Determination of Iodine Value of Palm Oil by Differential Scanning Calorimetry

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ABSTRACT: Iodine value (IV) is used as a parameter in process control as well as a quality parameter in traded palm oil products. IV measures the number of double bonds in the molecular structure of an oil. To form a double bond, carbon requires more energy (615 kJ/mol) than to form a single bond (350 kJ/mol). Therefore, the thermal behavior of an oil could reflect its iodine value. This study was conducted to demonstrate the use of a differential scanning calorimeter (DSC) to determine the IV of palm oil and its products as an attempt to reduce the use of chemicals in the analysis. The DSC thermograms of palm oil showed a clear separation of the substances that have low melting points (low-T), consisting of triunsaturated, monosaturated and disaturated triglycerides, from the high ones (high-T), consisting of trisaturated triglycerides. Regression analysis showed that the peak characteristics, namely, area and height of the low-T group and height of the high-T group in the heating thermogram and also the height of the high-T group in the cooling thermogram, can predict the IV of palm oil with R^2 higher than 0.99. This study concludes that DSC can be used to determine the IV of palm oil and its products.

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KEY WORDS: DSC, HPLC, iodine value, palm oil, thermal behavior, triglyceride.

A major concern of the International Union of Pure and Applied Chemistry (IUPAC) commission on oils, fats, and derivatives is the impact of analytical reagents on the environment as well as on the health of the analyst (1). Although the quantity of chemicals used in laboratories is much smaller than in industry, more toxic chemicals are encountered. Iodine value (IV) is an important parameter in oil and fat specifications; therefore, IV analysis is a routine activity in the palm oil industry.

Almost all specifications for palm oil and its products include IV. So, IV is used as a parameter in process control in the palm oil industry (2) and also as a quality parameter in traded goods. Usually, IV is determined by titration with carbon tetrachloride as a solvent (3). In general, chlorinated solvents (chloroform, carbon tetrachloride, or methylene chloride) make up about 25% of the solvents used in a typical IV determination (4). These solvents are considered to have the greatest impact on health and the environment by the IUPAC commission (1). Carbon tetrachloride is toxic and carcinogenic, with a threshold limit value of 5 ppm in air (5). An attempt was made to replace this solvent with cyclohexane or cyclohexane–acetic acid (4,6,7). IV determination by instrumental methods, e.g., refractive index, Fourier transform (FT)–nuclear magnetic resonance, near infrared (IR), and FT–IR, has been reported (5,8,9).

IV is a measure of unsaturation of oils and fats. It is defined as the percentage of iodine absorbed by the oil or fat under the test conditions (10). Differential scanning calorimetry (DSC) is a thermoanalytical technique for monitoring changes in physical or chemical properties of materials by directly measuring the specific heat of a material. The area enclosed by the curve of instrument signal recorded against time is directly proportional to the energy change (11). To form a double bond between two carbon atoms requires more energy (615 kJ/mol) than to form a single bond (350 kJ/mol) (12). Therefore, the thermal behavior of an oil might well reflect the IV of the oil.

In this study, DSC was used to determine the IV of palm oil and its products as a means to reduce the use of chemicals in the analysis.

MATERIALS AND METHODS

Malaysian refined, bleached, deodorized palm oil (RBDPO) with IV of 51, RBD-palm olein with IV of 56, RBD-palm stearin with IV of 29, and super olein with IV of 60 were used in this study. From these oils, 16 blends were prepared to obtain a range of IV from 29 to 60. All chemicals used were either of analytical or high-performance liquid chromatography (HPLC) grade.

Each blend was analyzed for its IV by a standard method (3) and for its cooling and heating thermograms by DSC. A Perkin-Elmer Model DSC-7 differential scanning calorimeter (DSC) (Norwalk, CT) was used for thermal analysis of the samples. The instrument was calibrated with indium and dodecane. Samples of *ca.* 3–10 mg were weighed into aluminum pans, and covers were crimped into place. An empty, covered pan was used as a reference. Both were placed in the instrument sample chamber. Heating and cooling thermograms were made on each sam-

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ple. The following temperature program was used for each sample: 80°C isotherm for 5 min, cool from 80 to −50°C at a rate of 5°C/min, hold at −50°C for 5 min. The same sample was then heated from −50 to 80°C at the same rate.

