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Experimental Determination of the Density, Viscosity and Surface Tension of Three Commercial Biodiesel Fuels up to 300°C

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Abstract

Data is unavailable for the physical properties of biodiesel fuels at temperatures above 100°C due to the limitation of conventional measurement equipment to operate at high temperatures. This lack of valid data gives rise to possible inaccuracies in simulating the atomization of biodiesel fuels in engines. This paper describes the equipment used in measuring the density, viscosity and surface tension at temperatures up to 300°C and gives some data.

A capacitance type liquid level meter was designed to measure the increase in volume of 50ml of the same three biodiesel fuels over the temperature range of 20°C to 300°C. Derived densities were found to be linear with temperature over the measured range. Used in this fashion, the level meter can be considered a precise densitometer with a repeatability to within 1%.

A modified Saybolt viscometer was used to measure the efflux times for 60mL of methyl esters of canola and soy and ethyl esters of fish-oil. The Modified Saybolt Viscometer was calibrated using a standard oil and can be considered an accurate and precise viscometer with an accuracy of 95% and repeatability to within 2%.

The surface tension of biodiesel fuels at temperatures up to 260°C was obtained using an apparatus developed for use with the method of pendant drop tensiometry and Axisymmetric Drop Shape Analysis – Profile (ADSA-P). At 260°C the surface tension of the methyl esters dropped to about a third of the value at 20°C, whereas the fish oil ethyl esters only dropped to about 2/3 of the value at 20°C. Pendant drop tensiometry combined with ADSA-P can be considered an accurate and precise method with an average accuracy of 95% and repeatability to within 5%.

INTRODUCTION

Fuel atomization is dependent on fuel properties such as density, viscosity and surface tension (Allen & Watts, 1998; Allen et al, 1999a). Current atomization and combustion models assume constant fuel temperature throughout the atomization process because the property values are not known above 100°C. Fuel atomization in an engine does not occur completely at the nozzle exit. Therefore the fuel must undergo some increase in temperature during the process. Knowledge of fuel properties relevant to atomization and combustion at both elevated temperatures and pressures is thus required, but this paper reports on the biodiesel properties at elevated temperatures only.

The experimental measurement of density, viscosity and surface tension of three commercial biofuels available commercially is discussed herein. For this work 100% methyl esters of canola (Milligan Bio-Tech, SK) and soy (West Central Soy, IA) and ethyl esters of fish-oil (Wilson's Fuels, NS) were obtained. These are referred to CME, SME and FEE in this paper.

DENSITY

Because density is the ratio of mass per unit volume, measuring the variation in volume of a given mass of oil as a function of temperature leads to the derivation of density at elevated temperatures. Thus the instrument noted below is referred to as a densitometer. Its use was selected since the effect of temperature on the results can be determined and since there are no components that could malfunction at high temperatures.

Apparatus

The main component of our capacitance type densitometer designed for use at elevated temperatures was a capacitor (Figure 1) specially constructed to fit inside the heated upper chamber of the Modified Saybolt viscometer described below and in Tate (2005) (Figure 2). The capacitor was attached to the lid of the viscometer. To calibrate the densitometer, aluminum spacing discs were used to vary the submergence depth. Variations in the submergence depth caused the dielectric constant of the capacitor to change, resulting in a measurable frequency output. The capacitance was measured using a Hex Schmitt-Trigger Inverter (MC74HC14AN), 5-volt power supply, and a Fluke 1900A Multi-Counter. The frequency counter had an input sensitivity of 20mV rms. The oil in the reservoir was continuously stirred to ensure a uniform temperature.

The individual effects of fuel type, temperature, and submergence depth on frequency output were examined to obtain a calibration equation for the densitometer.

Methodology

Prior to each fuel change, the capacitor and reservoir were cleaned with toluene, dried with acetone, and the baseline frequency was recorded in air at room temperature to ensure repeatability. The oil was placed in the reservoir, the apparatus was assembled, a flow of nitrogen was commenced to prevent oxidation of the oil during heating, and the stirrer was started. The temperature of the oil was measured using a Type K thermocouple calibrated to 980°C.

