Prediction of Specific Heat Capacity of Food Lipids and Foods

THESIS

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Xiaoyi Zhu

Graduate Program in Food Science and Technology

The Ohio State University

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Master's Examination Committee:

Dr. Dennis. Heldman, Advisor

Dr. F. Maleky

Dr. V.M. Balasubramaniam

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Abstract

The specific heat capacity of foods containing modest to significant amounts of lipid is influenced by the contribution of the lipid fraction of the composition. The specific heat capacity of the lipid fraction might be influenced by its fatty acid composition. Although published models for prediction of specific heat capacity based on composition provide reasonable estimates, it is evident that improvements are needed. The objectives of this investigation were to use advanced specific heat capacity measurement capabilities (Modulated Differential Scanning Calorimetry (MDSC)) to quantify potential effect of fatty acid composition on specific heat capacity of food lipids. In addition, the goal was to confirm or improve current prediction models in the prediction of specific heat capacity of food lipids and foods. The specific heat capacity of a series of triacylglycerols (TAGs) were measured over a temperature range from 40° C to 130° C by MDSC. Two parameters were used to characterize fatty acid composition of TAGs, one being average carbon number (C) and the other being average number of double bonds (U). Their impacts on specific heat capacity were determined respectively. A simple model was proposed to predict specific heat capacity of food lipids as a function of C, U and temperature (T) with specific heat capacity of TAGs. The proposed model was validated with measured specific heat capacity of vegetable oils. The proposed model, used in combination with current models, was used to predict specific heat capacity of food products based on composition. The results confirmed that the influence of temperature on specific heat capacity was linear

and the same for liquid TAGs. The specific heat capacity of liquid TAGs increased with C and decreased with U. The following model was proposed to predict specific heat capacity of food lipids based on fatty acid composition:

$$c_p^{18*} = 2.172 + 0.0022(T - 80) \tag{4.5}$$

$$c_p^* = c_p^{18*} + 0.0104(C - 18) \tag{4.7}$$

$$c_p = c_p^* - 0.0566U \tag{4.8}$$

The proposed model was validated to be able to predict specific heat capacity of food lipids. The influence of fatty acid composition on specific heat capacity was observed on vegetable oils as well. The proposed model had a percent average relative deviation of 0.83% in the prediction of specific heat capacity of vegetable oils and was better than other current models. The group contribution method was demonstrated as a good approach to predict specific heat capacity of food lipids as long as parameters were regressed appropriately. Experimental data has been provided to update group contribution parameters and thus improve performances of such models. The proposed model can be used to improve current models to predict specific heat capacity of foods with 1%-5% improvement by providing better estimate for the specific heat capacity of the lipid fraction based on fatty acid composition. Specific heat capacity measurement with MDSC was in agreement with specific heat capacity measurement with DSC. Both methods had the ability to detect a difference of 0.02kJ/kg·K.

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Vita

May 1991	Born, Changzhou, Jiangsu, China
2013	B.S. Food Quality and Safety, Nanjing
	Normal University
2013 to present	Graduate Student, Department of Food
	Science and Technology, The Ohio State
	University

Fields of Study

Major Field: Food Science and Technology

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Chapter 1: Introduction

Specific heat capacity is the amount of heat/energy per unit mass material absorbs for its temperature to increase 1°C/K. SI unit of specific heat capacity is kJ/kg·K. It is one of the fundamental thermophysical properties of materials. It is also thermodynamic in nature. It has wide applications in industrial settings. In most cases, it is used to establish energy balances in process and equipment design and optimization, though it is also used to obtain enthalpy and entropy and other thermodynamic functions. Specific heat capacity can be determined by several factors, including intermolecular interaction, thermal conductivity, phase stability and energy storage capacity, to name a few (White 1999). Specific heat capacity of food products, is of utmost importance in the modeling and design of heat transfer processes and manufacturing equipment in food industries, along with other basic thermophysical properties of foods. Efficient processes and manufacturing equipment partially rely on accurate specific heat capacity data of food products.

In the last decades, continuous efforts have been made to obtain specific heat capacity data of food products. Compiled experimental data of specific heat capacity of vegetable and fruit products, meat products, oils and dairy products can be found in Choi and Okos (1986). Updated experimental data of specific heat capacity of egg products (Coimbra and others 2006), meat products (Tavman and others 2007) and other food products is also available during recent years. In addition, Choi and Okos (1986) developed

group models to predict specific heat capacity of foods based on composition. Other empirical models to predict specific heat capacity of specific food products as a function of temperature and/or other parameters like water activity were also available in literatures (Constenla and others 1989; Njie and others 1998; Telis-Romero and others 1998, 2000; Minim and others 2002; Gratão and others 2004). These prediction models are critical in obtaining specific heat capacity of various food products.

In Choi and Okos' group models, specific heat capacity of individual food components (protein, carbohydrate, fat, fiber, ash, water and ice) was expressed as a function of temperature. A generalized expression for each food component category was an average of specific heat capacity of several common food components in the same category. As a result of that, the generalized expression ignores variation within the same category.

Parallel research in our group (Phinney and Heldman 2013) reevaluated specific heat capacity data in literatures and found that variation of specific heat capacity of each category can be significant, especially for the category of lipid. It is desirable to take variation within each category into account when predicting specific heat capacity to improve Choi and Okos' prediction models. As a start, this investigation intended to improve Choi and Okos' prediction models with lipid.

Lipid in food products mainly refers to animal fats and vegetable oils. For both animal fats and vegetable oils, their major constituents are triacylglycerols (TAGs). TAGs are fatty acid esters with three fatty acids esterified to the glycerol backbone. Basically, fatty acid is the building block for lipid in food products. Fatty acid differentiates in carbon number and number of double bonds. The hypothesis of this investigation was that specific heat capacity of lipid in food products was determined by fatty acid composition. And average carbon number and average number of double bonds of fatty acids were potential factors that impact specific heat capacity of lipid. The hypothesis was developed based on food lipid composition and reported specific heat capacity of TAGs and vegetable oils in Morad and others (2000) and Clark and others (1946). To our knowledge, potential effects of averaged carbon number and/or averaged number of double bonds on specific heat capacity of TAGs and vegetable oils might be indicated in literatures like Morad and others (1995a) and Clark and others (1946). However, there was evidence in literature that was against the relationships (Hampson and Rothbart 1983; Fasina and Colley 2008). The effects were not confirmed and quantified. So further study is needed to confirm effects of average carbon number and average number of double bonds on specific heat capacity on food lipids and predict specific heat capacity of food lipids based on fatty acid composition.

The overall objective was to improve Choi and Okos' prediction models by providing improved estimate for specific heat capacity of lipid. The specific objectives were as follows:

- To determine effects of average carbon number and average number of double bonds on specific heat capacity of TAGs
- To propose a model to predict specific heat capacity of TAGs and food lipids based on fatty acid composition and temperature
- To validate the proposed model with specific heat capacity of vegetable oils and compare model performances

- To use the proposed model as an improvement to Choi and Okos' prediction models to predict specific heat capacity of food products with modest to significant amounts of lipid and evaluate improvements
- To evaluate and compare methods for measurement of specific heat capacity magnitudes of food lipids

Chapter 2: Literature Review

2.1 Models to predict specific heat capacity of food products

The thermophysical properties of food products are fundamental to modeling for the design and optimization of heat-transfer processes within the food industry. Among these properties specific heat capacity is one of the most important for food processing.

Thermophysical properties (specific heat capacity) are influenced by variations in food product composition and processing parameters. Mathematical modeling is the most effective and economic method to determine such thermophysical properties in food products (Sweat 1995). Several mathematic models that estimate the specific heat capacity of food products based on composition and other parameters are reviewed in this section.

2.1.1 Composition-based models

Heldman and Singh (1981) proposed a composition-based model that was additive to predict specific heat capacity of food products as follows:

$$c_{p} (J/kg \cdot C) = 1424x_{c} + 1549x_{p} + 1675x_{f} + 837x_{a} + 4187x_{w}$$
(2.1)

where:

 $x_c = mass$ fraction of carbohydrate

 $x_p = mass$ fraction of protein

 $x_f = mass fraction of fat$

 $x_a = mass fraction of ash$

 $x_w = mass fraction of water$

 c_p = was specific heat capacity of food products

Based on data for specific heat capacity of unfrozen passion fruit juice of various water contents at two temperatures (Gratão and others 2004), this model was found to have moderate accuracy with a maximal percent error (% error) of 3.71%.

% error was defined as follows:

% error
$$\frac{|c_{p,exp} - c_{p,pre}|}{c_{p,exp}} \cdot 100$$
(2.2)

where:

 $c_{p,exp}$ = the experimental data

 $c_{p,pre}$ = the predicted value

Njie and others (1998) measured specific heat capacity of cassava, yam and plantain between 36°C and 51°C in the moisture range of 10%-68% and compared experimental values with predicted values by the model. The %error was within 10%. Considering that there might be 5% error in measurement as stated by the author, the model provided moderate accuracy.

Choi and Okos (1986) developed group models to estimate specific heat capacity of major food components (protein, fat, carbohydrate, fiber, ash, water and ice) as a function of temperature and expressed specific heat capacity of food products as a sum of products of specific heat capacity of major food components and their mass fractions.

It was assumed that:

$$\mathbf{c}_{\mathrm{p}} = \sum \mathbf{x}_{\mathrm{i}} \, \mathbf{c}_{\mathrm{pi}} \tag{2.3}$$

where:

 $c_{\text{pi}} = \text{specific heat capacity of major food component}$

 x_i = mass fraction of major food component i

Expressions of specific heat capacity of major food components as a function of temperature were summarized in Table 2.1 (Choi and Okos 1986).

Table 2.1 Expressions of specific heat capacity of major food components as a function of temperature*

Component	Expression	Average Standard Error	Average % Error
Protein	$c_p = 2.0082 + 1.2089 * 10^{-3} T - 1.3129 * 10^{-6} T^2$	0.1147	5.57
Fat	$c_p = 1.9842 + 1.4733 * 10^{-3} T - 4.8008 * 10^{-6} T^2$	0.0236	1.16
Carbohydrate	$c_p = 1.5488 + 1.9625 * 10^{-3} T - 5.9399 * 10^{-6} T^2$	0.0986	5.96
Fiber	$c_p = 1.8459 + 1.8306 * 10^{-3} T - 4.6509 * 10^{-6} T^2$	0.0293	1.66
Ash	$c_p = 1.0926 + 1.8896 * 10^{-3} T - 3.6817 * 10^{-6} T^2$	0.0296	2.47
Water ^a	$c_p = 4.0817 - 5.3062 * 10^{-3} T + 9.9516 * 10^{-4} T^2$	0.0988	2.15
Water ^b	$c_p = 4.1289 - 9.0864 * 10^{-5} T + 5.4731 * 10^{-6} T^2$	0.0159	0.38
Ice	$c_p = 2.0623 + 6.0769 \times 10^{-3} T$	0.0014	0.07

^a below 0 $^{\circ}C$

 b above 0 $^{\circ}C$

* C_p is in kJ/kg·°C, T is in °C

For example, the expression of specific heat capacity of protein as a function of

temperature in Table 2.1 was developed based on data of specific heat capacity of albumin, casein, whey and meat proteins as a function of temperature, using a curve to fit experimentally determined specific heat capacity values for all above mentioned samples as a function of temperature. Other expressions for major food components were also developed based on specific heat capacity of common components in each category. The model was used to estimate specific heat capacity of liquid juice products, milk products and some food component solutions in Choi and Okos (1986). Compared to literature specific heat capacity values of the preceding food products, the average % error was within 4%.

This model was built based on a relatively comprehensive specific heat capacity dataset and has been the most useful and widely used approach to predict specific heat capacity of food products to date as it provides moderately accurate estimations with acceptable % error.

Gratão and others (2004) used the model to predict specific heat capacity of unfrozen passion fruit juice of various water contents at two temperatures and found the maximal %error to be 3.24%. Pham (1996) compared specific heat capacity values provided by the model to those in literatures for unfrozen meat, fish and vegetables. Based on his analysis, the correlation between measured values and predicted values was 0.6, with 3.3% average %error. However, in Pham's analysis, the maximal %error was 16%, indicating that the model might have large deviations when applied to specific food products.

Choi and Okos (1986) used both linear and polynomial functions to express specific

heat capacity of major food components in preliminary analysis and concluded that polynomial functions provided better fit (data not shown in the thesis). However, Phinney and Heldman (2013) reevaluated their data and argued that for specific heat capacity, linear function was as good as polynomial function if not better. Additional literature has confirmed the linear relationship between specific heat capacity of food products and temperature over normal processing temperature ranges for apple juice (Constenla and others 1989), cassava, yam and plantain (Njie and others 1998), orange juice (Telis-Romero and others 1998), coffee extract (Telis-Romero and others 2000), milk (Minim and others 2002), and passion fruit juice (Gratão and others 2004). Improvements may be made to Choi and Okos' models.

2.1.2 Other models

The previously described generalized models are used to predict specific heat capacity of food products with moderate accuracy based on chemical composition. More simplified generalized models are used to predict specific heat capacity of food products when chemical composition of foods is unknown.

For example, Chen (1985) proposed the following model:

$$c_p(J/kg^{\circ}C) = 4190 - 2300x_s - 630x_s^3$$
(2.4)

where:

 $x_s = mass fraction of solids$

and Siebel proposed another model (ASHRAE Fundamentals Handbook 1985) for unfrozened foods as follows:

$$c_p(J/kg^{\circ}C) = 3350 x_w + 840$$
 (2.5)

where:

 $x_w = mass$ fraction of water

840 = an assumed base value that represented c_p of solids

Based on specific heat capacity of major food components (Choi and Okos 1986), major food components that are solids differ a lot in specific heat capacity. Thus the simplicity of this type of model comes at the cost of accuracy. The maximal %error was much higher for this type of generalized model than that for the above mentioned composition-based models for passion fruit juice (Gratão and others 2004).

