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VEGETABLE OILS: LIQUID COOLANTS FOR SOLAR HEATING AND
COOLING APPLICATIONS

Final Report

By
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February 1980

Work Performed Under Contract No. AC04-78CS34298

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U.S. Department of Energy

Solar Energy

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Vegetable Oils:
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I. ABSTRACT

As high temperature solar energy systems are developed for applications such as refrigeration, heating, cooking, electrical power generation, and industrial processes, the need for inexpensive, reliable heat transfer media (liquid coolants) will become more intense. At present petroleum distillates and synthetic coolants are being utilized for these purposes. Since the use of these substances represents a drain on our fossil fuel resources, it has been proposed that vegetable oils, renewable byproducts of agriculture processes, be investigated for possible use as liquid coolants. This research project was implemented for the purpose of researching such a use.

During the conceptual phase of the study, it was recognized that very little data are readily available for predicting the results of using vegetable oils as liquid coolants in high temperature solar systems. Therefore, the major thrust of the project was to investigate several thermophysical properties of the four vegetable oils selected. Vapor pressures, specific heat, viscosity, density and thermal conductivity were determined over a range of temperatures for corn, soybean, peanut and cottonseed oil. ASTM standard methods were used for these determinations.

In addition to the thermophysical property data acquisition, chemical analyses were performed on samples of each oil. The samples were collected before and after each experiment so that any changes in composition could be noted. The tests included iodine number, fatty acid, and moisture content determination.

II. NARRATIVE

A. Research Objectives

The research objectives included several tasks required to define the use of vegetable oils in high temperature (greater than 180°F, 82.2°C) solar systems:

1. A literature survey for existing thermophysical property data;
2. Thermophysical property experiments;
3. Stability and corrosion experiments;
4. Determination of potential for each oil as a liquid coolant for solar applications;
5. Evaluation of cost effectiveness of the selected oils;
6. Analysis of pumping power required to transfer a unit of heat energy with the selected vegetable oils.

The thermophysical properties were to be determined at a pressure of about one atmosphere at 20°F (11.1°C) increments from 70°F (21.1°C) up to the boiling point. Cottonseed, corn, peanut, and soybean oil were selected as the tentative candidates for use in solar systems.

B. Literature Survey/Formation of Research Plan

Previous research was conducted to determine the thermal properties of many of the commercially available natural oils. Published literature indicates that these data are not readily available in the temperature range of 70°F (21°C) to 700°F (371°C). Preliminary studies and existing data did indicate that fluid properties, such as viscosity, freezing point and density are in an acceptable range to indicate some potential in solar applications. A study by Wakeman and Magne (24, 25) defined flow properties of cottonseed oil between 86°F (30°C) and 410°F (210°C). Their data indicated that the viscosity of this oil fell in the range of viscosities given for commercially acceptable liquid coolants. Data on flow properties above 410°F (210°C) had not been adequately developed.

Vegetable oils have high temperature flammability properties. Jameson (22) has tabulated smoke, flash and fire points for several of these oils. Flash points have been recorded at approximately 620°F (327°C) and fire points at 670-680°F (354-360°C). The spontaneous ignition point is also an important property, and published data show that some of these oils (e.g. soybean) have ignition points as high as 833°F (445°C).

It is believed that the vegetable oils are much safer than other fluids. These oils are commonly used in or around food products and are non-toxic. Although some of these oils will produce corrosion in copper pipes if oxygen is present, there is no evidence to date that these oils will accelerate corrosion in closed systems, provided moisture content is low.

Their relative low cost is another attractive feature for using vegetable oils in solar systems. Prices range from \$3 to \$5 per gallon while petroleum based coolants and synthetic oils can cost as much as \$30

per gallon.

Research at the University of Florida (12, 18) has, in part, validated the use of these vegetable oils as liquid coolants. The use has dealt mainly with air conditioning and heating. In each case the research was designed to prove the feasibility of the concept and not to provide long term testing of the liquid coolant. If these oils are to realize wide-spread use in solar systems then reliable design data must be made available. This project has been designed to provide these data.

The more common oils; peanut, soybean, corn, and cottonseed, were selected for this study. A series of experiments were proposed in order to measure the thermophysical properties necessary for the proper design of solar equipment utilizing these oils. Coincident with these experiments, stability tests were run. The purpose of these experiments was to extend the thermophysical property data to higher temperatures and obtain the supplemental data needed to perform engineering calculations related to heat transfer and pumping power.

C. Experimental Facilities

The experiments performed under this contract were implemented at the University of Florida's Solar Energy and Energy Conversion Laboratories. As these experiments involved several physical chemistry procedures, the selective coating laboratory facilities provided an excellent base for this research. The laboratory provided air, gas, water, special ventilation requirements, sewage, and electrical power requirements. The laboratory facilities can accommodate the most delicate analytical equipment and yet still provide space for bench tests, such as the stability tests required by this research.

D. Experimental Equipment/Procedures

This study involved thermophysical property determinations for the oils at a pressure of approximately one atmosphere. Data were to be collected at 20°F increments from 70°F (21.1°C) to the boiling point.

1. Boiling Point

1.1 Introduction

When a pure liquid is placed in an evacuated bulb, molecules will leave the liquid phase and enter the gas phase until the pressure of the vapor in the bulb reaches a definite value which is determined by the nature of the liquid and its temperature.

If the pressure above the liquid is maintained at a fixed value, then the liquid may be heated to a temperature at which the vapor pressure is equal to the external pressure. At this point, vaporization will occur by the formation of bubbles in the interior of the liquid as well as at the surface. This is the boiling point of the liquid at the specified external pressure. If the external pressure is atmospheric pressure, the boiling process is called the normal boiling and the temperature is called the normal boiling point.

Clearly, the boiling temperature is a function of the external pressure; in fact, the variation of boiling point with external pressure is seen to be identical with the variation of the vapor pressure with temperature. One of the reasons that boiling point is an important physical property is that it is used to estimate other physical properties. These include viscosity, thermal conductivity, heat capacity and so forth.

In heat transfer systems, knowledge about the boiling point of the heat transfer media is important because the design of the pumps and piping should be such to prevent phase change or boiling.

1.2 Principles of measurement

Using ASTM standard method D1120-72, Standardized Method for Boiling Point of Engine Coolants (3), the boiling point was determined for each of the four oils selected for study; corn oil, peanut oil, cottonseed oil, and soybean oil. The apparatus used for these experiments is illustrated in Figures 1 and 2. Figure 1 is a schematic of the apparatus. The carbon dioxide (CO_2) gas was used to provide an inert atmosphere during boiling experiments. A more detailed discussion of the rationale for the use of CO_2 may be found in the Experimental Results section of this report.

Even though ASTM D1120-72 is specifically directed toward boiling points for automobile coolants (engine coolants that are miscible with water), the procedure lends itself easily to the determination of vegetable oil boiling points with the modifications shown in Figure 1. In the case of this research, a carbon dioxide atmosphere was used above the oil to prevent oxidation of the oil. The flask size was increased to 1000 milliliters to accommodate the CO_2 apparatus and the sample size was increased to 100 milliliters accordingly. The condenser subcooled the oil to the point that the reflux drops would create turbulence and fumes when they hit the hot boiling fluid in the flask.

The oils were heated at a rate sufficient to raise the temperature approximately 1°F (0.55°C) every 10 seconds until boiling and reflux were realized. After reflux was established, the temperature and barometric pressure were recorded.

Deviations in the thermometer readings were corrected with the use of the thermometer's correction chart. The variation of the boiling point, due to change in barometric pressure, was corrected with the Sidney-Young equation:

Thermometer

Condenser

Carbon
Dioxide
Supply

3-Neck
Distilling
Flask

Heater Controls

Electric Heater

Boiling Point Test Apparatus
Figure No. 1

Figure 2
Boiling Point Apparatus

$$C_f = 0.000095(760 - P)(273 + t_c) \quad (1)$$

where,

C_f = correction factor

P = barometric pressure, mm Hg

t_c = measured boiling point temperature, °C

In order to get an average value of boiling points of these oils five tests were run. The average value of the boiling points was then calculated.

2. Viscosity

2.1 Introduction

Viscosity, the resistance of adjacent fluid layers to shear, is one of the principle fluid properties. When shearing occurs between parallel planes, the shear stress is proportional to the velocity and inversely proportional to the distance between layers. A proportionality factor called dynamic viscosity relates the shear stress to the velocity and distance between planes. Both velocity and shear stress generally vary across the flow field and a differential expression results:

$$\tau = \mu \frac{dv}{dy} \quad (2)$$

where

τ = shear stress,

μ = dynamic viscosity,

$\frac{dv}{dy}$ = normal velocity gradient.

Another term frequently used in fluid dynamics is kinematic viscosity which involves only kinematic quantities and is expressed as

$$\nu = \frac{\mu}{\rho} \quad (3)$$

where

ν = kinematic viscosity,

μ = dynamic viscosity,

ρ = density.

Liquid viscosities are generally strongly dependent on temperature. The viscosity normally decreases with increasing temperature and first order estimates of kinematic viscosity as a function of temperature may be expressed as

$$\nu = A e^{B/T} \quad (4)$$

where

A, B = experimentally determined constants,

T = absolute temperature.

Several methods of predicting viscosity by empirical relationships and by improvements on the previously mentioned logarithmic expression are presented in Reference [28].

A variety of methods are available for measuring viscosity. These methods include the measurement of: pressure drop as a result of fluid flow in a tube; the drag on a body falling through a stagnant fluid. The drag on a rotating or oscillating body in a stagnant fluid. The procedure used in the vegetable oil testing, however, involves the measurement of the time required for the fluid to flow through a capillary.

2.2 Principles of viscosity measurement

The fundamental principle of the Saybolt viscosity method is the measurement of the time required for 60 ml of oil to flow through a calibrated capillary tube. The viscosimeter tube is an accurately machined cylinder of known volume which is filled with the oil being tested (see Figures 3, 4). The liquid is permitted to drain through the capillary under the head that results from the standing column of oil in the viscosimeter.

If the capillary tube was long enough, a fully developed laminar velocity profile would result. In this case the kinematic viscosity would be directly proportional to the efflux time. The capillary length, however, is short due to construction requirements (orientation constraints and difficulties in accurately machining long tubes to close tolerances). The lack of a fully developed flow pattern in the capillary caused by this effect

Sectional View of SAYBOLT Viscometer
Figure No. 3

Figure 4

Universal Saybolt Viscosimeter Tube and Orifice

requires that a correction term be added to the direct proportionality relationship.

$$\nu = C_1 t + \frac{C_2}{t} \quad (5)$$

where

ν = kinematic viscosity,

C_1, C_2 = constants,

t = corrected efflux time in seconds.

The accurate determination of the efflux time necessarily entails the use of a viscometer correction factor for each viscosimeter tube. This correction factor is determined by measuring the efflux time of a standard oil with accurately known viscosity at a specified temperature. The ratio of this standard efflux time to the measured efflux time results in the aforementioned correction factor which accounts for the presence of machining tolerances in both the cylinder and the capillary.

2.3 Saybolt equipment

The equipment necessary for the determination of Saybolt viscosity is outlined in Reference [6]. Basic requirements include a temperature bath, viscosimeter tubes, thermometers, timer and flasks. Although these devices are very simple by nature, their proper selection and utilization are essential to obtain acceptable data.

The temperature bath is provided as part of the Saybolt viscometer as shown in Figures 5 and 6. The bath must be filled to a level at least 1/4 inch above the viscosimeter tube overflow rim to ensure uniform sample temperatures.

