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Preparation and enhancement of thermal diffusivity of biodiesel from Nutrioli oil filled with Ag nanoparticles

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Abstract— **Liquid insulation plays a significant role in the design and operation of power system. There is good evidence in the literature that the addition of nanoparticles to conventional diesel can lead to significant increases in thermal characteristics. In this wok, spherical Ag nanoparticles with high thermal conductivity were added into biodiesel from soybean oil to form bionanofluids with the aim of enhancing thermal properties. Thermal diffusivity of biodiesel before and after modification were measured by mode mismatched dual-beam thermal lens technique. This was done in order to measure the effect of the presence of Ag nanoparticles on the biodiesel thermal diffusivity. The characteristic time constant of the transient thermal lens was estimated by fitting the experimental data to the theoretical expression for transient thermal lens. The thermal diffusivity of the bionanofluids (biodiesel, containing Ag nanoparticles) seems to be strongly dependent on the presence of metallic nanoparticles. The maximum diffusivity was achieved for the bionanofluids when concentration of nanoparticles increases from 0.1/1, 0.2/1, 0.4/1, 0.5/1, 0.7/1, 1/1 (mL/mL). A possible explanation for such thermal diffusivity of the bionanofluids with Ag nanoparticles is given. In order to characterize the bionanofluids, the following techniques were used: UV–Vis spectroscopy and transmission electron microscopy.**

Index Terms— **nanofluids, nanoparticles, soybean, thermal lens**

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I. INTRODUCTION

Biodiesel is defined by the ASTM as a liquid fuel that composed of the fatty acid alkyl ester of the long chain fatty acid derived from the vegetable oil and animal fats. Generally, there are four major types of feedstock available for the biodiesel production including oil seed (vegetable oil), animal fats, algae and different low quality material such as waste cooking oil, greases and soap stock [1]. Biodiesel production at industrial scale mostly utilized oil such as soybean, palm, and canola. However, the excess use of these vegetable oils (edible oil) leads to food versus crisis. The high cost of biodiesel is one the major hurdles towards its large-scale commercialization.

Cooling with nanobiodiesel possess one of the major technical challenges facing many industrial sectors such as transportation, microelectronics, and power generation. The common trend to address this problem is to enlarge surface of the heat sink by, for example, incorporating micro-channels into the heat transfer structure [2]. However, the performance of such systems could be further increased if novel fluids are engineered, which provide superior thermophysical properties to conventional fluids. Metals and metal oxides have much higher thermal conductivity than common fluids. Therefore, an innovative way to elevate the thermal conductivity of fluids is the addition of nanometer-sized metal or metal oxide particles into a base fluid. The use of nanometer-sized particles with large specific surface area could not only improve the heat transfer but also provides higher stabilization against particle sedimentation and prevent clogging of the heat sink. Various types of nanoparticles such as metallic and nonmetallic, with different shapes and sizes, can be suspended in different fluids forming so-called nanofluids. A number of the experimental studies on thermal properties of nanofluids show very large enhancements in the thermal conductivity of nanofluids. The extreme results were obtained for different allotropes of carbon. For example, enormous enhancement of thermal conductivity by 160% and by 70% were observed for a suspension containing 1% of MWCNTs in oil [3], [4]. Nevertheless, those materials are not very stable even at moderate concentration and need to be studied more carefully in different media. One promising way to characterize the thermal properties of both fat and oils from several sources and their respective biodiesels is by photothermal mehods [5]. Then, one of the most widely used techniques for photothermal characterization of liquids is the thermal lens technique. A thermal lens effect is created when the sample is exposed to an excitation laser beam with a Gaussian intensity profile. A fraction of absorbed energy is converted into heat, generating a radial temperature profile T (r,t). As a result of this local temperature increase a lens-like optical element in the heated region is created. The temporal evolution of such thermal lens is strictly related to optical and thermal properties of the sample and is detected by a probe beam, which impinges in a photodiode after passing through the sample [6]. Recently, the thermal lens technique has proved to be useful for the characterization of biodiesel [7]-[8]. The thermal lens technique can be used to estimate the thermal diffusivity (D) and the temperature coefficient of the refraction index (dn/dT) of biodiesel samples obtained from several oils, using both ethanol and methanol during transesterification processes [9]. Furthermore, the technique was applied to soybean biodiesel samples in order to evaluate the influence of residues and antioxidants on their thermo-optical properties [10]. The aim of this work is to characterize biodiesel with different concentrations of nanoparticles of Ag by thermal lens spectroscopy to attain experimental values of thermal diffusivity and a enhancement percentage of the thermal diffusivity with the nanoparticles of Au were found.