Empirical models have been developed to predict specific heat capacity of specific food products as a function of two to three important parameters, of which might be temperature, water content and fat content, with desired accuracy. For example, Gratão and others (2004) developed a model to predict specific heat capacity of passion fruit juice as a function of temperature and moisture content. Similar expressions were developed for other juice products (Constenla and others 1989; Telis-Romero and others 1998), cassava, yam and plantain (Njie and others 1998), coffee extract (Telis-Romero and others 2000) and milk (Minim and others 2002). More examples can be found in the literature. These empirical models, though accurate for specific food products, are not applicable to other food products. They are not focus of this investigation.

- 2.2 Specific heat capacity measurement methods
- 2.2.1 Method of Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter reports real-time differential heat flow signals of sample and reference in response to imposed temperature conditions. DSC is used in multi-

disciplines as it is an excellent technique in monitoring phase transitions and can also be used to measure specific heat capacity of materials in solid, liquid or gas states. This specific heat capacity measurement method has been gaining popularity for decades and is now more commonly found in specific heat capacity determination than other methods (Höhne and others 2003).

Using this method to measure specific heat capacity, sample and a reference crucibles are heated at a fixed rate in DSC. There are two platforms in DSC, used to hold the sample and the reference crucibles. The DSC cell with the two platforms and sensors are constructed symmetrically. The sample crucible has sample in it while the reference crucible usually is just empty. Differential rates of heat inputs $\left(\frac{dH}{dt}\right)$ are used to maintain the sample and the reference crucibles at the same temperature. Differential heat flow rate, which is proportional to $\frac{dH}{dt}$ due to instrument construction, is recorded in thermogram as a function of temperature. Specific heat capacity is related to the differential heat flow rate by equations as follows:

$d = \beta \frac{dH}{dt} = \beta \frac{dH}{dT} \frac{dT}{dt}$	(2.6)
---	-------

$$c_{\rm p} = \frac{1}{\rm m} \frac{\rm dH}{\rm dT}$$
(2.7)

$$d = \beta m c_p \frac{dT}{dt}$$
(2.8)

where:

d = differential heat flow rate

 $\frac{dT}{dt}$ = heating rate

 c_p = specific heat capacity

 β = a constant that is related to the instrument

 β can be determined with a reference material with known c_p like sapphire using the above equations.

One advantage of this method to determine specific heat capacity of materials is that it is a relatively rapid way to obtain data over a large temperature range with desired accuracy and precision (Höhne and others 2003). Another advantage is that only a small amount of sample (less than 0.1g) is used in thermal analysis with DSC, minimizing thermal lag effect and reducing cost.

Because DSC instruments are highly sophisticated and sensitive, expertise with instruments may be required to get reliable specific heat capacity measurement result with acceptable certainty (Höhne and others 2003). The evaluation of measured curves may be different as a result of operation procedure. Only a combination of precise measurement and qualitative or even special data evaluation can lead to reliable specific heat capacity measurement. The American Society for Testing and Materials has published a standard test method for specific heat capacity measurement with DSC which is similar to what is known as the three step procedure in the literature (ASTM International 2011).

The three step procedure is a temperature ramp procedure commonly found to be used to determine specific heat capacity of materials. The first step is to set up a run with empty weight-matched sample and reference crucibles using a predetermined heating rate over the desired temperature range to get a baseline which reflects asymmetry of sample and reference sides. The second step is to put a standard material with known specific heat capacity in the sample crucible and run the sample and reference crucibles under identical

experimental conditions. The third step is to run the sample and reference crucibles with actual sample of unknown specific heat capacity in the sample crucible under identical experimental conditions. Caution should be taken to assure constant heat flow rates at the beginning and end temperatures for each run. The first run is used to account for asymmetry of the instrument. The second run is used to obtain the constant β as mentioned in the proceeding content. Specific heat capacity of sample can be obtained after evaluation of signals from three runs. It is best to use only two-weight matched crucibles for all three runs. If a different sample crucible is used in the second/third run or crucibles of different masses are used in three runs, correction should be made in the evaluation process. Other procedures used to determine specific heat capacity of materials with DSC, and detailed precautions to take to obtain reliable results, can be found in Höhne and others (2003). With the proper precautions taken, uncertainty level is typically reported to be 1%-5% in literature (Höhne and others 2003). However, different researchers use different instruments, procedures and evaluation processes that are not published in most cases, without knowing complete procedures it is difficult to compare results (Höhne and others 2003).

2.2.2 Method of Modulated Differential Scanning Calorimetry (MDSC)

MDSC means temperature modulated differential scanning calorimetry method. Under development for the last 20 years, its most important application is in investigating change of apparent specific heat capacity quasi-isothermally during annealing or other reactions (Höhne and others 2003). In this method, a modulation term is added to the temperature change of conventional DSC. In the following equations and the following content, a sinusoidal temperature modulation is used for illustration of temperature modulation, while other forms of temperature modulation are also possible. Equations as follows describe overall temperature change of MDSC with a modulation term and change of heating rate with a modulation term.

$$T(t) = T_0 + \alpha t + T_A \sin(\omega t)$$
(2.9)

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \alpha + T_{\mathrm{A}}\omega\cos(\omega t) \tag{2.10}$$

where:

 T_0 = initial temperature

 T_A = modulation temperature amplitude

 ω = modulation period

 α = underlying heating rate (corresponding to the fixed heating rate in DSC)

 $T_A\omega \cos (\omega t) = modulated heating rate$

$$\omega = 2\pi f \tag{2.11}$$

where:

f = angular frequency of modulation

These terms are explained further in the following paragraphs.

There are four distinguished operation modes in this method; quasi-isothermal, heat-cool, heat-only and heat-isothermal (Höhne and others 2003). In the quasi-isothermal mode, the underlying heating rate is zero. Temperature changes periodically around a constant temperature. If the temperature modulation term is small, the temperature condition is almost isothermal. It is the only mode that makes it possible to investigate

change of apparent specific heat capacity quasi-isothermally. When this operation mode is used to measure specific heat capacity, specific heat capacity of sample at a certain temperature is measured continuously during the "isothermal" time with slight change in the heating rate. Only the heat flow signal that changes correspond to the heating rate is used to obtain specific heat capacity. And specific heat capacity value is an average of the continuous measurement, minimizing uncertainty in the measurement. In heat-cool mode, the modulated heating rate is larger than the underlying heating rate, so the total heating rate can sometimes be negative. This mode complicates data processing because it heats and cools the sample periodically which may trigger different processes. However, a relatively larger heating rate does provide a better signal-to-noise ratio compared to other modes. In heat-only mode, the modulated heating rate is smaller than the underlying heating rate, thus the total heating rate is always positive. This mode suppresses processes that happen during cooling to simplify data processing at the cost of signal-to-noise ratio. In heat-isothermal mode, the modulated heating rate equals to the underlying heating rate, which maximizes signal-to-noise ratio without involving cooling.

In any type of DSC, the measured total heat flow rate consists of two components, one being proportional to heating rate and specific heat capacity of sample, the other one representing the contribution of endo- or exothermic processes and other kinetic processes associated with the instrument. Typically when DSC is used to measure specific heat capacity, it is used at the temperature range in which no endo- or exothermic processes occur. Even so, due to the asymmetry of the instrument and other factors, there is some uncertainty using the total heat flow rate to obtain specific heat capacity as the total heat flow rate contains component that is not related to specific heat capacity. With the three step procedure to account for the asymmetry of the instrument, the level of uncertainty can be reduced. The MDSC separates these two components through more information obtained during modulation and complex mathematic analysis of the information and determines specific heat capacity of sample from the related component, by dividing the modulated heat flow amplitude by the modulated heating rate amplitude (Thomas and Aubuchon 1999). In this way, signals from change of specific heat capacity and from kinetic processes like crystallization, decomposition, evaporation, molecular relaxation and chemical reactions are separated. And the measurement is less dependent on the conditions of the instrument. Because of this separation specific heat capacity of sample can be determined with a single run instead of the three steps described above.

In applications to measure specific heat capacity with MDSC, temperature modulation amplitude and modulation period are critical parameters. The modulation period is the elapsed time for a whole sinusoidal modulation. The modulation period should be long enough to allow heat flow between sensor and sample for quantitative measurement of the heat flow signal. Temperature modulation amplitude is a compromise between sensitivity and resolution as larger temperature modulation amplitude provides better sensitivity but poorer resolution as a result of the heat-cool mode. Based on the instrument and software used, the manufacturer should have recommended values for temperature modulation amplitude and modulation period for specific heat capacity measurement of materials. In addition the underlying heating rate should not be too fast, allowing enough modulations to happen within the temperature range of interest. Optimal conditions for

temperature modulation amplitude, modulation period and underlying heating rate are impacted by weight, thickness and thermal properties of sample as well as that of crucible, and thus may be determined on a case-to-case basis.

Considering similarities between DSC and MDSC techniques, the same instrument typically can be used for both with some modifications. Currently MDSC is often a builtin feature in DSC instruments. The MDSC method measures specific heat capacity of sample in a single run and is less dependent on baseline conditions than DSC method. However, the development of MDSC technique and the discussion of applications of MDSC are still on-going.

2.2.3 Method of comparison calorimetry

In comparison calorimetry, a liquid sample in one container and distilled water in another container are heated to the sample temperature and then allowed to equilibrate with environment. The temperature of both liquids is recorded during cooling as a function of time. At a specific temperature, the heat loss rates of two liquids are equal and specific heat capacity of sample can be obtained.

$$(m_{a}c_{pa}+m_{w}c_{pw})\frac{\Delta T}{\Delta Ta} = (m_{b}c_{pb}+m_{s}c_{ps})\frac{\Delta T}{\Delta Tb}$$
(2.12)

where:

a, b, w, = crucible a, crucible b, distilled water and sample respectively

2.2.4 Method of guarded-plate

This method requires a relatively simple device with several thermal guards surrounding sample. Both sample and thermal guards can be heated electrically to the same temperature. It is assumed that there is no heat loss between sample and thermal guards, so specific heat capacity of sample can be obtained.

$$mc_{p}(T_{f}-T_{i})=VIt$$
(2.13)
where:
$$V = voltage$$

$$I = current$$

$$T_{f} = final temperature$$

$$T_{i} = initial temperature$$

$$L = L = L = L = L = L$$

2.2.5 Method of mixture

This method needs an adiabatic system in which a liquid sample is mixed with distilled water or other liquids with known specific heat capacity. Knowing the initial temperature of distilled water and liquid sample and final temperature of mixture, based on energy balance equation, the averaged specific heat capacity of liquid sample for the temperature range can be obtained. This method is widely used for its simplicity.

All of the above methods have been studied for a variety of applications. The choice of measurement method is determined by the specific application. In addition, other instruments/devices that are able to provide quantitative data of heat/energy transfer between environment, themselves and sample can be used for measurement of specific heat capacity with appropriate data processing.

2.3 Lipid and specific heat capacity

Lipid is a chemically diverse group that includes fatty acids, acyglycerols, phospholipids, sphingolipids, sterols, waxes and miscellaneous lipids. Commercial available lipids in food products from animal and plant origins are almost exclusively made

of triacylglycerols (TAGs) with insignificant amount of free fatty acids, mono-, diacylglycerols and other lipid components. A TAG is three fatty acids esterified to a glycerol. A TAG with three identical fatty acids is a "simple TAG" while a TAG composed of various fatty acids is a "mixed TAG". Fatty acids are building blocks of TAG and lipids. They are compounds with an aliphatic chain plus a carboxylic acid group. In nature most fatty acids have an even carbon number. Fatty acids are differentiated by carbon number and number of double bonds. Fatty acids containing double bonds in the aliphatic chain are classified as unsaturated while their counterpart is referred to as saturated because all carbons are "saturated" with hydrogen atoms. A fatty acid containing a single double bond is monounsaturated. If more than one double bond is present the fatty acid is polyunsaturated. It is most commonly found that in polyunsaturated fatty acid, two double bonds are one methyl group apart. An example of structures of TAG and fatty acid is shown in Figure 2.1.

$$\begin{array}{c} CH_{3}(CH_{2})_{7}CH=CH(CH_{2})_{7}C(O)O-CH_{2} \\ \\ CH_{3}(CH_{2})_{7}CH=CH(CH_{2})_{7}C(O)O-CH \\ \\ CH_{3}(CH_{2})_{14}C(O)O-CH_{2} \\ \end{array} \begin{array}{c} CH_{3}(CH_{2})_{7}C=C-(CH_{2})_{7}-C-OH \\ \end{array}$$

Figure 2.1 Structures of TAGs (OOP, left) and oleic acid (O, right)

The nomenclature of fatty acids is summarized in Table 2.2. A fatty acid can be named by association with carbon number and number of double bonds (Numerical

Abbreviation in Table 2.2).

