Journal of Engineering Physics and Thermophysics, Vol. 83, No. 1, 2010

A PHOTOACOUSTIC AND ULTRASONIC STUDY ON JATROPHA OIL

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UDC 536.2

Using the photoacoustic technique, the thermal diffusivity of a dimethoxymethane + jatropha liquid mixture and pure jatropha oil is measured at room temperature. The result is correlated with the result of ultrasonic measurements.

Keywords: *Photoacoustics, thermal properties, jatropha oil.*

Introduction. Due to the gradual depletion of world petroleum reserves and fossil fuels, to pollution from increasing exhaust emissions, and to the increasing cost of crude oil, there is an urgent need for suitable alternative fuels for use in diesel engines. Vegetable oil is a promising alternative because of several advantages: it is renewable, environment-friendly, and easily produced in rural areas where there is an acute need for modern forms of energy [1–3]. Many researchers [4, 5] have conducted engine tests using vegetable oils in a semi-adiabatic engine and found that they reduced particulate emission and increased thermal efficiency. Among oil seeds of forest origin, jatropha curcas, popularly known as ratanjyot, is a promising and commercially viable alternative to diesel oil since it has desirable physicochemical and performance characteristics comparable to the latter. Jatropha curcas is a large shrub or tree native to the American tropics but commonly found and utilized throughout most of the tropical and subtropical regions of the world. The seeds of jatropha contains about 38–40% nonedible oil. Jatropha oil cake is rich in nitrogen, phosphorous, and potassium and can be used as organic manure [6]. Because of its excellent drought resistance, it is suitable for preventing soil erosion and shifting of sand dunes. In addition, it is biodegradable, nontoxic, and therefore eco-friendly.

Pramanik [7] investigated in detail the effect of temperature on the viscosity of jatropha oil and its various blends with diesel oil in a compression ignition engine. Forson et al. [8] reported such an investigation on a direct injection single-cylinder diesel engine. It is also noted that the cetane number and calorific value of jatropha are comparatively high. Since most of the works reported are aimed at conversion efficiency, thermophysical properties such as thermal diffusivity, thermal conductivity, and thermal expansion are very sparse in the literature.

Recently dimethoxymethane (DMM) [9] is found to be an additive to diesel oil and petrol to reduce the particulate size and pollution, thereby increasing the efficiency. Since jatropha oil is used as a blend with diesel oil, it is necessary to study the thermal properties of this mixture. Moreover, reliable thermophysical data for pure jatropha oil have not been available so far in the literature, especially thermal diffusivity. In this paper an attempt is made to study the thermal diffusivity of pure jatropha oil using a photoacoustic technique. Addition of oxygenates to an automotive fuel, including both diesel oil and gasoline, clearly reduces NO_x and CO emissions by reducing the flame temperature. Therefore jatropha oil is blended with DMM at various mass fractions (0.05, 0.10, 0.15, 0.20, and 0.25), and photoacoustic measurements on these samples are carried out. Similarly, ultrasonic measurements on pure jatropha oil and mixtures of jatropha oil and DMM (JDM) are also carried out for the temperature range 303–313 K to correlate the results obtained in photoacoustics. The velocity from ultrasonic measurements is used to calculate the nonlinear acoustic parameter.

Photoacoustics. Among the various photothermal techniques, the photoacoustic (PA) technique offers a powerful tool for determining the thermal and optical properties of liquid samples [10, 11] since the periodic component of the surface temperature of a sample can be determined indirectly with high sensitivity. The thermal diffusivity of a

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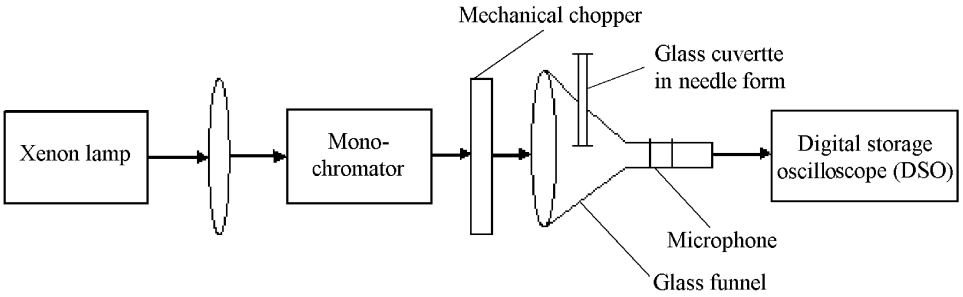

