Influence of Variety and Processing Methods on Specific Heat Capacity of Crude Palm Oil

Joseph S. Alakali, Sunday O. Eze, and Michael O. Ngadi

***Abstract*—Specific heat capacities of crude palm oils from the *Dura, Pisifera* and *Tenera* varieties of palm were measured. The oils were processed by hot and cold methods. Fresh and 12 month stored samples were analyzed using the Differential Scanning Calorimeter technique in the temperature range of -20 to 80°C. Results showed that variety of oil palm, processing method and storage history have significant effect ($P < 0.05$) on specific heat capacity of the samples. For all samples studied, the specific heat capacity increased in the temperature range from -10 to 10°C followed by a decrease to about 80°C. The specific heat capacity of *Dura* samples was highest followed by *Tenera,* whereas that of *Pisifera* was lowest. The specific heat capacity of cold processed palm oil was generally lower, ranging from 1.29 - 5.26 J/g°C while that of hot processed samples ranged from 1.80 – 6.24 J/g°C. Fresh samples had higher specific heat capacity compared to stored samples.**

***Index Terms*—Differential scanning calorimeter (DSC), Palm oil, processing methods, specific heat capacity.**

I. Introduction

Heat capacity is among the basic thermophysical and thermodynamic properties of food materials. It is directly linked with temperature derivatives of basic thermodynamic functions and therefore indispensable for the calculation of differences in these functions between different temperatures (Zabransky et al, 2001). It is used for establishing energy balances, entropy and for calculating changes in reaction enthalpies with temperature. Variations in heat capacities serve as a sensitive indicator of phase transitions and are an important tool for understanding changes in the structure of liquid solutions such as edible oils (Santos et al, 2005).

Heat capacities of edible vegetable oils are essential for a rigorous control of processes, realistic design of processes in industry (Morad et al, 1995) and setting up standards for each specific use (González et al, 2004). In order to analyse heat transfer during freezing or thawing, the specific heat capacity and heat capacity must be known (Ngadi et al, 2003). The specific heat capacities of oils and fats are also useful to determine their behaviour during different technological processes as they vary with chemical composition and temperature (Dieguez et al, 2010). It has been reported that specific heat capacities are similar for the triglycerides in their original physical state, but can increase as a function of the unsaturation of the fatty acids. Numerical values of the specific heat capacities of liquid fats are twice larger compared to that of solid fats, and the alfa (α) form has a higher heat capacity than the (beta) β form exhibits (Santos et al, 2005).

The Differential Scanning Calorimeter (DSC) is widely used to measure specific heat capacity of vegetable oils (Timms, 1985; Santos et al, 1995; Morad et al, 2000; Fasina and Colley, 2008, Narváez et al, 2008). Use of DSC to determine the specific heat capacity of triglycerides of palm oil has also been reported (Morad et al, 1995b). However, no work on the application of this technique to study the heat capacity of crude palm oil as affected by variety, processing and storage has been seen in literature. However, these factors are expected to introduce variations in the chemical composition of crude palm oil and influence its specific heat capacity. In this paper the DSC is used to study the specific heat capacity of crude palm oil from three varieties of oil palm, processed by the hot and cold method with varying storage history.

II. Materials and Method

A. Sample Preparation

Palm fruits from three oil palm varieties namely Dura, Tenera and Pisifera were collected from the Nigeria Institute for Palm Oil Research (NIFPOR) and used for the experiments. The fruits were subjected to either hot or cold processes to produce the palm oil. The processed samples were stored in sealed plastic containers and either used fresh ("Fresh") or stored for 12 months ("Stored"). The different samples were labelled as follows: DCPF (Dura, Cold Process, Fresh); DCPS (Dura, Cold Process, Stored); DHPF (Dura, Hot Process, Fresh); DHPS (Dura, Hot Process, Stored); TCPF (Tenera Cold Process, Fresh); TCPS (Tenera, Cold Process, Stored); THPF (Tenera, Hot Process, Fresh); THPS (Tenera, Hot Process, Stored); PCPF (Pisifera, Cold Process, Fresh); PCPS (Pisifera, Cold Process, Stored); PHPF (Pisifera, Hot Process, Fresh); and PHPS (Pisifera, Hot Process, Stored).

