Proceedings of ENCIT 2010
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13th Brazilian Congress of Thermal Sciences and Engineering
December 05-10, 2010, Uberlandia, MG, Brazil

STUDY OF VARIATION OF PHYSICAL PROPERTIES OF CRUDE AND REFINED VEGETABLE OILS

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Abstract. *The refining of vegetable oils for reduce the composition of oil is a complex procedure of multi-stages. With the grow-up of economy of refinery, it is very important the application of new technologies as the membrane process to improve of refining of vegetable oils. There are many advantages of membrane technology when compared with conventional process: low temperatures, minor waste energy and non-degradation of nutritional composites of oil. For the use of process with a good performance, the know of value and measurement of physical properties have fundamental importance. This work investigated the rheological behavior and the surface tension of the crude and refined oils of: canola, soybean and corn in the temperature range of 27ºC to 40ºC and palm oil in the temperature range of 40ºC to 60ºC, that is typical in membrane processing. The rheological measurements were obtained from the use of rheometers rotational with geometry of concentric cylinders and cone-plate by Brookfield (Rheometer DVIII +). Measurements of surface tension were carried out using a SensaDyne Tensiometer (Model QC6000). Rheograms were fitted according to the Ostwald-de-Waelle model or Power Law. It was found that the oils of canola, soybean and corn have Newtonian behavior for all temperatures studied and that its viscosity decreases with increasing temperature. The surface tension showed a decrease as a function of temperature in which the crude oils had a small deviation from this behavior.*

Keywords*: rheology, surface tension, vegetal oil, crude oil, membrane.*

1. INTRODUCTION

Vegetable oils represent one of the main products extracted from plants, approximately 80% of vegetable oils are used for food applications including salads, frying, mayonnaise and margarine. The remaining 20% are used in industrial applications which include detergents, cosmetics and lubricants (Kaufman and Ruebusch, 1990; Pryde and Rothfus, 1989).

Nowadays has been an increase in market demand for vegetable oils with different natural sources, which detach applications in the food industry covering the formulation of products in the viscosity for liquid foods is important parameter for characterization and evaluation of texture (Brock, 2008).

The refining of crude oil, in order to remove or reduce undesirable minor compounds, is an extensive procedure with many stages. Due the economic importance of the refining, great efforts have been made to improve it and simplify it (Gonçalves et al, 2005).

The application of membranes in the food industry has gained acceptance in the last years and have potential for application in oil processing industry. One of the biggest advantages of using membranes with respect to the conventional process is that low temperatures may be used, preserving oil components sensitive to high temperatures of high nutritional and technological interest, such as natural antioxidants. In general, the application of membrane processing of vegetable oils is associated with reduction in water consumption, energy and chemicals products. A quality product more stable and consequently better quality can be obtained by using membranes (Ribeiro, 2008; Snape and Nakajima, 1996).

In the investigation of the microfiltration process, some physical parameters and physical-chemicals are of special importance, among them, viscosity, pH, surface tension and concentration of suspended solids. The knowledge of the rheological behavior and their variations with the temperature is also useful as a parameter of quality control, and of great importance for the processing industry, the design of the stirring equipment, filtration, but also in the energy savings.

Several studies about rheological behavior to vegetables oils have been reported in the literature (Encinar et al., 2002; Santos et al., 2005). Brock et al (2008) experimentally determined the viscosity and thermal conductivity of oil refined corn, soybean, cotton, olive, sunflower, canola and rice bran. However, information about the physical properties of crude oils and surface tension are scarce.

In view of this, this paper aims to study the rheological behavior and surface tension of oils crude and refined: canola, soybeans and corn in the range of 27 º C to 40 º C and palm in the range of 40 º C to 60 º C, it typical range of processing with membranes

2. MATERIAL AND METHODS

2.1. Material

All crude vegetable oils and the refined palm oil used in this work were obtained from Department of Food Technology, University of Campinas (UNICAMP). The others refined oils (soybean - brands Lisa, corn - brands Lisa e canola - brands Purilev) were purchased from the local market. All oils used in this work were used without any free additional treatment.

2.2. Rheological measurements

Rheological measurements of the vegetables oils were carried out using rotational rheometer with cone-plate geometry with spindle CP-51 and concentric cylinders geometry with spindle SC4-18 from Brookfield (Rheometer DVIII+).

