

ABSTRACT

O'MEARA, MEGHAN. Determination of the Interfacial Tension between Oil/Steam and Oil/Air at Elevated Temperatures. (Under the direction of Dr. Brian Farkas.)

Immersion frying is a widely used cooking technique that involves heating foods in oil above 100°C. During frying, the heating profile of the product causes rapid moisture loss at its surface resulting in crust formation without burning. The rate of heat transfer, moisture loss and oil uptake are all affected, in part, by interfacial tension between the oil, steam and food surface. Understanding the relationship between frying oil temperature and the oil-steam interfacial tension may yield insight into the mechanism of boiling heat transfer and thus moisture loss. The pendant drop method was used to determine oil-air and oil-steam interfacial tension for five cooking oils (Canola, corn, olive, peanut, and soybean) at temperatures up to 200°C. Initial oil and air values started at room temperature and oil and steam values started at 110°C. The pendant drop method relates density difference, force of gravity, drop shape, and drop radius of curvature to interfacial tension. To determine interfacial tension, the density of the oil must to be known at each temperature. Density was determined from room temperature to the smoke point of each oil using the Archimedean method. This method relates fluid density to the buoyancy and volume of a submersed object of known physical properties. All oils demonstrated a nearly linear decrease in density with increasing temperature ($R^2 > 0.99$) from a high of 915.7 kg/m³ (soybean at 22°C) to a low of 801.5 kg/m³ (peanut at 200°C). Density trends for all oils were similar but density values were statistically different. Coefficient of variations of triplicate measurements at each temperature were less than 0.13%, indicating that the method demonstrated high precision for measuring the density of food oils at high temperatures. All interfacial tension values decreased linearly as temperature increased ($R^2 > 0.99$) from a high of 32.14 mN/m (Canola

oil at 23.5°C) to a low of 20.04 mN/m (fresh peanut and fresh corn oil at 200°C). Interfacial tension trends were similar for all oils but values were statistically different between oils at a given temperature ($p < 0.0001$). No significant difference was found between the oil-steam and oil-air interfacial tension values e.g. 25.21 mN/m, 25.29 mN/m, respectively, for Canola at 120°C. The coefficient of variation for quadruple measurements at each temperature ranged from 0.06 to 0.85%, indicating a precise method. The results indicate that oil-air interfacial tension may be used as an estimate for oil-steam interfacial tension. Additionally, the method and data generated through this research may be used in analysis of processes involving food oils at high temperatures including frying and atomization of biodiesel fuels.

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Determination of the Interfacial Tension between Oil-Steam and Oil-Air at Elevated
Temperatures

by
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DEDICATION

I dedicate this page to my mom and dad. I would also like to dedicate this to my wonderful fiancé, who helped me throughout this time.

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CHAPTER 1

1.1 INTRODUCTION

In the last 25 years, there has been a significant increase in the number of obese adults in the United States [1.1]. In 1985, the majority of states had less than 10% obesity, but in 2009, every state had above 20% obesity except Colorado. Obesity has been connected to coronary heart disease by the American Heart Association [1.2]. Oil consumption has also been linked to health concerns such as coronary heart disease [1.3]. In the United States, fried food is a multibillion dollar industry that relies heavily on deep-fat frying [1.4]. Frying is the process of cooking foods in edible oils at temperatures above the boiling point of water [1.5]. After frying, a 1.5 mm thick potato slice may contain up to 35% oil [1.3, 1.6]. One way to decrease the oil content in fried foods would be to reduce the length of frying. During frying, a product goes through four stages [1.7]. In the second stage, the moisture content at the surface of the product is rapidly lost and crust formation occurs. The rate at which the moisture escapes is related to the interfacial tension between the oil and the steam. In order to decrease oil content, the relationship between frying temperatures and the interfacial tension between oil and steam needs to be understood.

Interfacial tension (γ) is the force acting at the interface of two liquids or between a liquid and a solid. Molecules aligning at the interface of each liquid and the interaction between the molecules are what affect interfacial tension. The interface can also be between a gas and a liquid however, this tension is termed surface tension (σ). The tension at the surface of a liquid drop in a gas is what gives the liquid its shape. The interfacial between two liquids (oil-water 24.4 mN/m) is less than the surface tension of the liquid (oil 32.6

mN/m) [1.8]. Interfacial tension is seen throughout the food industry and in nature manifesting in emulsion formation (mayonnaise) to giving “water skaters” the ability to walk on water [1.9] to water beading up on a waxy leaf [1.10].

The ability for water skaters to walk on water, oil and water to form mayonnaise, and a food to fry all have one thing in common. That is that interfacial tension plays a role in the ability for each to occur. Water skaters are known as the insect that can walk on water. The ability for this to occur is because of two reasons. First, water skaters have hydrophobic hairs that line the legs and allow for a high interfacial tension between the water skaters and the water [1.9]. Second, water skaters have long, slender legs that distribute their weight over a large surface area. The combination of these two attributes allows water skaters to remain on the surface.

Oil and water are immiscible liquids. However, they can form a stable mixture when blended with a surfactant. An example is the use of soap while cleaning hands [1.10]. When trying to remove oil or grease, water will not “wet” the hands. This is because the interfacial tension between the oil and water is high. To remove the oil or grease, soap needs to be used. The soap is a surfactant and decreases the interfacial tension between the water and oil allowing for the oil to be removed from the hands.

Mayonnaise is one of many foods that use an emulsion to make a final product. An emulsion is a stable mixture of two immiscible liquids [1.10]. One way to assist the formation of an emulsion is to reduce the liquid-liquid interfacial tension to a point where the immiscible liquids will form a stable mixture. An emulsifier, or a surfactant, reduces interfacial tension and can be added to the oil or water fraction. The emulsifier also plays a

role in the stability of the emulsion, in which it reduces the ability of the oil or water drops to coalesce. One way to reduce coalescence of an emulsion is by forming smaller drops of the dispersed phase within the continuous phase [1.10]. To aid in formation of smaller drops an emulsifier needs to be added to reduce the interfacial tension between the two liquids.

Interfacial tension plays a role in heat and mass transfer during the frying process. During frying, moisture escapes the product as crust on the product is formed [1.7]. This moisture loss is dependent, in part, on the rate of heat transfer [1.5]. The rate of heat transfer during boiling may be related to interfacial tension by [1.11]:

$$\frac{q}{A} = \mu_L h_{fg} \left[\frac{g(\rho_L - \rho_v)}{\sigma} \right]^{1/2} \left[\frac{c_{pL}(T_s - T_{sat})}{c_{sf} h_{fg} Pr_L^{1.7}} \right]^3 \quad [1.11]$$

Where μ_L is the liquid viscosity (Pa s), h_{fg} is the latent heat of vaporization (J/kg), g is gravitational force (m/s^2), $(\rho_L - \rho_v)$ is the density difference between the liquid and vapor (kg/m^3), σ is the surface tension (N/m), c_{pL} is the heat capacity for the liquid (J/K), $(T_s - T_{sat})$ is the difference between the surface and saturated-liquid temperatures (K), c_{sf} is a coefficient that varies with surface-liquid combination, and Pr_L is the liquid Prandlt number.

After frying, as the product cools, oil uptake occurs and is in part related to the tension between the food and the oil through capillary flow [1.12]:

$$h = \frac{2\gamma \cos\theta}{\rho g r} \quad [1.2]$$

where h is the length of oil uptake (m), γ is interfacial tension between product and oil (mN/m), $\cos(\theta)$ is the contact angle between the oil and the product, ρ is the density of the oil (kg/m^3), g is gravitational acceleration (m/s^2) and r is the radius of the pore section [1.12].

Interfacial tension is affected by temperature and composition. For many pure liquids, an increase in temperature causes a linear decrease in interfacial tension [1.10]. The dependence of surface tension on temperature is described, for many liquids, by the Eötvös equation [1.10]:

$$\frac{d(\sigma(M/\rho)^{2/3}}{dT} = -2.12 \times 10^{-7} \text{ J mol}^{-2/3} \text{ K}^{-1} \quad [1.3]$$

where M is molar mass and ρ is density.

Also affecting interfacial tension is the presence of surfactants. Surfactants are ultimately used to decrease the interfacial tension between two liquids, a liquid and a solid, or a liquid and gas. Surfactants are amphiphiles that contain a hydrophobic tail and a hydrophilic head [1.10]. The balance between the two results in the hydrophilic-lipophilic balance (HLB). The higher the value the more hydrophilic the surfactant is and the lower the value, the more lipophilic the surfactant is. An HLB between 9 and 18 is desired for oil in water emulsions and a value between 3.5 and 6 is desired for water in oil emulsions [1.10]. For example, glycerol monostearate has an HLB of 3.8 which makes it a good surfactant for water in oil emulsion [1.10].

There are several common methods to measure interfacial tension. They may be divided into steady state and dynamic methods [1.10]. Steady state methods measure the interfacial tension when the system is at equilibrium and the interfacial tension is no longer changing. The Du Nouy ring, Wilhelmy plate, pendant drop and sessile drop can all measure steady state interfacial tension. The Du Nouy ring is a detachment method in which the required force to pull a ring through the interface is measured (Figure 1.1) [1.10]:

$$F = \gamma 2(2\pi r) \quad [1.4]$$

where F is the force (N) required to pull the ring and r (m) is the radius of the ring.

An advantage in using the Du Nouy ring method is that it is simple. A disadvantage for the method is that it is an approximation of interfacial tension [1.10].

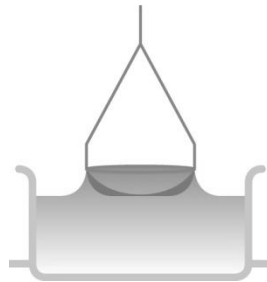


Figure 1.1: Schematic of Du Nouy ring method [1.13]

The Wilhelmy plate method is also a detachment method, but uses a plate instead of a ring to pull through the interface (Figure 1.2). The Wilhelmy plate method has the same advantages and disadvantages as the Du Nouy ring method [1.10]. Also, the Wilhelmy plate method must account for buoyancy of the plate which is dependent on the depth of immersion [1.10].

