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Surface Tensions of Jatropha and Soapnut Biodiesel and their Blends with Diesel at Elevated Temperatures and Pressures

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***Abstract** – Biodiesel is a renewable fuel derived from vegetable oils, animal fats, waste cooking oil and other lipids. Biodiesel can be used in its pure form as a blend with petroleum diesel in diesel engines with little or no modification. It can be produced domestically reducing the need to import petroleum products. As current biodiesel feedstocks are mostly derived from edible oils and fats, it is likely that biodiesel will compete with food sources. This research is focused on the characterization of the biodiesel sources such as jatropha and soapnut which are non-edible in nature. A high pressure pendant drop equipment (PD-E 1700) and drop shape analysis (DSA 100 V1.9) were used to measure the equilibrium surface tension of diesel and biodiesel fuels at elevated temperatures and pressures. The surface tension of diesel and biodiesel fuels showed a linear relationship with temperatures and pressures. A regression model was also developed using the measured data from the tests.*

Keywords – Biodiesel, jatropha, pressure, soapnut, surface tension, temperature.

1. INTRODUCTION

Biodiesel is a clean and renewable fuel with its properties similar to that of petroleum diesel. Biodiesel is produced from vegetables oils, animal fats, algae and other bio sources with lipid content in them. This fuel has recently been popular due to the concerns on depleting petroleum resources as well as the severe environmental impacts caused due to fossil fuel combustion. However, conventional sources of biodiesel mostly come from edible oil and fats creating a competing use of fuel and food. Recently some researchers have focused on developing and characterizing the biodiesel fuels derived from non-edible feedstocks including waste cooking oils [1], [2], jatropha and soapnut [3]-[5] and green canola *etc.* [6]. This paper has also focused on characterization of biodiesel fuels derived from non edible oils including jatropha and soapnut biodiesel and their blends.

2. ASSUMPTIONS

The blends of jatropha and soapnut biodiesel were prepared for B80, B50, B20 with proper shaking and was assumed that the solution is uniformly mixed. The surface tension of diesel was measured up to 448 K after which the samples start evaporating.

3. LITERATURE REVIEW

Surface tension is one of the important physical properties of the biodiesel fuels affecting the atomization in a diesel engine.

Enhanced atomization and proper air-fuel mixing helps complete combustion, increases engine efficiency and reduces air pollution [7]. Some previous studies have indicated that biodiesel fuels from different feedstock sources have different atomization properties [8], [9]. The differences in atomization properties are potentially due to the difference in their physical properties including surface tension. Some studies have also indicated that the physical properties are affected by the fatty acid content of the biodiesel feedstock [10]. These properties greatly affect the droplet formation and atomization [8], [11]. It has also been reported that the high surface tension of the liquid fuel makes the droplet formation more difficult [12] and leads to inefficient atomization [13]. The long fatty acid chain hydrocarbons and unsaturated bonds in biodiesel fuels make the surface tension to increase [12]. The surface tensions of pure biodiesel fuels can be reduced by using the blends of pure biodiesel with diesel fuels at different ratios [8], [14].

Several previous studies predicted the surface tensions of biodiesel fuels based on their fatty acid composition in mass percentage and their parachors [11], [15]. The parachor values were assigned to groups of atoms based on linkage and composition by Gibling [16]. Stalder *et al.* [17] presented a method for surface tension and contact angle measurement using low bond axisymmetric drop shape analysis. Joshi [18] measured the surface tensions of canola biodiesel and its blends from 293 to 533 K using the pendant drop method, analysed using Axisymmetric Drop Shape Analysis Profile (ADSA-P). Tate [19] measured the surface tensions of canola biodiesel, soybean biodiesel and fish oil biodiesel using pendant drop tensiometry.

In this work, a high pressure pendant drop equipment was used to measure the surface tension of petro-diesel, jatropha and soapnut biodiesel fuels and their blends with diesel. The experiment was carried out from atmospheric pressure to 7 MPa and from room temperature to 473 K, the maximum temperature allowed by the equipment.

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The surface tension was measured based on the principle that a drop hanging from a syringe needle, which is in hydrochemical equilibrium with its surrounding gas will assume a characteristic shape and size from which the surface tension can be calculated. The Young-Laplace equation, used to derive the surface tension for a pendant drop in hydrochemical equilibrium is presented below in Equation 1.

$$\Delta p = \sigma * \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (1)$$

where r_1 and r_2 are the principal radii of curvature at any point of the drop, σ is the surface tension, Δp is the difference in pressure between the outside of the pendant drop and its inside.

