Research article

The determination of the activation energy of diesel and biodiesel fuels and the analysis of engine performance and soot emissions

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ABSTRACT

The behaviors of a biofuel and a fossil fuel were evaluated by different techniques, namely thermal analysis (Thermogravimetry-TG and Differential Thermal Analysis-DTA) and engine performance tests. From TG and DTA curves, two decomposition phases were identified for diesel fuel with ignition temperature (IT) at 250 °C and three phases for biodiesel fuel with IT at 300 °C. Combining conversion (α) versus temperature and a model-free kinetics method, the range of activation energies (E_a) values were determined for both diesel (from 48.5 kJ mol^{-1} up to 61.0 kJ mol^{-1}) and biodiesel (from 58.6 kJ mol^{-1} up to 55.0 kJ mol^{-1}) fuels. At the initial phase of combustion, diesel fuel presents lower E_a and IT than biodiesel fuel. At the final phase of combustion, an opposite behavior is observed. These results provide subsides to predict that the behavior of diesel-biodiesel blends is the best option due to the lowering of E_a along the entire combustion process. As regards the engine tests, the B20 blend showed improvements compared with diesel fuel. In average, B20 presented increases of 1.2% in power, 1.0% in torque and 1.2% in thermal efficiency. In terms of soot, B20 presented 8.9% lower emissions than diesel fuel. Although thermal analysis and engine performance tests are executed under very different conditions, the results from both techniques showed the same trend, i.e., the best option for the combustion performance is a diesel-biodiesel blend.

1. Introduction

The global energy matrix is mainly based on non-renewable resources and extremely dependent on petroleum. The possible alternative energy sources are biofuels originated from numerous oleaginous plants. Normally, this fuel is produced by transesterification, which consists of a chemical reaction of vegetable oils or animal fats with ethyl or methyl alcohol, stimulated by a catalyst [1,2].

Biodiesel fuel obtained from soybean is widely significant in the substitution of mineral diesel fuel. In Brazil, it represents 64.84% of the national production of biodiesel fuel according to ANP (the Brazilian National Agency of Petroleum, Natural Gas and Biofuels) [3]. The diesel engine emits high levels of particles and NO_x due to high injection pressures and increased air-fuel ratio [4]. It is, in this sense, critical to diesel engines, the reason why its emissions must be reduced without

limiting its performance. Biofuels can positively contribute to this equilibrium showing its sustainable nature. The use of alternative fuels is increasingly attracting scientific interest [5], being biofuels widely used in diesel engines [6] due to its advantages and especially due to its environmental qualities [7,8].

Cardenas et al. [9] investigated the emissions and performance of rapeseed, soybean and sunflower biodiesel fuels and their 30% blends with diesel, comparing them with a reference mineral diesel fuel. The experimental tests were done according to the NEDC system. In terms of performance results, the biodiesel fuels displayed higher consumption over time than diesel fuel. Referring to pollutants, the biodiesel fuels presented higher emissions of CO, THC and NO_x, and lower values of smoke opacity. The accelerations during urban cycles showed considerable emissions peaks. An explanation for these emissions data is that biodiesel and its blends have a lower exhaust gas recirculation

valve opening, which decreases opacity and soot emissions, but increases other pollutants.

Bermudez et al. [5] investigated consumption and emissions behavior of soybean, rapeseed and palm biodiesel and an alternative Fischer Tropsch (FT) fuel, comparing them with a mineral diesel fuel in an engine under NEDC. The fuel consumption of all biodiesel fuels showed higher values compared to diesel and FT fuels. They also led to higher emissions of NO_x, CO and HC. By analyzing soybean biodiesel in comparison to the other biodiesel fuels, higher concentrations of HC and CO and lower of NO_x have been found. Because of the presence of aromatics in their formula, mineral diesel and FT fuels created benzene and toluene in HC emissions, which are cancer-causing compounds.

Bermudez et al. [10] studied the pollution rate and particle sizes of particulate matter from the burning of soybean, rapeseed and palm biodiesel, S10 and S50 mineral diesel and Fischer Tropsch fuels. As regards the total particulate matter production, the lowest emissions were from palm biodiesel, while soybean presented the third best results. It was observed that at low speed and load, the biodiesel fuels produced more PM than mineral diesel fuels. However, at medium speed and load, the biodiesel fuels showed lower total concentrations of particles on emissions. In terms of particle size from biodiesel fuels emissions, the particles are smaller than those produced by mineral diesel fuels. According to the author, the presence of sulfur in mineral diesel fuels is the reason why the particle size and geometry increase.