Temperature Effect

The effect of temperature on the dielectric constant on the meter was determined by fully submerging the capacitor in the filled reservoir to maintain a constant liquid level during expansion. Excess fuel (as the oil expanded on heating) drained into the overflow cup. The frequencies were recorded at seven specified temperatures as the oil was heated between 20°C and 300°C. The total time for this experiment for each fuel was 25 minutes.

Submergence Effect

To obtain the capacitance as a function of oil height for each of the three fuels, the reservoir was completely filled and the capacitor was submerged to three depths (3, 5, and 7 cm) using a combination of the aluminum spacer blocks machined to either 10 or 20 cm with a machining accuracy of ± 0.5 mm. These experiments were initially performed at a constant temperature of 20°C.

Calibration

Capacitance is governed by the following relationship

$$C = \frac{KA}{t} \quad (1)$$

where K is the effective dielectric constant of the total space between electrodes, A is the plate area and, t is the distance between the plates. The plate area is the product of plate width and submergence depth. For small changes in K and submergence depth (proportional to an increase in A), it can be seen that capacitance is proportional to variation in submergence depth, d , and dielectric constant as follows

$$C \propto (K_o + \Delta K)(d_o + \Delta d) \quad (2)$$

and

$$C \propto K_o d_o + d_o \Delta K + K_o \Delta d + \Delta K \Delta d \quad (3)$$

where the last term can be considered negligible.

Volume Change

To ensure that there was negligible evaporation of the oil, the maximum temperature of all experiments was at least 25°C below the boiling point of the lightest oil fraction. The experiments took 25 minutes each to complete. To further verify there was negligible evaporation of the oil, a sample was held at a constant temperature of 300°C for 25 minutes while the frequency output was monitored.

Density Results

A regression analysis was performed on the calibration data. The frequency of each fuel was regressed on temperature and liquid level. Regression coefficients (R^2) of 0.986 were obtained for each fuel data set. Based on these regression results and the results of the individual temperature and level experiments it was determined that

$$F = 0.04T - 2.74d + B \quad (4)$$

where F is frequency, d is the depth of submergence of the capacitor, T is temperature, and B is a constant that is dependent on fuel type.

Repeatability experiments were performed for the capacitor fully submerged at 20°C, 100°C and 200°C for each of the fuels. Five readings were taken at each temperature and a repeatability analysis was performed. The standard error of the densitometer was found to be 0.500 kHz, corresponding to 10 kg/m³. The repeatability was better than 1%.

Figure 3 shows the density of the three fuels as a function of temperature and a comparison with the results of Tat & VanGerpen (2000) and Yuen et al. (2003).

VISCOSITY

Apparatus

Saybolt viscometry was selected because of its adaptability of operation at elevated temperatures. This type of viscometer operates under the same principles as other capillary viscometers; the efflux time for a known volume of the fuel through a calibrated orifice is related to kinematic viscosity.

The Saybolt viscometer design (ASTM D88) was modified to allow for remote operation at temperatures ranging from room temperature to the boiling point of the most volatile fraction. An insulated, three part chamber was designed to house the Modified Saybolt system (Figure 2). In the lower chamber was a receiving flask made of 9.5 mm (3/8") stainless steel tubing and a 50.8 mm diameter steel sphere. Small holes were drilled at two heights on opposite sides of the tubing (Figure 2) and were compression sealed with Lexan discs and into which were placed two 14-volt lights and two photodiodes, to make up the level detection system. When the liquid level reached the holes the liquid impeded the amount of light transmitted to the diode and a distinct decrease in the signal voltage from the diode was observed. The receiving flask was heated to the test temperature with a 125W rope heater. An orifice diameter of 1.016mm was selected. The efflux time for water was measured as 105 Modified Saybolt Seconds (MSS) at 20°C and 91 MSS at 98°C. These efflux times correspond to kinematic viscosities of 1.004 mm²/s and 0.295mm²/s and dynamic viscosities of 1.00 mPa-s and 0.281mPa-s.

The oil in the reservoir was heated with two 250W band heaters controlled by an external on-off temperature controller purchased from Watlow. Three type K thermocouples were used to monitor and control the oil, chamber, and receiving flask temperatures. Type K wire thermocouples, calibrated to 480°C, were used for the control of the sample temperature and monitoring the receiving flask temperature. A type K thermocouple probe, calibrated to 980°C, was used for monitoring the sample temperature. The oil was continuously stirred during the heating process to ensure a uniform oil temperature. A remotely activated solenoid was used to control the stop.

