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Article

Quantitative GC-MS Analysis of Sawdust Bio-Oil

Anai L. dos Santos,[a] Ana Nadja L. Lucas,[b] Iuri D. P. da Mota,[b] Jaderson K. Schneider,[a] Allan S. Polidoro,[a] Andrea R. Pinho,[c] Fábio L. Mendes[c] and Elina B. Caramão *,[a,b,d]

[a]*Instituto de Tecnologia e Pesquisa (ITP), Universidade Tiradentes, Av. Murilo Dantas, 300, 49032-490 Aracaju-SE, Brazil*

[b]*Programa de Pós-Graduação em Biotecnologia Industrial, Universidade Tiradentes, Av. Murilo Dantas, 300, 49032-490 Aracaju-SE, Brazil*

[c]*CENPES, Conversão de Biomassa, Petrobras, 21941-915 Rio de Janeiro-RJ, Brazil*

[d]*Instituto Nacional de Ciência e Tecnologia em Energia e Ambiente (INCT E&A), 40170-115 Salvador-BA, Brazil*

Bio-oils from biomass pyrolysis have a highly promising potential as biofuels or sources of chemicals. The quantitative analysis of bio-oils is quite difficult and requires many standards. In this study, we developed a methodology using only 16 standards for determining the concentration of 49 compounds, representatives of the main chemical classes commons in bio-oils, using relative response factors (RRF) and analytical curves. Five *Pinus* sawdust bio-oils were analyzed using a GC-MS-DB-5 capillary column (60 m). SCAN mode (from 45 to 450 Daltons) and retention indices (LPTRI) were used for qualitative analysis. For quantitative analysis, SIM mode was preferred, and analytical curves were constructed from an initial solution at 400 mg g^{-1} of each of the 16 standards, with concentrations ranging from 1 to 150 mg g^{-1} added to the internal standard (methyl hexanoate) at 70 mg g^{-1}. After the positive identification and quantification of 9 compounds (among the 16 standards used), the other compounds were quantified using the RRF obtained from a standard solution at 30 mg g^{-1}, considering the similarities with those identified standards. 196 compounds were identified, while 49 compounds were quantified, highlighting the monoaromatic hydrocarbons, naphthalenes, benzofurans, alkyl phenols, and catechols.

Keywords: pyrolysis, bio-oil, GC-MS, quantitative analysis

Introduction

Bio-oil is a liquid organic product of lignocellulosic biomass pyrolysis[1] and can be widely used, after an appropriate upgrade, as advanced biofuels[1,2] or as a source of chemicals.[3]

The chemical composition of bio-oils is complex, containing many different compounds with a wide distribution of properties and concentrations. It is essential to detail the bio-oil composition for optimizing the pyrolysis processes and its subsequent upgrading process.[4] The main challenge in bio-oil analysis is identifying and quantifying the individual compounds and the total content of the compounds with distinct functional groups.[5,6]

One important review in the field of quantitative analysis of bio-oils was produced by Staš *et al*.[7] It discussed a state-of-the-art quantitative analysis of bio-oils and formulated strategies for obtaining in-depth information on the composition of the bio-oils and/or the products of their upgrading. The emphasis was placed on quantifying the oxygenated compounds (most important ones) in the bio-oils, including aldehydes, ketones, carboxylic acids, phenols, carbohydrates, ethers, and esters, among others. Also, methods for the quantification of the individual compounds were presented.

From this review, one can highlight gas chromatography, especially associated with a mass spectrometric technique (GC-MS) and/or a flame ionization detector (GC-FID), and more recently, the comprehensive two-dimensional gas chromatography (GC×GC), which have been used for bio-oil characterization. These methods enabled the

*e-mail: elina@ufrgs.br
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identification of several compounds with much structural information.[8] Extensive databases of bio-oil compounds were also presented in the literature, for example, the paper from Faix *et al*.[9] with detailed mass spectra of lignocellulosic degradation products.

The use of GC-MS has been reported not only for the general quantitative characterization of individual volatile and semi-volatile (less volatile) bio-oil compounds but also for the quantitative characterization of individual bio-oil compounds with specific functional groups, as, for instance, phenols, carbonyls, carboxylic acids, aliphatic alcohols, carbohydrates, furans, among others,[10-19] normally based on the peak areas obtained from the total ion current (TIC on SCAN mode), without any previous calibration.[20,21] This kind of quantification can be acceptable for comparing bio-oils obtained from the same pyrolysis process and analyzed at the same analytical conditions, but these concentrations do not correspond to the actual concentrations of the relevant bio-oil compounds.[10] However, when accurate concentrations are required, a complete calibration must be performed using selected-ion monitoring (SIM mode).

GC-FID has been typically applied for the quantitative analysis of bio-oils due to its better linearity than GC-MS,[18] being, in some aspects, preferred over GC-MS in this analysis. The difficulty is in the lack of standards for constructing analytical curves. If a similar GC-MS profile can be obtained in the same conditions for qualitative analysis, the GC-FID can be used for the quantitative purpose with more certainty.

The quantitative use of GC-FID for non-targeted compounds in bio-oil analyses, combined with GC-MS (qualitative analysis), is normally based on the use of relative response factors' (RRFs) prediction models that allowed one to predict the RRFs for the compounds for which no standards are available.[12,13,22]

In this sense, this study aimed to develop a quantitative method for analyzing bio-oils using only 16 standard compounds and calculating the relative response factor (RRF). The bio-oils used were produced from sawdust (Lignocel) in a pilot plant from CENPES (Petrobras, Brazil) in a fluid catalytic cracking (FCC) reactor with zeolite (ZSM-5) as a catalyst. Five samples of bio-oils obtained in different conditions were analyzed and compared.

Experimental

Materials

Analytical standards (16 compounds) and the internal standard (IS, hexanoic acid ethyl ester) were purchased from Sigma-Aldrich (São Paulo, Brazil) and used as received. Solvents dichloromethane and acetone, all reagent grade for liquid chromatography (LC) analysis, were purchased from Merck (São Paulo, Brazil) and used as received. A mixture of standard linear saturated hydrocarbons from 8 to 30 carbon atoms, obtained from Sigma-Aldrich (São Paulo, Brazil) was used in the determination of retention indexes.

Helium and nitrogen gases were provided, at a high purity degree, by White Martins (Aracaju and Rio de Janeiro, Brazil).

Commercial pinewood biomass (Lignocel BK40-90), supplied by J. Rettenmaier & Söhne GMBH+CO KG (Rosenberg, Germany), was used in the pyrolysis, with particle sizes smaller than 0.3 mm. The elemental composition of Lignocel (on a received basis) was 46.1 wt.% carbon, 6.3 wt.% hydrogen, 0.3 wt.% nitrogen, and 47.3 wt.% oxygen (by difference).