The viscosimeter tube must be properly cleaned per ASTM D-88 and fitted with the proper capillary tip. The universal tip must be utilized

ASTM Thermometer

Digital Timer

Figure No. 5

Figure 6
Universal Saybolt Viscometer

when testing vegetable oils as efflux times greater than 32 seconds, but less than 1000 seconds are expected. If the Furol orifice is used, the desired accuracy can not be obtained since Furol efflux times are about one-tenth of the Universal times.

ASTM Standard mercury thermometers with subdivisions of 0.05 were used to record the sample temperature. These thermometers also served as a means of stirring the oil in the tubes.

An electric timer with 0.1 second resolution was used to measure efflux time. The line frequency was monitored to ensure accurate readings. Miscellaneous equipment such as the withdrawal tube, filter, and receiving flask are detailed in Reference [6].

2.4 Saybolt procedure

For the determination of the vegetable oil viscosity, three methods were considered, ASTM D2515-74, ASTM E102-62 (reapproved 1973), and ASTM D88-56. In light of the temperature range proposed for the study, the availability of equipment, and the expected viscosity range, method D88-56 was selected for the tests.

The procedure described in ASTM D-88 can be broken into three major areas: 1) preparation and calibration; 2) data collection; and 3) calculation.

2.4.1 Preparation and calibration

The preparation of the equipment was discussed in the previous section. ASTM D-88 and the applicable technical manuals were consulted when the apparatus was initially set up. Once the viscometer was set up and temperature was under control, the viscometer was calibrated (6) at

several intervals periodically by measuring the efflux time at 100°F (37.77°C) with a Saybolt viscosity standard oil (S-60). The correction factor, F, for the viscometer tube was obtained from:

$$F = V/t \quad (6)$$

where:

V = certified Saybolt viscosity of standard oil, sec.

t = efflux time at 100°F (37.77°C), sec.

2.4.2 Data collection

While each step of the procedure was straightforward, attention to detail was imperative to prevent the introduction of unwanted experimental errors. These errors may arise due to changes in the sample or inattention to the specific test requirements. The detailed procedure is listed in ASTM D-88 and analyzed below.

First, the sample oils were carefully segregated and kept free from contamination. Separate filters and thermometers assisted in this regard. Even more significant changes in oil properties can result from inadvertent oxidation caused by excessive preheating. The preheating of relatively small batches should preclude temperature cycling and overheating while expediting the tests.

Second, the cork stopper was properly fitted into the air chamber to prevent the escape of air (see Figure 3). The fit must be tight so that oil does not enter the air chamber when the viscosimeter is filled. Leakage into this chamber would allow approximately 4 ml of sample to enter the receiving flask without passing through the orifice. This would cause a systematic error resulting in lower viscosity values.

Third, the sample was filtered, the proper level checked, and equilibrium established for each run on each oil. Proper sample stirring with the thermometer and level adjustment with the withdrawal tube will reduce random errors by standardizing the experimental technique.

Fourth, the cork and timer were consistently operated by the same experimenter. Various experimenters will have different reaction times and this would lead to inconsistencies in the data.

2.4.3 Calculations

The measured efflux time was multiplied by the previously determined correction factor. This corrected efflux time was used to determine the kinematic viscosity by the expression in Section 2.2.

Corrections were also applied for any changes in the power supply frequency during the period of the experiment.

The major source of uncertainty noted during this phase of the project was due to the time delay between the cork removal and starting the timer.

3. Density

3.1 Introduction

Density is described as the mass of material per unit volume at any given temperature. Liquid densities are readily determined by the use of simple, but precise test equipment. Several devices are available for measuring the density of liquids, but they all determine the same two quantities: weight and volume. From these data the density can be calculated directly

$$\rho = \frac{W}{V}$$

where

ρ = density, g/ml;

W = weight, g;

V = volume, ml.

Although density is easily determined and understood, it enters into numerous thermophysical relationships and thermodynamic processes. For example, density is used to relate dynamic and kinematic viscosities as well as to help relate specific heats at constant volume and pressure. Density is often used to assist in property predictions and finds its way into a variety of empirical equations. As one case in point, liquid thermal conductivity as a function of temperature can be predicted if the density is known at each desired temperature.

It can be seen that density data are required to enable certain other properties to be calculated. In addition to this function, density data enable the consistency of other measured property data to be checked by relating them to theoretical relationships determined with the aid of density information.

True density is described as the mass of material per unit volume at a

given temperature.

$$\rho = \frac{W}{V} \quad (8)$$

where,

ρ = density in gm/cm³ or lbm/ft³

W = weight (mass) in gm or lbm

V = volume in cm³ or ft³

True density is the measured density less the bouyant effect of air. The density of the liquid is determined by the above equation, and can be measured by very simple but precise test equipment.

Density of most liquids decreases as temperature increases. Changes in pressure affect the density of liquids; the change usually being such that at a given temperature, the density of a liquid increases as the pressure increases. The increase over a very wide range of pressures (1-3400 atm), for a low density liquid (0.3 gm/cm³ at 1 atm and 15°C) is about 20% and for a dense material (water with density of 1 gm/cm³ at 1 atm and 15°C) is about 7%.

3.2 Principles of density measurement

The apparent simplicity of the density expression presented in Section 3.1 must be tempered by several considerations. First, the vapor pressure at the test temperature must be evaluated to ensure evaporation losses are acceptable. Second, the volume of the sample must be corrected for container expansion. And third, the effect of air buoyancy on sample weight must be included.

3.2.1 Vapor pressure considerations

As mentioned, evaporation losses must be considered to prevent errors from being introduced by weight changes. These changes might be caused by

evaporation during the test. For vapor pressures less than 100 torr, ASTM D1481 can be used, which specifies a Lipkin pycnometer (open type). When vapor pressures exceed 100 torr, the Bingham pycnometer of ASTM D1480 (closed type) can be utilized to extend the density data to 600 torr. Above 600 torr, precision will suffer.

In light of the above discussion, the temperatures corresponding to 100 torr and 600 torr must be evaluated for each vegetable oil. The Clausius-Clapeyron equation can be used to obtain these temperatures since the boiling point data are available (boiling point temperature T_b at a known pressure). The equation is

$$\log \left(\frac{p_2}{p_1} \right) = \frac{\Delta H_v}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (9)$$

where

p_2, p_1 = pressures,

ΔH_v = molar heat of vaporization,

R = gas constant,

T_2, T_1 = absolute temperatures.

Letting p_1 and T_1 equal the boiling point values, the unknown temperatures T_2 can be evaluated at $p_2 = 100$ torr and 600 torr if ΔH_v is known;

$$T_2 = \left(\log \left(\frac{p_2}{p_1} \right) \frac{2.3R}{\Delta H_v} + \frac{1}{T_1} \right)^{-1} \quad (10)$$

The value of ΔH_v may be available in the literature for some vegetable oils. However, if the resultant temperatures are used conservatively to establish pycnometer usage ranges, Trouton's rule can be applied for an acceptable approximation. Trouton's rule states that the molar entropy of vaporization, ΔS_v , is constant for many liquids: 21 cal/°K mol.

Therefore, ΔH_v can be determined by the relation

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad (11)$$

where T_b is known from boiling point data and ΔS_v is approximated by Trouton's rule.

These calculations result in an average oil temperature of 350°F at 100 torr and 650°F at 600 torr. These nominal values should suffice for determining the range of applicability for each pycnometer.

3.2.2 Pycnometer volume calibration

Both the Bingham and Lipkin type pycnometers require that the expansion of the pycnometer be accounted for when used over a wide temperature range. Each pycnometer is filled with freshly boiled distilled water whose density is accurately known as a function of temperature. The pycnometer is weighed and the volume is calculated. This procedure is repeated at several levels for the Lipkin bicapillary pycnometer to ensure linearity.

This entire procedure is performed at three nominal temperatures and calibration curves are plotted. The corrected volume is also calculated by

$$V_t = V_r(1 + ct) \quad (12)$$

where

V_t = volume at any temperature,

V_r = volume at reference temperature,

c = volumetric coefficient of expansion for glass

t = temperature.

This expression is used to verify the calibration curve at the lower temperatures and to extend the calibration to higher temperatures.

3.2.3 Air buoyancy effect on weight

The weight of the sample must be adjusted for the effects of air buoyancy. These effects, although slight, occur whenever weights of different densities are used on the balance. The necessary correction factor (to be added to the apparent density) is determined by

$$C = \frac{\rho_a}{0.99823} \left(0.99823 - \frac{W}{V_t} \right) \quad (13)$$

where

C = air buoyancy correction factor;

ρ_a = room air density, g/cm³;

0.99823 = density of water at 20°C, g/cm³;

W = weight in air, g.

The air density can be determined by measuring the wet bulb and dry bulb temperatures and then entering the psychrometric chart to determine specific volume. The units in the equation must be consistent.

3.3 Density equipment

The equipment for measuring liquid density is straightforward in principle and relatively easy to use. The apparatus consists of three basic components: 1) the balance, 2) the pycnometer, and 3) temperature equipment. A Mettler balance accurate to ± 0.01 mg met the weighing requirements and was used for this work.

Both pycnometers are used to accurately measure sample volumes, but they accomplish the measurements in different ways. The Lipkin pycnometer is a bicapillary type with finely graduated arms, as shown in Figure 7. Readings are accurately obtained by reading the level of the fine oil thread that appears in each arm. Volume errors are minimized since the

Figure 7
Lipkin Bicapillary Pycnometer

surface area of the fluid is kept very small by the capillary. The Bingham pycnometer on the other hand, requires that a specific level be established. This type may take the form shown in Figure 8, but frequently an overflow technique is used. In the latter case, the sample expands and overflows into a removable chamber. Level is taken as completely full. Finally, it should be noted that the Bingham type pycnometer includes a stopper. This stopper must be used if the temperature range is to be extended.

The temperature equipment consists of: thermometers and thermocouples; temperature baths; and a constant temperature oven. This 100 - 150°C oven is used to dry the pycnometers prior to weighing as well as to preheat samples.

A liquid (oil) constant temperature bath (Figure 9) was used in order to bring the samples to the required temperature. A mercury thermoregulator was used to control the bath temperature within $\pm 0.002^{\circ}\text{C}$.

The temperature sensing devices used for the density determinations were thermocouples with an ice point machine as a reference temperature. The measuring system was a digital potentiometer capable of measuring to $\pm 1 \mu\text{volts}$.

3.4 Procedure

The specific procedures for the Lipkin and Bingham methods are presented in ASTM D1481 and ASTM D1480, respectively. Once the pycnometers were properly calibrated and air buoyancy effects are evaluated, the procedure reduced to measuring the volume and weight of the sample in the applicable pycnometer.

Several techniques were utilized to minimize experimental errors.

Figure 8
Bingham Pycnometer

Figure 9
Density Apparatus

1. The cleaning procedures outlined in References [5] and [13] were strictly adhered to so that neither sample contamination nor weighing errors were introduced.
2. Equilibrium was carefully established and maintained. When the Bingham pycnometer is used, temperature overshoots may result in the loss of too much sample. When either pycnometer is used, failure to allow equilibrium to occur will result in widely scattered data.
3. Drainage was minimized in the Lipkin pycnometer by filling near to the top of the scale. Specific guidelines are detailed in Reference [5].