Systematic Name	Common	Numerical	Abbreviation
	Inallie	AUDIEVIALIOII	
Hexanoic acid	Caproic acid	C6:0	
Octanoic acid	Caprylic acid	C8:0	
Decanoic acid	Capric acid	C10:0	
Dodecanoic acid	Lauric acid	C12:0	L
Tetradecanoic acid	Myristic acid	C14:0	М
Hexadecanoic acid	Palmitic acid	C16:0	Р
Octadecanoic acid	Stearic acid	C18:0	S
cis-9-Octadecenoic acid	Oleic acid	C18:1 9	0
cis-9, cis-12-Octadecadienoic acid	Linoleic acid	C18:2 9	Li
cis-9, cis-12, cis-15-Octadecatrienoic acid	Linolenic acid	C18:3 9	Ln
cis-5, cis-8, cis-11, cis-14-	Arachidonic	C20.4.5	
Eicosatetraenoic acid	acid	C20.4 3	
cis-5, cis-8, cis-11, cis-14,cis-17-		C20.5 5	ΓDA
Eicosapentaenoic acid		C20.3 3	EFA
cis-4, cis-7, cis-10, cis-13,cis-16, cis-19-		C22:6 4	
Docosahexaenoic acid			DΠA

Table 2.2 Nomenclature of fatty acid^a

a from Damodaran and others 2007

For example, Caproic acid, which has six carbons and zero double bonds can be named C6:0 or C6. Oleic acid, which has eighteen carbons and one double bond can be

named C18:1 or C18:1 9, with the last digit representing the position of the double bond. A TAG can be named by its fatty acid composition. For example, POS is the name of the TAG that has one palmitic acid (abbreviation P), one oleic acid (abbreviation O) and one stearic acid (abbreviation S). It could also be named as C16:0-C18:1-C18:0. Stereospecific numbering (*sn*) is used if the stereospecific locations of fatty acids are known. For example, sn-POS means 1-palmitoyl-2-oleoyl-3-stearoyl-*sn*-glycerol. Simple TAGs are often referred to by their common names in literature.

Both fatty acid and TAG have unique configurations. For example, nature double bond in unsaturated fatty acid is in *cis* configuration.

Previous research in our group (Phinney and Heldman 2013) found that specific heat capacity of food lipids varied a lot while Choi and Okos (1986) used an average specific heat capacity of food lipids to estimate specific heat capacity of all food lipids (Figure 2.2). It is desirable to obtain a better understanding of the cause of the variation of specific heat capacity and to improve the prediction of specific heat capacity of fat/lipid by Choi and Okos (1986). This kind of improvements is going to improve the prediction of specific heat capacity of food products by Choi and Okos (1986) or other models as well.

To maintain high food product quality and through-put, it has become a trend to apply advanced process control strategies in food manufacturing (Haley and Mulvaney 1995). The application of such strategies demands data on the thermophysical properties of food products for predictive mathematical modeling. This study certainly meets the trend. With the development of specific heat capacity measurement methods, advanced specific heat capacity measurement capabilities are accessible to provide specific heat capacity values to obtain a better understanding of the cause of the variation of specific heat capacity of lipids and to improve current predictive models.



Figure 2.2 Specific heat capacities of vegetable oils from 35°C to 180°C (Phinney and Helman 2013; Fasina and Colley 2008; Choi and Okos 1986)

In order to better understand the cause of the variation of specific heat capacity of lipids, literatures related to specific heat capacity of lipids were reviewed.

TAGs have the ability to exist in different crystalline structures as their molecular packing changes. The phenomenon is called polymorphism. Three major polymorphic forms of TAGs are typically designated as α , β ' and β . According to Hampson and Rothbart (1983), the magnitudes of specific heat capacity of three forms of LLL, MMM, PPP and SSS was $\alpha > \beta' > \beta$. In α form (hexagonal crystal), it was known that carbon chains rotated around an axis (Chapman 1962), which was expected to contribute to specific heat capacity. It was shown that different polymorphism forms of cottonseed oil had different specific heat capacity as well (Olive and Bailey 1945). The polymorphism formation is a kinetic event dependent on many factors such as composition and molecular structure of lipids, cooling, shearing, temperature profile. More importantly Olive and Bailey (1945) found that the trend of specific heat capacity of highly hydrogenated, hydrogenated, partially hydrogenated and unhydrogenated liquid cottonseed oils as a function of temperature was significantly different from that of solid samples. This was confirmed by Hampson and Rothbart (1983), it was found that liquid specific heat capacity of trilaurin, trimyristin, tripalmitin and tristearin increased more slowly as a function of temperature compared to solid specific heat capacity of these samples. To simplify, the focus of this study was determined to be specific heat capacity of liquid lipid for the following content.

Theoretically, the specific heat capacity of a substance is associated with excited degree of freedom of molecules at a certain temperature. The excited degree of freedom depends on bending and stretching of interacting atoms in the molecules as influenced by temperature. Theoretical calculation of specific heat capacity based on the excited degree of freedom is a multiple-step complicated process. Relatively rough approximations need

to be made in several steps. Due to the limitation of such calculations, constant pressure specific heat capacity is usually measured experimentally.

It was found that analytically molar specific heat capacity of a substance in gas state could be attributed to contributions of different functional groups (Benson and Buss 1958). Because of its desired characteristics, this group contribution estimation method was extended to substances in solid and liquid states (Domalski and Hearing 1988). The contribution of each functional group was described by parameters obtained from adequate experiment data as a function of temperature. This group contribution estimation method is discussed further in the next section.

Saturated fatty acids differ in the number of CH₂ groups in their chemical structures. According to the group contribution estimation method (Ceriani and others 2009), CH₂ group contributed positively to specific heat capacity, the incremental of CH₂ group in saturated fatty acids should increase specific heat capacity. As a result of that, the increment of CH₂ group in TAGs and food lipids should increase specific heat capacity. Considering the unique configuration of TAGs and food lipids, it was expected that the increase of average carbon number of TAGs and food lipids increases specific heat capacity. The average carbon number was defined as a sum of products of mole fractions and carbon numbers of fatty acids of TAGs and food lipids according to their fatty acid composition.

On the other hand, a saturated fatty acid and an unsaturated fatty acid with the same carbon number differ in that the unsaturated fatty acid contains CH=CH group. According to the group contribution estimation method (Ceriani and others 2009), CH=CH

contributed negatively to specific heat capacity. As a result of that, as the number of double bonds in the unsaturated fatty acid increases, specific heat capacity decreases. It was expected that the increase of average number of double bonds of TAGs and food lipids increases, specific heat capacity decreases. Average number of double bonds was defined as a sum of products of mole fractions and numbers of double bonds of fatty acids of TAGs and food lipids according to their fatty acid composition.

Above all, average carbon number and average number of double bonds of TAGs and food lipids were expected to impact their specific heat capacity.

Morad and others (1995a) found that specific heat capacity of simple TAGs almost evenly increased as a function of averaged carbon number of fatty acids of TAGs while uneven increase was found by Charbonnet and Singleton (1947). In contrast to their findings, Hampson and Rothbart (1983) found specific heat capacity of simple TAGs was not a function of average carbon number of fatty acids of TAGs. More evidence is needed to determine the relationship between the average carbon number of fatty acids and specific heat capacity of lipids. Thus one focus of this study was to quantify the relationship between the average carbon number of fatty acids and specific heat capacity of liquid lipid.

Clark and others (1946) measured specific heat capacity of hydrogenated cottonseed, castor, soybean, tung, linseed and perilla oils from 0°C to 280°C with a batch calorimeter. They also determined iodine numbers of these oil samples before and after specific heat capacity determination. Iodine number roughly determines level of unsaturation of lipid. They concluded that in general specific heat capacity was lower for oil samples with higher iodine numbers (higher levels of unsaturation). Bailey and others
(1944, 1945) found that specific heat capacity of refined cottonseed oil was higher than that of highly hydrogenated cottonseed oil which was higher than that of hydrogenated cottonseed oil and cottonseed oil. The level of hydrogenation is negatively related to the level of unsaturation of lipid. Thus it concluded that as the level of unsaturation of cottonseed oil increased, specific heat capacity decreased. Both works suggested that level of unsaturation might be a significant factor that impacted specific heat capacity of vegetable oils. However, as there was no quantitative definition of the level of unsaturation in both cases, their data is not suitable to be used to quantitatively correlate the level of unsaturation to specific heat capacity of lipid. This leads to another focus of this study, to quantify the relationship between level of unsaturation and specific heat capacity of lipid. In this investigation, the level of unsaturation was defined as average number of double bonds of lipid.

Based on the above, specific heat capacity of lipid might be potentially impacted by average carbon number and average number of double bonds, which means specific heat capacity of a lipid may be highly correlated with its fatty acid composition.

Kowalski (1988) reported fatty acid composition and specific heat capacity of rapeseed, soybean, sunflower, corn oils and lard from 70°C to 140°C. Kasprzycka-Guttman and Odzeniak (1991) published fatty acid composition and specific heat capacity of olive, rapeseed, soybean, sunflower, linen, castor oils and lard from 70°C to 140°C. These two works were the only ones in existence to report fatty acid composition and specific heat capacity of lipid. However, analysis based on their results did not reveal a clear correlation between fatty acid composition and specific heat capacity. It might because that difference

in specific heat capacity between lipid samples was difficult to detect or because of other unknown factors. Morad and others (2000) was able to correlate fatty acid composition of TAGs and two vegetable oils with specific heat capacity. This investigation was aimed to confirm the correlation with more food lipids and build a simple correlation between fatty acid composition and specific heat capacity of food lipids to improve specific heat capacity prediction of food products.

Morad and others (1995a) determined specific heat capacity of 4 simple and 4 mixed TAGs from above their melting points to 250 °C with DSC using a round robin test procedure under optimized conditions for measurement of specific heat capacity (Morad and others 1995b) (Figure 2.3). In this work, they concluded that there was a linear temperature dependency of specific heat capacity for these triacylglycerols up to 150°C. They noticed that oxidation began after 150°C and used nitrogen to eliminate oxygen to measure specific heat capacity after 150°C. Morad and others (1995a) published constants and equations to predict specific heat capacity of the TAGs (Table 2.3).



Figure 2.3 Specific heat capacity of liquid TAGs to 250 °C (Morad and others 1995a)

T 11 0 0 0		· · · 1	• , , •	201 1 1	(1 1005)
Table 2.3 Const	tants for spe	citic heat can	acity equation	1ª (Morad and	others (1995a)

Triacylglycerol	Temperature range /°C	А	В
Trilaurin	55-170	0.002443	1.8991
Trimyristin	65-181	0.00239	1.9565
Tripalmitin	75-184	0.002474	1.9793
Tristearin	80-187	0.00253	2.0208
1,2-dimyristoyl-3-palmytoyl	60-181	0.002078	1.9603
1,2-dimyristoyl-3-oleoyl	35-170	0.00239	1.8885
1,2 dipalmitoyl-3-oleoyl	50-180	0.002427	1.9213
1,2-dioleoyl-3-palmitoyl	35-162	0.002842	1.8916

a specific heat capacity equation is given: $c_p (J/g \cdot {}^{\circ}C) = AT + B$

The linear relationship between specific heat capacity and temperature for liquid TAGs to up to 150 $^{\circ}$ C concluded in Morad and others (1995a) was used in this investigation.

In addition, Morad and others (1995a) concluded (1) for simple triacylglycerols, specific heat capacity increased as carbon number increased while the same trend was not found for mixed triacylglycerols (2) mixed triacylglycerols had lowered specific heat capacity than simple triacylglycerols (3) the presence of double bonds might contribute to the reduction of specific heat capacity. The results from Morad and others (1995a) indicated that other factors like stereospecific locations of fatty acids and interactions of fatty acids might impact specific heat capacity of liquid lipid. In this study, it was assumed that stereospecific locations of fatty acids and interactions of fatty acids don't impact specific heat capacity of lipid for several reasons. First, impact of other factors, even if existed, should be small, negligible or non-quantifiable according to Morad and others (2000). In literatures, the most important factors that impact specific heat capacity of lipid were average carbon number and average number of double bonds. Yet the impact of average carbon number was known to be small and the impact was not consistently detectable. Second, it is difficult to qualitatively or quantitatively determine interactions of fatty acids for modeling purpose. This is exactly the same reason that group contribution estimation method assumed no interactions of neighboring functional groups. Also, analytical determination of stereospecific locations of fatty acids requires TAG composition determination of lipid, which requires advanced instrument and great effort and time. TAG composition of lipids under most processing conditions is not readily

available. Third, modeling specific heat capacity of lipids based on fatty acid composition will be simple and desirable.

2.4 Other models to predict specific heat capacity of triacylglycerols (TAGs) and food lipids as a function of temperature

Morad and others (2000) proposed a model to predict specific heat capacity of TAGs and vegetable oils based on fatty acid composition using Rowlinson-Bondi method. The model considered TAGs and vegetable oils as mixtures of fatty acids, and acquired satisfactory accuracy with a correction factor that accounted for TAG form. The Rowlinson-Bondi equation they used was as follows:

$$(c_{p}-c_{p}^{0})/R=1.45+0.45(1-T_{r})^{-1}+0.25\omega[17.11+25.2(1-T_{r})^{1/3}T_{r}^{-1}+1.742(1-T_{r})^{-1}]$$
(2.14)

where:

 c_p = liquid specific heat capacity

 c_p^0 = ideal gas specific heat capacity

 T_r = reduced temperature

 ω = acentric factor

 c_p^0 , T_r , ω of TAGs and vegetable oils were obtained based on fatty acid composition.

$$c_p^0 = \sum y_i c_{pi}^0$$
 (2.15)

where:

 y_i = mole fraction of fatty acid i

 c_{pi}^{0} = ideal gas specific heat capacity of fatty acid i

$$T_r = T/T_c$$
 (2.16)

$$Tc = \sum y_i T_{ci}$$
(2.17)

where:

 $T_c = critical temperature$

 T_{ci} = critical temperature of fatty acid i

$$\omega = \sum y_i \omega_i \tag{2.18}$$

 $P_{ci}V_{ci}/RT_{ci} = 0.291 - 0.08\omega_i$ (2.19)

where:

 ω_i = acentric factor of fatty acid i

 P_{ci} = critical pressure of fatty acid i

 V_{ci} = critical volume of fatty acid i

 c_{pi}^{0} , T_{ci} , P_{ci} and V_{ci} of fatty acids were estimated by additional group contribution estimation methods (Rihany and Doraisamy 1965; Fedors 1982; Joback and Reid 1987). A correction factor was developed to improve the prediction (Morad and others 2000).

