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THERMAL AND RHEOLOGICAL BEHAVIOR OF DIESEL AND METHANOL BIODIESEL BLENDS

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The most feasible alternative among fuels derived from biomass seems to be the biodiesel, having the required characteristics for a total or partial substitution of diesel oil. Therefore, the aim of this work is to evaluate the thermal and rheological behavior of the blends of diesel with the methanol biodiesel obtained from soybean oil, using B5, B15 and B25 blends. All thermogravimetric curves exhibited one overlapping mass loss step in the 35–280°C temperature range at air atmosphere and one step between 37–265°C in nitrogen. The rheological study showed a Newtonian behavior (n=1) for all blends.

Keywords: *biodiesel, blends, rheology*

Introduction

The biodiesel, a non fossil fuel derived from renewable sources, can be considered as a promising potential source for a gradual substitution of petroleum-based diesel all over the world. Therefore, many effects have been done in several countries in order to avoid the operating problems and to more adaptable in the diesel fuel engines [1, 2].

Biodiesel fuels are generally classified as fatty acid esters, derived from the catalyzed transesterification of fats and oils generally with methanol, although other alcohols also can be used. Graboski and McCormick [3] provided a recent extensive review of the utilization of biodiesel fuels in compression ignition engines. The general conclusion from the literature is that, in terms of power, wear, efficiency and emissions, biodiesel is a viable alternative. The reported results in the literature are somewhat different. Viscosity is one of the most important characteristic of biodiesels and should be maintained within pre-determined limits since it has great influence on the fluidodynamic properties of a fuel which concerns to the diesel engine operation (e.g. fuel circulation and fuel injection) [4].

Therefore, researchers tested several types of transesterified oils and these works showed good results upon the usage of these transesterified oils in diesel engines [5].

It was pointed out that the development of diesel–biodiesel blends in proper proportions cause less environmental problems and affect advantageously the operation time of the engine [6].

Thus, the present paper studies the thermal and rheological behavior of the blends of diesel and the methanol soybean biodiesel B5, B15 and B25. Pure diesel was used as reference.

Experimental

Samples

The reaction for the production of biodiesel was carried out with a 6:1 fixed ratio of methanol:soybean, with 1% catalyst (KOH), under constant mixing and controlled temperature. Thus, the cleavage of triacylglyceride molecules occurred, producing a mixture of the methyl esters of corresponding fatty acids and glycerin as a co-product [7]. After the purification step, the biodiesel was mixed with diesel with proper amounts, to form B5, B15 and B25 blends. A D type diesel was used in the blends. The pure diesel was represented by D100.

Methods

Thermal study

TG/DTA curves were recorded simultaneously using SDT 2960 TA Instruments Thermal Analyzer. A dynamic method was used, at a heating rate of 10°C min^{-1}. The initial sample mass was 10.00±0.5 mg, in synthetic air and nitrogen atmospheres, with a flow rate of 110 mL min^{-1}, in the 28–600°C temperature range [8–12].

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Rheological study

In the rheological study, diesel and diesel/biodiesel blend were evaluated. The rheological parameters were determined using a Brookfield LV-DVII viscosimeter.

Results and discussion

Thermal study

All the TG curves of the diesel/biodiesel blends, in synthetic air atmosphere present one complex mass loss step in the 35–280°C temperature range (Fig. 1a). This step comprises the evaporation and/or combustion of the methyl esters of the fatty acids of soybean oil (characteristic for pure biodiesel) and, as well as evaporation and/or combustion of the other components of the diesel, e.g. paraffins, naphthenes, olefins and aromatics, with a C12-18 carbon number [2].

TG curves of the diesel/biodiesel blends obtained in nitrogen atmosphere (Fig. 1b) present also only one mass loss between 37–265°C. Thus, this step included all the mass losses, which are due to the evaporation and/or pyrolysis of the previously listed compounds. It can also be observed that the TG curves are more similar in nitrogen atmosphere than in synthetic air. Between the diesel and the blends there are larger differences in the recorded mass loss values in the same temperature range.

For example for pure diesel, only one mass loss step takes place between 41 and 251°C in air, while in nitrogen it shifts to 44–254°C. As stated above, this mass loss is related to the evaporation and/or decomposition of the diesel compounds, either by combustion in air or by pyrolysis in nitrogen.

According to TG curves it should be emphasized that during thermal decomposition the diesel/biodiesel blends exhibit similar behavior to diesel, with the advantage of reduction of the emission of harmful gases.

