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Fuel 87 (2008) 1543–1551
FUEL
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A new test method for determination of wax content in crude oils, residues and bitumens

Xiaohu Lu [a,*], Björn Kalman [b], Per Redelius [a]

[a] AB Nynäs Petroleum, Bitumen Research, SE – 149 82 Nynäshamn, Sweden
[b] Swedish National Road and Transport Research Institute, SE – 581 95 Linköping, Sweden

Received 1 June 2007; received in revised form 17 August 2007; accepted 21 August 2007
Available online 19 September 2007

Abstract

A new method for determining wax content in petroleum materials is developed. It is based on thin layer chromatography with flame ionization detection (TLC-FID) and involves two-step development with two solvents. The principle of the test method is first to separate saturates from other more polar components based on good solubility of saturates in *n*-heptane and weak strength of interaction with an adsorbent (silica). Waxes are then separated from the saturate fraction using a poor solvent methyl-ethyl ketone (MEK) at such a low temperature (typically −20 °C) that waxes are in solid state. The separated fractions are quantified with FID. The test method is verified using various model compounds including *n*-alkanes of different molecular weight, isoalkane, as well as commercial waxes. Results indicate that the TLC-FID method detects the waxes mainly composed of *n*-alkanes ranging from C20 to C40, and large isoalkanes and cycloalkanes which are soluble in *n*-heptane. The method has been satisfactorily applied to a variety of samples of crude oils, residues, and bitumens. It is simple, quick, and reliable. By changing MEK temperature in the development chamber, waxes may be further characterized.

Keywords: Wax; Crude oil; Residue; Bitumen; Thin-layer chromatography with flame ionization detection

1. Introduction

High wax content could be disadvantageous in crude oils and in bitumens. In crude oils, wax may crystallize at low temperature and precipitate as a solid material, causing problems e.g., in pipelines, and in production and processing equipments [1–3]. In bitumen, which is a material produced by distillation of crude oils or found in nature as natural asphalt, the presence of wax was believed to be detrimental [4–6]. A previous study showed that wax in bitumen adversely influenced asphalt low temperature properties, but negative effects on wheel tracking resistance and moisture susceptibility were not found [7].

There is no universal definition of wax. Based on chemical composition, a distinction may be made between paraffin wax consisting of *n*-alkanes and microcrystalline wax containing isoalkanes and cycloalkanes [8–11]. Normally, paraffin waxes are highly crystalline materials with large crystal structures, whereas microcrystalline waxes are characterized by much finer crystals. In spite of the relatively simple definitions, the chemical components of waxes in petroleum materials are very complicated, and it is not possible to determine waxes with well-defined molecule types. Consequently, determination of wax content in crude oils, residues or bitumens is always test-method related. For example, the amount of materials which crystallize on cooling as determined by differential scanning calorimetry (DSC) may be used as a measure of wax content [12–14]. DSC measures energy change in the sample under a controlled heating or cooling rate. The content of crystallizing materials can be calculated providing that the enthalpy is known. It is however dependent on molecular weight and structure and is usually not known.

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[*] Corresponding author. Tel.: +46 8 52065007; fax: +46 8 52065454.
E-mail address: xiaohu.lu@nynas.com (X. Lu).

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doi:10.1016/j.fuel.2007.08.019

There are among others also two European standard methods for determination of wax content in bitumen, namely method by distillation [15], and method by extraction [16]. The first method determines the paraffin wax content of bitumen from a distillate obtained by a specified distillation process. The distillation takes place at very high temperatures (up to over 500 °C) at which cracking of molecules may occur [11]. Another method involves three steps: extraction of asphaltenes with petroleum spirit, extraction of most aromatic compounds with oleum, and finally crystallization of wax in ether/ethanol mixture at −20 °C. Both the methods are very laborious.

