

Thermal and Oxidative Degradation of Castor Oil Biodiesel

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Biodiesel is defined as the monoalkyl ester derivative of long-chain fatty acids, originated from renewable sources, such as vegetable oils or animal fats. The most common use of biodiesel is direct substitution of fossil fuels in compression–ignition engines. The heating of vegetable oils can cause complementary decomposition reactions, in which the results can also lead to the formation of polymeric compounds. This work has been carried out to study the degradation process of biodiesel in different temperatures and exposure times. The degradation process of biodiesel affected its thermogravimetric and calorimetric profiles, indicating the formation of intermediary compounds. The spectroscopic data of degraded biodiesel suggested oxidative polymerization, confirming thermal data. In the degraded biodiesel at 210 °C for 48 h, the formation of gum occurred, indicating that oxidative polymerization was completed.

Introduction

Triacylglycerides are the major constituents of castor oil. Ricinoleic acid constitutes about 90% of fatty acids. Because of this peculiar chemical composition, castor oil is highly valuable to industry.^{1–3}

The great demand of energy resources by production and transportation systems, associated with the shortage of fossil fuels, has been motivating the development of technologies that allow for the use of renewable energy sources. Biodiesel is among the better options.^{4,5}

Biodiesel is a renewable, biodegradable, and environment-friendly fuel substitute of fossil diesel. It constitutes a mixture of esters, which are obtained from the transesterification reaction of any triacylglyceride with a short-chain alcohol, for example, methanol.

The use of biodiesel brings about a series of environmental, economical, and social advantages. Several studies demonstrate that the substitution of fossil diesel for biodiesel decreases the emission of about 100% sulfur, 9.8% carbon dioxide, 14.2% unburned hydrocarbon, and 26.8% particulate materials.⁶ The impact of biodiesel, even as a blended fuel, on NO_x emissions is an area of great debate because of the influence of diesel types and engine models.

The environmental benefits can also generate economical advantages. Brazil can include biodiesel in the agreements established in the Kyoto Protocol and in the guidelines of Clean Development Mechanisms. There is already the possibility to sell carbon quotas, through the Carbon Fund, because of the emission reduction of pollutant gases, and also sell credits of “carbon sequestration”, through the Bio Carbon Fund, both funds managed by the World Bank.

Some properties of biodiesel are close to the fossil diesel, for example, volatilization temperature;⁷ then, biodiesel could be used in diesel engines without the need of any modification. However, some factors should be studied, mainly the degradation process of biodiesel.

The oxidation reaction of unsaturated fatty compounds affects the quality of fatty materials in diverse industrial applications, such as biodiesel. The issue of oxidative stability affects biodiesel mainly by contact with air during storage and factors such as elevated temperature, light, and other parameters that may accelerate oxidation. The exhaust emissions of a diesel engine operating on biodiesel are influenced by the oxidation of biodiesel.^{8,9}

The aim of this work is to characterize the degradation process of castor oil biodiesel in different temperatures and exposure times.

Experimental Section

The transesterification reaction was carried out in the molar ratio of 6:1 methanol/castor oil. The catalyst potassium hydroxide was used in the proportion of 1%. After the production and purification, biodiesel was characterized as indicated for Resolution 42 of the Brazilian National Agency of Petroleum, Natural Gas, and Biofuels (ANP).

