

COMPARATIVE METHODS IN THE DETERMINATION OF WAX CONTENT AND POUR POINTS OF CRUDE OILS

M. V. K ok^{1*}, J. M. Letoffe² and P. Claudy³

¹Department of Petroleum and Natural Gas Engineering, Middle East Technical University, 06531 Ankara, Turkey

²Laboratoire de Thermodynamique Appliqu e - UPRESA CNRS 5079, INSA Lyon Bat. 401, 69621 Villeurbanne Cedex, France

³Laboratoire des Mat riaux Organiques-Propri t s Sp cifiques, UPR CNRS 9031 BP 24, 69390 Vernaison, France

In this research, differential scanning calorimetry (DSC) and gas chromatography is used to determine the wax content of fourteen crude oils of different sources. Different empirical equations were applied to compare the wax content of crude oils. For the fourteen crude oil samples with the wax content ranging from 7.5 to 43.8 mass%, it was observed that the results of empirical equations were in good agreement with those determined by DSC and GC. Accordingly, a correlation between ASTM pour point and the temperature at which 2 mass% of wax has precipitated out from crude oil is developed.

Keywords: correlations, crude oil, DSC, empirical equations, gas chromatography, thermal effect, wax content

Introduction

Paraffin or wax deposition is one of the most severe problems for petroleum industry. Crude oils contain substantial amount of waxy materials. When a wax containing crude oil, is cooled below its wax appearance temperature (WAT), wax constituents tends to separate from the liquid phase of crude oil and starts to crystallize which causes several problems during production, storage and transportation. There are several methods for measurement of wax content of crude oils. The standard acetone method and its modified versions appear to be the industrial practice. In addition, gas chromatography, pulsed nuclear magnetic resonance (NMR), thermomicroscopy, and density measurements have been used for measuring the wax content. The procedure of the standard acetone method is very complex and some toxic solvents have to be used. The gas chromatographic method and pulsed NMR method have poor accuracy and low repeatability. The density measurement technique requires specialized equipment. In recent years, researchers have tried to find more convenient and reliable methods to determine the wax content of crude oils. DSC is well documented as a powerful technique for investigating the characteristics of crude oils and thermomicroscopy allows the observation of changes in the sample to be monitored at selected magnifications using an optical microscope. Thermomicroscopic investigations are useful for correlating morphological or structural changes with the thermal effects and can provide information regarding the internal structure of materials, including such phenomena as crystallization or phase separation [1–3].

Jiang *et al.* [4] used temperature modulated differential scanning calorimetry to measure the WAT of crude oil samples. Changes in the signals exhibit excellent correlations with WATs measured using conventional differential scanning calorimetry, DSC. For oil samples having low wax contents, it was observed that the ADSC is a more sensitive technique for identifying the onset of wax crystallisation and, specifically, the phase angle between the heating rate and heat flow modulations is extremely sensitive to this process. Chen *et al.* [5] developed a new method to measure the wax content of crude oils. The wax content of a crude oil is proposed and proved to be the Q (total thermal effect of wax precipitation in sample) ratio of the crude oil and its corresponding wax obtained by using standard acetone method. It is proposed that the new method can be applied to improve the accuracy in determining the amount of precipitated wax in a waxy crude oil at different temperatures. Elsharkawy *et al.* [6] studied the wax content by acetone precipitation techniques as well as WAT by viscosity measurements and DSC of eight different stock-tank crude oils. Comparison between predicted and measured results shows that measured WAT by DSC compares very well with that predicted from the model for most crudes. Li *et al.* [7] proposed correlation of the pour point on the basis of fourteen crude oils from eight countries. The development of the gel point correlation and further verification of the pour point correlation indicate that there is a relationship between the gelling of virgin waxy crudes and the amount of precipitated wax. According to these correlations and the amount of