The surface tension of the pendant oil drop surrounded by either air or nitrogen phase is determined by using the Young-Laplace equation of capillarity by finding the best numerically calculated surface profile to fit the physically observed drop profile. This method is considered one of the most accurate techniques for a large range of temperatures and pressures.

4. METHODOLOGY

Neat jatropha oil sample was obtained from Aaditya Aromedic and Bio Energies Pvt. Ltd., Tarsadi, Gujarat State of India. Soapnut oil sample was purchased from Satya Sai International Pvt. Ltd in western Nepal. The jatropha and soapnut oils were transesterified into methyl ester biodiesel fuels in the Dalhousie Laboratory. The two biodiesel fuels used for this work were characterized as per ASTM fuel quality standards and are summarized elsewhere [20]. The characteristics of the petro-diesel are also provided in the same reference.

4.1 Apparatus

High pressure pendent drop equipment (PD-E 1700) and drop shape analysis (DSA 100 V1.9) were used to measure the dynamic and equilibrium surface tension of different biodiesel blends at various temperatures and pressures. The PD-E-1700 built by Eurotechnica was used in this work and is shown in Figure 1. The DSA V1.9 is a drop shape analysis software built by KUSS (Germany). The DSA V1.9 software acquires and analyzes the picture of the pendant drop as shown in Figure 2.

The major component of this system is a high-pressure cell with windows on two sides. The maximum operating pressure and temperature of this cell is 69 MPa and 473 K respectively. The drop shape analysis DSA100 V1.9 consists of a high-resolution CCD camera with a light source. The high-pressure cell is located between the CCD camera and light source.

Fig. 1. High-pressure pendant drop equipment (PD-E 1700) and drop shape analysis (DSA100 V1.9).

Fig. 2. Pendant drop shape analysis acquiring pendant drop (DSA100 V1.9).

In this method, a pendant oil drop is formed on the tip of the stainless-steel needle installed at the top of the pressure cell in an air or nitrogen phase. With a digital image acquisition system from DSA100 V1.9, a digital image is acquired. The software requires the density of the test liquid (petro-diesel and biodiesel) and density of the gas phase (either air or nitrogen) surrounding the test liquid. The densities of the liquids at the respective temperatures and pressures have been reported elsewhere [20]. The densities of the surrounding gases were computed assuming the ideal gas law.

In this work, the surface tension readings were recorded for pressures 0.10, 1.83, 3.50, 5.30, 7.00 MPa and temperatures 293, 323, 373, 423, and 473 K respectively. In the case of the diesel, the temperature readings were recorded for 293, 323, 373, 423, and 448 K for all five pressures. The test was carried out for temperatures only up to 448 K because the boiling point of diesel starts at approximately 453 K and evaporation takes place after this temperature.

4.2 *Accuracy and Reproducibility of the Measurement*

The correct optical alignment, cleanliness and functionality of the system were confirmed by determining the surface tension of distilled water as 72.8±1.3% mN/m. This confirmation test was carried out after each test for different fuels. The instrument was cleaned with isopropyl alcohol (99% concentration) followed by acetone, and dried with nitrogen gas after completing the test of each blend of biodiesel fuel in order to avoid contamination from the subsequent test samples. Setting the instrument at a particular temperature was a difficult task. The control was manual and the temperature had an offset of ±273.5 K from the set point. As density was one of the inputs to the analyzer, any errors in density could also affect the accuracy of the surface tension results. For each pendant drop created during the test, the surface tension reading was repeated five times and an average was taken. Three pendant drops were created and corresponding measurements were taken to ensure the satisfactory repeatability at each specified temperature and pressure test.

5. RESULTS AND DISCUSSION

5.1. *Surface Tension of Petro-Diesel*

The surface tension of pure diesel B0 was measured and plotted as a function of temperature for five pressures and as a function of pressure for five temperatures (Figures 3 to 4). The results showed that the surface tension decreased linearly both for temperature and pressure variations. At atmospheric pressure, the surface tension of diesel decreased from 25.84 mN/m at 293 K to 15.84 mN/m at 448 K. The surface tension decreased from 19.67 mN/m at 293 K to 13.73mN/m at 448 K at 7.00 MPa. Dechoz and and Roze [21] also reported that the surface tension of diesel decreased linearly with increase in pressure up to 10 MPa. They also reported that the surface tension decreased nearly linearly with temperature.