THEORY

The thermal lens signal is defined as the normalized change of the transmission of the probe beam, centered at the beam axis and located at a distance much larger than the pump Rayleigh parameter. Shen et al have derived as expression for the signal using a diffraction approximation for Gaussian beams, which is given by [6]:

$$I(t) = I(0)\left[1 - \frac{\theta}{2}\tan^{-1}\left(\frac{2mV}{\left[(1+2m)^2+V^2\right]\frac{t_c}{2t}+1+2m+V^2}\right)\right]^2 \qquad (1)$$

In (1), I (0) is the signal intensity when either t or θ is zero; θ is proportional to the induced phase shift difference in the probe beam after it passes by the heated area of the sample and the equation for θ is [8]:

$$\theta = -\frac{P_e A L}{k\lambda_p}\frac{dn}{dT} \qquad (2)$$

where P_e (40 mW) is the incident power, A (cm^{-1}) is sample the absorption coefficient, λ_p (632.8 nm) is the wavelength of probe beam, L (1 cm) is the cuvette thickness, k (W / K cm) is the thermal conductivity, dn/dT (K^{-1}) is the refractive index temperature coefficient and tc is the so-called characteristic time constant of the TL effect´s formation, which is defined as $t_c = \omega_e^2/4D$ with $\omega_e = 3.98 \pm 0.02 \times 10^{-3}$ cm is the spot size of the excitation laser beam at the sample; D is the thermal diffusivity where $D = k/\rho c$ where k is the thermal conductivity, ρ is the density and c is the specific heat of the nanofluid; $m = (w_{1p} / w_e)^2$, with w_{1p} (cm) being the probe beam´s radius in the sample position and $V = Z_1/ Z_c$, with Z_1 (cm) being the distance between the minimum beam waist and the sample position; $Z_c = \pi\, \omega^2_{op} / \lambda p$, with ω_{op} (cm) being the minimum probe beam radius, the values of m and V are constants.

The formation of thermal lens in the nanofluid could be explained as follows: The pump laser wavelength is 532 nm, which is within the longitudinal plasmon resonance band of the silver nanoparticles, the conduction electrons absorb a part of the radiation, and they undergo plasmonic oscillation. The conduction electron in the silver nanorods oscillate along in different directions. This causes the generation of hot electrons. The electron relax down to ground state by the emission of phonons, giving rise to rapid lattice heating. The thermal equilibrium with the surrounding medium is reached by the heat transfer between the phonon modes and the base fluid. Consequently, a thermal gradient is created, which in turn induces a large refractive index variation in the medium and thereby creates a thermal lens. As the change of refractive index of the medium with temperature *dn/dT* is negative, it acts as a divergent lens. For calibration TL system, a trace amount (~ 0.0024 mg/mL) of Rhodamine 6G dye is added with the water, as the water has no optical absorption at the pump wavelength. The thermal diffusivity of the water is found to be $D = 1.43 \times 10^{-3}$ cm^2 /s which is comparable with the thermal diffusivity of water [11]. All the measurements are made under the same experimental conditions.

II. EXPERIMENTAL

Production of biodiesel by transesterification of refined soy oil

The reaction transesterification was carried out in a 250 ml Erlenmeyer flask containing 452 g of soy oil. This was conduced at 45 C, keeping the rate of magnetic stirring and oil (4.80 mol) to methanol (1.60) ratio constant at 250 rpm and 1:3, respectively. Catalyst of 1.0 % (w/w) of sodium hydroxide was used. The catalys was dissolved into methanol according to the oil to alcohol (1:3.) The oil was heated up to reaction temperature in Erlenmeyer flask and once the alkali got dissolved, the alcohol-alkali mixture was added to the oil, and the reaction was allowed for 60 min. This sample was allowed to settle overnight in a separating funnel by gravity, settling into a clear, golden liquid biodiesel on top with the light brown glycerol at the bottom. On the second day the glycerol was drained off from the bottom of the separating funnel. The raw biodiesel was washed with water three times to remove the unreacted catalysis and glycerol. To get a pure biodiesel, this was purified in a rotary evaporator to remove any excess methanol.

