STUDY ON TRIBOLOGICAL PERFORMANCE OF BIODIESEL MATERIAL[1]

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Abstract

The aim of this study was to compare the tribological performance of biodiesel and diesel fuels, through sliding tests of metallic specimens. Reciprocating pin-on-plate tests were conducted in a TE67 Plint&Partners tribometer, with plate specimens of gray cast iron sliding against edge-rounded pin specimens of steel bearing material, under lubricated bath with fuel materials, at room temperature. The tests were run with 2.5 Hz oscillation frequency, up to 50000 cycles. Wear track length was 10 and 20 mm, respectively corresponding to the maximum tangential velocities of 0.08 and 0.16 m/s. Two levels of loads, 200 and 400 N, were tested. The performance was analyzed in terms of friction coefficient and worn profiles of the plates. Physicochemical changes of the tested fuels were determined by DSC (Differential Scanning Calorimetry) and FT-IR (Infrared Fourier Transform Spectroscopy) techniques. The results have shown that friction coefficient depends on the load and velocity levels. At low load level, biodiesel promoted low friction than diesel, independently on the velocity level. At high load, the friction coefficient level was higher than that seen at low load, the tests with diesel being more dependent on the velocity level. Despite of high thermomechanical loading occurring in the sliding tests, analyses by FT-IR technique have indicated absence of chemical changes in both tested fuels. On the other hand, some change in the thermophysical behavior of biodiesel was seen by DSC analysis.

Key words: Biodiesel; Tribological performance; DSC, FT-IR.

ESTUDO DO DESEMPENHO TRIBOLOGICO DE BIODIESEL

Resumo

O objetivo deste trabalho foi comparar o desempenho tribológico dos combustíveis diesel e biodiesel, através de ensaios de deslizamento de metais. Os ensaios foram realizados com o dispositivo com movimento alternado pino-sobre-placa, do tribômetro TE67 da Plint&Partners, com placas de ferro fundido cinzento e pinos de aço para rolamento, lubrificados com o combustível à temperatura ambiente. A freqüência de oscilação da placa foi de 2,5 Hz), com total de 50000 ciclos. O comprimento da trilha de desgaste foi de 10 e 20 mm, correspondendo às velocidades tangenciais máximas de 0,08 e 0,16 m/s. Foram utilizados dois níveis de carga, 200 e 400 N. O desempenho foi analisado em termos do coeficiente de atrito e do perfil de desgaste das placas. Para a análise das modificações físico-químicas dos combustíveis, foram utilizadas as técnicas DSC (Calorimetria Diferencial de Varredura) e FT-IR (Espectroscopia de Infra-vermelho por Transformada Rápida de Fourier). De acordo com os resultados, o coeficiente de atrito dependeu dos níveis de carga e de velocidade do ensaio. Com a menor carga, o biodiesel resultou em atrito menor que o diesel, independentemente da velocidade. Com a maior carga, o coeficiente de atrito foi maior do que aquele com a menor carga, sendo que nos ensaios com diesel, foi observado efeito da velocidade de ensaio. Apesar do elevado carregamento termomecânico dos ensaios, não houve mudanças químicas dos combustíveis, de acordo com as análises por FT-IR. Por outro lado, análises por DSC indicaram uma mudança no comportamento termofísico do biodiesel.

Palavras-chave: Biodiesel; Desempenho tribológico; DSC, FT-IR.

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INTRODUCTION

Issues concerning what to do about energy policy and climate change is not new. Of all the possible solutions to the current energy problems, biofuels are probably the most aggressively promoted today. Relative to fuels for compression ignition engines, the interest in large-scale production of biodiesel has increased due to the need to ensure energy security, stimulate the agricultural business, reduce trade deficit of oil imports, and to provide an alternative transportation fuel. Large is the number of scientific papers found in electronic databases. As an example, since 1997, near 80 articles, where friction, wear or lubricity are mentioned, are found in SciencedDirect database, from around 420 concerning biodiesel.

