

Properties of biodiesel as a function of temperature

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Abstract: Biodiesel is a fuel with similar properties to diesel fuel but not produced from petroleum but from vegetable oil or animal fat. Biodiesel, in particular, or biofuel in general, is a type of renewable energy. From a chemical standpoint, biodiesel is the methyl ester of fatty acids. To produce biodiesel, people mix about 10% methanol into vegetable oil and use many different catalysts (especially potassium hydroxide, sodium hydroxide and alcohols). At normal pressure and temperatures around 60°C, the glycerol ester in vegetable oil is destroyed and the fatty acids will be esterified with methanol. The resulting glycerol must be separated from the biodiesel afterwards. Through the conversion of this ester biodiesel is much less viscous than vegetable oil and can be used as a substitute for diesel without having to modify the engine to match. It is also necessary to mention other suitable options for biodiesel. One can also use vegetable oil fuel directly without the need to convert esters. Depending on the engine type, some parameters of the diesel engine must be changed to adjust to other physical properties of the new fuel.

Keywords: biodiesel, properties, heat capacity, biofuels

1. INTRODUCTION

When you want to switch to biodiesel, the vehicle manufacturer's information policy can become a big problem. It is often only after it takes a long time for people to get information on whether a certain model is allowed to use biodiesel while biodiesel has been on the market for 10 years. Most mass-produced cars are not adapted to biodiesel. When using biodiesel fuel for a motor vehicle that is not adapted to PME, biodiesel destroys fuel lines and rubber seals. The reason is that biodiesel has the chemical nature of an emollient, causing the rubber material of these tubes and seals to initially inflate. In this case, using petroleum-derived diesel, this diesel will wash away biodiesel. Another issue to consider is when the fuel used for diesel engines has a direct fuel injection unit. The problem usually occurs during operation when the engine is operated with long idle periods. The less the amount of fuel injected, the less the dispersion quality of the nozzle is and therefore tends to form the unburnt droplets of fuel sticking to the cylinder wall and then they enter the lubrication circulation system. Here, due to the poor chemical stability of the RME, the RME decomposes gradually in the lubricating circulation system under the action of high temperatures, creating solid or gelatinous deposits, which can lead to engine failure more eroded. Therefore, it is recommended that when operating with PME, it is recommended to shorten the oil change period. One advantage of PME can become a disadvantage when used in practical motor vehicles: biodegradable and accompanying is not durable. Oxidation and water buildup will worsen the properties of PME after a period of storage. Therefore, PME is often less recommended for vehicles with less operating time. In addition, due to the different combustion process, the new engines have not been certified as adapted to PME. There may be a problem with the electronic parts of the engine, which have been tuned for use with conventional diesel. Particularly in motor vehicles equipped with soot filters in the exhaust gas, it is often problematic because these systems have been pre-adjusted to increase the amount of fuel injection after every 500 to 1,000 km of distance traveled to burn soot particles in the filter. It is good and reasonable to use this conventional diesel again as a bad thing when using biodiesel: if using biodiesel, increasing the amount of fuel injection will dilute the engine oil. If pure biodiesel is used, the combustion of soot particles in the filter becomes unnecessary. So in the future there will be fuel sensors to identify the quality of the fuel. The amount and timing of fuel injection can all be optimized. Experience in the field of transport vehicles shows that the use of biodiesel for many years can lead to fuel pump failures, especially in engines with pump-fuel injection components, although this vehicle has been permitted to operate with biodiesel, the manufacturer of the injection pump (Bosch AG) does not allow it to be used with RME. This is because the RME molecule is of a different size than conventional diesel and the RME molecules in sophisticated channels cannot fully lubricate at high pressure and become a cause of faster wear and tear. In recent years, biodiesel has received much attention because of ability to replace fossil fuels. Especially, the environmental matter concerned with the exhaust gases emission such as EN-590 in Europe, ASTM D 975 in USA in which the reduction in sulfur content is the most notable restriction (10 ppm by 2009 in Europe) from fossil fuels encourage the usage of biodiesel, which has proved to be economical, friendly more than fossil fuels. Biodiesel fuels are the fatty acid methyl or ethyl esters (FAME) derived from vegetable or animal fats and oils. In the European Union, FAMEs are mostly vegetable oil methyl esters from rapeseed and sunflower oils [1]. Ethanol is produced by alcoholic fermentation of sugar plants (beets, sugar cane) or of cellulose material (straw, wood). Moreover, biodiesel is known as a carbon