B. Measurement of Specific Heat Capacity

Specific heat capacity was measured using a DSC (Model V4.7A DSC 2000, TA Instruments, New Castle, DE, USA). Crude palm oil samples of approximately 5.30 mg were used in aluminum sample pans. Scan temperatures were from -20 to 80°C at a scan rate of 10°C/min with delay and dwell times of 2 and 1 min, respectively. Nitrogen was passed through the

Manuscript received August 9, 2012; revised September 25, 2012.

This work was supported in part by the Educational Trust Fund (ETF) of Nigeria and the Natural Science and Engineering Research Council of Canada (NSERC).

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heating chamber at atmospheric pressure and a flow of 13.3 mL/min measured at the bypass outlet. The DSC was fully computer controlled with rapid energy compensation and equipped with automatic data analysis software to calculate heat capacity from the heat flow data.

III. Results and Discussion

Fig. 1 and 2 present the effect of palm varieties and processing on specific heat capacity of crude palm oil. It is shown that the specific heat capacity of samples showed a general increase from -10°C to about 10°C followed by a sharp decrease to about 60°C. It then remained fairly constant afterwards to 80°C. This gives an indication that more heat was required to raise the temperature of oil samples in the lower temperature range (-10 to 10°C) than in the higher temperature range (10 to 80°C). According to Fasina and Colley (2010), increase in specific heat of oils with temperature is due to expansion of the materials during heating. The specific heat capacity of the samples peaked between 0 - 10°C corresponding to crystallization temperatures (Ng and Oh 1994). The peak values for the different samples were significantly different ($p \leq 0.05$). Mihara et al (2007) and Ng and Oh (1994) reported that peaks of thermograms are a function of crystallization temperature. According to the authors, crystallization temperatures of palm oils and some of their derivatives fall in the temperature range of 0 to 8°C, although it may also vary between 0 – 35°C depending on composition and cooling rate. In the crystalline state, palm oil requires more heat to break the intermolecular forces for melting. This energy demand decreases with temperature, higher or lower than the crystallization point (Mihara et al, 2007). The value of specific heat capacity obtained for the different oils in the range from 60 to 80°C are within the range reported by others authors for vegetable oils (Santos et al, 2005).

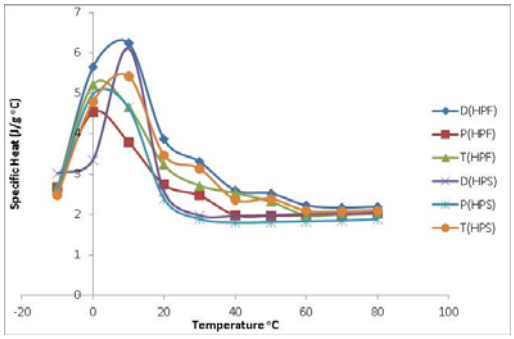

Fig. 1. Effect of oil palm variety on specific heat capacity of crude palm oil. d(HPF)- dura, hot process fresh. t(HPF)- tenera, hot process fresh. p(HPF)- pisifera, hot process fresh. d(HPS)- dura, hot process stored. p(hps)- pisifera, hot process stored. t(HPS)- tenera, hot process stored

Oils from different palm varieties presented different peak values of specific heat capacity. The specific heat capacity of *Dura* samples showed the highest peak followed by *Tenera*, while that of *Pisifera* was lowest. This indicates variation in chemical composition of samples based on variety of oil palm.

