Flow improver additives for gas condensate

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Abstract

This paper describes synthesis and evaluation of polymeric additives for improving the flow properties of gas condensate. The additives were prepared by the free-radical initiated polymerization of methacryl esters with styrene and acrylic or methacrylic acid. Polymerization was performed by initiator azo-bis isobutyronitrile in toluene or xylene at 80 °C. The influence of additives structure, composition and molar weight, as well as gas condensate properties on its flow properties was studied. Gas condensate samples from the fields of Kalinovac, Stari Gradac and Molve located in the northern Croatia were used for evaluation of the prepared additives. It was found that the additives efficiency was considerably influenced by their properties and by condensate n-paraffin content and distribution.

Keywords: Gas condensate; Flow improver; Polymeric additives

1. Introduction

Natural gas condensate is a by-product of natural gas. Hydrocarbon fractions, which are liquid at standard temperature and pressure, can if sufficiently light, become gaseous at high pressures of natural gas fields. When the gas is removed from the field and pressure reduced, some of the heavier fractions condense depending on the pressure. The liquid condensate can be refined like light crude oil. The condensate composition generally depends on the production field. Since the beginning of the 80s in the last century, INA-INDUSTRIJA NAFTE d.d., Zagreb, Croatia has been producing gas condensate from the fields of Molve, Kalinovac and Stari Gradac (St Gradac) situated in northern Croatia. The condensate samples differ in properties including distribution of n-paraffin content (up to C_{37}). The absence of heavier fractions (especially resins and asphaltenes) facilitates an unhindered paraffin crystallization causing gelling of condensate in installation facilities. Such behaviour is also characteristic of paraffinic crude oil,

therefore the problems concerning paraffin deposition in condensate and crude oil are usually treated in the same way. A separate treatment of condensate is also described in the literature [1–5]. It is well known that the presence of long-chain normal paraffin in crude oil and derivatives, as well as in gas condensate is responsible for the precipitation at near-ambient temperature that affects the bulk stream, characteristics, and influences the flow properties. In order to counteract the problems caused by n-paraffin deposition, several options are available, namely various mechanical, thermal and chemical means [6,7]. In most cases, paraffin problems can be resolved efficiently and economically with chemical products [8]. Paraffin precipitation may be treated chemically with solvents, dispersants and inhibitors (crystal modifiers, crystal distorters, wax modifiers). A preferred option would be to use wax modifier additives, commonly known as pour point depressants (PPDs), which are designed to improve cost- effectively the cold-flow properties of crude oil, gas condensate and derivatives. These compounds do not dissolve, disperse or remove paraffin that has already been deposited. They are applied in either continuous or squeeze-type treatment to restrict the crystal size and shape of precipitated paraffin, and help prevent

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re-agglomeration of paraffin crystals [8,9]. All PPDs are structured so that a part of the molecule is similar to paraffin wax crystals, which provide nucleation sites and co-crystallize with the paraffin wax crystals. The other part of the structure, dissimilar to wax crystals, blocks the extensive growth of wax matrices. Thus, it enables the bulk stream to persist as a fluid at lower temperatures and, consequently, to remain pumpable, pourable and filterable.

There are many polymeric compounds exhibiting such properties. Particular examples of the chemicals used in practice include: ethylene–vinyl acetate copolymers, vinyl acetate-α-olefin copolymers, alkyl esters of styrene–maleic anhydride copolymers, poly alkyl-acrylates, poly alkyl-methacrylates, and alkyl esters of unsaturated carboxylic acids, and α-olefin copolymers [9–16].

In this paper, the synthesis of efficient flow improver additives for gas condensate of different properties is described on the basis of octadecyl methacrylate copolymers with styrene and acrylic or methacrylic acid, as well as on the terpolymerization of these monomers in toluene or xylene.

2. Experimental

2.1. Materials

Monomers: acrylic acid (AA), >99%, Fluka; methacrylic acid (MAA), >99%, Fluka; dodecyl methacrylate (DDMA), polymerization grade, Rohm and Haas; octadecyl methacrylate (ODMA), polymerization grade, Rohm and Haas; styrene (St), >99.5%, Fluka.

Solvents: toluene, >99.5%, Fluka; xylene, isomers mixture, Fluka.