Temperature was controlled using a water bath. Analysis was done for crude and refined oils of: canola, soybean and corn in the temperature range of 27ºC to 40ºC and for crude and refined palm oil in the temperature range of 40ºC to 60ºC, typical membrane processing.

In both geometries of measurements for each rotational speed, the equipment measured the corresponding torque. From these values the equipment provided the shear rate and shear stress. The samples in this study were subjected to increasing and decreasing of rotation velocity (RPM). Thus measurements were performed in duplicates for each sample. The experiment was repeated three times for each of the temperatures and two samples were used for each oil. As the rheograms have not shown hysteresis, the final value of shear stress for each shear rate was the average value.

The rheological behavior was described using the Ostwald-de-Waelle or Power Law Model:

$$\tau = K\left(\dot{\gamma}\right)^n \tag{1}$$

where τ is the shear stress, $\dot{\gamma}$ the shear rate. In the Power Law Model, two rheological constants K and n are required to characterize the flow behavior. K is the Consistency Index and n is the Flow Behavior Index. The K value corresponds to the viscosity of Newtonian fluids (Krokida et al., 2001).

The results were analyzed with the software Origin 7.5. The curves data were fitted to rheological model using the software Origin 7.5. The Ostwald-de-Waelle Model or Power Law Model (eqn. l) was tested and the determination coefficient (R^2) was used as a parameter to verify the goodness-of-fit.

2.3. Surface tension

Surface tension measurements of the crude and refined vegetable oil were carried out with a tensiometer from SensaDyne (model QC6000). Temperature was controlled using a water bath. Analysis was done for crude and refined oils of: canola, soybean and corn in the temperature range of 27ºC to 40ºC and for crude and refined palm oil in the temperature range of 40ºC to 60ºC.

The method for measurement the surface tension by SensaDyne Instruments is the maximum differential pressure bubble. This method is completely independent of depth of immersion or the need to correct for differences in fluid density or specific gravity, when two probes of approximately equal length are inserted into a test fluid. Inert gas (Nitrogen) bubbles are blown into the body of a fluid through two orifices of different diameters. The pressures inside the bubbles are measured by a differential pressure transducer. The resulting differential bubble pressure is directly proportional o fluid surface tension.

3. RESULTS AND DISCUSSION

3.1. Rheological behavior

To evaluate the rheological behavior of the vegetal oils studied, graphs of shear stress in function of shear rate were analyzed, which were obtained from measurements performed in rheometers.

The Figure 1 shows the graph of shear stress in function of shear rate for refined and crude soybean oil with the rheometer of concentric cylinder (Fig.1.a) and cone plate (Fig.1.b). The behavior was analyzed for the range of temperature: 27ºC to 40ºC and none hysteresis was observed. In the Figures 1.a and 1.b with the same value of temperature, the profiles are similar as soon as crude and refined soybean oils. It shows that there is not changed of values of viscosity with the refinery of oil.

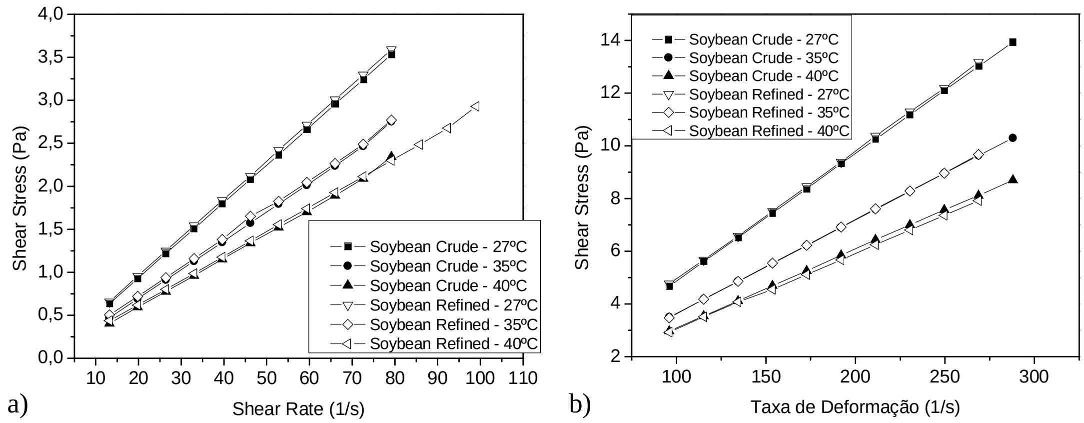

Figure 1. Graph of shear stress in function of shear rate for refined and crude soybean oil with the rheometer: a) concentric cylinder; b) cone plate.