A linear regression for surface tension (σ) on pressure and temperature was performed and the regression equation is presented below (Equation 2). The R^2 value was found to be 0.965.

$$\text{Surface tension } (\sigma) = 39.7-0.0519\,T- 0.000545\,P \tag{2}$$

where T is the absolute temperature in K, and P is the absolute pressure in kPa.

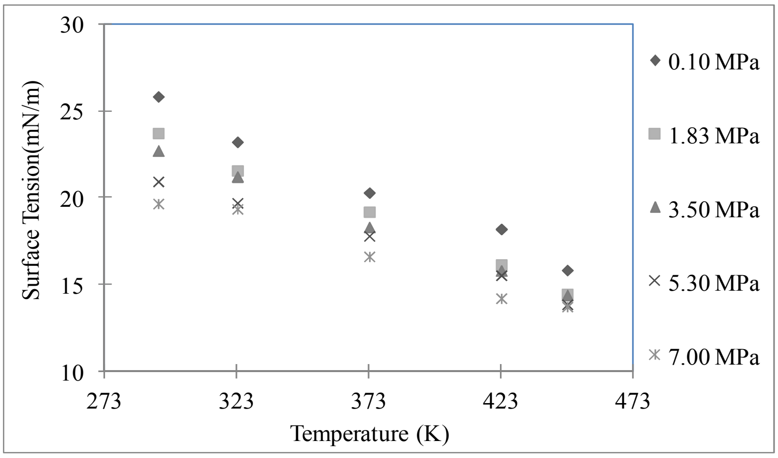

Fig. 3. Experimental surface tensions of diesel B0 as a function of temperature for five pressures [22].

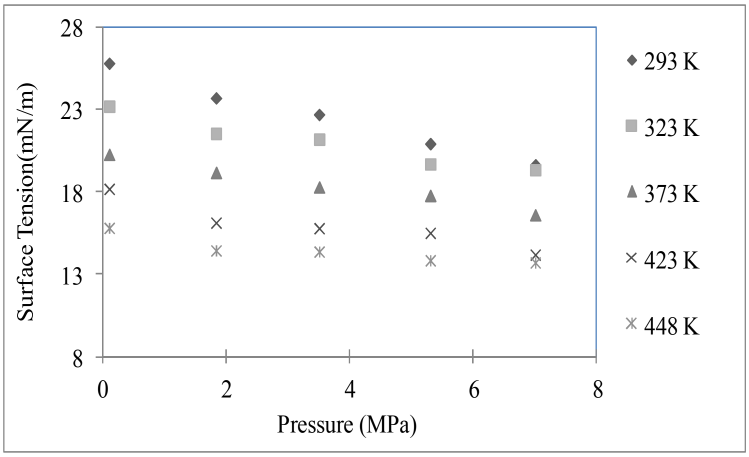

Fig. 4. Experimental surface tension of diesel B0 as a function of pressure for five temperatures [22].

The temperature and pressure dependent surface tension model can thus be generalized as the Equation 3 below.

Surface tension (σ) = C-A*T-B*P (3)

The maximum temperature at which the surface tension was measured for pure diesel was at 448 K. Above this temperature, the pendant drop could not be retained as some components of diesel had started evaporating before reaching this temperature.

5.2 *Surface Tensions of Jatropha Biodiesel and their Blends*

The surface tension of jatropha biodiesel blends B100, was measured and plotted for five pressures and five temperatures. As shown in Figure 5, the surface tension of jatropha biodiesel B100 was found to decrease from 30.10 mN/m at 293 K to 17.82 mN/m at 473 K for atmospheric pressure (0.10 MPa). Similar trends were observed for pressures 1.83 MPa, 3.50 MPa and 5.30 MPa. However for 7.00 MPa, the surface tension slightly increased from 20.65 mN/m at 293 K to 21.04 mN/m at 323 K and then decreased to 15.23 mN/m at 473 K. The model equation obtained from regression (Equation 3) of jatropha biodiesel surface tension data indicated that both the temperature and pressure coefficients are negative and should follow a decreasing trend. However, the data point at 323 K and 7.00 MPa slightly increased and the plot was slightly curved as an exception. The R^2 value of the temperature plot was 0.88 for this particular pressure. One of the probable reasons for such results is due to the difficulty in temperature stabilization during the data acquisition as it was manual temperature control. No discussion in the literature was found in support of this trend.