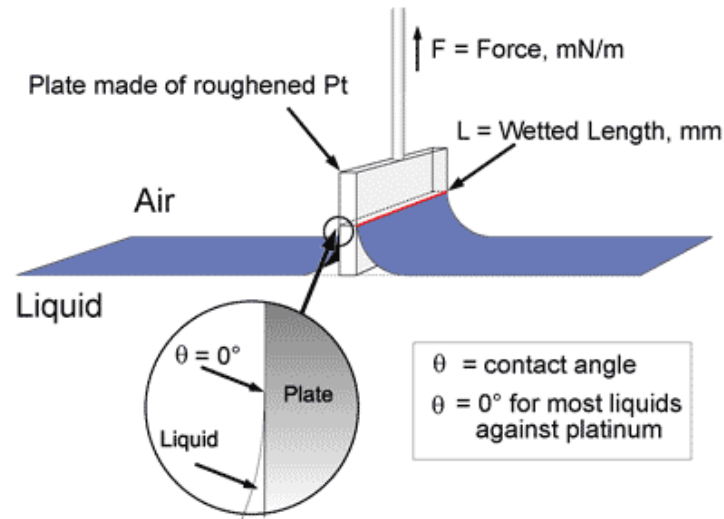


Figure 1.2: Schematic of Wilhelmy Plate method [1.14]

The pendant drop method measures the shape parameters (maximum diameter, height and the drop's diameter at the maximum diameter's distance from the drop's apex) of a drop hanging from a needle (Figure 1.3) to determine interfacial tension [1.15]:

$$\sigma = \frac{\Delta\rho g R_0^2}{\beta} \quad [1.5]$$

where, σ is surface tension (mN/m), $\Delta\rho$ is density difference between the drop and surrounding media (kg/m^3), g is gravitational force (m/s^2), R_0 is the distance from the drop apex to the maximum diameter (m), and β is a function of the width of the drop:

$$\beta = -0.12836 + 0.7577\delta - 1.7713\delta^2 + 0.5426\delta^3 \quad [1.6]$$

$$\delta = \frac{D_S}{D_E} \quad [1.7]$$

where D_E is the maximum diameter of the bubble and D_S is the diameter at distance D_E from the apex (Figure 1.3).

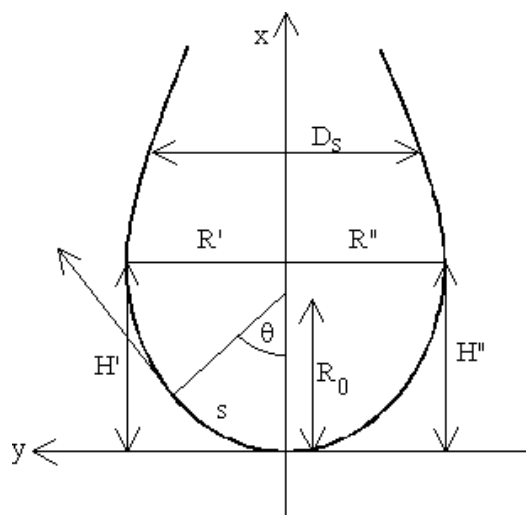


Figure 1.3: Schematic of Pendant Drop [1.15]

An advantage for this method is that it can be equipped with an environmental cell that can control the surrounding phase composition and temperature. A disadvantage for this method is it is not as simple as the Du Nouy ring and Wilhelmy Plate methods. This method requires a digital camera and a computer analysis program along with a location to dispense the drop to determine interfacial tension. The Du Nouy ring requires the device which measures the force and a simple calculation.

Similar to the pendant drop is the sessile drop method in which the contact angle between a solid and liquid is measured and then the interfacial tension determined (Figure 1.4). The surface tension values of the solid (γ_{sv}) and of the liquid (γ_{lv}) need to be known to calculate the interfacial tension between the solid and the liquid (γ_{sl}) [1.15]:

$$\cos(\theta) = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad [1.8]$$

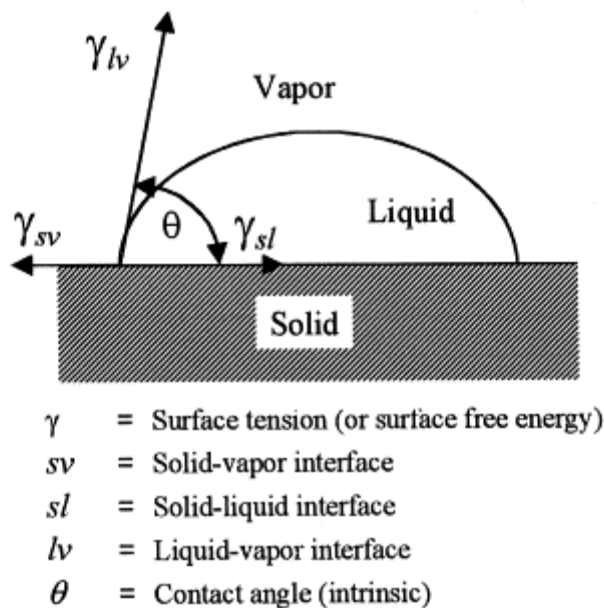


Figure 1.4: Schematic of sessile drop [1.16]

An advantage to sessile drop method is that it can be used to determine the interfacial tension between a liquid and a solid surface.

Dynamic methods measure tension over time. Therefore the interfacial tension is not at equilibrium and is not at its lowest value. The pendant drop method can be utilized to measure dynamic interfacial tension by oscillating the drop volume [1.16]. Maximum bubble pressure also measures dynamic tension (Figure 1.5). This method can only be used to measure the surface tension of a liquid and gas [1.17]. The surface tension for the liquid being tested is determined by measuring the pressure required to pump a gas through a capillary tube into a surrounding liquid. The maximum pressure is used to determine surface tension [1.18]:

$$\sigma = f \frac{rP}{2} \quad [1.9]$$

where r is the radius of the capillary, P is the maximum capillary pressure and f is a correction factor.

$$P = P_s - P_H - P_d \quad [1.10]$$

where P_s is the pressure of the system, P_H hydrostatic liquid pressure, and P_d is the excess pressure [1.18].

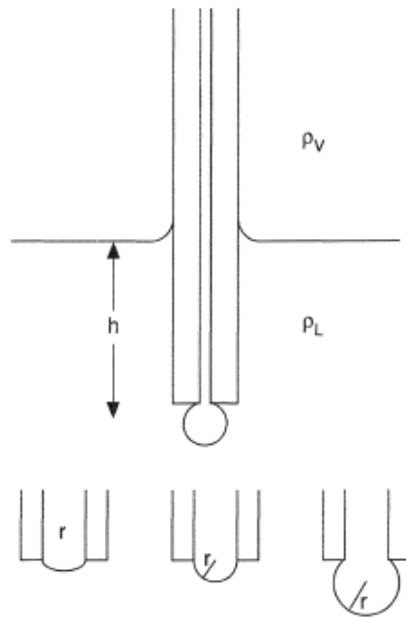


Figure 1.5: Schematic of maximum bubble method [1.17]

1.2 GOAL AND OBJECTIVES

The goal of this research was to quantify the interfacial tension between oil and steam using the pendant drop method. The objectives for this project were:

1. Develop a method and verify for measurement of Canola, Corn, Olive, Soybean, and Peanut oil density between 20 and 200°C;

2. Develop a mathematical model for density as a function of temperature;
3. Develop a method and verify for measurement of interfacial tension of the five oils previously mentioned with air at the interface from 20-200°C;
4. Measure interfacial tension between five oils and steam from 110°C-200°C;
5. Develop a mathematical model for interfacial tension as a function of temperature.

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CHAPTER 2

2.1 ABSTRACT

Cooking oils are widely used to fry foods at elevated temperatures. During frying, heat and mass transfer take place, in which both are affected by the density of the oil. However, for most cooking oils density values above room temperature are not well known. Density was determined from room temperature to the smoke point for each of five cooking oils (Canola, corn, olive, peanut, and soybean) using the Archimedean method. All oils demonstrated a nearly linear decrease in density with increasing temperature from a high of 915.7 kg/m^3 (soybean at 22°C) to a low of 801.5 kg/m^3 (peanut at 200°C). Density trends for all oils were similar but density values were statistically different. Coefficients of variation of triplicate measurements at each temperature were less than 0.13%, indicating that this method demonstrated high precision for measuring the density of food oils at high temperatures. Empirical formulae generated may be used in numerical simulation, process design, and instrumental analysis leading to improved efficiencies, product quality, and the understanding of transport fundamentals associated with immersion frying and other high temperature cooking processes.

2.2 INTRODUCTION

Density is a material property dependent on environmental conditions. Oil density has been experimentally shown to be dependent on temperature [2.1-2.8] and on material composition [2.2-2.6, 2.9] but is independent of pressure at standard processing conditions [2.10, 2.11]. During frying, oil density can impact the rate of heat and momentum transfer. Frying occurs at temperatures well above room temperature, e.g. 180°C [2.12], however

density of many common cooking oils is only known at temperatures less than 110°C [2.1]. To accurately determine transport rates in high temperature processes such as frying the density of oil at elevated temperatures should be known [2.1]. Specifically, the affect of temperature on the density of cooking oils should be determined up to the smoke point, since they are used in the food industry during frying and baking.

As an example, deep frying is a process in which a food is submersed in hot oil (180°C) [2.12]. During the frying process, bubble diameter, rate of heat transfer, and oil uptake are affected by frying oil density. During frying, steam escapes the product as bubbles with the departure diameter of the bubbles changing as a product fries and as the oil ages. Bubble's diameter is dependent on a number of properties such as the interfacial tension and density difference between the oil and the steam [2.13]. The rate of heat transfer during boiling is, in part, dependent on bubble diameter and therefore is dependent on oil/steam density difference [2.14]. As a product cools, oil enters the product and is in part driven by capillary flow. For capillary rise, the change in height of a fluid is dependent on the density of the fluid. Therefore, for the amount of oil uptake partially depends on oil density [2.15]. To be able to accurately determine bubble diameter, rate of heat transfer, and oil uptake, oil density at elevated temperatures must be known.

Bubble diameter, rate of heat transfer, and capillary flow are all affected by the interfacial tension. Determination of oil interfacial tension using the pendant drop method requires the density of the oil to be known at the test temperature. Therefore, to accurately examine the affect of interfacial tension on bubble diameter, rate of heat transfer and oil uptake, the density of the oil must be known.

Peanut oil density has been measured up to 200°C [2.2] and the density for corn, Canola, soybean oil has been measured up to 110°C [2.1], however the density for olive oil is only known at room temperature [2.16]. Mange and Wakeham (1944) investigated the effect of hydrogenation level and temperature (to 200°C) on peanut oil density and determined that density decreases as hydrogenation and temperature increase. Subrahmanyam et al. (1994) determined peanut oil density from 0°C to 80°C and saw the same inversely linear relationship ($R^2=0.9907$) as oil temperature increased. Canola, corn and soybean oil densities were determined from room temperature up to 110°C [2.1], and also showed an inverse linear relationship between density and temperature ($R^2= 0.9997, 0.9991, 0.9985$, respectively). Coupland and McClements (1977) used data from Nouredini et al. (1992) and Subrahmanyam et al. (1994) to develop oil specific empirical formulas, based on temperature, to determine density over a temperature range. The density for olive oil of various origins has only been determined at room temperature [2.16] and no predictive formulae have been proposed. Halvorsen et al. (1993) used a modified Rackett equation to determine density as a function of temperature and the physical properties (critical temperature, critical pressure and Rackett parameter) for the fatty acids components [2.9]. Although these empirical equations show good agreement with experimentally determined values, there remains a lack of data and predictive formulae for density at temperatures above 110°C.