For decades group contribution methods have been used to estimate specific heat capacity of organic molecules including fatty acids and TAGs. The core concept of a group contribution method is described in Section 2.3. The group contribution method is used for the estimation of most thermophysical properties as well.

Most recently, Ceriani and others (2009) proposed a group contribution method that was relatively simple to estimate specific heat capacity of fatty compounds as a function of temperature. They used functional groups: CH₃, CH₂, COOH, CH=CH, COO, OH and CH₂-CH-CH₂ to represent molecular structure of fatty compounds. The functional group specific parameters were regressed from experimental data of 86 fatty compounds while linear temperature dependency was assumed for each functional group. This was found to be as good as prediction methods provided by Morad and others (2000) and Kolská and others (2008).

Ceriani and others proposed the following model:

$$c_p = \sum N_k \cdot (A_k + B_k \cdot T)$$
(2.20)

where:

 N_k = the number of group k in TAG (group k could be CH₃, CH₂, COO, CH=CH, and CH₂-CH-CH₂)

 A_k , B_k = parameters (Table 2.4)

Table 2.4 Parameters for group contribution method (Ceriani and others 2009)

Group k	A_k	B _k
CH ₃	14.5504	0.05406
CH_2	19.539	0.038211
CH=CH	-130.42	0.54731
COO	26.261	0.12317
CH ₂ -CH-CH ₂	181.89	-0.37671

When this model was used to predict specific heat capacity of vegetable oils with known fatty acid composition, it was assumed that vegetable oils were mixtures of simple TAGs (Su and others 2011). And according to fatty acid composition, proportions of simple TAGs in vegetable oils were known. Specific heat capacity of vegetable oils were estimated with the following equation:

$$c_{p,veg} = \sum y_i c_{pi} \tag{2.21}$$

where:

 $c_{p,veg}$ = specific heat capacity of vegetable oil

 c_{pi} = specific heat capacity of simple TAG i

 y_i = mole fraction of simple TAG i

Zong and others (2000) found traditional group contribution methods too simplistic to estimate thermophysical properties (vapor pressure, enthalpy of vaporization, specific heat capacity and liquid viscosity) of TAGs. They considered a triacylglycerol molecule as a glycerol fragment and three fatty acid fragments and proposed a chemical constituent fragment approach. Specific parameters were assigned to each fragment to represent their contribution to specific heat capacity of TAGs. Fragment-specific parameters were regressed from limited experimental data. This method was used to predict specific heat capacity of several saturated TAGs, palm oil and cocoa butter based on composition. It was found to be as good as the group contribution method by Ruzicka and Domalski (1993a, 1993b).

Su and others (2011) compared the performance of Morad and others', Ceriani and

others' and Zong and others' methods in search of an optimal method to predict specific heat capacity of TAGs and food lipids based on fatty acid composition. Using the experimental data on TAGs and cocoa butter form Morad and others (2000), they found the three methods provided good estimates. When the author tried to further evaluate the three methods with fatty acid composition and specific heat capacity of vegetable oils in Kowalski (1988), they found deviation of predicted values from experimental data. And there was not more experimental data available to help explain the deviation or evaluate the three methods. This investigation was intended to provide more experimental data to validate the three methods as well.

Chapter 3: Materials and Methods

3.1 Materials

Pure triacylglycerols (TAGs) used in this study were as follows: tricaprin, trilaurin, trimyristin, tripalmitin, tristearin, triarachidin, tribehenin, triolein, trilinolein and trilinolenin. They were used because they were most commonly found in food products. As described in Chapter 2, quantitative relationship of specific heat capacity of the TAGs and potential factors that might impact specific heat capacity was not available. They were purchased from Sigma-Aldrich Co. Their melting point and molecular weight information used in this study was from Material Safety and Data Sheet (MSDS) provided by Sigma-Aldrich Co. (Table 3.1). Melting point of trilaurin was confirmed with Differential Scanning Calorimetry method. Melting profile of trilaurin will be found in Appendix A. No further confirmation of melting point was performed in this investigation. The information about purity of samples was obtained from MSDS provided by Sigma-Aldrich Co.. Purity of trilinolein was greater than 98% by thin layer chromatography (TLC). Purity of trilinolenin was greater than 97% by TLC. Purity of other TAGs was greater than 99% by analytical chromatography. No further purification was performed for all TAGs. Melting point of triolein, trilinolein and trilinolenin were not available from MSDS provided by Sigma-Aldrich Co.. Instead, it was stated they were liquid at room temperature. Supelco 37 component fatty acid methyl ester (FAME) mix was purchased from Sigma-Aldrich Co. to be external standard for fatty acid composition analysis of vegetable oils. The external standard contained 37 FAMEs. Each had a distinguished elution time in Gas Chromatography method for fatty acid composition analysis, which will be discussed in detail in the following content. The elution time was used to match that of FAMEs in vegetable oils to identify fatty acid. Vegetable oils used in this study were coconut oil, almond oil, vegetable oil (soybean oil), grapeseed oil and olive oil. They were bought from a local grocery (Kroger, Columbus, OH). They were chosen initially because according to typical fatty acid composition of vegetable oils (Dubois and others 2007), they had large variation in regards to fatty acid composition and the variation was expected to impact specific heat capacity of vegetable oils. They ranged from highly saturated to highly unsaturated according to their nutrition labels and was supposed to have largest difference in specific heat capacity according to Fasina and Colley (2008) and the assumption made in this investigation.

TAG	Numerical Abbreviation	Melting Point (°C)	Molecular weight (g/mol)
Tricaprin	C10:0-C10:0-C10:0	31	554.84
Trilaurin	C12:0-C12:0-C12:0	46.5	639
Trimyristin	C14:0-C14:0-C14:0	56-57	723.16
Tripalmitin	C16:0-C16:0-C16:0	66-67	807.32
Tristearin	C18:0-C18:0-C18:0	72	891.48
Triarachidin	C20:0-C20:0-C20:0	75-78	975.64
Tribehenin	C22:0-C22:0-C22:0	83	1059.8
Triolein	C18:1-C18:1-C18:1	NA^*	885.43
Trilinolein	C18:2-C18:2-C18:2	NA^*	879.38
Trilinolenin	C18:3-C18:3-C18:3	NA^*	873.34

Table 3.1 Numerical abbreviation, melting point and molecular weight of TAGs

* liquid at room temperature

3.2 Method

3.2.1 Terminology

To compare experimental values of specific heat capacity from different researchers and methods, percent difference (% difference) was used. Percent difference was defined as follows:

% difference
$$\frac{|c_{p,exp1} - c_{p,exp2}|}{c_{p,exp1}} \cdot 100$$
(3.1)

where:

 $c_{p, exp1}$ = experimental value by literature 1

 $c_{p, exp2}$ = experimental value by literature 2

For model comparison, several terms should be defined, including percent relative deviation (%RD), percent maximal relative deviation (%MRD), percent average relative deviation (%ARD) and %difference.

$$%RD = \frac{|c_{p,exp} - c_{p,prel}|}{c_{p,exp}} \cdot 100$$
(3.2)
where:

$$c_{p,exp} = \text{the experimental value}$$

$$c_{p,pre} = \text{the predicted value}$$

$$%MRD = \text{the maximum of } %RD$$

$$%ARD = \text{the average of } %RD$$

$$%difference = \frac{|c_{p,pre1} - c_{p,pre2}|}{c_{p,pre1}} \cdot 100$$
(3.3)

where:

 $c_{p, pre1}$, $c_{p, pre2}$ = the predicted values by model 1 and 2 respectively

3.2.2 Prediction models for specific heat capacity of vegetable oils and food products

These prediction models were used in comparison with the proposed model to evaluate abilities of different models to predict specific heat capacity of vegetable oils and food products. 3.2.2.1 Prediction models for specific heat capacity of TAGs, vegetable oils and food lipids

In the following chapter, a simple model will be proposed to predict specific heat capacity of food lipids. Three other models from literatures that were capable to predict specific heat capacity of TAGs, vegetable oils and food lipids were used to compare performances based on %ARD and %MRD. The three models were from Choi and Okos (1986), Morad and others (2000) and Ceriani and others (2009).

The proposed model predicted specific heat capacity of food lipids as a function of average carbon number (C), average number of double bonds (U) and temperature (T). Average carbon number and average number of double bonds were defined as follows:

$$C = \sum y_i C_i \tag{3.4}$$

$$U=\sum y_i U_i \tag{3.5}$$

where:

 x_i = mole fraction of fatty acid i

 C_i = carbon number of fatty acid i

 U_i = number of double bond of fatty acid i that composed food lipids

The proposed model will be introduced in the next chapter.

Choi and Okos (1986) used the following expression to predict specific heat capacity of fat including TAGs and vegetable oils as a function of temperature:

$$c_p = 1.9842 + 1.4733 * 10^{-3} T - 4.8008 * 10^{-6} T^2$$
(3.6)

The model of Choi and Okos (1986) was chosen for comparison as it was simple and widely used as discussed in the literature review. More importantly, the above mention equation, when used in combination with other expressions for other food components, can be used to predict specific heat capacity of food products based on composition.

Ceriani and others (2009) used a group contribution estimation approach to predict specific heat capacity of liquid TAGs with the following equation:

$$c_{p} = \sum_{k} N_{k} \cdot (A_{k} + B_{k} \cdot T)$$
(3.7)
where:

 N_k = the number of group k in TAG (group k could be CH₃, CH₂, COO, CH=CH, and CH₂-CH-CH₂in TAG)

 A_k , B_k = parameters specific to group k (Table 2.4)

When this model was used to predict specific heat capacity of vegetable oils with known fatty acid composition, it was assumed that vegetable oils were mixtures of simple TAGs. And according to fatty acid composition, proportions of simple TAGs in vegetable oils were known. Specific heat capacity of vegetable oils were estimated with the following equation:

$$\mathbf{c}_{\mathrm{p,veg}} = \sum \mathbf{y}_{\mathrm{i}} \mathbf{c}_{\mathrm{pi}} \tag{3.8}$$

where:

 $c_{p,veg}$ = specific heat capacity of vegetable oil

 c_{pi} = specific heat capacity of simple TAG i

 y_i = mole fraction of simple TAG i

This group contribution model was chosen because it was a simple group contribution model that was supposed to predict specific heat capacity accurately compared to other group contribution models (Ceriani and others 2009). It had the most updated parameters for the prediction of specific heat capacity of TAGs and vegetable oils.

Morad and others (2000) used a Rowlinson-Bondi method to predict specific heat capacity of liquid TAGs and vegetable oils based on their fatty acid composition. The Rowlinson-Bondi equation they used was as follows:

$$(c_{p}-c_{p}^{0})/R=1.45+0.45(1-T_{r})^{-1}+0.25\omega[17.11+25.2(1-T_{r})^{1/3}T_{r}^{-1}+1.742(1-T_{r})^{-1}]$$
(3.9)

where:

 $c_{p} = \text{liquid specific heat capacity}$ $c_{p}^{0} = \text{ideal gas specific heat capacity}$ $T_{r} = \text{reduced temperature}$ $\omega = \text{acentric factor}$ $c_{p}^{0}, T_{r}, \omega \text{ of TAGs and vegetable oils were obtained based on fatty acid composition.}$ $c_{p}^{0} = \sum y_{i} c_{pi}^{0} \qquad (3.10)$ where:

 y_i = mole fraction of fatty acid i c_{pi}^0 = ideal gas specific heat capacity of fatty acid i T_r =T/T_c (3.11)

$$Tc = \sum y_i T_{ci}$$
(3.12)

where:

 $T_c = critical temperature$

 T_{ci} = critical temperature of fatty acid i

$$\omega = \sum y_i \omega_i \tag{3.13}$$

$$P_{ci}V_{ci}/RT_{ci}=0.291-0.08\omega_i$$
 (3.14)

where:

 ω_i = acentric factor of fatty acid i

 P_{ci} = critical pressure of fatty acid i

V_{ci} = critical volume of fatty acid i

 c_{pi}^{0} , T_{ci} , P_{ci} and V_{ci} of fatty acids were estimated by additional group contribution estimation methods (Rihany and Doraisamy 1965; Fedors 1982; Joback and Reid 1987).

Additionally, this method used a correction factor (F_c), which was defined as follows:

For
$$Mw < 850$$
, $F_c = -0.3328 + 0.0001 | 850 - Mw |$ (3.15)

For Mw>850,
$$F_c = -0.2836 - 0.0005 |850 - Mw|$$
 (3.16)

$$Mw=3\sum y_i Mw_i + 38$$
 (3.17)

where:

Mw = molecular weight of TAG and vegetable oils

Mw_i = molecular weight of fatty acid i

where:

 c_p = specific heat capacity predicted by equation 3.9

 $c_{p,pre}$ = specific heat capacity predicted by this method

3.2.2.2 Prediction models for specific heat capacity of food products

Choi and Okos (1986) established models to predict specific heat capacity of food products based on composition with the following equation:

$$c_p = \sum x_i c_{pi} \tag{3.19}$$

where:

 c_p = specific heat capacity of food products

 c_{pi} = specific heat capacity of food component i, and food component i can be protein, carbohydrate, fat, fiber, ash, water and ice

 x_i = mass fraction of food components

 c_{pi} was calculated as a function of temperature. Expressions for the calculation of c_{pi} was shown in Table 2.1.

In this study, the proposed model was capable to predict specific heat capacity of liquid lipid. The proposed model, when used in combination with Choi and Okos' models that predict specific heat capacity of food components other than lipid and equation 3.19, should be able to estimate specific heat capacity of food products. This approached to predict specific heat capacity of food products were referred to as the proposed model in the following content.

The abilities of the two models to predict specific heat capacity of food products were compared based on %difference with proposed model being model 1 and Choi and Okos' models being model 2 for the definition of %difference.

