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Article

Synthesis of Triacetin and Evaluation on Motor

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Triacetin (or glycerol triacetate) was obtained by acetylating the glycerol by-product of biodiesel production process. This procedure is an interesting alternative that follows the principles of green chemistry. In this work, triacetin was synthesized using reactions between glycerol and acetic acid, as well as glycerol and acetic anhydride, using homogeneous and heterogeneous acid catalysis. The goal is to use this product as an additive for biodiesel produced from palm oil, which is a fuel with physical properties that require improvement. The products were characterized by Fourier transform infrared spectroscopy (FTIR), ^{13}C nuclear magnetic resonance (NMR) and gas chromatography (GC). The reaction between glycerol and acetic anhydride was the most effective for obtaining the desired product, with an approximate selectivity of 98% for triacetin. The triacetin was added to diesel fuel oil and biodiesel in proportions from 5 to 10% v/v, and the mixtures were tested in an electrical generator. In the test, the engine showed no problems during operation, and incorporating the mixtures did not result in significant consumption. Small reductions were detected in CO, O_2 and opacity, but no changes were observed in the emissions of NO_x and CO_2.

Keywords: triacetin, glycerol, acetic acid, acetic anhydride, gas emissions

Introduction

The search for clean, renewable and economically viable energy has encouraged the use of oxygenated additives that can enhance the combustion process and engine performance.[1]

Numerous investigations related to the search for fuel additives based on glycerol have been performed in recent years due to the large amounts of glycerol that are generated during biodiesel production.[2] This production has affected the market surplus of glycerol because the traditional pharmaceutical and cosmetic markets can no longer absorb it.[3,4] One promising application for this excess glycerol is transformation to 1,2,3-triacetoxypropane, which is also known as glycerol triacetate, triacetin or triacetylglycerol. When used as an additive, this product can prevent the crystallization of biodiesel, which is caused by changes in temperature and may cause blockages in the engine.[5,6]

The glycerol obtained during biodiesel production can be used to produce glycerol esters through acetylation. In the presence of a suitable acidic catalyst, this process can be achieved by combining glycerol and acetic acid[7,8] or glycerol and acetic anhydride;[9] the exothermic reaction favor the formation of triacetin, as reported by Silva *et al*.[9] This reaction produces mono, di and triacetin or glycerol triacetate; the two first compounds have applications in cryogenics and may serve as raw materials for the production of biodegradable polyesters.[10] Meanwhile, triacetin can be used in cosmetics, pharmaceuticals and fuel additives.[11-13]

Recent works[9,14-16] have demonstrated the interest in producing triacetin from glycerol. Liao *et al*.[14] proposed a two steps method to synthesize triacetin using glycerol and acetic acid in esterification and acetylation reactions with a 1:9 molar ratio of glycerol:acetic acid over Amberlyst A-35 and zeolites as catalysts. After 4 h at 105 °C over 5% Amberlyst A-35, authors obtained almost 100% selectivity for triacetin.

Silva *et al*.[9] studied the acetylation of glycerol with acetic anhydride in the presence of different solid acidic catalysts (zeolite H-Beta, K-10, and niobium phosphate and Amberlyst A-15). The following reaction conditions were tested: 1:3 and 1:4 molar ratios of glycerol:anhydride at temperatures from 60 to 120 °C over 20, 80 and 120 min. The authors were able

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to achieve 100% triacetin selectivity for all catalysts used under conditions of 1:4, 60 or 120 °C. The best parameters for catalysts H-Beta and K-10 were 60 °C and 20 min. For A-15 they were 60 °C and 80 min, and for niobium phosphate the best parameters used were 120 °C and 80 min.

Zhou *et al.*[15] studied the influence of varying the molar ratio of glycerol: acetic acid from 1:3 to 1:9 and the temperature from 80 to 110 °C while using Amberlyst A-15 as the catalyst. The conversion of glycerol increased as the molar ratio and temperature increased, but the molar ratio was the most important factor during the conversion of the studied groups.

