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Article

Upgrade of Biofuels Obtained from Waste Fish Oil Pyrolysis by Reactive Distillation

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Bio-oil is classified as second-generation biofuel and it is produced mainly through the pyrolysis of a waste lignocellulosic biomass base. The application of this product is still very limited, due to some of its chemical characteristics. This paper presents a proposal for the reduction of the acidity of bio-oil obtained from waste fish oil, previously produced and characterized as described in the literature, applying the reactive distillation process. This process is primarily based on the conversion of carboxylic acids into their corresponding esters by adding a widely available alcohol and a simple and cheap catalyst in the process for the fractional distillation of crude bio-oil to obtain light and heavy bio-oil, that is, fractions which are equivalent to the fossil fuels gasoline and diesel, respectively. The alcohols tested were methanol and ethanol and the catalysts were H_2SO_4, H_3PO_4, NaOH and Na_2CO_3, in proportions of 10 and 0.5 wt.%, respectively. The light bio-oil was obtained within a temperature range of 42 to 198 ºC with yields of 27.0 to 43.1% and the heavy bio-oil was recovered at 93 to 230 ºC with yields of 42.6 to 49.2%. The greatest acidity reduction was observed employing methanol+H_2SO_4 (95% and 43% for light and heavy bio-oils, respectively). The fractions produced were characterized by gas cromatography/mass spectrometry (GC-MS) and gas chromatography with flame ionization detector (GC-FID), applying the compound classification process PIONA (Paraffins, Iso-paraffins, Olefins, Naphtenes and Aromatics), revealing a homologous series of 1-alkenes and *n*-alkanes along with some aromatic compounds. The ^{1}H and ^{13}C NMR analysis showed that the process had no significant influence in relation to the carbons and hydrogens associated with the methyl, methylene, methyne and olefinic groups.

Keywords: bio-oil, waste fish oil, pyrolysis, biofuels, reactive distillation, acidity index, bio-oil upgrade

Introduction

Biofuels represent a concrete and promising solution for reducing the dependence on fossil fuels and the greenhouse gas emissions. Most of the production technologies are in the early stages of development and improvements are still required. Advanced biofuels are expected to become cost-competitive with conventional fossil fuels around 2030 and experts have indicated a possible ceiling in relation to the diffusion of vehicles running on biofuels in the private market being reached by 2050.[1] Based on the raw materials and technology used for their production, biofuels are classified as follows: (*i*) first generation, where the biomass is processed and produced in the form of solids (e.g. charcoal), liquids (e.g. ethanol, biodiesel and bio-oil) or gases (e.g. biogas); (*ii*) second generation, produced following two fundamentally different approaches, that is, biological or thermochemical processing, from agricultural lignocellulosic biomass; and (*iii*) third generation, specifically derived from microbes and microalgae. Second generation biofuels are characterized by the pyrolysis of waste material, leading to a lower cost being associated with the raw materials and limiting the competition between fuel and food.[2] According to the Food and Agriculture Organization, world production of fish in 2011 was 154 million tonnes, almost 131 million tonnes being directed toward human consumption. Around 50% of processed fish becomes waste material, in which the amount of oil ranges from 40 to 65%.[3]

Biomass in the form of vegetable oils, greases and animal fats (including waste fish oil) is based on triacylglycerols (TAGs). The main components of

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bio-oils obtained from the TAG pyrolysis process are alkanes, as in the case of petroleum-based diesel fuels, alkenes, alkadienes, aromatics and carboxylic acids.[4] This characteristic chemical composition is commonly found in bio-oils obtained from TAG pyrolysis and the proposed mechanism for the formation of these chemical constituents was discussed in 1947.[5] Bio-oils are viscous liquid biofuels with low pH, containing more than 300 compounds some of which are unstable and degrade over time and this hinders their use directly as diesel fuel or in diesel blends.[6] Some requirements for the use of bio-oil for industrial equipment like burners not intended for use in residential heating, small commercial boilers, and motor or marine applications, are detailed in ASTM D7544 - 2009.[7] Prior to their use as a substitute for fuels and chemicals derived from petroleum, bio-oils require considerable improvements in their features.[8] More recently, the international standard ASTM D7566 - 2014a and Resolution No. 20/2013 of the Brazilian National Agency of Petroleum, Natural Gas and Biofuel (ANP) have defined the specifications for synthesized paraffinic kerosene (SPK) produced from hydroprocessed esters and fatty acids (HEFA) for use as a synthetic blending component in aviation turbine fuels for civil aircraft and engines.[9,10] This results in a very promising perspective for the use and application of new biofuels for transport purposes.[11]