Fig. 1. Schematic diagram of PA setup.

material is a very important parameter, and it is closely related to the thermal conductivity, specific heat, and thermal expansion. The principle of the PA technique is that, when a modulated light is absorbed by the sample located in a sealed PA cell, the nonradiative decay of the absorbed light produces a modulated transfer of heat to the sample surface, which produces pressure waves in the gas inside the cell that can be detected by the microphone attached to the cell [12]. The present photoacoustic spectrometer consisted of a 400 W Xe-lamp (Jobin Yvon), an electromechanical chopper (Model number PAR 650), a monochromator (Model Triax 180, Jobin Yvon), a digital storage oscilloscope (DSO), and a PA cell. The sample (jatropha oil) is placed in the PA cell, and the microphone is located very close to the sample in a PA cell specially made for the liquid.

Photoacoustic Cell. The PA cell here is unconventional in the sense that it is made of a glass funnel of length 10 cm and diameter 5 cm, it is completely blackened inside with carbon black, and its wider end is sealed with a concave watch glass. Along the surface of the funnel on the top conical side, a small hole of diameter 1.5 mm is drilled. The liquid is injected into a needle-shaped cell (cuvette) with diameter 1 mm and length about 5 cm, which is sealed at the other end. This cuvette has to be placed in a glass funnel as shown in Fig. 1. A condenser microphone is inserted and placed close to the cuvette. The whole compartment should be airtight and soundproof. It is known that the amplitude of the PA signal will increase when the dimension of the PA cell is decreased, but cannot be decreased indefinitely through unwanted resonances. So, the dimension of the cell is very important. In general, the amplitude of the PA signal is very weak compared to solids, and as a consequence the PA cell was carefully designed. The signal after amplification is fed to a digital storage oscilloscope. The complete setup is shown in Fig. 1.

Photoacoustic Measurements. The thermal diffusivity is of direct importance in heat flow studies, as it determines the rate of periodic heating or transient heat propagation through the medium. The thermal diffusivity is measured by studying the variation in the amplitude of the PA signal for various chopping frequencies and a fixed wavelength of the incident light.

The intensity at the center of the beam coming out from the PA cell can be expressed as [13]

$$S = \frac{I_t - I_\infty}{I_t} = S_0 \frac{1}{\left(1 + 2n\,\frac{t}{t_c}\right)^2}, \qquad S_0 = \frac{I_\infty - I_0}{I_0}. \tag{1}$$

Twarowski and Kliger [13] reported multiphoton absorption spectra using thermal blooming, where a 1-mm diameter pin hole was placed at 10 cm from the sample, so that only the center of position of the chopped light (which has a diameter of 0.5 cm) was studied. In the present experiment, the same concept is used as follows.

The PA signal produced by the sample (jatropha oil and JDM) was measured for different chopping frequencies. The variation of the reduced PA signal $\sqrt{S_0/S}$ (where S_0 and S correspond to the signals at time t = 0 and time t) as a function of time is shown in Fig. 2 for a particular mass fraction of DMM in jatropha oil and chopping frequency. From the slope of the function $\sqrt{S_0/S}$ the characteristic time constant, t_c, corresponding to the liquid sample is found.

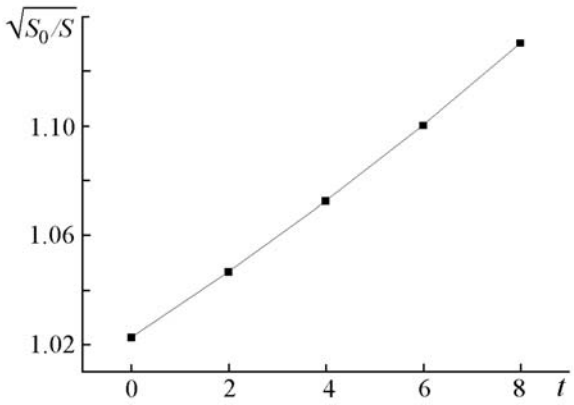

Fig. 2. Reduced PA signal as a function of time in JDM mixture at mass fraction of 0.05. t, msec.