Oilseed-based biodiesel is environmentally benign because it is a renewable fuel and has lower levels of sulfur dioxide and particulate matter emissions (since the oxygen in biodiesel enables more complete combustion to CO_2), contributing then for less environmental pollution. The use of biodiesel blended with petroleum diesel (also termed petrodiesel, or simply diesel) produces a fuel that is compatible with diesel engines, displaces the amount of imported petroleum and reduces harmful diesel emissions. Blends like B2 (2% biodiesel and 98% diesel) and B5 (5% biodiesel and 95% diesel) are becoming increasingly common as drivers become more aware of the many benefits. Although some researchers[1,2] have pointed out that emissions of nitrogen oxides can increase with the concentration of biodiesel in the fuel, more investigation is needed to resolve this issue.[3] Some biodiesel produces more nitrogen oxides than others, and some additives have shown promise in reducing the increases.

Several production processes for biodiesel are known.[4,5] The most applied route to biodiesel production involves the transesterification process, a chemical reaction between the vegetable oil (from soybean, palm, castor, rapeseed, sunflower, cotton, etc.) and an alcohol in the presence of a catalyst, whereby the glycerin is separated from the vegetable oil. The process leaves behind two products - methyl or ethyl - esters (the chemical name for biodiesel) and glycerin (a byproduct useful for soaps). The final product must meet certain physicochemical requirements in order to be qualified as biodiesel. Two international standards are: the European Standard, EN 14214:2002, and the US Standard, ASTM D 6751. Several specifications are listed in these standards, as water, sediment and solids content, flash point, cloud point, total acid number, cetane number, total glycerin and so on.

In terms of performance, one disadvantage of using biodiesel is its susceptibility to cold temperature problems, more than diesel. This effect can be moderated with blends. Another fact is that the energy content per gallon of biodiesel is slightly lower than that of petroleum diesel; vehicles might achieve a slight power loss with biodiesel fuels. Also, the solvent property of biodiesel can cause some fuel-system problems. On the other hand, an important characteristic for a fuel for diesel engines is its cetane number; it measures the readiness of the fuel to auto-ignite when injected into the engine. In general, cetane number is higher for biodiesel.[6] Another important characteristic is lubricity or slipperiness. Fuel injectors and some types of fuel pumps rely on fuel to lubricate moving parts that operate with close tolerances, high temperatures and high pressures. High lubricity of the fuel reduces wear on the engine and can increase the life of engine components.[7] Lubricity can be defined in many ways; one of them is the ability of a fluid to separate the interacting solid surfaces, besides that given by viscosity property. Then, lubricity can be related to wear and friction performance in boundary lubrication. Standards for lubricity tests are well known, one of those most frequently used is HFRR (High Frequency Reciprocating Rig, ASTM D 6079[8]) test method. SLBOCLE (Scuffing Load Ball-on-Cylinder Lubricity Evaluator, ASTM D 6078[9]) tests are also seen, but in less number. Both standards are related to laboratory methods. In HFRR test, the wear scar diameter is measured after 75 min test time; in SBOCLE test, one measures the minimum load for attaining a certain value of friction coefficient (0.175). The lubricity evaluation tests do not necessarily correlate between each other; the test conditions are distinct and different wear mechanisms occur. Most part of scientific publications on biodiesel lubricity employs HFRR tests; in most of cases, biodiesel blends display better lubricity than current low-sulfur diesel.[10,11]

This work presents some results, of both wear and friction performance of metallic samples tested with commercial fuels, biodiesel (B100) and diesel, under different levels of loads and tangential velocities. The tests were performed in a reciprocating pin-on-plate machine, in boundary lubrication regime. The obtained results could be indicatives of the tribological performance of both fuels. Lubricity could be better understood when related to friction results. At the most severe loading tests, some changes in the thermophysical behavior of the biodiesel fuel were apparent.