Initiators: azo-bis isobutyronitrile (AIBN), AKZO Chemie.

Gas condensate samples from the fields of Molve, Kalinovac, Stari Gradac (INA-INDUSTRIJA NAFTE d.d., Zagreb) the properties of which and n-paraffin distribution are listed in Tables 1 and 2.

2.2. Measurements

The average number of carbon atoms in methacrylic esters and additive compositions were obtained from FT NMR Bruker Avance 300, at room temperature, in $CDCl_3$ with TMS as internal standard.

Molar weights based on calibration with monodispersed polystyrene standards (Polymer Laboratories) were determined by GPC (Varian HPLC, Model 8500) using a set of 4-μ styrogel columns with THF as solvent, at room temperature.

Testing of flow improver additives was carried out by measurements of pour point (ASTM D 97), Linetronic Oil Lab Apparatus.

Table 2
Distribution of n-paraffin fractions in the gas condensate samples Molve 1, Molve 2, Kalinovac, St Gradac 1 and St Gradac 2; SIM DIS analysis

Fraction	Gas condensate sample, weight %				
	Molve 1	Molve 2	Kalinovac	St Gradac 1	St Gradac 2
C_5	0.79	0.69	2.56	1.87	1.69
C_6	1.53	1.09	3.05	2.60	2.37
C_7	2.52	1.87	3.49	3.22	3.03
C_8	3.32	2.77	3.63	3.53	3.48
C_9	3.53	3.40	3.41	3.43	3.60
C_{10}	3.39	3.88	3.08	3.27	3.67
C_{11}	3.29	3.86	3.06	3.25	3.58
C_{12}	2.85	3.45	2.70	2.92	3.16
C_{13}	2.56	3.14	2.47	2.74	2.88
C_{14}	2.41	2.94	2.27	2.56	2.65
C_{15}	2.26	2.62	2.05	2.41	2.48
C_{16}	1.89	2.18	1.81	2.13	2.06
C_{17}	1.63	1.86	1.49	1.74	1.75
C_{18}	1.44	1.64	1.27	1.51	1.51
C_{19}	1.28	1.50	1.11	1.32	1.33
C_{20}	1.08	1.25	0.92	1.11	1.11
C_{21}	0.95	1.09	0.78	0.99	1.00
C_{22}	0.80	0.92	0.63	0.81	0.82
C_{23}	0.71	0.82	0.55	0.72	0.74
C_{24}	0.59	0.68	0.44	0.59	0.60
C_{25}	0.49	0.60	0.39	0.53	0.51
C_{26}	0.45	0.51	0.33	0.45	0.47
C_{27}	0.38	0.42	0.28	0.39	0.41
C_{28}	0.34	0.36	0.24	0.34	0.35
C_{29}	0.28	0.29	0.20	0.29	0.29
C_{30}	0.23	0.21	0.14	0.26	0.25
C_{31}	0.16	0.09	0.11	0.21	0.18
C_{32}	0.11	0.12	0.09	0.13	0.14
C_{33}	0.08	0.08	0.05	0.10	0.10
C_{34}	0.05	0.05	0.05	0.07	0.08
C_{35}	0.04	0.03	0.04	0.06	0.05
C_{36}	0.04	0.02	0.03	0.04	0.04
C_{37}	0.03	0.02		0.04	0.04

Table 1
Characteristics of the gas condensate samples Molve 1, Molve 2, Kalinovac, St Gradac 1 and St Gradac 2

Property	Method	Gas condensate sample				
		Molve 1	Molve 2	Kalinovac	St Gradac 1	St Gradac 2
Specific gravity, d_4^{15} (kg/m^3)	ASTM D-4052/91	784.6	786.5	765.0	776.6	772.2
API degree	Calculated	48.8	48.3	53.4	53.2	51.7
Pour point (°C)	ASTM D-97/93	15	15	3	3	9
Dynamic viscosity, 40 °C (mm^2/s)	ASTM D-446/95	1.29	1.13	1.12	1.42	1.41
Refractive index, n_D^{20}	ASTM D-542	1.4460	1.4409	1.4381	1.4448	1.4364
Average molar weight, $\overline{M}_m$	Estimated	165	158	155	175	173