The Figure 2 shows the graph of shear stress in function of shear rate for refined and crude canola oil with the rheometer of concentric cylinder (Fig.2.a) and cone plate (Fig.2.b). The behavior was analyzed for the range of temperature: 27ºC to 40ºC and none hysteresis was observed. In the Figures 2.a and 2.b with the same value of temperature, the profiles are similar as soon as crude and refined soybean oils. The Figure 2 shows the same behavior as for soybean, for the same temperature canola oil showed curves close to the crude and refined oil.

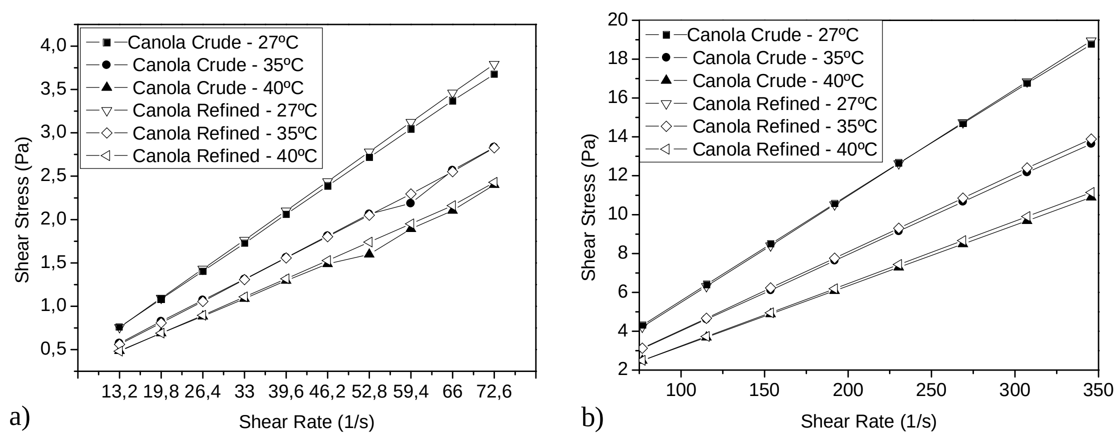

Figure 2. Graph of shear stress in function of shear rate for refined and crude canola oil with the rheometer: a) concentric cylinder; b) cone plate.

The Figure 3 shows the graph of shear stress in function of shear rate for refined and crude corn oil with the rheometer of concentric cylinder (Fig.3.a) and cone plate (Fig.3.b). The behavior was analyzed for the range of temperature: 27ºC to 40ºC and none hysteresis was observed. It is observed in the Fig. 3 that corn oil has a difference between the curves for crude oil and refined oil for the same temperature. This difference is most apparent in the rheometer of concentric cylinders.

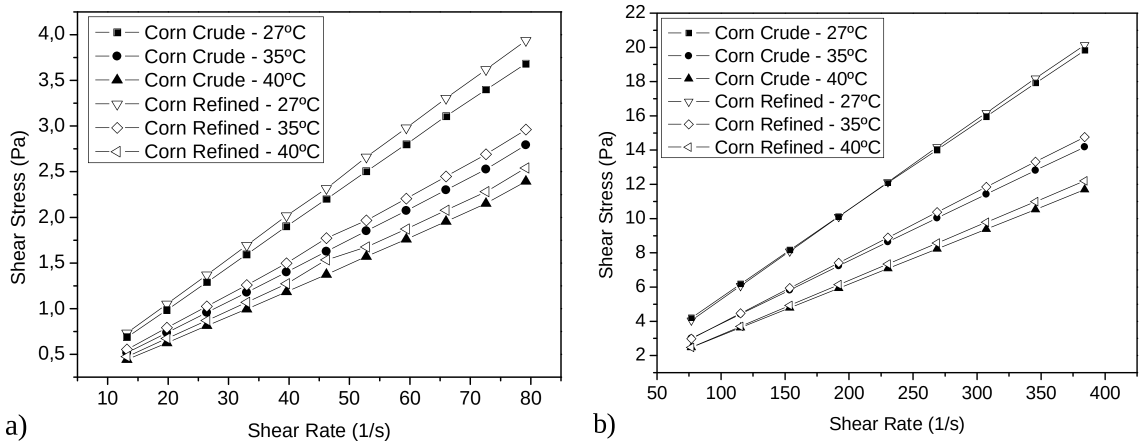

Figure 3. Graph of shear stress in function of shear rate for refined and crude corn oil with the rheometer: a) concentric cylinder; b) cone plate.