* Author for correspondence: kok@metu.edu.tr

precipitated wax, which can be determined only with a little sample by thermodynamic models or DSC experiment, the gel point and pour point of virgin waxy crude can be predicted even if the oil sample is very limited. Kök *et al.* [8–11] characterized the waxy crude oils by differential scanning calorimetry and thermomicroscopy in the temperature range from +80 to –20°C. Pour points were also determined. For crude oils which contain >10 mass% of *n*-paraffins, the pour point is reached when similar to 2 mass% of waxes have precipitated. By thermomicroscopy, it was observed for mixtures of pure paraffins and crude oil matrix that the size of the crystals is small and depends on the length of paraffinic chains at the pour point. Wax appearance temperatures of crude oils those determined by DSC, thermomicroscopy and rheometer are compared. Good agreement is obtained among the three techniques for crude oils having a significant precipitation rate. Effect of different additives was also discussed by analyzing the DSC and thermomicroscopy curves. Kök and Acar [12] investigated the thermal characterization and kinetics of Karakus crude oil in the presence of limestone matrix. In combustion with air, three distinct reaction regions were identified known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). Five different kinetic methods used to analyze the TG/DTG data to identify reaction parameters. On the other hand, different $f(\alpha)$ models from literature were also applied to make comparison. Kök [13] investigated the role of clay on the combustion and kinetic behavior of crude oils in limestone matrix. For this purpose, simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) experiments were performed at three different

heating rates at 10, 15 and 20°C min⁻¹, respectively. A uniform trend of decreasing activation energies was observed with the addition of clay. It was concluded that clay's surface area affects the values of Arrhenius constant, while it is the catalytic properties of clay, which lower the activation energies of all the reactions, involved in the combustion process.

Experimental

DSC and gas chromatography (GC) were used to determine the amount of wax content of fourteen crude oils from eight different sources. Before experiments, all the crude oils are heated to 80°C for two hours in closed containers and shaken thoroughly to ensure complete dissolution of wax. Then the closed containers are left to cool to room temperature. DSC experiments were performed using a computer controlled apparatus which was flushed with argon.

Experiments on heating/cooling were carried out in the temperature range of 80 to –20°C for heavy crude oils and 60 to 0°C for medium and light crude oils at 2°C min⁻¹ rate. Two parallel runs are made to improve precision. On the other hand, pour point of the samples was determined using ASTM method (D97-87) and pour point tester. All the experiments were performed twice for reproducibility.

Results and discussion

In DSC experiments, determination of the amount of precipitated waxes requires computation of baseline and knowledge of the experimental relation;

Table 1 Properties of crude oils

Origin	Crude oil	⁰ API grav.	DSC/mass%	GC/mass%	Difference*
Algeria	Es Sider	36.5	7.5	9.5	– 2.0
Angola	Palanca	38.0	8.8	10.5	– 1.7
France	Chaunay	36.1	10.3	9.7	+ 1.0
Libya	Bouri	26.6	10.5	9.3	+ 1.2
Syria	S. Light	37.5	12.4	11.1	+ 1.3
Angola	Takula	36.3	12.9	11.0	+ 1.9
Libya	Brega	40.0	16.9	15.6	+ 1.3
Gabon	Soyo	38.3	17.6	15.6	+ 2.0
Gabon	M Bya	35.7	18.5	15.5	+ 3.0
Libya	Sarir	36.5	20.4	17.5	+ 2.9
Indonesia	Handil	32.6	21.7	19.8	+ 1.9
Gabon	Caucal	36.3	23.8	21.7	+ 2.1
Tunisia	Ezzouia	39.0	33.0	28.3	+ 4.7
Libya	Bu Attifel	42.5	43.8	33.4	+10.4

* (DSC reading–GC reading)

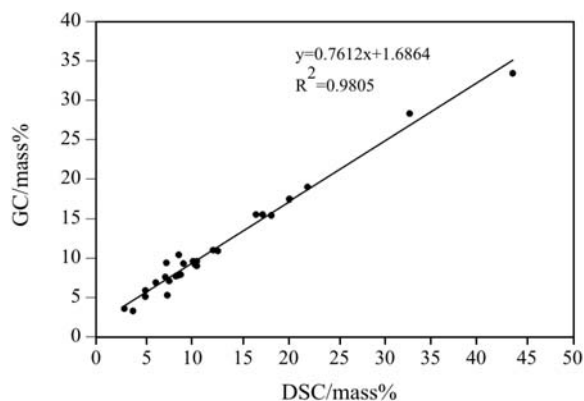


Fig. 1 DSC wax content (mass%) vs. GC wax content (mass%)