Methodology

The experimental procedure was based on ASTM D88, with the exception that some procedures were automated. Prior to each fuel change, the reservoir and receiving flask were cleaned with toluene and dried with acetone. The apparatus was assembled and a heated flow of nitrogen was started to prevent oxidation of the oil during heating.

Once the reservoir was filled and the chamber reassembled, operation of the Modified Saybolt viscometer was controlled via a program developed under LabWindows CVI. The sample and chamber temperature were continuously monitored. When a stable test temperature was attained, an indicator light on the computer monitor was lit. The solid-state relay and solenoid were then manually activated, releasing the reservoir plug. The light detecting diode signals were scanned simultaneously and continuously for a predetermined time greater than the estimated efflux time. At the completion of this time, the solenoid was deactivated and the reservoir plug closed.

Each experiment took between five and thirty minutes, depending on the test temperature. Three samples of each fuel were tested at 20°C intervals between 20°C and 300°C.

Calibration and Repeatability

In order to determine the relationship between MSS and kinematic viscosity, calibrations were performed using distilled water, Cannon viscosity oil standard No.1 and each of the biodiesel fuel samples at the specific temperatures for which the kinematic viscosity was known.

Three samples of fluid were tested at the temperature of known kinematic viscosity to determine the repeatability of the Modified Saybolt viscometer.

Viscosity Results

Calibration

The results of the calibration is shown in Figure 4. Regression analysis yielded $C_1 = 0.028$ and $C_2 = -199$ with an R^2 of 0.994. The repeatability of the Modified Saybolt viscometer was found to be 2%. The accuracy was 95%.

Viscosity

The more useful viscosity is the dynamic or absolute viscosity, which is obtained by multiplying the kinematic viscosity by the density. Thus Figure 5 shows the relationship between the dynamic (absolute) viscosity and temperature for CME, SME, and FEE.

SURFACE TENSION

Axissymmetric Drop Shape Analysis - Profile (ADSA-P)

Pendant drop tensiometry was selected for the determination of surface tension because of its applicability to elevated temperatures and ability to accurately determine low interfacial tensions. The principle of ADSA-P (Figure 6) is to determine the curvature of a pendant or sessile drop at the drop apex, b , and the capillary constant of the system, β . These droplet specific parameters can then be used to calculate the surface tension, σ . (Tate 2005) Reliable and accurate methods of ADSA-P have been developed (del Rio and Neumann, 1998, and Song and Springer, 1986) and form the basis of the analysis in this work. Significant errors result from misplacement of the origin, tilted drop profiles, and the aspect ratio, AR , and tilt angle, α , of an image but equations to correct for these have been developed. (del Rio and Neumann, 1998, and Song and Springer, 1986)

Experimental apparatus and procedure

A 500 μL syringe with 22-gauge removable needles was purchased from the Hamilton Company. The syringe was mounted in the injector port of a heated pressure chamber (Tate, 2005) with a Swagelok fitting. Nitrogen atmosphere was maintained at all times in the cylinder. A screw plunger on the adapter to the syringe enabled some control in the formation of droplets. Volumes less than 20 μL could be added to the droplets with one complete turn of the screw. The needle was cut to length and ground to a perpendicular edge. A cylinder was mounted flush with the bottom of the needle and ground smooth (Figure 7). This arrangement was used to form the pendant drops. An Olympus C-750 Ultra Zoom digital camera with a 10x optical zoom was used for the acquisition of droplet profiles. The camera was set up on a tripod with the field of view through both chamber view ports. A small bubble level was used to level the camera and syringe assembly. Backlighting was used to get a silhouette of the drops, Figure 7. The camera was set up to take black and white pictures in *.HQ format with a resolution of 2288 x 1712 pixels. After

the droplet pictures were obtained they were converted to *.GIF format with a resolution of 640 x 480 pixels and imported into OPTIMAS (BioScan Inc.) for the extraction of profile coordinates because higher resolutions caused image distortion in OPTIMAS. After the profile coordinates were extracted they were exported to Excel. The extraction of data points with OPTIMAS yielded a profile to which a second order polynomial was fit. The origin of the apex (X, Z) was determined by solving the resultant quadratic equation. The equations referred to above were then solved to obtain estimates of the surface tension.