After the data were collected, several simple calculations are made. First, the volume at the test temperature, V_t , is calculated as described in Section 2.2.2. Next, the buoyancy correction term, C , is determined in the manner presented in Section 2.2.3. Finally, the sample density is computed using the equation

$$\rho = \frac{W}{V} + C \quad (14)$$

4. Thermal conductivity

4.1 Introduction

Thermal conductivity is a fundamental thermophysical property that is essential for almost all heat transfer applications. Reliable thermal conductivity data are needed to interpret many physical and chemical processes as well as to design the equipment for thermal processes. The data that are available for liquids in general show variations of 10% to 20% for the same material at the same conditions. The data available for vegetable oils are inconclusive at the lower temperatures and almost nonexistent at higher temperatures.

The thermal conductivity of a material can be basically described as proportionality factor relating heat flux to the product of area and temperature gradient. This is defined by the Fourier equation

$$q_x = -kA \frac{\partial T}{\partial X} \quad (15)$$

where

q_x = heat transfer rate,

k = thermal conductivity,

A = Area normal to heat flow,

$\frac{\partial T}{\partial X}$ = temperature gradient in the direction of heat flow.

The thermal conductivity defined by this equation describes the ability of the material to conduct heat.

In gases this conduction or transfer of energy is a result of elastic collisions between molecules, while in liquids it has been postulated that the energy transfer occurs due to oscillations in the lattice structure. The theory concerning liquids, however, has by no means been quantified. The difficulty in this area can be clarified by examining the relationship of viscosity and thermal conductivity.

In light of the fact that both thermal conductivity and viscosity are transport properties (energy and momentum, respectively), a definitive relationship would be expected. For gases this relationship is well known as

$$\kappa = \mu C_v \quad (16)$$

where

κ = thermal conductivity of gas,

μ = dynamic viscosity,

C_v = specific heat at constant volume.

Unfortunately, expressions of this type do not hold for liquids. Numerous attempts have been made to derive theoretical expressions for liquid thermal conductivity but none can be applied over a significant range of liquids or temperatures. Empirical equations, while useful for individual liquids or classes of liquids, have not been successful to the extent that they can be applied to liquids different from the empirical base.

Therefore, it can be seen that accurate thermal conductivity data must rely heavily on experimental techniques rather than analytical or theoretical. Once both viscosity and thermal conductivity data are obtained, comparisons and relationships can be established for vegetable oils. Guidelines for relating these properties are available in Reference [33].

As a rule, thermal conductivity for most substances decreases with temperature and follows the relationship given by

$$k = B \rho^{4/3} \quad (17)$$

where

k = thermal conductivity,

B = experimentally determined constant for each liquid,

ρ = liquid density.

Methods of predicting thermal conductivity as a function of temperature are presented and evaluated in detail in Reference [28].

4.2 Principles of the hot wire method for thermal conductivity measurements

Measurement of thermal conductivity of liquids is not a simple task, because other heat transfer modes, particularly convection, come into play. Many attempts had been made to estimate the thermal conductivity of liquids based upon microscopic properties or other properties of material such as density, boiling point, molecular weight, critical properties, and so forth.

Several basic techniques are currently available for experimentally determining the thermal conductivity of fluids. These methods include: the plane layer method, the concentric cylinder method, the hot wire method the regular regime method, and the laminar regime method. Of these, the hot wire method is the most frequently used method for liquid measurements. This technique is established as the standard method by ASTM D2717.

4.2.1 Cell construction

The hot wire method is derived from the concentric cylinder method by replacing the internal cylinder with a thin platinum wire. The wire functions as a heater and as an internal RTD. This wire is accurately located on the axis of a precision bore glass tube by platinum lead-in wires and supports. The glass cylinder diameter is made as small as practical to reduce convective heat transfer. Such a cell is illustrated in Figure 10.

Platinum leads are extended through the glass and then changed to gold for routing through the side tube. The dimensions of these leads and their location is critical since heat losses through the ends must be minimized.

In addition, the cell dimensions must be precisely determined in light of the thermal conductivity expression and sources of error developed below.

4.2.2 Thermal conductivity equation for the glass system

When the heat transfer rate is constant in a cylinder (such as the apparatus in Figure 10), the Fourier equation can be integrated along a path of constant heat flow rate and the familiar expression for radial heat transfer through right circular cylinders obtained

$$Q = \frac{2\pi Lk(t_1 - t_2)}{\ln \left(\frac{r_2}{r_1} \right)} \quad (18)$$

where

Q = heat flux,

L = heated wire length,

k = thermal conductivity,

t_1, t_2 = internal and external temperatures,

r_1, r_2 = filament and inner cylinder radii.

Therefore, if the wire temperature, external temperature, and cell dimensions are known, the thermal conductivity can be calculated directly as

$$k = \frac{Q \ln \left(\frac{r_2}{r_1} \right)}{2\pi L(t_1 - t_2)} \quad (19)$$

For the specific cell being used, however, this equation must be modified to account for the temperature drop through the glass wall. The correction is derived as follows

$$\Delta t = \Delta t_{\text{meas}} - \Delta t_{\text{gl}} \quad (20)$$

Figure 10
Thermal Conductivity Cell

where

Δt = temperature difference across sample

Δt_{meas} = measured temperature difference (wire and bath),

Δt_{gl} = temperature difference across glass cylinder.

Now Δt_{gl} is calculated by

$$\Delta t_{\text{gl}} = \frac{Q \ln \left(\frac{r_3}{r_2} \right)}{2\pi L k_{\text{gl}}} \quad (21)$$

where r_3 and r_2 are the outer and inner cylinder radii, respectively, and k_{gl} is the thermal conductivity of the glass. Substituting the relationships for the various Δt 's results in

$$\frac{Q \ln \left(\frac{r_2}{r_1} \right)}{2\pi L k} = \Delta t_{\text{meas}} - \frac{Q \ln \left(\frac{r_3}{r_2} \right)}{2\pi L k_{\text{gl}}} \quad (22)$$

Solving for k and letting

$$A = \frac{\ln \left(\frac{r_2}{r_1} \right)}{2\pi L} \text{ and } B = \frac{\ln \left(\frac{r_3}{r_2} \right)}{2\pi L k_{\text{gl}}} \quad (23)$$

results in the expression

$$k = \frac{A}{\frac{\Delta t_{\text{meas}}}{Q} - B} \quad (24)$$

This expression is in the form presented in ASTM D2717 but it must be noted that only corrected RTD temperatures should be used in Δt_{meas} . The bath temperature reading can be used directly while the filament temperature must be obtained by extrapolating the apparent resistance reading to zero current. In this manner thermometer calibration differences do not

affect the temperature difference.

4.2.3 Errors resulting from the cell

Several errors may arise due to the manner in which the cell is constructed. Many of these errors are reduced by the cell design but some can not be avoided and must be considered during data analysis. Five major sources of error are enumerated in Reference [33] and are reviewed below.

1. Heat losses by conduction: These losses occur at the ends of the wire and are reduced by proper lead design. A detailed procedure for calculating these losses is available in Reference [33].
2. Heat losses by radiation: Radiation corrections are normally made for gases and ignored for liquids.
3. Convective heat transfer: This error is reduced by minimizing the cell diameter to reduce convective currents. A correction factor based on the Grashof and Prandtl numbers of the sample is presented in Reference [33].
4. Temperature "jump" effect: A jump in temperature at the boundary occurs when the mean free path of the sample molecules becomes comparable to the sample layer thickness. This effect is inversely proportional to pressure and is usually negligible at atmospheric pressure.
5. Eccentricity: When the filament does not coincide exactly with the cylinder axis, an eccentricity exists which results in high thermal conductivity values. A correction factor is derived in Reference [33] but the use of a universal measuring microscope with one micron divisions is required to evaluate the distance between axes.

4.3 Thermal conductivity equipment

The determination of thermal conductivity by the method outlined in Reference [7] entails the measurement of two temperatures as well as the power supplied to the filament. The need for these quantities necessitates two resistance measurements and one current measurement.

The entire electronic setup for gathering these data is presented in Figure 11. The experimental equipment can be separated into three sub-systems: 1) temperature measurement, 2) current supply, and 3) current measurement.

4.3.1 Temperature measurement

The two temperatures used in computing the temperature difference are measured by different platinum RTDs. The filament temperature is obtained from the cell resistance while the bath temperature is measured by the Standard Platinum Resistance thermometer (SPRT). Errors due to differences in calibration may be introduced unless the filament is calibrated against the SPRT and the effects of self heating are eliminated. This is accomplished by taking measurements at each calibration temperature at several low bridge currents. A curve was then plotted and the actual resistance is acquired by extrapolation of the measured apparent resistance to zero current.

4.3.2 Current supply

Both the SPRT and the thermal conductivity cell use a stable current that is supplied through a bridge circuit; however, the current requirements in each case are different. The circuit shown in Figure 11 provides both the 1 ma needed by the SPRT and the variable current (up to

Figure 11
Thermal Conductivity Electric Setup

approximately 25 ma) needed by the cell. However, these cannot be supplied simultaneously. Practically, this means that the temperature measurements must be taken sequentially.

The resistance connected at E in the figure is used in conjunction with the galvanometer keys on the Mueller bridge to limit the total current to the cell. A switch is provided so that additional resistance can be inserted to further reduce the current when the SPRT is used. The proper use of the circuit should prevent excessive currents from being applied to the RTDs.

4.3.3 Current measurement

The current measurement is accomplished by measuring the voltage drop across a precision one ohm standard resistor. The current supply circuit discussed in the previous section ensures that the maximum current rating of the one ohm resistor is not exceeded. Equipment used for these measurements included:

- a) precision potentiometer, K-3 Leeds & Northrup
- b) galvanometer, Leeds & Northrup Model 2230C
- c) standard cell, unsaturated electrochemical cell containing Cd SO₄ solution provided by Epply
- d) constant voltage power supply was used, provided with frequent standardization of potentiometer
- e) low thermal emf switches

4.4 Thermal conductivity procedure

Although the procedure is fairly simple in theory it is quite difficult to implement. The requirements for cleaning the cell between samples,

equilibrating the cell with the bath, and operating null balance equipment are extremely time consuming. The procedural discussion will be broken into two areas, standardization and data collection. Calculations are straightforward once the data are collected.

4.4.1 Cell standardization

The cell was standardized prior to use by calculating the cell constants, evaluating expansion effects, and calibrating the filament as an RTD.

First, the cell constants, A and B, were calculated from the information supplied by the manufacturer. The constants were verified by taking a series of measurements with a known material in the cell.

Next, since the testing will extend to high temperatures, the effects of cell geometry changes due to expansion were evaluated. This expansion causes an error in thermal conductivity which is given in Reference [33] as

$$\frac{\Delta k}{k} = a \alpha_{gl} t_{gl} - (a+1) \alpha_{pt} t_{pt} \quad (25)$$

where

$$\frac{\Delta k}{k} = \text{error in thermal conductivity,}$$

$$\alpha_{gl}, \alpha_{pt} = \text{linear expansion coefficients of glass and platinum,}$$

$$t_{gl}, t_{pt} = \text{temperatures of glass and platinum,}$$

$$a = \frac{1}{\ln \left(\frac{r_2}{r_1} \right)} \text{ using nominal cylinder and filament radii.}$$

Finally, the filament was calibrated against the SPRT and self heating effects were considered as previously described.

4.4.2 Data collection

The procedure for obtaining the required data is detailed in ASTM D2717. Although only three parameters must be monitored, an extensive amount of equipment is needed to accurately measure them (Figure 12). The procedure is further complicated by the use of null balance devices rather than direct reading devices.