The Figure 4 show the graph of shear stress in function of shear rate for refined and crude palm oil with the rheometer of concentric cylinder (Fig.4.a) and cone plate (Fig.4.b). The behavior was analyzed for the range of temperature: 40ºC to 60ºC and none hysteresis was observed. In the Figures 4.a and 4.b with the same value of temperature, the profiles are different for the crude and refined oils. The difference is bigger for 40ºC and the tendencies of change decrease with the increase of temperature until 60ºC.

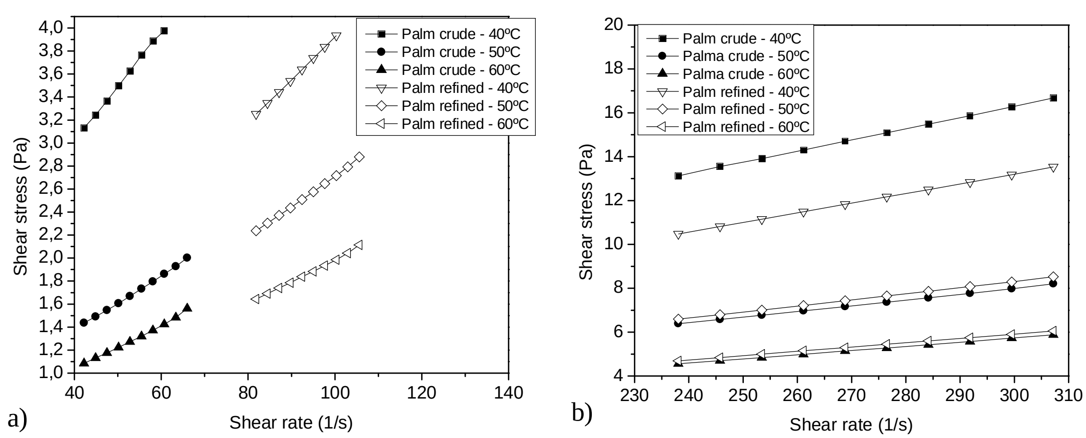

Figure 4. Graph of shear stress in function of shear rate for refined and crude palm oil with the rheometer: a) concentric cylinder; b) cone plate.

To emphasize, it was observed that rheograms obtained for both, the concentric cylinder rheometer and for the cone and plate, geometries showed no hysteresis.

The Tables 1 to 8 shows the rheological parameters of the Power Law Model. The vegetables oils showed a decrease in the consistency index in function of temperature. This behavior can be seen in all figures above, where a decrease of the slope of the curves with increasing temperature. This shows a decrease in apparent viscosity with increasing temperature.

Values obtained by the index of behavior, it was found that the rheological behavior of vegetable oils both crude and refined soybean, canola and corn can be classified as Newtonian for all temperature ranges in both geometries studied. The palm refined oil can also be classified as Newtonian for all temperature ranges and in both geometries. Such behavior is consistent with the results from literature for some vegetable oils (Brock et al., 2008; Conceição et al., 2005; Santos, 2005).

Table 1. Parameters for Power Law Model to the soybean refined oil.

	Concentric Cylinder			**Cone Plate**		
T (ºC)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.0538 ± 0.0008	0.039 ± 0.002	0.0351 ± 0.0008	0.050 ± 0.001	0.0378 ± 0.0003	0.035 ± 0.001
n	0.960 ± 0.004	0.97 ± 0.01	0.956 ± 0.005	0.995 ± 0.004	0.991 ± 0.001	0.968 ± 0.007
$\mathbf{R^2}$	0.99992	0.99909	0.99982	0.99990	0.99999	0.99968

Table 2. Parameters for Power Law Model to the soybean crude oil.

