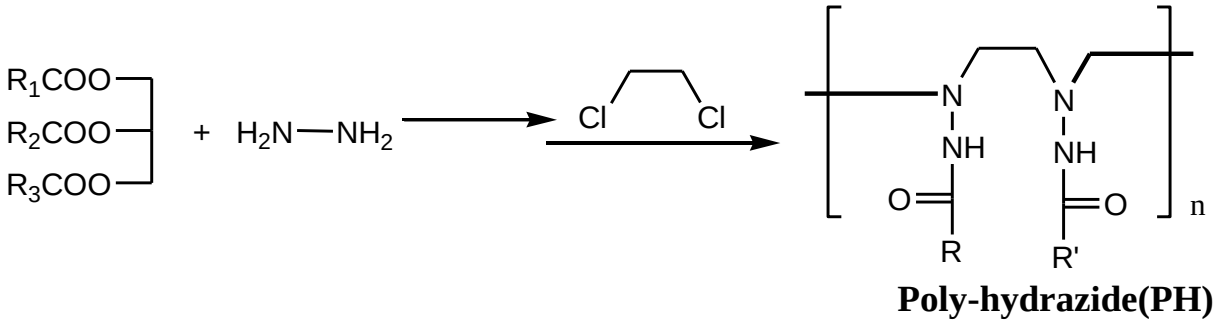
Canola oil and soybean oil were purchased from Xi'an Hengshun Oil and Grease Limited Company. All chemicals were purchased from Sinopharm Chemical Agent Co., Ltd. The four crude oil samples were produced from Nanyang Oil Field of China, and the main properties were shown in Table 1. Four compound groups, namely, saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (SARA), were separated by the column chromatography-based method according to industrial standard of China Petroleum SY/T 5119.

Tab. 1 Physical properties of the crude oil samples

Crude Oil	1	2	3	4
Pour point ℃	47.7	45.2	35.5	34.5
Density kg/m^3 (50℃)	830	922	895	885
Viscosity mPa·sec (50℃)	60.32	95.80	58.55	102.55
Salinity mg/L	591.50	859.60	335.65	691.85

Preparation of Poly-Hydrazide

Pretreated canola oil/ soybean oil and hydrazine hydrate solved in ethanol were added in a flask with the 1.1: 1 molar ratio of the ester group to amino group. 10wt% K_2CO_3 was added as catalyst, and the mixture was stirred under refluxing for 4 h. Then K_2CO_3 was removed by filtration, and dichloroethane was added under stirring with the 1.1 quantum of hydrazine hydrate. After refluxing for another 4 h, the solvent and the extra dichloroethane were distilled off under reduced pressure, and the poly-hydrazide (PH1/PH2) flow improver were obtained from further purification of the residues by washed with methanol.



Scheme 1 Synthesis of poly-hydrazide

Evaluation the Effect of Ph on Crude Oil

0.1 wt% xylene solution of PH was prepared firstly, according to ASTM, D 97-96 method, the solution was injected into the waxy crude oil with different volume and tested as pour point depressants, and a control experiment was carried out at the same time. The initial temperature is set at 2.0℃ above the temperature at which the oil became solid [15], and the detection limit is 0.1℃. Each test run was repeated three times to check repeatability and the maximum errors of the product distribution fell within a reasonable range of ±2.0%. Only the average data were reported hereinafter. The paraffin crystal in the saturated hydrocarbons of the heavy oil before and after aquathermolysis was examined under a BX41-P OLYMPUS polarizing microscope at temperature of 5℃.

Results and Discussion

The influence of the 500ppm PHs on the pour points of four crude oil samples from Nanyang Oil Field of China was tested, and the results were summarized in Table 1. From the table, it can be found that the two PH can reduce the pour points about under this low concentration for almost every sample. For 1# and 2#, PH1 is more effective than that of PH2, but in 3# and 4# PH2 is more effective. In all these results, the highest pour point depression, 10.6℃, was obtained by using PH1 in 2# crude oil.

Tab. 2 Effect of PH on the pour point of crude oil

PH	Δ pour point (℃)			
	1#	2#	3#	4#
PH1	3.5	10.6	8.3	6.6
PH2	2.6	7.5	9.2	7.1

Generally, a cold flow improver contains an oil-soluble long-chain alkyl group and a polar structure moiety in the molecular structure. The long-chain alkyl group can insert into the wax crystal in the fuels, and the polar moiety exists on the surface of the wax crystal, thereby inhibiting the crystal lattice formation and reducing the waxes crystal size[16]. The effect of PHs concentration on the pour point of 2# crude oil was screened in the following work, and the results were summarized in Figure 1. From this figure, it can be found that PH1 and PH2 are low effective under lower concentration (50-200ppm), and as the concentration increases up to 500 ppm, the pour point can be depressed by 10.6℃, further increase of the concentration will not depress the pour point effectively, so the proper concentration is 500 ppm.