Thin-layer chromatography with flame ionization detection (TLC-FID, known as Iatroscan technique) has been used to characterize petroleum related materials, including crude oils and bitumen [17,18]. For bitumen, the generic factions determined are named saturates, aromatics, resins, and asphaltenes (often abbreviated as SARA analysis). Based on the amount of saturates, the TLC-FID technique was suggested to predict wax content in bitumen [19,20]. However, the prediction was mainly based on measurement of the materials containing very high levels of wax. For more moderate levels of wax, correlation to the amount of saturates does not seem to exist. In [21], saturate fraction of bitumen was also used to determine wax content. The saturate faction was obtained by liquid chromatography after precipitation of asphaltenes with *n*-heptane.

This paper presents a simple method for determining wax content in petroleum products. The method is based on TLC-FID and involves two-step development with two solvents, *n*-heptane and methyl-ethyl ketone (MEK), respectively. The principle of the test method is first to separate saturates from other more polar components based on good solubility of saturates in *n*-heptane and weak interaction with an adsorbent (silica). Waxes are then separated from the saturate fraction using a poor solvent MEK at such a low temperature that waxes are in solid state. The separated fractions are quantified with FID. By the new method, waxes are defined as the saturated hydrocarbons that are soluble in *n*-heptane and insoluble in cold MEK. The test method is validated by various model compounds, as well as commercial waxes. It has been satisfactorily applied to a variety of samples of crude oils, residues, and bitumens.

2. Experimental section

2.1. Materials

In this study, five sets of materials were selected. They were model compounds, commercial waxes, pairs of crude oils and residues, and different bitumen products.

Model compounds included a series of *n*-alkanes ranging from *n*-hexadecane (*n*-C16) to *n*-hexatriacontane (*n*-C36), and one isoalkane, squalane ($C_{30}H_{62}$). All the substances are of synthesis grade, and their melting points range from 18 °C for *n*-C16 to 76.5 °C for *n*-C36.

Table 1
Characteristics of commercial waxes provided by producers

Source	Brand name	Type	Congealing point (CP) or melting point (MP) (°C)
Sasol wax	Sasolwax 5805	Paraffin	58–60 (CP)
	Sasolwax 5604	Paraffin	55–57 (CP)
	Sasolwax 5891	Microcrystalline	70–75 (CP)
	Sasolwax 0907	Microcrystalline	83–94 (CP)
Strahl & pitsch	SP 173P	Paraffin	61 (MP)
	SP 19	Microcrystalline	81 (MP)
	SP 60	Microcrystalline	82 (MP)
Hans-Otto Schumann GmbH & Co	Terhell paraffin JA 201	Slack wax	42.5 (CP)

CP and MP according to ASTM D938 and ASTM D127, respectively.

The commercial waxes selected were refined microcrystalline or paraffinic waxes from crude oils. The physical characteristics of the wax samples are given in Table 1. Compared with the paraffinic waxes, the microcrystalline waxes have higher melting points (or congealing points), indicating their molecular weights are considerably larger than the paraffinic waxes.

Three crude oils (one Boscan, two Russian) and their residues were analyzed. Residue is obtained as a bottom fraction in a distillation process which separates crude oils into fractions by selective boiling points (BP). It consists of the least volatile components at a specific boiling point (cut point). The cut points used for the three residues were 400 °C (Boscan), 555 °C (Russian A), and 560 °C (Russian B), respectively. As will be shown later by high temperature gas chromatography (HTGC), the crude oils and residues differ in chemical composition. Compared with the Boscan crude oil, the Russian crude oils are more paraffnic and contain more light fractions. Table 2 shows that these samples are also representative enough in terms of wax content.

As for bitumen, samples of different sources and of different wax contents were selected. The bitumens are 70/100 or 160/220 pen grade. Typical parameters of the bitumen samples are shown in Table 3.

2.2. TLC-FID procedure

The TLC/FID system used was Iatroscan TH-10 TLC/FID analyser MK-4. Quartz rods (10 in a rod holder) coated with a thin layer of silica (named Chromarod) were used for separations. FID signals were collected and amplified in an in-house assembled amplifier. Data were analyzed using software Spectrum Viewer Basic 2.6. Peaks in the chromatograms were quantified by the area above a horizontal baseline drawn from one side of the peak to the other side or extrapolated from a distinct baseline in the chromatogram.