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Review

Bio-Oil: The Next-Generation Source of Chemicals

Henrique Machado [1], Ana F. Cristino [2], Sofia Orišková [1] and Rui Galhano dos Santos [1,*]

[1] Centre for Natural Resources and the Environment (CERENA), Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; henrimac97@gmail.com (H.M.); sofia.oriskova@tecnico.ulisboa.pt (S.O.)

[2] Centro de Química Estrutural, Institute of Molecular Sciences and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal; afcristino@fc.ul.pt

* Correspondence: rui.galhano@ist.utl.pt

Abstract: Bio-oil, although rich in chemical species, is primarily used as fuel oil, due to its greater calorific power when compared to the biomass from which it is made. The incomplete understanding of how to explore its chemical potential as a source of value-added chemicals and, therefore, a supply of intermediary chemical species is due to the diverse composition of bio-oil. Being biomass-based, making it subject to composition changes, bio-oil is obtained via different processes, the two most common being fast pyrolysis and hydrothermal liquefaction. Different methods result in different bio-oil compositions even from the same original biomass. Understanding which biomass source and process results in a particular chemical makeup is of interest to those concerned with the refinement or direct application in chemical reactions of bio-oil. This paper presents a summary of published bio-oil production methods, origin biomass, and the resulting composition.

Keywords: bio-oil; hydrothermal liquefaction; pyrolysis; biomass

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1. Introduction

As the dialogue concerning climate change and carbon neutrality deepens, the human reliance on fossil fuels is greatly criticized. At the same time, climate change creates new concerns, which obligate us, as an inventive and adaptive species, to find strategies to battle adversity. This also presents a necessity to think seriously about how human activities influence the environment. Keeping these issues in mind while designing these new strategies is the key to carbon neutrality.

Frequent and severe forest fires are only preventable if there is a commitment to cleaning and caring for forested areas. During this process, significant volumes of organic matter are collected, which could be employed in new applications, such as using them as raw material, thus turning waste into an asset. Bio-oil production is an appealing concept for generating fuel from lignocellulosic biomatter, or other biomass, while also reducing dependence on fossil fuels. Recent approaches to reducing dependency on fossil fuels, such as biorefineries, may have lignocellulosic-rich biomass as a by-product [1], further increasing bio-oil feedstock availability. Bio-oil has a higher heating value when compared to its feedstock, and when burned, it can potentially generate a lower amount of greenhouse gas when compared to fossil fuels [2]. Therefore, its most studied application is still as a burning fuel, but other applications are emerging due to its composition, as is the case of foams and resins [3]. The latter applications emphasize the potential of bio-oil as a source of value-added chemicals.

Many sources of feedstocks have been studied [4–6] along with their applications as fuels, chemical sources, or raw materials in direct applications. A great deal of recent research has investigated ways to improve bio-oil performance as fuels: the use of catalysts, feedstock pre-treatment, and bio-oil upgrading to enrich the resulting bio-oil in hydrocarbons, therefore making it less abundant in N- and O-containing compounds [7]. However,

the presence of these compounds also highlights the possibility of having bio-oils as a source of chemical species or for direct application in chemical industries.

This work aims to give a brief introduction to bio-oil as a chemical source, serving as a referral point of the recent research on bio-oil production while commenting on the path previous research on the subject has taken.

2. Thermochemical Processes

Bio-oil is obtained via an array of thermochemical processes. The most common of these processes are pyrolysis and hydrothermal liquefaction [6–16]. These processes convert a given feedstock into bio-oil, biochar, and gas, with their composition dependent on feedstock type, pre-treatment, process, operating conditions, and later upgrading [5,8,9].

Pyrolysis processes are characterized by processing temperatures as high as 600 °C [10,11], shorter reaction times, and the necessity to dry feedstock before processing. Hydrothermal liquefaction eliminates the need for feedstock drying and utilizes water as a solvent at lower temperatures, but may require the application of pressures from 5 to 20 MPa [12]. Thermal liquefaction usually refers to processes, such as hydrothermal liquefaction, but utilizes organic solvents such as ethanol and acetone. In all of these processes, catalysts are frequently employed to modulate resulting bio-oil composition and improve the yield of total bio-oil or specific components [10].

Some authors also distinguish between light and heavy bio-oil, both making up for the entire bio-oil fraction extracted from a biomass source. The liquid fraction resulting from the thermochemical process is called light oil, and it is richer in phenols, ketones, and aldehydes than its source material. The solid portion is further extracted with an organic solvent, and a heavy oil is therefore obtained. It has a higher viscosity, associated with a higher content of longer hydrocarbons [13]. Two phases may be present when the water content in bio-oil exceeds a certain wt.%, thus creating the so-called water-soluble and organic phases [14].