Figure 6 shows surface tension of jatropha biodiesel B100 as a function of pressure for five temperatures. This also shows a linear relationship. At 293 K, the surface tension of canola B100 decreased from 30.10 mN/m at 0.10 MPa to 20.65 mN/m at 7.00 MPa. For 373 K, the surface tension decreased from 22.79 mN/m at 0.10 MPa to 19.88 mN/m at 7.00 mPa. Similarly, for 473 K, the surface tension decreased from 17.82 mN/m at 0.10 MPa to 15.23 mN/m at 7.00 MPa.

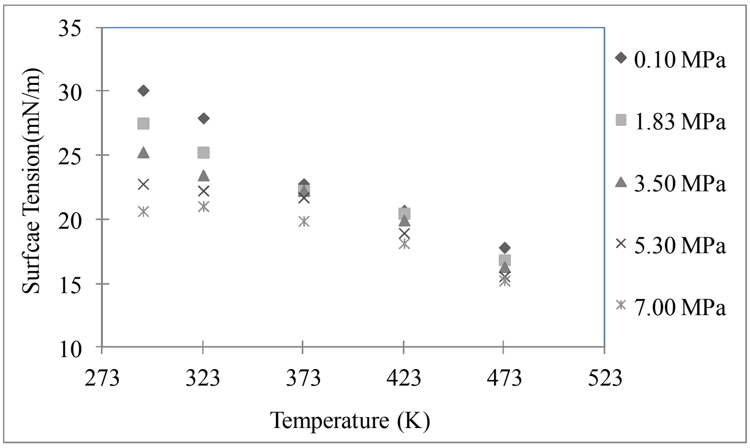

Fig. 5. Surface tension of jatropha B100 as a function of temperature for five pressures.

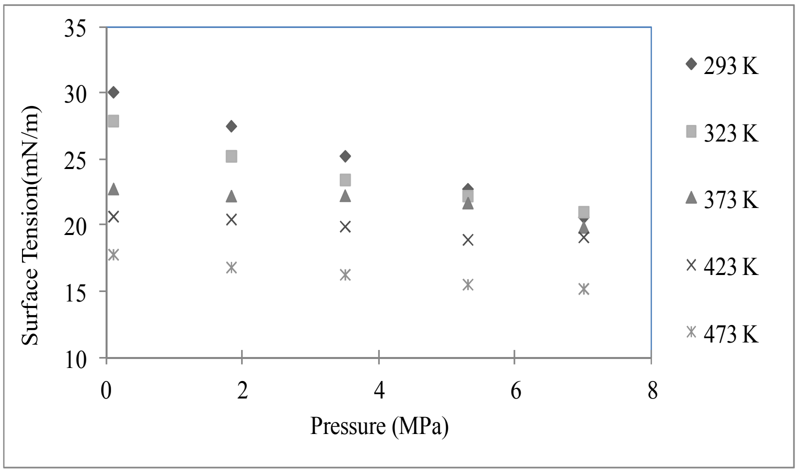

Fig. 6. Surface tension of jatropha B100 as a function of pressures for five temperatures.

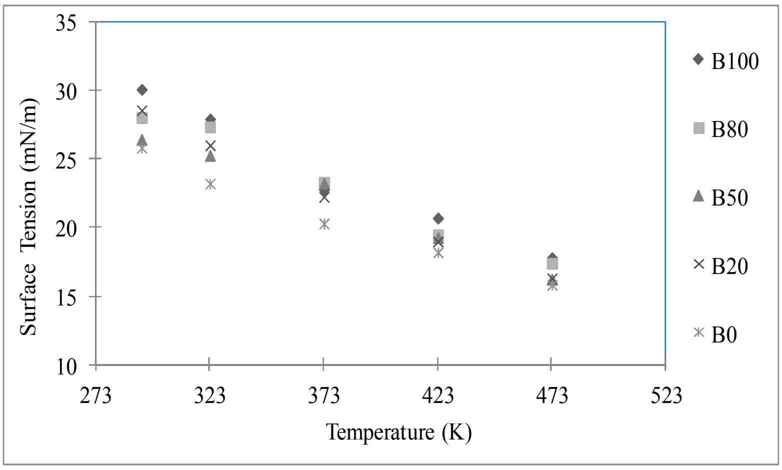

Fig. 7. Surface tension of jatropha biodiesel B100 and its blends and diesel at atmospheric pressure and different temperatures.