3.2.3 Fatty acid analysis

For sample preparation, 100mg of each vegetable oil was weighted in 20ml test tube with screw cap. 10ml hexane was added to dissolve vegetable oil sample. 10µl 2N potassium hydroxide in methanol was added. The test tube was vortexed for 30s with screw cap. Then 1.5ml sample was transferred into a 2.0ml centrifuge tube with a pinch of pre-added sodium sulfate anhydrous. The sample was centrifuged at 13.2 RPM and 24°C for 10min. The supernatant was transferred into a 2ml vial.

A Hewlett Packard 6890 Gas Chromatography with a flame ionization detector (FID) and a HP G1513A autosampler (Agilent Technologies) was used to analyze fatty acid composition of vegetable oils. A HP-88 column (60m*0.25mm*0.2µm) from Agilent Technologies was used. The split ratio was 1:20. The injection volume was 1.0µl. The carrier gas was helium and the flow rate was 40 ml/min. The oven conditions were: 120°C 1min, 10°C/min to 175°C, 5min, 15°C/min to 210°C, 5min, 30°C/min to 230°C, 2min. A hexane blank sample was run prior to samples. A FAME reference standard (Supelco 37 component FAME) sample was run to match retention time of the FAME in the reference standard and the FAME in the sample to identify fatty acid. Each sample was run in duplicates. Fatty acid composition was shown as the average of duplicates.

3.2.4 Specific heat capacity measurement

Specific heat capacity of TAGs and vegetable oils were measured with a TA Instruments Q2000 Differential Scanning Calorimeter (DSC) equipped with a refrigerated cooling system (RCS 90) with a built-in modulated differential scanning calorimeter (MDSC) feature. The Differential Scanning Calorimeter was connected to nitrogen cylinder and a computer. Nitrogen flow rate was 50ml/min during calibration and measurement.

3.2.4.1 Sample preparation

Tzero hermetic pans and lids were purchased from TA instruments and used. Prior to use, pans and lids were cleaned in mildly heated acetone (40°C) and dry. For each sample (TAGs or vegetable oils), a sample pan and a lid was weighted empty first. Then 5-7mg sample was carefully weighted into the sample pan. No sample was allowed on the seal. Then the sample pan was sealed with a TA Instruments blue press and weighted again. For the sample pan, a reference pan was prepared. The reference pan was weight matched with the empty sample pan to within 0.02mg. The reference pan was sealed with nothing in it with the same blue press. The weight of the sample pan, the reference pan and the sample was recorded as used as inputs in the operation software provided by TA instruments. For each sample, six replicates were conducted for specific heat capacity measurement.

An indium pan was prepared with 2-3mg indium. The indium pan and its reference pan were used for calibration. A sapphire pan was prepared with the sapphire in the accessory kit. The sapphire pan was used as standard. Pans and lids were handled all the time with cleaned tweezer. They were sealed with a TA Instruments blue press.

3.2.4.2 Calibration

Cleaning and calibration was performed according to manuals from TA instruments and more detailed information can be found there.

Prior to calibration, the cell of the DSC was gently cleaned with a fiberglass brush from the accessory kit. The residue in the cell was removed by compressed air. Then a cotton swab dipped with a little acetone was used to further clean the cell. A dry cotton swab was used to remove acetone residue. Compressed air was used after that to make sure residues were removed.

After cleaning, the DSC was run in the standard mode with empty cell from -90 °C

to 400°C at 20°C /min for several cycles. This was called a standard cyclic empty cell run.

It was performed to check the performance of the DSC. The curves obtained from the empty cell run were baselines. By analysis, if baselines were reproducible and had acceptable curvature and bow, calibration proceeds. The analysis of curvature and bow of baselines were performed according to the technical note from the TA instruments "How to analyze curvature and bow".

Otherwise, more cleaning of the cell was needed. The cell was burn out by heating it to 550°C at 20°C /min, opening lid for 60s and cooling. Then the fiberglass cleaning, acetone cleaning and empty cell run were performed again. The burn out procedure should

only be used as the last step to clean the cell as suggested by TA instrumenst because frequent burning out the cell shortened the use time of the DSC.

For calibration, the calibration wizard option was used. T4P heat flow and cell resistance and capacitance, cell constant and temperature calibration were chosen. Then there were three separate runs for calibration. The first was performed with the empty cell from -90 °C to 400°C at 20°C /min. The second was performed with two sapphire discs with matched weights from -90 °C to 400°C at 20°C /min. The second was performed with two sapphire discs the indium pan and its reference pan from 100 °C to 180°C at 10°C /min. The analysis of calibration was in technical note from the TA instrumenst. After the third run, a cell constant was generated and it should be within 0.9-1.1. The cell constant was calculated by dividing theoretical enthalpy of indium by the measured enthalpy. A standard cyclic empty cell run was performed again. If baselines were reproducible and had excellent curvature and bow (0.05mW), experiment proceeds. Otherwise calibration or even cleaning steps were repeated.

3.2.4.3 MDSC procedure

In this study, quasi-isothermal MDSC measurement for specific heat capacity was chosen because the TA instruments suggested that this type of measurement provided the most accurate absolute specific heat capacity value at each temperature measured. Parameters used for all runs were modulation amplitude 0.75°C, modulation period 100s

and isothermal time 10min. They were determined by preliminary analysis as optimal parameters.

Prior to each sample run, the sapphire pan and the corresponding reference pan were run under the same conditions as the next sample run. By dividing theoretical specific heat capacity of sapphire at each temperature by the measured one, a correction factor was obtained. The correction factor should be within 0.9 to 1.1. The next sample run was set to equilibrate at the highest temperature used for the measurement of specific heat capacity of the sample in this run for 5min to melt the sample. Then the specific heat capacity of the sample was measured from slightly above the melting point to 50°C above that at 10°C interval for saturated TAGs by quasi-isothermal MDSC. The temperature range was chosen so that there was enough data to determine relationship of specific heat capacity and temperature and a single run didn' t take too much time. Unsaturated TAGs were measured over similar temperature range for comparison purpose. Vegetable oils were measured from 40°C to 80°C. After each sample run, the sapphire was run again and correction factor at each temperature was calculated again. If two correction factors obtained before or after the sample run were in close agreement, measurement proceeds. The specific heat capacity of the sample at each temperature was obtained by multiplying the correction factor to the measured specific heat capacity at each temperature. If two correction factors were far from each other, it suggested that something might be wrong with the DSC (contamination might happen). The performance of DSC was checked by another empty cell run. If the result of empty cell run was not good, cleaning and calibration was repeated.

3.3 Data treatment

For each sample run, specific heat capacity was obtained by multiplying the correction factor to the measured specific heat capacity. The measured specific heat capacity was obtained from the software Universal analysis by plotting c_p vs temperature. The correction factor was obtained by dividing theoretical specific heat capacity of sapphire at each temperature by the measured one that was obtained with the software Universal analysis from the sapphire run. Each sample had six replicates and specific heat capacity of each sample was expressed as average.

3.4 Statistical Analysis

SPSS.21 (IBM, Inc,. USA) statistics software was used to perform statistical analysis. A One-Way ANCOVA with 95% confidence interval was used to evaluate the statistical difference of the intercept and slope between the linear regressions.

Chapter 4: Results and Discussions

In this chapter, the impacts of average carbon number (C) and average number of double bonds (U) on specific heat capacity of triacylclycerols (TAGs) will be discussed in detail. The discussion provides basis for predicting specific heat capacity of foods.

Seven (7) saturated TAGs were chosen to evaluate the influence of average carbon number on specific heat capacity. These TAGs differed in average carbon number from 10 to 22. In addition, three unsaturated TAGs (C=18, U=1,2,3) and tristearin (C=18, U=0) were chosen to investigate the influence of average number of double bonds on specific heat capacity. Average carbon number (C) and average number of double bonds (U) were defined in Section 3.2.2.1.

4.1 Effect of average triacylglycerol carbon number (C) on specific heat capacity

A triacylglycerol is derived from three fatty acids and a glycerol. Triacylglycerols (TAGs) differ in fatty acid composition. The specific heat capacity of TAGs is likely determined by fatty acid composition as well. Fatty acids are compounds with an aliphatic chain plus a carboxylic acid group. They are distinguished by their carbon number and the number of double bonds. According to fatty acid compositions, TAGs are distinguished by average carbon number (C) and average number of bonds (U). These factors might impact specific heat capacity of TAGs. Average carbon number of TAGs has been defined as the weighted average of the carbon numbers of fatty acids within the TAG. Average

number of double bonds has been defined as the weighted average of the numbers of double bonds of fatty acids in the TAG structure. Effects of average carbon number and average number of double bonds on specific heat capacity of TAGs will be discussed in Section 4.1 and 4.2.

The specific heat capacity of the seven saturated triacylglycerols (tricaprin, trilaurin, trimyristin, tripalmitin, tristearin, triarachidin and tribehenin) was measured using MDSC as described in Chapter 3. As mentioned in Section 3.2.4.3, the specific heat capacity measurement of one TAG was conducted at temperatures slightly above the phase change from solid to liquid. Five measurements were completed at 10°C intervals. The range of temperatures for specific heat capacity measurement varied slightly due to differences in the phase change temperature. The results in Figure 3 illustrated the increase in specific heat capacity as a function of temperature. The results indicated the pattern of specific heat capacity, depending on average carbon number of the TAGs. Two of the TAGs (tribehenin and triarachidin) had the highest specific heat capacity. A second cluster of the TAGs (tristearin, tripalmitin, trimyristin) had specific heat capacity in an intermediate magnitude range. Finally, a third set of the TAGs (trilaurin, tricaprin) had the lowest specific heat capacity.



Figure 4.1 Liquid specific heat capacity of saturated TAGs from 60°C to 130°C

Linear regression was used to generate a relationship between specific heat capacity and temperature based on Morad and others (1995a). More background was provided in Chapter 2. The linear regression coefficients were presented in Table 4.1. The correlation coefficients (R^2) in Table 4.1 described the ability of linear regressions to fit the experimental data. The R^2 were all higher than 0.998. The magnitude of R^2 confirmed that linear regression described the result very well and the relationship was linear.

Phinney and Heldman (2013) confirmed that the relationships of specific heat capacity to temperature for most food components (protein, carbohydrate, fat, ash) were best described by linear correlations. Earlier, Choi and Okos (1986) had previously suggested that a polynomial function was most appropriate.

TAG	С	U	Slope	Intercept	\mathbb{R}^2
tricaprin	10	0	0.002617±0.000134 ^a	1.891±0.019 ^a	1±0.0011
trilaurin	12	0	$0.002605 \pm 0.000174^{a}$	1.918 ± 0.014^{b}	0.9993 ± 0.0008
trimyristin	14	0	$0.002633 {\pm} 0.000103^{a}$	1.967±0.018°	$0.9988 {\pm} 0.0008$
tripalmitin	16	0	$0.002913{\pm}0.000305^a$	1.929±0.034°	0.9992 ± 0.002
tristearin	18	0	$0.002812{\pm}0.00007^{a}$	1.938±0.02°	$0.9987 {\pm} 0.0021$
triarachidin	20	0	$0.002678{\pm}0.000124^{a}$	$2.024{\pm}0.017^{d}$	$0.9988 {\pm} 0.0006$
tribehenin	22	0	$0.002939 \pm 0.000231^{a}$	$1.985{\pm}0.018^{d}$	0.9986±0.0014

Table 4.2 Regressions of liquid specific heat capacity of saturated TAGs as a function of

temperature*

regression was valid up to 150°C according to Morad and others (1995a)

One-Way Analysis of Covariance (ANCOVA) was used to evaluate the differences in the slopes and intercepts from the linear regression analysis. The slope represented the influence of temperature on specific heat capacity. The ANCOVA results presented in Table 4.1 indicated that there were no significant differences among the slope magnitudes for the seven TAGs. These results confirmed that the influence of temperature on liquid specific heat capacity was the same for all saturated TAGs. The ANCOVA then treated these regressions parallel and evaluated the differences in the adjust means of TAG groups. The adjusted means were the predicted specific heat capacity by ANCOVA of TAGs at the midpoint temperature of the entire temperature range or 80°C in this situation. Since these regressions were treated parallel, differences in adjusted means represented differences at any temperature or differences in intercepts. The results of ANCOVA was presented as differences in intercepts in Table 4.1 for consistency. The results of ANCOVA presented in Table 4.1 illustrated that there were significant differences among the intercept magnitudes for the seven TAGs. The intercept magnitudes for the TAGs (tribehenin and triarachidin) with largest carbon number were significantly larger than those for the second cluster (tristearin, tripalmitin and trimyristin) of TAGs. The intercept magnitudes of the second cluster of TAGs were, in turn, significantly larger than those of the third set of the TAGs (trilaurin and tricaprin) with the lowest carbon number. The intercept magnitude of trilaurin was significantly larger than that of tricaprin.

These results confirmed that the influence of temperature on liquid specific heat capacity was linear and the same for saturated TAGs and independent of average carbon number. The average carbon number (C) had a significant influence on the magnitudes of the specific heat capacity of TAGs. These observations were consistent with previous results from Morad and others (1995a). Morad and others (1995a) observed that liquid specific heat capacity of trilaurin, trimytistin, tripalmitin and tristearin, increased with carbon length. Statistical analysis completed in the current investigation provided stronger evidence of this relationship. This conclusion was in agreement with predictions by the group contribution method. That method suggested that CH₂ increments in organic molecules caused positive increases in specific heat capacity, as discussed in Section 2.3.