MATERIALS AND METHOD

Materials

In the tribological tests, rubbing specimens were pins and plates. The pins were of AISI 52100 steel, 63 HRc hardness, with test surface rounded to 5.5 mm radius and 0.5 μm Ra (mean height of asperities) roughness. The plates were of pearlitic gray cast iron, 250 HB hardness, with surface ground finished to 0.46 μm Ra roughness. Further details of specimens are described elsewhere.[12,13] As lubricants, diesel and biodiesel fuels were used. Both fuels are commercial, normally used in diesel engines.

Tribological Tests

Tests were performed in a TE67 Plint&Partners tribometer with reciprocating pin-on-plate device (see Figure 1). Plates were immersed in a bath with 10 ml of fuel. The test conditions were: room temperature, 2.5 Hz plate oscillation frequency, 5.5 h of total test time (total of 50000 cycles). Two levels of maximum tangential velocities, 0.08 m/s ("A" tests) and 0.16 m/s ("B" tests), corresponding to wear track lengths of 10 and 20 mm, and two levels of normal loads, 200 and 400 N, corresponding to 1.9 and 2.4 GPa of maximum hertzian pressure at the beginning of the tests,[14] were tested. Friction force was acquired along the tests at 0.1 Hz sampling rate. Friction coefficient was calculated as friction force divided by normal load.

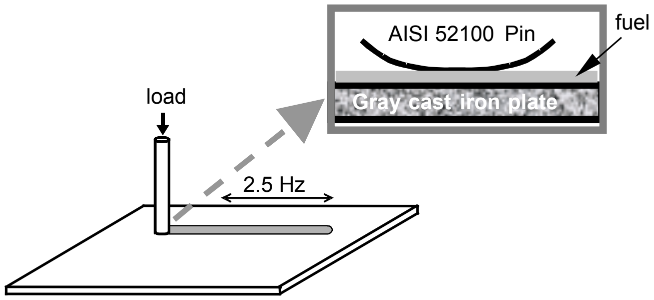

Figure 1: Schematics of the tribological test configuration.

Wear Analyses

The profiles of the worn track on the plates were measured at the middle position in the track, using a Dektak 6M stylus profiler (Veeco Instruments). The worn tracks on the plates were cross sectioned, metalographically prepared (polished with 1 μm diameter diamond abrasives) and examined with an optical microscopy (Olympus Bx51M) with image analysis program (Image-Pro Plus 5.1).

Fuel Analyses

Fourier Transform Infrared Spectroscopy (FT-IR) technique was employed to determine the chemical bonds of the fuels. All spectra were obtained using a diffuse reflectance accessory mounted in a Perkin-Elmer Spectrum GX. The diffuse reflectance accessory was aligned using KBr powder sample. This sample was also used so as to determine the background ratio spectrum. Fuel samples were homogeneously mixed to KBr, to 0.08 mg_{KBr}/mg_{fuel} concentration. An amount of 0.15 mg mass was used to fill the diffuse reflectance sampling cup. After filling, the surface was scraped with a spatula to packing the sample in the cup. Spectra were collected in the (500 to 5,000) cm^{-1} range, at 4 cm^{-1} resolution and average of 20 scans. The peaks of absorbance spectrum show at which wavenumbers the sample absorbs IR light, and allow interpretation of which functional groups are present.[15]

Differential Scanning Calorimetry (DSC) technique was used to obtain information on thermal behavior of the fuels, in terms of crystallization and melting temperatures, and volatilization and decomposition of existing components in the fuels.[16,17,18] Samples, with mass from 4 to 6 mg, were capsulated in hermetic aluminum crucible and were analyzed in a DSC Q1000 (TA Instruments). The applied thermal cycle, in nitrogen atmosphere (20 ml/min), was divided in two parts:

- First: cooling down from room temperature to -90ºC, holding for 600 s and subsequent heating up to 0ºC, with heating and cooling rates of 1.0ºC/min.
- Second: heating from 0 up to 550ºC with heating rate of 10.0ºC/min.