TABLE 1. Values of t_c, D, and k for pure jatropha oil and JDM mixtures at various mass fractions obtained by photoacoustic technique at room temperature

Characteristic	Mass fraction					
	0	0.05	0.10	0.15	0.20	0.25
t_c, msec	148	136	140	149	128	120
$D \cdot 10^8$, $m^2 \cdot sec^{-1}$	4.26	4.63	4.50	4.37	4.92	5.25
k, $W \cdot m^{-1} \cdot K^{-1}$	0.09	0.10	0.10	0.09	0.10	0.11

This constant is related to the thermal diffusivity D and the beam radius ω through the relation $t_c = \omega^2/(4D)$ [13]. A reference sample (water) with the known thermal diffusivity is used here to determine the thermal diffusivity of the unknown sample (to eliminate the uncertainty in the determination of the beam radius). Thus,

$$D = \frac{D_w t_{c,w}}{t_c} . \tag{2}$$

The observed values of the time constant and thermal diffusivity of jatropha oil and JDM for various mass fractions are presented in Table 1 (measurement error less than 3%). From the measured value of t_c, the thermal diffusivity is found using Eq. (2) (when Eq (1) is rearranged, it is found to be in exponential form and so the slope gives the time constant). The present experimental setup was first calibrated by measuring the thermal diffusivity of acetone, water, and toluene. The measured values of t_c for water (43 msec) and acetone (55 msec) and the thermal diffusivity of toluene ($9.8 \cdot 10^{-4}$ $cm^2 \cdot sec^{-1}$) are in good agreement with those reported in the literature [14]. From the measured value of the thermal diffusivities, the thermal conductivities can be calculated by using the relation $D = k/(C\rho)$. The specific heat of jatropha oil is determined experimentally from Newton's law of cooling, and for the JDM mixture it is found using Vegard's law with the known specific heat of DMM. In general, the thermal diffusivity is obtained from the characteristic frequency f_c of a sample (DMM + jatropha) and not from the chopping frequency. Since the characteristic frequency of any sample is a unique property, the thermal diffusivity will not change with the chopping frequency. That is why there is almost no variation in the thermal diffusivity, and the minor variations are due to experimental errors. Since no reports on the thermal conductivity of pure jatropha oil and JDM mixtures are available in literature, these results could not be verified immediately. However, here the results of PA technique are compared with those of ultrasonic measurements. Such ultrasonic results have also not been reported in the literature so far.

Ultrasonic Measurements. The study of molecular interactions in liquid mixtures is of considerable importance in the elucidation of the structural properties of molecules. Here ultrasonic measurements are carried out for pure jatropha oil (in the temperature range 303–333 K) and for JDM at various mass fractions in the temperature range 303–313 K (as the vaporization point of DMM is 314 K). The ultrasonic velocity in pure jatropha oil and JDM was measured at various temperatures using an ultrasonic interferometer (with a fixed frequency of 2 MHz), where the accuracy in measurements was 2%. The sample temperature was maintained constant by circulating hot water from a

TABLE 2. Values of ultrasonic velocity and parameter *B*/*A* for pure jatropha oil in the temperature range 303–333 K

Characteristic	*T*, K						
	303	308	313	318	323	328	333
u, m/sec	1400	1383	1370	1355	1342	1330	1315
B/*A*	10.4	10.2	10.1	10.0	9.9	9.8	9.7

TABLE 3. Values of ultrasonic velocity (m/sec) in JDM mixtures at various mass fractions in the temperature range 303–313 K

T, K	Mass fraction				
	0.05	0.10	0.15	0.2	0.25
303	1386	1375	1363	1350	1340
308	1377	1360	1350	1335	1325
313	1360	1346	1336	1320	1315