Techniques to improve the quality of the bio-oil should involve modifying the chemical composition and some properties, such as the viscosity, pH and thermal stability.[12] In this regard, the technologies available include catalytic cracking,[13,14] emulsification,[8] hydrodeoxygenation,[15] catalytic esterification,[16-20] molecular distillation,[21] catalytic hydrothermolysis[22] and reactive distillation.[8,23] All of these processes have advantages and disadvantages as upgrading techniques for bio-oil.[24] Reactive distillation is a separation process where fractional distillation is accompanied by chemical reactions in some or all stages of the distillation column. These reactions are triggered by the introduction of a reactive solvent which will react selectively with one of the components of the mixture inside the column. The products formed are removed from the column with relative ease.[25]

In previous studies,[26,27] some physico-chemical properties of the waste fish oil, crude bio-oil, light bio-oil and heavy bio-oil were determined and on evaluating the results the acidity index was found to be high considering the Brazilian fuel specifications.[26] Therefore, in this study, the reactive distillation of crude bio-oils obtained from the thermal cracking of waste fish oil was investigated as a method to upgrade these biofuels. The physico-chemical characteristics of upgraded biofuels were evaluated.

Material and Methods

Crude bio-oil

The raw material for this study was obtained from the thermal cracking of waste fish oil in a continuous pilot plant at 525 °C with a mass flow of up to 3.2 kg h^{-1} and characterized in terms of its physico-chemical properties.[27]

Upgrading of the bio-oil

A glass fractional distillation apparatus equipped with 14/20 joints, a round bottom flask (125 mL), a fraction distillation column (10 × 190 mm), a thermometer adapter, condenser and a heating mantle were used. A mass of 25 g of crude bio-oil (CBO) was added to the round bottom flask with 2.5 g of alcohol, methanol or ethanol (MeOH or EtOH) and 0.125 g of catalyst (H_2SO_4, H_3PO_4, NaOH or Na_2CO_3). The reactive distillation was started and the temperature of the vapor phase was measured at the top of fraction distillation column. The light bio-oil was removed with the condenser operating at 8 °C and at atmospheric pressure. The heat was turned off when the temperature of the vapor reached 200 °C and the fractionation distillation column was removed changing the system to a simple distillation apparatus. The distillate flask was replaced and the heat turned on again with the condenser now operating at ambient temperature. The heavy bio-oil (HBO) was then removed at a temperature of below 230 °C. The reagents used were of analytical grade. The experiments (Exp) carried out to obtain the light bio-oil (LBO) and HBO are shown in Table 1.

Table 1. Experimental planning for reactive distillation

Experiment	Alcohol → / Catalyst ↓	MeOH		EtOH	
		code	code	code	code
1 and 5	H_2SO_4	LBO1	HBO1	LBO5	HBO5
2 and 6	H_3PO_4	LBO2	HBO2	LBO6	HBO6
3 and 7	NaOH	LBO3	HBO3	LBO7	HBO7
4 and 8	Na_2CO_3	LBO4	HBO4	LBO8	HBO8
9 and 10	–	LBO9	HBO9	LBO10	HBO10
11[a]	–	–	–	–	–

[a]Experiment 11 (CBO without alcohol and catalyst) to produce LBO11+HBO11.

Physico-chemical characterization

The physical and chemical properties of the light and heavy bio-oils were determined using ASTM standard methods, including density (ASTM D 4052), acidity and iodine values (ASTM D 974 and *pr* EN 14111) and sulfur residue (ASTM D 4294).

^{1}H and ^{13}C NMR analysis of biofuels

The NMR spectra for the upgraded light and heavy bio-oil samples were recorded at 22 ºC 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 concentration of the samples was ca. 5 wt.%.

Gas chromatography conditions

The PIONA (Paraffins, Iso-paraffins, Olefins, Naphtenes and Aromatics) classification of the compounds of the light bio-oil into chemical classes and gas cromatography/mass spectrometry (GC-MS) analysis of the heavy bio-oil were carried out as described previously.[26] The gas chromatography with flame ionization detector (GC-FID) analysis of the heavy bio-oil was carried out on a Shimadzu GC-2010 chromatograph, equipped with a Rtx-1 (100% dimethyl polysiloxane, 30 m × 0.32 mm; film thickness 3 μm), using helium (99.999%) as the carrier gas with a constant flow of 1.2 mL min^{-1}, oven temperature of 150 °C (1 min) ramping at 5 °C min^{-1} to 280 °C (23 min), injector temperature of 250 °C, FID temperature of 280 °C and injection volume of 1.0 μL. The aqueous phase, produced only in the case of some upgraded light bio-oil samples, was analyzed for carboxylic acid determination in a Shimadzu GC-14B chromatograph with a Stabilwax column (100% polyethylene glycol, 30 m × 0.25 mm; film thickness 0.25 μm), using nitrogen (99.996%) as the carrier gas with a constant pressure of 100 kPa, oven temperature of 80 °C (3 min) ramping at 8 °C min^{-1} to 150 °C (5 min), injector temperature of 150 °C, FID temperature of 300 °C and injection volume of 0.3 μL.