According to Tan and Che Man (2002) and Vuillequez et al (2010), crystallization of palm oil depend on the fractions of its constituents (Olein and Stearin) as well as the polymorph (α, β', β) of its triglycerides. Samples with more Stearin and β polymorph fractions are more stable and have higher crystallization temperature (Vuillequez et al, 2010). The results imply that sample from *Dura* variety are likely to have higher Stearin and β fractions followed by *Tenera* and *Pisifera*. Also, palm oil from *Dura* stock may have higher saturated fatty acids, making it more stable and accounting for the higher thermograms peaks. Tan and Che Man (2002) also reported that specific heat capacity are higher for larger molecules of triglycerides and decrease with the degree of unsaturation. This further explains variations in specific heat of the palm oil samples based on varieties.

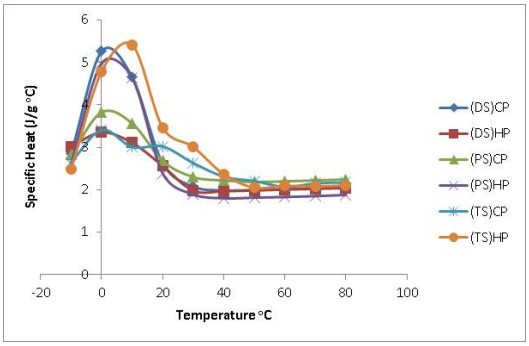

Fig. 2. Effect of processing method on specific heat capacity of crude palm oil. Legends are same as in Fig. 1.

For a given variety and storage history, the specific heat capacity of cold processed was lower (1.29- 5.26 J/g°C) than the hot processed samples (1.80 – 6.24 J/g°C). Exception to this trend was observed in the stored samples of Dura stock (Fig. 2). Similarly, specific heat capacity of stored samples tended to be higher than fresh samples of the same variety. Chemical changes occur in the oil during extraction. These changes influence the overall physical and chemical properties of the extracted oil. Normally, the degree of saturation of the fatty acids influences specific heat capacity values (Santos et al, 2005). Specific heat capacities tend to increase as a function of the unsaturation of fatty acids in the liquid and also in the solid state. Considering, thermal degradation that may have occurred during hot processing, it was expected that specific heat capacity would be higher for hot processed than cold processed oils. The results suggest that hot processed palm oil may require more energy to heat than cold processed oil. Rheology and mobility of oil and fat molecules in different states may have influence on values of specific heat capacity. Similarly, stored palm oil apparently went through quality degradation resulting in changes in its thermal properties. In particular, palm oil is likely to undergo oxidation and per-oxidation during storage leading to the breaking down of longer chain fatty acids to shorter chains (Rodenbush et al, 1999, Geller and Goodrum 2000), and resulting to reduction in its stability.

IV. Conclusion

Specific heat capacity of crude palm oil was affected by variety of oil palm, processing method and storage. The specific heat of *Dura* samples was higher followed by *Tenera* while *Pisifera* had the lowest. Cold processed oil and fresh samples had lower specific heat than the hot processed and

stored.

REFERENCES

[1] P. M. Dieguez, M. J. Beriain, K. Insausti, and M. J. Arrizubieta, "Thermal analysis of meat emulsion cooking process by computer simulation and experimental measurement," *International Journal of Food Engineering*, vol. 6, no. 1, 2010.

[2] S. O. Eze, J. S. Alakali, M. O. Ngadi, P. C. Njoku, and A. A. Ayuk, "Rheological properties of crude palm oil," *International Reviews of Chemical Engineering*, vol. 2, no. 5, pp. 598-605, 2010.

[3] O. O. Fasina and Z. Colley, "Viscosity and specific heat of vegetable oils as a function of temperature," *International Journal of Food Properties*, vol. 11, no. 4, pp. 738–746, 2008.

[4] D. P. Geller and J. W. Goodrum, "Rheology of vegetable oil analogs and triglycerides," *Journal of America Oil Chemical Society*, vol. 77, no. 2, pp. 111-114, 2000.