The primary consideration during data collection is the establishment of equilibrium. First, the bath must be at equilibrium as determined by constant SPRT readings. Second, the cell contents must be at equilibrium as determined by the zero current filament resistance. And third, the results must be fluctuating about a mean when readings are taken at various bridge currents. Ideally the results should be identical, as the power input to the cell and the resulting temperature difference are directly proportional. They are related by the thermal conductivity which should be constant at any specific temperature.

Figure 12
Thermal Conductivity Apparatus

5. Specific Heat

5.1 Introduction

In the design and evaluation of thermal systems, changes in properties such as enthalpy and internal energy are frequently required for various materials. These properties cannot be measured with instruments so they must be related to properties such as pressure, temperature, and volume that can be directly measured. Specific heats are defined to provide a connection between these unmeasurable and measurable properties for single phase materials. If vegetable oils are to be considered as liquid coolants, accurate specific heat data are essential.

There are three types of heat capacities defined for liquids. They are C_{pL} , C_{oL} , and $C_{sat L}$. The first represents the change in enthalpy with temperature at constant pressure; the second shows the variation in enthalpy of a saturated liquid with temperature; the third indicates the energy required to effect a temperature change while maintaining the liquid in a saturated state. The three heat capacities are defined and related as follows:

$$\begin{aligned} C_{oL} &= \frac{dH_{oL}}{dT} = C_{pL} + V_{oL} - T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{dP}{dT} \right)_{oL} \\ &= C_{sat L} + V_{oL} \left(\frac{dp}{dT} \right)_{oL} \end{aligned} \quad (26)$$

The term $\left(\frac{dP}{dT} \right)_{oL}$ represents the change in vapor pressure with temperature. Except at high temperature, all three forms of liquid heat capacities are in close numerical agreement. Most estimation techniques yield either C_{pL} or C_{oL} , although $C_{sat L}$ is often the quantity measured experimentally.

"Specific heat at constant pressure is defined in terms of enthalpy and its chosen measurable independent variables temperature and pressure"

[21]. Since the total differential of enthalpy can be expressed as

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp \quad (27)$$

and if the specific heat at constant pressure is defined as

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p \quad (28)$$

then the anticipated relationship between specific heat, enthalpy, pressure and temperature results

$$dh = C_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp \quad (29)$$

Specific heat can not be measured directly, but the above relationship suggests an indirect method if the experiment is performed at constant pressure. In this special case

$$C_p = \frac{dh}{dT} \quad (\text{at constant pressure}). \quad (30)$$

However, a change in the temperature of a substance usually causes the volume to change. Therefore, extra energy is required to overcome intermolecular forces; measurements at constant pressure conditions produce higher values than measurements at constant volume.

This fact can be used to advantage as a relationship between C_p and C_v is well known. The specific heat at constant pressure will be determined experimentally while the value at constant volume can be determined from the following equation as it is needed.

$$C_v = C_p - \alpha^2 \frac{T}{\rho \kappa} \quad (31)$$

where

T = temperature,

α = volumetric expansion coefficient,

ρ = density,

κ = compressibility.

All of these parameters are obtainable from other experimental methods.

It should be noted that since the specific heat is a function of temperature, measurements must be performed with small changes in temperature. If sufficiently small changes in temperature are used, C_p can be approximated by

$$C_p = \frac{\Delta h}{\Delta t} \quad (32)$$

in which both Δh and Δt are measured quantities. Although a "mean specific heat" is technically measured for the temperature range, these values can be plotted as point data and a curve can be fitted whose first derivative is C_p at any temperature in the range.

5.2 Principles of specific heat measurement

The experimental method used for determining the specific heats of vegetable oils involves the use of the drop calorimeter. This technique heats the oil sample to specified temperatures in a furnace and then drops the sample container into a calorimeter. Cooling is rapid as the sample gives up its heat to the calorimeter. Enthalpy is measured at the high temperature relative to the low temperature [15]. The heat effect produced by the sample in the calorimeter is measured as a rise in temperature of the calorimeter.

The practical application of this fundamental procedure necessitates the consideration of several important factors. First, the effects of vapor pressure must be resolved. Second, the heat effect ΔH must be

determined. And third, the temperature difference ΔT between the furnace T_f and calorimeter T_c must be accurately measured.

5.2.1 Vapor pressure considerations

If excessive amounts of vapor are present in the sample container, an error will result in the ΔH due to heat liberated by the condensation of the vapors. It has been determined that this effect is negligible for vapor pressures less than 100 torr [4]. At higher vapor pressures a correction is required.

The procedure for determining this correction is detailed in ASTM D2766 Appendix XI and is outlined as follows.

1. Determine the vapor pressure over the entire temperature range.
2. Determine the molar heat of vaporization as a function of pressure from the Clausius-Clapeyron equation.
3. Determine the average molecular weight.
4. Determine the volume of the sample container V_T .
5. Calculate vapor volume using the general relation

$$V_t = V_T - \frac{W}{\rho_t} \quad (33)$$

where

V_t = vapor volume at temperature t ,

V_T = total volume of container,

W = sample weight,

ρ_t = density at temperature t .

6. Determine the number of moles of vapor condensed as the difference between the moles at the initial and final temperatures. Use the ideal gas law.
7. Determine the correction factor to be subtracted from ΔH_T as

$$k = N\Delta H_V \quad (34)$$

where

k = correction factor,

N = moles of vapor condensed,

ΔH_V = molar heat of vaporization.

It should be noted that an extensive amount of information is required to make this correction. Some of the information must be predicted by using theoretical relationships, while other information may be obtained from the literature. Several of the items must be measured, some in previous experiments (density).

5.2.2 Determining heat effect, ΔH

The basis for ascertaining any of the ΔH values required by ASTM D2766 can be explained as follows: The unit under consideration (container or sample and container) is rapidly transferred from a hot furnace to the adiabatic calorimeter. The heating effect that occurs in the calorimeter is measured by the output of a thermistor bridge circuit in mv and is denoted as ΔE .

This effect is then related to ΔH by comparing it to another effect $\Delta e(\text{mv})$. This effect results from the application of an accurately known amount of heat (Q) to the calorimeter under similar circumstances. This last procedure involves the utilization of known electric power for a specified time following each calorimeter drop to determine a ΔH . The proper techniques for the calibration run are discussed in Section 5.4.

The heat effect ΔH caused by the drop can therefore be expressed as

$$\Delta H = Q \frac{\Delta E}{\Delta e} \quad (35)$$

5.2.3 Determining temperature difference

It must be realized that two temperature differences are effectively being measured. The first is the previously mentioned calorimeter temperature rise that is used in determining ΔH . This change however is measured in millivolts only.

The other temperature change, ΔT , is the difference between furnace temperature T_f and the initial calorimeter temperature T_c . This ΔT defines the range over which the measured ΔH occurs. An equation for ΔH as a function of ΔT must ultimately be determined over the entire range of determinations. This equation can then be differentiated and evaluated at any temperature within the specified range to determine C_p at that temperature.

5.3 Specific heat equipment

The standard test method for determining specific heats listed in ASTM D2766 involves the extensive use of electronic test equipment. This equipment (Figure 13) may be separated by function into four major subsystems: 1) drop calorimeter, 2) furnace control and indication, 3) heat effect monitoring, and 4) heater control and indication.

5.3.1 Drop calorimeter

The drop calorimeter portion of the apparatus consists of an adiabatic water filled jacket surrounding a tube-shaped basket that accepts the sample container. The unit is well insulated to prevent any appreciable heat losses from occurring during the short period of time when heat effects are being measured.

Figure 13
Specific Heat Apparatus

The calorimeter is fitted with an electric heater that is used to calibrate the calorimeter after each drop. This heater operates on 24 vdc and is limited to modest power outputs (much less than the drop).

The sample container is of stainless steel with a polytetrafluor-oethylene seal suitable for use at temperatures up to 260°C.

5.3.2 Furnace control and indication

A tubular furnace is mounted vertically as shown in Figure 14. The method of mounting allows the furnace to be swung directly over the calorimeter to drop the container, and then rapidly swung clear of the calorimeter. In this manner, radiation effects from the furnace are minimized.

A small catch supports the sample container in the furnace tube and an external trigger is provided. The system interrelations are shown in Figure 15.

The heat effect is then monitored by the change in a thermistor bridge output.

5.3.3 Heater control and indicating

The heater power is provided by a variable 24 vdc power supply and is determined by measuring the voltage and current at the heater. These systems are shown in Figure 15.

The energy supplied during the calibration run by the heater depends on the current, the voltage, and the length of time the heater is on. This energy, which manifests itself as heat in the calorimeter, can be expressed as

$$Q = \frac{E_1}{R_1} \left(\frac{R_{100} + R_{10,000}}{R_{100}} \right) E_{100} - E_1 \frac{t_c}{4.186} \quad (35)$$

Figure 14 Specific Heat Apparatus Block Diagram

Figure 15
Specific Heat Interrelations

where

Q = heat supplied,

E_x = voltage drop across x resistance,

R_x = resistance of x resistor,

t_c = time heater is on,

4.186 = conversion from joule to cal.

This expression is presented in Reference [4] without explanation but will be discussed below.

Referring to Figure 16 for clarity, it can be seen that R_{100} and $R_{10,000}$ form a simple voltage divider. The practical result of this technique is that only a fraction of the actual heater voltage is actually measured as E_{100} . The total supply voltage is then obtained by multiplying E_{100} by the characteristic resistance ratio. The supply voltage can then be obtained by applying Kirchoff's voltage law to the circuit. The heater voltage is found to be the difference between the supply voltage (as determined above) and the voltage drop across the one ohm standard, E_1 .

With the heater voltage known, the power can be calculated if the heater current can be found. In Figure 16, this current value is E_1/R_1 . The product of voltage and current is converted to calories by the indicated factor and multiplied by the elapsed time to produce the overall equation for the energy developed.

5.4 Specific heat procedure

The general procedure used in the specific heat testing can be broken into several distinct phases: calibration, data collection, and calculation. Each of these will be outlined and analyzed, but the specific

Figure 16

Specific Heat Voltage and Current Measurement

step-by-step procedure is listed in Reference [4] and will not be presented here.

5.4.1 Calibration

A prerequisite for making sample runs is the determination of the heat effect ΔH_C that is caused by an empty container. This value of ΔH_C depends on the physical characteristics of the container and on the furnace/calorimeter ΔT . Therefore, the ΔH_C must be determined over the entire test temperature range. Using guidelines provided in ASTM D2766, 25 determinations should be made at roughly 25°F intervals over the range. These data must be plotted accurately as ΔH_C vs. T for later use.

The value of ΔH_C is subtracted from the sample plus container enthalpy change, ΔH_T , to obtain the sample enthalpy change, ΔH_S . In addition, since both the ΔH_C and the ΔH_T drops are subject to heat losses from radiation as well as conduction, it cancels out those effects that occur during the drop.

Necessary care is taken to clean the cell with a 50% nitric acid solution. This is followed by a benzene rinse, distilled water rinse, acetone rinse and air drying.

5.4.2 Data collection

Both ΔH_C and ΔH_T were determined by the method explained in Section 5.2.2. The actual performance of the procedure necessitates a thorough understanding of the equipment and the technique.

The empty sample is brought to the desired temperature in the constant temperature furnace. The furnace temperature is monitored by a thermistor and the temperature of container by an inserted thermocouple. While the

container is equilibrating, the calorimeter temperature must be adjusted (by cooling or warming) to a temperature just below the selected initial starting point which has been fixed by the thermistor bridge (the thermistor bridge is adjusted for this temperature so that it has a zero output).

