EXPERIMENTAL INVESTIGATION ON THERMAL CONDUCTIVITY AND THERMAL DEGRADATION OF HONGE OIL METHYL ESTER WITH B-20 BLEND

Vinay Atgur1*, G. Manavendra2, G.P. Desai3 and B.Nageswara Rao4

ABSTRACT
Honge oil methyl ester (HOME) with B-20 blend is considered to examine thermal conductivity and thermal degradation of the biodiesel. Transient hot wire method is adopted to determine thermal conductivity of the samples. Heat source is clubbed with C-DAQ and LAB-VIEW software is utilized to record temperature and time. Following Sastry’s power law model, an improved empirical relation is developed for thermal conductivity of HOME with B-20 blend. Thermogravimetry (TG-DTG) analysis is performed under atmospheric conditions with 10°C/min heating rate of pure air flow. Diesel is exhibited one mass loss event from 55-334°C, whereas two mass loss event in case of biodiesel. Maximum decomposition temperature noticed for diesel, HOME and B-20 blend are 195°C, 227°C and 175°C respectively. Complete mass degradation takes place for diesel and HOME at 498°C, in case of HOME with B-20 blend complete mass degradation occurred at 377°C.

Keywords: Empirical Relation, Mass Degradation, Biodiesel, TG-DTG Analysis, Mass Loss.

INTRODUCTION
Depletion of oil reserves motivated the researchers on alternative energy resources. For the past couple of decades studies indicated on the use of pure vegetable oils in diesel engine or burners [1-3]. Developing countries need such type of resources for sustainability. Major problems related to the vegetable oils are on composition, structural studies, volatility and viscosity [4, 5]. Thermophysical properties study of pure vegetable oils play a vital role in heat transfer characteristics, life and performance of engines. In diesel engine minimum operation combustion temperature is 180°C which indicates the importance of transient phase [6, 7]. Biodiesels are composed of various fatty acids composition. The decomposition of these fatty acids differs from one source to another source. Combustion behavior of biodiesels depends on these properties. Transient hot wire method is adopted for measuring the thermal conductivity with nichrome wire (cylindrical) as heat source which is immersed in sample. Nichrome wire is connected to variable auto transformer, voltmeter, ammeter and data acquisition system for measurement of temperature with respect to time [8-10]. Data acquisition system RS232 helps us to measure for small intervals which can be further transmitted to MATLAB or Excel [11, 12].

Several authors studied the different methods for measurement of thermal conductivity among all of them transient hot wire is preferred because of its simple design, accuracy and time response. Several authors used the transient hot wire method to measure the thermal conductivity of low viscous fluids like water, ethylene glycol, Nanofluids and the mixture of them by using different heating materials elements like aluminum, platinum etc also by modifying their dimensions [13]. Some of the authors used 3ω hot wire method for the measurement of thermal conductivity. In the present work Honge oil methyl ester (Pongamia) is considered which is derived from the pongamia piñata seeds through the transterification process with the molar ratio is 5:1, and 1% of NaOH catalyst concentration. Since the pongamia seed are available thought the year its seeds (kernel) is having 38% of oil content.

This paper was recommended for publication in revised form by Regional Editor Baha Zafer
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Manuscript Received 17 February 2020, Accepted 2 July 2020
Properties of these biodiesel matches well with the diesel as discussed in table 1. Thermal analysis methods for the study of stability place a vital role for the analysis of combustion kinetics and decomposition [16]. Due to the presence of complex series and parallel reaction kinetics will differ from one source to another [17]. In the present work thermal conductivity and thermal degradation of the honge oil methyl ester and its B-20 blend are studied as function of temperature. Obtained results are modeled using the Sastry’s empirical model and the results are in good agreement with the literature. Thermal stability of the honge oil methyl ester and its B-20 blend is studied by using NETZSCH 449F3 simultaneous thermal analyzer with a heating rate of 10°C/min in atmospheric air. Reaction region, maximum decomposition temperature and weight loss are analyzed by the generated thermogravimetry and derivative thermogravimetry (TG-DTG) curve. Among the various blends tested on the engine, performance of B-20 blend is closely matches with diesel [18].