Results and Discussion

Reactive distillation

The reactive distillation of crude bio-oil (CBO) produced upgraded light bio-oil (LBO) and heavy bio-oil (HBO). After leaving the LBO to stand, an aqueous phase separated out spontaneously. The distillation ranges and the mass balances are given in Table 2. The yields were determined considering the mass of alcohol and catalyst and the difference in global yields was attributed to a crude oil waste present in the final stage of the distillation process.

The LBO was obtained as a light yellow to green liquid and the HBO as a dark brown fraction within the boiling ranges of gasoline and diesel, respectively. The main influence of the proposed reactive distillation processes observed was slight changes in the initial boiling point of the HBO fractions, and this could not be attributed to a specific type of catalyst or alcohol used. The global yields were around 89%; however, in the experiments with methanol catalyzed by sulfuric acid and phosphoric acid an aqueous phase was observed. Considering that in the reactive distillation the esterified carboxylic acid produces water as a sub-product, in Table 2 Exp1 and Exp2 show the highest water content values, which leads us to conclude that a greater amount of acids was converted into esters, decreasing the acidity of the final product. All of the aqueous phases were analyzed by GC-FID employing a polar column (Stabilwax) to investigate mainly the presence of residual unesterified carboxylic acids. The aqueous phase of the fraction obtained in the absence of alcohol and catalyst, LBO11, contained 59.5% (v/v) of acetic acid. The aqueous phase of the LBO fractions obtained from the reactive distillation process contained 3.4-7.8% (v/v) of

Table 2. Boiling point range and mass balance for reactive distillation

Exp.	LBO temp. range / °C	HBO temp. range / °C	LBO yield / wt.%	HBO yield / wt.%	Aqueous phase yield / wt.%	Global yield / wt.%
1	44-185	110-230	30.9	47.1	11.2	89.2
2	43-175	130-225	27.1	47.2	13.8	88.0
3	42-175	93-175	41.0	42.6	4.0	87.7
4	44 -187	105-173	39.0	45.0	4.3	88.3
5	43-184	95-217	37.4	46.4	5.5	89.9
6	47-180	110-160	40.4	42.6	1.0	89.4
7	47-198	80-157	41.8	44.6	1.0	84.0
8	44-187	75-172	43.1	46.4	0.5	87.5
9	45-180	100-226	37.9	49.2	3.9	90.9
10	46-193	95-185	42.9	48.5	0.0	91.4
11	42-185	130-215	35.2	46.2	0.5	81.9

acetic acid, showing the efficiency of the acidity reduction achieved with the esterification process. The fingerprint chromatograms of the aqueous phases also revealed the presence of many other compounds which cannot be identified by GC-FID due to the limitations of carboxylic acid standards. Considering the initial mass of waste fish oil and the conversion efficiency for the production of the crude bio-oil (CBO),[27] the yields for the upgraded biofuels were converted and reported based on the initial waste fish oil mass, to determine the yield expected from the raw material source. The results were 27.8% of LBO and 33.5% of HBO, which are close to the results obtained for the samples produced without treatment with an alcohol and a catalyst (Exp11), where the yields were 25.6% of LBO and 33.6 % of HBO.

Light bio-oil

The light bio-oils were characterized according to their physico-chemical properties (acidity index, iodine value, sulfur content and density) and the results are shown in Table 3.

The values for the acidity index shown in Table 3 were determined for all samples immediately after the reactive distillation, before the spontaneous separation of the aqueous phase, when the LBO presented a single homogeneous phase. The acidity of this fraction is attributed to the presence of carboxylic acids formed during the TGA pyrolysis. It is clear that the process with methanol and sulfuric acid (Exp1) provided the greatest reduction in acidity (around 94.3%) followed by Exp2 with the same alcohol and phosphoric acid as the catalyst (56.4% acidity decrease). It was observed that the acidity of the LBO samples decreased with better aqueous phase separation, for example, in the case of LBO5 it changed from 50.6 to 11.5 mg KOH g^{-1}, which can be explained by the strong affinity of polar carboxylic acids for the aqueous phase. The main problem found in relation to the product with the greatest acidity decrease was the increase in the sulfur content of the final product, which is attributed to the catalyst (H_2SO_4). All of the LBO samples obtained from the acid catalysis process were washed with a 0.1 mol L^{-1} solution of Na_2CO_3 in the proportion of 3:5 (LBO:Na_2CO_3) to remove the residual catalyst and the final acidity values were 0.8, 28.7, 1.7, and 52.0 mg KOH g^{-1}, respectively, for LBO1, LBO2, LBO5, and LBO6. As previously mentioned, the main objective of this study was to apply the distillation process employed to refine the crude product, in the form of a reactive process, to convert the residual carboxylic acids present in the crude bio-oil into their respective esters and decrease the acidity of the final products. In these experiments it was clear that the purpose was reached employing methanol as the reactant, for all catalysts (acid or basic, weak or strong). However, our proposed use of ethanol as the reactant, which is a less toxic alcohol and more abundant in Brazil, showed a significant reduction when sulfuric acid was used as the catalyst. The final sulfur contents are reported in Table 3. The density showed a slight improvement with a decrease in the values when compared to those for the fraction LBO11 obtained without any treatment. The iodine value did not show any significant difference after the processes, indicating that the unsaturated compounds were not modified.

