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Biofuels from waste fish oil pyrolysis: Chemical composition

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ABSTRACT

In a previous study, waste fish oil was converted into bio-oil by a fast pyrolysis process at 525 °C in a continuous pilot plant reactor with 72–73% yield. The bio-oil was distilled to obtain light bio-oil and heavy bio-oil and these biofuels were characterized in terms of their physico-chemical properties. In this study, the chemical composition of light bio-oil and heavy bio-oil was determined using GC-FID, GC–MS, ^{1}H and ^{13}C NMR techniques. The GC–MS analysis of waste fish oil showed the main composition of fatty acids to be the following: $C_{16:0}$ (15.87%), $C_{18:2}$ (20.96%), $C_{18:1}$ (17.29%), $C_{20:5}$ (5.11%), $C_{20:1}$ (7.59%), $C_{22:6}$ (4.53%), $C_{22:1}$ (10.42%) and others. The GC-FID analysis of the light bio-oil showed 482 compounds that were PIONA classified as paraffins (4.48%), iso-paraffins (8.31%), olefins (26.56%), naphthenes (6.07%) and aromatics (16.86%). The heavy bio-oil had a similar chromatographic profile as diesel oil, with a high content of carboxylic acids and olefins. These results are in good agreement with those for the gasoline and diesel oil fractions of petroleum.

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1. Introduction

According to the Food and Agriculture Organization (FAO), in 2005 the estimated world fish production was around 142 millions tons. Approximately 75% of this production is used for direct human consumption. The remaining 25% is destined for non-food products, in particular the manufacture of fishmeal and oil. For 2008 the estimated world fish production was 144 millions tons [1,2]. The volume of waste produced by processing plants is calculated to be around 50% of the total processed fish, for which the amount of oil varies from 40% to 65% [3].

The fast pyrolysis of triglycerides has been investigated with a view to biofuel production [4–11]. According to the pyrolysis reaction scheme, presented in Maher and Bressler [12], many different chemical groups can be produced during the pyrolysis reaction. The liquid product (bio-oil) obtained from triglyceride pyrolysis has a very complex composition [13] and requires the use of particular analytical techniques, and a precise determination of the bio-oil composition has not been carried out to date [6,14]. This bio-oil can be used directly as a fuel or can be fractionated to obtain purified hydrocarbons in the range of gasoline and diesel. These biofuels have been compared to fossil fuels and the results show partial agreement with fossil fuel specifications [4,9,10]. The need to improve the quality and the specific regulations of these biofuels has led to an increase in the number of studies related to the determination of their chemical composition [15,16].

Bio-oil has a large variety of compositions as a function of the feedstock [17,18]. It can be produced from biomass based on triglycerides like soybean, palm, castor and canola [5,9,13,19,20], as well as animal fats, lard, poultry fat and fish oil capsules [7,10,21], and the major products are alkanes, alkenes, ketones, aldehyde, aromatics and carboxylic acids.

Bio-oils based on lignin-cellulosic biomass contain phenols, benzenediols, furanes and their derivates as major compounds [16,22–25].

Several methods to determine the relative amounts of hydrocarbons in crude oil refining products can be employed [26]. A standardized method using high resolution gas chromatography (GC) with a 100-m capillary column can be used to determine individual components of spark ignition fuels [27]. The gas chromatography method for classification of gasolines into paraffin, iso-paraffin, olefin, naphthene and aromatic (PIONA) groups is based on the retention index [28–30]. Proton nuclear magnetic resonance (^{1}H NMR) is appropriate for the measurement of the concentrations of aromatic, olefinic and aliphatic fractions of gasoline samples [31]. Paraffin, aromatic and naphthene contents determined by the same spectroscopy method show a very good agreement when compared with the gas chromatography method [32,33].

In a previous study, some physico-chemical properties of waste fish oil (WFO), bio-oil (BO), light bio-oil (LBO) and heavy bio-oil (HBO) were determined and compared to Brazilian fuel specifications. LBO and HBO were also analyzed to determine the yields of

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compounds according to the carbon numbers in the chain by GC [34]. In this study, the chemical compositions of WFO, LBO and HBO were investigated. The biofuels were analyzed by GC-flame ionization detection (FID), mass spectrometry (MS) and proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy.

