Relationship Between Slip Melting Point and Pulsed NMR Data of Palm Kernel Oil

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A quantitative relationship between slip melting point (SMP) of palm kernel oil and pulsed nuclear magnetic resonance (NMR) data was established. Regression analysis on the SMP and solid fat content (SFC) data by NMR afforded the following relationship:

$$\text{SMP (°C)} = 0.03278 \times (\text{SFC 10}) + 0.1458 \times (\text{SFC 20}) + 19.1738$$

where SFC 10 was the solid fat content (%) at 10°C and SFC 20 was the solid fat content (%) at 20°C. The coefficient of multiple correlation was 0.87871. The equation was tested with 12 samples of crude and refined palm kernel oil. SMPs as determined indirectly by NMR correlated well with the conventional open capillary tube results (r = 0.99998). The maximum difference observed was 0.3°C. The correlation can be applied usefully for quality control.

KEY WORDS: Correlation, palm kernel oil, pulsed nuclear magnetic resonance, slip melting point, solid fat content.

The softening point (open tube melting point) or slip melting point (SMP) is often used to characterize oils and fats and is related to their physical properties, such as hardness and solidification/melting behavior. It is usually determined by the AOCS method (1) or, in the Malaysian palm oil industry, the PORIM method (2). Both the methods require 16 hr for conditioning the samples at 4-10°C. The methods, which are not applicable to all types of oils and fats, are time-consuming and therefore not suitable for quality control, especially during production such as controlled hydrogenation of oils to specified melting points. Hence a rapid method for SMP determination will certainly be useful and desired for quality control.

The nuclear magnetic resonance (NMR) method (3-7) has now become a standard technique and has replaced dilatometry as the preferred method for the determination of solid fat content (SFC) of oils and fats in the food industry. Reliable commercial NMR instruments are available which can give a direct read-out of SFC. The method has therefore been widely adopted for production quality control.

In view of the concern expressed over the empirical nature of the conventional methods used in the determination of SMP, and whether there is any quantitative relationship between SFC of oils and fats and their SMP, the objectives of this study were: i) To establish whether a quantitative relationship exists between SMP and SFC so that SMP can be interpolated from the measurement of SFC over a temperature range; and ii) to develop a rapid, reliable method for the determination of SMP of oils and fats from pulsed NMR data to facilitate quality control.

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As the NMR method for SFC determination has now become routine and standardized, and if the above two objectives are achieved, the NMR instrument can easily and advantageously be utilized to obtain SMP data in a much shorter time than otherwise obtained from the conventional methods.

EXPERIMENTAL PROCEDURES

Materials. Eighteen samples of refined, bleached and deodorized (RBD) palm kernel oil (PKO) from different sources were used for establishing the relationship, while another twelve samples of crude and RBD PKO were used for checking the validity and accuracy of the relationship established.

Slip melting point (SMP). SMP of the oil samples was determined by the PORIM method (2).

Nuclear magnetic resonance (NMR). The NMR measurement was performed using a pulsed NMR spectrometer (Bruker minispec pc 120, Bruker Analytische Messtechnik GmbH, Karlsruhe, Germany) with a 4.7 Kilogauss permanent magnet maintained at 40°C and providing hydrogen nuclei with a resonance frequency of 20 MHz. The Minispec pc 120 was calibrated and checked with standards having predetermined solids of 0, 30.3 and 74.1%.

Solid fat content (SFC). Unless otherwise specified, SFCs of the samples were analyzed according to the parallel tempering/measuring procedure by IUPAC (5). Total analysis time for each run is about 2 hr. The data on SMP and SFC for all the samples were prepared using the computer program "DATAPREP" (R. E. Timms, Swinderby, Great Britain) written in BASIC. The prepared data are shown in Table 1.

TABLE 1

Slip Melting Point and Solid Fat Content Data for RBD PKO Samples

Sample	SMP (°C)	SFC 10 (%)	SFC 20 (%)	SFC 25 (%)
1	27.7	69.27	41.74	16.98
2	27.4	70.37	41.33	15.97
3	27.6	70.13	41.19	17.16
4	27.8	70.50	42.10	17.50
5	27.8	69.62	41.90	18.28
6	27.6	69.51	41.79	17.89
7	27.4	69.91	42.11	17.95
8	27.5	69.10	42.07	17.68
9	27.5	69.88	42.02	17.51
10	27.7	69.58	42.97	17.11
11	27.2	66.91	40.35	16.00
12	27.6	71.75	42.47	17.99
13	27.8	68.05	43.95	18.45
14	27.2	66.80	40.70	17.90
15	27.4	72.61	40.46	17.58
16	27.8	73.38	42.46	18.79
17	27.2	65.85	40.35	16.24
18	27.0	63.80	39.08	12.52

Regression analysis of the data was performed using the program "REGRESS" (R. E. Timms), which was run with the Y variable specified as SMP and the X variables specified as SFC 10, SFC 20 and SFC 25, where SFC 10 was SFC (%) at temperature 10°C; SFC 20 was SFC (%) at temperature 20°C; and SFC 25, SFC (%) at temperature 25°C.