There are plenty of results from experimental tests of biodiesel-fueled internal combustion engines. Most of them present data on performance and emissions. However, detailed analyses of the combustion are needed to better understand the biodiesel burning process. A technique which has been extensively used to determine the activation energy of various solid and liquid fuels is the thermal degradation assessed by thermogravimetry. These studies have been performed based on fuels to be used under different combustion conditions, i.e., for different kinds of thermal machines. Kok et al. [11] studied the nature of the combustion of agricultural solid residues using thermal analysis techniques. Luo et al. [12] investigated the combustion chemical kinetics of coke on deactivated catalysts with the use of thermogravimetry. Borsato et al. [13] adopted the thermogravimetric analysis to determine the activation energy of the soybean biodiesel fuel mixed with three kinds of synthetic antioxidants. Crnkovic et al. [14] determined the activation energies of the crude glycerin and of the beef tallow for their application in engines. Also for that purpose, Conconi et al. [15] analyzed the behavior of the activation energies of three kinds of fuels produced in Brazil: mineral diesel, sugarcane farnesane and soybean biodiesel.

The objective of the present study is to determine the activation energy for the thermal decomposition of diesel and soybean biodiesel fuels, to specify which fuel or fuel blend leads to the best combustion quality under atmospheric pressure on a thermogravimetric balance. Additionally, it tries to make the same estimations from engine performance and soot emissions experimental test, i.e., under high pressure and high heating rates. The fuels tested were: Brazilian commercial diesel fuel, pure soybean biodiesel (100% biodiesel, B100) and blends of 20% (B20) and 50% (B50) biodiesel in diesel.

2. Experimental tests

2.1. Materials

Two different fuel samples, diesel and biodiesel, were used in this study. The diesel fuel is commercialized by Petrobras as S10 which is a blend of 93% pure diesel and 7% biodiesel fuels. The biodiesel fuel sample for the tests was obtained from the Brazilian company Granol, processed by transesterification with methanol. Properties of the pure fuels are shown in Table 1. In the engine experimental tests, in addition to pure fuels, two blends with different proportions of diesel and biodiesel fuels were also used: B20 and B50.

Table 1
Fuel properties.

Property	Unit	Diesel	Soybean B100
Mass fractions			
Carbon	(−)	0.870	0.769
Hydrogen		0.126	0.118
Oxygen		0.003	0.113
Sulfur		0.001	(−)
Cetane number	(−)	50.5	50.6
Viscosity at 40 °C	(mm^2/s)	2.68	4.24
Density at 15 °C	(kg/L)	0.84	0.88
Lower heating value	(MJ/kg)	42.9	36.8
Stoichiometric air-fuel ratio	(−)	14.66	12.49
Distillation 10 vol%	(°C)	195	316
Distillation 50 vol%	(°C)	262	328
Distillation 90 vol%	(°C)	339	334

2.2. TG and DTA experiments

Thermogravimetric (TG) and Differential Thermal Analysis (DTA) experiments were carried out in the Shimadzy 51H and 50H analyzers, respectively. Experimental conditions were: heating rates of 5, 10 and 20 °C min^{-1}, temperature range from room temperature up to 600 °C, sample mass of 10 ± 0.5 mg of each fuel for each test and a 100 mL min^{-1} flow rate of synthetic air atmosphere (80% nitrogen and 20% oxygen).

2.3. Activation energy determination. Mathematical model

The model-free kinetics is based on the calculation of the activation energy as a function of the conversion (α). In several reactive processes, the determination of the reaction rate depends on conversion α, temperature (T) and time (t). Conversion is given by:

$$\alpha = (m_0 - m)/(m_0 - m_\infty), \tag{1}$$

in which m is the sample mass which is a function of time, m_0 is the initial mass of the sample and m_∞ is the final mass of the sample.

The reaction rate given as a function of conversion, $f(\alpha)$, is different for each process and the reaction model must be determined experimentally. For a simple reaction, the estimated $f(\alpha)$ has the value of the reaction order n. For complex reactions, $f(\alpha)$ is complex and generally unknown, in which case the algorithm of order n results in inaccurate chemical kinetics data.

The use of model-free kinetics based on the Vyazovkin theory [16–18] makes it possible to retrieve kinetic information about complex reactions. This model is based on isoconvertional techniques for the calculation of the effective activation energy (E_a) as a function of the conversion (α) of the chemical reaction, i.e. $E_a = f(\alpha)$. Hence, this approach follows all the conversion points collected from the numerous experimental tests, avoiding uncertainties that can result from a single experiment. The theory states that:

$$d\alpha/dt = k(T)f(\alpha), \tag{2}$$

in which t is the time, T is the temperature and α is the conversion, $f(\alpha)$ represents the reaction model and $k(T)$ is the Arrhenius reaction rate coefficient, so:

$$d\alpha/dt = A \exp\left(\frac{-E_a}{RT}\right)f(\alpha), \tag{3}$$

in which R is the universal gas constant, A is a pre-exponential factor, E_a is the activation energy and $d\alpha/dt$ is the reaction rate [s^{-1}].

The global relations of a multi-step process can be represented by combining a single-step equation, so Eq. (3) is representative of the whole process. In effect, the global relation of the process is approximated by the combination of a few (commonly two or three) relations of equations and each one of them influences the whole temperature