The surface tension of jatropha biodiesel and its blends B100, B80, B50, B20 and B0 were measured and plotted for five pressures and five temperatures. Figure 7 represents the surface tension values for jatropha biodiesel and its blend with diesel. It was found that the surface tension values decreased linearly as the temperature increases. At atmospheric pressure, the surface tension of jatropha B100 decreased from 30.10 mN/m at 293 K to 17.82 mN/m at 473 K. For jatropha B80, the surface tension decreased from 28.95 mN/m at 293K to 17.41 mN/m at 473 K. Similarly the surface tension for jatropha B50 and B20 decreased from 26.45 mN/m and 28.57 mN/m at 293 K to 16.23 mN/m and 16.31 mN/m at 473 K respectively. The surface tension was found to decrease with increases in pressure for all blends.

Table 1 shows the regression coefficients for surface tensions of jatropha B100 and its blends and diesel for temperatures between 293 K to 473 K at atmospheric pressure, 3.5 MPa and 7.00 MPa using Equation 3. The average surface tension decreased by of 0.06 mN/m/K for all blends at atmospheric pressure. Similarly, the average surface tension decreased by 0.04 mN/m/K at 3.50 MPa and 0.03 mN/m/K at 7 MPa, respectively.

Table 1. Regression coefficients of surface tension for jatropha biodiesel and its blends with respect to diesel at atmospheric pressure, 3.50 MPa and 7.00 MPa.

Fuel Type	Slope (mN/m/K)	Intercept (mN/m)	R^2	Slope (mN/m/K)	Intercept (mN/m)	R^2	Slope (mN/m/K)	Intercept (mN/m)	R^2
	0.10 MPa			3.50 MPa			7.00 MPa		
B100	-0.06	49.70	0.976	-0.04	39.09	0.968	-0.04	36.65	0.992
B80	-0.06	48.67	0.983	-0.05	41.21	0.989	-0.03	33.20	0.967
B50	-0.06	48.16	0.993	-0.04	36.07	0.967	-0.03	31.52	0.941
B20	-0.05	43.92	0.983	-0.05	39.12	0.979	-0.03	30.04	0.959
B0	-0.05	40.99	0.985	-0.04	36.52	0.986	-0.03	27.49	0.951

Jatropha B100 and its blends were also plotted as a function of temperature at 3.50 MPa (Figure 8). The surface tension decreased from 25.27 mN/m at 293 K to 16.30 mN/m at 473 K for jatropha B100. For jatropha B80, B50 and B20, the surface tension values decreased from 25.67 mN/m, 22.45 mN/m and 23.63 mN/m at 293 K to 16.25 mN/m, 15.06 mN/m and 14.84 mN/m respectively at 473 K. The surface tension of jatropha biodiesel and its blends including diesel were plotted as a function of temperature at 7 MPa (Figure 9). The surface tension for all blends is found to decrease linearly from 293K to 473 K at an average rate of 0.03 mN/m/K. The high R^2 values show a high correlation for the observed data sets.

5.3 Surface Tension of Soapnut Biodiesel

The surface tension of soapnut biodiesel showed a very similar trend as seen in the case of biodiesel from jatropha oil. For each pressure, the surface tension was found to decrease linearly with temperature. Figure 10 shows the surface tensions of soapnut biodiesel for five temperatures and five pressures. For soapnut biodiesel B100, the surface tensions decreased from 29.50 mN/m at 293 K to 16.95 mN/m at 473 K at atmospheric pressure. A similar trend was observed for 1.83 MPa, 3.50 MPa and 5.30 MPa. At 7.00 MPa, the surface tension of soapnut B100 decreased from 22.78 mN/m at 293 K to 14.84 mN/m at 473 K. The R^2 value using Equation 3 for all pressures and temperatures was 0.929. The R^2 values from regression for soapnut biodiesel B100 at 5.30 and 7.00 MPa were found to be 0.903 and 0.851 respectively. However, there was a significant decrease in surface tensions values at 323 K for 5.30 MPa and 7.00 MPa. The decrease in surface tensions at 323 K for 5.30 and 7.00 MPa could have occurred due to sudden temperature increase because of the manual control mechanism. Ignoring these two data points, the R^2 values for the regression become 0.970 and 0.966 for 5.30 and 7.00 MPa, respectively. The R^2 value using Equation 3 for all pressures and temperatures was still 0.929 ignoring the two data points at 323 K for 5.30 and 7.00 MPa.