Triglyceride composition was determined by HPLC. The HPLC system used was composed of a Shimadzu (Kyoto, Japan) LC-10 AD liquid chromatograph, Shimadzu SIL-10A Auto injector, Shimadzu system controller SCL-10A, and RID-6A Shimadzu refractive index detector. The column was a Nova-Pak C18 (3.9 × 300 mm) Waters (Milford, MA) packed with a particle size of 5 μm. The mobile phase was a mixture of acetone/acetonitrile (63.5:36.5), and the flow rate was 1 mL/min. The injection volume was 10 μL of 5% (wt/vol) oil in chloroform. Sensitivity was adjusted to 16×10^4 refractive index units full-scale deflection. Triglyceride peaks were identified based on earlier results (13,14).

The relationship between peak characteristics of DSC and IV was determined by stepwise regression in statistical analysis system (SAS) release 6.08 (SAS Institute, Cary, NC). It is hypothesized that, if IV can be predicted from these peak characteristics, the DSC method could be used to determine the IV of palm oil.

RESULTS AND DISCUSSION

The standard analysis showed that the IV of the samples ranged from 29 to 60. Typical crude palm oil has an IV of around 50, typical stearin between 30 and 40, olein around 56, and double fractionation of olein gives an IV of around 60. Thus, this range covered almost all of the palm oil products.

The thermograms showed clear differences among samples as shown in Figure 1 for the heating thermogram and in Figure 2A,B,C for the cooling thermograms. Five peaks were found in the heating thermogram and three in the cooling thermograms. Basically, the peaks can be classified into high-temperature melting points (high-T group) and low-temperature melting points (low-T group) (15). The thermograms showed that the higher the IV, the larger and higher the peak of the low-T peak group but the smaller and shorter the peak of the high-T peak group. The glyceride composition of samples with the lowest IV (IV = 29) consisted of diglyceride (4.01%), triunsaturated triglyceride (TG) (5.24%; OOL, OOO), monosaturated TG (21.52%; PLO, POO, OOS), disaturated TG (52.13%; MPL, PPL, PPO, POS, SOS), and trisaturated TG (36.46%; LaLaM, MMM, PPP) where La stands for lauric, M for myristic, P for palmitic, O for oleic, L for linoleic, and S for stearic acid. The oil with IV of 48 consisted of diglyceride (5.41%); triunsaturated (6.16%), monosaturated (35.21%), disaturated (46.22%), and trisaturated (7.01%) TG. The oil with the highest IV (IV = 60) consisted of diglyceride (5.89%); triunsaturated (10.75%), monosatu-

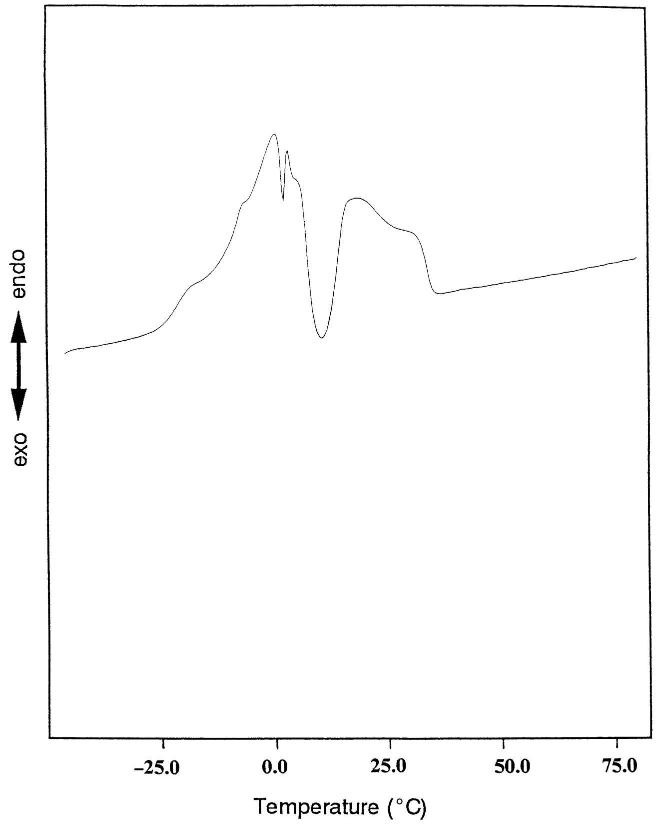

FIG. 1. Heating thermogram of palm oil with iodine value of 48, run from −50 to 80°C at a heating rate of 5°C/min.