The acidic zeolite catalyst used in the experiments was a commercial sample based on ZSM-5 and supplied by FCC S.A. (Rio de Janeiro, Brazil). This catalyst presents a surface area of 127 $m^2\ g^{-1}$ and a micropore volume of 0.003 $cm^3\ g^{-1}$. A material composed of silica and clay was used as an inert bed medium. A hydrothermal deactivation procedure was employed on the fresh materials at 805 °C.

Five different samples of sawdust bio-oils produced in the pyrolysis plant of CENPES, Petrobras, under different conditions, will be described below. The samples are part of a pyrolysis test carried out in the FCC reactors at CENPES (Petrobras, RJ, Brazil), using pine sawdust as biomass and different catalyst/biomass ratios (CTB varied from 8.1% in sample A to 34.8% in sample E) as can be seen in the Results section, being this the main difference between the samples of bio-oils analyzed.

Pyrolysis process

A FCC pilot plant was adapted to perform biomass pyrolysis in a circulating fluidized bed. This configuration allows high heat transfer rates for maximizing liquid production and minimizing secondary reactions.[23] The heat required for endothermic reactions is provided by burning the coke/coal deposited in the bed particles (sand or catalyst). The acidic zeolite catalyst used in the experiments was a commercial sample based on ZSM-5 and supplied by FCC S.A. (Rio de Janeiro, Brazil). A hydrothermal deactivation procedure was carried out on the fresh materials at 805 °C for five hours under 100% steam atmosphere in a fluidized bed unit, commonly used for evaluation tests of catalytic cracking catalysts. The ZSM-5 zeolite, after its deactivation, presented a surface area of 127 $m^2\ g^{-1}$ and a micropore volume of 0.937 $cm^3\ g^{-1}$. The pilot plant consists of a pyrolysis

reactor and a regenerator, besides a system to introduce biomass and equipment for liquid recovery products. The solid flow rate is 1.0 kg h^{-1}, using a variable speed screw conveyor. The independent electrical heaters allow an isothermal profile along the system. Nitrogen was introduced at the bottom of the reactor to maintain the particles fluidized, and a mixture of oxygen and air was injected at the bottom of the regenerator.

The vapors produced during the pyrolysis passed through a cyclone to separate the spent catalyst and minimize the entrainment of solid particles into the recovery system. Injections of heated nitrogen (400 °C) were used to prevent the condensation of the bio-oil heavier fractions in the reactor and cyclone exit lines.

To increase the efficiency, the condensation of bio-oil was done through three systems: (*i*) a dry-ice cooled trap aiming for retaining the heavier fraction of bio-oil; (*ii*) a tower cooled by Freon passing through an internal coil; and (*iii*) two parallel vessels with an internal demister, immersed in a bath with dry ice, to prevent the condensable compounds from passing through the liquid collection system. The incondensable gas pass through a filter upstream of the wet gas meter (WGM) that was used to measure the gaseous product from the pyrolysis reactor.

The reaction temperature employed in all experiments was set as 500 ºC with base in data from the thermogravimetric analysis (TGA) of sawdust.[24] The regenerator fluidized bed temperature was kept at 670 °C, enabling proper coke burning.

GC-MS analysis

Gas chromatographic analyses were performed using a Shimadzu GC-MS QP2010-plus (Shimadzu company, Kyoto, Japan) equipped with a capillary column DB-5 (60 m length, 0.25 mm diameter, 0.25 μm stationary phase) using He (99.999 purity, flow rate 1 mL min^{-1}) as the carrier gas, with electron impact of 70 eV, T_{INJ} (injector temperature) and T_{DET} (detector temperature) = 300 ºC. Splitless injection with a volume injected of 1 μL was used. Data treatment was performed using the GCMS solution software. The bio-oils were analyzed without any derivatization.

For qualitative analysis, SCAN mode was used in a mass range from 45 to 450 Daltons. The oven was heated from 40 to 300 °C at 3 °C min^{-1}, total time = 202 min. The software calculated retention indices (LPTRI) after injecting a mixture of *n*-alkanes (from 7 to 40 carbons in the chain).

For quantitative analysis, SIM mode was used, and the oven was heated from 40 to 160 ºC at 2 ºC min^{-1} and from this temperature to 300 ºC at 20 ºC min^{-1}, remaining at this temperature for 5 min. Total time = 72 min. Analytical curves were plotted using solutions prepared from an initial solution at 400 mg g^{-1} of each of the 16 standards. The solutions were prepared in concentrations varying from 1 to 150 mg g^{-1} being added the IS (methyl hexanoate) at 70 mg g^{-1}. The bio-oil samples were analyzed in a concentration of 10.000 ppm (mg g^{-1}), with the addition of the IS at 70 mg g^{-1}.

To determine RRF, after the positive identification of 9 compounds (among the 16 standards used), other compounds could be quantified using the RRF obtained from a standard solution at 30 ppm.

Example of RRF determination: all alkyl phenols in the samples were quantified using the RRF of *m*-cresol; benzenediols were quantified based on 4-methyl catechol; quantification of benzaldehydes used 5-hydroxy-benzaldehyde curve; and so on. These quantifications used the following equations:

$$RFi = \frac{Ci}{Ai} \quad (1)$$

$$RFis = \frac{Cis}{Ais} \quad (2)$$

$$RRFi = \frac{Ci}{Ai} \times \frac{Ais}{Cis} \quad (3)$$

where RFi: response factor for the compound 'i' and RFis: response factor for the internal standard, Ci: concentration of the compound "i" and Cis: concentration of the internal standard, Ai: area of the peak of the compound "i" and Ais: area of the peak of the internal standard.

Dividing RFi/RFis, it is obtained the RRFi (relative response factor for the compound 'i'), which was used in the quantitative determination of the concentration of the compound 'i' in each sample.

Results

Preliminary analysis

According to the CTB (catalyst to biomass ratio) applied, five different samples were obtained where the major quantitative effect was the variation on the yield in coke formation, as can be seen in Table 1.

The mass yield of the products was around 47% of liquids, which generated around 14% of bio-oil (organic phase). The average elemental composition of the bio-oils (organic phases) was: 70% carbon, 7% hydrogen, and 23% oxygen (by difference).