TABLE 4. Values of u, L_f, and k for JDM mixtures obtained by ultrasonic technique at room temperature

Characteristic	Mass fraction				
	0.05	0.10	0.15	0.20	0.25
u, m/sec	1386	1375	1363	1350	1340
L_f, Å	1.9	2.0	2.1	2.2	2.2
k, $W \cdot m^{-1} \cdot K^{-1}$	0.070	0.073	0.075	0.077	0.078

TABLE 5. Values of thermal conductivity (W/(m·K)) of JDM mixtures obtained by ultrasonic and PA techniques at room temperature

Technique	Mass fraction				
	0.05	0.10	0.15	0.20	0.25
PA	0.09	0.10	0.10	0.09	0.10
Ultrasonic	0.070	0.073	0.075	0.077	0.078

thermostatically controlled water bath (with an accuracy of $\pm 0.1^{\circ}$C). The results for the ultrasonic velocity in pure jatropha oil and JDM (for various mass fractions) as a function of temperature are presented in Tables 2 and 3, respectively. It is found that the ultrasonic velocity decreases as the temperature increases. This behavior is also seen in other liquids [15].

The thermal conductivity can be computed from the intermolecular distance, which is found from the ultrasonic velocity. The intermolecular free length can be deduced from the available volume per mole V_a as follows [16]. According to Schaaffs, V_a can be expressed as

$$V_a = V\left(1 - \frac{u}{u_\infty}\right), \tag{3}$$

where u_∞ = 1600 $m \cdot sec^{-1}$. The intermolecular free length L_f is calculated using the following equation:

$$L_f = \frac{2V_a}{Y}, \tag{4}$$

where the surface area per mole Y can be written as

$$Y = (36\pi N V_0^2)^{1/3}. \tag{5}$$

The ultrasonic velocity is used to calculate the intermolecular free length, which in turn is used to compute the thermal conductivity.

TABLE 6. Calculated values of *B*/*A* for JDM mixtures in the temperature range 303–313 K

T, K	Mass fraction				
	0.05	0.10	0.15	0.20	0.25
303	10.3	10.2	10.0	9.9	9.9
308	10.2	10.0	9.9	9.8	9.8
313	10.0	9.9	9.8	9.7	9.7

As a first approximation, we can evaluate the thermal conductivity in liquids from the intermolecular free length L_f if we assume the latter to be the mean free path; thus, the thermal conductivity is

$$k = \frac{1}{3} C L_f u . \tag{6}$$

To calculate the thermal conductivity, the Brownian motion for heat diffusion was assumed, which is a very good approximation. With the mean free length and the velocity of sound in JDM, the thermal conductivity is calculated at room temperature and given in Table 4 (error in measurements is less than 2%). Then a comparison can be made between the results of photoacoustic and ultrasonic measurements for the thermal conductivity (see Table 5). It is found that the results of the PA technique agree fairly well with those of the ultrasonic technique.

Nonlinear Parameter. It should be noted that the equations used earlier are strictly valid for linear liquids, i.e., molecular displacements in liquids should be very small compared to the free path when an ultrasonic energy propagates through a liquid. To make a meaningful comparison between the results of photoacoustic and ultrasonic measurements, the amount of nonlinearity should be estimated in pure jatropha oil and JDM, which is known as the nonlinear parameter *B*/*A*. The study of nonlinearity in organic liquids, in particular, is an important topic of researches and a lot of corresponding works are reported in the literature [17, 18]. This can be understood as follows. If the equation of state of a medium is represented by a Taylor series, only the quadratic and linear terms are considered. The higher-order terms are considered when the displacements are higher, and the ratio of the respective coefficients of these terms, *B*/*A*, is used as a parameter to describe the nonlinearity of the medium. Due to the growing applications of nonlinear acoustics in a number of areas, which range from underwater acoustics to biomedicine, there has been increasing interest in estimating the nonlinear acoustical property of materials.