Preparation of silver bionanofluids

In order to obtain biodiesel containing metallic nanoparticles, the silver nanoparticles were first synthesized by the reduction of AgNO3 with sodium citrate using a modified version of a previously reported procedure [12]. In brief, an aqueous solution of AgNO3 (0.0013 M, 25 mL) was refluxed for 30 min. Next, aqueous sodium citrate (0.097 M, 1 mL) was injected into the solution and then refluxed for 60 min to produce the yellow aqueous solution of silver nanoparticles of 16.3 nm average size. To 10 ml of the silver colloidal solution thus prepared, 10 ml of 0.0013 M solution of octadecylamine (ODA) in biodiesel of soy oil was added to yield immiscible layers of the colourless organic solution on top the yellowish silver hydrosol. Vigorous shaking of the test-tube resulted in transfer of the silver colloidal nanoparticles into the biodiesel and this was observed by the yellow colouration on the biodiesel and a corresponding loss of colour the aqueous phase when the two layers separated out. The process of washing with ethanol removes uncoordinated ODA molecules from biodiesel. Finally, the bionanofluid (which are mixture of silver nanoparticles in a biodiesel) was placed in a quartz cuvette of 1 cm thick for the optical and thermal measurement. Bionanofluids with lower concentrations of silver nanoparticles were obtained by adding of biodiesel (0.1/1, 0.2/1, 0.4/1, 0.5/1, 0.7/1, and 1/1 (nP / biodiesel) (mL/mL).) All the experiment were performed at room temperature and subjected to ultrasonic processing prior to each measurement.

III. RESULTS AND DISCUSSION

Fig. 1 displays a typical TEM image showing particle distributions of the 16.32 nm Ag nanoparticles and shape of the particle.

The UV-vis absorption spectra of biodiesel without nanoparticles of Ag is shown in the Fig. 2, also are show the optical absorption spectrum for biodiesel for different concentrations of Ag nanoparticles. This set of spectra shows an absorption peak strong at around 240 nm, and the crescent band around 435 nm, which is generally assigned to the surface plasmon resonance (SPR) of nanoparticle [10]. It can be seen that with increasing concentration of nanoparticles for example, 1 mL/ 1mL) there is an increase in the absorption peak with respect to the high concentration (1 mL/1 mL.) In these spectra shows the low absorption of the compounds around the wavelength of the excitation laser (514 nm) in the experiment.

To check the reliability of the TL experimental setup, measurements of the thermal diffusivity of nanoparticles/biodiesel concentrations and biodiesel were performed. The TL signal from biodiesel with concentration of Au/Biodiesel (0.2 mL/1mL) is show in Fig. 3. The signal decreases in time indicating that the thermal lens defocuses the probe beam on the detector, and the sample behaves like a divergent lens. The symbols represent the experimental data, and the solid line is the result of best fit by (1) with m=22.54 ± 0.1 and V = 0.62 ± 0.01 given by the experimental measurement of beam waist and θ =9.8 ± 0.2 × 10^{-2} and t_c = 19.6 ± 0.2 × 10^{-4} as adjustable parameters. Using the expression $t_c = \omega_e^2/4D$, a thermal diffusivity D = 22.8 ± 0.3 × 10^{-4} cm^2 /s for Au / Biodiesel (0.2 mL/1mL) concentration was obtained.

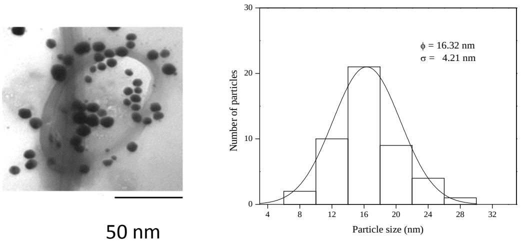

Fig. 1 TEM images and particles size histograms of Ag particles with a nominal size of 16.32 nm.

