Fuel Processing Technology 128 (2014) 349–353

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Novel high-molecular multifunctional reagent for the improvement of crude oil properties

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ARTICLE INFO

Article history:
Received 11 February 2013
Received in revised form 25 July 2014
Accepted 26 July 2014
Available online xxxx

Keywords:
Water–oil emulsion
Demulsifier
Depressor

ABSTRACT

New high-molecular nonionic surfactant "SMATWEEN" was synthesized by catalytic esterification of styrene-co-maleic anhydride copolymer (styromal) with polyoxyethylene sorbitantrioleate (Tween-85) and used as a demulsifier and depressant for multiple high-paraffinic oils from Kazakhstan oilfields. The structure of the synthesized surfactant was studied and proven.

The high demulsibility efficiency of new macromolecular surfactant was shown. It was found that it is necessary to enter the demulsifier SMATWEEN before the pour point. Rheological parameters of the reagent show improvement by introducing it in high-paraffinic oil before the crystallization of the most high-molecular paraffins.

1. Introduction

Crude oil by process of oilfield exploitation includes water, which generates a stable water-in-oil or oil-in-water emulsion. The dispersion process of water droplets in the oil emulsion is followed by the presence of surface-active reagents in crude oil, such as asphaltenes, paraffins, resins, naphthenic acids and small particles of clays, silica and salts [1]. It was found that the concentration of these natural surfactants is higher in the heavy oils than in light oils [2].

Preparation of oil is an important step in the process of oilfield exploitation, as it influences the price and quality of commercial oil and oil products. The formation of stable oil–water emulsions reduces the efficiency of preparation of oil transportation and the efficiency of refinery process [3].

Most of the crude oil from Kazakhstanian oilfields is high-paraffinic and resinous. Water content in oilfields reaches 20–80% and causes significant problems in the preparation of oil transportation.

Applied destruction methods of oil–water emulsion are based on the heating methods or methods of addition of chemical additives (demulsifiers). The used reagent plays the role on both as a depressant and as an inhibitor of paraffin precipitation [4].

At the present time, the main method of oil preparation is chemical demulsification. Chemical demulsification is the most important property of a demulsifier, i.e. its ability to ensure maximum depth of oil dehydration at a minimum flow and processing temperature. The effect of chemical demulsifiers decreased by the transferring of oil components to the oil volume [5]. Numerous studies show the highest efficiency of reagents in which hydrophobic groups compared with hydrophilic ones [6–11].

The study of technical and patent literature has allowed the definition of the search path of raw materials and conditions of the synthesis of the new demulsifier. The method of catalytic esterification of styrene and maleic anhydride copolymer with polyoxyethylene sorbitan trioleate was developed. As a result of the synthesis new high-molecular surface active agent "SMATWEEN" was obtained, which combines functions of demulsifier and depressant additives. Comprehensive laboratory testing of the reagent on high-paraffinic oil of Kazakhstan oilfields was studied.

This article presents the results of laboratory tests of "SMATWEEN" on water–oil emulsion of Kyzylkiya and Kenlyk oilfields, commercial oils of Kumkol and Akshabulak oilfields of South Turgai basin of the Republic of Kazakhstan.

2. Experimental section

2.1. Materials and methods

All reagents were purchased from Sigma-Aldrich and used as received without additional purification. Fourier transform infrared (FTIR) spectra were recorded with a Shimadzu FTIR-8400. Spectra were taken with a resolution of 4 cm^{-1} and were averaged over 320 scans. Scanning was carried out from 4000 to 400 cm^{-1}. ^{1}H nuclear

Abbreviations: Stiromal, styrene-co-maleic anhydride copolymer; Tween-85, polyoxyethylene sorbitantrioleate; GOST, State Standard of the Republic of Kazakhstan.

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http://dx.doi.org/10.1016/j.fuproc.2014.07.039
0378-3820/

magnetic resonance (NMR) and ^{13}C NMR spectra were recorded in deuterated dimethylsulfoxide on a Bruker Avance-3-400 spectrometer and were averaged over 120 scans. The chemical shifts were recorded in δ relative to the residual solvent peaks at 2.50 ppm (^1H for $(CD_3)_2SO$) and 39.5 ppm (^{13}C for $(CD_3)_2SO$).

2.2. Sample characteristics

Oil samples obtained from oilfields in South Turgai basin and South Mangishlak basin of the Republic of Kazakhstan. The samples were characterized by the standard procedures: ASTM D445-01 (American Petroleum Institute (API) kinematic viscosity) [12], ASTM D5453-05 (sulfur content) [13], ASTM 5853 (pour point) [14], GOST 8 559-2003 (State Standard of the Republic of Kazakhstan) (the density and volume of oil) [15], GOST 1756 (determination of saturated vapors pressure) [16], GOST 21534-76 (the content of chloride salts) [17], GOST 6370 (mechanical impurities content) [18], GOST 2477-65 (water content) [19] and GOST 20287-91 (flow point temperature) [20].

2.3. Demulsification test

Evaluation of the effectiveness of the synthesized nonionic surfactant was carried out by Bottle Test.