Zhou *et al.*[16] evaluated the catalytic characteristics and parameters to optimize the esterification of glycerol with acetic acid over solid acid catalysts: Amberlyst A-15 and zeolites HZSM-5 and HUSY. The catalytic tests utilized molar ratios of glycerol:acetic acid from 1:3 to 1:9 and temperatures between 80 and 110 °C. The authors found that the A-15 showed better activity and higher selectivity for diacetylglycerol and glycerol triacetate. According to the authors, the A-15 resin has sufficient porosity and acid sites, facilitating the formation of reactive electrophilic intermediates and larger molecules such as di- and glycerol triacetate. Similar to the previous study,[15] the authors observed that the highest molar ratio and temperature positively affected the conversion of glycerol and selectivity for di- and glycerol triacetate.

Casas *et al.*[17] evaluated the physical and chemical characteristics of a mixture of biodiesel containing 20% triacetin by weight. The authors analyzed properties such as: density, kinematic and dynamic viscosities, cloud point, pour point, point of clogging, cetane number and flash point. The results suggest that the freezing point of triacetin is responsible for the decreased cloud and pour points, while the point of blockage is directly connected to the high viscosity of triacetin. Adding more triacetin increased the density and the viscosity, and decreased flash point value and cetane number of the mixtures.

Venkateswara Rao *et al.*[18] carried out a comparative study using diesel oil, coconut oil biodiesel and coconut oil biodiesel and triacetin mixtures in different proportions (0, 5, 10, 15, 20 and 25%, v/v) in a direct injection diesel engine. The authors indicated that the blend with 10% triacetin showed better engine performance, with reduced gas emissions (HC, CO, CO_2, NO_x and opacity).

Pathak and Paul[19] studied the effect of triacetin and ethanol as additives for neem oil biodiesel on the performance and emissions characteristics of a diesel engine. The authors used 5 and 10% of additive, with constant engine speed. Compared with biodiesel, it was observed that there was a slight reduction in specific energy consumption, adding triacetin and/or ethanol to biodiesel. According to the authors, at higher loads, the emissions of CO, HC and particles were significantly lower in all mixtures compared with biodiesel, but there was an increase in the NO_x emission values. As observed by the authors, triacetin is also an antiknock agent and has high oxygen content improving fuel combustion.

In this work, the acetylation of glycerol was studied by combining acetic acid (1:6) and acetic anhydride with glycerol (1:3) while using Amberlyst A-15 and H_2SO_4 as catalysts. A small diesel generator was used to test mixtures of 5 and 10% triacetin in palm oil biodiesel and diesel oil to assess the influence of the additive on the engine performance.

Experimental

Table 1 shows the conditions and catalysts used in the tests to obtain triacetin. The reactions were conducted at reflux in a 500 mL round bottom flask with a condenser under constant magnetic stirring. During the experiments, 5% Amberlyst A-15 was used *per* mole of glycerol (40 mL). For the homogeneous process, sulfuric acid was added to match the acid equivalents present in the resin. After 2 h, the product was vacuum distilled in a fractionating column to remove the excess acetic acid. The triacetin-rich fraction was then washed with saturated sodium chloride solution (30 g sodium chloride *per* 100 g of water). After washing, the product was placed on rotary evaporator to remove the excess water.

Chemical analysis

The products were characterized using ^{13}C nuclear magnetic resonance (NMR) spectroscopy on a Varian

Table 1. Reaction conditions

Catalyst	Molar ratio		Temperature / °C	time / min	Activation temperature / °C
	Anhydride:glycerol	Acetic acid:glycerol			
Amberlyst A-15	3:1	–	60	120	100
Amberlyst A-15	–	6:1	120	120	100
H_2SO_4	–	6:1	120	120	–

Table 2. Selectivity to glycerol acetates in reactions of glycerol with acetic anhydride and acetic acid

Catalyst	Molar ratio glycerol		Temperature / °C	time / min	Conversion / %	Selectivity to acetins / %		
	Acetic anhydride	Acetic acid				Mono	Di	Tri
A-15	1:3	–	60	120	100	0.7	1.3	98.1
A-15	–	1:6	120	120	100	3.5	8.7	87.8
H_2SO_4	–	1:6	120	120	100	8.4	24	66.4