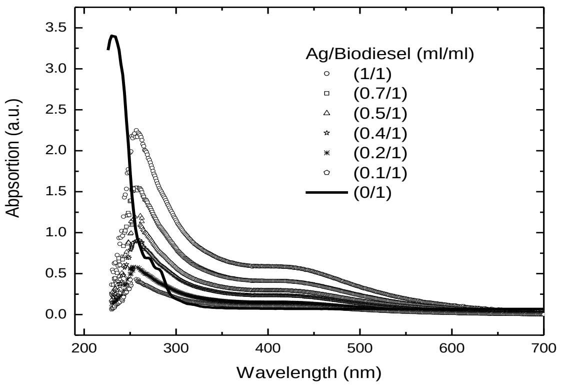

Fig. 2. UV-vis absorption spectra for: biodiesel, Ag nanoparticles, Ag/Biodiesel at different concentrations.

In a similar way, from the best fit of (2) to the experimental data, the thermal diffusivities of the other nanofluid samples were obtained at room temperature: D = (29.5±0.4) × 10^{-4}cm^2· s^{-1}, D = (28.1±0.2) × 10^{-4}cm^2· s^{-1}, D = (26.6±0.3) × 10^{-4}cm^2· s^{-1}, D = (26.6±0.3) × 10^{-4}cm^2· s^{-1}, and D = (20.5±0.5) × 10^{-4}cm^2· s^{-1}, for samples with Ag nanoparticle concentrations 1/1, 0.7/1, 0.5/1, 0.4/1 and 0.1/1 (mL/mL), respectively. The thermal diffusivity values obtained for biodiesel with gold nanoparticles are (slightly) higher than the one of pure biodiesel, 16.3±0.2 × 10^{-4}cm^2· s^{-1} (the reported value in the literature for pure biodiesel is 14.0 × 10^{-4}cm^2· s^{-1} [11], [13]-[14]). The increment in the thermal diffusivity goes from 25 % to 75 % for the different Ag nanoparticle concentrations. All results are in Table 1. There is a significant increases in thermal diffusivity with increasing Ag nanoparticle concentration.

The observed increase in the thermal diffusivity can be attributed to the great thermal diffusivity of the Ag nanoparticles contained in the biodiesel (oil.) Many authors have reported the enhancement in the thermal diffusivity of oleic acid attributed to the thermal diffusivity of individual carbon nanotubes for suspensions with 0.5 %, there was an increase in thermal diffusivity of 20 % [7] and for 1.0 vol % nanotubes the increase was 136 % [4].

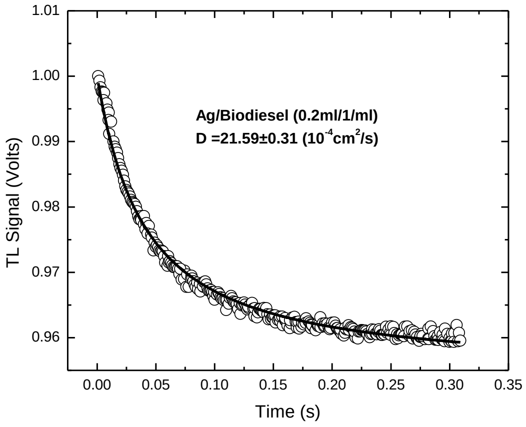

Fig. 3. Thermal lens signal of the Ag/Biodiesel (0.2 mL/1mL); empty circles (o) represent experimental points and the red line is the best fit with (1).

Table I. Dependence of the thermal diffusivity and other fitting parameters values of biodiesel on the concentration of Ag nanoparticles

nP/ Biod (mL/mL)	**$t_c(10^{-4}s)$**	**θ $(x10^{-2})$**	**$D(10^{-4}cm^2/s)$**	**% e**
1/1	14.8±0.2	10.0±0.2	29.5±0.4	75
0.7/1	15.9±0.1	13.4±0.3	28.1±0.3	61
0.5/1	16.8±0.2	13.9±0.3	26.6±0.3	53
0.4/1	17.7±0.2	10.8±0.2	25.3±0.2	45
0.2/1	19.6±0.2	9.8±0.2	22.8±0.3	31
0.1/1	21.8±0.2	9.1±0.2	20.5±0.2	18
Biod	27.4±0.3	39.9±0.11	16.3±0.2	Pure Biod

Biod= biodiesel; e= enhancement

In the literature, authors have pointed out many causes for the thermal increase of nanofluids. It is possible to list some physical reasons to explain this improvement in the heat transfer performance of nanofluids as follows: (1) the suspended nanoparticles increase the surface area and the heat capacity of fluid; (2) the suspended nanoparticles increase the effective thermal conductivity of the fluid; (3) the interaction and collision among particles, fluid and the flow passage surface are intensified; (4) the mixing fluctuation and the turbulence of the fluid are intensified; and (5) the dispersion of nanoparticles slightly modifies the transverse temperature gradient of the fluid.