PIONA (Paraffins, Iso-paraffins, Olefins, Naphtenes and Aromatics)

All LBO fractions were submitted to Detailed Hydrocarbon Analysis (DHA), where the constituents of light biofuels are grouped into their respective chemical classes and, using the detector response factor, the

Table 3. Physico-chemical properties of LBO

Fraction	Acidity index / (mg KOH g^{-1})	Iodine value / (cg I_2 g^{-1})	Density / (kg m^{-3})	Sulfur content / wt.%
LBO1	7.6	127.3	843.8	0.05
LBO2	57.8	143.0	842.5	0.01
LBO3	85.9	140.6	844.7	–
LBO4	88.3	142.8	848.7	–
LBO5	50.6	128.0	835.5	0.05
LBO6	114.6	117.4	842.0	0.01
LBO7	140.2	125.7	842.2	–
LBO8	137.8	120.8	844.4	–
LBO9	130.4	138.5	844.4	–
LBO10	136.5	144.3	842.2	–
LBO11	172.7	121.1	857.0	0.01
CBO	132.5	83.7	896.5	0.01

relative peak area on the chromatogram is converted into a theoretical v/v percentage, as shown in Table 4.[26,28,29] The predominance of aromatics and olefins is characteristic of products obtained from the thermal cracking of triglycerides and the contents present in the LBO fractions are equivalent to those in Brazilian gasoline (petroleum-based fuel). The presence of oxygenates was more evident in the LBOs obtained from poor reactive processes, as a residue of the alcohols used in the reactive distillation, and the other chemical classes of the upgraded LBO samples did not differ notably from those observed for the LBO11 obtained with no reactive process.

LBO1 showed the best physico-chemical aspects and contained more than 450 compounds, with 44 major compounds representing 50% of the total composition of this sample. The main compounds are listed in Table 5.

Table 4. Hydrocarbon classification (%) for LBO fractions (DHA)

Sample	Paraffin	Iso-paraffin	Olefin	Naphthene	Aromatic	C_{14+}	Oxygenate	Unclassified
LBO1	3.55	4.60	17.02	4.57	19.25	11.07	1.88	38.05
LBO2	3.76	5.50	18.61	4.69	15.56	8.20	6.17	37.50
LBO3	3.57	5.46	17.52	4.31	15.73	7.59	14.19	31.66
LBO4	3.47	5.85	17.04	4.66	14.80	6.64	17.09	30.46
LBO5	5.92	5.57	17.77	5.06	14.45	9.28	8.04	33.90
LBO6	3.45	4.96	18.22	4.56	14.35	6.57	17.62	30.27
LBO7	3.14	6.16	16.01	4.29	14.68	9.22	17.16	29.34
LBO8	3.47	5.99	16.70	4.50	14.48	7.23	18.15	29.48
LBO9	3.41	5.67	16.21	4.01	14.28	7.76	19.21	30.45
LBO10	3.28	6.13	16.80	4.42	13.15	7.47	17.44	31.31
LBO11	3.80	6.70	18.70	5.44	16.33	10.21	1.02	37.78
GA[a]	14.83	21.98	16.78	17.34	18.25	0.00	0.88	9.93

[a]GA: gasoline (petroleum-based fuel).