Table 1. Elemental analysis and product yield distribution for catalytic pyrolysis (biomass: sawdust of *Pinus* wood, catalyst: ZSM-5, and reaction temperature: 500 ºC)

Sample/condition		Mass yield of the pyrolysis products / wt.%						Elemental analysis of OP		
		Gases		Liquids		Solids	Mass balance			
Code	CTB / %	Light HC	Others	OP	AP	Coke		C / %	H / %	O / %
Sample A	8.1	2.5	30.2	14.8	34.9	9.9	92.2	67.3	6.8	25.9
Sample B	13.9	2.1	30.8	13.0	30.7	13.9	90.5	68.7	7.1	24.2
Sample C	16.9	1.9	29.8	14.5	33.5	14.6	94.4	66.5	6.8	26.7
Sample D	22.1	3.0	24.9	12.5	40.2	15.1	95.7	72.4	7.1	20.5
Sample E	34.8	3.9	33.2	14.6	27.5	23.6	102.7	74.9	7.2	17.9
Average value		2.7	29.8	13.9	33.3	15.4	95.1	70.0	7.0	23.0

CTB: catalyst/biomass ratio; OP: organic phase (bio-oil); AP: aqueous phase.

The increase of CTB enhanced coke yields from 9.9 to 23.6 wt.%. Higher heat transfer accelerates some reactions, favoring polymerization and coke formation of biomass components. CTB presented intrinsic relation with the oxygen content of bio-oils, which decreased significantly as its CTB increased. This is linked with deoxygenation reactions ($-CO_2$, $-CO$, and $-H_2O$), probably enhanced by the higher CTB. Generally, studies with ZSM-5 obtained liquid products with oxygen content above 20 wt.%.[25,26] Sources in the literature[27,28] indicated that oxygen content (< 20 wt.%) makes the mixture with fossil streams reliable for co-processing in conventional refining. Besides, it is worth noticing that yields of the organic phase did not decrease as the quality increased, being kept around 14 wt.%.

Qualitative analysis

Figure 1 shows the chromatograms of the bio-oils (from A to E) by GC-MS method in SCAN mode. As seen in these chromatograms, the samples shown remarkable similarity in their qualitative profiles. The results of peak identification are shown in Tables S1 and S2 in the Supplementary Information (SI) section for the five samples. These tables contain retention times, areas, LPTRI, and NIST webbook data. Area values are not directly related to concentration since this analysis was performed in SCAN mode, a situation in which the proportionality between concentration and area is not direct.

Table 2 summarizes the results obtained from GC-MS analysis in SCAN mode, considering the number of compounds found and the chemical classes' relative peaks area.

Quantitative analysis

Table 3 presents the list of the 16 standards and the internal standard, their RRFi, and data for determining the linearity range, the straight-line equation, and the R^2 (coefficient of determination), while Figure S1 (SI section) shows the calibration curves (y = Ai/Ais *versus* x = Ci/Cis), for each standard compound, divided into phenols, other oxygenated compounds, and hydrocarbons. The internal standard was ethyl hexanoate at a constant concentration of 70 ppm. Table S3 (SI section) presents the identification using LPTRI and the values of RRFi for the identified and quantified compounds in the five samples. The analyses were done in triplicate (in some cases quadruplicate) and the standard deviation values was between 0.2 to 9%, which can be considered a good result.

With these values, the concentrations of the compounds were calculated by the equation 4, using the RRFi of the standard with the most remarkable structural similarity with the compound in question:

$$Ci = RRFi \times (Ai/Ais) \times Cis \quad (4)$$

As the IS concentration is fixed and equal to 70 mg mL^{-1}, the concentration in mg mL^{-1} is obtained first. Considering the mass used to analyze each sample, the mass (in mg) and the concentration (mg g^{-1} of bio-oil) can be calculated. The compounds were divided into classes, using the ions chosen for each class, and a new injection of each sample was performed in these conditions.

Figure 2 shows the chromatograms, in the SIM mode, with the identification of the quantified compounds in sample A. Three different conditions were used: (*i*) only ions for phenols (with peaks identified in blue); (*ii*) other oxygenated compounds (with peaks identified in red) and in (*iii*) only the hydrocarbons, with green numbers. The GC profile of the other samples, in these same conditions, are similar.

Table 4 presents the quantification data of all samples, divided into the same classes shown in Figure 2, while Table 5 presents a summary of these data.

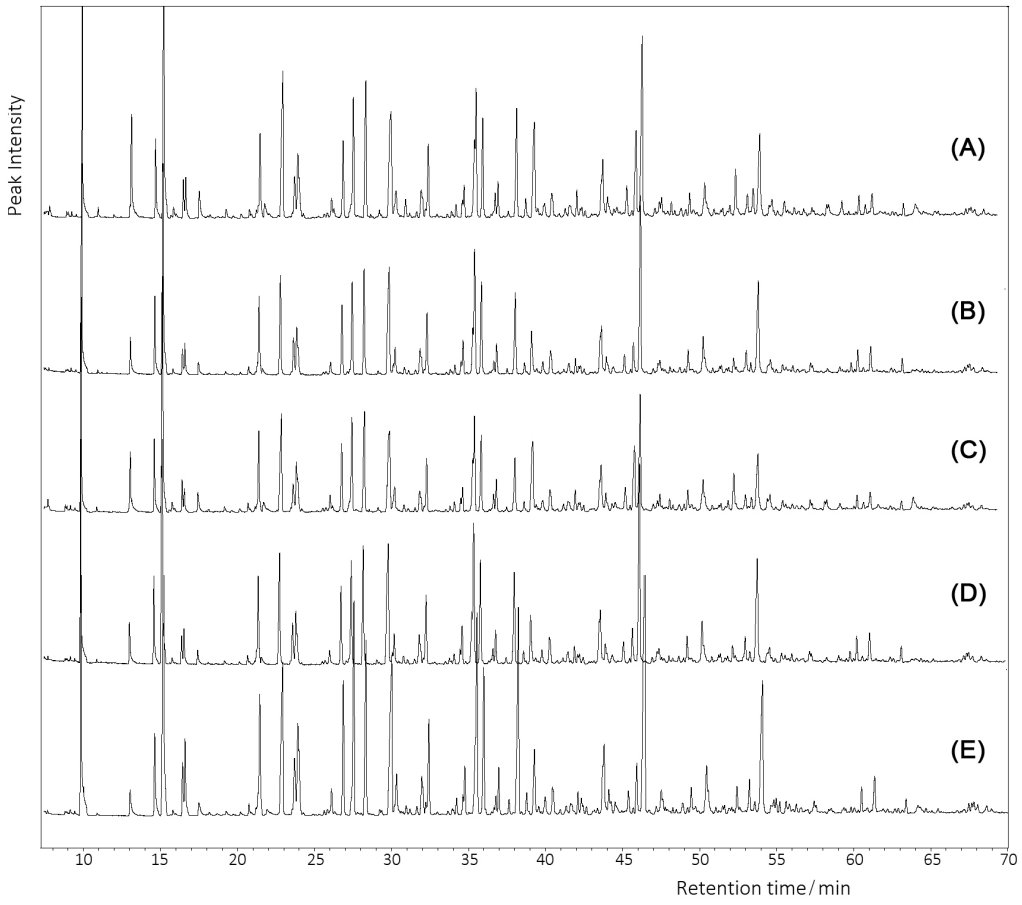

Figure 1. Total ion chromatograms (GC-MS, SCAN mode) of the five samples (A, B, C, D, and E) analyzed. Chromatographic conditions are described in the Experimental section.