As the calorimeter approaches the initial setting temperature, the output of the bridge becomes less negative and approaches zero. Just before the output reaches zero, the temperature of the sample capsule is determined by reading the output of the copper-constantan thermocouple to the nearest $1 \mu\text{v}$. At the moment of zero output, the furnace is swung over the calorimeter and the sample container dropped. As the calorimeter equilibrates with the sample container, the "bias potentiometer" is adjusted to bring the recorded temperature trace onto the scale. This temperature (which resumes a linear drift) must be recorded. The total heat effect in millivolts is calculated by taking the algebraic sum of the initial and final potentiometer biases and the extrapolated differences in the temperature traces. A typical temperature trace is shown in Figure 17.

The characteristic initial and final drift rates illustrated by this figure are due to departure from adiabatic conditions caused by stirring and insulation heat losses. The total heat effect should be determined only after extrapolating these drift rates to time $t_{1/2}$, where half of the total effect has occurred. For heater runs, the bias should be preset such that the smaller heat effect Δe due to heater will occur over the mid-range portion of the effect caused by the drop. This technique compensates for thermistor nonlinearity and an example is provided in Reference [4].

In addition to the temperatures, heat effects, and electrical

Figure 17

Typical Calorimeter Temperature Trace

measurements described in Sections 5.2 and 5.3, the weight, W , of the sample must be known. This weight was corrected for air buoyancy as outlined in Section 3.2.3.

5.4.3 Calculations

Once the data are collected, several calculations must be performed. The necessary calculations can be summarized as: 1) preliminary, 2) deriving $\Delta H_S = f(\Delta T)$, and 3) calculating specific heat.

The preliminary calculations include the determination of ΔH_C and ΔH_T as described in Sections 5.2.2 and 5.3.3. Once these values are known the ΔH_S per gram can be found

$$\Delta H_S = \frac{(\Delta H_T - \Delta H_C)}{W} \quad (36)$$

Next, a least squares analysis is used (assuming a quadratic relationship) to derive $\Delta H_S = f(\Delta T)$. The equation takes the form

$$\Delta H_S = B\Delta T + C(\Delta T)^2 \quad (37)$$

where B and C are constants determined from a system of equations that are related to the ΔH_S and ΔT data.

Finally, the resulting equation is differentiated for ΔH_S with respect to ΔT resulting in

$$\Delta H = B + C\Delta T \quad (38)$$

The values for furnace temperature, T_f , and calorimeter temperature, T_C , are appropriately substituted for ΔT , and ΔH_S can be evaluated at T_f for any temperature in the range of experimental determinations. Extrapolation outside this range is not recommended.

6. Chemical Analyses

Samples of oil were taken throughout the study and subjected to chemical analyses. Each sample was tested for iodine number, fatty acid content, and moisture content. These data provided information related to the possible degradation of the sample during the property determinations. At the high temperatures encountered during these property experiments, it is possible that the chemical bonds of the hydrocarbons comprising these oils could break or react with other substances such as oxygen or water.

The chemical analyses were performed by an independent research laboratory. The following methods were utilized:

Iodine Absorption Number (19)	Methods 28.018 Hanus Method
Free Fatty Acid Content (19)	Method 28.029
Moisture and Volatile Matter (19)	Method 28.002

E. Experimental Results

Table 1 presents the boiling point data obtained by the procedures outlined in Section D-1. These data have been corrected for thermometer inaccuracies and for barometric pressure.

Tables 2 - 6 present the viscosity data for the four vegetable oils in terms of kinematic viscosity and Universal Saybolt seconds. These data were obtained using the procedures discussed above. The kinematic viscosity values were calculated using the equation

$$v = 2.201 \times 10^{-3} t - \frac{1.802}{t} \quad (39)$$

where:

t = corrected efflux time, sec

v = kinematic viscosity, cm^2/sec

The absolute viscosity can be calculated from

$$\mu = \rho \cdot v \quad (40)$$

where

ρ = density of liquid at corresponding temperature

μ = absolute viscosity in $\text{gm}/\text{cm sec}$ (poise)

The density data may be obtained from Tables 7 and 8 of this section. These data are expressed in gm/cm^3 for temperatures ranging from approximately 70°F (21.4°C) to 386°F (196.8°C). These data were subjected to linear regression analyses and equations derived for the correlation of the density data to temperature ($^\circ\text{C}$).

The thermal conductivity data for the vegetable oils are presented in Tables 9 through 12 for temperatures ranging from approximately 77°F (25°C) to 380°F (193°C). The thermal conductivity data are reported in $\text{cal}/\text{sec cm}^\circ\text{C}$ with appropriate conversions to $\text{Btu}/\text{hr ft}^\circ\text{F}$. The data obtained through a linear regression analysis are also reported for each oil.

In determining the specific heat relationships for the four vegetable oils studied by this research project, it was necessary to evaluate the enthalpy change of the sample at several temperatures throughout a range from 68°F (20°C) to 540°F (282°C). The least squares method was used to evaluate a quadratic equation of the form:

$$\Delta H_S = AT + BT^2 \quad (41)$$

where

ΔH_S = sample enthalpy change

T = sample temperature.

This equation was differentiated with respect to temperature in order to determine the specific heat functions. Tables 13 through 16 illustrate the sample enthalpy change data. Table 17 summarizes the specific heat data.

The data reported in Table 18 represents several chemical analyses performed on oil samples taken during one phase of the experimentation. The control samples were representative samples of oil taken before any tests were performed.

After the oil was subjected to a boiling point determination, a sample was taken and chemical analyses were performed. These data are also reproduced in Table 3. The data for experiment No. 5, soybean oil, are for a boiling point determination in an environment of air; a color change was observed when the oil was heated. The data for experiment 7 were for the determination in an environment of CO₂. The iodine number in each case is lower than the control value, with the sample from experiment 5 exhibiting the lowest value. This is an indication that oxidation may have occurred. The fact that the sample for experiment No. 7 is lower than the control value illustrates that other chemical reactions such as pyrolysis

may have also taken place. In each of the other experiments reported for the oils, the iodine value of the sample taken after the boiling point determination (in an inert atmosphere) was lower than the control.

The values given for percent moisture and percent free fatty acids are also indicative of trends observed when oils degrade due to overheating. During the boiling point determination, free fatty acids and moisture were produced, which indicated that the oils were breaking down.

The literature (1, 20, 27) was surveyed for fire, flash and fire point data for the oils under study. These data are reported in Table 19.

TABLE 1
BOILING POINT DATA*
VEGETABLE OILS

	Mean Boiling Point (Uncorrected) $t_{bp}, ^\circ\text{F}$	Barometric Pressure, mmHg	Mean Boiling Point (Corrected) $t_{bp}, ^\circ\text{F}$	Standard Error $^\circ\text{F}$
Soybean Oil	708.6 (375.9°C)	771.5	707.3 (375.2°C)	2.6°F
Cottonseed Oil	712.8 (378.2°C)	772.6	711.4 (377.4°C)	0.9°F
Peanut Oil	719.4 (381.9°C)	772.6	718.0 (381.1°C)	0.8°F
Corn Oil	707.8 (375.4°C)	770.7	706.6 (374.8°C)	0.2°F

* ANSI/ASTM D 1120-72

TABLE 2
VISCOSITY DATA
VEGETABLE OILS
SOYBEAN OIL

Oil Temperature		Universal Saybolt Viscosity		Kinematic Viscosity, ν	
$^{\circ}\text{F}$	$(^{\circ}\text{C})$	Ave., Sec	Corrected, Sec	$10^{-6}\text{m}^2/\text{sec}$	Uncertainty, %
84.0	(28.88)	219.32	209.0	45.1	0.09
96.0	(35.55)	172.00	164.0	35.0	0.13
116.6	(47.00)	120.50	115.0	23.7	0.19
137.0	(58.33)	94.13	90.0	17.8	0.27
157.0	(69.44)	75.20	71.5	13.2	0.38
176.0	(80.00)	66.08	63.0	11.0	0.48
196.0	(91.11)	56.20	53.5	8.40	0.67
216.5	(102.50)	51.00	48.5	6.96	0.85
235.5	(113.05)	46.61	44.5	5.74	1.00
254.0	(123.33)	44.40	42.0	4.95	1.30
273.5	(134.16)	41.74	40.0	4.30	1.54
294.0	(145.55)	40.20	38.5	3.80	1.80
313.5	(156.38)	38.70	37.0	3.27	2.10
337.0	(169.44)	37.45	35.5	2.73	2.60
354.0	(178.88)	36.02	34.5	2.37	3.10
372.0	(188.88)	35.15	33.5	1.99	3.80
373.0	(189.44)	34.95	33.3	1.91	3.98
380.0	(193.33)	34.92	33.0	1.80	4.20

Equation: $\ln \nu = -18.8535 + (2.64028 \times 10^3/T)$

$\nu \equiv \text{m}^2/\text{sec}$, $T \equiv ^{\circ}\text{K}$, coefficient of correlation = 0.998

TABLE 3
VISCOSITY DATA
VEGETABLE OILS
COTTONSEED OIL

Oil Temperature		Universal Saybolt Viscosity		Kinematic Viscosity, ν	
$^{\circ}\text{F}$	$(^{\circ}\text{C})$	Ave., Sec	Corrected, Sec	$10^{-6} \text{ m}^2/\text{sec}$	Uncertainty, %
83.75	(28.75)	243.06	236.0	51.2	0.08
96.26	(35.70)	188.92	185.5	39.8	0.10
117.50	(47.50)	127.65	124.0	25.8	0.17
137.12	(58.40)	97.50	95.0	19.0	0.25
157.00	(69.44)	78.30	76.0	14.3	0.35
176.00	(80.00)	67.48	65.5	11.6	0.44
196.00	(91.11)	57.38	56.0	9.10	0.60
216.00	(102.22)	51.96	50.5	7.50	0.77
235.00	(112.77)	47.61	46.5	6.36	0.95
253.40	(123.00)	44.56	43.5	5.43	1.10
273.00	(133.88)	42.41	41.0	4.63	1.40
293.00	(145.00)	40.50	39.5	4.13	1.60
311.49	(155.27)	38.98	38.0	3.62	1.90
335.00	(168.33)	37.87	37.0	3.27	2.10
352.00	(177.77)	36.28	35.0	2.55	2.80
369.75	(187.64)	34.75	34.0	2.20	3.40
376.00	(191.11)	34.35	33.5	1.99	3.80

Equation: $\ln \nu = -18.78096 + (2.64772 \times 10^3)/T$

$\nu \equiv \text{m}^2/\text{sec}$, $T \equiv ^{\circ}\text{K}$, coefficient of correlation = 0.997

TABLE 4
VISCOSITY DATA
VEGETABLE OILS
PEANUT OIL

Oil Temperature		Universal Saybolt Viscosity		Kinematic Viscosity, ν	
$^{\circ}\text{F}$	$(^{\circ}\text{C})$	Ave., Sec	Corrected, Sec	$10^{-6}\text{m}^2/\text{sec}$	Uncertainty, %
84.00	(28.88)	225.40	220.0	47.6	0.09
96.50	(35.83)	174.05	170.0	36.3	0.12
117.70	(47.60)	122.50	120.0	25.0	0.18
137.50	(58.60)	93.75	91.5	18.1	0.26
157.50	(69.72)	77.00	75.0	14.1	0.35
176.00	(80.00)	66.78	65.0	11.5	0.45
196.00	(91.11)	55.94	54.5	8.68	0.64
216.00	(102.22)	50.60	49.5	7.25	0.80
235.00	(112.77)	46.94	46.0	6.20	0.98
253.40	(123.00)	44.86	44.0	5.58	1.20
273.00	(133.88)	41.75	41.0	4.63	1.40
293.00	(145.00)	40.52	39.5	4.13	1.60
311.50	(155.27)	38.90	38.0	3.02	1.90
335.00	(168.33)	37.85	37.0	3.27	2.10
352.00	(177.77)	37.03	36.0	2.92	2.40
369.00	(187.22)	36.25	35.5	2.73	2.60
372.00	(188.88)	36.05	35.0	2.55	2.87
376.00	(191.11)	35.10	34.0	2.18	3.00