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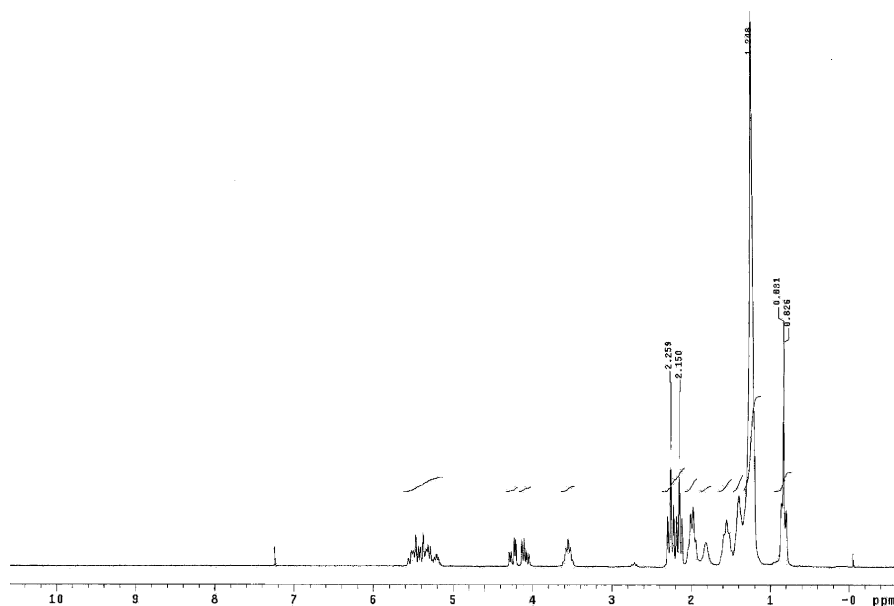


Figure 1. ^1H NMR spectrum of castor oil.

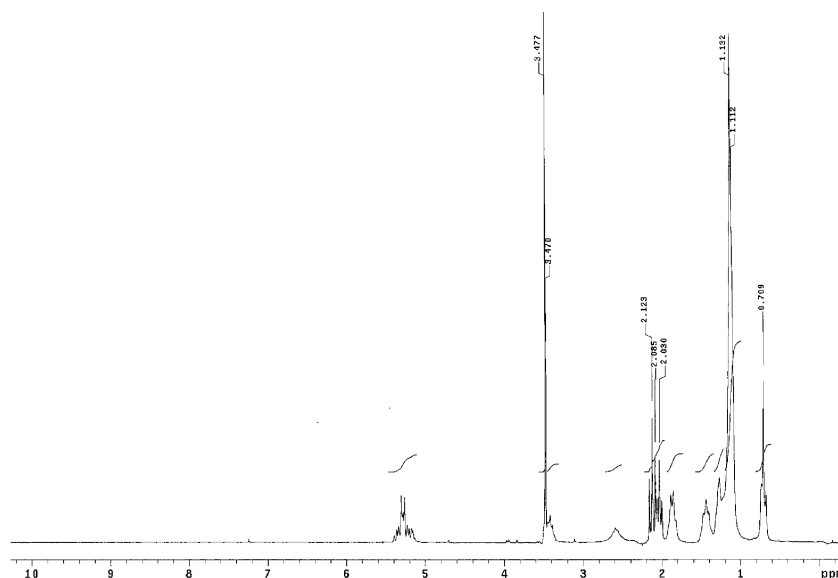


Figure 2. ^1H NMR spectrum of biodiesel.

In the degradation process, biodiesel (350 mL) was heat-treated at 150 and 210 °C, in a synthetic air atmosphere, in a system similar to a distillation one.¹⁰ Samples were withdrawn after times of 1, 6, 12, 24, 36, and 48 h. Thermogravimetry (TG), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and infrared spectroscopy characterized degraded biodiesel.

Infrared spectra were performed in a MB 102 Bomem spectrometer, using KBr pellets, in the region of 4000–400 cm^{-1} .

NMR of the proton (Varian 200 MHz) was performed at ambient temperature with CDCl_3 as the solvent.

The thermogravimetric (TG/DTG) and calorimetric (DSC) curves were obtained in a SDT 2960 TA Instruments thermal analyzer, in a synthetic air atmosphere, with a flow of 100 mL min^{-1} , sample mass of 10.0 ± 0.5 mg, heating rate of 10 °C min^{-1} , and temperature interval of 28–900 °C.

Results and Discussion

Transesterification reactions of different oils are reported in the literature. The use of methanol combined with soybean or

rapeseed oil as a precursor for biodiesel production is commonly observed. These reactions are usually carried out using alkoxides as the catalyst.¹¹

In this work, castor oil biodiesel attended the requirements of ANP; therefore, it becomes able to be applied as fuel. Castor oil biodiesel presented a higher flash point and viscosity than fossil diesel. A greater flash point guarantees security in the handling and storage.