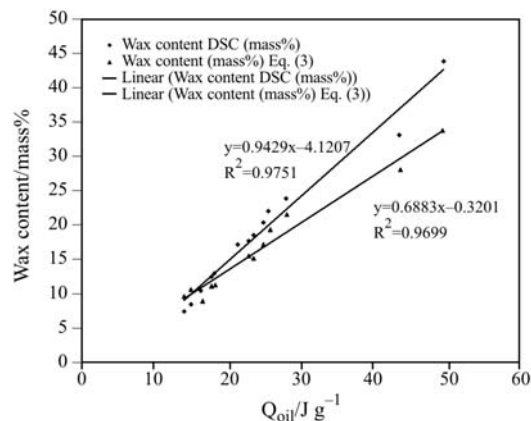


Fig. 2 Q_{oil} ($J g^{-1}$) vs. DSC wax content (mass%) and GC wax content (mass%)

$$\Delta H_{diss}=f(T) \quad (1)$$

The baseline for crude oils is assumed to be the line between the end of the exothermic effect after T_g , and the end of the dissolution of the paraffins. If dS are the area between the calorimetric signal and the baseline in the temperature interval T and $T+dT$, a thermal effect dQ can be computed as follows:

$$dQ=kdS \quad (2)$$

where dQ is the heat absorbed by the sample for the dissolution of the mass of paraffins and k is the calibration factor. Using the relationship $\Delta H_{diss}=f(T)$, a corresponding mass of paraffins is computed. Integration from the beginning to the end of the thermal effects gives the mass of paraffins. During this procedure the mass of precipitated waxes is directly calculated from enthalpy measurements [8–11]. The amount of wax, which is obtained with good reproducibility in DSC experiments, is higher

than the values obtained by GC. In fact, GC evaluates *n*-alkanes and DSC evaluates the total amount of crystallized species (*n*-alkanes isoalkanes, cycloalkanes, ...). The results are given in Table 1 and Fig. 1 respectively.

A new method which is used to determine the wax content of crude oil more accurately has been proposed [5]. In this method, the total thermal effect, Q_{oil} , of the wax precipitation is computed by integrating the area between DSC signal curve and the baseline. The linear relation between Q_{oil} and the corresponding wax contents determined by DSC and GC are given in Eqs (3) and (4) respectively (Fig. 2).

$$C_{wax}=0.944 Q_{oil}-2.2475; (R^2=0.9767) \quad (3)$$

$$C_{wax}=0.69 Q_{oil}-0.2577; (R^2=0.9651) \quad (4)$$

In a similar study [5], which is performed using fourteen waxy crude oils with wax content ranging from

Table 2 Comparison of the wax determination methods

Crude oil	$Q_{oil}/K g^{-1}$	Wax content DSC/mass%	Wax content/mass% Eq. (3)	Wax content GC/mass%	Wax content/mass% Eq. (4)
El Sider	14.1	7.5	4.8	9.5	6.3
Palanca	14.9	8.8	6.1	10.5	7.0
Chaunay	16.2	10.3	7.5	9.7	6.5
Bouri	16.3	10.5	7.7	9.3	6.2
S. Light	17.7	12.4	9.5	11.1	7.4
Takula	18.2	12.9	9.9	11.0	7.3
Brega	21.3	16.9	13.7	15.6	10.5
Soyo	22.7	17.6	14.4	15.6	10.5
M Bya	23.6	18.5	15.2	15.5	10.4
Sarir	24.8	20.4	17.0	17.5	11.8
Handil	25.6	21.7	18.3	19.8	13.4
Caucal	27.9	23.8	20.2	21.7	14.7
Ezzouia	43.6	33.0	28.9	28.3	19.3
Bu Attifel	49.5	43.8	39.1	33.4	22.8