2. Experimental

2.1. Chemical composition of waste fish oil

The WFO was esterified with methanolic sulfuric acid (90:10, v/v) [35] before being submitted to gas chromatography/mass spectrometry (Varian CP-3800/Saturn 2000) and quantified by gas chromatography/flame ionization detection analysis. The esterified WFO was compared with standard solutions of Fatty Acid Methyl Esters (FAMEs) and homologous n-alkanes obtained commercially from Supelco®. The FAME standards were utilized to identify the unsaturated fatty acids through the similarity of their retention time (RT). The n-alkane standards were applied to determine the retention index (RI) [36] of all fatty acids in the sample, which can be used as a reference. The analysis was performed using a CP-Sil 8 Cb Low Bleed capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium (99.999%) was used as the carrier gas with a constant flow rate of 1 mL min^{-1} for GC–MS and 1.2 mL min^{-1} for GC-FID, and oven temperature of 80 °C (3 min), 5 °C min^{-1} to 250 °C (15 min). Injector temperature for both analyses was 250 °C and FID temperature was 280 °C. The MS was conducted with the following operation conditions: transfer line 240 °C, manifold 80 °C, ion trap 175 °C and electron energy 70 eV.

2.2. Waste fish oil pyrolysis

The bio-oil was obtained in a previous study in a continuous reactor pilot plant at 525 °C with mass flow rate of 3.2 kg h^{-1} and underwent simple distillation to produce light bio-oil and heavy bio-oil. The physico-chemical properties of these biofuels have been previously described in the first part of this study [34].

2.3. ^{1}H and ^{13}C NMR of biofuels

The NMR spectra of BO, LBO and HBO, obtained as described in [34], were recorded at 22 °C using a Bruker AC-300 spectrometer at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). Chemical shifts were referenced in parts per million (ppm) relative to the signal of tetramethyl silane (TMS). The sample was dissolved in deuterated chloroform.

2.4. PIONA analysis of light bio-oil

The GC-FID and GC–MS analysis were conducted in a CP-Sil PONA (100 m × 0.25 mm; film thickness 0.5 μm). Helium (99.999%) was used as the carrier gas with a constant pressure of 50.5 psi for FID and a constant flow of 1.0 mL min^{-1} for MS; oven temperature of 35 °C (15 min), 1 °C min^{-1} to 60 °C (20 min), 2 °C min^{-1} to 200 °C (10 min); injector temperature of 250 °C; FID temperature of 280 °C; and injection volume of 0.3 μL. The GC–MS analysis was conducted with the following operation conditions: transfer line 240 °C, manifold 80 °C, ion trap 175 °C and electron energy 70 eV. The LBO was compared with a Nafta standard solution obtained commercially from Supelco®. The retention indexes of the Nafta standards were determined [36] and the hydrocarbons were identified by retention time similarity.

2.5. Chemical composition of heavy bio-oil

The GC-FID and GC–MS analysis of HBO was performed using a CP-Sil 8 Cb Low Bleed capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium (99.999%) was used as the carrier gas with a constant flow rate of 1.2 mL min^{-1} for FID and 1.0 mL min^{-1} for MS; oven temperature of 100 °C (5 min); 5 °C min^{-1} to 250 °C (20 min); injector temperature of 250 °C; FID temperature of 280 °C; and injection volume of 0.5 μL. The MS was conducted with the following operation conditions: transfer line 240 °C, manifold 80 °C, ion trap 175 °C and electron energy 70 eV.

3. Results and discussion

3.1. The chemical composition of waste fish oil

The analysis of methyl esters of WFO revealed 13 peaks and the chemical composition is shown in Table 1. The unsaturated acids $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ were identified by comparison of their retention times with the FAME standard. Others were identified by comparison of GC–MS spectra with those in the NIST 02 Mass Spectral Database. The major fatty acids found were $C_{16:0}$, $C_{18:1}$, $C_{18:2}$ and $C_{22:1}$, responsible for 64% of the total composition. Eicosapentaenoic acid ($C_{20:5}$) and docosahexaenoic acid ($C_{22:6}$), typical fatty acids of fish oils, were identified and quantified as 5.11% and 4.53%, respectively.

3.2. Light bio-oil fraction of bio-oil

The GC-FID analysis of LBO (Fig. 1) shows 482 peaks with relative concentrations higher than 0.01%.