RESULTS AND DISCUSSION

In the present paper, the equation was determined by means of regression analysis. A constant was included in the regression analysis because it gave significant improvement in results. Initially, multiple regression was run with the Y variable specified as SMP and the other three variables as SFC 10, SFC 20 and SFC 25. However, since SFC 25 had a t value which was not significant at the 95% confidence level, it was eliminated and a new regression equation was computed with the X variates, SFC 10 and SFC 20. The output produced is shown in Table 2, from which the following regression equation (relationship) with constant (intercept) that links SMP with SFC for PKO was obtained.

Relationship. The correlation is:

$$\text{SMP of RBD PKO} = 0.03278 \times (\text{SFC 10}) + 0.1458 \times (\text{SFC 20}) + 19.1738$$

where SMP denotes slip melting point; SFC 10 denotes SFC at 10°C; and SFC 20 denotes SFC at 20°C. The correlation coefficient (0.87871) indicated the closeness of fit. The observed and predicted values obtained from the computer are shown in Table 3. The equation was able to describe the data well, and can be used to predict the SMP of PKO whose SFCs have previously been determined with a reasonably high degree of accuracy. The goodness of fit is indicated below in terms of 95% confidence limit (res.std. dev. × t), and maximum deviation of predicted from observed. The dependent variable was SMP of RBD PKO; 95% CL, 0.26; and max. deviation, 0.24.

Example of the use of the equation. To predict or determine the SMP of a palm kernel oil sample having the following SFCs (and SMP determined by conventional method): SFC at 10°C, 71.5%; 20°C, 41.7%; 25°C, 17.6%; and SMP (conventional), 27.8°C. Using the established equation, SMP of PKO = 0.03278 × (SFC 10) + 0.1458 × (SFC 20) + 19.1738 = 27.6°C. The figure determined from the equation compares favorably with the actual result.

TABLE 2

Outputs of Regression Analysis on Palm Kernel Oil Data

Correlation Matrix
Degrees of freedom = 16

	SFC 10	SFC 20	SMP (°C)
SFC 10	1.0000	0.5162	0.6623
SFC 20		1.0000	0.8365
SMP (°C)			1.0000
Mean	69.28	41.61	27.51
Range	9.58	4.87	0.80
Std. Dev.	2.3	1.1	0.2

Regression Coefficients
Y Variate: SMP (°C)

	Estimate	Std. Error	T
Constant	19.1738	1.1699	16.3894
SFC 10	0.03278	0.01501	2.1839
SFC 20	0.1458	0.03111	4.6855

Multiple Correlation Coefficient = 0.87871
Residual Standard Deviation = 0.12434

Analysis of Variance

	DF	SS	MS	F
Regression	2	0.7858	0.3929	25.41
Residual	15	0.2319	0.01546	
Total	17	1.01768	0.05986	

TABLE 3

Observed and Predicted SMP of PKO

Sample	SMP observed (°C)	SMP predicted (°C)	Difference (°C)
1	27.7	27.53	0.17
2	27.4	27.51	−0.11
3	27.6	27.48	0.12
4	27.8	27.62	0.18
5	27.8	27.56	0.24
6	27.6	27.54	0.06
7	27.4	27.60	−0.20
8	27.5	27.57	−0.07
9	27.5	27.59	−0.09
10	27.7	27.72	−0.02
11	27.2	27.25	−0.05
12	27.6	27.72	−0.12
13	27.8	27.81	−0.01
14	27.2	27.30	−0.10
15	27.4	27.45	−0.05
16	27.8	27.77	0.03
17	27.2	27.21	−0.01
18	27.0	26.96	0.04

