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Determining the wax content of crude oils by using differential scanning calorimetry

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Abstract

By the use of differential scanning calorimetry (DSC), a new method to measure the wax content of crude oil has been developed. In this paper, 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, i.e. $Q_{\text{oil}}/Q_{\text{wax}}$. For the 14 studied crude oils with the wax content ranging from 1 to 27 wt.%, the wax contents determined by the presented method are in good agreement with those determined by standard acetone method, with an absolute average deviation of only 0.82 wt.%. This method has an advantage over reported DSC methods in which the exact dissolution or precipitation enthalpy of wax is a must. It is also found that the wax contents determined by either of the two methods show good linear relationship with the total thermal effect Q_{oil}, with the correlation coefficients over 0.96. According to the empirical correlations, the wax content of a crude oil can be easily determined by using the DSC total thermal effect Q_{oil}. In addition and more significantly, 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.

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Keywords: Crude oil; Wax content; Differential scanning calorimetry (DSC)

1. Introduction

Determining the wax content of crude oil is of great importance for petroleum industry, especially for production, storage and transportation of waxy crude oils. There have been some methods for wax content measurement. The standard acetone method (UOP method 46–64) and its modified versions [1,2] appear to be the industrial practice to determine the wax content of crude oils. Besides, gas chromatography [3], pulsed nuclear magnetic resonance (NMR) [4] and density measurement technique [5] have been used for measuring the wax content. However, the procedure of standard acetone method is very complex and some toxic solvents (such as toluene, benzene, etc.) have to be used. Gas chromatographic method and pulsed NMR method bear poor accuracy and low repeatability [3,4]. Density measurement technique requires specialized equipment, and no further application has been reported in determining the wax content of crude oils.

In recent years, researchers are trying to find more convenient and reliable methods to determine the wax content of crude oils. Differential scanning calorimetry (DSC) is well documented as a powerful technique for investigating the characteristics of crude oils [6–13]. Previous work has reported that determining the wax content by DSC generally requires the base-line computation [6–12] and the knowledge of the experimental equation $\Delta H_{\text{diss}} = f(T)$ (the dissolution enthalpy) [7–10] which allows transformation of the measured heat in the wax mass and therefore the computation of wax content. The base-line for a crude oil is generally assumed to be a line between the end of the exothermal effect after the glass transition temperature and the end of the dissolution of the wax [9], or a straight line computed by least-squares fitting with the values of the calorimetric signal included in the temperature range from wax appearance temperature (WAT) to 10 K above [11]. However, in most cases, the values of the calorimetric signal between WAT and 10 K above it are not straight enough for base-line computation, and the glass transition temperature of crude

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oil is generally hard to reach when liquid N_2 cooling is applied. Furthermore, every crude oil has its own unique experimental equation $\Delta H_{\mathrm{diss}} = f(T)$, which is very difficult to determine accurately. Some studies were reported that the average precipitation enthalpy ΔH_{prec} [11,12] of pure wax in the crude oil was used for the computation of wax content. Unfortunately no satisfied ΔH_{prec} or related equations have been achieved.

In the present work, a new method has been proposed and approved to determine the wax content of crude oil more accurately. Wax contend can be determined by using the total thermal effect Q ratio of the crude oil and the corresponding wax sample obtained by standard acetone method, i.e. $Q_{\mathrm{oil}}/Q_{\mathrm{wax}}$. Empirical correlations have been established, which made the determination of wax content competitively easier than earlier reported methods.

2. Experimental details

2.1. Samples

Fourteen crude oils used in this work cover a large range of fluid compositions and properties. A brief description of the crude oils investigated is given in Table 1. The wax contents are determined by both the presented DSC method and the standard acetone method. Before experiment, all the crude oils are thermally pretreated, namely, the samples are heated to 80 °C for 2 h in closed containers and shaken thoroughly to ensure complete dissolution of wax. Then the closed containers are left to cool to environmental temperature.

2.2. Differential scanning calorimetry

All thermal analyses are performed using a TA2000/MDSC2910 DSC apparatus. Calibration for temperature and heat flow is carried out using the melting point and the heat of melting high purity metal indium. Dry N_2 gas is purged through the DSC cell, and the cooling is accomplished with a liquid-nitrogen cooling-accessory. A 4–8 mg thermally pretreated crude oil specimen is then transferred into an aluminum crucible, which is then sealed and weighed. Experiments are carried out by heating the crucible to 80 °C and keeping the temperature for 1 min, and then cooling it at a cooling-rate of 5 °C/min from 80 to −30 °C. Four to five parallel runs are made and averaged results are used to improve precision.