Equation: $\ln \nu = -18.421427 + (2.51102 \times 10^3)/T$

$\nu \equiv \text{m}^2/\text{sec}$, $T \equiv ^{\circ}\text{K}$, coefficient of correlation = 0.995

TABLE 5
VISCOSITY DATA
VEGETABLE OILS
CORN OIL

Oil Temperature		Universal Saybolt Viscosity		Kinematic Viscosity, ν	
$^{\circ}\text{F}$	$(^{\circ}\text{C})$	Ave., Sec	Corrected, Sec	$10^{-6}\text{m}^2/\text{sec}$	Uncertainty, %
83.50	(28.61)	225.5	215.0	46.5	0.09
96.00	(35.55)	177.4	169.0	36.1	0.12
116.50	(46.94)	127.5	121.5	26.6	0.17
136.67	(58.15)	94.9	90.5	18.0	0.27
156.50	(69.16)	80.7	77.0	14.6	0.34
176.00	(80.00)	65.5	62.5	10.8	0.48
196.00	(91.11)	58.0	55.0	8.83	0.63
216.00	(102.22)	51.4	49.0	7.10	0.83
235.00	(112.77)	47.4	45.0	5.90	1.00
253.50	(123.05)	44.9	43.0	5.30	1.20
273.00	(133.88)	41.9	40.0	4.30	1.50
283.00	(145.00)	40.7	39.0	3.96	1.70
313.50	(156.38)	39.5	37.5	3.45	2.00
337.00	(169.44)	37.8	36.0	2.92	2.40
354.00	(178.88)	36.4	35.5	2.73	2.60
372.24	(189.02)	36.0	34.5	2.37	3.00
378.00	(192.22)	35.5	34.0	2.18	3.40

Equation: $\ln \nu = -18.55493 + (2.55349 \times 10^3)/T$

$\nu \equiv \text{m}^2/\text{sec}$, $T \equiv ^{\circ}\text{K}$, coefficient of correlation = 0.997

TABLE 6

SUMMARY

VISCOSITY EQUATIONS OF CORRELATION

VEGETABLE OILS

 ν , m²/sec

T, °K

Soybean Oil

$$\ln \nu = -18.8535 + 2.64028 \times 10^3 (T)^{-1}$$

coefficient of correlation = 0.998

Cottonseed Oil

$$\ln \nu = -18.78096 + 2.64772 \times 10^3 (T)^{-1}$$

coefficient of correlation = 0.997

Peanut Oil

$$\ln \nu = -18.421427 + 2.51102 \times 10^3 (T)^{-1}$$

coefficient of correlation = 0.995

Corn Oil

$$\ln \nu = -18.55493 + 2.55349 \times 10^3 (T)^{-1}$$

coefficient of correlation = 0.997

TABLE 7
DENSITY DATA
VEGETABLE OILS

		gm/cm ³			
Temperature °F (°C)		Soybean Oil	Cottonseed Oil	Peanut Oil	Corn Oil
70.60	(21.44)	0.91849	-----	0.91266	0.92176
81.36	(27.42)	0.91338	0.90756	0.91248	0.91668
107.40	(41.89)	0.90360	0.90210	0.90314	0.90473
120.00	(48.89)	0.90185	0.89802	0.89844	0.90276
140.00	(59.99)	0.89068	0.88695	0.89246	0.89362
160.07	(71.15)	0.88516	0.87981	0.88497	0.88531
180.16	(82.31)	0.87654	0.87678	0.87920	0.87824
200.08	(93.38)	0.87115	0.86436	0.86838	0.87114
220.06	(104.48)	0.86155	0.85961	0.86112	0.86298
240.17	(115.65)	0.85708	0.85472	0.85623	0.85758
262.40	(128.00)	0.85320	0.85165	0.85419	0.85351
288.81	(142.67)	0.84478	0.84337	0.84542	0.84498
304.32	(151.29)	0.83843	0.83779	0.84007	0.84057
323.74	(162.08)	0.83425	0.83271	0.83635	0.83422
344.86	(173.81)	0.82559	0.82357	0.82753	0.82700
365.74	(185.41)	0.82163	0.81974	0.82257	0.82214
386.28	(196.82)	0.81464	0.81355	0.81553	0.81620

TABLE 8
DENSITY DATA
VEGETABLE OILS

ρ , gm/cm³ T, °C

Soybean Oil

$$\rho = -5.847 \times 10^{-4} T + 0.92755$$

coefficient of correlation = 0.998

Cottonseed Oil

$$\rho = -5.583 \times 10^{-4} T + 0.92180$$

coefficient of correlation = 0.995

Peanut Oil

$$\rho = -5.611 \times 10^{-4} T + 0.92497$$

coefficient of correlation = 0.997

Corn Oil

$$\rho = -5.937 \times 10^{-4} T + 0.92976$$

coefficient of correlation = 0.997

TABLE 9
THERMAL CONDUCTIVITY DATA
VEGETABLE OILS

SOYBEAN OIL

Temperature		Thermal Conductivity, k
°F	(°C)	10^{-4} cal/sec cm °C
77.56	(25.31)	0.8268
92.68	(33.71)	1.0901
136.02	(57.79)	2.0670
168.87	(76.04)	3.3352
189.77	(87.65)	3.5178
216.60	(102.55)	3.5895
234.05	(112.25)	3.6722
257.00	(125.00)	4.4740
282.74	(139.30)	4.8625
320.36	(160.20)	5.1105
359.96	(182.20)	7.6408

Equation: $k = 0.216476 \times 10^{-4} + (3.494014 \times 10^{-6})T$

$k \equiv \text{cal/sec cm } ^\circ\text{C}$ $T \equiv ^\circ\text{C}$

coefficient of correlation = 0.970

$(\text{cal/sec cm } ^\circ\text{C}) \times 241.90 = (\text{Btu/hr ft } ^\circ\text{F})$

TABLE 10
THERMAL CONDUCTIVITY DATA
VEGETABLE OILS

COTTONSEED OIL

Temperature		Thermal Conductivity, k
°F	(°C)	10^{-4} cal/sec cm °C
77.00	(25.00)	2.8633
92.86	(33.81)	3.1808
117.75	(47.64)	3.8204
144.21	(62.34)	4.2120
188.55	(86.97)	5.1714
199.85	(93.25)	5.3286
214.81	(101.56)	5.6284
234.46	(112.48)	5.9379
257.36	(125.20)	6.4818
281.77	(138.76)	6.9716
323.37	(161.87)	7.1058
359.92	(182.18)	8.5410
376.05	(191.14)	9.4423

Equation: $k = 1.9600 \times 10^{-4} + (3.61218 \times 10^{-6})T$

$k \equiv \text{cal/sec cm } ^\circ\text{C}$ $T \equiv ^\circ\text{C}$

coefficient of correlation = 0.991

$(\text{cal/sec cm } ^\circ\text{C}) \times 241.90 = (\text{Btu/hr ft } ^\circ\text{F})$

TABLE 11
THERMAL CONDUCTIVITY DATA
VEGETABLE OILS

PEANUT OIL

Temperature		Thermal Conductivity, k
°F	(°C)	10^{-4} cal/sec cm °C
77.34	(25.19)	2.2495
99.21	(37.34)	2.8595
115.25	(46.25)	4.3320
136.20	(57.89)	4.4322
159.62	(70.90)	4.5143
188.49	(86.94)	4.9888
209.66	(98.70)	5.2728
234.10	(112.28)	5.4999
234.52	(112.51)	5.7676
265.32	(129.62)	8.2012
326.21	(163.45)	9.2963
337.59	(169.77)	9.3717
359.98	(182.21)	10.3671
365.92	(185.51)	10.6479

Equation: $k = 1.04388 \times 10^{-4} + (4.94985 \times 10^{-6})T$

$k \equiv \text{cal/sec cm } ^\circ\text{C} \quad T \equiv ^\circ\text{C}$

coefficient of correlation = 0.977

$(\text{cal/sec cm } ^\circ\text{C}) \times 241.90 = (\text{Btu/hr ft } ^\circ\text{F})$

TABLE 12
THERMAL CONDUCTIVITY DATA
VEGETABLE OILS

CORN OIL

Temperature		Thermal Conductivity, k
°F	(°C)	10^{-4} cal/sec cm °C
77.00	(25.00)	2.5483
92.86	(33.81)	2.8797
115.39	(46.33)	3.3368
131.65	(55.36)	3.6910
159.62	(70.90)	3.9911
181.87	(83.26)	4.7424
207.81	(97.67)	5.2837
234.82	(112.68)	6.3273
263.16	(128.42)	6.4410
290.68	(143.71)	7.0165
326.17	(163.43)	7.7875
338.00	(170.00)	8.0059
358.45	(181.36)	8.2255

Equation: $k = 1.6074 \times 10^{-4} + (3.7640 \times 10^{-6})T$

$k \equiv \text{cal/sec cm } ^\circ\text{C}$ $T \equiv ^\circ\text{C}$

coefficient of correlation = 0.996

$(\text{cal/sec cm } ^\circ\text{C}) \times 241.90 = (\text{Btu/hr ft } ^\circ\text{F})$

TABLE 13
SPECIFIC HEAT DATA
VEGETABLE OILS

Temperature		ΔH_s cal/gm
$^{\circ}\text{F}$	$(^{\circ}\text{C})$	
100.00	(37.77)	16.7300
175.30	(79.61)	36.6620
248.00	(120.00)	57.2500
321.04	(160.58)	79.3000
392.00	(200.00)	102.0300
428.90	(220.50)	114.3600
520.39	(271.33)	146.4025

$$\text{Equation: } H_s = 0.42758 T + 0.0004128 T^2$$

$$\Delta H_s \equiv \text{cal/gm} \quad T \equiv ^{\circ}\text{C}$$

TABLE 14
SPECIFIC HEAT DATA
VEGETABLE OILS

Temperature		ΔH_s cal/gm
$^{\circ}\text{F}$	$(^{\circ}\text{C})$	
100.00	(37.77)	18.1476
175.30	(79.61)	39.2069
248.00	(120.00)	60.4726
321.04	(160.58)	83.2014
392.00	(200.00)	105.9762
428.90	(220.50)	118.3002
520.39	(271.33)	149.6866