RESULTS AND DISCUSSION

Friction Coefficient

Figure 2 presents the results of friction coefficient along the test time, obtained from the four tested conditions. The values of friction coefficient increased along the time with both fuels, excluding the tests with biodiesel under 200 N load. Another observation is that friction coefficient was roughly independent on the velocity, excluding the tests with diesel under 400 N.

Under 200 N load, biodiesel produced lower level and more steady friction behavior than diesel. Lubricity of biodiesel is clearly superior than that of diesel under this load level, independently on the tested velocity level.

Under 400 N load, friction phenomena at the contacting interface between pin and plate were more unstable: graphs show instants of sudden decreases and increases. These are indicative of very high severity of the test condition. In this case, there was a strong effect of velocity on friction coefficient in the test with diesel fuel. The final value of 0.26 under higher velocity test is well above the limiting value stipulated in SBOCLE test, where a friction coefficient greater than 0.175 indicates the diesel fuel fails the lubricity evaluation.[9] Comparing both fuels, friction behavior was more predictable with biodiesel.

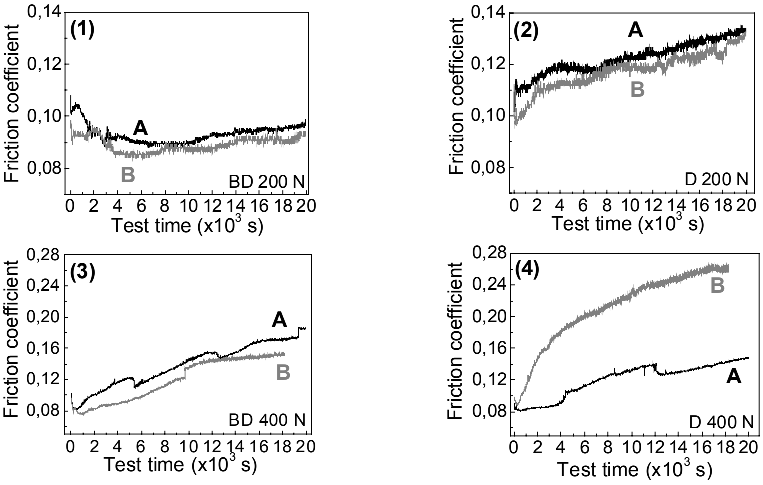

Figure 2: Friction coefficient along test time, A (0.08 m/s); B (0.16 m/s). (1) biodiesel 200 N, (2) diesel 200 N, (3) biodiesel 400 N, (4) diesel 400 N.

Wear

Figure 3 shows the worn profiles of the plates. If one analyses the scar width, it is possible to see a proportionality of it with its scar height in most of cases: larger width corresponded to a taller height. Differences are clearer in terms of height. Clearly, there was a marked effect of load on wear; this fact was expected, according to the Archard equation.[14] Concerning the velocity effect on wear, there is no explanation for the changes seen with velocity up to this moment. However, due to the fact that deviations in wear information are always high, more tests are necessary to determine the deviation values of wear in each of the tested conditions. In addition to that, comparing the graphs of Figure 2 to those of Figure 3, it is apparent that correlation between friction and wear results is not evident. On the other hand, taking a general observation of the graphs, it is possible to see that wear was greater with diesel fuel, “B” test. The scar height was out the profiler measuring range. Figure 4 also evidences that the track on plate was more heterogeneous (rougher) with diesel fuel.

