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Short communication

Investigation of cyclohexanone pentaerythritol ketal as a clean flow improver for crude oil

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ABSTRACT

The decomposition of polymer in the oil refining process is the main problem for the application of typical polymer flow improvers, so there is a requirement to seek for new small molecular flow improvers. In this work, a small molecular flow improver, cyclohexanone pentaerythritol ketal, was synthesized and fully characterized. The further evaluation test showed that the synthesized compound can improve the flow properties of crude oil samples by reducing the viscosity of crude oil by 70% at most and depressing the pour point slightly. With the composition group's content of different crude oil samples and the response to the additive, it was found that the high content of saturated HC makes for the effective viscosity reduction. The role of cyclohexanone pentaerythritol ketal in limiting the degree of cocrystallization can be further confirmed by the average particle size and the particle morphology analysis of saturated HC component illustrated from microscopic crystal morphology. Besides, cyclohexanone pentaerythritol ketal is a cleaner crude oil additive with its decomposition at relatively low temperature in light of the result of thermal analysis.

1. Introduction

As we know, heavy crudes account for a large fraction of the world's potentially recoverable oil reserves, and the production, storage and transportation of crude oil products have become a complex and highly technical operation. One of the major difficulties is the highly viscous fluids that require economical ways to transfer the heavy crude [1,2]. Therefore, different methods are used to reduce the viscosity of the heavy crude for easier production and transportation. For instance, dilution with lighter crudes or alcohols, and heating are some of those common methods, while the preferred option is the use of chemical additives referred to as wax crystal modifiers, also known as viscosity-reducer, pour point depressants, flow improvers, and paraffin inhibitors [3–8]. Most of the chemical additives typically have a wax-like paraffinic part that cocrystallizes with wax, forming components of oil and a polar component limiting the degree of cocrystallization. Polymers with these properties are homo and copolymers of alpha olefins [4], ethylene-vinyl acetate copolymers [5], polyalkyl acrylates, methacrylates [6], alkyl esters of styrene-maleic anhydride copolymers, and alkyl fumarate-vinyl acetate copolymers [7]. But they are very selective, that is, not all additives are sufficiently effective for every crude oil [8]. Besides, the long molecular chain, large molecular weight and high thermo stability of these polymers are hard to decompose in oil refine process [9]. So there is a requirement to seek for new small molecular compounds as clean flow improvers [10]. In this paper, a spiro compound with short molecular chain and low molecular weight, cyclohexanone pentaerythritol ketal, was synthesized and evaluated as a clean flow improver for crude oil.

2. Experimental

2.1. General

The crude oil samples of JH17P27 and JH32P1 used in this study were obtained from Jinghe Oilfield, China, and crude oil samples of SY01 and XT01 were obtained from Xinjiang Oilfield, China. The physical parameters are shown in Table 1. Initially, the crude oil was homogenized by shaking it for an hour to ensure that the physical properties of the heavy crude oil are homogeneous. Then the crude oil was used for measurements. NMR spectrum was recorded in the stated solutions, on a Bruker Drx-400 spectrometer, operating at 400 MHz for H; δ values are reported in mg/L and *J* values in Hertz. Mass spectrum was recorded on a Micromass Platform II spectrometer, using the direct-inlet system operating in the electron impact (EI) mode at 75 eV. Thermal analysis was performed on a TGA/SDTA851e Thermal Analyzer, where the heating rate was 10 K min^{-1} in the range of 298–880 K.

2.2. Synthesis of cyclohexanone pentaerythritol ketal [11]

Cyclohexanone and pentaerythritol were added in a flask with the molar ratio of 2:1, and the toluene was added as water carrier and solvent. Then, 5% (wt) solid acid, $NaHSO_4$ was added as catalyst. The mixture was refluxed under stirring until no water could be carried out, and then cooled to room temperature. The $NaHSO_4$ was filtrated,

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Table 1
The physical parameters of the crude oil.

Oil sample	Pour point (°C)	ρ^{20} (g·cm^{-3})	Saturated HC (%)	Aromatic HC (%)	Resin (%)	Asphaltene (%)
JH17P27	17.8	0.880	71.41	15.15	13.28	0.16
JH32P1	15.0	0.884	57.43	13.67	28.12	0.78
SY01	10.2	0.949	44.46	16.11	38.29	1.14
XT01	14.8	0.957	42.13	19.70	24.73	13.44

and the solvent was evaporated to produce the crude product. After recrystallization in methanol, the pure product was obtained as a colorless block, with a yield of 85.0%. The reaction is described in Scheme 1.

2.3. X-ray data collection and structure refinement

All H atoms were positioned geometrically, with C–H = 0.93–0.98 Å, and refined with a riding model, with $U_{iso}(H) = 1.2U_{eq}$(carrier). Data collection: SMART [12]; cell refinement: SAINT [12]; data reduction: SAINT [12]; program (s) used to solve structure: SHELXS97 [13]; programs used to refine structure: SHELXL97 [14]; molecular graphics: DIAMOND for Windows [15]; software used to prepare material for publication: WinGX [16].