Table 2. Summary of data of the bio-oils (from A to E) obtained by GC-MS in the SCAN mode

Chemical classes			Area / %					Number of peaks				
			A	B	C	D	E	A	B	C	D	E
Hydrocarbons	indanes		5.8	11	5.49	10.4	11.9	5	5	3	7	5
	indenes		6.48	5.18	7.44	6.57	7.67	6	5	5	4	4
	alkyl benzenes		20.1	25.3	23.1	31.1	23.5	15	14	14	15	16
	naphthahlenes		14.2	18.1	11.9	17.8	20.6	9	8	9	11	11
	polyaromatics		0.67	0.66	0.61	0.61	1.74	2	2	3	2	7
Oxygenated	alcohols		0.87	0.94	1.18	0.18	1.21	2	2	3	1	3
	aldehydes		1.87	1.17	2.78	0.31	0.42	5	3	5	1	2
	ketones		7.45	5.32	6.89	3.92	3.18	14	12	15	12	10
	ethers		8.16	7.38	8.5	6.01	7.44	9	7	7	7	7
	phenols	alkyl phenols	23.9	19.5	21.7	18.2	17.6	18	16	14	17	17
		cathecols	8.54	3.49	8.72	3.19	3.21	5	3	4	3	3
		guaiacols	0.91	0.26	0.25	0.28	0.19	3	1	1	1	1
		naphthols	1.02	1.72	1.53	1.62	1.47	3	4	4	5	4
Total			100	100	100	100	100	96	82	87	86	90

The compounds with higher concentration in each sample can be viewed in Figure 3, for comparative purposes. From this figure is possible to see the predominance of phenols, highlighting the concentration of catechol (mainly in samples C and E), and *o*-cresol (3-methyl phenol). Toluene also appears in highly

Table 3. Details of the 16 standard compounds used in this work and the construction of the calibration curves, including the range of linearity and the coefficient of determination (R^2)

t_R / min	Compounds		RRFi	MW / Da	Formula	Ions (*m/z*)			Linearity range / (mg mL^{-1})	Calibration curve	R^2
	Abbreviation	Name									
14.47	m-Xyl	*m*-xylene	1.963	106	C_8H_{10}	105	91	78	1 to 50	$y = 1.7032x - 0.0241$	0.9844
14.94	p-Xyl	*p*-xylene	0.305	106	C_8H_{10}	105	91	78	15 to 125	$y = 0.8119x - 0.0076$	0.9875
16.42	o-Xyl	*o*-xylene	0.906	106	C_8H_{10}	105	91	78	1 to 50	$y = 0.3524x - 0.0079$	0.9801
16.54	cycloC6	cyclohexanone	1.141	98	$C_6H_{10}O$	98	68	55	1 to 100	$y = 1.7143x - 0.0761$	0.9963
22.69	PH	phenol	2.103	94	C_6H_6O	94			15 to 125	$y = 2.6852x - 0.1137$	0.9928
29.67	mCr	*m*-cresol	1.392	108	C_7H_8O	108	107	94	1 to 150	$y = 1.7623x - 0.1178$	0.9925
35.34	2,5-Ph	phenol 2,5 dimethyl	2.824	122	$C_8H_{10}O$	121	108	107	1 to 50	$y = 3.7910x - 0.1130$	0.9924
36.61	4-Ph	phenol 4 ethyl	3.072	122	$C_8H_{10}O$	121	108	107	1 to 50	$y = 3.8138x - 0.1652$	0.9862
36.80	3,5-Ph	phenol 3,5 dimethyl	2.158	122	$C_8H_{10}O$	121	108	107	1 to 50	$y = 2.4773x - 0.0566$	0.9922
37.94	Naph	naphthalene	6.611	128	$C_{10}H_8$	128			1 to 30	$y = 6.6469x - 0.0593$	0.9973
38.61	3,4-Ph	phenol 3,4 dimethyl	2.568	122	$C_8H_{10}O$	121	108	107	1 to 50	$y = 3.0580x - 0.1061$	0.9898
40.69	2 Ph	phenol 2 propyl	3.257	136	$C_9H_{12}O$	136	108	107	1 to 50	$y = 3.7910x - 0.1130$	0.9924
45.31	Resor	resorcinol	1.087	110	$C_6H_6O_2$	110			5 to 150	$y = 2.0548x - 0.4066$	0.9922
45.82	4-Cat	catechol 4 methyl	0.150	124	$C_7H_8O_2$	124	78		15 to 150	$y = 1.4230x - 0.6621$	0.9911
50.83	OH-Bz	benzaldehyde 4-hydroxy	0.994	122	$C_7H_6O_2$	122	121		15 to 150	$y = 2.1567x - 0.4455$	0.9963
53.31	Van	vanillin	1.525	152	$C_8H_8O_3$	152	151		1 to 150	$y = 2.3638x - 0.2123$	0.9930
23.88	IS	ethyl hexanoate (IS)	1.000	144	$C_8H_{16}O_2$	88					

MW: molecular weight; y = Ai/Ais; x = Ci/Cis; Ai: area of the compound 'i'; A_{IS}: area of the internal standard; C_i: concentration of the compound 'i'; C_{IS}: concentration of the internal standard; RRFi: relative response factor for the compound 'i'; IS: internal standard.

concentration in sample B. Naphthalene and their alkyl derivatives presents higher concentrations in all the samples too.

The comparison of the chemical classes found in each sample, according to the CTB and content of oxygen (% obtained in the elemental analysis), can be visualized in Figure 4.

Discussion

This study aimed to develop a quantitative process based on a few standards for the quantitative determination of the main constituents of bio-oils of lignocellulosic origin.

This way, five bio-oils obtained from pine sawdust, under similar conditions (same equipment and temperature) but with slight variations in the use of catalysts, were analyzed.

The qualitative analysis (Tables S1 and S2 and Figure 1) allowed the identification of 126 compounds, which, according to the literature, are expected for this type of biomass.[1,4-6,24] Oxygen compounds (74) predominated over hydrocarbons (52). Among these compounds, phenols, some ethers (derived from furan), and aromatic hydrocarbons (monoaromatics and naphthalene) stand out. The analysis using only the comparison between chromatographic peak relative areas has been used in many studies[20,21,29] as a semi-quantitative evaluation. However, it has a fundamental error: disregarding response factors, that is, the individual relationship of each compound between area and concentration. However, it is quite useful for fast comparing different samples.