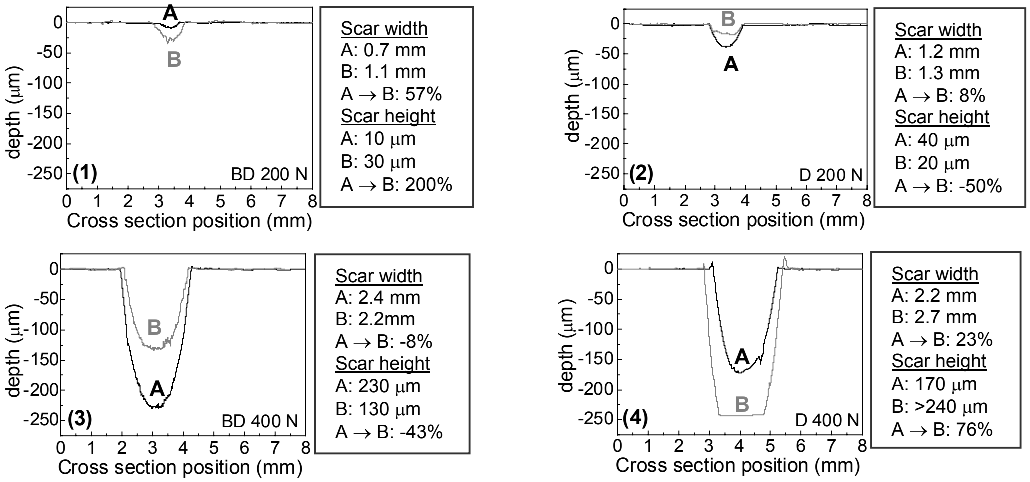

Figure 3: Worn profile of the plates, A (0.08 m/s); B (0.16 m/s). (1) biodiesel 200 N, (2) diesel 200 N, (3) biodiesel 400 N, (4) diesel 400 N.

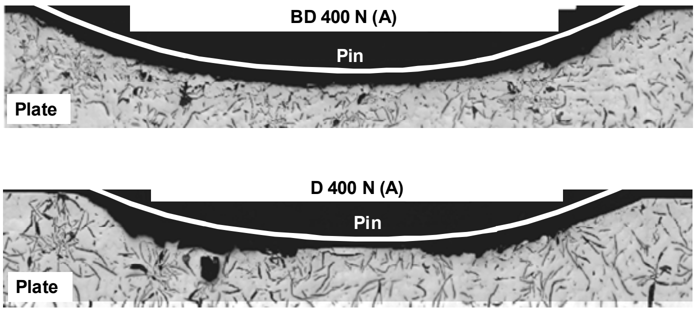

Figure 4: Cross section of the worn tracks of the plates after A test.

FT-IR Analyses

Figure 5 presents the FT-IR absorbance spectra for diesel and biodiesel, prior to the tests. Several contrasts between diesel and biodiesel material can be noticed. Diesel spectra should display the absorption peaks mainly related to saturated hydrocarbon bonds (alkanes, H-C-H, near 2900 cm^{-1} and at (4070 to 4420) cm^{-1}). There are no absorption peaks from diesel at (1500 to 1900) cm^{-1} and (3000 to 3700) cm^{-1}, where biodiesel absorbs well. Absorption around 1750 cm^{-1} can be related to stretching vibration of carbonyl bands of esters. Peaks around 1200 cm^{-1} may be assigned to the axial deformation of CC(=O)–O bonds of esters, while peaks around 1183 cm^{-1} may be assigned to asymmetric axial deformation of O–C–C bonds.[15,19] Absorption around 3500 cm^{-1} can be assigned to axial deformation of O–H bond of hydroxyls. Also can be the peak around 1700 cm^{-1}.[15] The range from (900 to 1300) cm^{-1} is known as the “fingerprint” region of spectra, related to many coupled vibration bands. It is clear that the main differences among the FT-IR spectra of fuels are mostly related to the oxygen bonds in biodiesel. A work in the literature has shown that increasing the oxygen content can improve wear and friction performance.[20]

The spectra of Figure 6 are related to the fuels after being tribologically tested under 400 N and 0.16 m/s (“B” test). This test condition was considered the most severe one for the fuel; therefore, changes in the chemical bonds of fuel material were expected because of severe thermomechanical action during rubbing. However, the spectra show that, even at such severe test condition, no changes, in terms of functional groups with fundamental vibrations in the middle infrared range, are noticed, either for diesel or biodiesel. It is apparent that high friction coefficient, seen particularly in the tests with diesel, does not affect the chemical stability of fuel material. High temperature instead of high load may bring other consequences to the chemical bonds of fuels. In the tests, warming of the fluid bath was negligible.

