Fuel Synthesis with Biocidal activity and lubricating grease from industrial oil waste

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Introduction

Just access the news sites, especially the sections where the theme is science and industries, which appear, highlighted subjects on environmental preservation and sustainability. These actions are also linked to cost reduction. With a careful eye on the sustainable process, it was proposed to these industrialists the transformation of the oily waste into value-added products that could be used in the factory itself. They would be fuel to be used in transport and grease lubricants for the process machines.

This paper shows us attractive results to be applied as activities of innovation and conservation of the environment by these institutions, such as the proposal of transformation of waste into value - added products. Initially, two competing aluminum cans factories were selected in order to unify a proposal that would be applicable to any factory that operates in the segment. The previous tests of the basic composition of this oily waste and part of the characterization were carried out as proposals for the destination of the material, are produced with a fuel production with a biocide and a production of lithium grease.

As greases were produced with oily waste and lithium soap and characterized in the laboratory of lubricants of the National Agency of Natural Gas and Biofuel (ANP), in Brazilia, They were classified as resistant to high temperatures and with NLGI grade 0 and 2.

The fuel was produced by successive reactions of: Thermal cracking, esterification reaction with methanol and aluminum oxide as catalyst and Hydrodeoxygenation reactions using as catalyst nickel molybdenum sulphide supported on alumina ($NiMoS_2/Al_2O_3$) the fuel is similar to diesel, and have Biocidal activity, inhibiting the growth of the main fungi (*Fusarium solani* and *Aspergilus niger)* and bacteria (*Acinetobacter sp.* and *Bacillus subtilis)* commonly found in the diesel oil (Ramalho et. Al 2016).

A general objective of this research was produced: a lubricating grease and fuel from the waste oil of the aluminum cans factories and investigate of the Biocidal activity. In order to obtain the fuel, successive reactions were made: thermal cracking, esterification and hydrotreatment, for Hydrodeoxygenation and hydrogenation reactions. The characterization of waste and fuel, are presented by techniques such as: spectroscopy in the Infra red region, gas chromatography coupled to the mass spectrum and by physical chemical analyzes that apply to the fuel for road use.

Material and Methods

The waste oil were collected from two competing cans from the aluminum packaging sector for beverages, one located in the city of São Paulo, which we will call Factory 1 *(F1)* and another in Federal District, which we will call *(F2). Synthesis of fuel* – To make the *Thermal Cracking reaction* - 500 g of the sample was weighed in a three - necked flask accommodated in a heating mantle and coupled to a condenser, reaction time was to 1h and 30min and the temperature to 400 º C. *Esterification Reaction*- In a closed reactor, 150 g of each sample were weighed, 1,5gof catalyst (Al_2O_3) added and 90 g of methanol PA at 180 ° C for 1 h. *Hydrodeoxygenation and hydrogenation Reaction* - 150 g of the cracked product were weighed, 12 g of catalyst ($NiMoS_2/Al_2O_3$) added and 450 psi of hydrogen gas pressure inserted at 340 ° C for 6 h. *The characterization* of the products and waste oil was made to: elementary analysis to determine the percentage of Carbon, Nitrogen and Hydrogen (C, H, and N). Infrared absorption (IR) using an ATR (attenuated total reflectance). Gas chromatography coupled to mass spectrum GC/MS and some analyzes were performed, using methods validated by the ANP (National Agency of Natural Gas and Biofuels): Specific mass (ASTM D 442 method), Ash Content (ASTM D 482), Kinetic Viscosity (ASTM D 445 method), acidity index (AOCS Method Cd 3d-63), Carbon residue (ASTM D 189), Flash point (ASTM D 93), Cetane number (ASTM D 4737 method), Cold clogging (ASTM D 6371). For B*iocidal activity* was made a test of inhibition of growth of microorganisms with weighing of fungal biomass. L*ubricating grease* - lithium hydroxide and commercial soybean oil was reacted in the molarratio3:1mol, to 12 h to produce the fatty acid salt. Grease was produced in two mass proportions, 1: 1 and 1: 1.5 being respectively fatty acid salt and residual organic oil. Grease tests: Penetrationat 25 ° C (worked 60 times) ASTM Method D 217 and Drop Point (ASTM D556 method).