Premium COMPACT 600 MHz spectrometer. The samples were dissolved in deuterated chloroform and tetramethyl silane was used as an internal reference. The Fourier transform infrared absorption spectra (FTIR) were obtained with a Prestige 21 model Shimadzu FTIR spectrometer. Liquid samples of the raw materials and products were placed between KBr plates. The resolution of the spectra was 16 cm^{-1}, and the scan range from 400-4000 cm^{-1}. Reaction conversion and selectivity were calculated using two-dimensional gas chromatography (GC) in a system consisting of two GC-2010 chromatographs coupled to a quadrupole mass spectrometer MS-QP2010. The first gas chromatograph was equipped with a CG Solgel-wax (30 m × 0.25 mm × 0.25 mm) column, and the second was equipped with a BP5 column (30 m × 0.25 mm × 0.25 mm). Helium was used as the carrier gas, the injector temperature was 250 °C and the flame ionization detector (FID) was maintained at 250 °C. The heating rate was 15 °C min^{-1}.

To evaluate the influence of the additive on the performance of a diesel engine, an Agrale M90 motorized generator driven by a diesel air-cooled monocylinder engine with an output of 12.2 cv was used. This generator does not allow changes in the rotation of the engine (angular speed of 1800 rpm). However, the load could be varied through a bank containing 9 lamps operating from 160 to 500 W. In these tests, the emissions from a diesel engine fueled with commercial diesel oil (D100), palm oil biodiesel (B100) from Agropalma, blends of diesel and/or biodiesel with proportions 5 and 10% of triacetin by volume were also analyzed, which were known as D5 (diesel + 5% triacetin), D10 (diesel + 10% triacetin), B5 (biodiesel + 5% triacetin) and B10 (biodiesel + 10% triacetin). The density and viscosity of the fuels with and without triacetin were measured. The density was evaluated based on NBR 14065 using an automatic density meter (Rudolph research analytical, DDM 2911). The viscosity was measured according to NBR 10441 with a Herzog HVM 472 multiviscosimeter. A MODAL 2010-AO gas analyzer was used for emission gas analysis. Smoke opacity was measured using a NA-9000 opacimeter, providing an indirect measure of diesel particulate emissions.

Results and Discussion

Catalytic tests

Table 2 shows the results for the catalytic reactions at molar ratios of 1:6 (glycerol:acetic acid) and 1:3 (glycerol:acetic anhydride). The reaction between glycerol and acetic anhydride was highly selective for triacetin (98%), confirming the results obtained by Silva *et al.*[9] under similar reaction conditions. Silva *et al.*[9] used a 1:4 molar ratio of glycerol:acetic anhydride in reactions over 20 min (Amberlyst-A15 without heat treatment) and 80 min (Amberlyst-A15 with heat treatment), obtaining 90 and 100% selectivity for triacetin, respectively. For all reactions the conversion was 100% as observed by Silva *et al.*[9]

Product analysis

Figure 1a shows the spectra of a standard triacetin sample and Figure 1b a sample obtained from a reaction between glycerol and acetic anhydride. At 1750 cm^{-1}, a signal from the carbonyl stretch of the product esters was observed, confirming that the triacetin was obtained. At approximately 3000 cm^{-1}, a characteristic C–H (alkane) signal was observed, while at 3500 cm^{-1}, a band characteristic of OH was observed. The similarities between

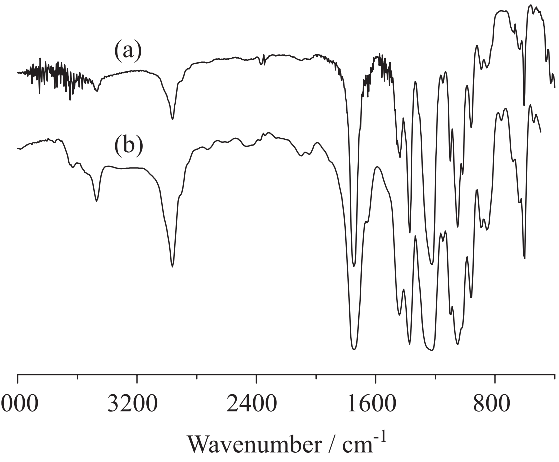

Figure 1. FTIR spectra (a) standard triacetin and (b) riacetin 1: 3 (glycerol: acetic anhydride with A-15).

the spectra in Figure 1 suggest that the procedure adopted for purifying triacetin was efficient.