Table 3 Comparison between the amount of precipitated waxes and pour points of crude oils

Crude oil	Wax content 1% prec./°C	Wax content 2% prec./°C	Wax content 3% prec./°C	Pour point, ASTM/°C	Pour point, *PPT/°C
Es Sider	12.7	5.8	0.1	9.0	6.0
Palanca	9.4	1.8	-5.2	9.0	6.0
Chaunay	15.2	8.0	1.0	6.0	6.0
Bouri	23.5	17.4	11.8	12.0	18.0
S. Light	13.2	6.4	0.4	9.0	3.0
Takula	19.0	14.8	10.3	18.0	12.0
Brega	7.4	-1.7	12.8	3.0	9.0
Soyo	19.4	14.8	10.8	15.0	15.0
M Bya	16.7	12.8	11.2	18.0	18.0
Sarir	25.1	20.3	16.0	24.0	21.0
Handil	28.1	26.3	24.8	27.0	27.0
Caucal	32.1	29.8	27.8	24.0	24.0
Ezzouia	37.6	30.8	28.8	36.0	36.0
Bu Attifel	48.0	38.8	34.3	39.0	39.0

*PPC (pour point tester)

1.58–26.29 mass%, the best correlation between the Q_{oil} and wax content is obtained by least square fitting is:

$$C_{wax}=0.75 Q_{oil}+0.20; (R^2=0.9937) \quad (5)$$

The comparison of measured and computed wax contents are given in Table 2. Equations (3) and (4) will be use to improve the accuracy of computation the amount of precipitated wax in crude oils at different temperatures.

Concerning the crude oils, the knowledge of the enthalpy of precipitation allows to calculate the amount of precipitated waxes vs. temperature and to compare the results of pour point. Temperatures corresponding

to 1, 2 and 3 mass% of precipitated *n*-alkanes and the pour points measured by ASTM method and pour point tester are given in Table 3. The best correlation is obtained when 2 mass% of waxes have precipitated into the crude oil matrix, in the case of crude oils which contain more than 10 mass% of *n*-paraffins (Fig. 3). In other words, pour point is reached when 2 mass% of waxes have precipitated. A correlation between the ASTM–PPT (pour point tester) and T_c (2 mass%) is obtained.

$$T_c(2 \text{ mass\%, ASTM})=1.0224T_{pp}-2.0344; \quad (R^2=0.8926) \quad (6)$$

Table 4 Comparison between calculated and measured temperatures at which 2 mass% wax is precipitated

Crude oil	ASTM pour point/°C	Measured 2% prec/°C	Calculated °C Eq. (6)	Calculated °C Eq. (8)	Pour point tester/°C	Calculated °C Eq. (7)
Es Sider	9.0	5.8	7.2	7.2	6.0	5.2
Palanca	9.0	1.8	7.2	7.2	6.0	5.2
Chaunay	6.0	8.0	4.1	4.4	6.0	5.2
Bouri	12.0	17.4	10.2	10.0	18.0	17.0
S. Light	9.0	6.4	7.2	7.2	3.0	2.2
Takula	18.0	14.8	16.4	15.6	12.0	11.1
Brega	3.0	-1.7	1.0	1.6	9.0	7.2
Soyo	15.0	14.8	13.3	12.8	15.0	14.0
M Bya	18.0	12.8	16.4	15.6	18.0	17.0
Sarir	24.0	20.3	22.5	21.1	21.0	19.9
Handil	27.0	26.3	25.6	23.9	27.0	24.9
Caucal	24.0	29.8	22.5	21.1	24.0	21.1
Ezzouia	36.0	30.8	34.8	32.3	36.0	32.3
Bu Attifel	39.0	38.8	37.8	35.1	39.0	35.1