A liquid pycnometer and the Archimedean method are two methods to determine density of a liquid at temperatures above room temperature. A liquid pycnometer has been used most often to determine oil density at a specific temperature [2.1-2.4, 2.17]. The

Archimedean method has been used to find density of liquids at high temperatures (molten igneous rocks) [2.18], but has not been applied to food grade oils. The method utilizes an object of known mass and volume, suspended from the bottom of a scale. To measure the density of a liquid, the object's mass is measured out of the liquid and while being submersed in the liquid. The difference in mass of the object in and out of the liquid to the volume of the object is then used to determine liquid density as [2.13]:

$$\rho = \frac{\beta+s}{V^o+v'} \quad [2.1]$$

$$\beta = m_v - m_f \quad [2.2]$$

where, ρ is the liquid density (kg/m^3), β is buoyancy affect (kg), V^o is the volume (m^3) of the object, v' is the volume (m^3) of any submersed suspended wire and s is the surface tension affect (kg) between the liquid and suspending wire. The buoyancy affect is the difference in mass of the suspended mass *in vacuo* (m_v) and in the test fluid (m_f).

The objective of this work was to determine density for five common cooking oils (Canola, olive, soybean, corn, and peanut) from room temperature to 200°C, using the Archimedean method.

2.3 MATERIAL AND METHODS

2.3.1 Materials

Canola oil (ConAgra, Omaha, NE), extra virgin olive oil (American Rice Inc., Houston, TX), soybean oil (ALDI, Batavia, IL), peanut oil (Ventura Foods, Brea, CA), and corn oil (ACH Food, Memphis, TN) were purchased from a local grocery store (Harris Teeter, Raleigh, NC). A 0.076 cm diameter stainless steel wire (Hobart Welders, NorthernTools, Raleigh, NC) was welded to a 2.54 cm stainless steel ball (Precision

Instrument Machine Shop, North Carolina State University, Raleigh, NC). Test oil was contained in an insulated (Heatshield Products, Valley Center, CA $k=0.0418$ W/mK, $x=0.16$ cm) beaker. A hot plate with mixing was used to heat the oil.

2.3.2 Archimedean Method

Oil density was determined using the Archimedean method [2.19] from room temperature to 200°C (180°C for olive oil) in 20°C increments. A hole was cut into the top of a platform and a scale was placed on top such that the wire/ball assembly could be suspended from the bottom of the scale. The mass of the wire/ball *in vacuo* was determined to be 69.67 g. The oil was heated to the test temperature while continuously mixed to ensure uniformity. The wire/ball was placed in the beaker during heating to maintain uniform temperatures. Once at the desired temperature the mass of the wire/ball was determined while suspended in the oil. Density was then calculated (equation 2.1) while assuming the surface tension effect (s) was negligible. This assumption was later verified. The volume of the stainless steel ball (V^0) and the submerged portion of the wire ($v^?$) was determined as 8.58 cm³ and 0.01 cm³ respectively.

Measurements were performed in triplicate and statistical analysis was performed to determine the precision of the instrumentation by examining coefficient of variation. T-tests were used to test the equality of means across oil types to determine similarity between the oils.

2.4 RESULTS AND DISCUSSION

Oil density was determined at each temperature (Table 2.1). Corn and soybean oil and peanut and olive oil were statistically similar (Tuckey's test, confidence interval = 95%).

Canola oil was statistically similar to corn and soybean oil (Table 2.1) at some test temperatures. The variability of the Archimedean method, determined by the coefficient of variation, was less than 0.13% for all oils.

Table 2.1: Density values for five common cooking oils from room temperature to 200°C

Temperature (°C)	Density (kg/m ³)*				
	Canola	Corn	Soybean	Peanut	Olive
22.2±1	913 ^b	915 ^a	916 ^a	912 ^b	909 ^c
40	902 ^c	904 ^a	903 ^b	899 ^d	897 ^e
60	890 ^b	893 ^a	892 ^a	887 ^c	886 ^c
80	878 ^b	881 ^a	880 ^{a,b}	875 ^c	874 ^c
100	867 ^a	868 ^a	868 ^a	862 ^b	862 ^b
120	854 ^b	856 ^a	856 ^a	850 ^c	850 ^c
140	842 ^b	844 ^a	845 ^a	838 ^c	837 ^c
160	829 ^b	832 ^a	833 ^a	826 ^c	825 ^c
180	817 ^b	819 ^a	820 ^a	814 ^c	814 ^c
200	807 ^a	808 ^a	807 ^a	801 ^b	N/A

*means with in a row with a common subscript do not differ significantly.

Density as a function of temperature was plotted (Figure 2.1) and it was determined that oil density is inversely proportional to temperature and that each of the oils follows the same trend. This is in agreement previous studies [2.1, 2.2].

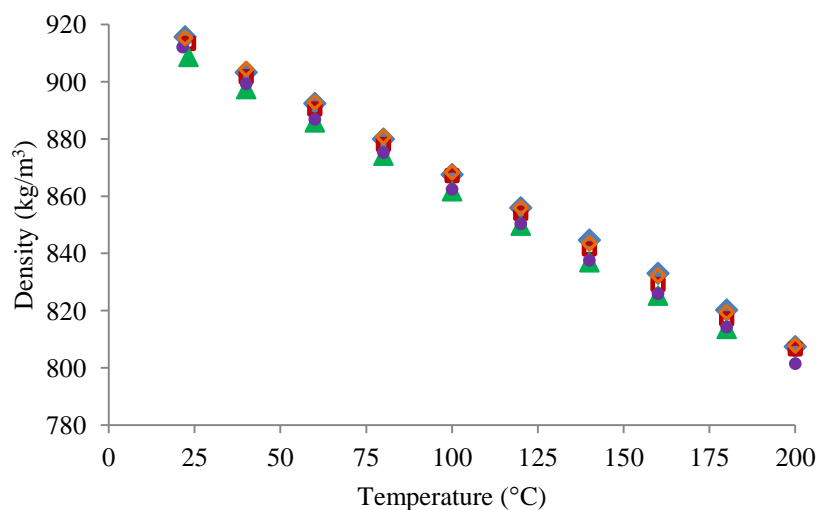


Figure 2.1: Density data for various oils from room temperature to 200°C. (◆) soybean oil, (□) canola oil, (▲) olive oil, (●) peanut oil, (◇) corn oil

Density of all oils decreased at similar rates (slope, Table 2.2) with increasing temperature; and all had similar y-intercepts (Table 2.2) indicating that temperature affects oil density in a similar fashion for all oils tested.

Table 2.2: Y-intercept, slope and correlation coefficient

Oil	Canola	Corn	Olive	Soybean	Peanut
y-int	926.73	928.88	922.24	928.18	924.24
Slope	-0.6057	-0.6063	-0.6055	-0.6005	-0.6146
R ²	0.9996	0.9999	0.9999	0.9997	0.9998

Verification of negligible surface tension effect was done using density values in Table 2.1 and calculated oil volume (5.54 mm^3) that wicked up the wire. In initial density calculations (Table 2.1), the surface tension effect (s) was assumed to be zero. The surface

tension effect is the oil mass that adheres to the wire due the surface tension between the oil and the wire and thus adds to the mass of the object. The mass of oil adhered to the wire was calculated using density values (Table 2.1) and a calculated oil volume. New densities (Table 2.3) were calculated using equation 2.1 and the calculated values for s . The new densities were compared to those in Table 2.1, they differ by ± 0.5 (kg/m^3). It was concluded that assuming a negligible surface tension effect was appropriate for this study as the calculated oil mass on the wire (Table 2.3) was negligible when compared to the mass of the object and did not affect calculated density.

Table 2.3: Determined surface tension effect and corrected densities

Temperature (°C)	Surface Tension effect (kg)					Corrected Density (kg/m^3)				
	Canola	Corn	Soybean	Peanut	Olive	Canola	Corn	Soybean	Peanut	Olive
22.2±1	5.06E-03	5.07E-03	5.07E-03	5.05E-03	5.03E-03	914	916	916	913	909
40	4.99E-03	5.01E-03	5.00E-03	4.98E-03	4.97E-03	902	905	904	900	898
60	4.93E-03	4.94E-03	4.94E-03	4.91E-03	4.90E-03	891	893	893	887	886
80	4.86E-03	4.88E-03	4.87E-03	4.84E-03	4.84E-03	879	881	881	876	875
100	4.80E-03	4.81E-03	4.80E-03	4.77E-03	4.77E-03	868	869	868	863	862
120	4.73E-03	4.74E-03	4.74E-03	4.71E-03	4.70E-03	855	856	856	851	850
140	4.66E-03	4.67E-03	4.68E-03	4.64E-03	4.63E-03	842	844	845	838	837
160	4.59E-03	4.61E-03	4.61E-03	4.57E-03	4.57E-03	830	833	834	826	826
180	4.52E-03	4.54E-03	4.54E-03	4.51E-03	4.50E-03	818	820	821	815	813
200	4.47E-03	4.47E-03	4.47E-03	4.44E-03	N/A	807	808	808	802	N/A

Peanut oil densities determined in the present study were found to agree with the densities determined by Magne and Wakeham (1944) and by Subrahmanyam et al. (1994) (Figure 2.2). In comparing the coefficient of variation (Table 2.4), the current study's coefficients of variation were consistent with those previously found (Mange and Wakeham

(1944), Nouredдини et al. (1992), Mange and Skau (1945), Johnstone et al. (1940), and Rice and Hamm (1988)).

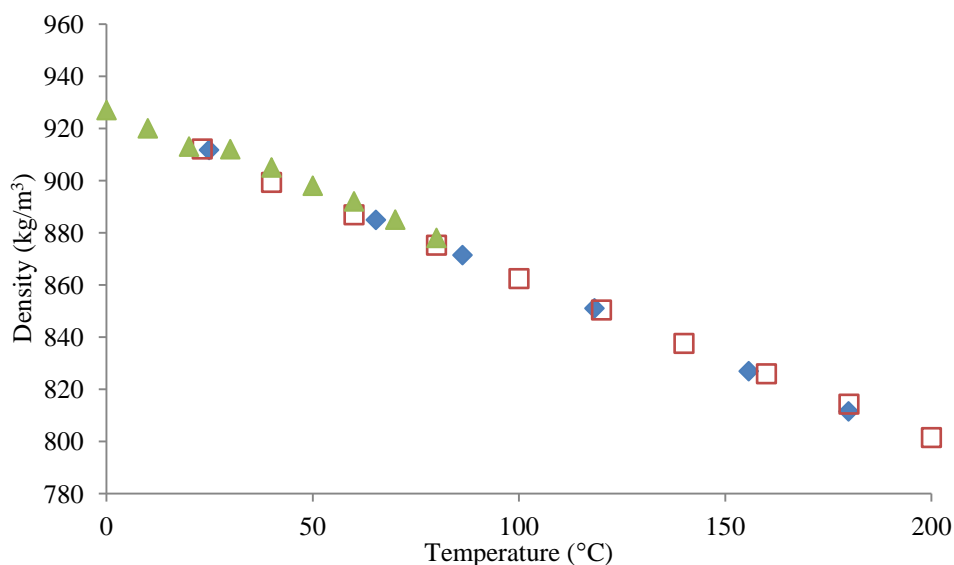


Figure 2.2: Comparison of peanut oil published densities to experimental densities. Mange and Wakeham (1944) (◆), current study (□), Subrahmanyam et al. (1994) (▲)

Table 2.4: R^2 values from experimental densities compared to different literature densities

Oil	Coefficient of Variation (R^2)						
	Current Study	Magne and Wakeham (1944)	Subrahmanyam et al. (1994)	Nouredдини et al. (1992)	Mange and Skau (1945)	Johnstone et al. (1940)	Rice and Hamm (1988)
Peanut	0.9998	0.9999	0.9907	--	--	--	--
Soybean	0.9997	--	--	0.9985	0.9998	0.9999	0.9860
Canola	0.9996	--	--	0.9997	--	--	--
Corn	0.9999	--	--	0.9991	--	--	--

Soybean oil densities were compared to published data [2.1, 2.2-2.5, 2.17] and were found to be in agreement with literature values (Figure 2.3). Experimental data for Canola oil

was in agreement with Ackman and Eaton (1977), but had some discrepancies when compared to Nouredдини et al. (1992), however they were still in agreement (Figure 2.4). Corn oil's density was found to be in agreement with Nouredдини et al. (1992) (Figure 2.5). Olive oil's density was only able to be compared to room temperature data for various origins of olive oil and it was found to be in agreement with the different varieties [2.16] (Table 2.5). Taking into account these comparisons and the comparison of the coefficient of variation, it was determined that the Archimedean method provides data that is in agreement with published data and is a suitable method for measuring oil density at elevated temperatures.