Results and Discussion

Characterization of Waste oil factories F1 and F2 - Elemental analysis of the crude wastes, F1 and F2 was carried out, where the F1 Plant was defined by (C, H, N) and have, 72.45 % of Carbon, 12.37 % of Hydrogen and 0.59 % of nitrogen. The Factory F2, Carbon 85.42 %, 14.97 % and 0.72% of Nitrogen. It is noted that the greatest composition of both is carbon, which leads us to expect the compounds to have long chains of hydrocarbons. After these, the analysis of spectroscopy results was performed. Figure 1, shows the spectra in the infra red (IR) region of the F1 and F2 factory waste. The bands are identifying by numbers. Bands appearing in the 3500 cm^{-1} and 3200 cm^{-1}, **(1)** on regions refer to the (O-H) bond. The bands appearing in the region between 2960 cm^{-1} **(2)**, 2920 cm^{-1} **(3),** and 2850 cm^{-1} **(4)** refer to (CH_3) of methyl groups and methylene (CH_2) respectively. The band appearing in the region between 1740 cm^{-1}**(5)** and 1720 cm^{-1} refer to the absorption band (C=O) of esters and aldehydes, and 1710 cm^{-1} to 1700 cm^{-1} **(6)** refer to fatty acid carbonyls and some ketones. The band appearing at 1640 cm^{-1}**(7)** refers to the C = C bonds. The bands in the regions between 1460 cm^{-1}**(8)** and 1375 cm^{-1}**(9)** refer to (CH_2) plane of methylene groups and (CH_3) vibration of methyl groups. Bands in the region between 1380 cm^{-1} and 1150 cm^{-1}**(10)** correspond consecutively to CH_3 groups and the (C-O) group of esters. Bands appearing in the region between 1100 cm^{-1}**(11)** and 1150 cm^{-1}**(12)** are related to (C-O) esters. In the region at 720 cm^{-1}**(13)** it can be said that the Rocking effect occurs, that is, a plane flexion in which the structural unit in the case (-CH_2) does not oscillate back and forth in the plane of symmetry of the molecule. (Silverstein, 2013)

The chromatograms of wastes from factories F1 and F2 are presented in Figure 2, characteristic picks of hydrocarbons, alcohols, aldehydes, ester and carboxylic acids (Junior, 2016). The functional groups are identified and substances suggested: **1**-ethylhexanol, **2**-ác.hexanóic, **3**-Tetradecene, **4**-Tetradecane, **5**-Pentadecane, **6**-Hexadecane, **7**-Pentadecane, **8**-Octadecane, **9**-Octadecanal, **10**-Nonadecane, **11** - Methyl ester pentadecanoic acid, **12** - Eiconsane, **13** - Nonadecanol, **14** - Methyl ester heptadecanoic acid, **15** - Methyl ester Octadecanoic acid, **16** - Docosanol e **17** – Tetracosane. (NIST, 2016) Some picks don't appear on chromatogram of F2 because they are present just in the F1waste oil. The sample of F1 have more oxygenated compounds and an acids compounds shows in points **2, 11, 14** e **15** . For hydrocarbons, alkenes and alkenes that exist in the residual mixture, in addition to the compatibility of the digital library in all spectra having shown compatibility above 90% (Silverstein, 2013).