Figure 2 shows the ^{13}C NMR spectra of commercial and experimentally obtained for triacetin. The signals with chemical shifts of approximately 20 ppm correspond to carbons 5 and 6, which are linked to the carbonyl esters. The peak at 62 ppm corresponds to carbon 4. The signals at 70 ppm revealed three carbons present between the two carbons 4 that were linked to the carbonyl of the ester. At 170 ppm, the signals observed represented carbons 1 and 2, and the signal at 77.2 ppm corresponds to the deuterated solvent ($CDCl_3$).

Fuels and blends properties

Table 3 shows some of the properties of the diesel, biodiesel and their mixtures with triacetin. According to Altabani *et al.*[20] viscosity is considered one of the most important properties of fuels because it affects the operation of fuel injectors and spray atomization equipment. This problem is exacerbated at low temperatures; the increased viscosity affects the fluidity of the fuel. Incorporating an additive can prevent these issues, especially for the biodiesel derived from palm oil; this fuel tends to be more viscous than petroleum diesel, as shown in Table 3. Adding 5 and 10% triacetin to the diesel oil decreased the viscosity by 3 and 2%, respectively. For the biodiesel the reduction was less sensitive: 1% for 5 and 10%; blends were not significant. Altabani *et al.*[20] measured 4.69 mm^2 s^{-1} for biodiesel from palm oil. Despite our results do not corroborate with Altabani *et al.*,[20] the viscosity values observed agree with the specified ASTM D6751 with limits between 1.9 and 6 mm^2 s^{-1} standards.

The density of a fuel is a fundamental property that affects engine performance because it influences the air-fuel relationship and energy content inside the combustion chamber.[21] According to the literature,[21] the density of biodiesel is slightly higher than that of diesel oil. This property is affected by the degree of unsaturation of the vegetable oil: the greater the unsaturation level is, the greater the density is. According to the European norm EN 14214, the density limits for biodiesel are between 0.860 and 0.900 g cm^{-3}, while diesel standard EN 590 sets the limits between 0.820 and 0.845 g cm^{-3}. The results in Table 3 indicate that adding triacetin increases the density of both fuels, although the values remain within the standard limits.

Power generator tests

The tests in Figure 3 were performed at an angular velocity of 1800 rpm while varying only the load through a bank of lamps. Figure 3a shows the specific fuel consumption (g kW h^{-1}) relative to the required motor power (kW) to D100, B100 and their mixtures with triacetin. The specific fuel consumption is larger when less power