The identification of compounds by Detailed Hydrocarbon Analysis (DHA) was carried out using the retention index according to ASTM D 6729-01 and was confirmed by GC–MS through a comparison of the MS spectra with those in the NIST 02 Mass Spectral Database. A correction coefficient related to the detector factor response for specific hydrocarbons was multiplied by the GC-FID relative concentration to obtain the theoretical absolute quantification to express their concentration in percent volume/volume (% DHA). Table 2 shows 31 compounds with a GC-FID relative concentration above 0.5%, which represent almost 44% of the total LBO chemical composition. It can be noted that the major compounds identified are aromatics such as benzene, toluene and ethylbenzene and olefins including 1-pentene, 1-hexene, 1-heptene and 1-octene.

The DHA results were classified according to PIONA. Table 3 shows the PIONA classification of light bio-oil in comparison with

Table 1
Chemical composition of waste fish oil.

Peak	RT (min)	RI	Methyl ester of	% Relative GC-FID
1	21.945	1723	$C_{14:0}$	6.02
2	25.659	1903	$C_{16:1}$	4.38
3	26.102	1926	$C_{16:0}$	15.87
4	29.041	2082	$C_{18:4}$ + $C_{18:0\ branched}$	1.49
5	29.278	2095	$C_{18:2}$	20.96
6	29.393	2101	$C_{18:1}$	17.29
7	29.472	2105	$C_{18:1}$	2.43
8	29.830	2126	$C_{18:0}$	3.06
9	32.218	2263	$C_{20:5}$	5.11
10	32.847	2301	$C_{20:1}$	7.59
11	35.247	2448	$C_{22:6}$	4.53
12	35.481	2462	$C_{22:5}$	0.85
13	36.098	2499	$C_{22:1}$	10.42
			Total	100.00

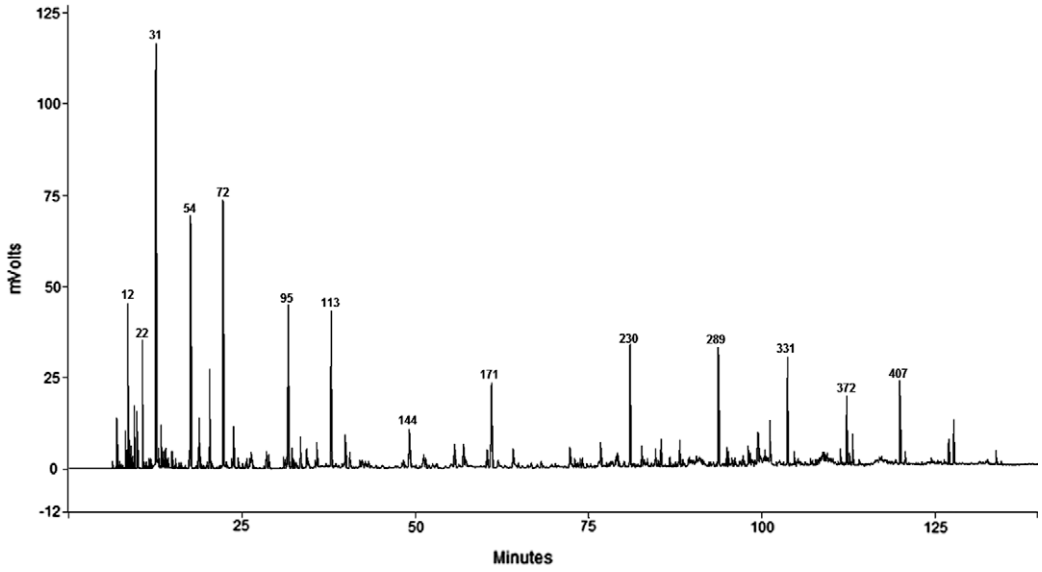

Fig. 1. GC-FID analysis of light bio-oil.

Table 2
Main chemical composition of light bio-oil.