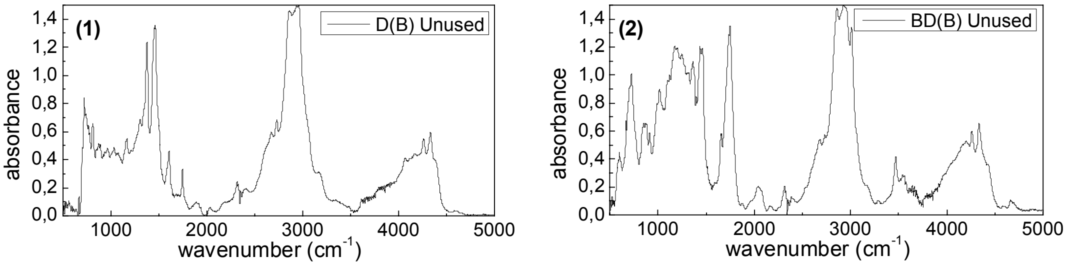

Figure 5: FTIR spectra from 500 to 5000 cm^{-1}, of unused diesel (1) and biodiesel (2).

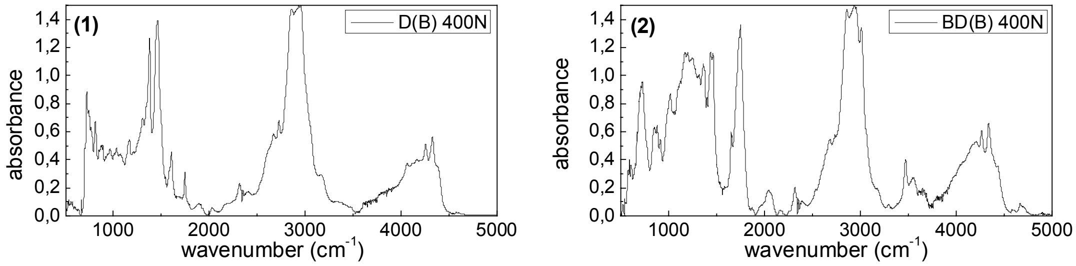

Figure 6: FTIR spectra from 500 to 5000 cm^{-1}, of biodiesel (1) and biodiesel (2) after tribological test (400 N, 0.16 m/s).

DSC Analyses

Figures 7, 8 and 9 show the results obtained by DSC measurements, of the fuel samples in the conditions prior to (unused) and after the tribological tests.

Figure 7 are related to the thermophysical behavior of unused samples of both diesel and biodiesel fuels. Figure 7.1 shows crystallization during cooling from 0 to -90ºC (exothermic peaks) and melting during heating up to 0ºC (endothermic peaks). At this temperature range, it is clear that biodiesel undergoes more transformations than diesel. For biodiesel, a crystallization process starts at approximately -1ºC and finishes around -67ºC. The melting process starts at -60ºC and finishes around 0ºC. For diesel, no crystallization is detected during its freezing up to –90°C; consequently, melting peak is also not detected. Figure 7.2 shows material volatilization and decomposition (endothermic peaks) during heating from 0 to 550ºC. For biodiesel, the volatilization and decomposition processes are represented by one large endothermic peak (around 210°C) followed by another small endothermic peak (around 350°C). For diesel, there is one large peak at 125ºC (peak temperature) representing the volatilization and decomposition processes.