The ^1H NMR spectrum of castor oil presented glyceride protons at 4.2 ppm (Figure 1). In the ^1H NMR spectrum of biodiesel, the strong singlet at 3.4 ppm indicates methyl ester formation. The signals at 2.1 ppm result from the protons on the CH_2 groups adjacent to the methyl ester (Figure 2). The major differences between the ^1H NMR spectrum of castor oil and the resulting fatty acid methyl ester are the disappearance of the glyceride protons at 4.2 ppm and the appearance of methyl ester protons at 3.7 ppm.

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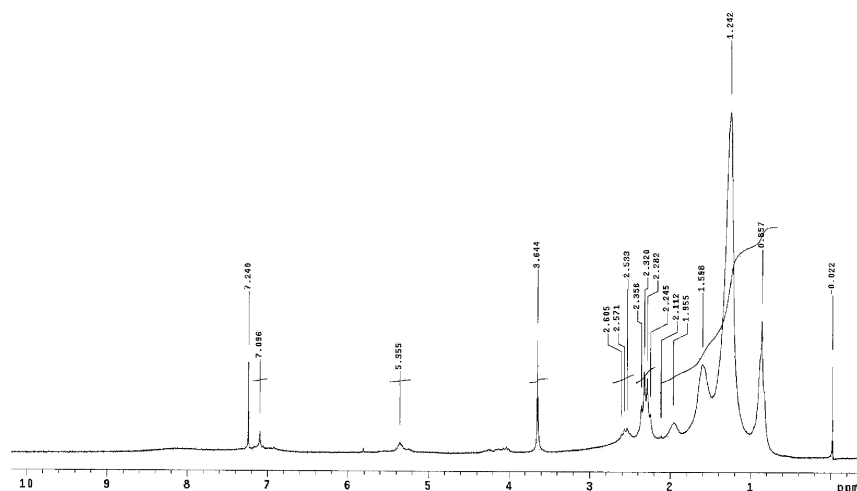


Figure 3. ^1H NMR spectrum of degraded biodiesel at 210 °C for 48 h.

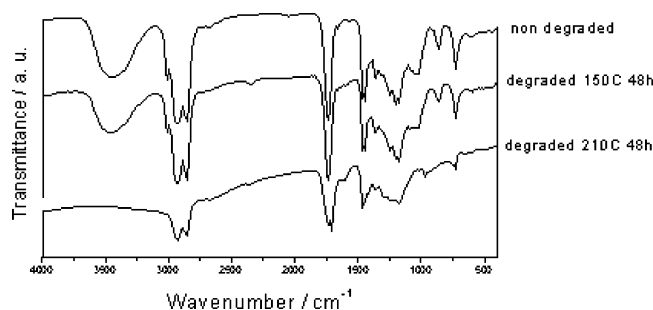


Figure 4. Infrared spectra of nondegraded and degraded biodiesel.

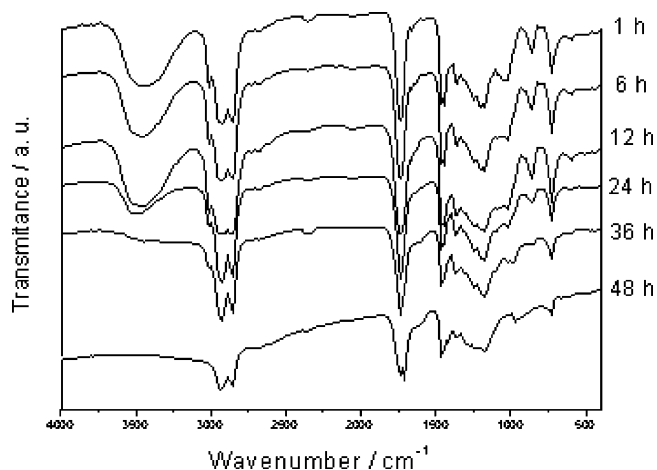


Figure 5. Infrared spectra of degraded biodiesel at 210 °C.