2.3.1. Bottle test

Graduated glass test tube of 100 ml poured with natural water–oil emulsion. Synthesized demulsifier was added to the emulsion at various concentrations (30 g/t, 60 g/t, 90 g/t). The tube content was mixed 5 min and stored in a water bath at 60 °C for 1 h. Aliquots of experimental samples were taken after 5, 10, 20, 40 and 60 min. Calculation of received data performed by the following formula: WS (vol.%) $= V/V_o * 100$ where, WS (vol.%) — the degree of demulsification in %, V — volume of released water in ml, and V_o — water emulsion volume in ml.

2.4. Estimation method of depressant reagents effectiveness

Pour point was determined according to ASTM 5853. Kinematic viscosity measurement was performed according to ASTM D445.

2.5. Depressants agent injecting method

The calculated amount of depressant was injected into the sample which was heated up to 60 °C. The sample was mixed by an electromechanical mixer at a given temperature for 30 min. Then the mixed sample was cooled to 20 °C and further measurements were carried out.

2.6. Synthesis of nonionic "SMATWEEN" surfactant

Reaction was carried out in three-necked flask equipped with stirrer, reflux condenser, thermometer and connecting pipe to enter the catalyst, solvent and diluent. 0.001 mol of copolymer of styrene and maleic anhydride (stiromal) was dissolved in 0.001 mol of dimethylsulfoxide. Then polyoxyethylene sorbitan trioleate (Tween-85) was gradually added to the flask through the connecting pipe. The molar ratio of maleic anhydride and Tween-85 was 1:1. 0.002 mol of pyridine catalyst was injected to the reaction flask. The temperature was raised to 110 °C and this temperature was maintained for 2 h with constant stirring and temperature control. Solvent vapors were trapped in a condenser (refrigerator) and poured back into the flask. After reaction copolymer was precipitated in diethyl ether and was dried in a vacuum oven to constant mass.

3. Results and discussion

3.1. Chemical analysis of formation water from Kyzylkiya and Kenlyk oilfields

The data on chemical analyses of formation water of Kyzylkiya and Kenlyk oilfields are shown in Table 1.

Results show that the formation water of Kyzylkiya and Kenlyk oilfields contains a mixture of salts of sodium, potassium, calcium and magnesium in different concentrations. And it can be attributed to calcium chloride and low pH of formation water and cause high corrosion activity. The content of sodium chloride, magnesium and calcium dissolved in formation water mixture depends significantly on the oil fields.

3.2. Oil characteristics

Oil emulsions of Kyzylkiya and Kenlyk oilfields, commercial oil of Akshabulak, commercial oil of Kumkol oilfields, commercial oil mixture of Kumkol-Akshabulak (60:40) and commercial oil of Zhetybai oilfield were used to the study of high-molecular multifunctional reagent. Physical–chemical characteristics and chemical composition of oils are shown in Tables 2 and 3.

It was found that samples of South Turgai basin oils are high-paraffinic, low-sulfuric and low-resinous (Tables 2 and 3 [21]). According to the State Standard R 51858-2002 [22] oil from South Turgai basin is classified to special light oil type. Oils of Zhetybai oilfields of South Mangishlak basin are high-paraffinic, low-sulfuric, medium resinous and according to the State Standard R 51858-2002 classified as light oil. Due to the high content of paraffins, oils of South Turgai basin have high pour point. There are characteristic features for the high-paraffinic and resinous oil of Zhetybai oilfield of South Mangyshlak basin – high viscosity and level of density, acceptable flow characteristics only at high temperatures.

Therefore, transportation of such crude oils in the spring, autumn and winter is difficult and can lead to a shutdown of the pipeline.

3.3. Demulsifying and desalting activity of SMATWEEN

Demulsifying and desalting activity of synthesized high-molecular nonionic surfactant was investigated on natural water–oil emulsions of Kyzylkiya and Kenlyk oilfields of South Turgai basin of the Republic of Kazakhstan. Water contents in oil emulsions of Kyzylkiya oilfield were 43% and 29% in Kenlyk oilfield. Fig. 1 shows the dependence of dewatering degree on sedimentation temperature of water–oil emulsions with synthesized reagent. Fig. 1a shows that the reagent "SMATWEEN" exhibit fairly good activity at 25 °C for Kenlyk oilfield

Table 1
Chemical analysis of the formation water of Kyzylkiya and Kenlyk oilfield.

Sample		Kyzylkiya	Kenlyk
Density, kg/cm^3		1.052	1.082
Refraction coefficient		9.4	13.8
pH		6.14	6.11
Anions, mg/l	Cl^-	56,090.0	85,200.0
	SO_4^{-2}	480.3	292.2
	CO_3^{-2}	Absent	Absent
	HCO_3^-	259.2	183.0
Cations, mg/l	Ca^{+2}	5931.8	9218.4
	Mg^{+2}	875.5	1751.0
	$Na^+ + K^+$	28,243.5	41,577.5
General mineralization, mg/l		91,880.3	138,222.1
Ba^{+2}		891.0	1684.5
General hardness, mg-equiv/l		368.0	604.0
General Fe content, mg/l		Absent	Absent
Temperature °F		70	70
Resistance Om-m^2/m		0.11	0.16