Table 1
Brief description of oil samples used in this investigation

Sample no.	Crude oil	WAT[a]	Pour point[b]	Wax content[c] (wt.%)
1	Qinhai	46.5	38	20.18
2	Daqing	43.2	36	26.29
3	Zhongyuan	49.7	35	21.51
4	Mahuining	28.9	18	10.12
5	Shengli	34.3	17	9.62
6	Qiuling	21.5	15	10.93
7	Nanhai	44.4	33	19.60
8	Sudan	57.8	35	21.23
9	Donghetang	17.2	<-30	1.58
10	Oil blend 1	39.3	25	9.71
11	Oil blend 2	35.1	30	15.99
12	Oil blend 3	42.8	29	12.51
13	Oil blend 4	34.9	13	8.37
14	Oil blend 5	31.8	5	6.08

[a] The wax appearance temperatures were determined using DSC technique.
[b] The pour points were determined using standard ASTM D97-2001.
[c] The wax contents were determined by standard acetone method.

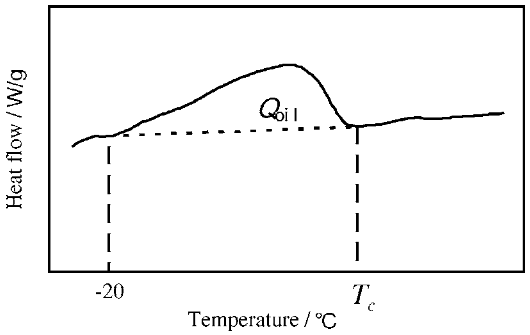

Fig. 1. A sample of DSC curve of crude oil.

In this paper, the total thermal effect Q of the wax precipitation in specimen can be computed by integrating the area between DSC calorimetric signal curve and the line connecting the two signals at temperatures of −20 °C and WAT (see Fig. 1). This procedure can easily be carried out by using a software from TA instrument thermal analyst.

2.3. Modified standard acetone method

The wax contents of crude oils are determined according to the Chinese Petroleum Test Standard SY/T 7550–2000, a slightly modified version of the standard acetone method. The specimen of thermally preheated crude oil is mixed with petroleum ether (1:30 (v/v)), left for about 1 h to ensure complete dissolution, then transferred to a glass chromatographic column packed by calcined F-20 alumina which is prewetted by petroleum ether. Then add the eluant of benzene, simultaneously collect eluate at the rate of 2–3 ml/min into a clean weighted Erlenmeyer flask. Take away the flask when the obvious black ring of cut-point reaches the bottom of the alumina bed. Evaporate the collected eluate at 120 °C to remove most of the solvent, and the left is dissolved in the 1:1 mixture of toluene and acetone. Then place the flask in a cold bath of −20 °C, keep it for 30 min to ensure the wax completely precipitate. Next, filtrate and evaporate the solvent to dry, reweigh the bottle to obtain the percentage of total wax in the original oil sample. According to the standard, the repeatability of this method is within ±10% relative.

3. Results and discussion

3.1. Experiment results

The wax contents of all the fourteen crude oils are determined using both the presented DSC technique and the standard acetone method. The results given in Table 2 show that the Q_{oil}/Q_{wax} values are in good agreement with wax contents determined by standard acetone method, and therefore Q_{oil}/Q_{wax} can be used to determine the wax content. The average absolute deviation is 0.82 wt.%, and the average relative deviation is 6.996%.

3.2. Empirical equations

Good linear relations can be found between the Q_{oil} and the corresponding wax contents determined by both standard acetone method and Q_{oil}/Q_{wax} method (see Fig. 2).

The linear relation between the Q_{oil} and the corresponding wax contents determined by Q_{oil}/Q_{wax} method can be expressed as Eq. (1) with a correlation coefficient of $R^2 = 0.9837$.

$$c_{wax} = 0.75Q_{oil} + 0.20 \tag{1}$$

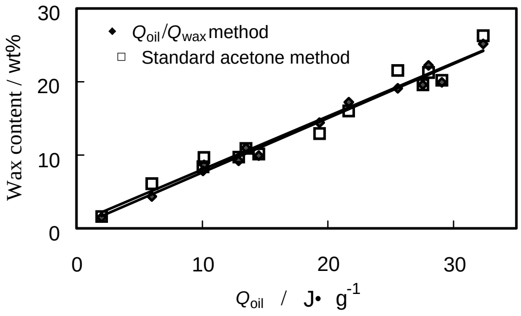

Fig. 2. The relationship between wax content and the Q_{oil}.

where c_{wax} (wt.%) is wax content of crude oil, Q_{oil} (J/g) is the total thermal effect Q of crude oil between WAT and −20 °C.

The linear relation between the Q_{oil} and the corresponding wax contents determined by the standard acetone method can be described as Eq. (2) with a correlation coefficient of $R^2 = 0.9651$.

$$c_{wax} = 0.73Q_{oil} + 0.74 \tag{2}$$

The comparison of measured wax contents and computed ones by Eqs. (1) and (2) is shown in Table 3 and Fig. 3. The average absolute deviation of wax contents between Eq. (1) and the Q_{oil}/Q_{wax} method or between Eq. (2) and the standard acetone method is within an acceptable level. Because the wax content results from the two methods are in good agreement, there is minor difference between the two empirical equations with only less than 0.5 wt.% of absolute deviation within the wax content range of 0–27 wt.%. According to Eq. (1) or Eq. (2), the wax content of any crude oil can be easily computed provided that the total thermal effect Q of the wax precipitation in crude oil between WAT and −20 °C was obtained.