**Table 1** Comparison of biodiesel and diesel properties

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Calorific value (MJ/kg)</th>
<th>Kinematic Viscosity (@ 40°C cSt)</th>
<th>Cetane value</th>
<th>Density (kg/m³)</th>
<th>Flash point (°C)</th>
<th>Pour point (°C)</th>
<th>Cloud point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIESEL</td>
<td>44.22</td>
<td>2.87</td>
<td>47.8</td>
<td>840</td>
<td>76</td>
<td>-3</td>
<td>6.5</td>
</tr>
<tr>
<td>HOME</td>
<td>38.66</td>
<td>4.92</td>
<td>51.0</td>
<td>870</td>
<td>140</td>
<td>4.3</td>
<td>13.2</td>
</tr>
<tr>
<td>B-20 HOME</td>
<td>43.85</td>
<td>2.98</td>
<td>-</td>
<td>835</td>
<td>86</td>
<td>2.8</td>
<td>7.8</td>
</tr>
</tbody>
</table>

**Table 2** Chemical composition of HOME

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Structure</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated fat</td>
<td>-</td>
<td>20.5</td>
</tr>
<tr>
<td>Monounsaturated fatty acid</td>
<td>-</td>
<td>46</td>
</tr>
<tr>
<td>Polysaturated fatty acid</td>
<td>-</td>
<td>33.4</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>16:00</td>
<td>10.8</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>18:00</td>
<td>8.7</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>18:01</td>
<td>46</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>18:02</td>
<td>27.1</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>20:00</td>
<td>0.8</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>18:03</td>
<td>6.3</td>
</tr>
<tr>
<td>Behenic acid</td>
<td>22:00</td>
<td>3.2</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>14:00</td>
<td>0.23</td>
</tr>
<tr>
<td>Capric acid</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>12:00</td>
<td>0.1</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

MATERIAL

Biodiesel samples of Honge oil methyl ester (HOME), were acquired in the local commerce and there B-20 blends were prepared in the laboratory. For the transient hot wire equipment nichrome wire of 5mm diameter and 20 cm length was used as the heat source. In the Thermogravitometry experimentation alumina crucible pan (Al₂O₃) has considered with atmospheric air as inert gas and oxygen as purge gas.

EXPERIMENTAL PROCEDURE

In the Transient Hot Wire Method, the thermal conductivity of the medium is determined by observing the rate at which the temperature of a metallic heater increases with time after an initial set of voltage has been connected to it. The heater is with the dimensions of 21cm height and 6.5mm of radius. The heater is electrified with the given power source. To know whether the heater is conducting the heat uniformly or not we had to check it by using thermocouples connected to the heater at three different places on it. To observe the obtained temperature from three different places we connected the other ends of the thermocouples to temperature indicator.

Thermocouples used to read the temperature are of K-Type thermocouples, because of two reasons: are 1) K-Type thermocouples are economical in cost, easily available and has a good precisson ranges. 2) Temperature indicator we used is itself a K-Type indicator. To start experiment we need to connect each and everything component and check. A tube made of plastick has been applied to hold the liquid to be heated. We carefully inserted the heater in to the sample holded tube. To start the experiment we need to put the voltmeter and ammeter in a steady state. Introduce the C-DAQ (Data Acquisition System) here to get the time vs temperature values. Initially we have to give the set up instructions to the C-DAQ by using LAB-VIEW software to read time vs temp values at 0.001 level for time and temperature also. Main advantage of the C-DAQ is its fine way of giving results. Conducted the experiments for Diesel, HOME and B-20 HOME and taken out the time and temperature readings by using the LAB-VIEW software. Experiment done until 100°C and calculated the thermal conductivity values by using a standard formula from a reference paper. NI 9219 module is used in the C-DAQ to acquire the time, temperature data which is specifically made to acquire the data of mechanical responses like frequency, vibrations, thermocouple data etc., To restrict the heat which is easily releases from the sample tube, it is wounded with glass wool with a thickness of 1.5 to 2cm. The heat releases from the sample tube is nothing but the natural convection, and we use glass wool to restrict that heat. Voltmeter, ammeter and thermocouple used in the experiments processes accuracy of 1% each. 3.41% of uncertainty involved in the measurement which has been taken care during the thermal conductivity calculation.

TG-DTG COMBUSTION EXPERIMENTS

T-zero calibration i.e. temperature calibration is done by using two experiments, first calibration will be performed using no pans or without samples to get the baseline. Second experiment is carried out using the sapphire material alumina without a pan placing on both the reference position. In both the experiments cell is preheated, followed by an initial equilibrium temperature then holding isothermal for 5 minutes. Temperature zero mass aluminum pans are appropriate since the samples are liquids and volatile. Temperature as well as sensitivity calibration done Al₂O₃ furnace.