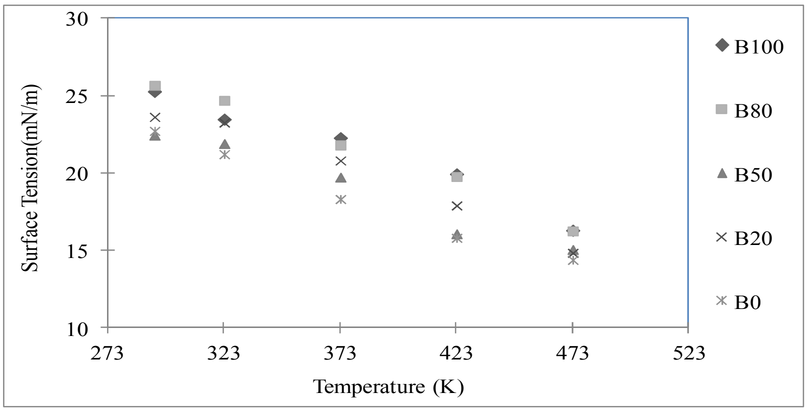

Fig. 8. Surface tension of jatropha biodiesel and its blends and diesel at 3.50 MPa.

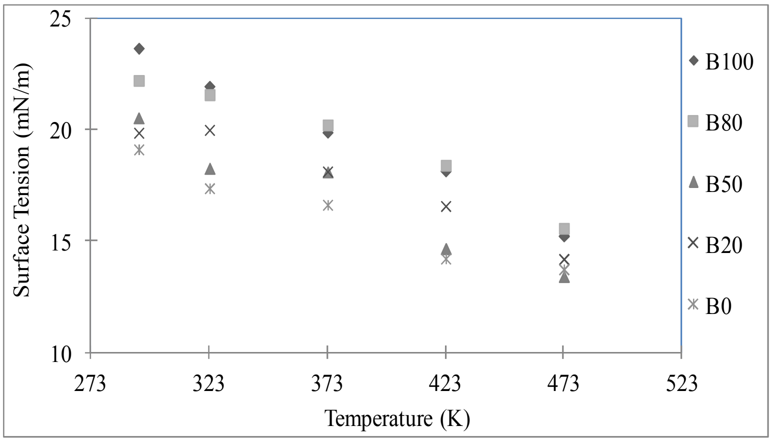

Fig. 9. Surface tension of jatropha biodiesel and its blends and diesel at 7.00 MPa.

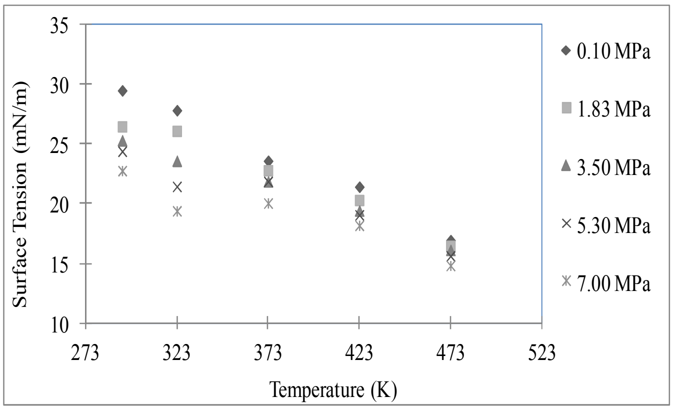

Fig. 10. Experimental surface tension of soapnut biodiesel B100 as a function of temperature for five pressures.

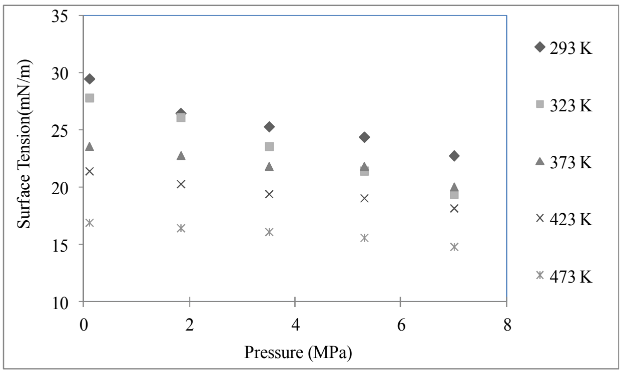

Fig. 11. Experimental surface tension of soapnut biodiesel B100 as a function of pressure for five temperatures.