The thermal diffusivity of various concentrations of silver nanoparticles suspended in soybean biodiesel has been measured. The soybean biodiesel thermal diffusivity increase with the increase of silver nanoparticles concentration. We attributed this increment in thermal diffusivity to phonon scattering at interface of particle-liquid and rich contact between the nanoparticle and surrounded liquid.

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REFERENCES

[1] W. C. Silva, A. M. Rocha, M. P. Castro, M. S. Sthel, H. Vargas, G. F. David, V.H. Pérez, Fuel, 14 (2014), 00-01.

[2] Shahriari, W. M. Mat Yunnus, R. Zamiri, J. Europ. Opt. Soc. Rap. Public., 8 (2013), 13026-1 – 13026-2.

[3] S.U.S. Choi, G.Z. Zhang, W.Yu, E.F. Lockwood, A. E. Grolke, Appl. Anomalus thermal conductivity enhancement in nanotube suspensions, Phys. Lett.. 79 (2001) 2252.

[4] S. Shaikh, K. Lafdi, R. Ponnappan, Thermal conductivity improvement in carbon nanoparticle doped PAO oil: an experimental study, J. Appl. Phys. 101 (2007), 064302-1 – 064302-7.

[5] J.A. Balderas López, A. Mandelis, Self-consistent phototermal technique: Application for measuring thermal diffusivity in vegetable oils, Rev. Sci. Instrum. 74 (2003) 700-702.

[6] J. Shen, R.D. Lowe, R.D. Snook, A model for cw laser induced mode-mismatched dual-beam thermal lens spectrometry, Chem. Phys. 165 (1992), 385-396.

[7] M. Ventura, E. Simionatto, L.H.C. Andrade, E.L. Simionatto, D. Riva, S.M. Lima, Fuel, 103 (2013) 506-511.

[8] L.C. Meher, D. Sagar, D. Vidya, S.N. Naik, Technical aspects of biodiesel production by transesterification – a review. Renew Sust. Energy Rev. 10, (2006) 248-268.

[9] G. Knothe, Analyzing biodiesel: standards and other methods, JAOCS, 83, (2006) 1097 – 1107.

[10] E. Shahriari, W. M. Mat Yunus, R. Zamiri, J. Europ. Opt. Soc. Rap. Public. 8, (2013) 13026-1 - 13026-4.

[11] R.C. Weast, Handbook of Chemistry and Physics 67 ed. (Chemical Ruber Corp., Boca Raton, FL., 1986-1987).

[12] J. F. Sánchez-Ramírez, U. Pal, L. Nolasco-Hernández, J. Mendoza-Álvarez, and J. A. Pescador-Rojas 2008, Journal of Nanomaterials, Volume 2008, 620412, 9 pages.

[13] S. M. Lima, M. S. Figueiredo, L. H.C. Andrade, A. R. L. Caíres, S. L. Oliveira, F. Aristone, Applied Optics 48, (2009) 5728-5732

[14] R. F. Souza, M. A.R.C. Alencar, C.M. Nascimento, M. G. A. da Silva, M. R. Meneghetti, J. M. Hickmann, Proc. of SPIE 6323, (2006) 63231T-1- 63231T-8

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- J .L. Jiménez-Pérez, R. Gutiérrez Fuentes, Z. N. Correa-Pacheco, J. Tánori-Cordova, A. Cruz Orea, G. López Gamboa, Study of Vegetable Biodiesel Enhanced by Gold Nanoparticles Using Thermal-Lens Technique. Int. J. Thermophys 36 (2015) 1086-1092
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- Z. N. Correa-Pacheco, A. Cruz-Orea, J .L. Jiménez-Pérez, S. C. Solorzano-Ojeda, C. L. Tramón-Pregnan, Measurement of thermal properties of Triticale starch films by using photothermal techniques. Int. J. Thermophys. 36 (2015) 873-879