In the ^1H NMR spectrum of degraded biodiesel at 210 °C, the intensity of the 1, 12, 24, and 48 h peaks decreased. In the exposition time of 48 h (Figure 3), the sample presented a peak at 7.2 ppm, attributed to oxidation products. The oxidized fatty acid chains may break apart, producing shorter chain acids and aldehydes.¹²

Ricinoleic acid is the major component in castor oil, which contains a hydroxyl component, presenting bands at 3440, 850, and 1000 cm^{-1} . In the infrared analyses of biodiesel, the intense $\text{C}=\text{O}$ stretching band of methyl ester was presented at 1742 cm^{-1} and medium $\text{C}-\text{O}$ bands were presented at 1173, 1200, and 1246 cm^{-1} . The infrared spectrum of degraded samples, mainly at 210 °C, suggested an oxidation process (Figure 4).

Table 1. Steps of Mass Loss of Degraded Biodiesel at 150 °C

samples	steps	temperature (°C)	mass loss (%)
biodiesel degraded for 1 h	first	114–292	86.58
	second	292–363	9.08
biodiesel degraded for 12 h	first	143–292	78.11
	second	292–359	13.63
	third	359–566	6.95
biodiesel degraded for 24 h	first	157–312	69.87
	second	312–346	14.36
	third	346–368	4.26
	fourth	375–471	5.79
	fifth	471–588	5.19
biodiesel degraded for 48 h	first	148–309	60.03
	second	309–366	16.03
	third	366–472	17.97
	fourth	472–612	6.63

Table 2. Steps of Mass Loss of Degraded Biodiesel at 210 °C

samples	steps	temperature (°C)	mass loss (%)
biodiesel degraded for 1 h	first	136–293	98.48
	second	293–370	3.13
biodiesel degraded for 12 h	first	165–310	60.30
	second	310–390	25.22
	third	390–465	8.18
	fourth	465–557	6.77
biodiesel degraded for 24 h	first	175–289	26.22
	second	289–356	34.77
	third	356–414	14.84
	fourth	414–467	11.22
	fifth	467–528	12.82
biodiesel degraded for 48 h	first	166–342	18.07
	second	342–461	63.09
	third	461–517	26.94

In the infrared spectrum of degraded biodiesel at 210 °C for 1, 6, 12, 24, 36, and 48 h, the bands at 3007 cm^{-1} ($\text{HC}=\text{CH}$ stretching) and 724 cm^{-1} (out-of-plane bending) decreased intensity, indicating a decrease in unsaturation. It can be attributed to oxidative polymerization (Figure 5).

The oxidation reactions produce hydroperoxides, which can polymerize with other radicals to produce insoluble sediments and gums. In the degraded biodiesel at 210 °C for 48 h, the formation of gum occurred, suggesting that oxidative polymerization was completed.

TG/DTG curves of castor oil presented three steps of mass loss, attributed to decomposition and/or volatilization of triacylglycerides (mainly ricinoleic acid), in the temperature ranges of 221–395, 395–482, and 482–573 °C, with a mass loss of 56, 31, and 12%, respectively (Figure 6). The DSC curve of

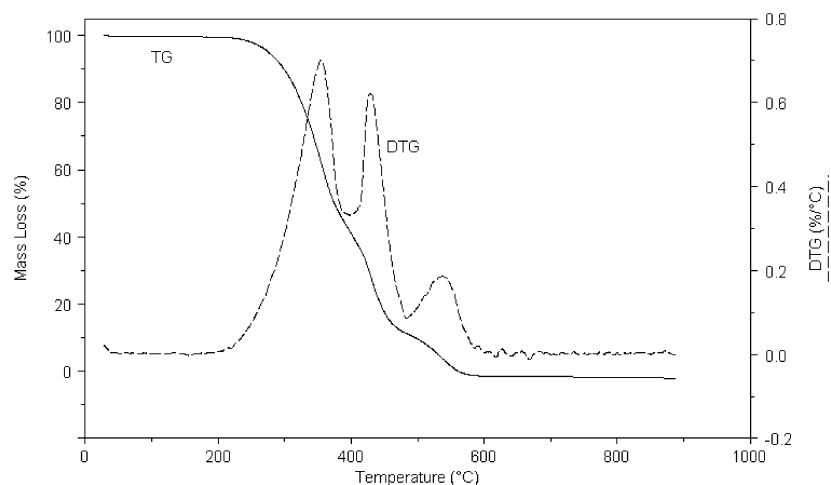


Figure 6. TG/DTG curves of castor oil.