neutral fuel because the carbon present in the exhaust was originally fixed from the atmosphere [2]. Biodiesel fuels have higher lubricity than conventional fuels, but there are some disadvantages such as formation of deposits, the degradation of materials, the filter plugging, the degradability, the cold flow properties, and the quality specifications [3]. Many researchers have presented a growing and developing interest in modeling combustion processes with alternative fuels to understand clearly the combustion and emission characteristics of these fuels which are renewable, biodegradable and oxygenated such as animal fat, vegetable oils, their derivative and mixtures. An accurate prediction of the alternative fuel properties is necessary and critical in order to study the spray, atomization, mixtures and combustion process in the combustion chamber of engine. Some research results have proven that the physical properties of the fuel can affect directly combustion performance and emissions. The physical properties of the fuel such as density, surface tension and viscosity affect the atomization quality. Therefore, predicting and establishing the physical properties of the biofuels is a crucial step to predict accurately the spray atomization and combustion processes. The paper presents the results of predicting and establishing some thermal properties of biodiesel such as density, viscosity, surface tension, heat capacity, heat of vaporization and conductivity. These results orientate and improve the biodiesel using in diesel engine in order to reduce environment pollution.

2. Properties of biodiesel

Biodiesel is made up of a very simple chemical reaction. Biodiesel has many advantages to the environment compared to conventional diesel. Biodiesel from rapeseed generates far less emissions than fossil fuels. Dust in the exhaust gas is halved, hydrocarbon compounds are reduced by up to 40%. Biodiesel is nearly sulfur free, nontoxic and easily biodegradable. Biodiesel is now considered to be one of the most environmentally friendly fuels on the market. Although it is now possible to buy biodiesel at many petrol stations (particularly in Germany, 1,900), biodiesel has not been used much by consumers because they do not believe the car can run on a complete fuel all from plants. Another problem is that many people are not sure whether their cars can use biodiesel. Lack of information to consumers about the future damage caused by biodiesel for vehicles could be the biggest problems that need to be solved in order to gain widespread acceptance of biodiesel. In Europe, it has been suggested several times that 3% to 5% of biodiesel should be added to conventional diesel fuel because this biodiesel part is considered not harmful even to motor vehicles equipped with proper equipment. In France, this has been done for a long time: Ordinary diesel is added with the biodiesel that French agriculture is capable of producing. The reality of France shows that the quality of conventional diesel with biodiesel content is 5%, avoiding technical disadvantages. The critical properties are used to estimate the properties such as liquid density, viscosity, surface tension, heat capacity, diffusion coefficient, heat of vaporization and thermal conductivity. The critical properties are also used to estimate the fuel boiling point and establish a correlation for vapour pressure. Hence it is particularly important to accurately predict the fuel critical properties, as they will influence the prediction of the other fuel properties. Critical pressure (P_c), critical temperature (T_c) and critical volume (V_c) are the three widely used pure component constants, which cannot be easily obtained through experiments. In physical properties prediction, they are usually used as key inputs.

$$T_c = \frac{T_b}{0.567} + \Sigma \Delta_T - (\Sigma \Delta_T)^2 ; P_c = \frac{MW}{(0.34 + \Sigma \Delta_p)^2}$$