Peak	RT (min)	RI	Compound	% Relative GC-FID	% DHA
12	8.442	483.19	1-Pentene	0.88	1.04
22	10.601	541.23	Cyclopentene	0.91	0.88
31	12.517	583.56	1-Hexene	3.69	4.16
54	17.534	640.17	Benzene	3.74	1.79
57	18.743	651.82	Olefin C_7	0.65	0.72
64	20.278	666.62	3-Methylcyclopentene	1.36	1.61
72	22.215	685.30	1-Heptene	4.28	4.66
77	23.740	700.00	n-Heptane	0.73	0.83
95	31.619	748.64	toluene	2.95	2.43
101	33.387	759.67	2-Methyl-3-ethylpentane	0.64	0.73
113	37.811	787.29	1-Octene	3.14	3.34
120	39.847	800.00	n-Octane	0.69	0.76
144	49.087	837.35	Ethylbenzene	1.44	1.19
161	55.615	863.75	3-Ethylheptane	0.80	0.85
164	56.914	868.99	o-Xylene	0.75	0.61
170	60.318	883.74	Unclassified C_8	0.58	0.64
171	60.934	886.41	Isobutylcyclopentane	2.83	2.76
178	64.072	900.00	n-Nonane	0.64	0.69
200	72.252	944.12	n-Propylbenzene	0.67	0.57
215	76.680	968.00	1-Methyl-2-ethylbenzene	0.74	0.61
230	80.918	990.86	1-Decene	2.54	2.60
252	85.399	1022.72	Unclassified C_{10}	0.59	0.62
263	88.090	1044.65	n-Butylbenzene	0.51	0.43
289	93.652	1090.00	1-Undecene	2.24	2.28
315	99.380	1146.17	n-Pentylbenzene	1.21	1.03
322	101.105	1163.87	Naphtalene	1.22	0.89
331	103.623	1189.70	1-Dodecene	1.94	1.96
360	109.384	1248.80	n-Hexylbenzene	0.55	0.47
372	112.164	1277.31	1-Tridecene	1.16	0.83
374	113.035	1286.24	2-Methylnaphtalene	0.66	0.68
407	119.841	1356.05	1-Tetradecene	1.50	1.53
			Total	46.22	44.17

petroleum-based fuels (gasolines A and C[1]). The parameters that differed most between light bio-oil and gasoline A were the contents of paraffins, iso-paraffins and naphthenes compounds, which were lower in the former. On the other hand, the light bio-oil shows a higher content of olefins in comparison with gasolines A and C. Olefins are known to provide more desirable octane ratings than n-paraffins, but are more unstable in the presence of oxygen and can contribute to the production of gum deposits during long-term storage. This means that fuels with high levels of olefins require the use of antioxidants. The aromatic compounds, like olefins, have good octane numbers, but tend to be more toxic and some countries have specific regulations for certain compounds, for example, benzene. On the other hand, olefins and aromatics are added to gasolines to replace other more toxic compounds used as octane enhancers, for example, organometallic compounds.

The results for the PIONA classification also show high contents of C_{14+} compounds which can be reduced by optimization of the fractionation process to obtain greater similarity between the bio-

[1] Gasoline A is a petroleum-based fuel and gasoline C is the Brazilian gasoline commercialized with a 20% content of ethanol, as an anti-knocking additive.

Table 3
PIONA classification of light bio-oil.

Classes	% (v/v) Light bio-oil	% (v/v) Gasoline C	% (v/v) Gasoline A
Aromatics	16.86	14.81	18.85
Iso-paraffins	8.31	19.35	23.67
Naphtenes	6.07	16.26	19.89
Olefins	26.56	11.72	13.53
Oxygenates	0.06	17.76	0.16
Paraffin	4.48	13.65	16.55
C_{14+}	5.30	0.00	0.00
Unclassified	32.38	6.44	7.36
Total	100.00	100.00	100.00

fuel fraction and fossil fuels. The 32% of unclassified compounds were distributed across a high number of compounds (~272) and each one contributes with a relatively low concentration. The difficulty in identifying all of these compounds by GC reflects the complex composition of biofuels obtained from bio-oil derivates, and there is also a lack of studies and standards. The use of complementary techniques like NMR, as described below, shows that these compounds can be classified according to the PIONA classification system.

3.3. Heavy bio-oil fraction from bio-oil

The results of the GC-FID analysis of HBO are shown in Fig. 2. The chromatogram of HBO was compared with that of diesel oil (DO) and homologous n-alkane standards. The similarity between the chemical compositions of HBO and DO is clear, basically with n-alkanes C_{10}–C_{26} in the composition. The major peaks for HBO show a small difference in the retention times in relation to those of n-alkane standards. The peaks on the MS spectra were identified as being homologous terminal olefin compounds with a number of carbons lower than C_{22}.