TABLE 15

SPECIFIC HEAT DATA
VEGETABLE OILS

PEANUT OIL

Temperature °F (°C)		ΔH_s cal/gm
100.00	(37.77)	19.1538
175.30	(79.61)	41.3563
248.00	(120.00)	64.4213
321.04	(160.58)	88.4275
392.00	(200.00)	112.8643
428.90	(220.50)	126.1511
520.39	(271.33)	160.0836

$$\text{Equation: } H_s = 0.4936818 T + 0.0007114 T^2$$

$$\Delta H_s \equiv \text{cal/gm} \quad T \equiv ^\circ\text{C}$$

TABLE 16

SPECIFIC HEAT DATA
VEGETABLE OILS

CORN OIL

Temperature °F (°C)		ΔH_s cal/gm
100.00	(37.77)	17.5028
175.30	(79.61)	38.2155
248.00	(120.00)	59.5305
321.04	(160.58)	82.2516
392.00	(200.00)	105.5767
428.90	(220.50)	118.1948
520.39	(271.33)	150.9228

$$\text{Equation: } H_s = 0.4483933 T + 0.0003975 T^2$$

$$\Delta H_s \equiv \text{cal/gm} \quad T \equiv ^\circ\text{C}$$

TABLE 17

SPECIFIC HEAT DATA

VEGETABLE OILS

SPECIFIC HEAT EQUATION*

C† = Specific Heat, cal/gm °C

T = temperature, °C

Soybean Oil

$$C = 0.4276 + 0.0008 T$$

Cottonseed Oil

$$C = 0.4690 + 0.0006 T$$

Peanut Oil

$$C = 0.4937 + 0.0007 T$$

Corn Oil

$$C = 0.4484 + 0.0008 T$$

*Equations are for the temperature range 20°C to 280°C

† To convert from cal/gm °C to Btu/lbm °F, multiply values calculated from the equations above by 1.00

TABLE 18

CHEMICAL ANALYSIS

OF VEGETABLE OIL

SAMPLES

		% Moisture	% Free Fatty Acid	Iodine Number
Soybean Oil	Control	0.32	0.50	127
	Exp. No. 5	2.80	33.00	75
	Exp. No. 7	0.81	13.7	85
Cottonseed Oil	Control	0.07	0.28	81
	Exp. No. 12	2.30	5.40	62
Peanut Oil	Control	0.05	0.28	85
	Exp. No. 19	3.60	9.30	67
Corn Oil	Control	0.01	0.28	108
	Exp. No. 24	0.39	2.8	82

TABLE 19
SMOKE, FLASH AND FIRE POINTS
SELECTED VEGETABLE OILS

Oil	Smoke Point	Flash Point	Fire Point
Corn	352°F (178°C)	562°F (294°C)	655°F (346°C)
Cottonseed	420 - 450°F (216 - 232°C)	615 - 625°F (324 - 329°C)	670 - 685°F (354 - 363°C)
Peanut	450°F (232°C)	625°F (329°C)	685°F (363°C)
Soybean	410°F (210°C)	603°F (317°C)	670°F (354°C)

F. Discussion of Results/Statistical Analysis

1. Introduction

Though present in many parts of a plant, fats generally occur in the greatest quantity either in the pulp of the fruit (fruit-coat fat) and/or in the seed. There are several differences in the properties of the constituents of these fatty compounds or fatty acids. Vegetable oils, which are vegetable fats in liquid form at room temperature, are classified according to their major component acids. These classes are generally defined as follows:

Class 1: It is thought that oleic and linoleic acid, together, make up at least 80% of all fatty acids produced in seed fats. Palmitic acid accounts for 7-8% and all other familiar acids such as linoleic, elaeostearic, ricinoleic, erucic, etc. constitute the remainder.

There is a subclassification in this group depending upon which component predominates the others. They are:

- a) "drying" (linolenic and linoleic acids)
- b) "semi-drying" (linolenic and oleic acids)
- c) "non-drying" (oleic and palmitic acids).

Class 2: This group is divided into two subgroups:

- a) In the first subgroup, the additional acid is characteristic of an entire plant family (or nearly so).
- b) The second subgroup is restricted to the species of one genus or to an even narrower range; that is, to one or two species.

2. Structure and Composition of Oils

As mentioned, fats and oils are water-insoluble substances of plant (or animal) origin which consist predominantly of glyceryl esters of fatty acids or triglycerides. Structurally, triglyceride is the condensation product of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water and one molecule of a triglyceride:

A mixed triglyceride may have three different isomers depending upon which fatty acid is in the middle position, while a mixed triglyceride, with two different fatty acids, has four isomer forms.

Having discussed the component acids of fats, it is worth mentioning the way in which these acids combine in the glyceride molecules. It is shown that, with few exceptions, despite the wide variation in the components of acids of fats from vegetable or even animal origin, these all are woven into triglycerides in one way or another. Several patterns of acid distribution have been suggested and among them are:

- a) Random distribution: distribution of acids among the glycerides is by chance (corn oil, soybean oil).
- b) Even distribution: each acid present is distributed evenly among the glyceride molecules (most of the vegetable seeds fat).
- c) Partial random distribution (corn oil).

d) Restricted random distribution.

The molecular weight of the glycerol portion ($C_3H_8O_3$) of a triglyceride molecule is 41. The combined molecular weight of a fatty acid radicals ($RCOO$), comprising the remainder of a molecule, will vary with different oils from about 650 to 970. Thus, fatty acids contribute from 94 to 96% of the total weight of the molecule. Since fatty acids are present in large quantities, they comprise the most reactive portion of the fats.

Most of the fatty acids contain an even number of carbon atoms. They differ mainly in the number of carbon atoms in their chain and by the number and position of double bonds between the carbon atoms.

The fats which have no double bonds are called "saturated". Many of the unsaturated fatty acids have more than one double bond in their structure, for example, Linoleic acid ($C_{18}H_{32}O_2$) with two double bonds may be found in cottonseed oil.

Some vegetable oils contain a cyclic compound named STEROL which has the structure shown below:

STEROL

Table 20 below shows the percent of this compound in the different oils.

TABLE 20

Percent of STEROL in Vegetable Oils

Corn Oil	0.58 - 1%
Cottonseed Oil	0.26 - 0.31
Peanut Oil	0.19 - 0.25
Soybean Oil	0.15 - 0.38

The composition of the four major oils, subject of this research, are listed in Tables 21 through 24.

TABLE 21
Representative Composition of Soybean Oil

Iodine value	135.8
Saturated acids, %	14.1
Composition from thiocyanogen analysis	
Oleic acid, %	26.0
Linoleic acid, %	49.4
Linolenic acid, %	10.6
Composition by spectrophotometric analysis	
Saturated acids, %	14.0
Oleic acids, %	23.0
Dienoic acids, %	55.1
Trienoic acids, %	8.0

TABLE 22
Representative Composition of Cottonseed Oil

Iodine value	104.7
Saturated glycerides	27.5
Oleic glycerides	22.9
Linoleic glycerides	49.2

TABLE 23
Representative Composition of Peanut Oil

Iodine value	95.1
Fatty acid composition	
(wt. % of total fatty acid)	
Palmitic	9.5
Stearic	4.8
C ₂₀ , C ₂₂ , C ₂₄	7.9
Oleic	44.9
Linoleic	32.9
Component glycerides	
(mol. %)	
3 unsaturated groups	41.0
2 linoleic groups	14.7
1 linoleic group	64.0
No linoleic group	21.3
3 oleic groups	2.0
2 oleic groups	40.0
1 oleic group	53.0
No oleic group	5.0

TABLE 24

Representative Composition of Corn Oil

Iodine value	122.2
Composition of fatty acids	
Weight % total fatty acids	
Myristic	0.6
Palmitic	12.7
Stearic	3.0
C ₂₀ -C ₂₂ saturated acids	0.6
Total saturated acids	17.6
Oleic	0.8
Linoleic	51.6
Linolenic	0.8
Acids above C ₁₂	1.7

The iodine value is a measure of the unsaturation of the oils and is expressed in terms of the number of centigrams of iodine per gram of sample (percentage absorbed by weight of iodine absorbed). As illustrated by Table 18, these values ranged from 81 to 127 for the oils studied. The literature reports values ranging from 95 to 136. Table 25 below illustrates this comparison.

TABLE 25

Iodine Values

	Experimental Iodine Value	Range of Published Values
Soybean	127	117 - 141
Cottonseed	81	99 - 113
Peanut	85	84 - 102
Corn	108	103 - 128

In all cases but for cottonseed, the experimental oils yielded iodine values falling in the range of published values. It was noted in the literature that a representative iodine value for cottonseed oil which has been hydrogenated is 78. It maybe that the experimental oil sample was slightly hydrogenated.

As might be expected, the composition of a vegetable oil affects its thermophysical properties. In fact, some researchers have not only correlated these properties to temperature but also iodine values. Because of the time limitation on this project, only one iodine value (that of the experimental oil) was considered.

As was mentioned earlier in this report, it was observed early in the research that the vegetable oils were sensitive to heat in an atmosphere of air. During the boiling point determination, the oils changed color and spontaneous ignition of the vapors occurred. Table 18 illustrated the change in iodine value during the boiling point determinations. The decrease in iodine value (indicating that double bonds are being saturated) and the increase in % free fatty acid and moisture both indicate that changes,

due to heating and the presence of oxygen, are taking place. Subsequent experiments (e.g. No. 7, Table 18) under a carbon dioxide blanket illustrated that even in a substantially inert atmosphere, the oils experienced a decrease in iodine number and an increase in free fatty acids and moisture.

Several chemical reactions may have taken place, including oxidation, isomerization, polymerization and pyrolysis. These reactions can occur spontaneously with the addition of heat. The subsequent changes in chemical composition can affect the heat transfer properties of the vegetable oils as well as the properties related to pumping power.

Oxygen reacts more readily with unsaturated organic acids than with saturated acids. Since the oils are 70 - 80% unsaturated acids, this is certainly a potential problem. At low temperatures, oxidation will occur at a relatively slow rate. This rate of oxidation will remain fairly low for some period of time, called the induction period. After the induction period, oxidation rates will increase greatly. The length of the induction period is halved for every 18°F (10°C) increase in temperature.

In the presence of atmospheric oxygen (auto oxidation) several compounds may be formed by the oxidation process. These include peroxides, enediols, poxides and moloxides.

There are two methods of reducing the oxidation of these oils: 1) heat the oil in a closed system or under an inert atmosphere and 2) use natural antioxidants such as lecithin ($C_{42}H_{48}O_9PN$) or gossypol (29). Typically a very small quantity of gossypol will have dramatic effects on reducing the rate of oxidation. The effect of concentration of lauryl caffeate on the oxidation of corn oil is illustrated in Figure 19.

Generally, oxidation reactions would be expected to break the oils into lower molecular weight substances; however, oxidation is also accompanied by

Oxygen uptake at 90°C of (a) corn oil, (b) corn oil plus 0.02% lauryl caffeate, (c) corn oil plus 0.10% lauryl caffeate

Figure 19

polymerization which has the opposite effect. The overall effect is reported to result in an increase in viscosity (8). Polymerization can occur spontaneously within vegetable oils with the addition of sufficient heat. In the temperature range of 482 to 572°F (250 to 300°C) the rate of polymerization increases rapidly. This thermal polymerization can result in the formation of a variety of organic molecules, including ring or cyclic types. Ralston (27), Anderson and Porter (2) elaborate on several of these polymerization reactions.

Isomerization is another reaction associated with heating. This reaction results in a rearrangement of atoms within an organic molecule so that the chemical formula does not change. This may involve a change as simple as moving the location of a double bond. Eckey (16) cites experimental evidence that heating oleic acid to 356°F (180°C) will result in approximately 8% isomerization; thereby changing the thermophysical properties of the vegetable oil containing substantial percentages of oleic acid.

The term generally used to describe the decomposition of oils due to the addition of heat is pyrolysis. In some vegetable oils, pyrolysis occurs at temperatures as low as 572°F (300°C). At temperatures above 752°F (400°C), this decomposition is extensive, resulting in the production of compounds such as ketones, water, and miscellaneous gaseous and liquid hydrocarbons. Egloff and Morrell (17) obtained a 54% yield of gasoline through pyrolysis of cottonseed oil.