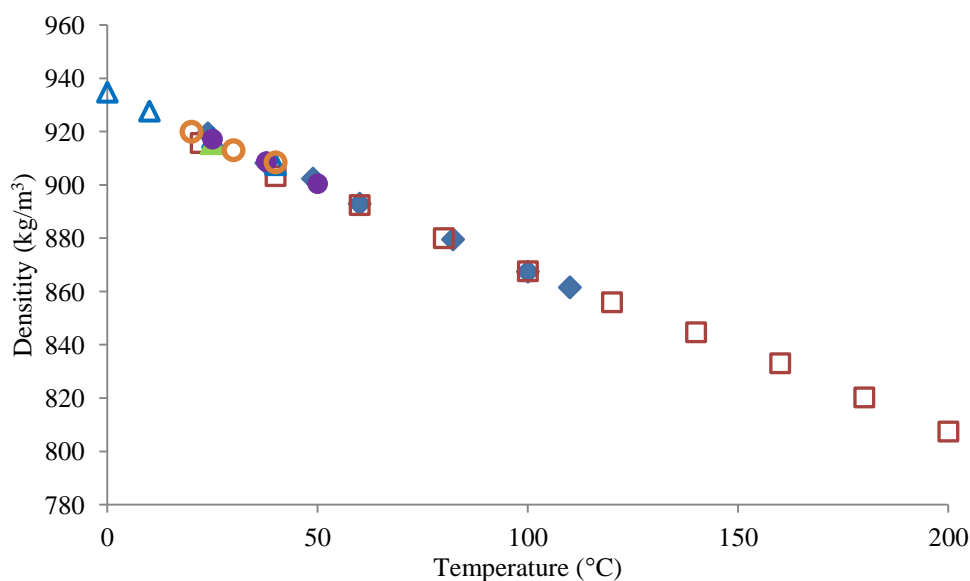


Figure 2.3: Comparisons of soybean oil published densities to experimental densities. Nouredinni et al. (1992) (◆), Current study (□), Mange and Skau (1945) (▲), Ackman and Eaton (1977) (▲), Johnstone et al. (1940) (●), Rice and Hamm (1988) (○)

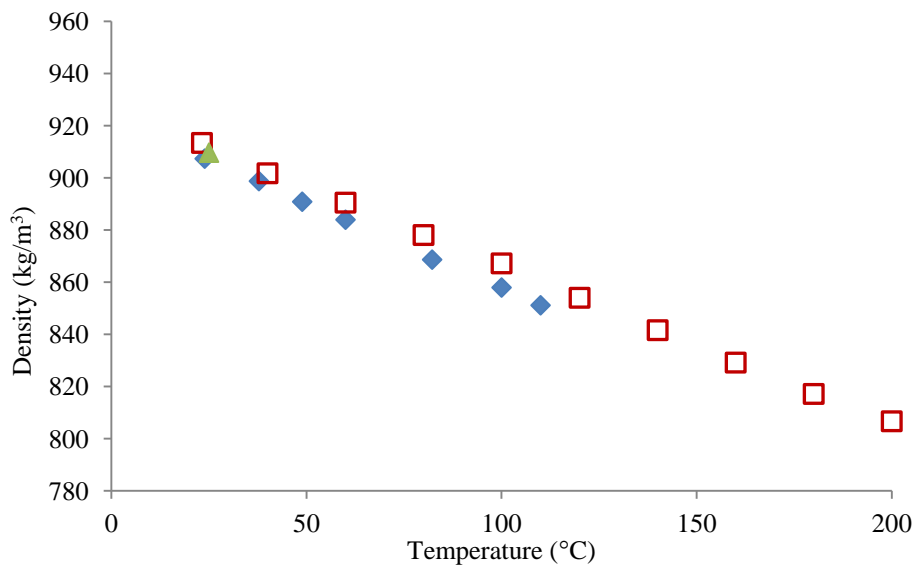


Figure 2.4: Comparison of Canola oil's published densities to experimental densities. Nouredinni et al. (1992) (◆), Current study (□), Ackman and Eaton (1977) (▲)

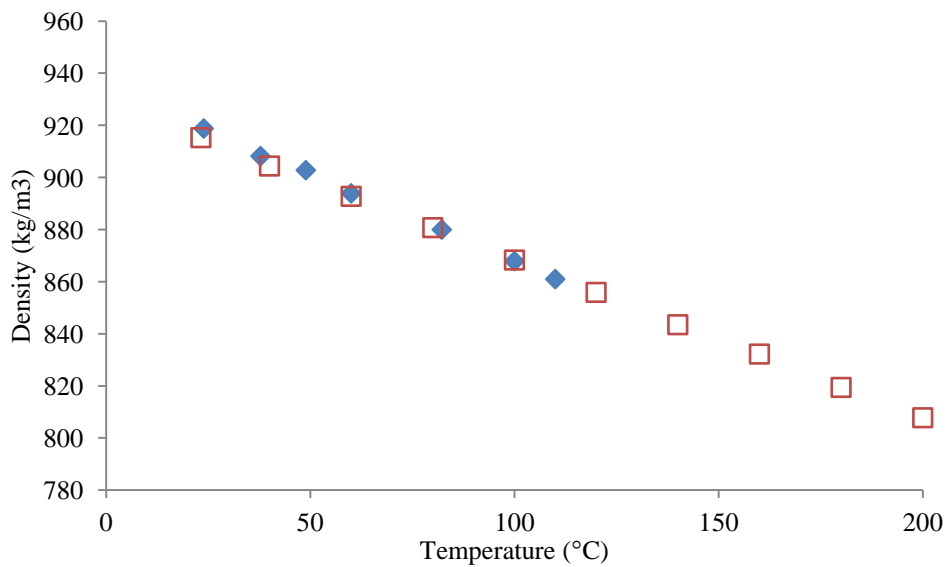


Figure 2.5: Comparisons of experimental corn oil's density to Nouredinni et al. data. Nouredinni et al. (1992) (◆), Current study (□)

Table 2.5: Comparison of current study olive oil density to Jamieson (1927) densities at room temperature

Current Study	Jamieson			
	Spanish	Italian	Tunisian	Californian
908.7	908.9	909.3	910.4	909.2

Experimental density data were analyzed using two types of equations [2.7, 2.9]. The first was the modified Rackett equation developed by Halvorsen et al. (1993):

$$\rho_{oil} = \frac{(\sum x_i MW_i)}{R(\sum \frac{x_i T_{c_i}}{P_{c_i}}) [\sum (x_i Z_{RA_i}) (1 + (1 - T_r)^{2/7})]} + F_c \quad [2.3]$$

where ρ_{oil} is the density of the oil, R is the universal gas constant, T_r is the reduced temperature, F_c is the correction factor, and x_i is the mole fraction and MW_i is the molecular weight of each fatty acid (i) [2.6].

$$T_r = \frac{T}{T_{c,mix}} \quad [2.4]$$

where

$$T_{c,mix} = \sum x_i T_{c_i} \quad [2.5]$$

$$F_c = 0.0236 + k|875 - MW_{oil}| \quad [2.6]$$

The value of k is dependent on MW_{oil} . For MW_{oil} greater than 875, k equals 0.000082. For MW_{oil} less than 875, k equals 0.000098 [2.6].

$$MW_{oil} = 3 \sum x_i MW_i + 38.0488 \quad [2.7]$$

P_{c_i} is the critical pressure, Z_{RA_i} is the Rackett parameter, and T_{c_i} is the critical temperature [2.6] of each fatty acid and were calculated using data provided in Halvorsen et al. (1993) for fatty acid concentrations of oils in the current study.

To compare the predicted density values from the Modified Rackett equation to the current study's density values, percent absolute error was used:

$$\% \text{ absolute error} = \frac{(\rho_{\text{experimental}} - \rho_{\text{MR}})}{\rho_{\text{experimental}}} \times 100 \quad [2.8]$$

Where ρ_{MR} is density determined by the Modified Rackett equation, $\rho_{\text{experimental}}$ is density determined in the current study. Percent absolute error values indicated a difference between densities from the current study to densities by the Modified Rackett equation (Table 2.6). Also, the percent absolute error from the current study (Table 2.6) was significantly greater than the percent absolute errors (0.00-0.70) presented in Halvorsen et al. (1993). From this, it is concluded that the Modified Rackett equation is not a good predictive equation for density, contrary to what Halvorsen et al. (1993) determined.