The main biofuels obtained from the biomass pyrolysis, as with the heavy bio-oil, had a high acid index as previously reported [34]. In the chromatogram "a" of Fig. 2, the presence of three peaks (225, 257 and 275) can be noted close to the retention time of n-alkanes C_{18}, C_{20} and C_{22} as asymmetric chromatographic bands. The HBO was submitted to the methanolic sulfuric acid procedure to esterify

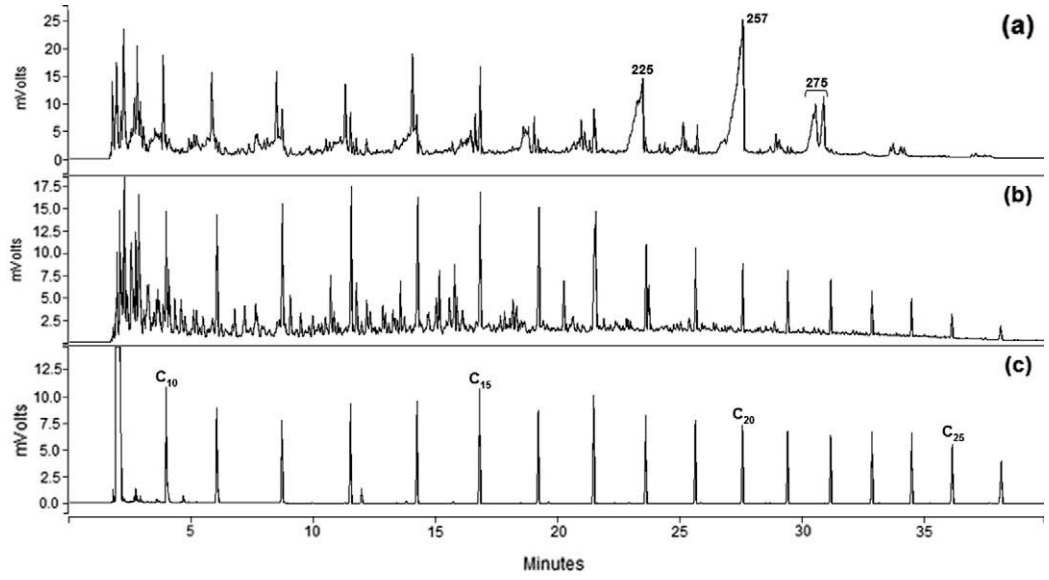

Fig. 2. GC-FID chromatogram of HBO (a) DO (b) and n-alkanes standards (c).

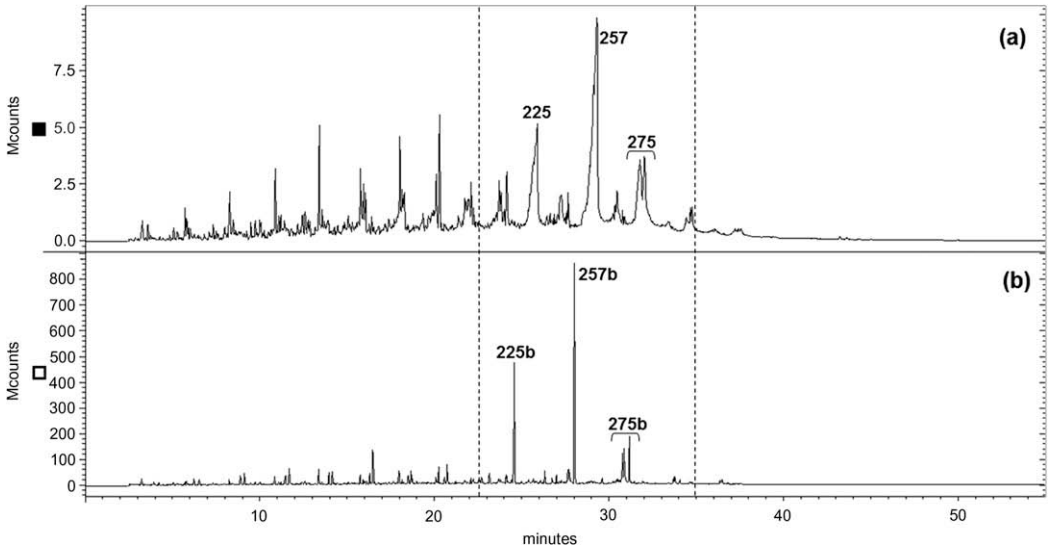

Fig. 3. Total ion chromatogram of HBO (a) and esterified HBO (b).

the possible fatty acid residues. Fig. 3 shows the total ion chromatogram of HBO and an esterified sample of HBO.