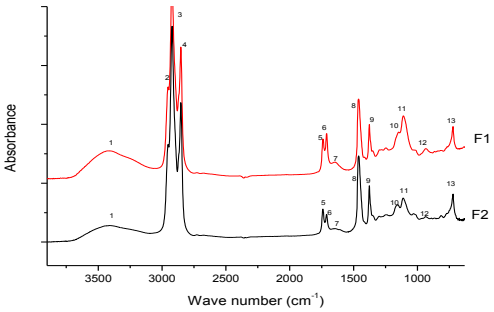


Figure1 IR Waste oil factories F1 and F2

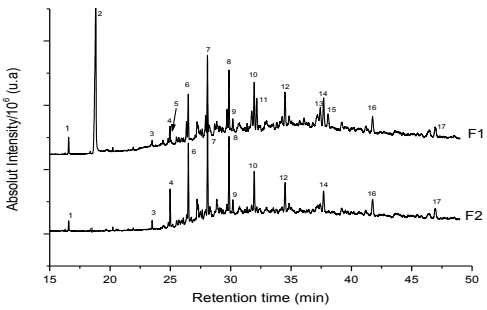


Figure2 Chromatogram Waste oil factories F1 and F2

Thus, in the chromatogram presented in Figure 2 suggests the identification of the main substances of the gross wastes. It is clearly noticed that the raw material of the F1 plant, have more components in its mixture than those of the F2 Plant, which shows the difference between the F1 and F2 samples, is a peak referring to an intense carboxylic acid in the F1 Plant and absent in the F2 (NIST, 2016), **s**uch evidence can be confirmed by the acid value of F1 was 35.5 mg/g and F2 22.0 mg/g. In addition, the physicochemical analyzes are described: as specific mass F1 = 888.7 g/cm^3 and F2 = 888.4 g/cm^3 and viscosity F1 = 59.45 mm^2/s e F2 = 60.93 mm^2/s. The composition of the wastes oils are similar and show us that we saw in chromatograms, compounds with a long carbon chain. Values of carbon residue F1 = 0,089 mg and F2 = 0,086 mg and ash both F1 and F2 = 0,009 mg are low, which indicates that in these residues are not present or are at very low levels, salts and non-volatile compounds.

Synthesis Fuel- Based on the analysis of the wastes composition from F1 and F2 factories, as a function of the long carbon chains and oxygenated compounds, the thermal cracking reaction was performed to break the long chains into smaller chains (Bandeira et. Al 2013). With the cracked products, two reactions were carried out: esterification to obtain blends BX ,ester and hydrocarbons fuels (Lei 13.033, 2014); and Hydrodeoxygenation and hydrogenation with the production of fuel basically composed of hydrocarbons (Chorkendorff, I.; Niemantsverdriet, 2003)

The results of an elemental analysis of the esterified products, where F1 Plant 24.04% of Carbon, 6.75% of Hydrogen and 0.69% of Nitrogen. The results of Factory F2 is, Carbon 37.15%, 9.61% of hydrogen and 0.41% of Nitrogen, the lower values of N, H and C for these compounds are justified as a function of the esterification reaction will in fact produce more oxygenated compounds not present or are at very low levels, salts and non-volatile compounds, the proposal of mechanism was explained by (Martins et. Al 2013) Physical chemical analyzes such as: acid value of F1 was 3.51 mg/g and F2 4.02 mg/g, specific mass F1 = 820.3 g/cm^3 F2 = 816.0 g/cm^3, viscosity F1 = 4.13 mm^2/s and F2 = 4.84 mm^2/s , values of carbon residue F1 = 0.0334 mg and F2 = 0.039 mg, flash point F1 and F2 = 42 ° C, and ash point F1 = 0.001 mg and F2 = 0.003 mg are low, which indicates that these product can be used like a fuel, according with the specifications and limits described in the ANP technical regulation nº 4 (ANP, 2013).

Figure 3 shows the IR spectrum of these products, when comparing them with commercial diesel, the evidence of the band between1740 cm-1 e 1720 cm-1 relative to the C=O bond of esters that together with the physical analyzes Chemical properties make it possible to use it as a substitute for blends (diesel and biodiesel).