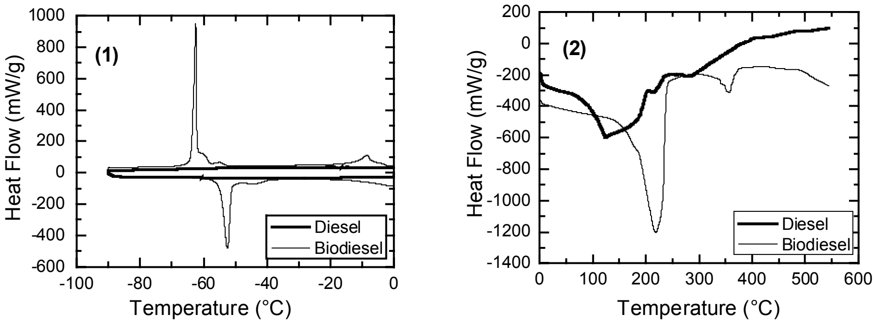

Figure 7: DSC curves of unused fuels (diesel and biodiesel): (1) crystallization and melting and (2) volatilization and decomposition.

Figures 8 and 9 respectively present the thermophysical behavior of samples of diesel and biodiesel fuels after being tribologically tested. It is possible to notice from Figure 8 that diesel has not experienced any relevant changes in the thermophysical behavior, if compared to the unused sample.

In contrast, the curves in Figure 9 reveal that some structural changes occurred in the biodiesel material, specifically after the test under 400 N, the most severe load condition. In the crystallization process, the small peak (around -60ºC), originally overlapped with the largest peak at -63ºC, has disappeared (see Figure 9.3). In the melting process, the small peak (around -45ºC), close to the largest peak at -53ºC, has also disappeared (see Figure 9.3). In the volatilization and decomposition process, the largest peak, originally around 210°C, is shifted to high temperatures (maximum at 352°C), and superposes the original small peak around 350ºC. One possible explanation for the changes in the thermophysical behavior of the biodiesel sample after tribological test may be related to some decrease in its water content. The test at the most severe condition can cause heating and then moisture evaporation. FT-IR analyses of biodiesel material have indicated the presence of certain chemical bonds (hydroxyl groups), possibly from water. This hypothesis must be better investigated. Analysis of thermogravimetry coupled to mass spectrometry may confirm if the mentioned change in the thermophysical behavior was due to water evaporation. Nevertheless, despite the apparent thermophysical changes, it was observed that the tribological performance of biodiesel was still superior to diesel.

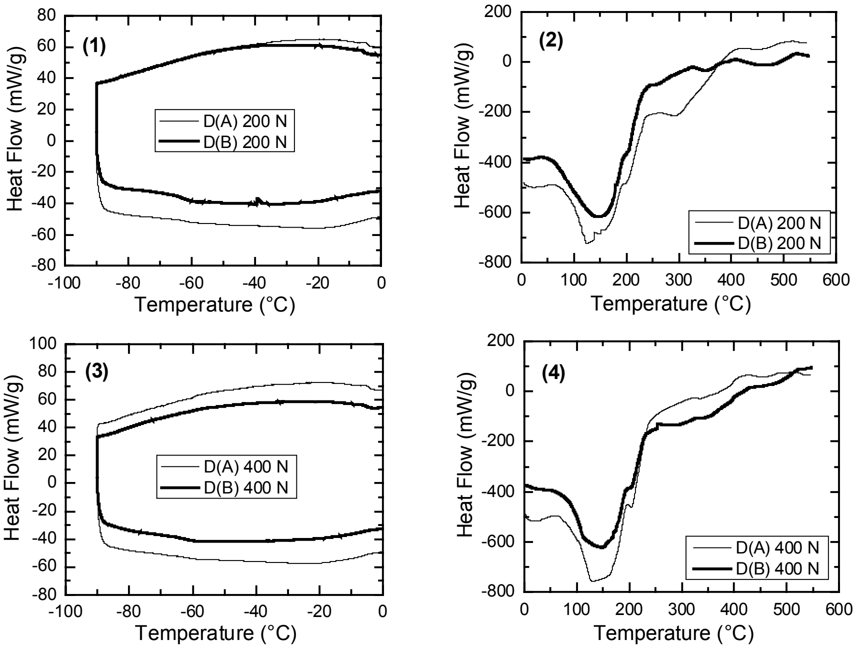

Figure 8: DSC curves of diesel after tribological tests, A (0.08 m/s); B (0.16 m/s). (1) 200 N, crystallization & melting; (2) 200 N, volatilization & decomposition; (3) 400 N, crystallization & melting; (4) 400 N, volatilization & decomposition.