Figure 11 represents the surface tensions of soapnut biodiesel B100 as a function of pressure. The surface tensions decreased linearly with pressure for each temperature. At 293 K, the surface tension decreased from 28.18 mN/m at 0.10 MPa to 21.27 mN/m at 7.00 MPa. For 473 K, the surface tension decreased from 14.31 mN/m at 0.10 MPa to 13.64 mN/m at 7.00 MPa. However, the slope of the line was found to be higher due to an increase in temperature as compared to an increase in pressure which indicates that temperature has a higher impact on surface tension compared to pressure. B100 as a function of pressure for five temperatures [22].

Figure 12 represents the surface tension of soapnut biodiesel and its blends and diesel at atmospheric pressure. The surface tension for soapnut biodiesel B100 decreased from 29.50 mN/m at 293 K to 16.95 mN/m at 473 K at atmospheric pressure. Surface tension for all blends linearly decreased with temperature by an average rate of 0.06 mN/m/K. Similarly, Figure 13 shows the surface tensions of soapnut biodiesel at 3.50 MPa. The surface tension decreased at an average rate of 0.044 mN/m/K. For 7.00 MPa, it was found that the surface tension decreased linearly as the temperature was raised from 293 K to 473 K (Figure 14).

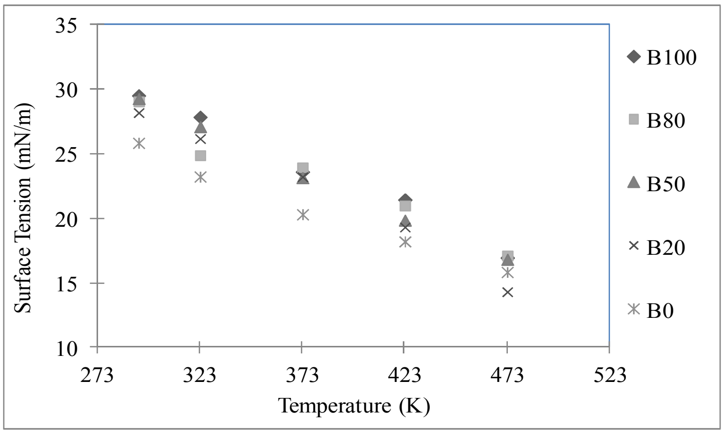

Fig. 12. Surface tension of soapnut biodiesel and its blends with diesel at atmospheric pressure.

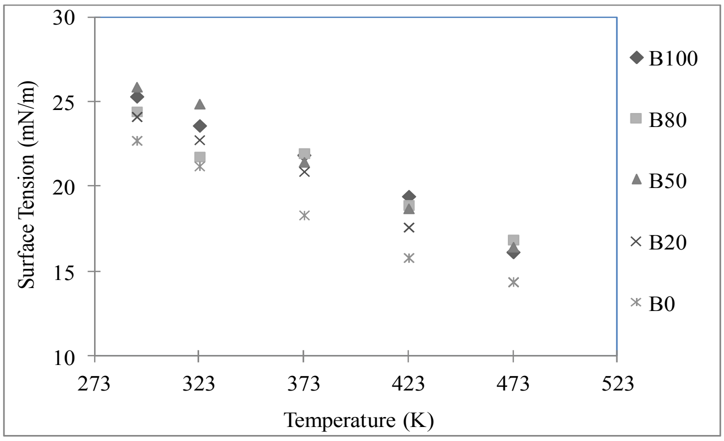

Fig. 13. Surface tension of soapnut biodiesel and its blends and diesel at 3.50 MPa.

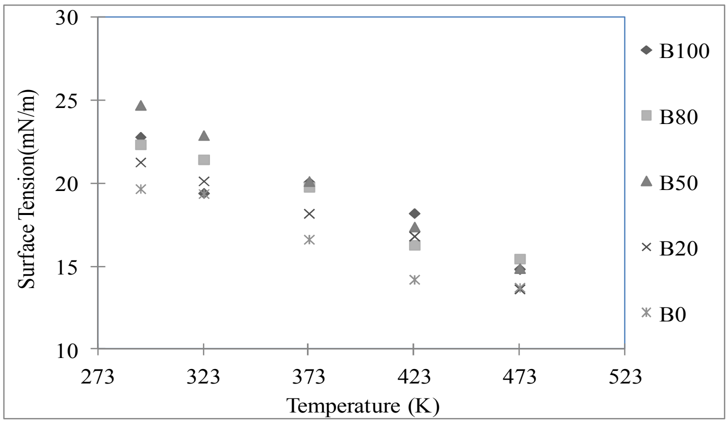

Fig. 14. Surface tension of soapnut biodiesel and its blends and diesel at 7.00 MPa.