Table 2.6: Current study, predicted density using Modified Rackett equation (Halvorsen et al. (1993), Percent absolute error (%AE) for each oil at various temperatures

Temperature (°C)	Soybean Oil			Canola Oil			Olive Oil		
	Density (kg/m ³)		Percent Absolute Error	Density (kg/m ³)		Percent Absolute Error	Density (kg/m ³)		Percent Absolute Error
	Current study	Predicted density		Current study	Predicted density		Current study	Predicted density	
22.2±1	915.7	894.0	2.37	913.3	890.7	2.47	908.7	887.2	2.37
40	903.3	882.5	2.30	901.7	879.9	2.42	897.4	876.3	2.35
60	892.4	869.4	2.57	890.4	866.9	2.65	885.8	863.3	2.54
80	880.0	856.1	2.71	878.0	853.6	2.78	874.2	850.0	2.76
100	867.6	842.7	2.87	867.2	840.2	3.11	861.7	836.6	2.92
120	855.9	829.0	3.15	854.0	826.5	3.21	849.7	822.9	3.15
140	844.7	815.0	3.51	841.6	812.7	3.43	836.9	809.0	3.33
160	833.0	800.8	3.86	829.1	798.5	3.69	825.3	794.9	3.68
180	820.2	786.4	4.13	817.1	784.1	4.04	813.6	780.4	4.08
200	807.4	771.6	4.43	806.6	769.4	4.62	N/A	N/A	N/A
Average %AE			3.19			3.24			3.02

Table 2.6: Continued

Temperature (°C)	Peanut Oil			Corn Oil		
	Density (kg/m ³)		Percent Absolute Error	density (kg/m ³)		Percent Absolute Error
	Current study	Predicted density		Current study	Predicted density	
22.2±1	912.1	907.8	0.47	915.3	878.4	4.03
40	899.3	895.6	0.40	904.4	867.1	4.13
60	886.8	882.3	0.51	892.8	854.2	4.32
80	875.2	868.8	0.73	880.7	841.1	4.50
100	862.4	855.2	0.84	868.3	827.9	4.66
120	850.4	841.2	1.07	855.9	814.4	4.85
140	837.6	827.1	1.25	843.5	800.7	5.07
160	825.9	812.7	1.60	832.2	786.8	5.46
180	814.3	798.0	2.00	819.4	772.6	5.72
200	801.5	783.0	2.30	807.8	758.1	6.16
Average %AE			1.12	4.89		

The second approach to modeling the data was an empirical curve fit. A linear equation relating density to temperature was used by Coupland and McClements (1997). This empirical approach generated unique equations for each oil type. The equations developed by Coupland and McClements (1997) were used in the current study to determine oil density at specific temperatures and the values were compared to the current study's data. Coupland and McClements (1997) used oil density data from Nouredini et al. (1992) and Subrahmanyam et al. (1994) to develop empirical equations (Table 2.7) based on:

$$\rho = \rho_0 + \rho_1 T \quad [2.9]$$

The predictive densities from Coupland and McClements (1997) empirical equations agree with the current study's data (less than 0.80 average %AE, Table 2.8). However, densities could only be compared up to 80°C for peanut oil and 110°C for corn, Canola and soybean oil, because Subrahmanyam et al. (1994) and Nouredini et al. (1992) data's maximum

(Table 2.8). New empirical formulas were developed for a temperature range from room temperature to 200°C using the current study's data (Table 2.7).

Table 2.7: Variables for equation 5 from Coupland and McClements (1997)

Oil	Coupland and McClements		Current Study	
	ρ_0	ρ_1	ρ_0	ρ_1
Corn	934.23	-0.65	928.88	-0.6063
Peanut	927.13	-0.60	924.24	-0.6146
Canola	923.05	-0.66	926.73	-0.6057
Soybean	934.41	-0.67	922.24	-0.6055
Olive	-	-	928.18	-0.6005

Table 2.8: Comparison of predicted density from Coupland and McClements (1997) and current study predicted data

Corn				Soybean			
Temperature	Coupland & McClements	Current study	% AE	Temperature	Coupland & McClements	Current study	% AE
22.2	920	915	0.48	22.2	920	916	0.51
40	908	904	0.40	40	908	903	0.38
60	895	893	0.31	60	894	892	0.23
80	882	881	0.21	80	881	880	0.08
100	869	868	0.11	100	867	868	0.08
Average %AE			0.30				0.26

Table 2.8: Continued

Peanut				Canola			
Temperature	Coupland & McClements	Current study	% AE	Temperature	Coupland & McClements	Current study	% AE
21.5	914	912	0.35	23.2	908	913	0.54
40	903	899	0.39	40	897	902	0.65
60	891	887	0.42	60	883	890	0.78
80	879	875	0.46	80	870	878	0.91
-	-	-	-	100	857	867	1.05
Average %AE			0.41				0.79

2.5 CONCLUSION

Densities from the current study agree with currently published data and extend the range of knowledge up to 200°C found commonly in frying and baking. The Archimedean method provided precise data and new empirical formulas were developed from this data to determine density as a function of temperature. The modified Rackett equation was found to be less accurate than empirical formulations, but has the advantage of being predictive based on oil composition and temperature. The current study's data can be used as an aid in determination of heat and mass transfer.

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CHAPTER 3

3.1 ABSTRACT

Immersion frying is a widely used cooking technique that involves heating foods in oil above 100°C. During frying, the heating profile of the product causes rapid moisture loss at its surface resulting in crust formation without burning. The rate of heat transfer, moisture loss and oil uptake are all affected, in part, by interfacial tension between the oil, steam and food surface. Understanding the relationship between frying oil temperature and the oil-steam interfacial tension may yield insight into the mechanism of boiling heat transfer and thus moisture loss. The pendant drop method was used to determine oil-air and oil-steam interfacial tension for five cooking oils (Canola, corn, olive, peanut, and soybean) at temperatures up to 200°C. Initial oil-air values started at room temperature and oil-steam values started at 110°C. All interfacial tension values decreased linearly as temperature increased ($R^2 > 0.99$) from a maximum of 32.14 mN/m (Canola oil at 23.5°C) to a low of 20.04 mN/m (fresh peanut and fresh corn oil at 200°C). Interfacial tension trends were similar for all oils but values were statistically different between oils ($p < 0.0001$). The coefficient of variation for quadruple measurements at each temperature ranged from 0.06 - 0.85 %, which indicated a precise method. No significant difference was found between the oil-steam and oil-air interfacial tension values, e.g. 25.21 mN/m vs. 25.29 mN/m, respectively, for Canola at 120°C. The results indicate that oil-air interfacial tension may be used as an approximation for oil-steam interfacial tension. Additionally, the method and data generated through this research may be used in analysis of processes involving food oils at high temperatures including frying and atomization of biodiesel fuels.

3.2 INTRODUCTION

Interfacial tension (γ) can be found in nature when water beads up on a waxy leaf, or in food products made from an emulsion. Interfacial tension is the force acting at the interface of two liquids or between a liquid and a solid [3.1]. It is the energy required to increase the surface area of a liquid by a unit of area. Interfacial tension is affected by the type of interface, composition of liquid, solid or air, and temperature. Interfacial tension for oil in steam is significantly different than the interfacial tension between oil and water, 21 mN/m, 44 mN/m, respectively [3.2]. If surfactants are added to an oil and water mixture, the interfacial tension between the oil and water decreases [3.3].

Surface tension (σ) is affected by temperature and composition of test material. For many pure liquids, an increase in temperature causes a linear decrease in the surface tension [3.1]. The dependence of surface tension on temperature, for many liquids, is described by the Eötvös equation [3.1]:

$$\frac{d(\sigma(M/\rho)^{2/3}}{dT} = K \quad [3.1]$$

where M is the molar mass, ρ is the density, and K is the Eötvös constant ($-2.12E-7$ J/mol^{2/3}K).

Temperature affects interfacial tension and this change in interfacial tension has the potential to affect the physics that occur in the production of food. Rate of heat transfer and mass transfer are both determined, in part, from the interfacial tension. Rate of heat transfer during boiling is inversely related to the square root of the interfacial tension [3.4]. To understand and mathematically model the rate of heat transfer or mass transfer at elevated temperatures; the interfacial tension needs to be determined at elevated temperatures.

Frying is a process in which a food is submersed in hot (180°C) oil [3.5]. The rate of heat transfer, moisture loss, and oil uptake are all aspects of frying that are influenced by the interfacial tension between the oil and either the product or the steam that is escaping. As the product fries, heat transfer and moisture loss take place. Moisture loss is dependent on the rate of heat transfer [3.6], and therefore the interfacial tension. As frying occurs, the interfacial tension between the oil and steam changes as the temperature difference between the product and the oil decreases. This change in interfacial tension influences the rate of heat transfer and moisture loss.

As a product cools after frying, steam generation ceases and oil enters the product. Oil uptake is driven in part by capillary flow as oil enters the porous matrix of the crust. During capillary flow, the degree of oil uptake depends on the interfacial tension of the oil [3.7]. The interfacial tension of food oils is unknown at elevated temperatures, but to better understand frying heat transfer, moisture loss and oil uptake, the interfacial tension needs to be understood.

Currently no studies report food oil interfacial tension between steam or air at elevated (>100°C) temperatures. Huygens et al. (1992) studied the interfacial tension of hydrocarbons and either steam or water from 100°C to 135°C. It was determined that there was a significant difference between the two interfacial tensions and that as temperature increased interfacial tension decreased. Kalogianni et al. (2010) measured the interfacial tension of olive oil and air at 50°C after various cycles of heat treatments. It was determined that the interfacial tension was 30.7 mN/m after no heat treatments and decreased with increased heat treatments to a minimum of 29.5 mN/m after 40 cycles.

During frying, the oil encounters different interfaces and will have different interfacial tensions. The oil interfaces can be between the food, the water within the product, or the steam escaping. Various studies have examined the interfacial tension of food oil with interfaces such as a potato, water, or air [3.3, 3.9-3.12]. The relationship of oil uptake and water loss to interfacial tension (measured at room temperature) between soybean oil and a potato product was examined [3.9]. It was found that as interfacial tension decreased, the degree of water loss increased and the amount of oil uptake increased.

The interfacial tension between soybean oil and water was determined as a function of different amounts of surfactants [3.3]. Gil and Handel (1992) showed that as surfactant concentration increased, interfacial tension decreased. Silva and Singh (1995) determined that the surface tension for corn oil decreased by 2% as the length of frying increased. Tseng et al. (2003) found the same relationship between soybean oil and air and frying times. Dana and Saguy (2006) utilized contact angle measurements to determine interfacial and surface tension values between oil and water or oil and air. There was no change in the surface tension between Canola oil and air as frying length increased, however the interfacial tension between Canola oil and water decreased. This decreased in interfacial tension was due to surfactants produced as par-fried frozen french fries were finish-fried in Canola oil. The surfactants produced during frying affected the oil-water interfacial tension, but not the oil-air surface tension indicating that the surfactants were likely hydrophilic.

Interfacial tension can be measured by many methods including: pendant drop, Du Nouy ring, Wilhelmy plate, maximum bubble pressure, and contact angle. The pendant drop method determines interfacial tension as it relates to the drop's shape parameters, density

difference, and gravitational force. Pendant drop has been used by Huygens et al. (1992) to study the interfacial tension of hydrocarbons at elevated temperatures. The Du Nouy ring and Wilhelmy plate are detachment methods in which a ring or plate, respectively, is pulled out of the liquid. The interfacial tension is related to the force required to detach the ring or plate from the surface of the liquid [3.7]. These methods have been used most often [3.3, 3.7, 3.9, 3.11] to determine interfacial tension at room temperature. The maximum bubble pressure method measures the surface tension by monitoring the pressure required to form a bubble. This method is employed to measure dynamic interfacial tension and can be used for liquid-air interfaces [3.8, 3.13]. Finally, the contact angle method or sessile drop method measures the angles between a liquid drop and a hard surface and uses the Young's equation to determine the interfacial tension between a liquid and the solid [3.10]. For the current study, the pendant drop method was used because it is a steady state method and the environment and temperature can easily be controlled by an environmental cell.