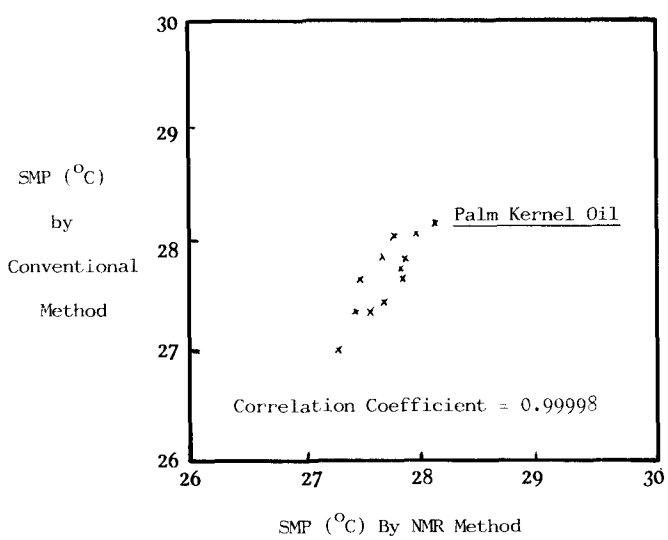

FIG. 1. Correlation of SMP by conventional and NMR methods.

TABLE 4

Comparison of SMP of RBD and Crude PKO by Conventional and NMR Methods

	RBD PKO					CRUDE PKO					
	1	2	3	4	5	6	7	8	9	10	11	12
SFC (% by NMR)												
10°C	66.8	66.6	71.0	62.8	71.8	68.1	69.7	67.6	69.0	67.9	67.9	67.9
20°C	41.7	41.5	45.4	41.2	40.9	44.0	43.7	42.5	42.0	43.8	43.6	44.8
25°C	17.7	17.6	19.5	17.6	18.4	18.5	20.7	20.2	19.9	21.9	21.3	21.5
SMP (°C-NMR)	27.4	27.4	28.1	27.2	27.5	27.8	27.8	27.6	27.6	27.8	27.7	27.9
SMP (°C-Conventional)	27.3	27.6	28.1	27.0	27.3	27.8	27.6	27.4	27.8	27.7	28.0	28.0

TABLE 5

SFC and SMP Data for PKO Determined by AOCS Method[a]

	1	2	3	4	5	6	7	8
SFC (% by NMR)								
10°C	62.3(71.0)[b]	60.8(68.1)	60.1(69.7)	58.8(67.6)	58.6(69.0)	59.7(67.9)	59.4(67.9)	59.3(67.9)
20°C	39.6(45.4)	38.5(44.0)	38.2(43.7)	37.5(42.5)	37.4(42.0)	38.4(43.8)	38.0(43.6)	38.2(44.8)
25°C	22.2(19.5)	20.8(18.5)	20.6(20.7)	20.3(20.2)	19.5(19.9)	20.9(21.9)	20.9(21.3)	20.8(21.5)
SMP (°C-NMR)	27.0(28.1)	26.8(27.8)	26.7(27.8)	26.6(27.6)	26.5(27.6)	26.7(27.8)	26.7(27.7)	26.7(27.9)
SMP (°C-Conventional)	28.0	27.8	27.6	27.4	27.8	27.7	28.0	28.0

[a]Reference 6. [b]Values given in parentheses are the results obtained by the IUPAC Method (5).

The relationship thus established for SMP and SFC permits one to determine the SMP of PKO in a shorter time (2 hr) than the normal AOCS procedure (16 hr).

Accuracy and repeatability. In order to test the accuracy of the equation for determining SMP, 12 samples of crude and refined PKO were determined for their SMP (conventional) and SFC (NMR). Their results are shown in Table 4, together with their corresponding SMPs derived from the equation. The correlation between the SMP of PKO determined by the conventional open capillary tube method and that from SFC by NMR is shown in Figure 1. There is good correlation between the two methods (correlation coefficient = 0.99998). The maximum difference in SMP observed between the two methods is 0.3°C. The good accuracy and repeatability of results offers the NMR method a faster way of determining the SMP of PKO.

The SFC data obtained by NMR can be usefully applied in quality control to predict the SMP of refined as well as crude PKO satisfactorily. The agreement between the results from the conventional and NMR methods is reasonably good. With more data available the mathematical model can be further refined and the correlation improved.

In Table 5 the SFCs of PKO determined by the AOCS tempering procedure (6) are compared with those by the IUPAC method (5). Generally, SFC 10 and SFC 20 determined by the AOCS method are about 8-9% and 5-6% lower than those obtained by the IUPAC method, respectively. Consequently, the predicted SMP is about 1°C lower (see Table 5) than that derived from the NMR data obtained by the procedure described in this paper.

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