Although quantitative evaluation using calibration curves and standards is more reliable, it becomes unfeasible in most cases due to the lack of all necessary standards, the difficulty in acquiring them (especially in countries like Brazil), and the total cost of the process.

For this reason, we chose to develop a procedure based on a reduced number of standard compounds, representative of the main classes found in the studied bio-oils, thus composing a "synthetic bio-oil" and from this bio-oil to develop the analytical methodology with the construction of the curves and relative response factor calculations using the method of standard addition. The concentrations of the other compounds that presented chemical structure and/or chemical function similar to one of the standards used were calculated from this.

The results made it possible to quantitatively determine 49 compounds representing more than 90% of the total weight of identified compounds in each sample (Tables 4 and 5).

The predominance of the classes of phenols, ethers, and hydrocarbons was confirmed (Figure 3), thus indicating the

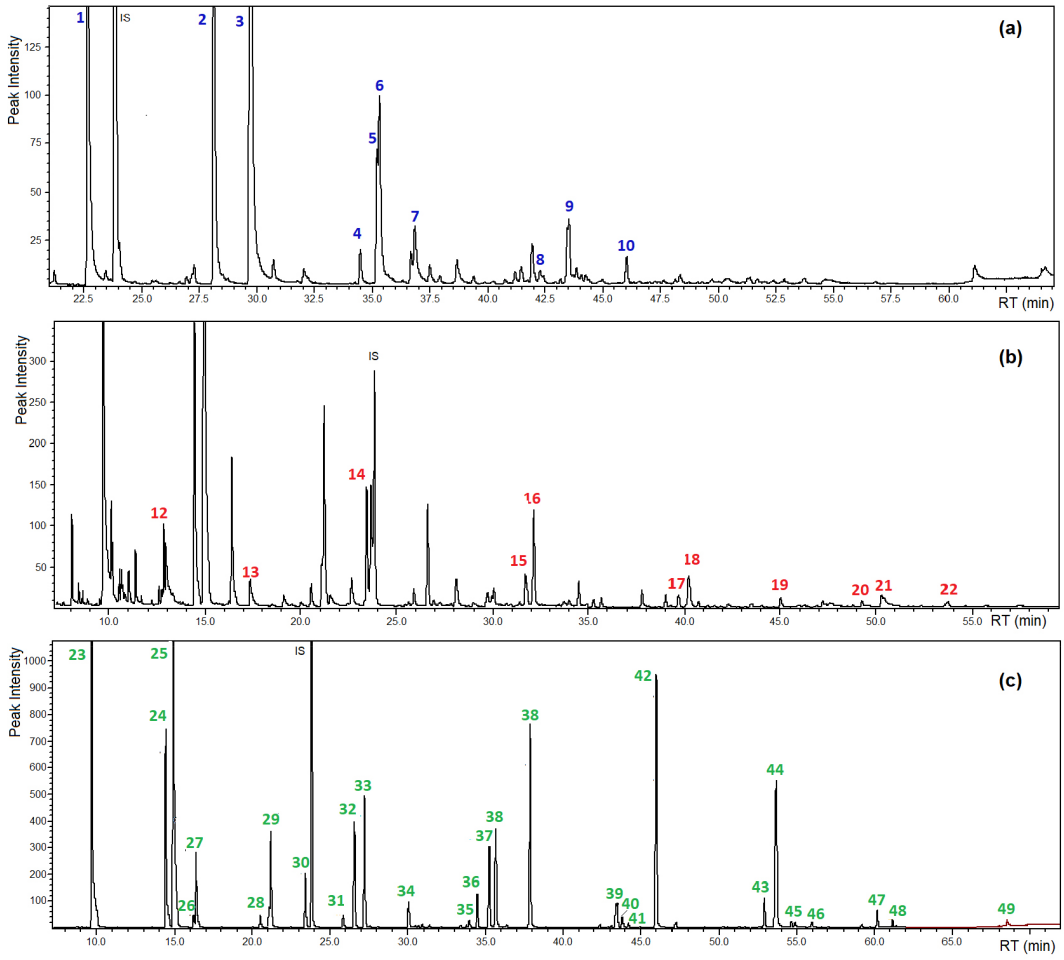

Figure 2. GC-MS chromatograms of sample A with selected ions (SIM mode): (a) ions related to phenols (*m/z* in Daltons = 88 (internal standard), 94, 107, 108, 110, 121, 124,136); (b) ions related to other non-phenolic oxygenated compounds (*m/z* in Daltons = 55, 67, 68, 82, 88 (IS), 91, 96, 105, 118, 120, 131, 132, 134, 145, 151); and (c) ions related to hydrocarbons (*m/z* in Daltons = 78, 88 (IS), 91, 105, 115, 117, 119, 128, 129, 130, 132, 141, 142, 155, 156, 166, 168, 170, 178). Chromatographic conditions are described in the Experimental section.

Table 4. Quantitative analysis of samples of the bio-oils (samples A to E)

Compound		RRFi	Bio-oil A		Bio-oil B		Bio-oil C		Bio-oil D		Bio-oil E	
t_R / min	Name		m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})
9.69	toluene	1.9633	3.42	67.59	6.75	134.73	3.90	77.53	3.47	68.71	2.81	56.43
14.42	*m*-xylene	1.9633	3.01	59.49	0.50	9.98	0.50	9.94	0.60	11.88	0.72	14.46
14.97	*p*-xylene	0.9062	0.69	13.64	0.80	15.97	0.92	18.29	1.35	26.73	1.01	20.28
16.23	styrene	1.9633	0.73	14.43	0.22	4.39	0.14	2.78	0.10	1.98	0.13	2.61
16.38	*o*-xylene	0.3052	0.48	9.49	0.02	0.40	0.03	0.60	0.04	0.79	0.04	0.80
20.51	benzene, propyl	1.9633	0.54	10.67	0.16	3.19	0.10	1.99	0.06	1.19	0.07	1.41
21.20	benzene, 1-ethyl-3-methyl	1.9633	0.30	5.93	0.01	0.20	0.80	15.90	0.55	10.89	0.57	11.45
23.45	benzene, 1,3,5-trimethyl	1.9633	0.25	4.94	0.40	7.98	0.33	6.56	0.22	4.36	0.28	5.62
25.87	styrene, 2-methyl	1.9633	0.44	8.70	0.14	2.79	0.10	1.99	0.06	1.19	0.09	1.81
26.62	indane	6.6107	1.99	39.33	2.57	51.30	1.81	35.98	1.36	26.93	2.01	40.36
27.29	indene	6.6107	1.56	30.83	3.74	74.65	2.84	56.46	1.80	35.64	2.57	51.61
30.08	m,α-dimethylstyrene	1.9633	0.14	2.77	0.19	3.79	0.12	2.39	0.09	1.78	0.16	3.21
34.00	benzene, 1-pentenyl-	1.9633	0.94	18.58	0.07	1.40	0.06	1.19	0.02	0.40	0.08	1.61
34.52	indane, 5-methyl	6.6107	0.60	11.86	0.87	17.37	0.62	12.33	0.40	7.92	0.15	3.01

Table 4. Quantitative analysis of samples of the bio-oils (samples A to E) (cont.)