At each temperature, drops were formed and allowed to set for five minutes to reach thermal equilibrium. The drops were of unknown and random volumes. Three drops of each fuel were formed at 20°C intervals up to 60°C and at 40°C intervals from 60°C to the boiling point of the lightest oil fraction. Two pictures were taken of each drop formed.

Accuracy and repeatability

Distilled water at room temperature was used to determine the accuracy and repeatability of this method. For a typical water-air system the expected surface tension is 72.80mN/m.

Surface Tension Results

The prediction models proposed by Allen *et al.* (1999b) and Yuan *et al.* (2003) were used to predict the surface tension of the biodiesel fuels based on their fatty acid composition. The linear relationships for the measured densities derived by Tate (2005) were used directly in the calculation of the temperature dependant surface tension.

From Figures 8, 9, and 10 it is observed that the predicted surface tensions do not agree very well with the measured surface tensions.

CONCLUSIONS

1. A capacitance type level meter was shown to give the variation of volume of biodiesel fuels up to the boiling point of the lightest fraction with a precision of 1%. The densities of three commercial B100 biodiesel fuels, canola methyl esters, soy methyl esters, and fish oil ethyl esters decreased linearly with temperature by 1.23 kg/m³°C for temperatures of 20°C to 300°C. The predicted values in the literature for densities beyond 100°C deviate from the experimental densities obtained in this work.
2. A Modified Saybolt Viscometer was shown to give the efflux time of 60 ml of biodiesel fuels up to the boiling point of the lightest oil fraction with 95% accuracy and 5% repeatability. The viscosities of three commercial biodiesel fuels, canola methyl esters, soy methyl esters, and fish oil ethyl esters, decreased with temperature.
3. The Pendant Drop tensiometry and Axisymmetric Drop Shape Analysis – Profile (ADSA-P) method can be used to measure the surface tension of biodiesel fuels up to the boiling point of the lightest oil fraction. The surface tension of three commercial biodiesel fuels, canola methyl ester, soy methyl ester, and fish oil ethyl ester decreased with temperature.

ACKNOWLEDGEMENT

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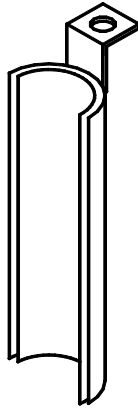