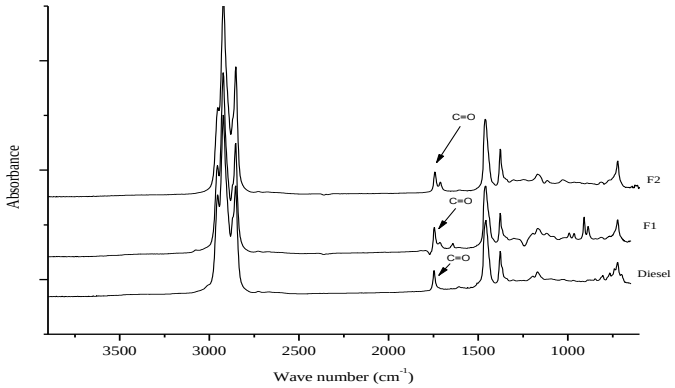
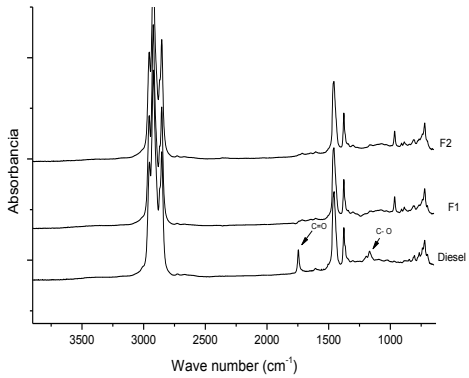


Figura3 IR of esterificated products factories F1, F2 and diesel oil.

The results of an elemental analysis of the fuel products, where F1 Plant 75.84% of Carbon, 12.58% of Hydrogen and 0.96% of Nitrogen. The Factory F2, Carbon 67.66%, 11.83% of Hydrogen and 0.88% of Nitrogen, the high values of these compounds are justified because the reactions with Hydrogen gas they produced reactions of decarboxylation (release CO_2)and decarbonilation (release CO) producing water and alkanes and other reactions and routes was proposal in (Junior,2016) this authors show us, some mechanism proposal for it. The IR of the Fuel obtained of Hydrodeoxygenation e hydrogenation reaction are presented in Figure 4, compare the spectra of F1 and F2 with that of diesel oil appear in diesel oil spectra bands corresponding to C=O between 1740 cm^{-1}and 1720cm^{-1}and bands between 1150 cm^{-1} e 1100 cm^{-1}corresponding to C – O bonds that characterize esters. The IR spectra show the same compounds. In addition, the spectra present similar compositions of the two fuels (F1 and F2) confirming that the proposal can be applied to any industry that operates in the same segment. Further expanding the alternatives for a possible industrial scale application of these proposed routes. The Chromatogram presented in Figure 5, suggested except the pick of the ester in diesel chromatogram oil spectra, the others picks, clearly show a similarity in their composition The chromatograms of fuel produced are identified, and the principal functional groups Hydrocarbons (alkanes) the compounds suggested are: **1**-Heptane, **2**-Methyl heptane, **3**-Octane, **4**-Nonane, **5**-Decane, **6**-Undecane, **7**-Dodecane, **8**-Tridecane, **9**-Tetradecane, **10**-Pentadecane, **11** - Hexadecane, **12** - Heptadecane**13** –Octadecane.



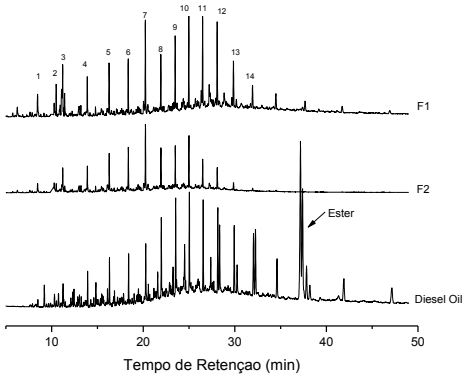


Figura4 IR Esterified products (F1 and F2) and Diesel Oil Figura5 – Chromatogram of Fuel (F1 and F2) and Diesel oil