Earlier research (Phillip and Mattarnal 1976; Hampson and Rothbart 1983) did not reveal relationship between average carbon number and specific heat capacity of TAGs. The differences from results presented in the current investigation may be associated with improved detection limits. The differences in specific heat capacity of TAGs, like the difference between tricaprin and trilaurin or between trilaurin and trimyristin, were 0.02 kJ/kg·K as indicated by the current investigation and by results from Morad and others (2000). If the detection limits of the instrumentation were larger than the differences, the method may not detect the differences. Phillip and Mattarnal (1976) indicated that experimental error was 5% for their measurements and equal to a variance of 0.1 kJ/kg·K. For these measurement methods, the differences in specific heat capacity of the TAGs may not be detected.

It should be noted that the ANCOVA did not reveal significant differences in specific heat capacity between tribehenin and triarachidin and among tristearin, tripalmitin and trimyristin, possibly due to detection limits of MDSC.

The experimental values of specific heat capacity for TAGs were compared to literature values in order to evaluate the capabilities of the MDSC. The specific heat capacity of the TAGs (trilaurin, trimyristin, tripalmitin and tristearin) measured during this investigation was in close agreement with data reported by Morad and others (2000). The maximum percent differences was 2.31%, when the percent difference was defined to be the absolute difference between specific heat capacity reported in this investigation and value reported in the literature, dividing by the value from this investigation. Similar comparisons with results from other published researches were 4% when compared to data by Phillip and Mattarnal (1976) for trilaurin, trimyristin, tripalmitin and tristearin, and 2.18% when compared to results reported by Eiteman and Goodrum (1994) for tricaprin at 100°C.

ТАС	Temperature	c _{p,exp}	$c_{p,exp}^{a}$	%difforance	c _{p,exp} ^b	%differ
IAU	(°C)	$(kJ/kg\cdot K)$	(kJ/kg·K)	/ourrerence	$(kJ/kg\cdot K)$	ence
trilaurin	100	2.179	2.143	1.64	2.135	2.04
	80	2.126	2.094	1.49	NA	NA
trimyristin	100	2.232	2.180	2.31	NA	NA
	80	2.176	2.136	1.86	NA	NA
	60	2.126	NA	NA	2.048	3.66
tripalmitin	120	2.28	2.276	0.17	2.306	-1.15
	100	2.219	2.227	-0.35	NA	NA
	80	2.164	2.177	-0.61	NA	NA
tristearin	120	2.277	2.276	0.04	NA	NA
	100	2.218	2.227	-0.39	NA	NA
	80	2.165	2.177	-0.56	2.218	-2.43
triolein	100	2.188	2.163	1.16	NA	NA
	80	2.127	2.123	0.20	NA	NA
	60	2.068	2.083	-0.71	NA	NA
					c _{p,exp} ^c	
					(kJ/kg·K)	
tricaprin	100	2.153	NA	NA	2.2	-2.183

Table 4.3 Comparisons of specific heat capacity with published literatures

^a Morad and others 2000

^b Phillip and Mattarnal 1976

^c Eiteman and Goodrum 1994

Specific heat capacity from the current investigation was measured by MDSC while data from other researches in Table 4.2 was measured by DSC. These comparisons

suggested that specific heat capacity measurements with MDSC were in close agreement with specific heat capacity measurements with DSC. Both methods were able to distinguish TAGs with differences of 0.02 kJ/kg·K.

4.2 Effect of average number of double bonds (U) on specific heat capacity

The specific heat capacity of three unsaturated triacylglycerols (TAGs) (triolein, trilinolein and trilinolenin, C=18, U=1,2,3) was measured. The temperature range described in Section 4.1 was used for these measurements. The results, along with specific heat capacity of tristearin (C=18, U=0) were presented in Figure 4.2. The four TAGs had the same average carbon number (C) but four different levels of average number of double bonds (U). The results indicated that specific heat capacity decreased as average number of double bonds increased.

The relationships between specific heat capacity and temperature were analyzed using linear regression analysis, as described in Section 4.1. The results in Table 4.3 presented linear regression coefficients and correlation coefficients (R²). These results confirmed the linearity of the relationship between specific heat capacity and temperature for both saturated and unsaturated liquid TAGs based on Morad and others (1995a).

The coefficients from linear regression analysis were analyzed by One-Way ANCOVA, as described in Section 4.1. The results from the ANCOVA indicated that there were no significant differences among slopes. These results confirmed that temperature effect on specific heat capacity was the same for all TAGs. In addition, the ANCOVA revealed that there were significant differences among linear regression intercepts or specific heat capacity decreased as average number of double bonds increased.



Figure 4.5 Liquid specific heat capacity of TAGs from 40°C to 100°C

Table 4.4 Regressions of liquid specific heat capacity of TAGs as a function of temperature^{*}

7±0.0021
8±0.0007
9±0.0004
8±0.0019

* regression was valid up to 150 °C according to Morad and others (1995a)

The same relationship between specific heat capacity and average number of double bonds was reported by Parks and Huffman (1930) for liquid n-pentane and pentene-2. The significant decrease in specific heat capacity along with the formation of double bond was due to the decrease of vibrations of carbon atoms that were adjacent to the double bond. The loss of vibrations of the two hydrogen atoms that were replaced by the double bond might contribute slightly to the decrease as well. Anand and others (2011) reported that specific heat capacity of C18 methyl esters decreased as the number of double bonds increased and these researchers suggested that this was a result of increased fluidity and volatility of methyl esters as a result of the formation of double bonds. The results from this investigation provide a quantitative effect of unsaturation on specific heat capacity of TAGs.

When comparing reported specific heat capacity of triolein at 60, 80 and 100° C from Morad and others (2000) to results from this investigation, the maximum percent difference was 1.16%.

4.3.A Prediction model for specific heat capacity of TAGs

The results discussed in Section 4.1 and 4.2 can be used to quantify the influences of average carbon number (C), average number of double bond (U) and temperature (T) on specific heat capacity of liquid triacylclycerols (TAGs). In this section, the prediction model will be developed and discussed.

Based on the results from Section 4.2, the results in Table 4.4 were developed. A linear regression was used to describe the average number of double bonds on specific heat

capacity from 60°C to 100°C. The correlation coefficients (R^2) of 0.955 to 0.999 indicated that the linear regression described the relationship very well.

Temperature (°C)	C range	U range	Slope	Intercept	R ²
100	18	0-2	-0.048 ^a	2.224 ^a	0.9552
90	18	0-2	-0.0495 ^a	2.196 ^b	0.9643
80	18	0-3	-0.0566 ^a	2.172 ^c	0.9881
70	18	1-3	-0.0635 ^a	2.159 ^d	0.999
60	18	1-3	-0.0635 ^a	2.13 ^e	0.9975

Table 4.5 Specific heat capacity of TAGs as a function of U

The specific heat capacity of TAGs as a function of average carbon number was presented in Table 4.5 from 60°C to 120°C. The results in Table 4.5 indicated that specific heat capacity increased linearly with average carbon number. Based on Morad and others (1995a), these linear relationships were valid for liquid TAGs to up to 150°C.

Temperature (°C)	C range	U range	Slope	Intercept	R ²
120	16-22	0	0.0121ª	2.081 ^a	0.7143
110	16-22	0	0.0115 ^a	2.059 ^b	0.7776
100	10-22	0	0.0104 ^a	2.058 ^b	0.8365
90	10-22	0	0.0104 ^a	2.03 ^c	0.8402
80	10-20	0	0.0114 ^a	1.99 ^d	0.806
70	10-14	0	0.0192 ^a	1.878 ^{de}	0.9603
60	10-14	0	0.0194 ^a	1.850 ^e	0.9699

Table 4.6 Specific heat capacity of TAGs as a function of C

Based on the analysis presented in Table 4.4, the following relationship applied:

$$c_p^{18} = \mathbf{A} + \mathbf{B}\mathbf{U} \tag{4.1}$$

where:

 c_p^{18} = specific heat capacity of TAGs with an average carbon number of 18

B = slope coefficient

A = intercept coefficient

The slope coefficient (B) discussed the influence of average number of double bonds on specific heat capacity when average carbon number was 18. Since the One-Way ANCOVA indicated that significant differences among the slope coefficients did not exist
at different temperatures. The specific slope coefficient selected was for the full range of average number of double bonds (0 to 3) or -0.0566. This value was very close to the mean of the five values over the entire range of temperatures or -0.0562.

The intercept coefficient (A) represented the specific heat capacity of tristearin (C=18, U=0) at a defined temperature. It should increase linearly as temperature increased as discussed in Section 4.1. This relationship was confirmed by the ANCOVA.

Thus the relationship between specific heat capacity at average carbon number of 18 and average number of double bonds of U became:

$$c_p^{18} = c_p^{18*} - 0.0566U \tag{4.2}$$

where:

$$c_p^{18*}$$
 = specific heat capacity of tristearin (C=18, U=0)
Plotting intercepts against temperatures in Table 4.5:

$$c_p^{18*} = 1.996 + 0.0022T \tag{4.3}$$

By selecting a reference temperature of 80°C, the relationship became:

$$c_p^{18*} = 2.172 + 0.0022(T - 80) \tag{4.4}$$

The results in Table 4.5 indicated that the relationship of specific heat capacity and average carbon number can be described by:

$$c_p^* = \mathbf{A}' + \mathbf{B}'\mathbf{C} \tag{4.5}$$

where:

 c_p^* = specific heat capacity of saturated TAGs

A'= intercept coefficient

B'= slope coefficient

The slope coefficient (B') indicated the influence of average carbon number on specific heat capacity. The One-Way ANCOVA showed that significant differences among the slope coefficients did not exist at different temperatures. The slope coefficient selected was B'=0.0104. The selection of B' was based on the full range of average carbon number. The intercept coefficient (A') was the base value for specific heat capacity of TAGs and was a function of temperature.

The relationship became:

$$c_p^* = \mathbf{A}' + 0.0104\mathbf{C} \tag{4.6}$$

This expression can be used to predict specific heat capacity of saturated TAGs (U=0).

Using c_p^{18*} as reference specific heat capacity, the expression became:

$$c_p^* = c_p^{18*} + 0.0104(C - 18) \tag{4.7}$$

Equation 4.2 can be generalized to obtain the following equation:

$$c_p = c_p^* - 0.0566U \tag{4.8}$$

In summary, the prediction model for specific heat capacity of TAGs involved three equations applied in the follow sequences:

$$c_p^{18*} = 2.172 + 0.0022(T - 80) \tag{4.5}$$

$$c_p^* = c_p^{18*} + 0.0104(C - 18) \tag{4.7}$$

$$c_p = c_p^* - 0.0566U \tag{4.8}$$

Equation 4.5 can be used to predict specific heat capacity of the liquid TAG with C=18 and U=0 as a function of temperature with reference temperature of 80°C to up to

150°C. Equation 4.5 was used as reference specific heat capacity in equation 4.7. As discussed in Section 4.1 and 4.2, the temperature effect on specific heat capacity of T was the same. Equation 4.5 took into account the impact of temperature on specific heat capacity of the TAGs. Equation 4.7 can be used to predict specific heat capacity of saturated TAGs. It accounted for the impact of average carbon number on specific heat capacity. Equation 4.8 referenced equation 4.7 and can be used to predict specific heat capacity of unsaturated TAGs. Based on the proposed model, the following equation also applied:

$$c_p = 2.172 + 0.0022(T - 80) + 0.0104(C - 18) - 0.0566U$$
(4.9)

4.3. B Validation of the prediction model using specific heat capacity of vegetable oils

The proposed prediction model developed in Section 4.3.A was expected to predict specific heat capacity of a food lipid because food lipid contained mostly triacylglycerols. The proposed model will be validated with specific heat capacity of vegetable oils in this section. To use the proposed model to predict specific heat capacity of vegetable oils, fatty acid composition of vegetable oils was determined (Table 4.6) and used to develop average carbon number and average number of double bonds in Table 4.6.

Percent (%)	Coconut oil	Almond oil	Grapeseed oil	Cocoa butter	Vegetable oil	Olive oil
C6	0.7 ± 0.04	0.0	0.0	0.0	0.0	0.0
C8	9.0±0.4	0.0	0.0	0.0	0.0	0.0
C10	6.9±0.2	0.0	0.0	0.0	0.0	0.0
C12	53.5±0.2	0.0	0.0	0.0	0.0	0.0
C14	19.1±0.2	0.0	0.0	0.0	0.0	0.0
C16	6.8±0.7	6.7±0.04	9.3±0.04	31.5±0.6	12.1±0.08	15.1±0.3
C16:1	0.0	0.4±0.01	0.0	0.0	0.0	1.6±0.2
C18	0.7 ± 0.02	0.7 ± 0.08	2.0±0.1	31.6±0.2	2.5±0.08	1.7±0.07
C18:1	2.6±0.3	66.4±0.2	20.8±0.03	34.5±0.4	21.0±0.05	73.1±0.6
C18:2	0.6±0.1	25.8±0.1	67.7±0.03	2.4±0.03	57.8±0.3	8.0±0.1
C18:3	0.0	0.0	0.3±0.01	0.0	6.6±0.2	0.5±0.02
Averaged carbon number (C)	12.353	17.856	17.815	17.370	17.759	17.666
Average number of double bonds (U)	0.03891	1.184	1.571	0.3932	1.565	0.9213

Table 4.7 Fatty acid composition of vegetable oils

The predicted specific heat capacity and experimental specific heat capacity of vegetable oils were compared in Table 4.7. Percent relative deviation (%RD) was used to evaluate the comparison. Percent relative deviation (%RD) and its related coefficients like percent average relative deviation (%ARD) and percent maximal relative deviation (%MRD) used in this section were defined in Section 3.2.1.