The objective of this work was to determine the interfacial tension for five common food oils (Canola, corn, soybean, olive, and peanut oil) between either air or steam from room temperature (air) or 110°C (steam) to 200°C using the pendant drop method. Oil-steam interfacial tension was compared to oil-air interfacial tension to determine if it can be used as approximation for oil-steam interfacial tension. Interfacial tensions for different brands of soybean oil were evaluated to determine if there is a difference between brands of oil. To determine accuracy of the method, the interfacial tension of decane was measured over a temperature range and was compared to reference data.

3.3 MATERIAL AND METHODS

3.3.1 Materials

Canola oil (ConAgra, Omaha, NE), olive oil (American Rice Inc., Houston, TX) soybean oil (Ventura Foods, Brea, CA; Smucker Company, Orrville, OH; ConAgra, Omaha, NE; ALDI, Batavia, IL), peanut oil (Ventura Foods, Brea, CA), and corn oil (ACH Food, Memphis, TN) were purchased from a local grocery store (Harris Teeter, Raleigh, NC). Decane was purchased from TCI America, Portland, OR. A goniometer (Ramé-Hart, Advanced Goniometer, model 300, Succasunna, NJ) equipped with a CCD digital camera and software (DROPimage Advanced), and an environmental cell (model P/N 100-07) were used to measure interfacial tension. A 22 gauge needle (Ramé-Hart, Succasunna, NJ) and manual dispensing micro-syringe (Ramé-Hart, model 100-10-20, Succasunna, NJ) were used to dispense a drop. A high temperature resistant pipe, high temperature heating tape (O.E.M. Heaters, Saint Paul, MN), thermal insulation (Heatshield Products, Valley Center, CA) with a thermal conductivity of 0.0418 W/mK, and aluminum foil were used for the transport of steam from the source to the environmental cell.

3.3.2 Pendant Drop

The pendant drop method was used to determine the interfacial tension for oil-air and oil-steam interfaces. The method entails a drop being dispersed, using a micro-syringe, from a stainless steel needle whose tip is in an environmental cell. This drop is analyzed for maximum diameter ($R' + R''$), length of drop, and the drop's diameter (D_s) at the maximum diameters distance from the drop's apex to determine interfacial tension (Figure 3.1).

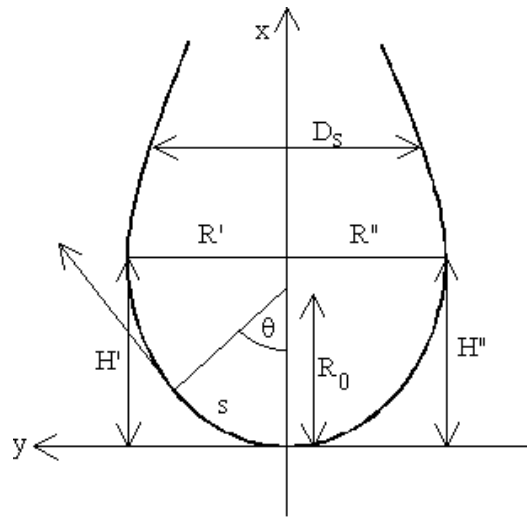


Figure 3.1: Dimensions of drop [3.14]

3.3.3 Interfacial Tension Instrumentation

During measurement of interfacial tension, the environment around the drop was controlled using a temperature controlled environmental cell (Figure 3.2). The temperature was monitored at the drop's location inside the cell. The drop was dispensed at a location within the sight windows on the cell. The environmental cell was also equipped with two portals that could be opened to control the composition of the environment inside. For oil-air interfacial tension, the portals were closed on the environmental cell.



Figure 3.2: Environmental cell used to control environment during pendant drop method [3.14]

The environmental cell fit on the goniometer's base in the assembly (Figure 3.3). The drop's size was monitored using the CCD digital camera and software program.



Figure 3.3: Advanced goniometer model 300 and CCD digital camera for drop image analysis [3.14]

3.3.4 Steam Delivery

To add steam to the environment, the portals on the environmental cell were opened and the steam was piped into the cell. The pipe was wrapped with heating tape to ensure that the steam did not condense and that the steam's temperature was constant. The pipe was wrapped with thermal insulation to prevent heat loss and condensation. One end of the pipe was connected to the environmental cell via one of the open portals on the cell (Figure 3.4). The other end of the pipe was connected to a steam source (Erlenmeyer flask with boiling water). To ensure that there was a steam environment within the cell, the other open portal had a piece of tubing connected to it to allow the steam to escape. As the steam moved through the cell, it would exit only through this tube. The tube sat in a beaker and condensation was monitored on the beaker's wall. Seeing condensation forming on the beaker wall confirmed that steam was flowing through the environmental cell.

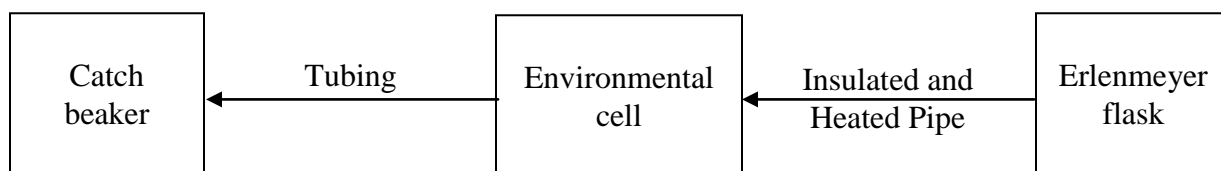


Figure 3.4: Schematic of instrumentation with steam flow

3.3.5 Interfacial Tension Determination

The CCD digital camera, along with a software analysis program, was used to measure the drop parameters (Figure 3.1) to determine the interfacial tension [3.14]:

$$\gamma = \frac{\Delta\rho g R_0^2}{\beta} \quad [3.2]$$

where, γ is surface tension (mN/m), $\Delta\rho$ is density difference between oil and steam or air (kg/m^3), g is gravitational force (m/s^2), R_o is the distance from the drop apex to the maximum diameter (m), and β is a function of the width of the drop:

$$\beta = -0.12836 + 0.7577\delta - 1.7713\delta^2 + 0.5426\delta^3 \quad [3.3]$$

$$\delta = \frac{D_S}{D_E} \quad [3.4]$$

where D_E is the maximum diameter of the bubble and D_S is the diameter at distance D_E from the apex (Figure 3.1).

Measurements were performed in quadruplet and t-tests were used to test the equality of means across oil types. Coefficient of variation calculations were used to determine precision of instrumentation. Interfacial tension of decane was determined and compared to published data to determine accuracy of the instrumentation and method.

3.4 RESULTS AND DISCUSSION

3.4.1 Accuracy of Method

The interfacial tension of decane was determined from 23°C to 60°C and the results compared to those in Rolo et al. (2002), Jasper (1953) and Jasper (1972) (Table 3.1). The current study's data had an overall relative error to published values of 2.5% and a maximum relative error of 3.0% at 40°C, compared to Jasper (1953). Following the verification process outlined in Rolo et al. (2002), a relative error of 2.5% and difference in literature values, it was concluded that the method and instrumentation provides accurate data.

Table 3.1: Current study interfacial tension of decane compared to literature data for decane

Temperature (°C)	Current Study (mN/m)	Rolo et al. (2002)	Jasper (1953)	Jasper (1972)
20	-	24.47	23.89	23.83
23.5	23.00	-	-	-
40	21.40	22.45	22.06	21.99
60	19.87	20.6	20.22	20.15

3.4.2 Oil-Air Interfacial Tension

Interfacial tension for oil and air (Table 3.2) was determined using the pendant drop method. When comparing each oil type at each temperature, it was determined that some interfacial tensions were significantly different ($p < 0.0001$). With a coefficient of variation of less than 0.85%, the Ramé-Hart goniometer was precise in measuring the interfacial tension by pendant drop method.

Table 3.2: Oil-Air interfacial tension for five common cooking oils for various temperatures

Temperature (°C)	Interfacial Tension (mN/m)*				
	Canola	Corn	Soybean	Peanut	Olive
23.5±0.6	32.41 ^D	32.15 ^{BC}	29.43 ^A	32.23 ^C	32.03 ^B
40	31.29 ^D	30.63 ^B	28.42 ^A	30.90 ^C	30.91 ^C
60	29.67 ^D	29.28 ^B	27.19 ^A	29.16 ^B	29.47 ^C
80	28.17 ^D	27.78 ^C	25.89 ^A	27.61 ^B	28.11 ^D
100	26.71 ^D	26.33 ^B	24.16 ^A	26.20 ^B	26.51 ^C
120	25.33 ^E	24.98 ^B	23.03 ^A	25.29 ^D	25.13 ^C
140	23.96 ^C	23.71 ^B	21.76 ^A	23.94 ^C	23.68 ^B
160	22.66 ^D	22.24 ^B	20.86 ^A	22.70 ^D	22.49 ^C
180	21.22 ^B	21.12 ^B	19.49 ^A	21.47 ^C	21.14 ^B
200	20.08 ^B	20.04 ^B	18.98 ^A	20.04 ^B	N/A

*: means with in a row with a common subscript do not differ significantly.

It was determined for all oils that interfacial tension is linearly inversely proportional to temperature ($R^2 > 0.99$) (Figure 3.5). Differences in the slopes and the y-intercepts (Table 3.3) are not significant except for soybean oil. Soybean oil interfacial tension, at all temperatures, was lower compared to the other oils' interfacial tension. Upon further study, it was discovered that an expired bottle of soybean oil was purchased and it was hypothesized that this was the reason for the difference between the interfacial tension of soybean oil and the interfacial tension of the other oils. To further investigate this hypothesis, different brands of soybean oil were purchased to see how the interfacial tension changed between brands and compare the unexpired brands with the one expired soybean oil (discussed in detail later).

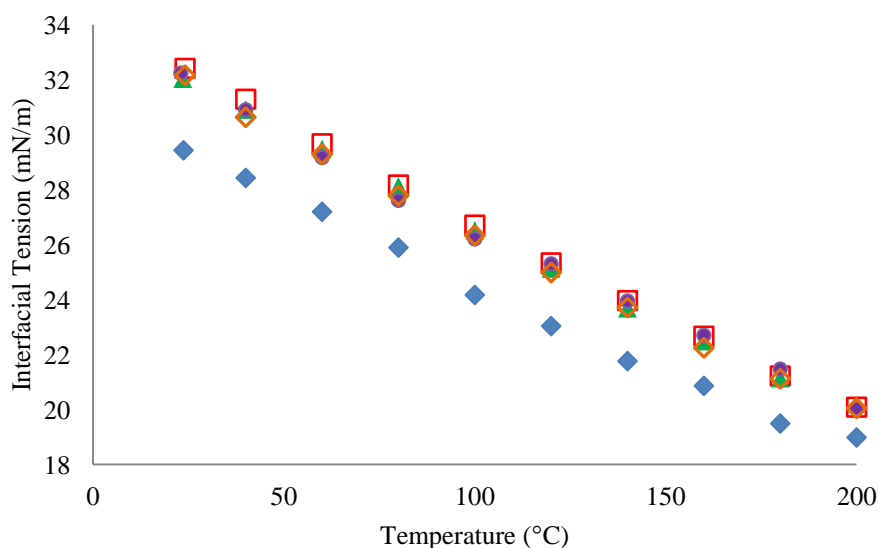


Figure 3.5: Interfacial tension for various oil's from room temperature to 200°C with air as the interface. Soybean oil (◆), Canola oil (□), olive oil (▲), peanut oil (●), corn oil (◇)

Table 3.3: Y-intercept, slope and correlation coefficient

Oil	Canola	Corn	Olive	Soybean	Peanut
y-int	33.94	33.41	33.67	30.74	33.38
Slope	-0.0706	-0.0687	-0.0703	-0.0618	-0.0637
R ²	0.9987	0.9972	0.9993	0.9935	0.9954

3.4.3 Oil-Steam Interfacial Tension

The oil and steam interfacial tension results showed the same decrease in interfacial tension with increasing temperature relationship as was seen in oil and air interfacial tension results (Table 3.4). Again, the expired soybean oil was noticeably different from the other four oils.