Compound		RRFi	Bio-oil A		Bio-oil B		Bio-oil C		Bio-oil D		Bio-oil E	
t_R / min	Name		m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})	m_i / mg	Ci / (mg g^{-1})
35.32	indane, 4-methyl	6.6107	0.85	16.80	1.04	20.76	0.72	14.31	0.65	12.87	0.67	13.45
35.74	indane, 3-methyl	6.6107	1.04	20.55	1.59	31.74	1.21	24.06	0.82	16.24	0.93	18.67
37.97	naphthalene	6.6107	2.03	40.12	1.44	28.74	2.60	51.69	3.70	73.27	1.46	29.32
43.55	indene, C2	6.6107	0.91	17.98	1.42	28.34	1.01	20.08	0.61	12.08	0.94	18.88
43.89	indene, C3	6.6107	0.22	4.35	0.53	10.58	0.35	6.96	0.20	3.96	0.37	7.43
46.18	naphthalene, 2-methyl	6.6107	4.63	91.50	4.43	88.42	4.63	92.05	4.33	85.74	2.13	42.77
53.02	naphthalene, 2-ethyl	6.6107	0.37	7.31	0.50	9.98	0.42	8.35	0.31	6.14	0.48	9.64
53.84	naphthalene, 1-ethyl	6.6107	1.40	27.67	1.64	32.73	0.02	0.40	1.28	25.35	1.32	26.51
54.98	naphthalene, 1,6-dimethyl	6.6107	1.03	20.36	0.04	0.80	1.47	29.22	0.06	1.19	0.09	1.81
56.06	naphthalene, 1,5-dimethyl	6.6107	0.24	4.74	0.08	1.60	0.06	1.19	0.04	0.79	0.13	2.61
60.28	naphthalene, C3	6.6107	0.23	4.55	0.41	8.18	0.34	6.76	0.20	3.96	0.41	8.23
62.14	naphthalene, 1,2,5-trimethyl	6.6107	0.15	2.96	0.01	0.20	0.00	0.00	0.01	0.20	0.07	1.41
67.10	phenanthrene	6.6107	0.10	1.98	0.13	2.59	0.17	3.38	0.11	2.18	0.11	2.21
Subtotal hydrocarbons			28.29	559.09	29.70	592.81	25.27	502.39	22.44	444.36	19.80	397.59
22.88	phenol	3.5253	0.08	1.58	1.73	34.53	1.32	26.24	1.56	30.89	2.25	45.18
28.30	phenol, 2-methyl	2.3333	0.38	7.51	0.42	8.38	0.53	10.54	0.84	16.63	0.58	11.65
29.95	phenol, 3-methyl	2.3333	4.34	85.77	3.54	70.66	4.24	84.29	4.18	82.77	5.64	113.25
34.61	phenol, 2-ethyl	5.1507	0.11	2.17	0.12	2.40	0.16	3.18	0.13	2.57	0.18	3.61
35.39	phenol, 3,4-dimethyl	4.305	0.59	11.66	0.38	7.58	0.34	6.76	0.60	11.88	0.81	16.27
36.75	phenol, 4-ethyl	5.1507	1.10	21.74	1.37	27.35	1.13	22.47	0.94	18.61	1.92	38.55
36.94	phenol, 3,5-dimethyl	3.6176	1.28	25.30	1.18	23.55	0.94	18.69	1.22	24.16	2.35	47.19
39.25	catechol	1.8225	3.74	73.91	4.16	83.03	5.98	118.89	4.44	87.92	4.62	92.77
42.08	phenol, 2,3,6-trimethyl	5.4608	0.14	2.77	0.25	4.99	0.30	5.96	0.32	6.34	0.25	5.02
45.89	catechol, 4-methyl-	0.2511	0.05	0.99	0.17	3.39	0.15	2.98	0.07	1.39	0.52	10.44
61.34	2 naphthol	11.083	0.31	6.13	0.24	4.79	0.27	5.37	0.61	12.08	0.38	7.63
Subtotal phenols			12.12	239.53	13.56	270.66	15.36	305.37	14.91	295.25	19.50	391.57
48.89	1*H*-indanol	11.083	0.12	2.37	0.03	0.60	0.04	0.80	0.08	1.58	0.14	2.81
50.42	1*H*-indenol	11.083	0.10	1.98	0.22	4.39	0.21	4.17	0.39	7.72	0.56	11.24
53.55	vanillin	2.5559	0.33	6.52	0.49	9.78	0.66	13.12	0.21	4.16	0.36	7.23
13.00	2-cyclopenten-1-one	1.9124	0.32	6.32	0.48	9.58	0.54	10.74	0.38	7.52	0.34	6.83
17.46	2-cyclopenten-1-one, 2-methyl-	1.9124	0.12	2.37	0.13	2.59	0.15	2.98	0.11	2.18	0.10	2.01
45.32	1*H*-inden-1-one, 2,3-dihydro-	1.9124	0.12	2.37	0.07	1.40	0.07	1.39	0.07	1.39	0.15	3.01
23.88	benzofuran	11.083	1.98	39.13	1.16	23.15	2.64	52.49	3.20	63.37	2.16	43.37
31.92	benzofuran, methyl-	11.083	1.47	29.05	0.78	15.57	0.90	17.89	1.51	29.90	1.14	22.89
32.39	benzofuran, 2-methyl-	11.083	1.23	24.31	1.26	25.15	1.78	35.39	3.00	59.41	2.12	42.57
39.96	benzofuran, 2,3-dihydro-	11.083	0.16	3.16	0.13	2.59	0.21	4.17	0.21	4.16	0.12	2.41
40.44	benzofuran, 4,7-dimethyl-	11.083	1.35	26.68	0.68	13.57	0.76	15.11	1.14	22.57	1.01	20.28
Subtotal other oxygenated compounds			7.30	144.27	5.43	108.38	7.96	158.25	10.30	203.96	8.20	180.94
Total			47.71	942.89	48.69	971.86	48.59	966.00	47.65	943.56	47.50	970.10

m_i: mass of the compound "i"; C_i: Ci: concentration of the compound "i"; RRFi: relative response factor for the compound "i".

possibility of using this bio-oil both for energy purposes with biofuel, due to the high content of monoaromatic hydrocarbons, as an industrial raw material, due to the high phenol content.