The results in Table 4.7 confirmed that the proposed model provided an estimate of specific heat capacity of vegetable oils in very good agreement with experimental value, with %RD within 2% and a %ARD of 0.83%. When using the proposed model to predict specific heat capacity of vegetable oil or other lipid, it was assumed that lipids were exclusively TAGs. However, there was minor components other than TAG in all lipids, like free fatty acid. The amount and composition of components other than TAGs might affect the prediction. It was noticed in Table 4.7 that the proposed model had smaller %RD for some vegetable oils as compared to others. These differences might be attributed to the amount and composition of other components in vegetable oils.

	Temperature (°C)	Cp exp	Cp pre	%RD
	80	2.081	2.079	0.1
1	70	2.059	2.053	0.29
grapeseed	60	2.037	2.024	0.64
011	50	2.015	1.996	0.97
	40	1.993	1.967	1.33
	80	2.103	2.132	1.35
almond oil	70	2.081	2.105	1.12
	60	2.059	2.078	0.87
	50	2.037	2.05	0.61
	40	2.015	2.023	0.37
				continued

Table 4.8 Comparison of specific heat capacity of vegetable oils

	80	2 081	2 096	0.72
		2.001	2.070	0.72
. 1 1	70	2.059	2.07	0.54
vegetable	60	2.037	2.043	0.3
011	50	2.015	2.016	0.05
	40	1.993	1.989	0.2
	80	2.116	2.133	0.78
	70	2.094	2.106	0.55
olive oil	60	2.072	2.079	0.32
	50	2.05	2.051	0.03
	40	2.028	2.025	0.17
	80	2.143	2.188	2.05
	70	2.121	2.164	1.98
cocoa butter	60	2.099	2.137	1.77
butter	50	2.077	2.11	1.55
	40	2.055	2.084	1.38
	80	2.111	2.143	1.49
	70	2.089	2.115	1.23
coconut	60	2.067	2.087	0.96
011	50	2.045	2.06	0.73
	40	2.023	2.034	0.54
% ARD				0.83

Table 4.7 Comparison of specific heat capacity of vegetable oils (continued)

The proposed model was compared to other published models proposed to predict specific heat capacity of vegetable oils (Table 4.8). The results in Table 4.8 indicated that the proposed model had the smallest %ARD and %MRD when compared to other models. The percent average relative deviation and percent maximal relative deviation of the proposed model was much smaller than the Choi and Okos' model. As previous described, the Choi and Okos' model used an average to estimate specific heat capacity of all lipids

within a given product. The model will be expected to deviate depending on the type of lipid in the product. The percent average relative deviation and percent maximal relative deviation of the proposed model was much smaller than predictions from the Ceriani and others' group contribution model because the proposed model quantified the influence of double bonds within food lipid on specific heat capacity better.

Table 4.9 %ARD and %MRD of models predicting specific heat capacity of vegetable oils

	The proposed	Choi and Okos'	Ceriani and	Morad and
	model	(1986)	others (2009)	others (2000)
%ARD	0.83	1.83	1.63	0.85
%MRD	2.05	5.33	5.15	2.33

The proposed model and the Morad and others' model had the same magnitude of %ARD and %MRD. These models were based on fatty acid composition. It was confirmed that it was important to consider fatty acid composition when predicting specific heat capacity of vegetable oils and food lipids. Morad and others' model was based on corresponding state theory and complex as discussed in Section 2.4. In addition, an experimental correction factor was used to adjust the performance of the model. The

proposed model provided a more desired method to predict specific heat capacity of vegetable oils and food lipids.

4.4 Prediction of specific heat capacity of food products with modest to significant lipid fraction

The proposed model has been demonstrated better in predicting specific heat capacity of food lipids than other models as discussed in Section 4.3. If the proposed model was used to predict specific heat capacity of the lipid in a food product with known fatty acid composition and Choi and Okos' expressions (Table 2.1) was used to predict specific heat capacity of major food components other than lipid in the food product, the proposed model can be used to predict specific heat capacity of the food products with equation 2.3.

Specific heat capacity of several food products with modest to significant lipid fraction was predicted by Choi and Okos' models and by the proposed model. A beef product, a pork product, a lamb product, a cream product, a margarine product, a mayonnaise product and an egg yolk product were selected and composition was determined from USDA nutrient database. The compositions were used as inputs. For the proposed model, fatty acid composition of the lipid fraction of food products was also required. This information was extracted from literatures. The two models were compared from 50°C to 150°C because (1) the corresponding lipid in each product was generally liquid above 50°C (Langworthy and Hunt 1913; Martin 2013) and the proposed model predicted specific heat capacity of liquid lipid up to 150°C as discussed in previous

sections, (2) Choi and Okos' models were used in the temperature range from 40°C to

150°C, (3) 50°C to 150°C was a typical range for processing of food products.

4.4.1 Beef product

A beef product with modest lipid composition was chosen from USDA nutrient database (13347, Beef, cured, corned beef, brisket, cooked). Composition for the beef product was listed in Table 4.9. Typical fatty acid composition of beef tallow in Table 4.10 was used in the proposed model to estimate the contribution of the lipid fraction.

	Beef
	Product
Protein (%weight)	18.17
Fat (% weight)	18.98
Carbohydrate (% weight)	0.47
Fiber (% weight)	0
Ash (% weight)	2.6
Water (% weight)	59.79

Table 4.10 Composition of the beef product

	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	С	U
Beef tallow	2.5	27	10.8	7.4	47.5	1.7	0	16.586	0.617

Table 4.11 Typical fatty acid composition of beef tallow (Gunstone and Padley 1997)

The performances of the two models were shown in Figure 4.3. In Figure 4.3, estimates of two models were very close around 50°C with %difference 0.05%. However, as temperature increased, a difference could be found between two estimates and %difference kept increasing until maximal %difference 1% was reached at 150°C. The trend- increased %difference with temperature increases, was observed in other food products investigated as well. This was because that the impact of temperature on specific heat capacity of food lipid was larger in the proposed model than in Choi and Okos' models according to coefficients assigned to temperature.



Figure 4.6 Prediction of specific heat capacity of the beef product by Choi and Okos' models and the proposed model

Percent difference in this case was small. The two models were in agreement. As discussed earlier, Choi and Okos' models used an empirical expression to estimate specific heat capacity of the lipid fraction in foods. In their models, specific heat capacity of fat was an average of specific heat capacity of several common lipids. Based on average carbon number and average number of double bonds of all lipid investigated in this study as listed in Appendix B, beef tallow had close average carbon number with most lipids and its average number of double bonds fell in the middle of lipids. Thus its specific heat capacity should be in the middle of the lipid group, which explained why the two models were in agreement.

4.4.2 Pork product

A pork product with modest lipid composition was chosen from USDA nutrient database (07225, OSCAR MAYER, Pork Sausage Links (cooked)). Composition for the pork product was listed in Table 4.11. Typical fatty acid composition of lard in Table 4.12 was used in the proposed model to estimate the contribution of the lipid fraction.

	Pork
	Product
Protein (%weight)	16.3
Fat (% weight)	30.5
Carbohydrate (% weight)	1
Fiber (% weight)	0
Ash (% weight)	2.7
Water (% weight)	49.5

Table 4.13 Typical fatty acid composition of lard (Gunstone and Padley 1997)

	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	С	U
Lard	2	27.1	4	11	44.4	11.4	0	17.28	0.712

The performances of the two models were shown in Figure 4.4. In Figure 4.4, %difference ranged from 0.11% to 1.73%. Percent difference was small. The two models

were in agreement because specific heat capacity of lard was close to average specific heat capacity of fat provided by Choi and Okos (1986) according to average carbon number and average number of double bonds.



Figure 4.7 Prediction of specific heat capacity of the pork product by Choi and Okos' models and the proposed model

4.4.3 Lamb product

A lamb product with significant lipid composition was chosen from USDA nutrient database (17285, Lamb, Australian, imported, fresh, separable fat, cooked). Composition for the lamb product was listed in Table 4.13. Typical fatty acid composition of mutton tallow in Table 4.14 was used in the proposed model to estimate the contribution of the lipid fraction.

	Lamb
	Products
Protein (%weight)	9.42
Fat (% weight)	66.4
Carbohydrate (% weight)	0
Fiber (% weight)	0
Ash (% weight)	0.45
Water (% weight)	24

Table 4.14 Composition of the lamb product

Table 4.15 Typical fatty acid composition of mutton tallow (Gunstone and Padley 1997)

	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	С	U
Mutton tallow	5.6	27	1.6	31.7	31.7	1.6	0	17.06	0.365

The performances of the two models were shown in Figure 4.5. In Figure 4.5, %difference was 0.47% at 50°C and 4.79% at 150°C. Significant difference was found between estimates from two models. The proposed model provided better estimate. It was because that specific heat capacity of mutton tallow should be above average according to

the magnitudes of average carbon number and average number of double bonds. The proposed model provided better estimate based on fatty acid composition while Choi and Okos' models provided the average.



Figure 4.8 Prediction of specific heat capacity of the lamb product by Choi and Okos' models and the proposed model

It was also noticed that the magnitude of specific heat capacity of the lamb product was significantly lower than that of the beef and the pork products. It was because that the lamb product contained significant amount of lipid.

4.4.4 Cream Product

A cream product with modest lipid composition was chosen from USDA nutrient database (01053, Cream, fluid, heavy whipping). Composition for the cream product was listed in Table 4.15. Typical fatty acid composition of milk fat in Table 4.16 was used in the proposed model to estimate the contribution of the lipid fraction.

	Cream
Protein (%weight)	2.05
Fat (% weight)	37
Carbohydrate (% weight)	2.79
Fiber (% weight)	0
Ash (% weight)	0.45
Water (% weight)	57.71

Table 4.16 Composition of the cream product

Table 4.17 Typical fatty acid composition of milk fat (Gunstone and Padley 1997)

C4	C6	C8	C10	C12	C14	C15	С	U
3.85	2.35	1.7	2.4	2.6	9.8	1.2		
C16	C17	C18	C18:1	C18:2	C18:3		14.636	0.389
24.05	0.9	12.95	27.6	2	2.45			
				_	_			

The performances of the two models were shown in Figure 4.6. In Figure 4.6, %difference ranged from 0.03% to 1.88%. The two models were in agreement because specific heat capacity of cream should be close to the average based on average carbon number and average number of double bonds.



Figure 4.9 Prediction of specific heat capacity of the cream product by Choi and Okos' models and the proposed model

4.4.5 Margarine product

A margarine product with significant lipid composition was chosen from USDA nutrient database (04683, Margarine, margarine-like vegetable oil spread, 67-70% fat, tub). Composition for the margarine was listed in Table 4.17. Typical fatty acid composition of sunflower oil in Table 4.18 was used in the proposed model to estimate the contribution of the lipid fraction.

	Magarine
Protein (%weight)	0.07
Fat (% weight)	68.29
Carbohydrate (% weight)	0.59
Fiber (% weight)	0
Ash (% weight)	1.53
Water (% weight)	29.52

Table 4.18 Composition of the margarine

Table 4.19 Typical fatty acid composition of sunflower oil (Gunstone and Padley 1997)

	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	С	U
Sunflower oil	0	6	0	6	18	69	0	17.88	1.56

The performances of the two models were shown in Figure 4.7. In Figure 4.7, %difference ranged from 0.5%-6.04%. The percent difference was 0.5% at 50°C. Then it decreased with temperature and then increased with temperature again. This was because the temperature effect was larger in the proposed model as discussed before. And the percent difference was obtained with absolute difference of estimates from the two models. And the proposed model provided a smaller estimate at 50°C than that of Choi and Okos' models because based on fatty acid composition, specific heat capacity of sunflower oil was among the lowest within the lipid group. The proposed model thus better predicted specific heat capacity of sunflower oil.



Figure 4.10 Prediction of specific heat capacity of the margarine by Choi and Okos' models and the proposed model

4.4.6 Mayonnaise product

A mayonnaise with significant lipid composition was chosen from USDA nutrient database (43598, Mayonnaise dressing, no cholesterol). Composition for the mayonnaise was listed in Table 4.19. Typical fatty acid composition of egg yolk and soybean oil in Table 4.20 was used in the proposed model to estimate the contribution of the lipid fraction. Egg yolk was expected to provide 6% fat.

	Mayonaise
Protein (%weight)	0
Fat (% weight)	77.8
Carbohydrate (% weight)	0.3
Fiber (% weight)	0
Ash (% weight)	0.4
Water (% weight)	21.7

Table 4.20 Composition of the margarine

Table 4.21 Typical fatty acid composition of sunflower oil (Gunstone and Padley 1997)

	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	С	U
Soybean oil	0	11	0	0	22	53	8	17.78	1.7
Egg Yolk	1	23	5	4	47	16	2	17.04	0.9

The performances of the two models were shown in Figure 4.8. In Figure 4.8, % difference ranged from 1.03%-4.01%. Significant difference was because that specific heat capacity of soybean oil was among the lowest within the lipid group. The proposed model thus better predict specific heat capacity of soybean oil.



Figure 4.11 Prediction of specific heat capacity of the mayonaise by Choi and Okos' models and the proposed model

4.4.7 Egg yolk product

A egg yolk with modest lipid composition was chosen from USDA nutrient database (01125, Egg, yolk, raw, fresh). Composition for the egg yolk was listed in Table 4.21. Typical fatty acid composition of egg yolk in Table 4.22 was used in the proposed model to estimate the contribution of the lipid fraction.

	Egg
	Yolk
Protein (%weight)	15.86
Fat (% weight)	26.54
Carbohydrate (% weight)	3.59
Fiber (% weight)	0
Ash (% weight)	1.71
Water (% weight)	52.31

Table 4.22 Composition of the egg yolk

Table 4.23 Typical fatty acid composition of egg yolk (National Research Council 1976)

	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	С	U
Egg Yolk	1	23	5	4	47	16	2	17.04	0.9

The performances of the two models were shown in Figure 4.9. In Figure 4.9, %difference increased from 0.4% to 0.8% as temperature increased for the same reason discussed earlier. The estimates of two models were close because average carbon number and average number of double bonds of egg yolk was in the middle of the lipid group as discussed earlier.