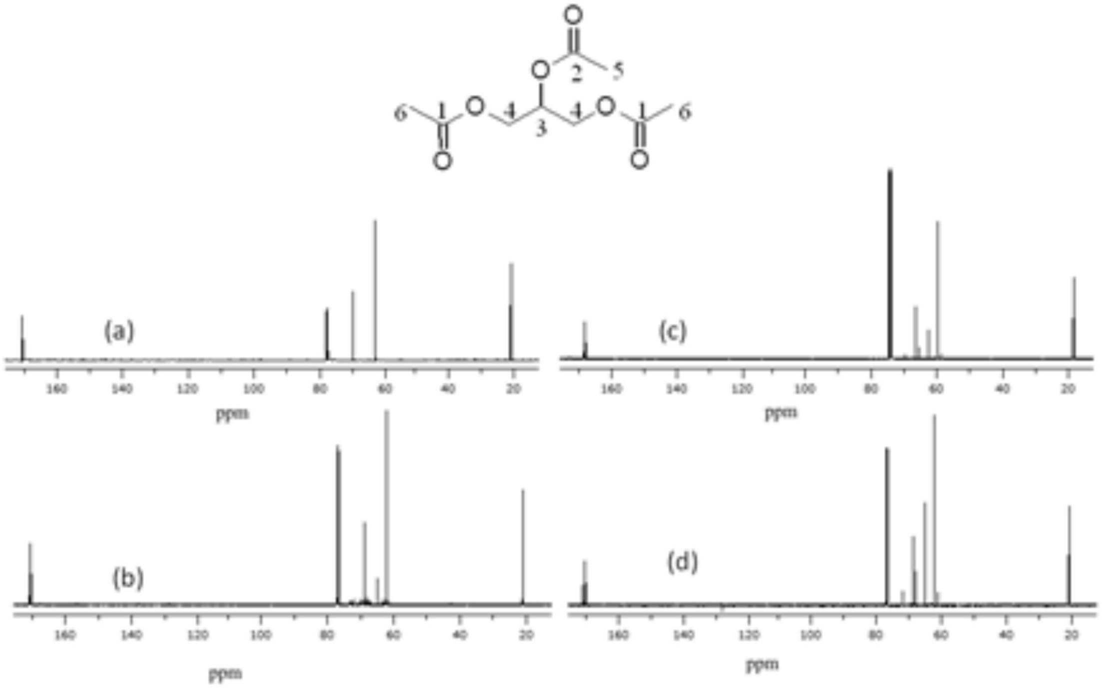

Figure 2. ^{13}C NMR (a) standard triacetin; (b) triacetin 1:6 (glycerol:acetic acid and A-15); (c) triacetin 1:3 (glycerol:acetic anhydride with A-15); (d) triacetin 1:6 (glycerol:acetic acid and H_2SO_4).

Table 3. Diesel, biodiesel and blends physical properties

Fuel property	D100	D5	D10	B100	B5	B10
Density at 20 °C / (g cm^{-3})	0.8330	0.8362	0.8361	0.8755	0.8886	0.9013
Viscosity at 40 °C / (mm^2 s^{-1})	3.13	3.04	3.06	4.67	4.63	4.63