Sample E had the highest content of phenols and total oxygenates (383.55 and 564.49 mg g^{-1}, respectively). However, the original value of oxygen obtained by elemental analysis for this sample (17.9%) was the lowest

Table 5. Summary of quantitative data of bio-oils (samples A to E) including CTB and O

Class	Ci / (mg g^{-1})				
	A	B	C	D	E
Hydrocarbons	547.91	592.42	502.86	444.57	393.4
Phenols	233.4	270.71	325.37	295.2	383.55
Oxygenated compounds (others)	136.36	132.09	157.92	243.59	180.94
Total of oxygenated compounds	369.76	402.8	483.29	538.79	564.49
Total	917.67	995.22	986.15	983.36	957.88
Initial mass / mg	51.6	50.1	50.3	50.5	49.8
Unidentified / %	2.19	0.12	0.35	0.42	1.04
CTB	8.12	13.87	16.9	22.12	34.75
O / %	25.9	24.2	26.7	20.5	17.9

Ci: concentration of the compound "i"; CTB: catalyst to biomass ratio; O: content of oxygen obtained in the elemental analysis.

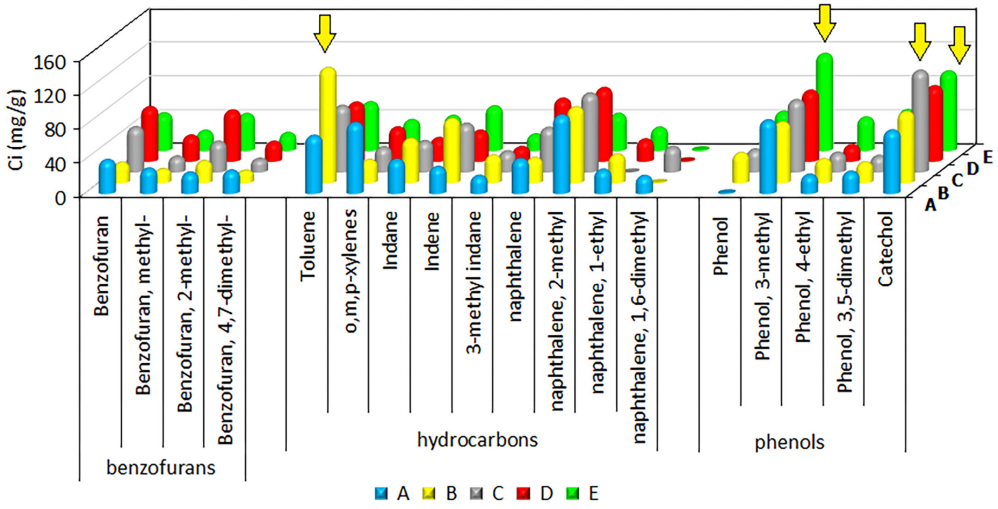

Figure 3. Distribution of the majority compounds in each sample of bio-oil analyzed. Compounds signaled with a yellow arrow (catechol (118.9 and 92.3 mg g^{-1} in samples C and D), *m*-cresol (113.3 mg g^{-1} in sample E and toluene (134.7 mg g^{-1}) in sample B) were the most abundant compounds in the bio-oils.

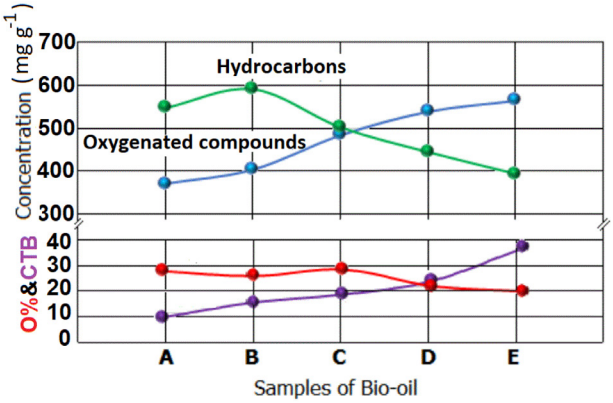

Figure 4. Distribution of the chemical classes found in bio-oils produced at different CTB (catalyst to biomass ratio).

among the 5 bio-oils produced and must be important to emphasize that this was the bio-oil obtained with the highest CTB (34.75%). This result allows us to conclude that the predominant factor for the production of phenols is the correct choice of catalyst and the proportion used. The higher catalyst/biomass ratio, the higher the phenol and total oxygenated compounds obtained in the process.

This improvement of the bio-oil needs a relatively simple upgrade process, isolating oxygenated and polar compounds from the hydrocarbons. Several procedures have been indicated in the literature[30-34] for this type of upgrade of bio-oils aiming at their final application.

Conclusions

This study developed a quantitative methodology based on adding standards and using GC-MS (SIM mode) to analyze bio-oils and relative response factors referring to only 16 standard compounds. At the end of the process, after the construction of the analytical curves, the linearity of the process was verified in the range of 1 to 150 mg mL^{-1}, and 49 compounds were identified and quantified in five

samples of bio-oils obtained from sawdust pyrolysis of pine, in pyrolytic conditions very similar.

Alkyl phenols, catechols, benzofurans, monoaromatic hydrocarbons, and naphthalenes stand out among these compounds. This composition indicates the possibility of using these bio-oils as biofuels or industrial raw materials after separating oxygenates (polar) and hydrocarbons (nonpolar).

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Author Contributions

Elina B. Caramão, Andrea R. Pinho, Fábio L. Mendes were responsible for conceptualization; Iuri D. P. da Mota, Ana Nadja L. Lucas, Jaderson K. Schneider, Anai L. dos Santos for investigation, analysis, and data interpretation; Jaderson K. Schneider, Anai L. dos Santos, Allan S. Polidoro for calculations; Elina B. Caramão, Anai L. dos Santos, Allan S. Polidoro for writing original draft, writing-review and editing; Elina B. Caramão for resources, funding acquisition and project administration. All the authors have participated in drafting and revising the manuscript.