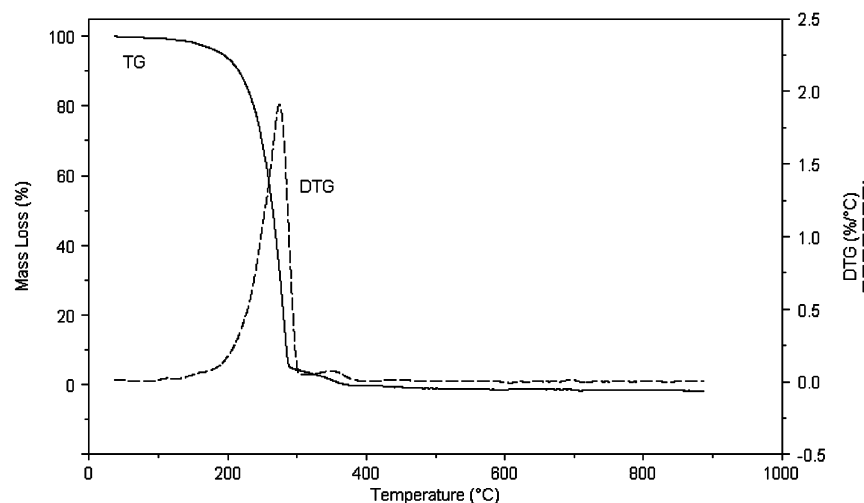


Figure 7. TG/DTG curves of biodiesel.

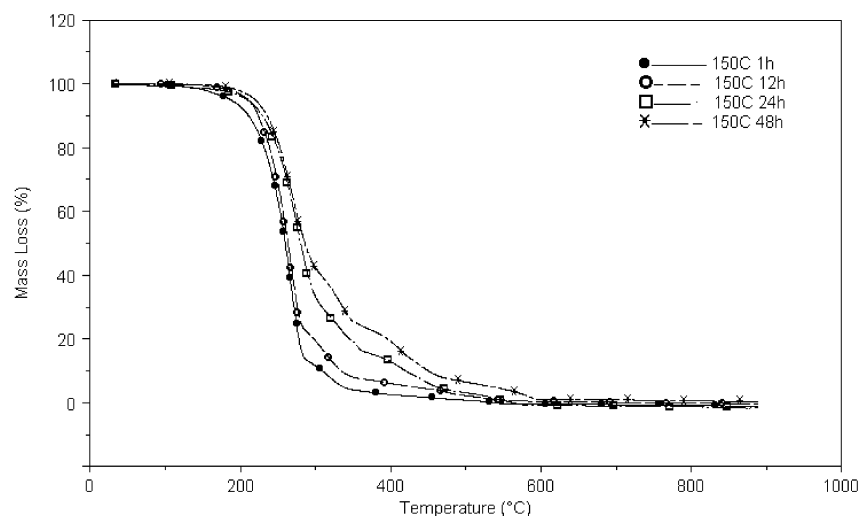


Figure 8. TG curves of degraded biodiesel at 150 °C.

castor oil presented three exothermic transitions, attributed to the combustion process, in the peak temperatures of 347, 434, and 541 °C, with enthalpies of 2041, 66, and 1314 J g⁻¹, respectively.