Table 3.4: Oil-Steam interfacial tension for five common cooking oils for various temperatures

Temperature (°C)	Interfacial Tension (mN/m)*				
	Canola	Corn	Soybean	Peanut	Olive
110	26.00 ^D	25.73 ^C	24.44 ^A	25.46 ^B	25.68 ^C
120	25.21 ^C	24.98 ^B	23.67 ^A	25.03 ^B	25.07 ^B
140	23.95 ^C	23.75 ^B	22.33 ^A	23.71 ^B	23.66 ^B
160	22.54 ^C	22.48 ^{B,C}	21.06 ^A	22.39 ^B	22.76 ^D
180	21.60 ^D	21.16 ^B	20.18 ^A	21.28 ^B	21.45 ^C
200	20.33 ^C	20.02 ^B	19.00 ^A	20.22 ^C	N/A

*: means with in a row with a common subscript do not differ significantly.

The same linear inverse relationship was seen ($R^2 > 0.99$) as was in the oil and air interfacial tension (Figure 3.6). Again, it is noticeable that all of the interfacial tensions lay on top of each other except for expired soybean oil.

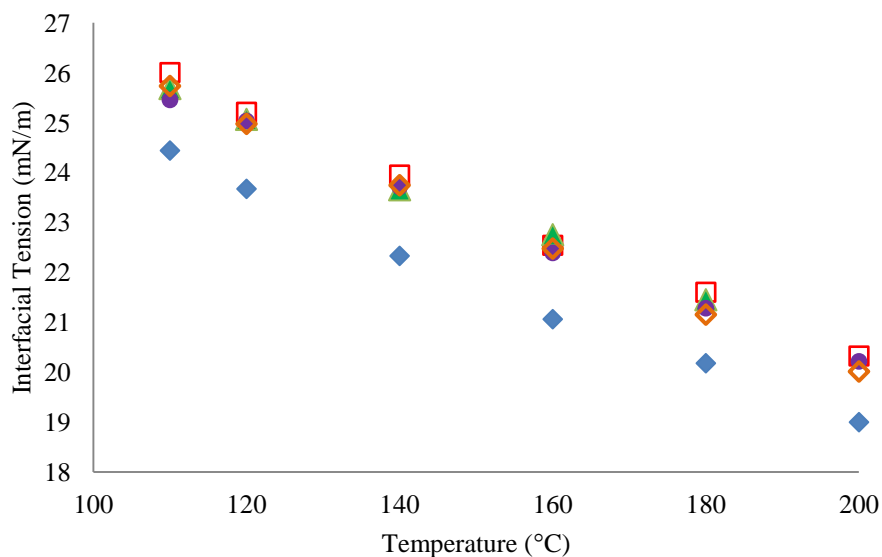


Figure 3.6: Interfacial tension for various oil's from 110 °C to 200°C with steam as the interface. Soybean oil (◆), Canola oil (□), olive oil (▲), peanut oil (●), corn oil (◇)

When comparing the oil and steam interfacial tensions to oil and air interfacial tensions, small differences were found (Figures 3.7-3.11) by overlaying the values on one plot. From figures 3.7-3.11, it was concluded that oil-air interfacial tensions are a good approximation for the oil-steam interfacial tensions in the temperature range tested (110-200°C).

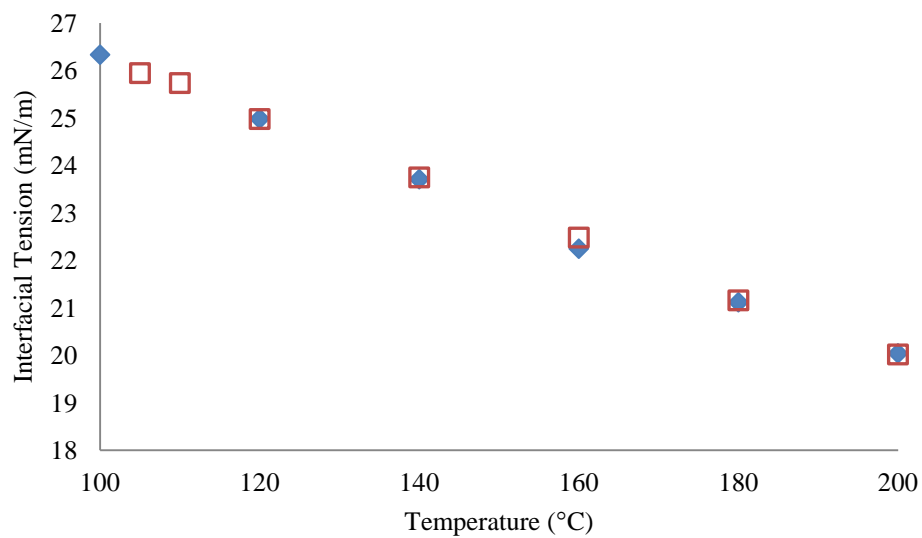


Figure 3.7: Interfacial tension for corn oil from 100 °C to 200°C with steam or air as the interface. Corn oil and air (◆), corn oil and steam (□)

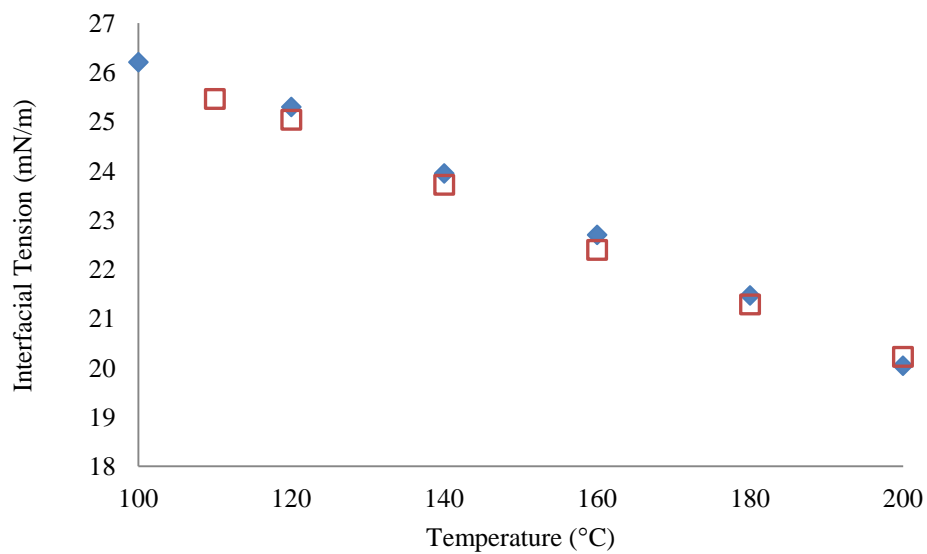


Figure 3.8: Interfacial tension for peanut oil from 100 °C to 200°C with steam or air as the interface. Peanut oil and air (◆), peanut oil and steam (□)

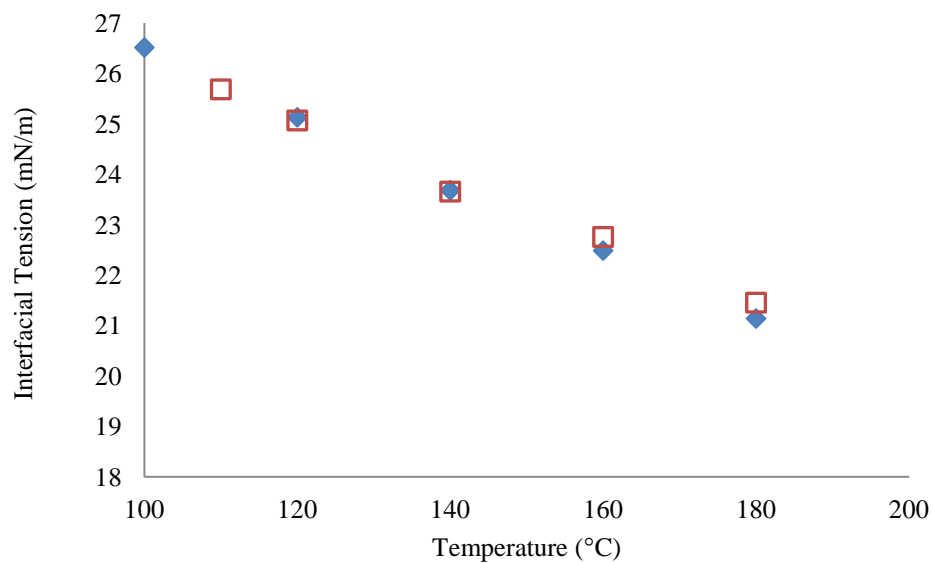


Figure 3.9: Interfacial tension for olive oil from 100 °C to 180°C with steam or air as the interface. Olive oil and air (◆), olive oil and steam (◻)

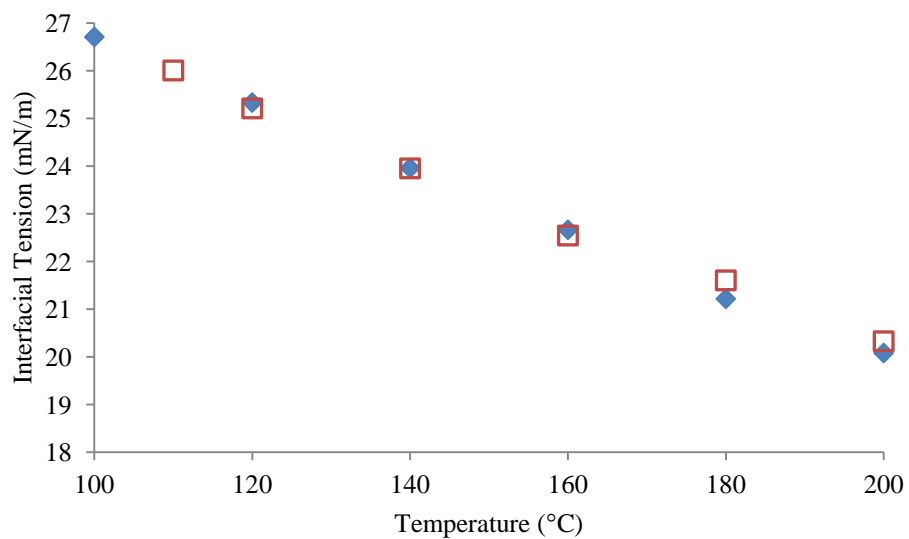


Figure 3.10: Interfacial tension for Canola oil from 100 °C to 200°C with steam or air as the interface. Canola oil and air (◆), Canola oil and steam (◻)