The total ion chromatogram of the esterified sample of HBO indicates the disappearance of the previously described asymmetric peaks and the appearance of peaks at 225b, 257b and 275b, as shown in the Fig. 3b. These compounds were identified by MS and the relative concentrations were determined by FID (Fig. 2a) and represent 36.8% of the chemical composition of HBO (Table 4). Aromatics, olefins and carboxylic acid residues were the main compounds found in the HBO biofuel.

Table 4
Main chemical composition of heavy bio-oil (Fig. 2a).

Peak	RT GC-FID (min)	% Relative GC-FID	Compounds identified by GC–MS
6	1.941	1.32	Alkenes + benzene derivatives
10	2.216	1.75	
18	2.768	1.02	
31	3.833	1.33	Decene
50	5.827	1.80	Undecene
73	8.479	1.36	Dodecene + naphtalene
101	11.288	1.34	Tridecene
129	14.037	1.52	Tetradecene
161	16.811	1.09	Pentadecene
225	23.147	6.46	Tetradecanoic acid ($C_{14:0}$)
249	25.119	0.93	Pentadecanoic acid ($C_{15:0}$)
257	27.239	11.88	Hexadecanoic acid ($C_{16:0}$)
275	30.416	3.13	Octadecenoic acid ($C_{18:1}$)
276	30.830	1.87	Octadecanoic acid ($C_{18:0}$)
	Total	36.80	

The main characteristics of biofuels such as HBO, a diesel-like fuel, are their high content of olefins and a high temperature value for the cold filter plugging point (+14 °C), as discussed in a previous paper. The presence of carboxylic acid residues is the result of the unreacted carboxylic acids from the feedstock. The acidity of biofuels can reflect in an increased corrosion rating. The advantage is that the origin of this acidity is from weak organic acids, in contrast to fossil fuels where the acidity is from sulfur compounds. Changes in the residence time, the use of a specific catalysts and a post esterification reaction of these biofuels are currently under study, aiming to adapt these biofuels to comply with national regulations.

3.4. ^{1}H and ^{13}C NMR of bio-oil, light bio-oil and heavy bio-oil

The ^{1}H NMR spectrum of the bio-oil is shown in Fig. 4a. As expected, the light bio-oil and heavy bio-oil proton spectra show the same signals with different mol% hydrogen distribution, as listed in

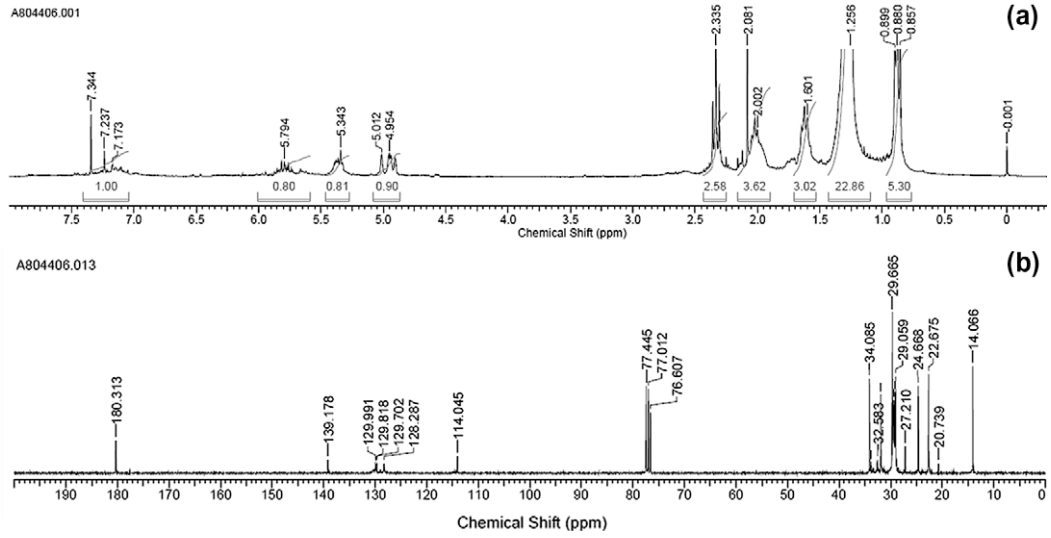

Fig. 4. ^{1}H NMR (a) and ^{13}C NMR (b) spectral regions for bio-oil.