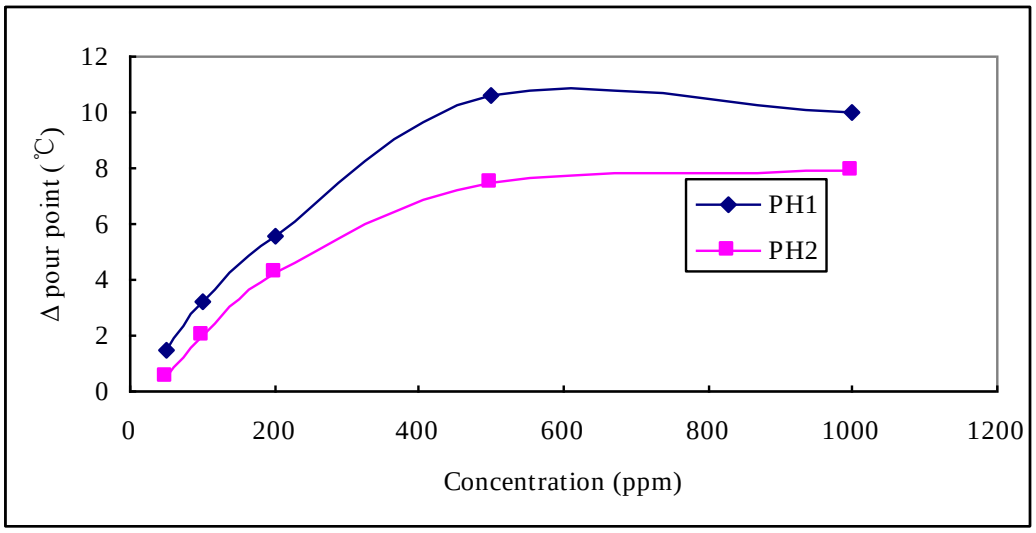


Fig. 1 The effect of PH concentration on the pour point of 1# and 2# crude oil samples

Below the pour point of the crude and processed oils, paraffin crystals will deposit and tend to plug flow lines and filters. The saturated hydrocarbons were separated and the effect of PH1 on it was investigated. Visual observations suggest that paraffin crystals are larger size and more numerous in the crude heavy oil (a) than after being processed (b), as shown in Figure 2. This may suggest that some of the longer paraffinic chains were also decomposed in the aquathermolysis reaction[16].

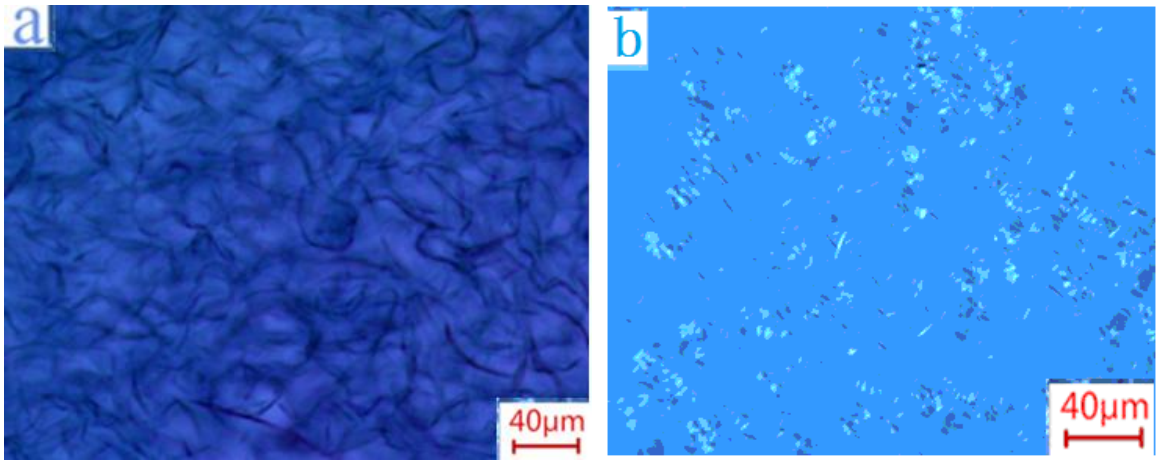


Fig. 2 Photography of paraffin crystal in saturated HC of the heavy oil before (a) and after (b) adding PH1

Conclusion

A series of poly-hydrazide (PH) was prepared by free-radical polymerization. The PAEs were used as pour point depressant for crude oil from Yumen Oil Field. PH1 and PH2 showed potent activity for 2#, 3# and 4# samples under the concentration of 500 ppm. Further study of the effect of the concentration on the pour point showed the proper concentration is 500 ppm. Besides, the added PH1 can modify the paraffin crystal of saturated HC, which indicates the poly-hydrazide can interact with the paraffin to improve the flow property.

Acknowledgments

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