Table 5. Chemical composition LBO1 (main compounds)

Peak	RT / min	RI[a]	Compound	DHA%[b]
1	6.675	390.84	Methanol	1.60
13	9.142	510.17	*cis*-2-pentene	0.67
24	12.409	583.41	1-hexene	1.45
40	17.334	640.17	Benzene	0.92
57	21.935	685.12	1-heptene	2.31
80	31.239	748.64	Toluene	1.29
95	37.384	788.74	1-octene	2.00
96	37.942	791.83	*trans*-1,2-dimethylcyclohexane	0.50
100	39.414	800.00	*n*-octane	0.52
121	48.480	837.38	Ethylbenzene	0.82
133	54.859	863.74	3-ethylheptane	0.70
135	56.127	868.99	o-xylene + 1,1,2-trimethylcyclohexane	0.49
140	60.092	885.30	1-nonene	2.38
146	63.340	900.00	*n*-nonane	0.59
150	65.247	910.14	Isopropylbenzene	0.60
161	71.668	944.30	*n*-propylbenzene	0.49
192	80.442	990.94	1-decene	2.33
204	83.090	1007.67	1-methyl-3-isopropylbenzene	1.31
251	93.225	1090.04	1-undecene	2.45
260	95.132	1106.99	1,2,3,5-tetramethylbenzene	1.33
280	98.956	1146.17	*n*-pentylbenzene	0.85
288	100.657	1163.61	Naphthalene	0.89
301	103.207	1189.73	1-dodecene	2.14
346	111.748	1277.25	2-methylnaphthalene	1.23
389	119.415	1355.80	*n*-hepthylbenzene	1.78
			Total	31.64

[a]RI: Retention Index and [b]DHA% is a theoretical absolute quantification to express the concentration in percent v/v.

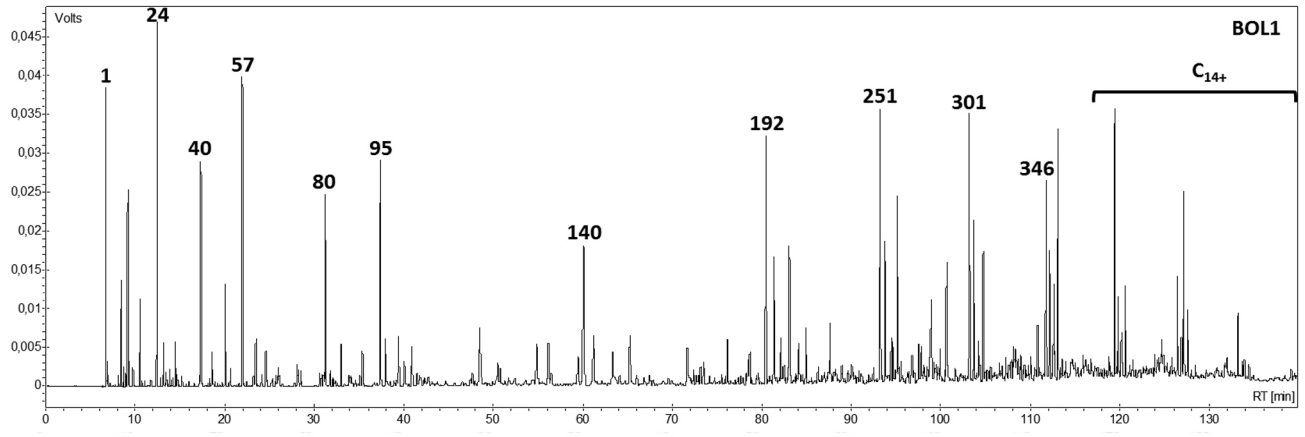

Figure 1. Detailed hydrocarbon analysis of LBO1.

Figure 1 shows the chromatogram for LBO1 with the numbered identification of the main compounds, such as aromatics and olefins, revealing the presence of 1-alkanes as well as monoaromatics and naphthalene derivatives (as shown in Table 5). Aromatics and olefins are known for their high octane numbers (anti-knocking properties) and these results verify the possibility of applying the LBO fraction directly as a biofuel or blended with gasoline fuel and/or other biofuel derivatives.[30]

It can be noted from the C_{14+} content and the high concentration of compounds above peak 192 that this fraction needs to be improved, perhaps with the use of a more efficient fractional distillation column for possible use as a gasoline additive.

Heavy bio-oil

The physico-chemical properties of the upgraded HBOs are shown in Table 6. It is clear that there were no significant changes in the parameters investigated, with the exception of the acidity. The best result was obtained for a sample too rich for the methanol/sulfuric acid process, with an acidity decrease of 42.5%. The value of 86.9 mg KOH g^{-1} differed considerably from the legally stipulated values (for example, 0.5 mg KOH g^{-1}) for the acidity of Brazilian biodiesel blended with diesel (5%). This high acidity value was attributed to residual fatty acids ($C_{14:0}$ and $C_{16:0}$) present in the HBO fractions.

A further test was performed applying 0.5 g of an ion exchange resin (mixed cationic/anionic) to 2, 4, 8, 12 and 16 mL of HBO11 at 23 °C for 30 min. This procedure was previously tested for biodiesel purification and no effect on the acidity was noted.[31] However, for HBO11, reductions in the acidity of 4% for a ratio of 0.5 g:16 mL and 8% for 0.5 g:4 mL were observed.