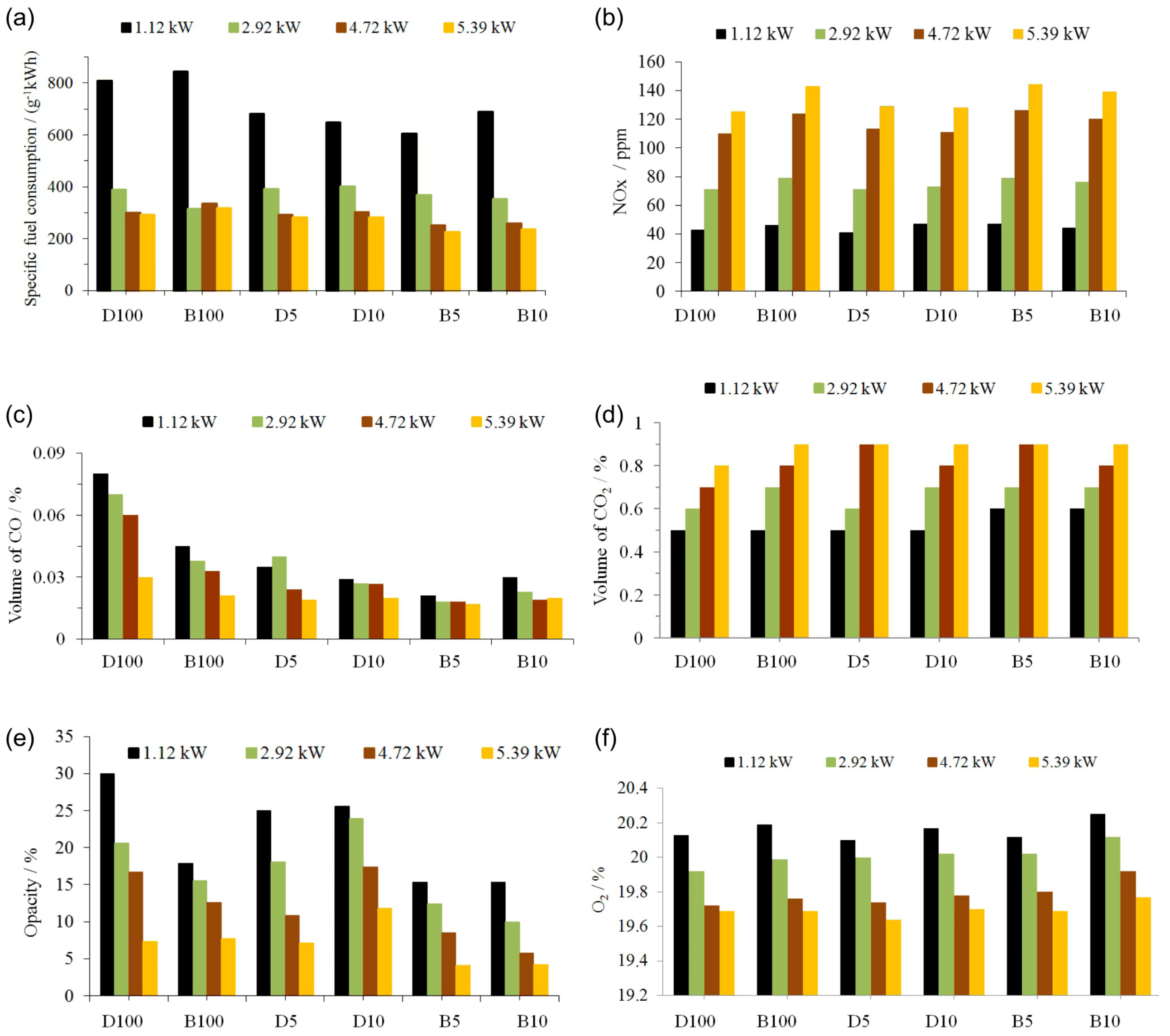

Figure 3. (a) Specific fuel consumption *vs.* engine speed; (b) NOx emission; (c) CO emission; (d) CO$_2$ emission; (e) opacity emission and (f) O$_2$ emission.

is supplied by the generator, and the same behavior was observed by Roskilly *et al.*[22] It was found that the specific consumption was lower for diesel and mixtures thereof relative to biodiesel and mixtures thereof.

Kalam and Masjuki[23] reported that this behavior was expected and best explained by the efficiency of burning the diesel fuel. After adding triacetin to diesel and biodiesel, however, no improvements were observed. The consumption was almost the same as the pure fuel, and for biodiesel, the addition of the additive slightly increased specific fuel consumption.

Figure 3b shows the NO$_x$ emissions. As expected, the values increase when increasing the engine power. In addition, the emissions were higher for biodiesel and mixtures thereof. The D5 and D10 mixtures produced lower NO$_x$ values. In the reviews conducted by Lapuerta *et al.*[24] and Xue,[25] the authors found different results regarding NO$_x$ emissions. In some cases, emissions are reduced in the presence of biodiesel, while they are increased in others. In some works, the differences are not significant, similar to the present study. The NO_x emissions of biodiesel are normally higher than those of diesel oil when measured on a test bench engine, but not when they are measured from vehicles, possibly explaining the varied results. In addition, the loads of vehicular engines are generally smaller than those imposed in experimental tests.[24] Our results suggest that the addition of triacetin do not make a significant difference in this case. According to the survey conducted by Xue,[25] the properties of biodiesel, including its higher oxygen content and higher cetane number, and the improvements to injection and combustion technologies have strongly affected NO_x emissions for biodiesel. However, some authors argue that the oxygen content of biodiesel does not directly influence the NO_x emissions, suggesting that more research is needed regarding the other properties of biodiesel and their effects on combustion and the fuel system to explain the increased NO_x emissions.