Figure 1. Capacitance Densitometer

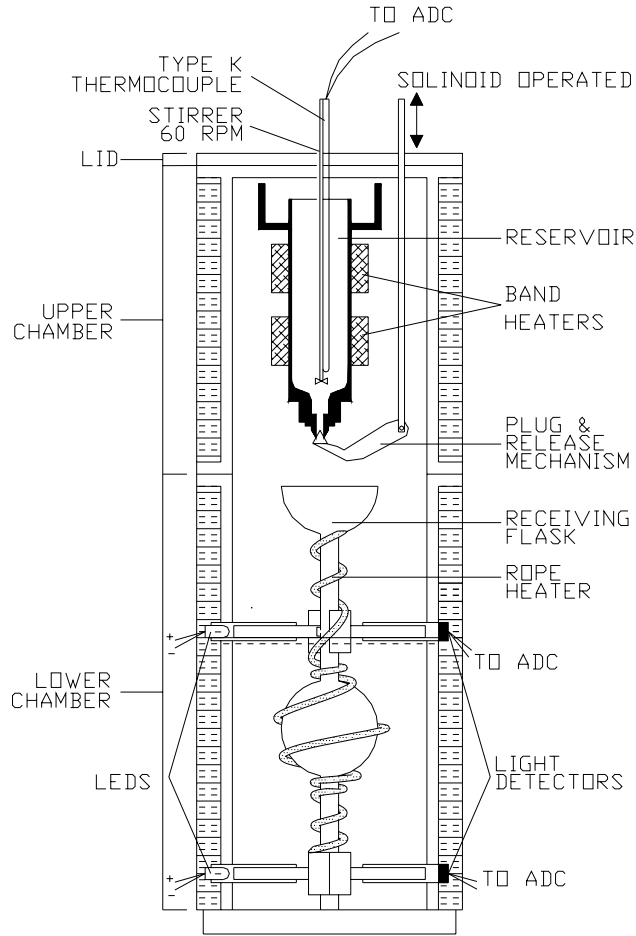


Figure 2. Modified Saybolt Viscometer

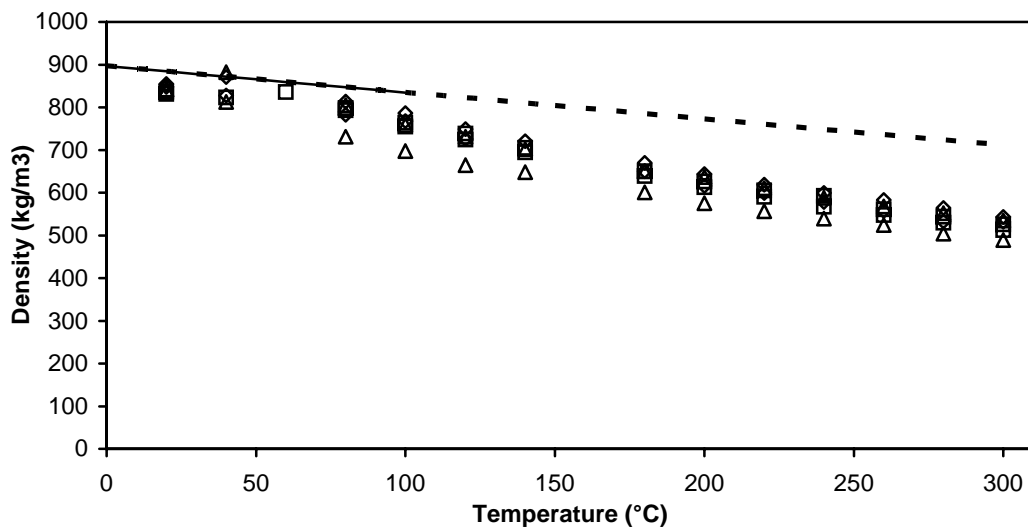


Figure 3. Comparison of experimental and predicted densities to 300°C. \diamond CME, \square SME, Δ FEE, — Tat and Van Gerpen (2000), - - - Yuan et. al. (2003)

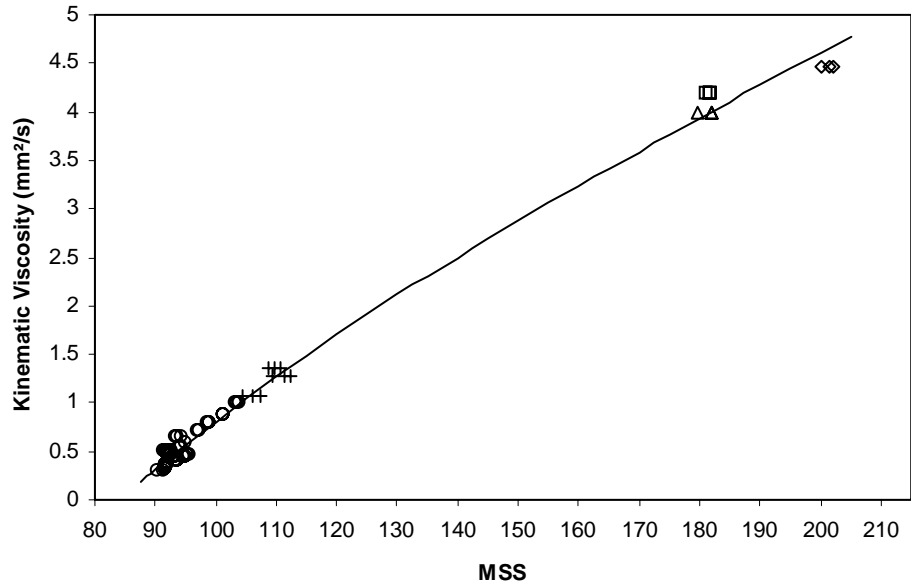


Figure 4. Modified Saybolt viscometer calibration results. \diamond CME, \square SME, Δ FEE, + Cannon oil standard no. 1, \circ Distilled water, — Calibration curve.