TG-DTG combustion experimentation is performed using NETZSCH STA 449F3, aluminum pan with heating rate of 10°C/min and the curve is analyzed in terms of heat flow and reaction intervals. In air some material undergoes char formation due to partial combustion that will affect results but in oxygen environment most organic will go through complete combustion for this reason combustion experiment is performed in oxygen environment. Pans are hermetically sealed to avoid the damage for the TG-DTG cell. Initially place the sample (3-5ml) in to the
pan and load the pan into the equipment. While starting the experimentation select the required temperature range as 30-500°C and select the heating rate 10°C/min. Purge gas as oxygen is selected for experiments.

Figure 1. Experimental set up of transient hot wire method ((A-C-DAQ, B-Thermocouple, C-Heater, D-Test Cell, E-Variac, F-Ammeter, G-Voltmeter, H-RS230 Cable and I-Computer.)

Figure 2. Outline of transient hot wire method, (A-C-DAQ, B-thermocouple, C-top cap, D-glue, E-heating wire, F-coolant, G-testing Sample, H-sample container, I-bottom Cap, J-A.C.power supply, K-resistance, L-multimeter, M-variac, N-RS230 cable and O-computer)
RESULT AND DISCUSSION

THERMAL CONDUCTIVITY

For performing the numerical simulation of combustion process transport properties of the fuel plays a vital role, for biodiesel and its blend these properties data are not sufficiently available. Therefore the present study investigates one of the important property i.e thermal conductivity has been experimentally determined.

Figure 3 shows the comparison of the variation of thermal conductivity with respect to temperature of (30°C–100°C) diesel by using transient hot wire method to its theoretical value by taking the average of the three runs. Theoretical vs. experimental value matches well with the averaged error of 0.4 (+/-). As temperature increases the thermal conductivity value for diesel decreases due to the reason that as we heat the diesel there exists a buoyancy force by density gradient which opposes by the viscous resistance of the fluids leading to the thermal non equilibrium in the diesel there by thermal conductivity of the diesel decreases with respect to the diesel.

Figure 5 shows the variation of thermal conductivity values for diesel, HOME and JOME with respect to temperature from (30°C–100°C). It is observe decrement in thermal conductivity with increase in temperature for all the three fuels. Since the FAME profile of HOME indicates that there is more contain of oxygen compared to JOME [19]. Due to the presence of weaker double bonds both the biofuels exhibit decrease in the thermal conductivity, the elemental composition of the carbon and hydrogen in HOME is less compared to JOME and diesel molecules have long chain hydrocarbons and low ignition temperature due to this JOME exhibits a lesser thermal conductivity value when compared to HOME and diesel. Since both HOME and JOME are having merely same fatty acid profiles thermal conductivity of both the biodiesels will follow the same trend [20].

Figure 6 indicates the variation of thermal conductivity for diesel, HOME and B-20. As the biodiesel percentage increases with the diesel the physical properties tends towards the diesel [21]. In the table 1 the properties of the B-20 blend matches merely with diesel. Kinematic viscosity of the diesel, HOME and B-20 are 2.87 cSt, 4.92 cSt, 2.98cSt respectively. Density value for diesel, HOME and B-20 are 840 kg/m³, 870 kg/m³ and 834 kg/m³ respectively [22].
Figure 4. Comparison of thermal conductivity of diesel with literature

By considering both the properties we can say that B-20 home matches well with the diesel therefore the thermal conductivity of B-20 will follow the same trend as diesel with nearly the same value. As the temperature increases both density and viscosity decrease, density leads to the buoyancy force which will be opposed by the viscous force for the flow therefore the thermal conductivity decreases with increase in the temperature.
Figure 6. Comparison of thermal conductivity for HOME and its blend with diesel.