Figure 3c shows the emission of CO as a function of the generator load for different fuels. A reduction in CO emissions was observed when increasing power output. These emissions were higher for the D100 and lower for B5. The presence of 5 and 10% triacetin in the diesel oil reduces the CO emission by approximately 50%. The biodiesel experienced a lower reduction due to the presence of oxygen in the fuel. Therefore, adding triacetin to diesel and biodiesel decreased the amount of CO released in the atmosphere. This result is expected due to the high oxygen content of the biodiesel and triacetin, which favors complete combustion.[23,24]

Figure 3d shows the emission of CO_2 *versus* the generator load for different fuels. The concentration of CO_2 increased with the generated power. In general, lower CO_2 emissions were observed for the diesel oil. All of the other fuels exhibit very similar behaviors except for B5 and D5 under a load of 4.72 kW. This behavior was also observed by McCarthy *et al.*[26] who observed increased CO_2 emissions when increasing the proportion of biodiesel in diesel. According to the authors, this increase was expected because a decrease in CO usually coincides with an increase in CO_2 emissions. These results suggest that the addition of triacetin do not make a significant difference in this case.

The data presented in Figure 3e show a reduction in the opacity when burning fuel with an increase in generated power. The percentage opacity for biodiesel is significantly lower than for diesel oil. The presence of triacetin decreased the opacity of the mixtures with diesel oil and those with biodiesel. Previous reports indicate that the oxygen present in the biodiesel and the additive is the primary factor when reducing particulate emissions through better combustion.[26] The absence of aromatic compounds, soot precursors and the addition of triacetin to biodiesel also contribute to the reduction in haze.[25] The higher cetane number of biodiesel can also improve combustion.[27]

The results in Figure 3f indicate that the oxygen consumption and the concentration of this gas in the exhaust decrease when the generated energy is increased. However, the emissions were highest for samples B10 and B100. The other fuels also generated very close values. In work performed by Reis *et al.*[28] noted that the oxygen emissions increased after adding biodiesel to diesel oil and decreased when increasing the load applied to the generator. According to the literature,[29] the presence of oxygen in the biodiesel chains contributes to the emission of O_2 when compared to mineral diesel fuel. This contribution improves the fuel combustion by reducing the formation of particulate material in the combustion chamber, which is an advantage of using higher percentages of biodiesel in the blend.[30]

Conclusions

The best results of the triacetin synthesis were obtained by acetylating of glycerol with acetic anhydride. The FTIR, NMR and GC analyses confirmed the high selectivity for triacetin (98%).

Adding the triacetin with diesel reduced the viscosity by 3 and 2% for the blends with 5 and 10%, v/v, respectively. For biodiesel, the viscosity was less dramatic: 1% for both blends. The viscosity values are obtained based on the ASTM D6751 standard with limits between 1.9 and 6 $mm^2\ s^{-1}$. Adding triacetin increased the density of both fuels; in all cases, however, the values remained within the limits of the standard.

When analyzing the engine performance, adding triacetin did not significantly alter the specific consumption. An increase in NO_x emission rates was observed when increasing the engine power, and these rates were higher for biodiesel and mixtures thereof. CO emissions were reduced for increased power output and the presence of 5 and 10% triacetin diesel oil reduces the emission of CO by approximately 50%. Biodiesel in this reduction was lower, most likely due to the presence of oxygen in the fuel. The CO_2 emissions were increased due to the increased load on the generator, as reported by McCarthy *et al.*[26] It was observed that the emission of CO_2 was lower for D100.

The opacity decreased as the load on the engine increased. The B100, B5 and B10 showed lower percentages of opacity. There was a small increase in the percentage of opacity for D10. The O_2 concentration decreased when increasing the power output. The emissions were higher for B10 and B100, while the other maintained similar values.

Consequently, adding triacetin to biodiesel subtly contributed to the reduction in emissions as pointed before by Pathak and Paul.[19] Complementary analyses of other parameters, such as the cetane numbers, cloud points and distillation curves, are important for validating the applicability of the additive.

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