The calorimetric data of the diesel/biodiesel blends and pure diesel, obtained in synthetic air and nitrogen are presented in Table 1. A higher number of transitions are observed in air. In this analysis, the first transition is endothermic, attributed the evaporation of small carbon chains, while the other ones are exothermic, related to the combustion of the organic compounds. In nitrogen there was an endothermic transition attributed to the evaporation and/or pyrolysis of the organic compounds (Fig. 2).

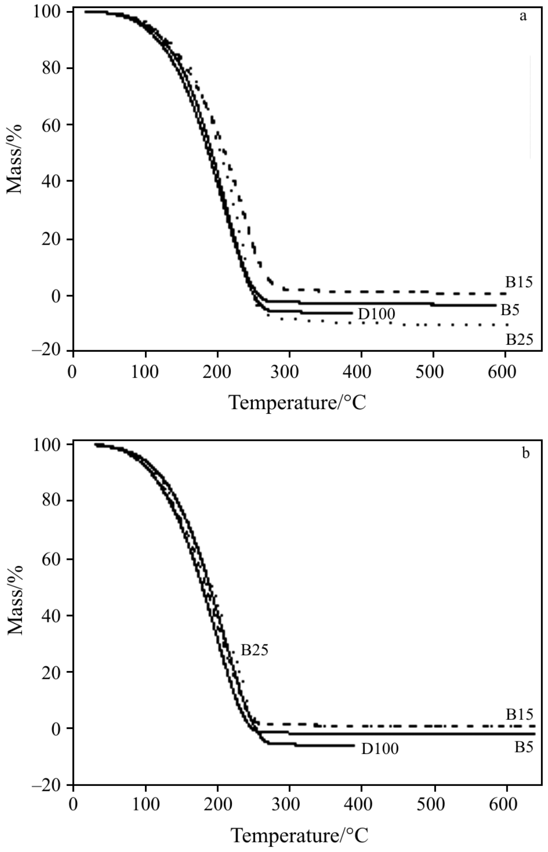

Fig. 1 TG curves of diesel and diesel/biodiesel blends in a – synthetic air and b – nitrogen

Table 1 Calorimetric data of diesel and diesel/biodiesel blends in different atmospheres

Sample	Temperature/°C–enthalpy change/J g^{-1}	
	synthetic air	nitrogen
B5	223–422 419–19.2	149–414
B15	238–548 365–5.73 447–20.9	182–323
B25	102–68.9 246–107 371–19.5 511–60.8	154–420
D100	174–505	159–415

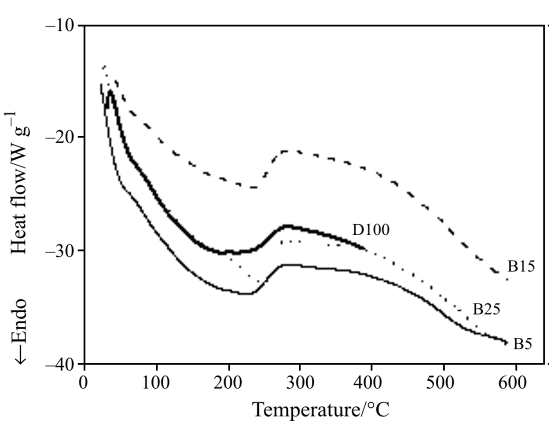

Fig. 2 DTA curves of diesel and diesel/biodiesel blends in nitrogen atmosphere

Rheological study

Most low molecular mass fluids obey the Newtonian model over a wide shear range rates – typically over several log cycles of shear. However, with high molecular mass and more complex liquids, deviations from the Newtonian model are observed [13, 14].

For the case of time-independent fluids, the apparent viscosity may increase, remains unchanged or decreases with the shear rate. These fluids are known as dilatent, Newtonian and pseudoplastic, displaying values of $n>1$, $n=1$ and $n<1$, respectively.

All the diesel/biodiesel blends (B5, B15 and B25) as well as the pure diesel (D100) exhibited a virtual Newtonian behavior, displaying a power index, $n\approx1.004$ (Fig. 3). Such behavior is evidenced by the linear variation of shear stress with the shear rate.

Compared to the pure diesel, pure biodiesel has a high viscosity, which may lead to operating difficulties during its application in an unadapted diesel engine which can be solved by blending of pure biodiesel with diesel (with about 25% (*v*/*v*) proportions in B25) Despite of their higher viscosity compared to the pure diesel (Fig. 4), the blends are still fulfil the requirements diesel oil of ANP (The Brazilian National Agency for Petroleum, Natural Gas and Biofuels).