Table 2 represents the values of regression coefficients for biodiesel blends and diesel in atmospheric pressure, 3.50 MPa and 7.00 MPa. The surface tension decreased at an average rate of 0.06 mN/m/K at atmospheric pressure and 0.04 mN/m/K for 3.50 MPa and 7.00 MPa. All R^2 values are higher than 0.95 indicating a high correlation of the experimental data sets recorded. Even though the slopes are very similar, it is noted that there is more unexplained scatter in the B80 data Figures 12 to 14.

A linear regression was performed to determine the relationship between surface tension and temperature and pressure for all blends for biodiesel and diesel. This regression model follows the model Equation 3 above. Table 3 shows the summary of regression data including R^2 and the constants A, B and C. The constants for temperatures are higher than for pressures implying that the temperature has a higher effect on surface tension than pressure for all blends of soapnut biodiesel and diesel.

For both jatropha and soapnut biodiesels, no surface tension values were found in the literature against which to compare our results. However, as jatropha and soapnut biodiesel fuels meet the ASTM fuel quality standards, a general comparison can be made with other biodiesel surface tension values. The surface tensions of jatropha and soapnut biodiesel at 313 K in this work were found to be 28.50 mN/m and 28.46 mN/m respectively. They are comparable with the canola surface tension value of 27.67 mN/m [22]. The surface tensions predicted by Allen *et al.* [11] for 15 biodiesel fuels at 313 K varies between 27.69 -29.24 mN/m. These surface tension values were also comparable with the surface tension of peanut biodiesel (28.45 mN/m), coconut oil biodiesel (26.23 mN/m), palm biodiesel (27.94 mN/m), soybean biodiesel (28.33mN/m) and canola biodiesel (29.49 mN/m) as reported by Shu *et al.* [12]. The surface tension values reported by Freitas *et al.* [13] for palm and rapeseed biodiesel at 313 K were 30.55 and 31.17 mN/m respectively, which are higher than the values noted above.

Table 2. Regression coefficients of surface tension for soapnut biodiesel and its blends and diesel at atmospheric pressure, 3.50 MPa and 7.00 MPa.

Fuel Type	Slope (mN/m/K)	Intercept (mN/m)	R^2	Slope (mN/m/K)	Intercept (mN/m)	R^2	Slope (mN/m/K)	Intercept (mN/m)	R^2
	0.10 MPa			3.50 MPa			7.00 MPa		
B100	-0.06	49.74	0.990	-0.04	39.76	0.988	-0.04	32.87	0.851
B80	-0.06	45.67	0.953	-0.04	35.40	0.927	-0.04	34.61	0.966
B50	-0.06	49.50	0.997	-0.05	42.06	0.993	-0.05	40.54	0.999
B20	-0.07	50.73	0.988	-0.05	40.29	0.986	-0.04	33.29	0.980
B0	-0.05	40.99	0.984	-0.04	36.52	0.986	-0.03	30.74	0.952

Table 3. Regression coefficients for surface tension for soapnut biodiesel and its blends at atmospheric pressure.

Fuel Type	C	A	B	R^2
B100	43.0	-0.0508	-0.000670	0.929
B80	39.1	-0.0426	-0.000650	0.886
B50	43.8	-0.0609	-0.000476	0.989
B20	43.3	-0.0570	-0.000627	0.949
B0	37.8	-0.046	-0.000545	0.971

6. CONCLUSION

Surface tensions of jatropha and soapnut biodiesels were measured for elevated temperatures, 293-473K, and pressures, 0.1-7.00 MPa, and were found to decrease linearly with increase in both temperature and pressure. At 293 K and 0.1 MPa, the surface tension was 30.1 mN/m for jatropha oil and 29.5 mN/m for soapnut oil. An increase in temperature was found to have a higher impact in reducing surface tensions than an increase in pressure. The surface tension of blends of diesel fuel with jatropha and soapnut oil consistently decreased with increase in diesel fuel - varying from 0 to 50%, depending on the fuel, temperature and pressure. Although the surface tensions for jatropha and soapnut biodiesel were not available in the literature, the results obtained showed very similar surface tension values when compared with other biodiesel fuels including canola, peanut and soybean biodiesel fuels found in the literature.

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