At last, a general observation concerning the DSC curves is that the energy involved in volatilization and decomposition of biodiesel is slightly higher, compared to that of diesel. The high endothermic peaks of biodiesel during the volatilization and decomposition processes may be associated to more complete combustion process of this type of fuel.

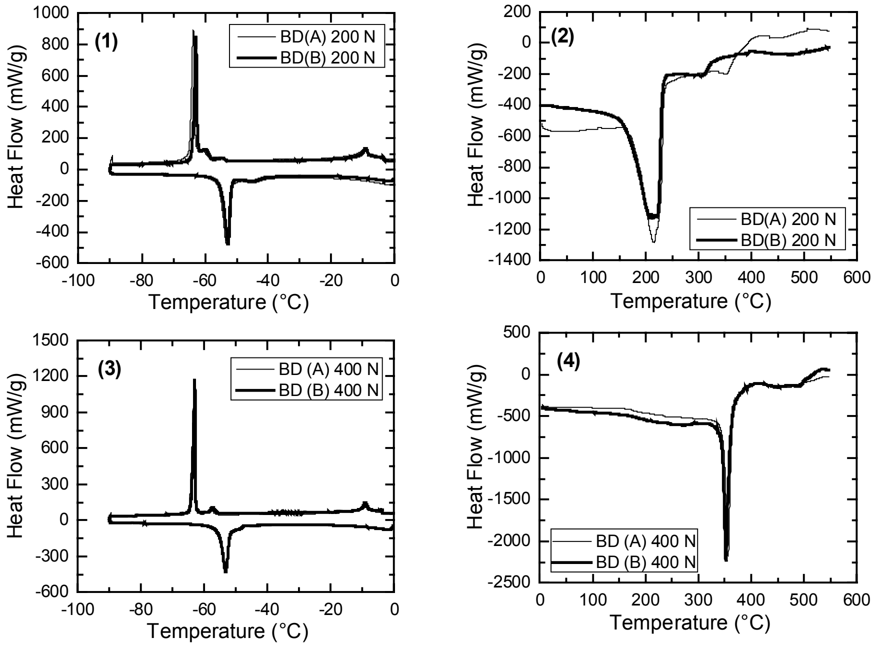

Figure 9: DSC curves of biodiesel after tribological tests, A (0.08 m/s); B (0.16 m/s). (1) 200 N, crystallization & melting; (2) 200 N, volatilization & decomposition; (4) 400 N, crystallization & melting; (4) 400 N, volatilization & decomposition.

CONCLUSIONS

This work presented some results obtained from tribological tests of metallic specimens in boundary lubrication sliding, with diesel and biodiesel fuels as lubricants. Wear and friction depended on the test condition; in general, both were lower with biodiesel. This fact confirms superior lubricity of biodiesel material. DSC analyses have shown that biodiesel material starts crystallization transformations at low temperature (-1ºC), differently from diesel. Also by DSC analyses, it was seen that the biodiesel used in the most severe load condition had its thermophysical behavior changed. Decrease in water content due to its evaporation during the tribological test is a possible cause for the observed change. More investigation is needed to confirm this hypothesis. Despite of changes in its thermophysical behavior, biodiesel material was not affected in terms of chemical degradation, according to FT-IR analyses. Diesel material has not shown any changes regarding either thermophysical behavior or chemical bonds, despite being worst for lubricity concern.

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