Table 6. Physico-chemical properties of HBO samples

Sample	Acidity index / (mg KOH g^{-1})	Iodine value / (cg I_2 g^{-1})	Density / (kg m^{-3})	Sulfur content / wt.%
HBO1	86.9	75.6	881.9	0.02
HBO2	108.1	76.8	873.7	–
HBO3	109.4	81.4	862.7	–
HBO4	122.6	83.8	869.3	–
HBO5	123.6	81.6	863.0	–
HBO6	94.8	79.4	865.2	–
HBO7	116.3	77.0	861.7	–
HBO8	122.9	82.8	867.9	–
HBO9	134.8	75.0	882.1	–
HBO10	135.9	75.9	876.2	–
HBO11	151.1	67.0	872.1	0.01
CBO	132.5	83.7	896.5	0.01

HBO chemical composition

The GC-FID analysis of the HBO fractions revealed that the major compounds were a homologous series of 1-alkene and *n*-alkanes. Figure 2 shows the chromatograms for HBO1 and diesel. The HBO1 sample obtained by fractional reactive distillation showed a lower amount of fatty acid residues, in contrast to previously reported results obtained applying a simple distillation process.[26] This optimization of the distillation process, together with the reactive process, contributed to decreasing the acidity of the heavy bio-oils.

The distribution of the HBO fractions according to the relative area on the GC-FID spectra into hydrocarbon ranges shows a high content (around 22%) of *n*-C_4 to *n*-C_{10} for all fractions. This is a high level when compared with diesel (ca. 8%). All other homologous hydrocarbon ranges

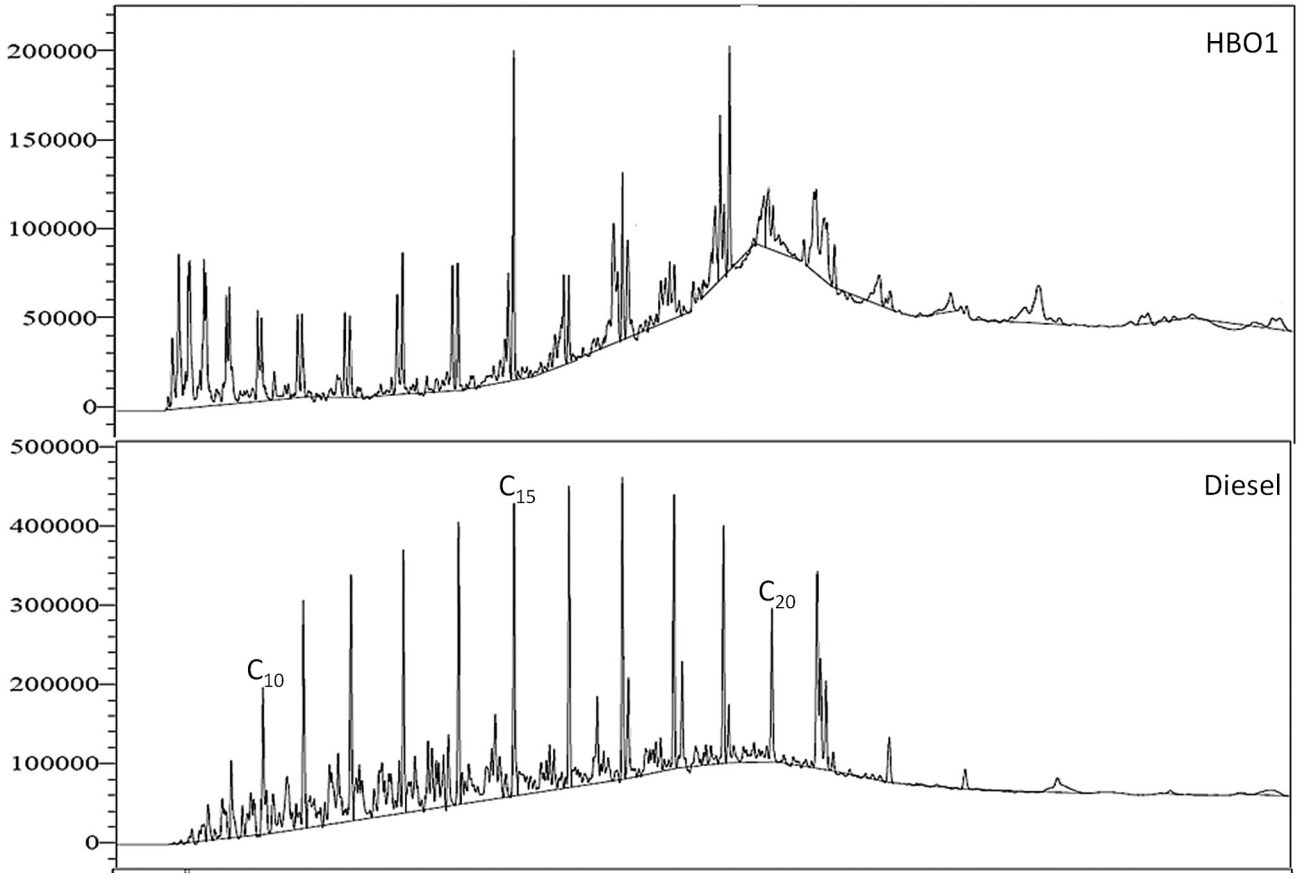

Figure 2. Detailed hydrocarbon analysis of HBO1 and diesel.