2.4. Evaluation tests

Crude oil sample was doped with cyclohexanone pentaerythritol ketal butanol solution with concentrations of 100, 300, 500, 800 or 1000 mg/L at 50 °C, stirred for 30 min for homogenization. The viscosity was measured at the temperatures of 20–50 °C. Cyclohexanone pentaerythritol ketal was tested for its effectiveness as a flow improver for the crude oil samples through the pour point test according to the ASTM-97 procedure. 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 hereafter.

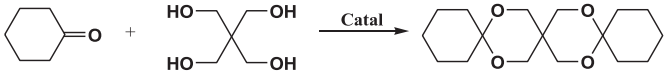
2.5. Optical microscopy

The saturated hydrocarbon component was separated from the crude oil using the standard method for the optical study. Wax crystal morphologies were observed using a BX41-P OLYMPUS polarizing microscope. Samples were initially heated to 50 °C and then cooled to 10 °C for 5 min. A small amount of wax crystal was loaded onto the glass slide inside a copper stage with a central window. During the measurement, the temperature of the copper stage was controlled at 10 °C in a circulating bath.

3. Results and discussion

3.1. Structure

Cyclohexanone pentaerythritol ketal was characterized by HNMR, and the spectrum is shown in Fig. 1. The data can be summarized as: ^{1}H-NMR (D_6-DMSO, 400 MHz), δ: 3.62 (8H, s), 1.76 (4H, t, J = 7.2 Hz), 1.55 (4H, td, J = 7.6, 1.2 Hz), 1.35 (2H, t, J = 7.6 Hz). The single peak at δ 3.62 for 8 H is assigned to the four CH_2 groups from pentaerythritol. The presence of large amounts of hydrogen signal from δ1.35–1.76



Scheme 1. Synthesis of cyclohexanone pentaerythritol ketal.

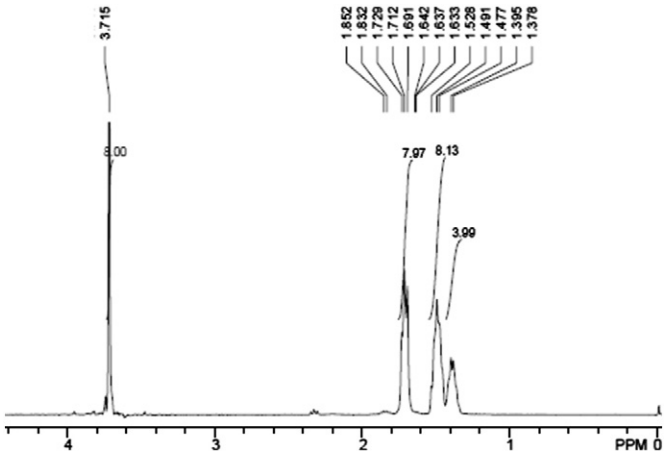


Fig. 1. The HNMR spectrum of cyclohexanone pentaerythritol ketal.

demonstrates the three kinds of H existing in the two cyclohexyl groups, which are in great agreement with the ratio of product structure. Besides, the MS (EI) shows a peak of 296 (M^+), which agrees with the molecular weight of cyclohexanone pentaerythritol ketal as well.

Furthermore, the stereo structure of the title compound was corroborated by X-ray diffraction analysis. Geometric parameters of the title crystal structure are in the usual ranges. The main experimental data is displayed in Table 2. The molecular structure is shown in Fig. 2, and the packing of the molecules is depicted in Fig. 3. The X-ray structural determination of the title compound confirms the assignment of its structure from NMR and MS spectrum data. There are two independent molecules with different conformations in the crystal, varying in bond lengths and angles. In each molecular, there are four six-membered cycles, two cyclohexyl groups and two 1,3-dioxane groups. The four six-membered cycles all display typical stable boat conformations, as shown in Fig. 2. There is no typical hydrogen bond in the two compound crystals since there is no hydrogen donor in the molecule. As shown in Fig. 3, the stacking interaction is responsible for the crystal's 1-D supra-molecular structure, and it is obvious that the two cyclohexyl groups stack in different directions one by one because of the fixed spiro structure, which indicates that cyclohexanone pentaerythritol ketal may interact with the paraffin in crude oil in a similar way to modify the formation of wax crystal lattices.

3.2. Thermal gravimetric analysis

As shown in Fig. 4, there are two stages of weight loss in the TGA curve of cyclohexanone pentaerythritol ketal. The first stage of weight loss is about 9% between 30 °C and 200 °C, which corresponds to the loss of absorbed solvent during the recrystallization process. In the second step, between 200 °C and 300 °C, the large amount of weight loss about 83% indicates the decomposition of cyclohexanone pentaerythritol ketal. Above 300 °C, the remaining weight ratio is less than 8%, corresponding to the carbon residue. The thermal performance

Table 2
The main information of the crystal.

Parameter	Data
Formula sum	$C_{34}H_{56}O_8$
Formula weight	592
Crystal system	Monoclinic
Space group	P 21
Cell parameters	a = 11.1214(9) Å b = 13.9216(6) Å c = 11.6658(10) Å β = 118.07(1)°
Cell ratio	a/b = 0.7989 b/c = 1.1934 c/a = 1.0490
Cell volume	1593.81(935) Å^3
Z	4