3. Boiling Points

The pressure corrected boiling points observed for these vegetable oils were in the range of 707-718°F (375-381°C). Considering the standard errors for these data, the boiling points of the four oils were very close to each other. Neglecting all other properties of the oils, this range of temperatures would indicate that these oils would be satisfactory as high temperature solar system coolants. These data may be compared to water with a normal boiling point of 212°F (100°C) or a 50 weight percent aqueous ethylene glycol solutions with a boiling point of approximately 225°F at a pressure of atmosphere (see Figure 20). Obviously the decision to use these oils as heat transfer media cannot be based on boiling point data alone. Other thermophysical properties must be considered.

B Curves = Boiling Point vs Composition
C Curves = Condensation Temperature vs Composition

Figure 20 Boiling Point
and Condensation of Aqueous
Solutions of Ethylene Glycol

4. Viscosity

Tables 2 through 6 indicated viscosities for the four vegetable oils over a range of temperatures from 84°F(28.9°C) to 380°F(193.3°C). In all cases the viscosities decreased with temperature. The correlation equations were summarized in Table 6. As illustrated by this table, the coefficients of correlation were very good. For comparison the viscosities of water and a water/ethylene glycol solution are illustrated in Table 26. These data will be used later in the report to compare heat transfer characteristics.

TABLE 26
VISCOSITIES
WATER AND WATER - ETHYLENE GLYCOL SOLUTIONS
50% by Weight

Temperature	Water-Ethylene Glycol Solution	Water
°F (°C)	Viscosity, 10^{-6} m /sec	Viscosity, 10^{-6} m /sec
0 (-17.8)	17.58	-
25 (-3.9)	8.37	-
50 (10.0)	4.86	1.20
75 (23.9)	3.10	0.90
100 (37.8)	2.09	0.70
125 (51.7)	1.53	0.56
150 (65.6)	1.16	0.43
175 (79.4)	0.88	0.37
200 (93.3)	0.68*	0.31*

* extropolated values

The viscosities of the water/glycol solution and water are considerably lower than those values noted for the vegetable oils in the same temperature range. The effects of these differences will be quantified later in this report when pumping energy requirements and heat transfer rates are discussed.

5. Density

The densities of the oils are illustrated in Table 7. There are minor differences in density but for the purpose of engineering calculations, these differences will not be significant. Table 27 below illustrates densities of water and the water/glycol 50-50 solution. In all cases the densities of the oils were less than those densities of water and the water/glycol solution at the same temperature.

TABLE 27

DENSITY DATA*

gm/cm³

Temperature	50% by Weight	Water
°F (°C)	Water-Ethylene Glycol Solution	
0 (-17.8)	1.0809	-
25 (-3.9)	1.0749	-
50 (10.0)	1.0689	0.9997
75 (23.9)	1.0629	0.9973
100 (37.8)	1.0539	0.9930
125 (51.7)	1.0449	0.9872
150 (65.6)	1.0369	0.9806
175 (79.4)	1.0279	0.9718

* to convert to lb/gal multiply by 8.34

6. Thermal Conductivity

Thermal conductivity data were presented in Tables 9 through 12. The lowest thermal conductivities were recorded for soybean oil. Cottonseed oil and corn oil had similar conductivities. Peanut oil was observed as having the highest thermal conductivity at temperatures in excess of 50°C. For comparison purposes, thermal conductivities of water and a 50-50 mixture of ethylene glycol and water are given in Table 28.

TABLE 28

THERMAL CONDUCTIVITY

10⁻⁴ Cal/Sec cm°C

Temperature	50% by Weight	Water
°F (°C)	Water-Ethylene Glycol Solution	
0 (-17.8)	10.1	-
25 (-3.9)	10.1	-
50 (10.0)	10.0	14.4
75 (23.9)	-	14.7
100 (37.8)	9.96	15.0

TABLE 28 (Cont.)

Temperature	50% by Weight	Water
°F (°C)	Water-Ethylene Glycol Solution	
125 (51.7)	-	15.3
150 (65.6)	9.9	15.6
175 (79.5)	-	15.9
200 (93.3)	9.8	16.2

* to convert to Btu/hr ft°F multiply by 241.9

It is obvious from these data that the thermal conductivities of water and ethylene glycol/water solutions are higher than those of the vegetable oils at temperatures less than 200°F. At higher temperatures the vegetable oil conductivities rise to values that would exceed the water/glycol conductivity, assuming the water/glycol values continued their downward trend.

7. Specific Heat

The specific heats of the vegetable oils are presented in Table 17. These data are summarized below for the temperature range 0°F (-17.8°C) to 200°F (93.3°C). Corresponding data for water and a 50% solution of ethylene glycol in water are also illustrated for comparison.

TABLE 29

SPECIFIC HEAT DATA

Cal/gm°C

Temperature	Peanut	Soybean	Corn	Cottonseed	Water/Glycol	Water
°F (°C)	Oil	Oil	Oil	Oil	Solution	
0 (-17.8)	-	-	-	-	0.730	-
25 (-3.9)	-	-	-	-	0.753	-
50 (10.0)	-	-	-	-	0.775	1.002
75 (23.9)	0.510	0.447	0.468	0.483	0.795	0.999
100 (37.8)	0.520	0.458	0.479	0.492	0.815	0.999
125 (51.7)	0.530	0.469	0.490	0.500	0.830	0.999
150 (65.6)	0.540	0.480	0.501	0.508	.845	1.001
175 (79.5)	0.549	0.491	0.512	0.517	0.858	1.003
200 (93.3)	0.559	0.502	0.523	0.525	0.870	1.006

As is evident by inspecting the data, the specific heats of the vegetable oils are less than those of water and ethylene glycol-water solutions at comparable temperatures. However, the specific heats of the oils are in a range which would still justify consideration as heat transfer and storage media.

8. Chemical Stability

Several sources of information were considered in studying the chemical stability of the vegetable oils. These included literature searches and experimental work.

The literature (1, 20, 27) reported various combustion properties of the vegetable oils including smoke, flash and fire points. As these data illustrate, there are health and safety hazards in handling these oils at temperatures in excess of 400°F (204°C). If a leak should develop in a fluid line or storage vessel and the oils come in contact with the atmosphere, then there would be a possibility of smoke production or auto-ignition and fire. These conditions were observed during the initial stages of this project when boiling points were being determined. Unless there was a blanket of inert gas kept on the oils, smoke was produced and in some cases the volatile vapors from the oil would flash in the neck of the reflex condenser.

An attempt was made to qualify the effects of high temperature on oil stability. Table 18 illustrates the results of chemical analyses performed on oil samples taken during the boiling point determinations. As discussed previously, there was a significant change in iodine number when the oils were heated to boiling. This change was observed whether or not there was an inert atmosphere over the oil. This indicates that chemical reactions (possibly pyrolysis) other than oxidation may have been taking place.

The funding and time constraints on this project did not allow for long term stability testing. This work, however, is being continued and the

results should be available in a future report. In conjunction with the stability work, corrosion studies are being made to determine the capability of the oils with common metals used in solar systems. Problems have already been noted with the use of copper. This will be substantiated along with tests on aluminum and steel.

9. Corrosion

Observations made at the laboratory indicate that the oils maybe mildly corrosive to copper and iron. In one case the copper seemed to complex with the oils, causing the oils to break down with the ultimate production of a sticky lacquer-like material. Due to the complexity of the thermophysical property experimental work, the laboratory was not able to substantiate the corrosion phenomena. Work will continue in this area and this work will hopefully provide additional information related to corrosion and material capability.

10. Transport Phenomena

A preliminary study was performed to determine the fluid flow and heat transfer characteristics of the oils in a design situation. These calculations will be verified later in a series of experiments to be performed at the University of Florida Energy Research and Education Park.

The following case study was used:

1. A system comprised of 100 feet (30.48 meters) of 3/4" (1.9 cm) ID copper tubing was selected.
2. A maximum velocity of 4 ft/sec (1.22 m/sec) was assumed. This set the flow rate at $0.01227 \text{ ft}^3/\text{sec}$ ($3.47 \times 10^{-4} \text{ m}^3/\text{sec}$).

Calculations were conducted for a fluid temperature of 200°F (93.3°C) and 300°F (148.9°C). An iterative calculation using the Newton-Raphson rearrangement of the Colebrook equation was used to calculate head loss in the pipe. The following results were obtained:

TABLE 30

Head Loss/Heat Transfer Data
200°F

	Peanut Oil	Cottonseed Oil	Corn Oil	Soybean Oil	Water	50% glycol/ water solution
Pipe Length, ft.	100	100	100	100	100	100
Pipe ID, ft.	.0625	.0625	.0625	.0625	.0625	.0625
Flow rate, ft ³ /sec	.01227	.01227	.01227	.01227	.01227	.01227
Velocity, ft/sec	4	4	4	4	4	4
Head loss, ft.	18.1	18.3	18.1	17.9	7.9	9.3
Heat Transfer Coefficient Btuh/ft ² °F	150.6	140.6	139.1	111.2	1471.0	749.8

TABLE 30, Cont'd.

300°F

	Peanut Oil	Cottonseed Oil	Corn Oil	Soybean Oil	Water	50% glycol/ Water Solution
Pipe Length, ft.	100	100	100	100	100	100
Pipe ID, ft.	.0625	.0625	.0625	.0625	.0625	.0625
Flow rate, ft ³ /sec	.01227	.01227	.01227	.01227	.01227	.01227
Velocity, ft/sec	4	4	4	4	4	4
Head Loss, ft.	14.4	14.2	14.2	13.9	7.3	8.5
Heat Transfer Coefficient, Btu/h/ft ² °F	277.9	252.4	251.3	216.5	1725.6	917.1

In real applications velocities would be set at lower values (1-2 ft/sec) but these data represent the worst situation as far as head loss is concerned and the best situation in the case of convection heat transfer. As is evident from these data, the head losses for the vegetable oils under these conditions are twice those realized with water or glycol/water solutions. The heat transfer coefficients are approximately 80% lower than the values for water and glycol/water solutions. In simple terms it will take much more pumping power with the vegetable oils to achieve comparable heat transfer rates to those of water and water/glycol solutions.

F. Summary

This project has resulted in the development of comprehensive data for the thermophysical properties of vegetable oils for temperatures ranging from 77°F (25°C) to approximately 400°F (204°C). Because of the low fire and flash points of these oils, it was not possible to expand the scope of this project to higher temperatures. However, work is underway to develop the instrumentation necessary to explore those data at higher temperatures. It may be that because of the chemical instability of these oils at higher temperatures that it will not be a fruitful venture to exceed temperatures of 400°F (204°C).

For the temperature range studied, the oils seem to be fairly compatible (noncorrosive) with steel although there were problems observed with copper. This will be substantiated in future studies.

The pumping power required to obtain heat transfer coefficients comparable to those which can be obtained with the use of water or glycol/water solutions at the same conditions is much higher for the vegetable oils. However, there is one distinct advantage due to lower operating pressures. At 300°F water has a vapor pressure of 4.56 atmospheres and a 50% glycol/water solution has a vapor

pressure over two atmospheres. This would allow low pressure operation of solar collection subsystems. Because of the flammability of these oils, they would have to be used in air free, closed systems or in systems under inert gas pressure. Carbon dioxide proved to be a suitable gas for this purpose in the research performed at the University of Florida.

In general, the vegetable oils provide us with a renewable, inexpensive coolant for high temperature solar systems. There are certain advantages as well as disadvantages in using these oils. Actual experience with these oils will provide the additional information required to determine the long range effectiveness of vegetable oils as liquid coolants. Work is underway to construct a pilot scale system utilizing one of the oils as a coolant. The research will also investigate the use of these oils in high temperature storage systems.

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