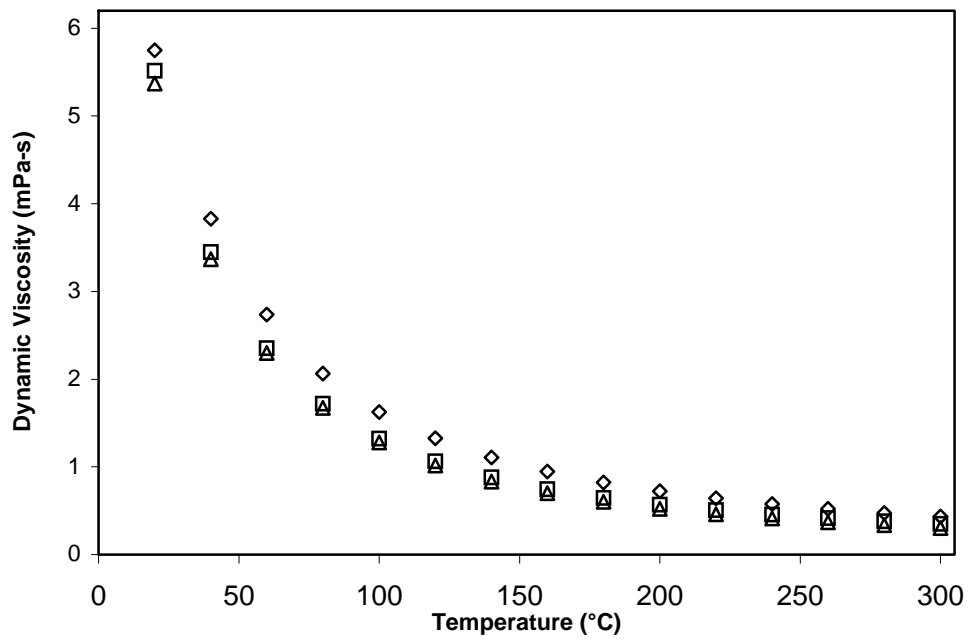


Figure 5. Dynamic viscosities of three biodiesel fuels from 20°C to 300°C. \diamond CME, \square SME, Δ FEE.

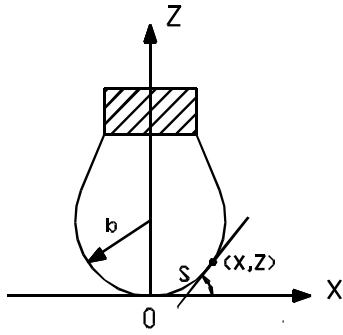


Figure 6. Pendant drop, showing the parameters for analysis.



Figure 7. Photograph of a pendant drop, showing the calibration cylinder.