	Concentric Cylinder			**Cone Plate**		
T (ºC)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.0509 ± 0.0008	0.034 ± 0.002	0.029 ± 0.002	0.0496 ± 0.0004	0.0385 ± 0.0003	0.0338 ± 0.0004
n	0.969 ± 0.004	0.99 ± 0,01	0.99 ± 0.01	0.996 ± 0.001	0.994 ±0,001	0.980 ± 0.002
$\mathbf{R^2}$	0.99992	0.99932	0.99890	0.99999	0.99999	0.99997

Table 3**.** Parameters for Power Law Model to the corn refined oil.

	Concentric Cylinder			**Cone Plate**		
T (ºC)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.059 ± 0.001	0.045 ± 0.002	0.038 ± 0.002	0.0535 ± 0.0006	0.0399 ± 0.0003	0.03344 ± 0.00008
n	0.958 ± 0.005	0.956 ± 0.009	0.96 ± 0.02	0.996 ± 0.002	0.994 ± 0.001	0.9914 ± 0.0004
$\mathbf{R^2}$	0.99983	0.99942	0.99862	0.99998	0.99999	1,00000

Table 4**.** Parameters for Power Law Model to the corn crude oil.

	Concentric Cylinder			**Cone Plate**		
T (ºC)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.0573 ± 0.0007	0.040 ± 0.002	0.033 ± 0.002	0.0625 ± 0.0003	0.0444 ± 0.0003	0.0357 ± 0.0006
n	0.952 ± 0.003	0.967 ± 0.009	0.98 ± 0.01	0.9679 ± 0.0008	0.969 ± 0.001	0.973 ± 0.003
$\mathbf{R^2}$	0.99994	0.99945	0.99896	1.00000	0.99999	0.99996

Table 5. Parameters for Power Law Model to the canola refined oil.

	Concentric Cylinder			**Cone Plate**		
T (ºC)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.061 ± 0.001	0.045 ± 0.001	0.037 ± 0.002	0.0545 ± 0.0002	0.0421 ± 0.0004	0.0327 ± 0.0003
n	0.962 ± 0.004	0.966 ± 0,007	0.97 ± 0.01	1.000 ± 0.001	0.992 ± 0.002	0.997 ± 0.001
$\mathbf{R^2}$	0.99989	0.99971	0.99907	1.00000	0.99999	0.99999

The palm oil shows an increase in the behavior índex and a decrease in the consistency índex with the increase in the temperature to both geometries. The behavior index indicates the pseudoplasticity, so that the further away from unity the greater the thinning of the product. Such behavior was observed by Freitas (1998).

Analyzing the rheological parameters obtained, values were different for the two geometries studied. Gehrke (1996) measured the apparent viscosity of the concentrated juice of cashew apple, orange, lemon and passion fruit with the aim of comparing the results obtained in the measurement systems and parallel plate and concentric cylinders. In this work differences in the value of apparent viscosity for the two rheograms was observed for the same temperature and concentration. From the above observations, one can see the importance in indicating the measuring system used in any rheological test.

Table 6. Parameters for Power Law Model to the canola crude oil.

	Concentric Cylinder			Cone Plate		
T (°C)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.063 ± 0.001	0.048 ± 0.005	0.037 ± 0.005	0.0616 ± 0.0004	0.0423 ± 0.0005	0.0341 ± 0.0004
n	0.947 ± 0.005	0.95 ± 0.002	0.97 ± 0.03	0,979 ± 0.001	0.989 ± 0.002	0.963 ± 0.002
R^2	0.99983	0.99658	0.99398	0.99999	0.99999	0.99998

Table 7. Parameters for Power Law Model to the palm refined oil.

	Concentric Cylinder			Cone Plate		
T (°C)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.061 ± 0.001	0.045 ± 0.001	0.037 ± 0.002	0.0545 ± 0.0002	0.0421 ± 0.0004	0.0327 ± 0.0003
n	0.962 ± 0.004	0.966 ± 0.007	0.97 ± 0.01	1.000 ± 0.001	0.992 ± 0.002	0.997 ± 0.001
R^2	0.99989	0.99971	0.99907	1.00000	0.99999	0.99999

Table 8. Parameters for Power Law Model to the palm crude oil.