TG/DTG curves of biodiesel presented two steps of mass loss, attributed to decomposition and/or volatilization of methyl esters (mainly methyl ricinoleate), in the temperature ranges of 151–297 and 297–382 °C, with a mass loss of 93 and 4%,

respectively (Figure 7). The DSC curve of biodiesel presented three exothermic transitions, attributed to the combustion of methyl esters, in the peak temperatures of 200, 331, and 443 °C, with enthalpies of 17, 249, and 117 J g⁻¹, respectively.

The degraded biodiesel at 150 and 210 °C for 1 h (Figures 8 and 9) presented the same number of steps of mass loss of nondegraded biodiesel. The increase of the degradation time (12 and 24 h) changed the thermogravimetric profile, increasing

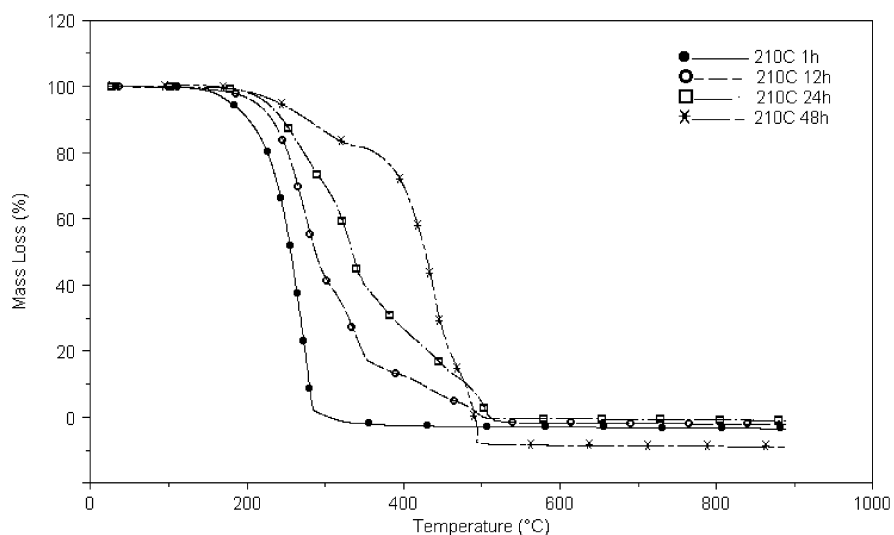


Figure 9. TG curves of degraded biodiesel at 210 °C.

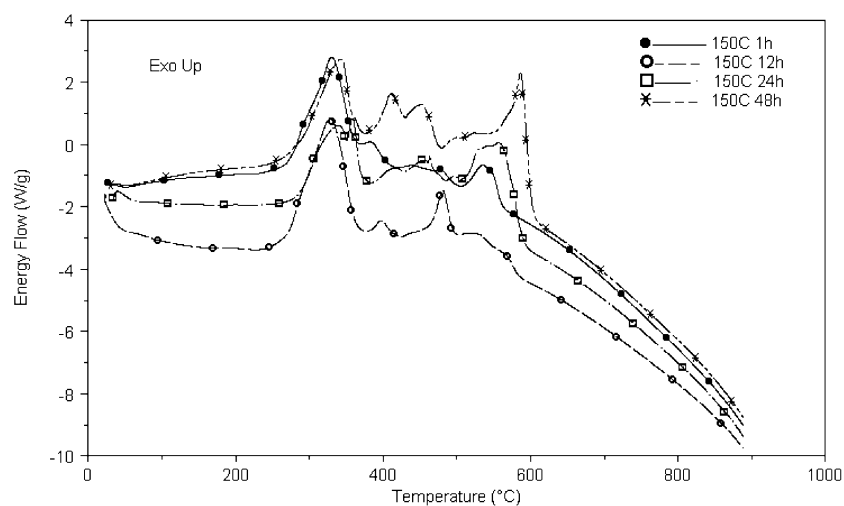


Figure 10. DSC curves of degraded biodiesel at 150 °C.