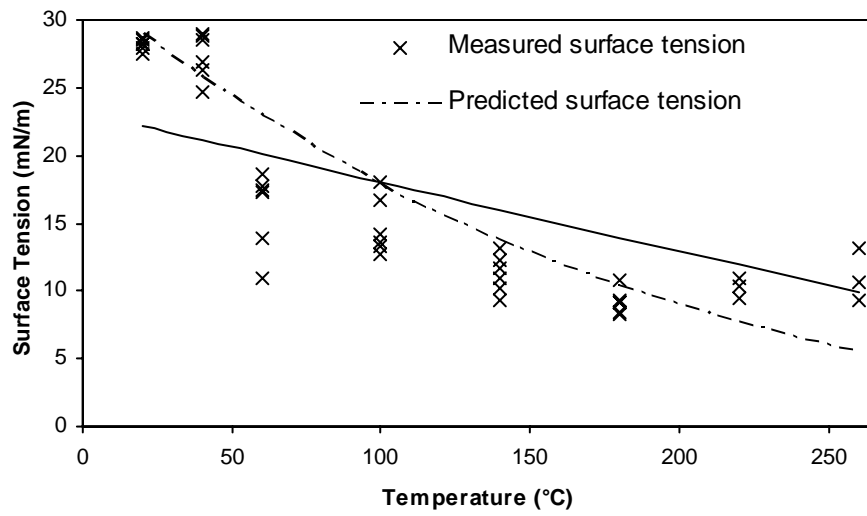


Figure 8. Surface Tension of Canola Methyl Ester CME

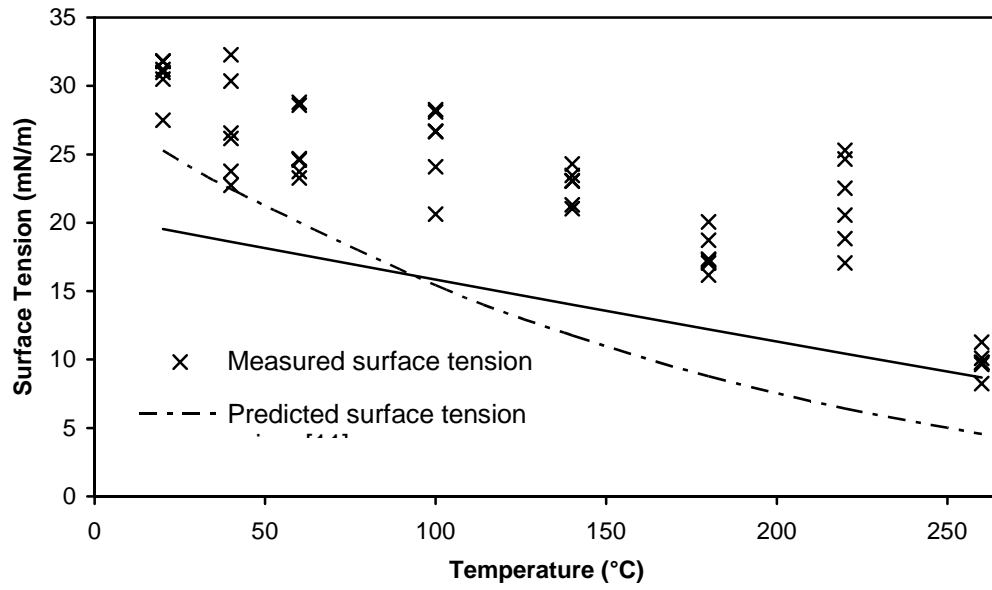


Figure 9. Surface Tension of Soy Methyl Ester SME

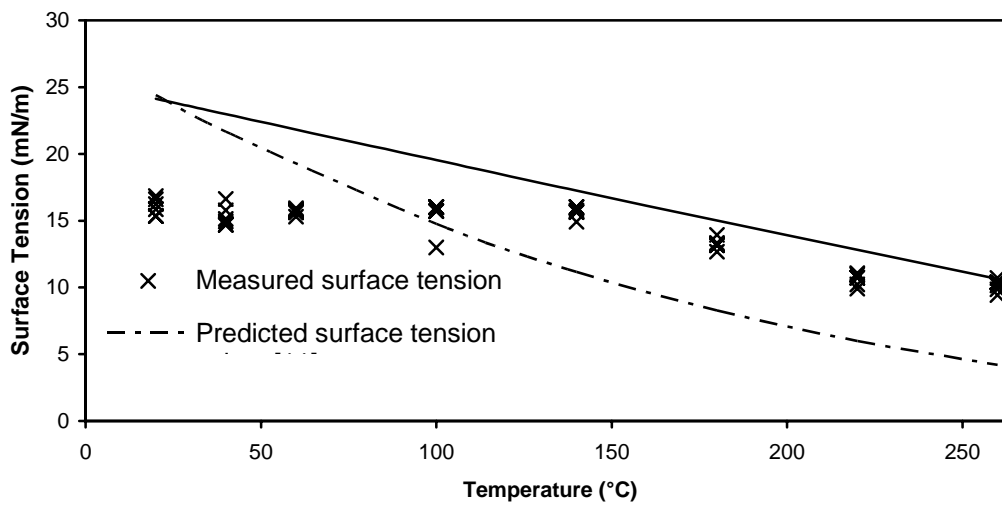


Figure 10. Surface Tension of Fish-oil Ethyl Ester FEE