References

1. Moraes, M. S. A.; Migliorini, M. V.; Damasceno, F. C.; Georges, F.; Almeida, S.; Zini, C. A.; Jacques, R. A.; Caramão, E. B.; *J. Anal. Appl. Pyrolysis* **2012**, *98*, 51. [Crossref]
2. Oasmaa, A.; Van De Beld, B.; Saari, P.; Elliott, D. C.; Solantausta, Y.; *Energy Fuels* **2015**, *29*, 2471. [Crossref]
3. Czernik, S.; Bridgwater, A. V.; *Energy Fuels* **2004**, *18*, 590. [Crossref]
4. Lazzari, E.; Schena, T.; Primaz, C. T.; da Silva Maciel, G. P.; Machado, M. E.; Cardoso, C. A. L.; Jacques, R. A.; Caramão, E. B.; *Ind. Crops Prod.* **2016**, *83*, 529. [Crossref]
5. Barros, J. A. S.; Krause, M. C.; Lazzari, E.; Bjerk, T. R.; do Amaral, A. L.; Caramão, E. B.; Krause, L. C.; *Microchem. J.* **2018**, *137*, 30. [Crossref]
6. Schena, T.; Farrapeira, R.; Bjerk, T. R.; Krause, L. C.; Mühlen, C.; Caramão, E. B.; *Sep. Sci. plus.* **2019**, *2*, 89. [Crossref]
7. Staš, M.; Auersvald, M.; Kejla, L.; Vrtiška, D.; Kroufek, J.; Kubička, D.; *TrAC, Trends Anal. Chem.* **2020**, *126*, 115857. [Crossref]
8. Stas, M.; Kubicka, D.; Chudoba, J.; Pospisil, M.; *Energy Fuels* **2014**, *28*, 385. [Crossref]
9. Faix, O.; Meier, D.; Fortmann, I.; *Holz Roh- Werkst.* **1990**, *48*, 351. [Crossref]
10. Auersvald, M.; Shumeiko, B.; Staš, M.; Kubička, D.; Chudoba, J.; Šimáček, P.; *ACS Sustainable Chem. Eng.* **2019**, *7*, 7080. [Crossref]
11. Ferrell III, J. R.; Olarte, M. V.; Christensen, E. D.; Padmaperuma, A. B.; Connatser, R. M.; Stankovikj, F.; Meier, D.; Paasikallio, V.; *Biofuels, Bioprod. Biorefin.* **2016**, *10*, 496. [Crossref]
12. Undri, A.; Abou-Zaid, M.; Briens, C.; Berruti, F.; Rosi, L.; Bartoli, M.; Frediani, M.; Frediani, P.; *J. Anal. Appl. Pyr.* **2015**, *114*, 208. [Crossref]
13. Charon, N.; Ponthus, J.; Espinat, D.; Broust, F.; Volle, G.; Valette, J.; Meier, D.; *J. Anal. Appl. Pyrolysis* **2015**, *116*, 18. [Crossref]
14. Artigues, A.; Puy, N.; Bartrolí, J.; Fábregas, E.; *Energy Fuels* **2014**, *28*, 3908. [Crossref]
15. Thangalazhy-Gopakumar, S.; Adhikari, S.; Gupta, R. B.; Fernando, S. D.; *Energy Fuels* **2011**, *25*, 1191. [Crossref]
16. Ingram, L.; Mohan, D.; Bricka, M.; Steele, P.; Strobel, D.; Crocker, D.; Mitchell, B.; Mohammad, J.; Cantrell, K.; Pittman Jr., C. U.; *Energy Fuels* **2008**, *22*, 614. [Crossref]
17. Branca, C.; Giudicianni, P.; Di Blasi, C.; *Ind. Eng. Chem. Res.* **2003**, *42*, 3190. [Crossref]
18. Marathe, P. S.; Juan, A.; Hu, X.; Westerhof, R. J. M.; Kersten, S. R. A.; *J. Anal. Appl. Pyrolysis* **2019**, *139*, 233. [Crossref]
19. Thangalazhy-Gopakumar, S.; Adhikari, S.; Ravindran, H.; Gupta, R. B.; Fasina, O.; Tu, M.; Fernando, S. D.; *Bioresour. Technol.* **2010**, *101*, 8389. [Crossref]
20. Liu, Y.; Shi, Q.; Zhang, Y.; He, Y.; Chung, K. H.; Zhao, S.; Xu, C.; *Energy Fuels* **2012**, *26*, 4532. [Crossref]
21. Aho, A.; Kumar, N.; Eränen, K.; Salmi, T.; Hupa, M.; Murzin, D. Y.; *Fuel* **2008**, *87*, 2493. [Crossref]
22. Olcese, R.; Carré, V.; Aubriet, F.; Dufour, A.; *Energy Fuels* **2013**, *27*, 2135. [Crossref]
23. Akhtar, J.; Amin, N. S.; *Renewable Sustainable Energy Rev.* **2012**, *16*, 5101. [Crossref]
24. Schneider, J. K.; da Cunha, M. E.; dos Santos, A. L.; Maciel, G. P. S.; Brasil, M. C.; Pinho, A. R.; Mendes, F. L.; Jacques, R. A.; Caramão, E. B.; *J. Chromatogr. A* **2014**, *1356*, 236. [Crossref]
25. Mendes, F. L.; Ximenes, V. L.; de Almeida, M. B. B.; Azevedo, D. A.; Tessarolo, N. S.; Pinho, A. R.; *J. Anal. Appl. Pyrolysis* **2016**, *122*, 395. [Crossref]
26. Atutxa, A.; Aguado, R.; Gayubo, A. G.; Olazar, M.; Bilbao, J.; *Energy Fuels* **2005**, *19*, 765. [Crossref]
27. Mercader, F. M.; Groeneveld, M. J.; Kersten, S. R. A.; Way, N. W. J.; Schaverien, C. J.; Hogendoorn, J. A.; *Appl. Catal., B* **2010**, *96*, 57. [Crossref]
28. Thegarid, N.; Fogassy, G.; Schuurman, Y.; Mirodatos, C.; Stefanidis, S.; Iliopoulou, E. F.; Kalogiannis, K.; Lappas, A. A.; *Appl. Catal., B* **2014**, *145*, 161. [Crossref]
29. Farrapeira, R. O.; Andrade, Y. B.; Schena, T.; Schneider, J. K.; von Muhlen, C.; Bjerk, T. R.; Krause, L. C.; Caramão, E. B.; *Ind. Eng. Chem. Res.* **2022**, *61*, 9567. [Crossref]

30. Panwar, N. L.; Paul, A. S.; *Environ. Eng. Res.* **2020**, *26*, 200382. [Crossref]
31. Rahman, S.; Helleur, R.; MacQuarrie, S.; Papari, S.; Hawboldt, K.; *Sep. Purif. Technol.* **2018**, *194*, 123. [Crossref]
32. Suota, M. J.; Simionatto, E. L.; Scharf, D. R.; Meier, H. F.; Wiggers, V. R.; *Energy Fuels* **2019**, *33*, 9886. [Crossref]
33. Ren, S.; Ye, X. P.; Borole, A. P.; *J. Anal. Appl. Pyrolysis* **2017**, *123*, 30. [Crossref]
34. Zhang, X.; Ma, H.; Wu, S.; Jiang, W.; Wei, W.; Lei, M.; *Fuel* **2019**, *242*, 587. [Crossref]

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