above *n*-C_{10} presented contents of around 5%, with the exception of *n*-C_{15} due to the presence of average levels of 10% in the HBO fractions. The baseline drift near *n*-C_{20} observed on the chromatogram for the HBO1 fraction (Figure 2) and for all other HBO fractions was investigated with a hard methanolic/sulfuric acid esterification process and the fatty acid residue was identified as tetradecanoic and hexadecanoic acids.

^{1}H and ^{13}C NMR analysis of upgraded and non-upgraded light bio-oil and heavy bio-oil

The ^{1}H NMR spectra for all samples of light and heavy bio-oils showed spectral similarities, except in the case of the mol% hydrogen distribution. The data for the unreacted and upgraded fractions are given in Table 7. It is clear from the results that for the light fraction of the bio-oil the reactive distillation decreased the presence of olefins and increased significantly the presence of type 3 and 4 hydrogens correlated with esters that affect the acidity of the upgraded bio-oil.

The ^{1}H and ^{13}C NMR spectra for LBO1 are shown in Figure 3. A simple analysis of the three distinct chemical classes (aliphatic, olefins and aromatics) shows that the light fractions have less aliphatic hydrogens than the heavy fractions. The LBO1 data and spectrum clearly revealed the effect of esterification, observed in the shift at 3.0-5.0 ppm, and this influence was not observed for the heavy fractions of the bio-oil. This indicates that the major acid contribution in these bio-oils originates from small carboxylic acids, as verified in the analysis of the aqueous phase separated from the light fractions.

The significant changes observed in the ^{13}C NMR spectra (Figure 3) were the disappearance of a common signal at 180 ppm (characteristic of the carbonyl carbon of carboxylic acids) and the appearance of the signals at 51 and 174 ppm, attributed to the methoxyl carbon and C=O of esters, respectively, as a consequence of the esterification during the reactive distillation. The other signals confirm the presence of olefins (ca.114 and 139 ppm), aromatics (125-130 ppm) and methylene/methyl carbons (10-40 ppm) as previously reported.[26]

Conclusions

Strong and weak commercially available acids and bases were tested as catalysts in the upgrading of bio-oil fractions employing methanol and ethanol as raw materials,

Table 7. ^{1}H NMR of LBO and HBO

Hydrogen type	^{1}H Chemical shift / ppm	mol% / % of total hydrogen			
		LBO11	LBO1	HBO11	HBO1
1) Aromatics	7.0-9.0	3.77	4.45	3.11	3.14
2) Olefins (–HC=CH–)	5.0-6.5	8.23	5.22	2.43	2.06
3) CH_3, CH_2 and CH, adjacent to –OH 3) CH_3, CH_2 and CH, adjacent to –OC(=O)R	3.0-5.0	–	4.40	–	–
4) CH_2, adjacent to –C=C 4) CH_3, adjacent to –Ph 4) CH_3, CH_2 and CH, bound to –(C=O)OR; –(C=O)OH; –(C=O)H	2.0-2.5	11.11	18.08	14.72	15.12
5) CH, adjacent to –C–C=C 5) CH, adjacent to –C–CH_2 5) CH_3, adjacent to –C=C	1.5-2.0	12.87	10.13	10.22	8.97
6) CH_2 and CH, adjacent to –CH_2R 6) CH_2, adjacent to –C–CH_2 6) CH_2, adjacent to –C–C=C	1.0-1.5	47.33	43.20	57.18	58.38
7) CH_3, adjacent to –CH_2R 7) CH_3, adjacent to –C–CH_2 7) CH_3, adjacent to –CC=C	0.5-1.0	16.67	14.51	12.33	12.32
8) Aliphatics (total)	0.5-3.0	87.98	85.92	94.45	94.79