Biocidal activity - The samples were tested 100% pure, in the amount of 100 microliters in each well. The values are determined by the mean values of the inhibition halos in millimeters found in the triplicates. The analyzed substances presented an efficient Biocidal action, to be active in the test of diffusion in agar the inhibition halo must be greater than 10mm, only the hydrogen presented the lowest results of inhibition halo, but we can perceive that of a general outside, the hydrogenated ones have a lower Biocidal activity than the other substances. The best results were with the cracked ones independently of the origin and the worst ones with hydrogenated ones. Another analysis is that the substances appear to be better for fungi than for bacteria (Ramalho et. Al 2016).

Sample	**Fungi**		**Bacterial**	
	Fusarium solani	*Aspergillus niger*	*Acinetobacter sp.*	*Bacillus subtilis*
Waste F2	33,20 mm	50,00 mm	55,00 mm	30,50 mm
Fuel F2	22,00 mm	30,00 mm	23,50 mm	20,00 mm
Esterificated F2	22,33 mm	24,20 mm	12,20 mm	12,50 mm
Cracking F2	38,00 mm	35,50 mm	50,50 mm	56,00 mm
Fuel F1	20,50 mm	25,00 mm	13,33 mm	10,00 mm
EsterificatedF1	24,00 mm	28,50 mm	12,60 mm	14,33 mm
Cracking F1	36,00 mm	33,33 mm	55,00 mm	56,50 mm
Waste F1	39,00 mm	32,50 mm	60,00 mm	58,00 mm
Diesel oil	-	-	-	-

Grease Lubricating - The greases are basically composed of a dispersing agent, usually metallic soap and mineral, vegetable or synthetic long chain of oil. They are classified by some tests, among them the cone penetration, which follows a scale developed by the NLGI (National Lubricating Grease Institute).The less resistant to the impact of the cone, the lower the NLGI grade, the greases are worked on a specific equipment and designed for that purpose whose best description of the procedure will be presented in the methodology. Thus, the methodology of the synthesis of the grease produced with the residue was based on the physical chemical characteristics of the raw waste from the can mills that gave rise to the residue (Carretero, 2006).The greases were characterized in the laboratory of lubricants of the National Agency of Natural Gas and Biofuel (ANP), in Brazilian- Brazil. The cone penetration test to F1 grease 1:1 and 1:1,5 (waste x lithium soap) produced in thents of millimeters, 376 and 281 classified than in NLGI, 0 and 2 respectively, and the drop point to 1:1 and 1: 1,5 in, 175 ° C and 128,5 ° C. The results of F2 factory to cone penetration for 1:1 and 1:1,5 proportions grease 324 and 310 thents of millimeters classified the F2 grease in NLGI number, 1 to both. The drop point is 155 º C to 1:1 and 139 ° C to 1:1,5. The types of greases purchased by these factories have the same classifications by varying the number of NLGI consistency between 0 and 2 for work at temperatures above 130 ° C. It can therefore be used as a sustainable process practice. The greases of 1: 1 lithium metal soap residue presented better application and quality than those in which more soap was used than residual oil.

Conclusions and perspectives

Biocidal fuel and lubricating grease were produced from the oily residue of aluminum can factories. The fuel had similar physical and chemical properties to the fuels currently used in diesel-powered engines, which use blends (diesel-biodiesel) or pure diesel. The use of the residue as fuel presented a significant differential, the Biocidal activity, for inhibiting the growth of common fungi and bacteria in fuels. It is also verified that these products can be obtained from competing industries but that work in the same segment, present variations in the composition but that do not interfere in the final product. By investing in the process of transforming the oily residue, in value-added products, these industrialists invest in a sustainable process and work to reduce costs by failing to acquire inputs such as fuel and lubricating greases. It is an innovative work, with promising results and significant environmental impact.

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