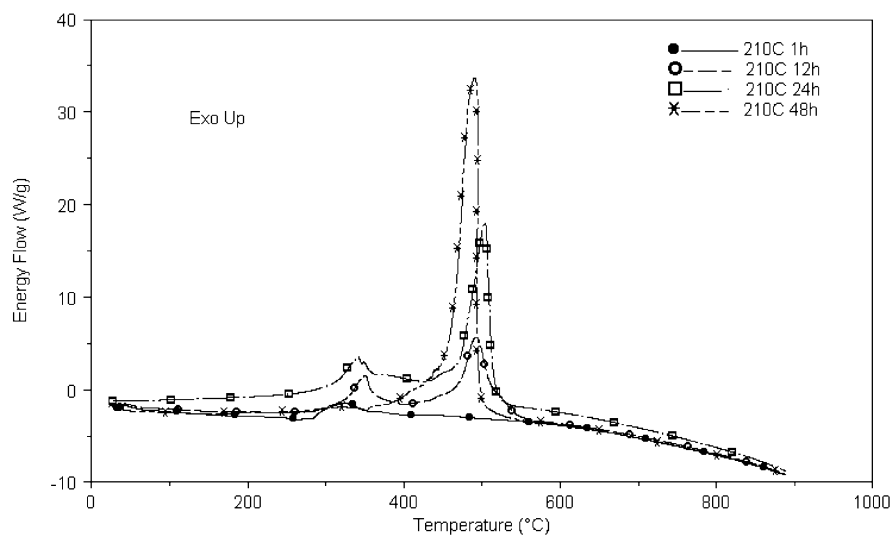


Figure 11. DSC curves of degraded biodiesel at 210 °C.

the number of steps and initial temperature, indicating the formation of intermediary compounds (Tables 1 and 2). In the degraded biodiesel for 48 h, the number of steps and initial temperature decreased, with the probability that compounds formed were decomposed at higher degradation times.

In the degraded biodiesel at 150 and 210 °C for 1, 12, and 24 h, the mass loss of the first step decreased with degradation times. The mass loss of the second step increased (Tables 1 and 2), indicating the formation of high-molecular-weight compounds, which decomposed at higher temperatures.

Table 3. Transitions Observed in the Degraded Biodiesel at 150 °C

data of transitions	1 h	12 h	24 h	48 h
peak temperature (°C)	328	326	315	339
enthalpy (J g ⁻¹)	960	1302	251	847
peak temperature (°C)	387	398	360	408
enthalpy (J g ⁻¹)	49	48	77	131
peak temperature (°C)	495	480	405	455
enthalpy (J g ⁻¹)	31	199	30	129
peak temperature (°C)	548	568	463	587
enthalpy (J g ⁻¹)	165	110	88	953
peak temperature (°C)			561	
enthalpy (J g ⁻¹)			731	

The increase of the degradation time (1, 12, and 24 h) changed the calorimetric profile of degraded biodiesel at 150 and 210 °C (Figures 10 and 11), increasing the number of exothermic transitions and indicating the formation of intermediary compounds (Tables 3 and 4). In the degraded biodiesel for 48 h, the number of exothermic transitions decreased, with the probability that compounds formed were decomposed at higher degradation times.

The most likely impact of the formation of sediment and gum will be fuel filter plugging and varnish deposits on fuel system components. The acid formation may cause corrosion in the

Table 4. Transitions Observed in the Degraded Biodiesel at 210 °C

data of transitions	1 h	12 h	24 h	48 h
peak temperature (°C)	230	349	340	317
enthalpy (J g ⁻¹)	79	751	558	105
peak temperature (°C)	307	492	427	494
enthalpy (J g ⁻¹)	188	2111	214	7348
peak temperature (°C)			503	
enthalpy (J g ⁻¹)			2897	

fuel system. In addition, hydroperoxides are very unstable and have a tendency to attack elastomers.¹³

Conclusions

The biodiesel presented stability up to 150 °C. The degradation process of biodiesel altered its thermal profile, indicating the formation of intermediary compounds, which decompose during higher degradation times. The spectroscopic data of degraded biodiesel indicated oxidative polymerization, confirming the thermal data. In degraded biodiesel at 210 °C for 48 h, the formation of gum occurred, suggesting that oxidative polymerization was completed.

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