Formally, viscosity is the ratio of the shearing stress (F/A) to the velocity gradient in a fluid. Viscosity is one of the most important physical properties of a fluid system (Fasina et al). Viscosity is the quantity shown the resistance to the flow of liquid. The higher the viscosity is, the more unfavorable the use is because it reduces the possibility of dispersing while injection into the combustion as well as increasing the ability of the sedimentation in the equipment. Viscosity is inversely proportional to temperature. Krisnangkura et al gave an experimental database of viscosity and provided a set of parameters for the description of the viscosity of pure fatty acid methyl esters (FAMES). These equations were developed by considering the viscosity as the integral of the interaction forces of molecules. The temperature dependency of the viscosity for short-chain methyl esters (C_6 - C_{12}) can be estimated by equation. Surface tension is measured as the energy required to increase the surface area of a liquid by a unit of area. The surface tension of a liquid results from an imbalance of intermolecular attractive forces, the cohesive forces between molecules. While the surface tension of the fuel is high, the mist injection will be less so this adversely affects the quality of the combustion in diesel engines. Besides, the experimental researches show the relationship between surface tension and temperature. Surface tension is proportional to viscosity and inversely proportional to temperature. Therefore, surface tension of biodiesel is able to be calculated via heating temperature. There are many various methods for estimating densities (ρ). Furthermore, Spencer has conducted an extensive evaluation of the available methods for predicting the saturated liquid density of pure hydrocarbons as a function of temperature. They concluded that, the most

accurate mean of predicting the effect of temperature on the saturated liquid densities is by the modified Racket equation. Biodiesel density is lightly higher than traditional fuels at 300K (880 kg/m³ in compared with 790 kg/m³ of kerosene and 850 kg/m³ of diesel fuel). An increase in fuel density will have a slight direct effect on spray compactness and penetration, resulting in less air resistance, since for the same volume, the fuel mass flow will be increased. The enthalpy of vaporization also called the latent heat of vaporization, it is considered as the difference between the enthalpy of the saturated vapour and the enthalpy of the saturated liquid at the same temperature. The higher the enthalpy of vaporization is, the more the energy is required for fuel vaporization. The Pitzer was used to determine the latent heat of vaporization H_{lv} up to the biodiesel critical temperature. An analytical representation of this correlation for $0.6 < T_r < 1.0$ is given as equation:

$$\frac{H_{lv}}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456}$$

However, while the latent heat of vaporization at low temperatures ($T_r < 0.6$) the following relationship suggested by Fish and Lielmezs were used:

$$H_{lv} = H_{lvb} \frac{T_r}{T_{br}} \frac{\chi + \chi^{0.3598}}{\chi + \chi^{0.13856}} ; \chi = \frac{T_b}{T_r} \frac{1 - T_r}{1 - T_{br}}$$

The latent heat of vaporization of the biodiesel shown in Fig.1 is much lower than fossil fuels and ethanol, and that means energy for biodiesel vaporization is much less than ethanol and fossil fuels. Giannelose quation

$$H_{lv} = RT_c \Delta Z_{vb} (T_{br} \frac{\ln(P_c / 1.01325)}{1 - T_{br}}); H_{lv} = RT_c T_{br} \frac{3.978T_{br} - 3.958 + 1.555 \ln P_c}{1.07 - T_{br}}$$

Here ΔZ_{vb} is set to be unity and P_c is the critical pressure

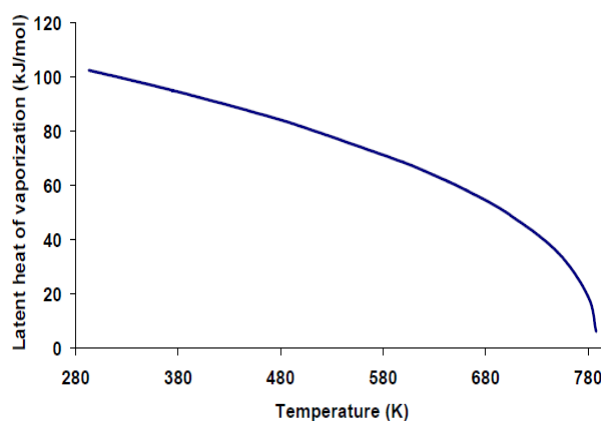


Fig.1. Relationship between latent heat of vaporization and temperature

Liquid heat capacity is not function of temperature while $T_r < 0.7$ (Reid et al). However, at high reduced temperatures, liquid heat capacities are functions of temperature. In order to calculate the liquid heat capacity, the relatively simple approach of Chueh and Swanson for liquid heat capacity (C_p) at 293.15K has proposed as:

$$C_p^o = \sum_{i=1}^n N_i \Delta C_{pi} + 18.83m$$

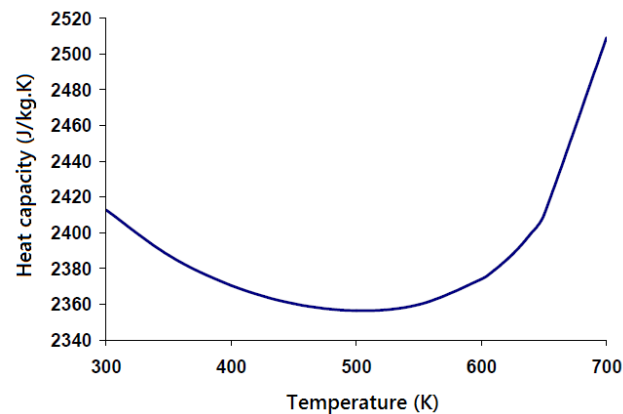
Where:

N_i is the number of different atomic groups in the compound;

C_{pi} is the numeric value of the contribution of element i ;

m represents the number of carbon groups requiring an additional contribution.

Relationship between heat capacity and temperature is shown in Fig.2.

Fig.2. $C_p = f(T)$

For liquids at reduced temperature from 0.25 to 0.8 and at a pressure below 3.4 MPa, the equation proposed by Pachaiyappan et al may be used to determine the thermal conductivity (λ - W/m.K):

$$\lambda = 1.811 \cdot 10^{-4} \rho M \cdot W^{1.001} \left[\frac{3 + 20(1 - T_r)^{2/3}}{3 + 20(1 - \frac{293.15}{T_c})^{2/3}} \right]$$

Besides, Reid R.C et al. proposed a method to calculate Thermal conductivity as:

$$\lambda = \frac{A_3(1 - T_r)^{0.38}}{T_r^{1/6}} ; A_3 = \frac{A^* T_b^\alpha}{M^\beta T_c^\gamma}$$

where A^* , α , β , γ can be found in. Biodiesel is ester of fatty acid and ethanol therefore the parameters A^* , α , β , γ are respectively 0.0415; 1.2; 1.0; 0.167. Furthermore, it has suggested the method to determine thermal conductivity through molecular weight, such as:

$$\lambda(T_b) = \frac{1.11}{M^{1/2}}$$

And, the equation from [26] is also used to estimate λ at different temperature:

$$\lambda = \lambda(T_b) \left[3 + 20(1 - T_r)^{2/3} \right]$$

Diffusion coefficient is not only encountered in Fick's law but also in numerous other equations of physics and chemistry. Diffusion coefficient is generally prescribed for a given pair of species. For a multi-component system, it is prescribed for each pair of species in the system. The higher the diffusivity (of one substance with respect to another), the faster they diffuse into each other. For the prediction of the gas diffusivity of binary air-biodiesel, the method of is recommended:

$$\delta = \frac{0.00143 T^{1.75}}{P M^{1/2} \left[(\Sigma v_A)^{1/3} + (\Sigma v_B)^{1/2} \right]^2} ; M = 2[(1/M_A) + (1/M_B)]^{-1}$$

3. CONCLUSION

Another problem is that the fuel enters the engine oil at diesel engines with direct fuel injection. This problem usually occurs during operation when the engine is operating with long idle periods. The less the amount of fuel injected, the less the dispersion quality of the nozzle is and therefore tends to form the unburnt droplets of fuel sticking to the cylinder wall and then into the lubrication circulation system. In particular, motor vehicles equipped with soot filters often have problems because these systems have been pre-adjusted to increase the amount of fuel injected every 500 to 1,000 km to burn soot particles in the filter. It is good and reasonable to use this conventional diesel again as a bad thing when using biodiesel: if using biodiesel, increasing the amount of fuel injection will dilute the engine oil. If pure biodiesel is used, the combustion of soot particles in the filter becomes unnecessary. So in the future there will be fuel sensors to identify the quality of the fuel. The amount and timing of fuel injection can all be optimized. For each physical property, the best

prediction model has been identified and the calculated properties can be used as key references for biodiesel combustion modeling. The results show that, the higher the temperature is, the more increasing the volatility and diffusion coefficient are, otherwise the lower the viscosity, surface tension, density, enthalpy of vaporization are. These mean that, the biodiesel will be easy to spray and atomize, evaporate and mix with gas in combustion chamber if they are heated up to suitable temperature.

4. REFERENCE

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