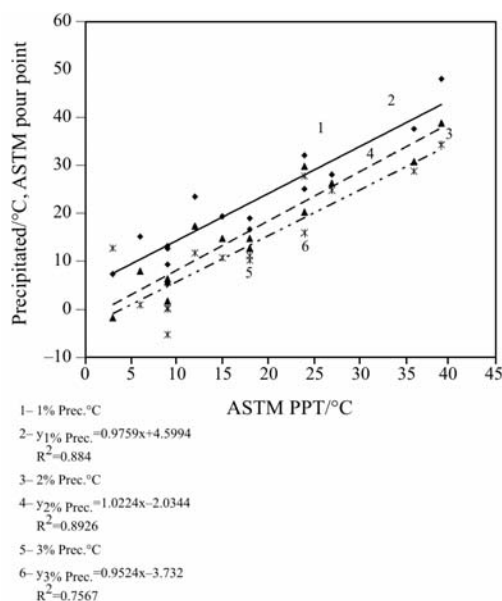


Fig. 3 ASTM pour point (°C) vs. 1, 2 and 3 mass% wax precipitated (mass%)

$$T_c(2 \text{ mass\%}, \text{PPT}) = 0.9847T_{pp} - 0.731; \quad (7)$$

$$(R^2 = 0.875)$$

In a similar study [7], which is performed using twenty-four waxy crude oils with wax content ranging from 2.7–25.0 mass%, the best correlation between the pour points and T_c (2 mass%), is obtained by least square fitting is:

$$T_c(2 \text{ mass\% ASTM}) = 0.9308T_{pp} - 1.2164; \quad (8)$$

$$(R^2 = 0.9886)$$

The comparisons between the measured T_c (2 mass%) and the calculated T_c (2 mass%) are given in Table 4. According to these correlations and the amount of precipitated wax, the pour point of waxy crude oils can be determined easily.

Conclusions

DSC and GC was used to determine the wax content of crude oils. Empirical correlations were also established and good correlations were determined between the Q_{oil} and wax content determined by DSC and GC.

In the case of crude oils the best correlation between ASTM pour point and the DSC results is obtained when 2 mass% waxes has precipitated from the crude oil. The results further demonstrate that there is a definite relation between the pour point and 2 mass% precipitated wax.

References

- 1 P. Claudy, J. M. Letoffe, B. Chague and J. Orrit, *Fuel*, 67 (1988) 58.
- 2 P. Claudy, J. M. Letoffe, B. Neff and B. Damin, *Fuel*, 65 (1986) 861.
- 3 P. Claudy, J. M. Letoffe and B. Damin, *Fuel*, 74 (1995) 92.
- 4 Z. Jiang, J. M. Hutchinson and C. T. Imrie, *Fuel*, 80 (2001) 367.
- 5 J. Chen, J. J. Zhang and H. Y. Li, *Thermochim. Acta*, 410 (2004) 23.
- 6 A. M. Elsharkawy, T. A. Al-Sahhaf and M. A. Fahim, *Fuel*, 79 (2000) 1047.
- 7 H. Y. Li, J. J. Zhang and D. F. Yan, *Petr. Sci. Technol.*, 23 (2005) 1313.
- 8 M. V. K ok, J. M. Letoffe, P. Claudy, D. Martin, M. Garcin and J. L. Volle, *J. Therm. Anal. Cal.*, 49 (1997) 727.
- 9 M. V. K ok, J. M. Letoffe, P. Claudy, D. Martin, M. Garcin and J. L. Volle, *Fuel*, 75 (1996) 787.
- 10 M. V. K ok, J. M. Letoffe and P. Claudy, *J. Therm. Anal. Cal.*, 56 (1999) 959.
- 11 M. V. K ok, J. M. Letoffe, P. Claudy, M. Garcin and J. L. Volle, *Fuel*, 7 (1995) 810.
- 12 M. V. K ok and C. Acar, *J. Therm. Anal. Cal.*, 83 (2006) 445.
- 13 M. V. K ok, *J. Therm. Anal. Cal.*, 84 (2006) 361.

Received: February 6, 2007

Accepted: March 20, 2007

OnlineFirst: July 5, 2007

DOI: 10.1007/s10973-006-8254-2