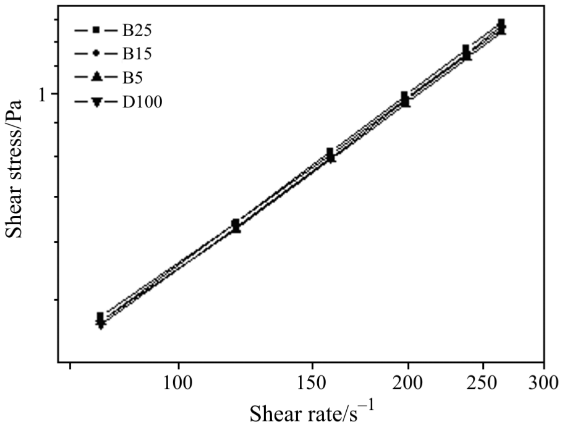

Fig. 3 Shear stress *vs*. shear rate for diesel and its blends containing biodiesel

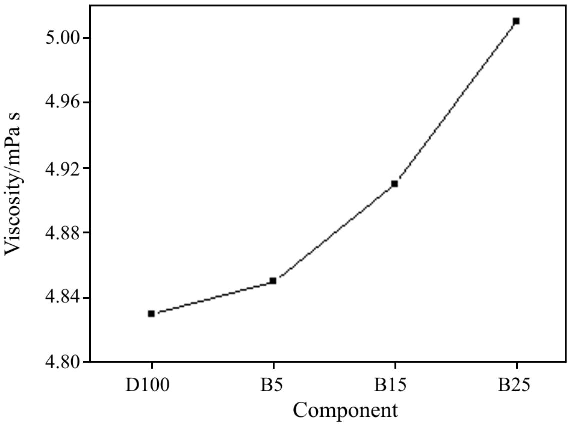

Fig. 4 Viscosity of diesel and diesel/biodiesel blends

This viscosity increase is caused by the high molecular mass of the original triglycerides containing long length chain fatty acids. The transesterification process reduces the molecular mass of the compounds minimum by 30% of its original value leading to lower viscosity.

Conclusions

Based on the TG and DTA curves, the thermal profiles of diesel and diesel/biodiesel blends could be evaluated in synthetic air and nitrogen atmosphere. These results indicate similar thermal behavior meanwhile the blends emitted less amount of harmful substances.

The rheological study showed that all the blends presented a nearly Newtonian behavior. Despite of presenting a higher viscosity than diesel, the viscosity of the blends fulfils the requirements of ANP.

Acknowledgements

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References

1 M. Canakci, A. Erdil and E. Arcaklioğlu, Appl. Energ., 83 (2006) 594.
2 A. Srivastava and R. Prasad, Renew. Sustain. Energ. Rev., 4 (2000) 111.
3 M. S. Graboski and R. L. McCormick, Prog. Energ. Combust., 24 (1998) 125.
4 C. A. W. Allen, K. C. Watts, R .G. Ackman and M. J. Pegg, Fuel, 78 (1999) 1319.
5 R. A. Ferrarri. V. S. Oliveira and A. Scabio, Quim. Nova, 28 (2005) 19.
6 The Non Technical Barriers Network, Agence de l'Environnement et de la Maîtrise de l'Energie, Paris 1998.
7 M. M. Conceição, R. A. Candeia, H. J. Dantas, L. E. B. Soledade, V. J. Fernandes Jr. and A. G. Souza, Energ. Fuel, 19 (2005) 2185.
8 R. G. Ferrillo and A. Granzow, Thermochim. Acta, 38 (1980) 27.
9 R. G. Ferrillo and A. Granzow, J. Thermal Anal., 29 (1984) 1237.

10 S. A. Silva, M. M. Conceição, A. G. Souza and R. O. Macedo, Thermochim. Acta, 328 (1999) 177.

11 M. M. Conceição, A. M. L. Melo, N. Narain, I. M. G. Santos and A. G. Souza, J. Therm. Anal. Cal., 67 (2002) 273.

12 M. M. Conceição, R. A. Candeia, F. C. Silva, A. F. Bezerra, V. J. Fernandes Jr. and A. G. Souza, Ren. Sustain Energ. Rev., in press.

13 G. Schramm, A Practical Approach to Rheology and Rheometry, Gebrueder Haake GmbH, Karlsruhe 1998.

14 Site http://sst-web.tees.ac.uk/external/U0000504/Notes/foodstruct/fsc06/FdRheo02.html, accessed at June 28, 2006.

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