[5] C. González, J. M. Resa, R. G. Concha, and J. M. Goenaga, "Enthalpies of mixing and heat capacities of mixtures containing alcohols and n-Alkanes with corn oil at 298.15 K," *Journal of America Oil Chemical Society*, vol. 81, no. 9, pp. 1415-1419, 2004.

[6] N. A. Morad, M. Idrees, and A. A. Hasan, "Improved conditions for measurement of specific heat capacities of pure triglycerides by differential scanning calorimeter," *Journal of Thermal Analysis*, vol. 44, pp. 823–835, 1995.

[7] N. A. Morad, M. Idrees, and A. A. Hasan, "Specific heat capacities of pure triglycerides by heat-flux differential scanning calorimetry," *Journal of Thermal Analysis*, vol. 45, pp.1449-1461, 1995.

[8] N. A. Morad, A. A. M. Kamal, F. Panau, and T. W. Yew, "Liquid specific heat capacity estimation for fatty acids, triacylglycerols, and vegetable oils based on their fatty acid composition," *Journal of America Oil Chemical Society*, vol. 77, no. 9, pp. 1001-1006, 2000.

[9] H. Mihara, T. Ishiguro, H. Fukano, S. Taniuchi, and K. Ogino, "Effect of crystallization temperature on its crystallization. IV. The influence of tripalmitoglycerol (PPP) on the crystallization of 1, 3-dipalmitoyl 2-oleoyl glycerol (POP) and 1, 2-dioleoyl-3-palmitoyl glycerol," *Journal of Oleo Science*, vol. 56, no. 5, pp. 223-230, 2007.

[10] C. C. Narváez, S. M. Rincón, Z. Castañeda, and D. F. J. Sánchez, "Determination of some physical and transport properties of palm oil and of its methyl esters," *Latin American Applied Research*, vol. 38, pp. 1-6, 2008.

[11] W. L. Ng and C. H. Oh, "A kinetic study on isothermal crystallization of palm oil by solid fat content measurements," *Journal of America Oil Chemical Society*, vol. 71, no. 10, pp. 1135-1139, 1994.

[12] M. O. Ngadi, M. S. Chinnan, and P. Mallikarjunan, "Specific heat capacity and heat capacity of fried shrimp at freezing and refrigeration temperatures," *Lebensm.-Wiss. U.-Technol*, vol. 36, pp. 75–81, 2003.

[13] C. M. Rodenbush, F. H. Hsieh, and D. S. Viswanath, "Density and viscosity of vegetable oils," *Journal of America Oil Chemical Society*, vol. 76, no. 12, pp. 1415-1419, 1999.

[14] J. C. O. Santos, M. G. O. Santos, J. P. Dantas, M. M. Concei, P. F. A. Filho, and A. G. Souza, "Comparative study of specific heat capacities of some vegetable oils obtained by DSC and microwave oven," *Journal of Thermal Analysis and Calorimetry*, vol. 79, pp. 283–287, 2005.

[15] C. P. Tan and Y. B. Che, "Differential scanning calorimetric analysis of palm oil, palm oil based products and coconut oil: effects of scanning rate variation," *Food chemistry*, vol. 76, no. 1, pp. 89-102, 2002.

[16] R. E. Timms, "Physical properties of oils and mixtures of oils," *Journal of America Oil Chemical Society*, vol. 62, no. 2, pp. 241 -239, 1985.

[17] A. Vuillequez, L. Koza, B. Youssef, M. Bridier, and J. M. Saiter, "Thermal and structural behavior of palm oil: Influence of cooling rate on fat crystallization," *Macromolecular Symposia*, vol. 290, no. 1, pp. 137-145, 2010.

[18] M. Zabransky, V. Ruzicka, and E. S. Domalski, "Heat capacity of liquids: Critical review and recommended values," *Journal of Physical and Chemical Reference Data*, vol. 30, no. 5, pp. 1199 -1205, 2001

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