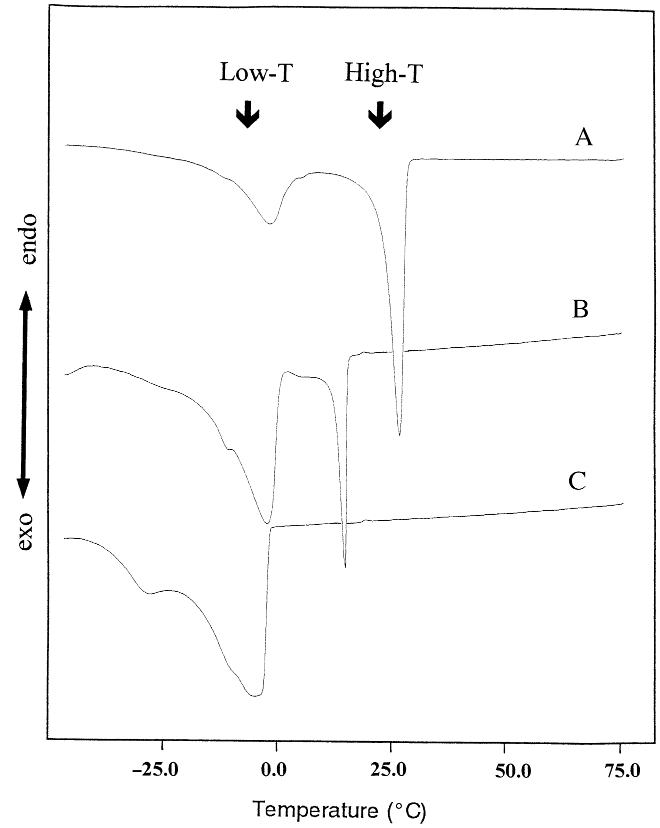

FIG. 2. Cooling thermograms of palm oil samples run from 80 to −50°C at a cooling rate of 5°C/min; (A) oil having iodine value (IV) of 29, (B) IV = 48, (C) IV = 60. Abbreviations: Low-T, low-temperature melting points; High-T, high-temperature melting points.

TABLE 1
Stepwise Regression with Heating and Cooling Thermograms as the Independent Variables[a]

Step	Regression equation	R^2
1	IV = 55.11505 – 3.1965 HhTco	0.945
2	IV = 50.0982 + 2.3853 HlThe – 3.1335 HhTco	0.973
3	IV = 50.9586 + 6.1395 HlThe – 0.0206 AlThe – 3.0132 HhTco	0.980
4	IV = 54.0444 + 6.6844 HlThe – 0.02882 AlThe + 3.4935 HhThe – 5.6889 HhTco	0.992

[a] Abbreviations: IV, iodine value; HhTco, peak height (H) of the high-temperature (hT) cooling (co) thermogram; HlThe, peak height (H) of the low-temperature (lT) heating (he) thermogram; AlThe, peak area (A) of the low-temperature (lT) heating thermogram; HhThe, peak height (H) of the high-temperature (hT) heating thermogram.

rated (43.05%), disaturated (38.18%), and trisaturated (2.13%) TG. In the DSC cooling thermogram of the highest IV sample (Fig. 2C), the high-T peaks did not appear, while the oil with an IV of 48 (Fig. 2B) and that with the lowest IV (Fig. 2A) showed these peaks. Based on the TG composition, the highest IV oil has low trisaturated TG (2%), the oil with IV of 48 has 7%, and the lowest IV oil has 36%. Therefore, the high-T peaks reflected the presence of trisaturated TG.

From each sample, there were eight variables, namely, peak area (A) and peak height (H) of the low-T (lT) group in the heating (he) thermogram (AlThe and HlThe) and in the cooling (co) thermogram (AlTco and HlTco), peak area and peak height of the high-T (hT) group in the heating thermogram (AhThe and HhThe) and in the cooling thermogram (AhTco and HhTco). These variables were used as the independent variables in the stepwise regression analysis with IV as the dependent variable. The summary of the stepwise regression is presented in Table 1.

The stepwise regression analysis showed that four variables were adequate to estimate the iodine value of the oil with $R^2 = 0.992$. The variables were HlThe, AlThe, HhThe, and HhTco. Therefore, the regression model to predict IV is shown in the following equation with $R^2 = 0.992$:

$$\begin{array}{lllll} \text{IV} = 54.044 & + 6.6844\ \text{HlThe} & - 0.0288\ \text{AlThe} & + 3.4935\ \text{HhThe} & - 5.6889\ \text{HhTco} \\ \quad (1.21) & (1.2828) & (0.007) & (0.8709) & (0.6742) \\ & [0.03\%] & [0.17\%] & [0.20\%] & [0.01\%] \end{array} \qquad [1]$$

Figures in parentheses are the standard deviations of the respective parameters. The *P* values of these variables are listed in brackets.