	Concentric Cylinder			Cone Plate		
T (°C)	**27°C**	**35°C**	**40°C**	**27°C**	**35°C**	**40°C**
K (Pa.s)	0.25 ± 0.01	0.090 ± 0.005	0.059 ± 0.004	0.079 ± 0.002	0.030 ± 0.001	0.0191 ± 0.0004
n	0.68 ± 0.01	0,74 ± 0.01	0.78 ± 0.02	0.780 ±0.004	0.800 ± 0.006	0.850 ± 0.004
R^2	0.99842	0.99771	0.99728	0.99985	0.99968	0.99988

3.2. Surface tension

To evaluate the surface tension of the vegetable oils studied, graph of the surface tension in function of temperature were evaluated, which were obtained from measurements performed using the tensiometer. Figure 5 shows the graph of surface tension in function of temperature for refined and crude oils of soybean, corn and canola in the range of temperature: 27 ° C to 40 ° C.

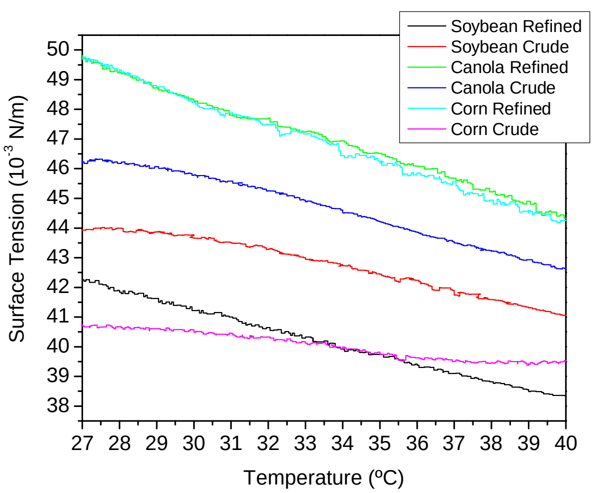

Figure 5. Graph of surface tension in function of temperature for refined and crude oils of soybean, corn and canola.

Figure 6 shows the graph of surface tension in function of temperature for refined and crude oils of palm with the range of temperature: 40ºC to 60ºC.

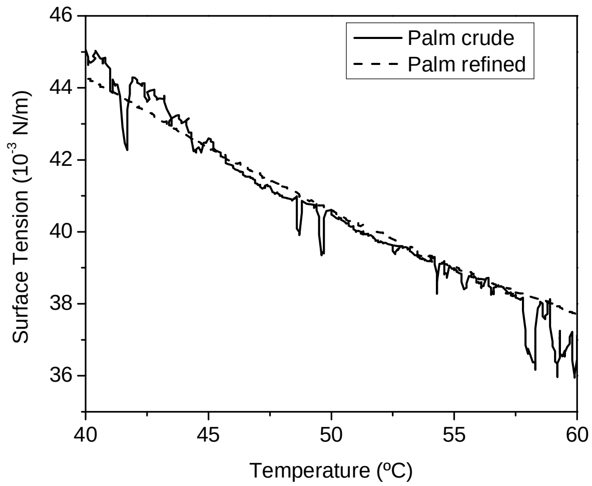

Figure 6. Graph of surface tension in function of temperature for refined and crude oils of palm.

The vegetables oils showed a decrease in the surface tension in function of temperature. This behavior is in agreement with the literature (Palmer, 1976). The crude oils showed a small deviation from this behavior and indeed must be due to the amount of impurities in these products.

4. CONCLUSIONS

The physical properties of various crude and refined vegetable oils were investigated, where rheological and surface tension measurements were carried out. The apparent viscosity of vegetable oils was influenced by temperature, an increase in the temperature causes a decrease in viscosity of vegetable oils. With relation to the rheological behavior, soybean, corn and canola oil, both crude and refined, and refined palm oil showed Newtonian behavior for all ranges of temperature and in the two geometries used. The Power law Model shows a good fit for the different oils studied and in the whole temperature range.

Distinct values of rheological parameters in both geometries studied were found. It can be concluded that there is great importance in indicating the measuring system used in any rheological test, thus enabling future comparisons and reproduction of data.

There was a decrease of the surface tension as a function of temperature in which the crude oil showed a small deviation from this behavior. The results reported in this study may be valuable in the design and operation of processes involving vegetable oils.

5. ACKNOWLEDGEMENTS

The authors are grateful to FAPESP, CNPq and CAPES for their financial support.

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