Kittel [19] and Hartman [20] studied this nonlinearity in the beginning using ultrasonic velocity. The Schaaff theory is one of the well-accepted theories for organic liquids, and recently Tong and Dong [21] in the study of the ultrasonic velocity and nonlinear acoustic parameter *B*/*A* in an organic liquid modified Schaaff's equation for *B*/*A* and obtained the following:

$$\frac{B}{A} = (\gamma - 1)\frac{1}{T\beta} + J(x) = J_0 + J(x) , \tag{7}$$

where

$$J(x) = \frac{2(3-2x)^2}{3(x-1)(6-5x)} .$$

Here x is the real volume of a molecule, which is the ratio of the molecular weight to ρb, where

$$b = \frac{16}{3}\pi r_0^3 N . \tag{8}$$

We calculated the nonlinear parameter *B*/*A* for pure jatropha oil in the temperature range 303–333 K using the modified Tong and Dong equation [21] (see Table 6). It is observed that there is a change in *B*/*A* with temperature. The experience gained with other organic liquids [22] reveals that the nonlinear parameter is above 8 for most of the liquids. Here we get a value of the same order for both pure jatropha oil and JDM (see Tables 2 and 6), i.e., the nonlinearity does not increase because of the addition of DMM to pure jatropha oil.

Results and Discussion. Jatropha oil as such is a viscous liquid and cannot be used straightaway for automobile engines, even though this is one of the best substitutes for fossil or petroleum fuels. Similarly, DMM is recently found to be a very good additive to diesel oil in enhancing the efficiency and reducing the emission of particulate matter, despite the fact that DMM is explosive. Here, the binary mixture of jatropha oil and DMM was studied in detail for determination of thermal properties by photoacoustics. The results on the thermal diffusivity of pure jatropha oil and JDM mixtures for various mass fractions are given in Table 1. The thermal diffusivities reported are averaged over at least five measurements. Since the thermal properties of jatropha oil are not available in the literature, a direct comparison could not be made. It has already been noted that the calorific value and cetane number of jatropha oil, which are comparable to those for diesel oil, makes it an ideal alternative fuel compared to other edible vegetable oils [7]. Thus, by the same photoacoustic technique, the thermal diffusivity of petrol was found to be $7.2 \cdot 10^{-8}$ $m^2 \cdot sec^{-1}$, which is in good agreement with the literature value [23]. Similar measurements on JDM were made by photoacoustics and ultrasonics. The thermal conductivity calculated from ultrasonics is comparable with the results of photoacoustic measurements. To the best of our knowledge, this is the first report on photoacoustic and ultrasonic measurements of the thermal properties of jatropha oil and JDM mixtures.

Conclusions. Thermal properties obtained from photoacoustics show that the thermal diffusivity and conductivity of jatropha are not affected by addition of DMM (despite its large oxygen content). Thus, when it is used, the engine will not be heated, but at the same time one can expect low particulate emission and hence improved efficiency.

One of the authors, G. Krishna Bama, acknowledges the University Grants Commission, New Delhi, India for providing a fellowship under the FIP scheme to carry out this work in the School of Physics, Madurai Kamaraj University, Madurai.

NOTATION

A and *B*, first and second terms in the Taylor expansion series, respectively; *b*, Van der Waals constant; *C*, specific heat, J/(kg·K); *D*, thermal diffusivity, m^2/sec; f_c, characteristic frequency, Hz; *I*, signal intensity; *k*, thermal conductivity, W/(m·K); L_f, intermolecular free length, m; N, Avogadro number; *n*, number of photon adsorbed; r_0, molecule radius, m; *S*, relative signal intensity; *T*, temperature, K; *t*, time, msec; t_c, characteristic time constant, msec; *u*, ultrasonic velocity, m/sec; *V*, molar volume at temperature *T*, m^3/mol; V_a, available volume, m^3/mol; V_0, molar volume at zero temperature, m^3/mol; *x*, real molecule volume, m^3; *Y*, surface area per mole, m^2/mol; β, isobaric expansibility; γ, ratio of specific heats; ρ, density, kg/m^3. Subscripts: c, characteristic; *t* refers to time *t*; w, water; 0, initial value; ∞, steady state.

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