Figure 4.12 Prediction of specific heat capacity of the egg yolk by Choi and Okos' models and the proposed model

In summary, ranges of % difference of food products were listed in Table 4.23. The percent difference increased with increasing temperature in the prediction. It was significantly larger when the food product contained food lipid whose specific heat capacity deviated from the average. And the maximal percent difference was larger when the food product contained a larger amount of lipid. The proposed model was able to improve prediction of specific heat capacity of food products.

Food		
Product	%difference	%fat
Beef	0.05-1	18.98
Egg Yolk	0.4-0.8	26.54
Pork	0.11-1.73	30.5
Cream	0.03-1.88	37
Lamb	0.47-4.79	66.4
Margarine	0.5-6.04	68.29
Mayonnaise	1.03-4.01	77.8

Table 4.24 %difference of the proposed model and Choi and Okos' models of food

product from 50°C to 150°C

4.5 The abilities of DSC and MDSC to measure specific heat capacity of triacylglycerols and food lipids

As discussed in Section 4.1, DSC and MDSC were powerful in measuring specific heat capacity of triacylglycerols (TAGs), although they had detection limits. Specific heat capacity of vegetable oils was used to evaluate their abilities further. Despite composition difference between cocoa butter used in this study and that used in Morad and others (2000) and difference in measurement method, specific heat capacity of cocoa butters from two works were quite close (differences within 0.02 kJ/kg·K, %differences were 0.86% and 0.33% at 60°C and 80°C). Fatty acid compositions of cocoa butters used in both works were known. The similarity in fatty acid composition contributed to the small difference in specific heat capacity. This can be seen as an experimental confirmation to the statement

of Su and others (2011), which declared that specific heat capacity of different varieties of a vegetable oil should be very close if their fatty acid composition didn't vary much from typical composition. This also confirmed MDSC's ability to measure specific heat capacity.

Kowalski (1988), Kasprzycka-Guttman and Odzeniak (1991) and Fasina and Colley (2008) provided specific heat capacity of vegetable oils by DSC. Specific heat capacity of vegetable oils was different in these researches. It was very difficult to compare results especially considering that fatty acid composition in some researches was unknown.

Chapter 5: Conclusion

The results showed that specific heat capacity measurement for triacylglycerols (TAGs) and vegetable oils with Modulated Differential Scanning Calorimetry (MDSC) was in good agreement with specific heat capacity measurement with Differential Scanning Calorimetry (DSC). Both methods were able to distinguish TAGs with differences of 0.02 kJ/kg·K. The influence of temperature on liquid specific heat capacity was linear and the same for TAGs. The average carbon number (C) and the average number of double bonds (U) had a significant influence on the magnitude of the specific heat capacity of TAGs. The specific heat capacity of TAGs increased with average carbon number and decreased with average number of double bonds. These trends were also found in vegetable oils. The prediction model of specific heat capacity of TAGs and food lipid was established through equations as follows:

$$c_p^{18*} = 2.172 + 0.0022(T - 80) \tag{4.5}$$

$$c_p^* = c_p^{18*} + 0.0104(C - 18) \tag{4.7}$$

$$c_p = c_p^* - 0.05660 \tag{4.8}$$

Equation 4.5 took into account the impact of temperature on specific heat capacity of food lipid. Equation 4.7 accounted for the impact of average carbon number. Equation 4.8 accounted for levels of unsaturation.

The proposed model was also expressed by:

$$c_p = 2.172 + 0.0022(T - 80) + 0.0104(C - 18) - 0.0566U$$
(4.9)

The proposed model provided good prediction for specific heat capacity of vegetable oils. The prediction was in agreement with experimental data. Percent relative deviation was within 2% and percent average relative deviation was 0.83%. The proposed model had the smallest %ARD and %MRD compared to other models. It was suited to be used to predict specific heat capacity of food lipids. The model in Morad and others (2000) provided good estimates as well. The two models were based on fatty acid composition thus it was important to include fatty acid composition in the prediction of specific heat capacity of food lipids. The group contribution method was demonstrated as a good approach to predict specific heat capacity of food lipids as long as parameters were regressed appropriately. Experimental data has been provided to update group contribution parameters and thus improve performances of such models. The proposed model can be used to improve current models to predict specific heat capacity of foods with 1%-5% improvement by providing better estimate for the specific heat capacity of the lipid fraction based on fatty acid composition.

References

- Choi Y, Okos MR. 1986. Effects of temperature and composition on the thermal properties of foods. In Maguer M, Jelen P, editors. Food Engineering and Process Applications. London: Elsevier Applied. Science Publishers. pp 93–101.
- Coimbra JS, Gabas AL, Minim LA, Rojas EEG, Telis VR, Telis-Romero J. 2006. Density, heat capacity and thermal conductivity of liquid egg products. Journal of Food Engineering. 74 no. 2: 186-190.
- 3. Tavman S, Kumcuoglu S, Gaukel V. 2007. Apparent specific heat capacity of chilled and frozen meat products. International Journal of Food Properties. 10(1): 103-112.
- 4. Constenla DT, Lozano JE, Crapiste GH. 1989. Thermophysical properties of clarified apple juice as a function of concentration and temperature. J. Food Sci. 54: 663–668.
- Telis-Romero J, Telis VRN, Gabas AL, Yamashita F. 1998. Thermophysical properties of Brazilian orange juice as affected by temperature and water content. Journal of Food Engineering. 38(1): 27-40.
- 6. Njie DN, Rumsey TR, Singh RP. 1998. Thermal properties of cassava, yam and platain. Journal of food engineering. 37(1): 63-76.
- Telis-Romero J, Gabas AL, Polizelli MA, Telis VRN. 2000. Temperature and water content influence on thermophysical properties of coffee extract. Int J Food Prop. 3: 375–384.
- Minim LA, Coimbra JS, Minim VP, Telis-Romero J. 2002. Influence of temperature and water and fat contents on the thermophysical properties of milk. Journal of Chemical & Engineering Data. 47(6): 1488-1491.
- 9. Gratão ACA, Junior VS, Polizelli MA, Telis-Romero JAVIER. 2004. Thermal properties of passion fruit juice as affected by temperature and water content. Journal

of food process engineering. 27(6): 413-431.

- 10. Phinney D, Heldman D. 2013. Unpublished.
- 11. Morad NA, Kamal AM, Panau F, Yew TW. 2000. Liquid specific heat capacity estimation for fatty acids, triacylglycerols, and vegetable oils based on their fatty acid composition. Journal of the American Oil Chemists' Society. 77(9): 1001-1006.
- 12. Clark PE, Waldeland CR, Cross RP. 1946. Specific heats of vegetable oils from 0 to 280 °C. Industrial & Engineering Chemistry. 38(3): 350-353.
- 13. Hampson JW, Rothbart HL. 1983. Triglyceride specific heat determined by differential scanning calorimetry. Journal of the American Oil Chemists' Society. 60(6): 1102-1104.
- 14. Fasina OO, Colley Z. 2008. Viscosity and specific heat of vegetable oils as a function of temperature: 35 to 180 °C. International Journal of Food Properties. 11(4): 738-746.
- 15. Sweat VE. 1995. Thermal properties of foods. In Rao MA, Rizvi SSH, editors. Engineering Properties of Foods. New York: Marcel Dekker. pp 99-138.
- 16. Heldman DR, Singh RP. 1981. Food process engineering. AVI, Westport, CT, USA.
- 17. Pham QT. 1996. Prediction of calorimetric properties and freezing time of foods from composition data. Journal of Food Engineering. 30(1): 95-107.
- 18. Chen CS. 1985. Thermodynamic analysis of the freezing and thawing of foods: enthalpy and apparent specific heat. J Food Sci. 50: 1158–1162.
- 19. American society of heating, refrigeration and air conditioning engineers. Inc. 1985. Thermal properties of food. In 1985 ASRHAE Fundamentals Handbook. Atlanta, Ga: ASHRAE. pp. 31.3-31.28.
- 20. Höhne G, Hemminger W, Flammersheim HJ. 2003. Differential scanning calorimetry. 2nd ed. Springer Science & Business Media.
- 21. ASTM E1269-11, Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry, ASTM International, West Conshohocken, PA, 91

2011, www.astm.org

- Thomas L, Aubuchon S. 1999. Heat capacity measurements using quasi-isothermal MDSC 1–5. TA Instruments Technical Bulletin No. 230.
- Damodaran S, Parkin KL, Fennema OR (Editors.). 2007. Fennema's food chemistry. CRC press.
- 24. Haley TA, Mulvaney SJ. 1995. Advanced process control techiques for the food industry. Trends Food Sci. Technol 6: 103–110.
- Chapman D. 1962. The Polymorphism of Glycerides. Chemical Reviews. 62(5): 433-456.
- Oliver GD, Bailey AE. 1945. Thermal properties of fats and oils. Oil & Soap. 22(2): 39-41.
- Oliver GD, Singleton WS, Todd SS, Bailey AE. 1944. Thermal properties of fats and oils. II. Heat capacity and latent heat of cottonseed oil. Oil & Soap. 21(10): 297-300.
- Benson SW, Buss JH. 1958. Additivity rules for the estimation of molecular properties. Thermodynamic properties. The Journal of Chemical Physics. 29(3): 546-572.
- Domalski ES, Hearing ED. 1988. Estimation of the Thermodynamic Properties of Hydrocarbons at 298.15 K. Journal of physical and chemical reference data. 17(4): 1637-1678.
- Ceriani R, Gani R, Meirelles AJ. 2009. Prediction of heat capacities and heats of vaporization of organic liquids by group contribution methods. Fluid Phase Equilibria. 283(1): 49-55.
- Morad NA, Idrees M, Hasan AA. 1995a. Specific heat capacities of pure triglycerides by heat-flux differential scanning calorimetry. Journal of thermal analysis. 45(6): 1449-1461.
- Charbonnet GH, Singleton WS. 1947. Thermal properties of fats and oils. Journal of the American Oil Chemists Society. 24(5): 140-142.

- Kowalski B. 1988. Determination of specific heats of some edible oils and fats by differential scanning calorimetry. Journal of Thermal Analysis and Calorimetry. 34(5): 1321-1326.
- Kasprzycka-Guttman T, Odzeniak D. 1991. Specific heats of some oils and a fat. Thermochimica acta. 191(1): 41-45.
- 35. Morad NA, Idrees M, Hasan AA. 1995b. Improved conditions for measurement of the specific heat capacities of pure triglycerides by differential scanning calorimetry. Journal of Thermal Analysis and Calorimetry. 44(4): 823-835.
- Rihani DN, Doraiswamy LK. 1965. Estimation of heat capacity of organic compounds from group contributions. Industrial & Engineering Chemistry Fundamentals. 4(1): 17-21.
- 37. Fedors RF. 1982. A relationship between chemical structure and the critical temperature. Chemical Engineering Communications. 16(1-6): 149-151.
- Joback KG, Reid RC. 1987. Estimation of pure-component properties from groupcontributions. Chemical Engineering Communications. 57(1-6): 233-243.
- 39. Kolská Z, Kukal J, Zábranský M, Ruz`ic`ka V. 2008. Estimation of the heat capacity of organic liquids as a function of temperature by a three-level group contribution method. Industrial & Engineering Chemistry Research. 47(6): 2075-2085.
- 40. Zong L, Ramanathan S, Chen CC. 2009. Fragment-based approach for estimating thermophysical properties of fats and vegetable oils for modeling biodiesel production processes. Industrial & engineering chemistry research. 49(2): 876-886.
- 41. Růžička JrV, Domalski ES. 1993a. Estimation of the heat capacities of organic liquids as a function of temperature using group additivity. I. Hydrocarbon compounds. Journal of physical and chemical reference data, 22(3): 597-618.

- 42. Růžička JrV, Domalski ES. 1993b. Estimation of the heat capacities of organic liquids as a function of temperature using group additivity. II. Compounds of carbon, hydrogen, halogens, nitrogen, oxygen, and sulfur. Journal of physical and chemical reference data. 22(3): 619-657.
- 43. Su YC, Liu YA, Diaz Tovar CA, Gani R. 2011. Selection of prediction methods for thermophysical properties for process modeling and product design of biodiesel manufacturing. Industrial & Engineering Chemistry Research. 50(11): 6809-6836.
- 44. Phillips JC, Mattamal MM. 1976. Correlation of liquid heat-capacities for caboxylic esters. Journal of Chemical and Engineering Data. 21(2): 228-232.
- 45. Eiteman MA, Goodrum JW. 1994. Heat capacity of the triglycerides: Tricaproin, tricaprylin and tricaprin. Journal of the American Oil Chemists' Society. 71(5): 549-550.
- 46. Parks GS, Huffman HM. 1930. THERMAL DATA ON ORGANIC COMPOUNDS. IX. A STUDY OF THE EFFECT OF UNSATURATION ON THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF SOME HYDROCARBONS AND OTHER COMPOUNDS1. Journal of the American Chemical Society, 52(11): 4381-4391.
- Anand K, Sharma RP, Mehta PS. 2011. A comprehensive approach for estimating thermo-physical properties of biodiesel fuels. Applied thermal engineering. 31(2): 235-242.
- 48. Gunstone FD, Harwood JL, Padley FB (Eds). The Lipid Handbook. 2nd ed. CRC Press. pp 23,45-46.
- 49. National Research Council. 1976. Fat Content and Composition of Animal Products. Washington DC: National Academy of Science. pp 203.





Figure A.1 Melting profile of trilaurin



Appendix B: Average carbon number (C) and average number of double bonds (U) of food lipids

Figure B.1 Average carbon number (C) and average number of double bonds (U) of food lipids