Table 5
Assignment of ^{1}H NMR spectral regions to triglyceride pyrolysis biofuels.

Hydrogen type	^{1}H Chemical shift (ppm)	Mol% (% of total Hydrogen)		
		Bio-oil	Light bio-oil	Heavy bio-oil
Aromatics	7.0–9.0	2.44	5.11	2.37
Olefins (–HC=CH–)	5.0–6.5	6.14	10.53	4.32
CH_2, adjacent to –CH=CH CH_3, adjacent to -Ph CH_3, CH_2 e CH, adjacent to –(C=O)OR; –(C=O)OH; –(C=O)H	2.0–2.5	6.31	19.84	15.15
CH, adjacent to $–CH_2–CH=CH$ CH, adjacent to $–CH_2–CH_2$ CH_3, adjacent to –CH=CH	1.5–2.0	16.23	10.44	9.47
CH_2 e CH, adjacent to $–CH_2R$ CH_2, adjacent to $–CH_2–CH_2$ CH_2, adjacent to $–CH_2–CH=CH$	1.0–1.5	55.91	37.63	54.59
CH_3, adjacent to $–CH_2–R$ CH_3, adjacent to $–CH_2–CH_2$ CH_3, adjacent to $–CH_2–CH=CH$	0.5–1.0	12.96	16.44	14.08
Aliphatics (total)	0.5–3.0	91.41	84.35	93.29

Table 5. The simple spectrum can be divided into three distinct bands: aromatics, olefins and aliphatic hydrogens.

Resonances between 7 and 9 ppm were assigned to aromatic structures, and between 5 and 6.5 ppm they were attributed to non-conjugated olefins (centered at 5.3 ppm). The region between 0.5 and 2.5 ppm is strongly overlapped and contains signals mainly due to cycloalkanes (naphthenes), and normal- and iso-paraffins. The total aliphatic hydrogen intensity (0.5–2.5 ppm) is predominant in both biofuels.

The ^{1}H NMR integration results show that the contents of aromatic and olefin compounds in LBO are twice those in HBO. It is possible to consider that in the pyrolysis of triglycerides, the formation of unsaturated compounds occurs with small chains and lower boiling points (BP < 220 °C).

The BO, LBO and HBO were also analyzed by ^{13}C NMR (Fig. 4b). The biofuels show the same signals on the ^{13}C NMR spectra. The signal with a chemical shift of 180 ppm confirmed the information obtained from the GC–MS analysis regarding the presence of carboxylic acids in these biofuels with more relative intensity in the HBO sample. The identification of carbons with a chemical shift of 114 ppm as terminal-CH_2 and 139 ppm as vinyl confirms the presence of alkenes with terminal unsaturation. Carbons with a chemical shift between 30 and 40 ppm were assigned to naphthenes. Aromatics (127–130 ppm), and methyl and methylene carbons (10–30 ppm) were also identified.

4. Conclusions

The full determination of the chemical composition of waste fish oil as described herein shows the carboxylic acids characteristic of fish oil, that is, eicosapentaenoic and docosahexaenoic acids. The carboxylic acids $C_{16:0}$, $C_{18:1}$, $C_{18:2}$ and $C_{22:1}$ are the main compounds found in the feedstock.

The pyrolysis at 525 °C of waste fish oil as an animal source of triglycerides shows that it is possible to obtain biofuels like light bio-oil and heavy bio-oil with a good similarity to petroleum-based fuels. The PIONA analysis identified olefin and aromatic compounds as the main components of light bio-oil. The MS technique was very important to confirm the chemical structure of the PIONA compounds classified. Heavy bio-oil contains basically 1-olefins and carboxylic acid residues of the pyrolysis process. The H^1 NMR showed a high content of aliphatic hydrocarbons in all biofuels investigated in this study. The ^{13}C NMR analysis confirmed the presence of carbon in the biofuel composition as aliphatics, olefins and aromatics.

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