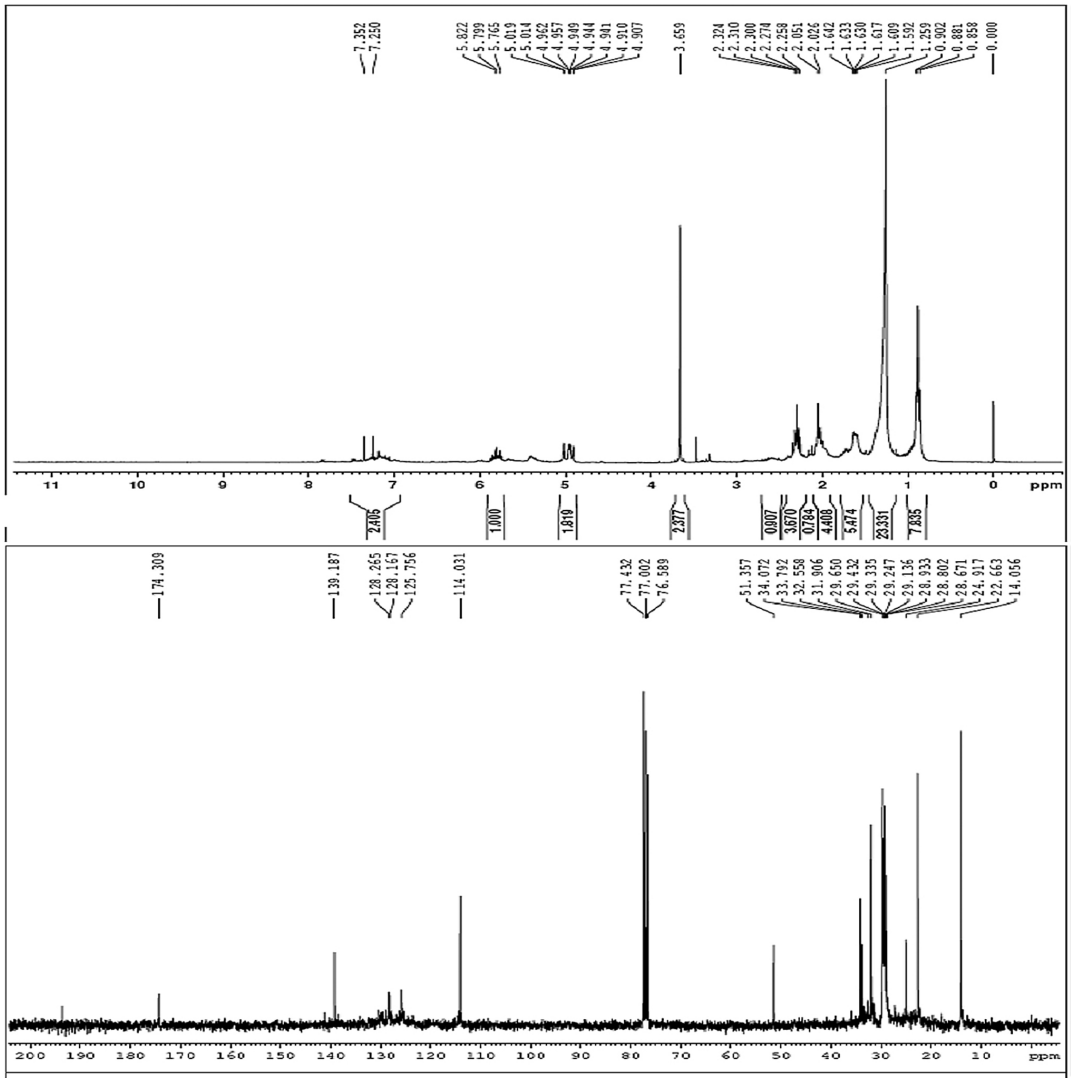

Figure 3. ^{1}H and ^{13}C NMR spectra for LBO1.

through reactive distillation. A crude bio-oil, which had been previously obtained and characterized, produced two kinds of upgraded biofuels, light and heavy bio-oils, with boiling point ranges similar to those of gasoline and diesel produced from petroleum, respectively. The main objective was to decrease the acidity of these biofuel fractions. The best results were achieved with the methanol/sulfuric acid system, which decreased the acidity by 94.3% and 42.5% for the light and heavy bio-oil fractions, respectively. The other characteristics (iodine value, specific gravity and sulfur content) of the obtained fractions were only slightly modified by the reactive process. The investigation of the chemical composition showed the influence of small carboxylic acids, like acetic acid, on the acidity of the light bio-oil and tetradecanoic and hexadecanoic acids on that of the heavy bio-oil. These results highlight the need for a pre-reflux to be carried out before the fractional distillation and the recovery of an intermediary fraction between the light and heavy bio-oil to eliminate the C_{14+} contamination of the light fraction. These results also highlight the main problem of the second generation biofuels, the acidity, and reveal a simple condition which can enable their use in other combustion applications. The authors propose that this upgrade could be performed in a system coupled to the pyrolysis reactor.

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