3.3. Application in determination of precipitated wax at different temperatures

Eqs. (1) and (2) help improving the accuracy of computing the amount of precipitated wax in crude oils at different temperatures when the precipitation enthalpy or dissolution enthalpy of pure wax and the base-line computation are difficult to determine.

When the values of the DSC calorimetric signal between WAT and 10 K above it are straight enough for base-line computation, an adjustment of the precipitation or dissolution enthalpy of pure wax can be used to make the computed

Table 2
Comparison of the two wax content determination methods

Sample no.	Total thermal effect Q (J/g)		Wax content[a] (wt.%)		Deviation (wt.%)	Relative deviation (%)
	Q_{wax}	Q_{oil}	A	B		
1	145.6	29.07	19.96	20.18	−0.22	−1.09
2	128.6	32.34	25.14	26.29	−1.15	−4.37
3	133.6	25.54	19.11	21.51	−2.40	−11.16
4	145.9	14.49	9.93	10.12	−0.19	−1.88
5	117.1	10.12	8.65	9.62	−0.97	−10.08
6	122.8	13.48	10.97	10.93	0.04	0.37
7	139.8	12.89	9.22	9.71	−0.49	−5.05
8	140.5	27.56	19.61	19.60	0.01	0.05
9	125.9	27.99	22.23	21.23	1.00	4.71
10	133.4	2.00	1.50	1.58	−0.08	−5.06
11	125.9	21.67	17.21	15.99	1.22	7.63
12	134.3	19.32	14.39	12.91	1.48	11.46
13	128.0	10.06	7.86	8.37	−0.51	−6.09
14	138.3	5.98	4.32	6.08	−1.76	−28.95
Absolute average					0.82	6.996

Deviation = $A - B$; relative deviation = $((A - B)/B) \times 100\%$.

[a] Wax content A was determined by Q_{oil}/Q_{wax}; wax content B, standard acetone method.

Table 3
Deviations of computed and measured wax contents

Item	Number of data, *n*	Absolute deviation			Relative deviation		
		Maximum (wt.%)	Average (wt.%)	Standard deviation	Maximum (%)	Average (%)	Standard deviation
Eq. (1)	14	1.75	0.72	0.51	12.00	6.14	3.58
Eq. (2)	14	2.12	1.07	0.70	39.24	10.36	9.71

Note: Absolute average deviation $= (1/n)\sum_1^n |c_c - c_m|$; average relative deviation $= (1/n)\sum_1^n |c_c - c_m|/c_m$; standard deviation $= \sqrt{\left(n\sum(c_c - c_m)^2 - \left[\sum|c_c - c_m|\right]^2\right)}\,/n(n-1)$, where c_c, c_m are calculated and measured wax contents.

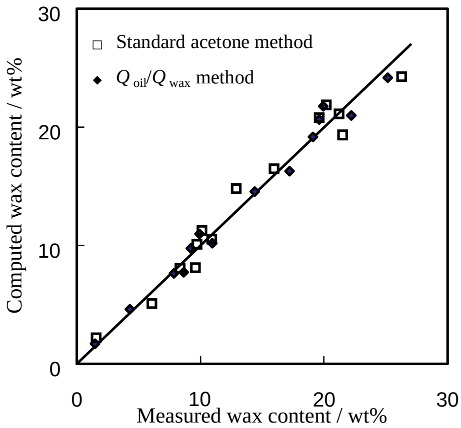

Fig. 3. Computed wax contents vs. measured ones.

wax content by reported DSC methods equal to the results from Eq. (1) or Eq. (2). Thus, the amount of precipitated wax at different temperatures can be computed more accurately.

When the values of the DSC calorimetric signal between WAT and 10 K above it are not straight enough for base-line computation, an approximate average enthalpy of precipitation of pure wax can be assumed between 200 and 230 J/g [11,12], and then adjust an assumed base-line to make the computed wax content equal to that from Eq. (1) or Eq. (2). Therefore, the amount of precipitated wax at different temperatures can be achieved.

4. Conclusions

Through experimental studies, we can come to the conclusions as follows:

1. The wax content of crude oil can be determined by the ratio of total thermal effect Q of the crude oil and that of its precipitated wax obtained by using standard acetone method.
2. Two empirical correlations have been established on the basis of good linear relations between Q_{oil} and the wax contents determined by both standard acetone method and Q_{oil}/Q_{wax} method. Those make it easier to determine the wax content of crude oils.
3. The new established correlations open a new way to improve the accuracy of computing the amount of precipitated wax in crude oils at different temperatures.

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