The role of the liquid fraction in determining IV is represented by both the height (HlThe) and the area (AlThe) of the peaks with different regression coefficient signs. H1The has a positive coefficient whereas AlThe has a negative sign. These two variables are highly correlated ($r = 0.944$), which means that the height increases or decreases in harmony with the area. For each change in the liquid fraction, the area changes on a much bigger scale than the height, which results in a much bigger variability, i.e., standard deviation of 125.43 compared to 0.66 for the height. Consequently, the big change was complemented by a small coefficient in the regression. The probability value (*P* value) of the coefficient of HlThe (0.03%) is much smaller than that of AlThe (0.17%), which indicates that the height is more significant. Therefore, in aggregate, the low-T peaks contribute positively to IV.

The role of the solid fraction in the regression was represented by the peak heights in both the heating and cooling thermograms, i.e., HhThe and HhTco, which are highly correlated ($r = 0.987$). The regression coefficient of HhThe is positive, whereas that of HhTco is negative. The *P* value of HhThe (0.20%) is much bigger that that of HhTco (0.01%), which indicates that the latter is much more significant. Therefore, in aggregate, the solid fraction contributes negatively. These results agree well with the theory: the more liquid the fraction, and consequently the less solid the fraction, the higher the IV.

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REFERENCES

1. Dieffenbacher, A., New Standard Methods for the Analysis of Oils and Fats, *Mal. Oil Sci. Tech. 4*:167–170 (1995).
2. Hoffmann, G., *The Chemistry and Technology of Edible Oils and Fats and Their High Fat Products*, Academic Press, London, 1989, pp. 384.
3. AOCS, *Official and Tentative Methods of the American Oil Chemists Society*, 15th edn., American Oil Chemists' Society, Champaign, 1990.
4. Mozayeni, F., G. Szajer, and M. Walters, Determination of Iodine Value Without Chlorinated Solvents, *J. Am. Oil Chem. Soc. 73*:519–522 (1996).
5. Gee, P.T., Iodine Value Determination by FTIR Spectroscopy, *Mal. Oil Sci. Tech. 4*:182–185 (1995).
6. AOCS, *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th edn., American Oil Chemists' Society, Champaign, 1989.
7. PORIM, *PORIM Test Methods,* Palm Oil Research Institute of Malaysia, Ministry of Primary Industries, Malaysia, 1995, 170 pp.
8. Haryati, T., T. Herawan, and L. Buana, Use of Refractive Index for Controlling Iodine Value in the CPO Refinery and Fractionation Plants, in *Proceedings 1993 PORIM of the International Palm Oil Congress, Kuala Lumpur*, 1993, pp. 141–146.
9. Van de Voort, F.R., J. Sedman, E. Emo, and A.A. Ismail, Rapid and Direct Iodine Value and Saponification Number Determina-

tion of Fats and Oils by Attenuated Total Reflectance/Fourier Transform Infrared Spectroscopy, *J. Am. Oil Chem. Soc. 69*:1118–1123 (1992).

10. Rossell, J.B., Classical Analysis of Oils and Fats, in *Analysis of Oils and Fats*, edited by R.J. Hamilton and J.B. Rossell, Elsevier Applied Sciences, London, 1987, pp. 10–12.
11. Biliaderis, C.G., Differential Scanning Calorimetry in Food Research—A Review, *Food Chem. 10*:239–265 (1983).
12. McQuarrie, D.A., and P.A. Rock, *General Chemistry*, 3rd edn., W.H. Freeman and Co., New York, 1991, 1083 pp.
13. Swe, P.Z., Y.B. Che Man, and H.M. Ghazali, Improved NARP-HPLC Method for Separating Triglycerides of Palm Olein and Its Solid Fractions Obtained at Low Temperature Storage, *Food Chem. 56*:181–186 (1996).
14. Ghazali, H.M., A. Maisarah, S. Yusof, and M.S.A.M. Yusoff, Triglyceride Profiles and Melting Properties of Lipase-Catalyzed Transesterified Palm Stearin and Coconut Oil, *Asia Pacific J. Mol. Biol. and Biotechnol., 3*:280–289 (1995).
15. Haryati, T., Y.B. Che Man, P.Z. Swe, H.M. Ghazali, and A.B. Asbi, Thermal Analysis of Crude Palm Oil and Its Products by DSC, presented at the 87th AOCS Meeting & Expo, April 28–May 1, 1996, Indianapolis, Indiana.

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