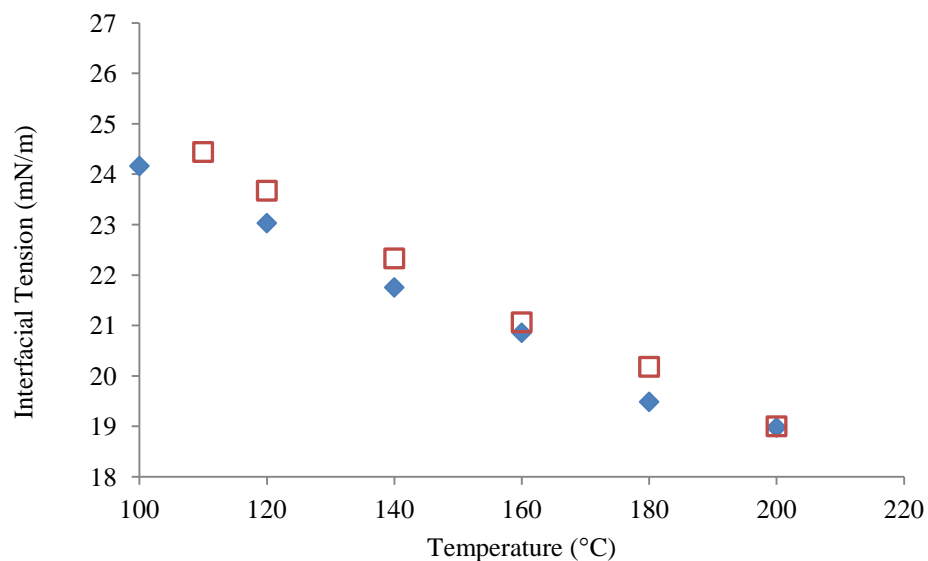


Figure 3.11: Interfacial tension for soybean oil from 100 °C to 200°C with steam or air as the interface. Soybean oil and air (◆), soybean oil and steam (◻)

3.4.4 Predictive Equations

The Eötvös equation describes the affect of temperature on surface tension for many liquids (equation 3.1) [3.9]. The Eötvös equation was used to predict the surface tension of Canola oil (Figure 3.12). The Eötvös equation with the $K = 2.1\text{E-}7 \text{ J/mol}^{2/3}\text{K}$ inaccurately predicted the slope of surface tension vs. temperature. If K was adjusted to $2.83\text{E-}7 \text{ J/mol}^{2/3}\text{K}$, the Eötvös equation accurately predicted the surface tension of the oil.

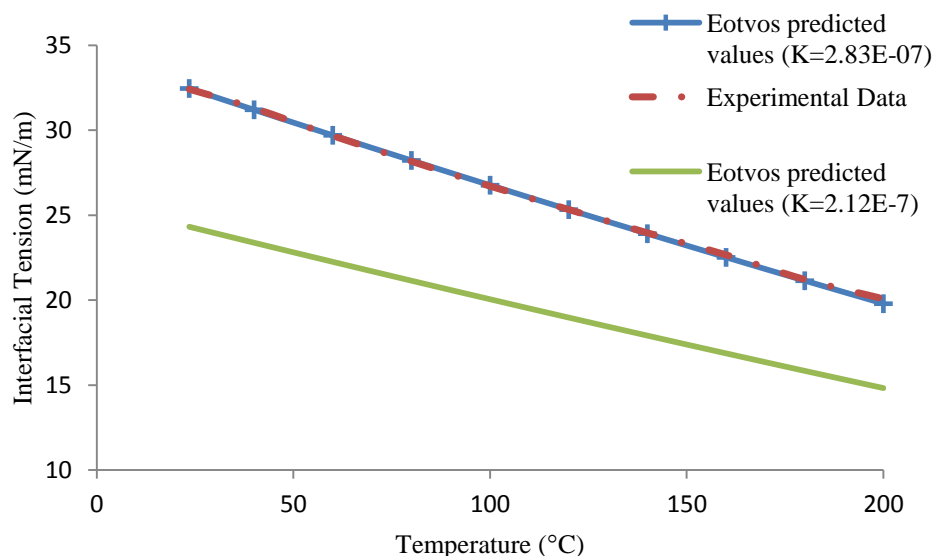


Figure 3.12: Comparison of Eötvös equation with two different values for K to experimental interfacial tension for Canola oil.

The Eötvös constant is a measure of the entropy of formation on the surface and the entropy change that occurs when liquid molecules move from inside the liquid to the surface of the liquid [3.16]. It is the same for all non-polar liquids and about the same for all liquids. However, the excess entropy on the surface is based on the configuration of the molecules and the Eötvös constant is higher for geometrically complicated molecules [3.16]. It is proposed that the increase value of K for Canola oil is because the configuration is more complicated.

Another approach to model interfacial tension as a function of temperature would be an empirical curve fit. Empirical equations are based on:

$$\gamma = \gamma_0 + \gamma_1 T \quad [3.5]$$

Empirical formulas were developed for a temperature range from room temperature to 200°C for each oil (Table 3.5).

Table 3.5: Variables for equation 5 from current study

Oil	γ_0	γ_1
Corn	33.41	-0.0687
Peanut	33.38	-0.0637
Canola	33.94	-0.0706
Soybean	32.92	-0.0660
Olive	33.67	-0.0703

3.4.5 Soybean Oil Brands

Four brands of soybean oil were studied to determine the change in interfacial tension as depending on brand. All interfacial tension verses temperature plots had the same inverse relationship but the y-intercepts were different (Figure 3.13). There was a noticeable difference between the Carlini brand (expired oil) interfacial tension and the three other brands. It was hypothesized that this occurred because the oil had degraded due to light and oxygen exposure over time and therefore had a lower interfacial tension (Table 3.6). When comparing the other three brands' interfacial tensions to the other oil types interfacial tension, there was not a substantial difference. To explain why there is a difference in interfacial tension after oil ages in a bottle verses frying, it is hypothesized that a different type of surfactant was produced during aging of oil compared to ones produced during frying.

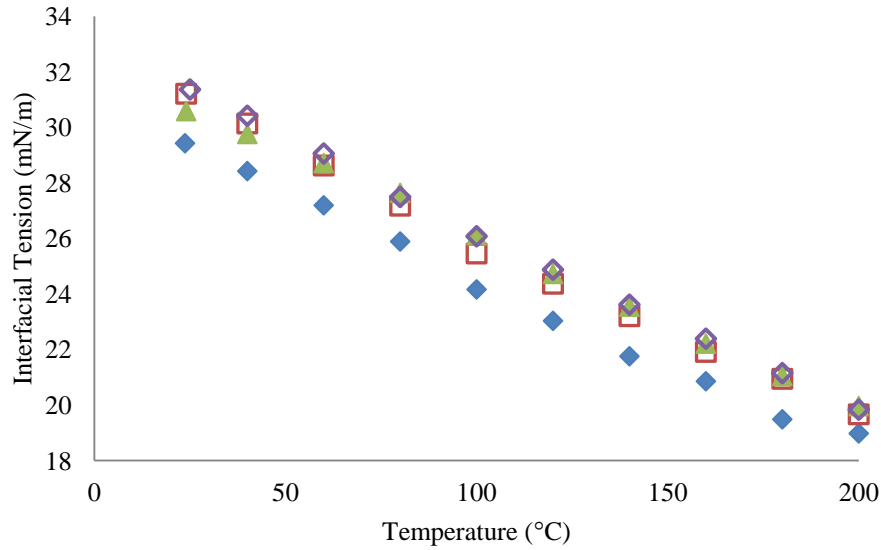


Figure 3.13: Interfacial tension for different brands of soybean oil from room temperature to 200°C with air as the interface. Carlini (◆), Crisco (◻), LouAna (▲), Wesson (◇)

Table 3.6: Interfacial tension for four brands of soybean oil for various temperatures

Temperature (°C)	Interfacial Tension (mN/m)			
	Carlini	Crisco	LouAna	Wesson
24±1.0	29.43±0.03	31.21±0.06	30.58±0.10	31.36±0.07
40	28.42±0.10	30.14±0.09	29.76±0.13	30.42±0.09
60	27.19±0.06	28.62±0.07	28.71±0.08	29.06±0.07
80	25.89±0.11	27.18±0.07	27.64±0.01	27.49±0.02
100	24.16±0.08	25.46±0.16	26.11±0.11	26.08±0.05
120	23.03±0.07	24.37±0.15	24.72±0.01	24.87±0.04
140	21.76±0.09	23.20±0.10	23.54±0.08	23.61±0.01
160	20.86±0.10	21.91±0.17	22.21±0.06	22.39±0.06
180	19.49±0.10	20.94±0.04	21.05±0.04	21.15±0.04
200	18.98±0.07	19.67±0.12	19.96±0.04	19.83±0.08

3.4.6 Effect on rate of Heat Transfer

The rate of heat transfer is inversely related to square root of interfacial tension [3.4]:

$$\frac{q}{A} = \mu_L h_{fg} \left[\frac{g(\rho_L - \rho_v)}{\sigma} \right]^{1/2} \left[\frac{c_{pL}(T_s - T_{sat})}{C_{sf} h_{fg} Pr_L^{1.7}} \right]^3 \quad [3.6]$$

Where μ_L is the liquid viscosity (Pa s), h_{fg} is the latent heat of vaporization (kJ/kg), g is gravitational force (m/s^2), $(\rho_L - \rho_v)$ is the density difference between the liquid and vapor (kg/m^3), σ is the surface tension (N/m), c_{pL} is the heat capacity for the liquid (J/K), $(T_s - T_{sat})$ is the difference between the surface and saturated-liquid temperatures (K), C_{sf} is a coefficient that varies with surface-liquid combination, and Pr_L is the Prandlt number for the liquid. Using density (O'Meara, 2012) and oil-air interfacial tension, the effect of using room temperature values instead of the values at temperature of frying was evaluated. From equation 3.6:

$$\left[\frac{\rho_L - \rho_v}{\sigma} \right]^{1/2} \quad [3.7]$$

was used to determine this effect (Table 3.7).

Table 3.7: Results from equation 6 at room temperature and at 200°C

Temperature (°C)	Value ($s/m^{3/2}$)
22.2	168
200	200

If room temperature values were used to determine rate of heat transfer at 200°C, it would introduce a 16% error. The rate of heat transfer would be under quantified and models of the system would be wrong.

3.5 CONCLUSION

All interfacial tensions are inversely related to temperature and have similar values. These values can then be used to accurately determine the rate of heat transfer, moisture loss

and oil uptake during frying. The interfacial tensions for oil-air are a good approximation for oil-steam interfacial tension.

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