MATHEMATICAL MODELLING

Sastry [23] has suggested empirical relation for thermal conductivity of the liquids as a function of temperature in the power-law form including boiling and critical temperature as

\[ \lambda_L = \lambda_b \times a^m \]  

where

\[ m = 1 - \left( \frac{1 - T_r}{1 - T_{br}} \right)^n \]  

\[ T_r = \frac{T}{T_c} \]  

\[ T_{br} = \frac{T_b}{T_c} \]

\[ \lambda_L \] is the thermal conductivity of the liquid; \( \lambda_b \) is thermal conductivity of the liquid at boiling point; \( T_b \) is the boiling point temperature; \( T_c \) is the critical point temperature; and \( T \) is the temperature at which thermal conductivity needs to find. The constants in the power-law model are \( a = 0.6 \) and \( n = 0.2 \). Equation (1) is further simplified as follows.
\[ m = 1 - \left( \frac{T_c - T}{T_c - T_b} \right)^{0.2} = 1 - \left[ \left( \frac{T_c - T_b + (T_b - T)}{(T_c - T_b)} \right) \right]^{0.2} = 1 - \left[ 1 + 0.2 \left( \frac{T_b - T}{T_c - T_b} \right) \right]^{0.2} \]  

Using (5) in (1) and the value of \( a=0.16 \) one can write

\[ \log \lambda_L = \log \lambda_p - 0.2 \left( \frac{T_b - T}{T_c - T_b} \right) \times \log (0.16) \]

\[ \log \lambda_L = \log \lambda_p + 0.15917 \left( \frac{T_b - T}{T_c - T_b} \right) \]  

Specifying \( \lambda_L = \lambda_{L1} \) at \( T = T_1 \) equation (6) becomes

\[ \log \lambda_{L1} = \log \lambda_p + 0.15917 \left( \frac{T_b - T_1}{T_c - T_b} \right) \]  

Similarly specifying \( \lambda_L = \lambda_{L2} \) at \( T = T_2 \) equation (6) becomes

\[ \log \lambda_{L2} = \log \lambda_p + 0.15917 \left( \frac{T_b - T_2}{T_c - T_b} \right) \]  

Subtract eq. (8) from (7) and simplifying

\[ \log \left( \frac{\lambda_{L1}}{\lambda_{L2}} \right) = 0.15917 \times \left( \frac{T_b - T_1}{T_c - T_b} \right) \]  

**Table.3** Boiling temperature and critical temperature of diesel and HOME

<table>
<thead>
<tr>
<th>Fuel</th>
<th>( T_b ) in °C</th>
<th>( T_c ) in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>360</td>
<td>450</td>
</tr>
<tr>
<td>HOME</td>
<td>316</td>
<td>415</td>
</tr>
</tbody>
</table>

Using the boiling point temperature \( (T_b) \), measured thermal conductivity \( (\lambda_{L1} \text{ and } \lambda_{L2}) \) at temperatures \( (T_1 \text{ and } T_2) \), one can find the critical temperature \( (T_c) \) from (9). Table. 3 gives the critical temperature for diesel and HOME, using the physical properties \([24, 25]\) empirical relation for the thermal conductivity of diesel and HOME are presented below

For diesel:

\[ \lambda_L = 0.15061 \times 0.16^{0.0011T} \]  

(10)

For HOME:

\[ \lambda_L = 0.15559 \times 0.16^{0.002T} \]  

(11)

Figure 7 and 8 shows the comparison of the developed empirical relation (10) and (11) for thermal conductivity of diesel and HOME with measured data.
From Figure 7 and 8 it can be seen that thermal conductivity decreases with increasing temperature of liquids. This could be mainly due to expansion of liquids with increasing temperature and movement of molecules. The empirical relation (10) and (11) confirms the trend of thermal conductivity of liquids. The maximum deviation of 1.24% observed at 70°C for diesel, whereas 1.13% deviation observed for HOME.

Figure 7. Variation of thermal conductivity ($\lambda_L$) of diesel with temperature.

Table 4 shows the thermal conductivity value for diesel, HOME and B-20 HOME. From the below values can say that the B-20 blend properties matches closely with the diesel. Generated thermal properties data can be used for the design and optimization of combustors and for the simulation purpose.

Figure 8. Variation of thermal conductivity ($\lambda_L$) of HOME with temperature.
Table 4: Thermal conductivity of biodiesel and diesel properties

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Thermal Conductivity in W/mK at 40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIESEL</td>
<td>0.141</td>
</tr>
<tr>
<td>HOME</td>
<td>0.133</td>
</tr>
<tr>
<td>B-20 HOME</td>
<td>0.137</td>
</tr>
</tbody>
</table>

THERMOGRAVIMETRIC ANALYSIS (TG-DTG)

TG-DTG combustion mechanism of hydrocarbons since too complicated. As hydrocarbons have different number of carbons and different type of bonding, complex parallel and serial reactions take place. Whereas combustion mechanisms of biofuels are still under study as vegetable oils ingredients vary according to their origins due to this conversion of triglycerides to monoglycerides occurs with severities and different combustion behavior [26]. Generally the combustion mechanism of crude oil exhibits two steps of reaction, low temperature oxidation (LTO) where mass loss of free moisture, volatile hydrocarbons such as ketones, aldehydes, alcohols and peracids takes place. During high temperature oxidation (HTO) molecules of hydrocarbons are oxidized by air during this bigger molecules are converted into smaller fractions and smaller molecules takes the combustion reaction easily. Combustion mechanism of diesel takes place only one step of reaction where as it loses small volatile components.

Figure 9 shows TG/DTG curve of Diesel shows two steps of mass loss related to the evaporation in the first step where as second step represents the decomposition, volatilization of typical carbon chains C₉ to C₂₅ .in which largest mass loss occurs around 97.38%.Diesel contains 75% of saturated hydrocarbons mainly paraffin’s (n-iso, and Cyclo paraffins) and 25% of aromatic hydrocarbons (including naphthalene’s and alkyl benzenes)[27].Combustion reaction zone occurs between 55°C-334°C with mass loss of 97.38% at 334°C.Complete combustion occurs at 498°C with 0.50% residual mass. Flash point of diesel is around 75°C in between 55°C-75°C.
preparation for the burning phase takes place i.e physical delay takes place [28, 29]. Diesel stable up to 55°C further onwards the combustion phenomena will takes place with peak temperature of 195°C.

![TG-DTG analysis graph of HOME](image1)

**Figure 10.** TG-DTG analysis graph of HOME

TG/DTG curve of Honge oil Methyl Ester (HOME) shows two steps of mass loss related to the volatilization and combustion of triglycerides in a synthetic air atmosphere. Figure.10 presented two mass step loss between 130-498°C with a residual mass of 1.49% and with a maximum temperature of 227°C. The mass of loss is related to the volatilization and combustion of methyl esters with a major content of oleic acid 46% such results are in good agreement with literature [30, 31]. HOME is thermally stable up to 130°C further which the first step of reaction takes place.

![TG-DTG Analysis graph of B-20 blend of HOME](image2)

**Figure 11.** TG-DTG Analysis graph of B-20 blend of HOME
TG/DTG curve Figure 11 of B-20 HOME shows similar behavior as compared to diesel with combustion reaction zone 53-302°C. At 372°C complete combustion occurs with 100% degraded mass. Maximum decomposition temperature occurs at 175°C with 37% mass loss [32]. Onset temperature for both Diesel its B-20 HOME is similar which indicates that B-20 blend approaching the petrodiesel characteristics [33, 34]. Compared to diesel peak temperature is slightly less temperature occurs in B-20 HOME which indicates that the thermal efficiency of B-20 HOME while operating in the engine is greater than the diesel with reduced pollutions.

**Table 5** TGA/DTG Combustion reaction intervals, peak temperatures, and weight losses

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Reaction Region, °C</th>
<th>Peak Temperature, °C</th>
<th>Weight Loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIESEL</td>
<td>55-334</td>
<td>195</td>
<td>99.50 at 498°C</td>
</tr>
<tr>
<td>HOME</td>
<td>105-335</td>
<td>227</td>
<td>98.51 at 498.1°C</td>
</tr>
<tr>
<td>B-20 HOME</td>
<td>53-302</td>
<td>175</td>
<td>100 at 377°C</td>
</tr>
</tbody>
</table>

**CONCLUSION**

This article presents the experimential studies made on thermal conductivity and thermal degradation of Diesel, HOME and its B-20 blend. Following Sastry’s power law model, a simple empirical relation is developed for thermal conductivity as a function of temperature. The developed empirical relation is validated with test data. HOME with B-20 blend data properties are comparable with diesel properties. TG-DTG analysis results indicated that B-20 blend of HOME behaves similar to diesel with reduced peak temperature of combustion, reduced pollutant formation and provides better thermal efficiency. This data can be utilized in the process of simulation and combustion studies.

**NOMENCLATURE**

B-20 – biodiesel 20% and diesel 80%.
DTG- Differential Thermal Degredation
HOME- Jatropha oil methyl ester.
TG- Thermal Degradation
THW- Trasiet Hot Wire

**ACKNOWLEDGEMENT:**
The authors acknowledge the support received from the Sophisticated Analytical Instrumentation Facility Center IIT-Madras and Visvesvaraya Technological University Belagavi for Thermal Analysis.

**REFERENCES**