Most researchers choose pyrolysis processes over hydrothermal and thermal liquefaction, which only represent about 30% of recent studies. In addition to resulting in different bio-oil compositions, their associated costs are also different. One study, which compared the economic viability of bio-oil production from palm residues, found pyrolysis to have almost double the cost of a hydrothermal process [15]. The authors also concluded that achieving higher bio-oil yields would reduce costs more than improving the energetic efficiency of the applied process. Research on producing bio-oil in the last 5 years has also mostly focused on fuel making, about 70%, when compared to other applications, as seen in Figure 1.

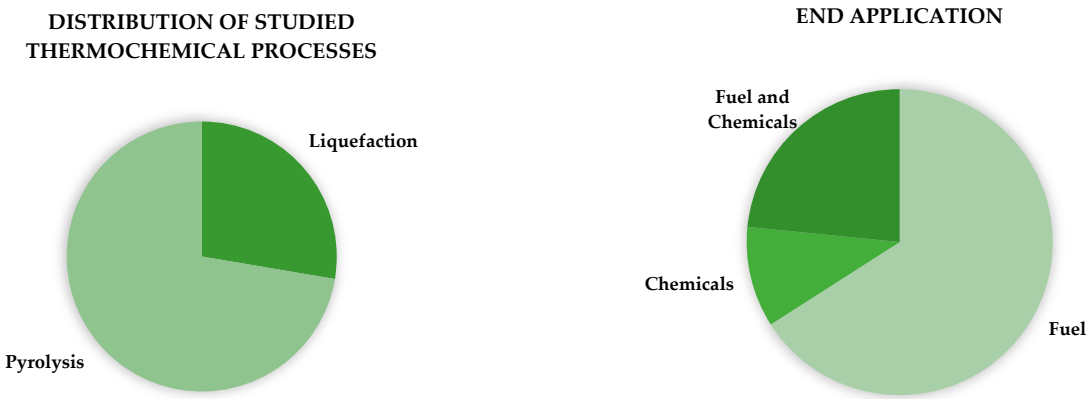

Figure 1. Distribution of thermochemical processes and end application from bio-oil production research in the last 5 years (according to a search made in Web of Science).

Previous literature has already observed that pyrolysis bio-oil research frequently uses some sort of high-volume and low-value agricultural residue (rice husk or straw, wheat

straw or some form of oil palm residue) as feedstock [5]. This is still somewhat true today, as many of the works presented in this paper still make use of one of these feedstocks. Research that focuses on other, more uncommon biomasses mostly focus on fuel production and thus are often absent in information useful for other applications.

In Tables 1 and 2, an overview is given on the most recent studies involving the thermo-chemical liquefaction and pyrolysis of several feedstocks to produce bio-oil. The application and conversion yields (%) are presented for all studies.

Table 1. Summary of thermochemical liquefaction bio-oil references.

Feedstock	Thermochemical Process	Application	Yield (%)	Ref.
Amphiroa fragilissima	HTL	Fuel	29	[16]
Animal manure	HTL	Fuel and Chemicals	31	[17]
Cellulose	HTL	Fuel	-	[18]
Corn stover	HTL	Fuel	29	[19]
Corn straw	HTL	Fuel and Chemicals	8	[20]
Cow dung	HTL	Fuel and Chemicals	57	[21]
Dunaliella sp	HTL	Fuel	13	[22]
Eucalyptus	TL	Chemicals	30	[23]
Eucalyptus globulus	TL	Fuel	96	[24]
Hay	HTL	Fuel	-	[18]
Karanja press seed cake	TL	Fuel	99	[25]
Lemon Peel and Spirulina Platensis	HTL	Fuel	26	[26]
Lignin	TL	Fuel and Chemicals	63	[27]
Miscanthus	HTL	Fuel	26	[28]
Nostoc ellipsosporum	HTL	Chemicals	25	[29]
Oak wood	HTL	Fuel	-	[18]
Palm kernel shell	HTL	Fuel and Chemicals	16	[30]
Peanut straw	HTL	Fuel and Chemicals	15	[20]
Pinewood shaves	TL	Fuel	99	[31]
Pinus ponderosa	HTL	Fuel	16	[1]
Poplar	HTL	Fuel	20	[32]
Potato peels	TL	Fuel and Chemicals	80	[33]
Rhodococcus opacus	HTL	Fuel	27	[34]
Rice husk	HTL	Fuel and Chemicals	60	[21]
Rice straw	CHTL	Chemicals	-	[35]
Rice straw	CHTL	Fuel	67	[36]
Rice straw	HTL	Chemicals	48	[35]
Rice straw	HTL	Fuel	30	[13]
Rice straw	TL	Fuel	23	[37]
Rice straw	HTL	Fuel and Chemicals	15	[20]
Rice Straw and municipal sewage sludge	TL	Fuel	32	[37]
Scenedesmus obliquus	HTL	Fuel	40	[38]
Sewage sludge	HTL	Fuel	25	[28]
Soybean straw	HTL	Fuel and Chemicals	16	[20]
Spirulina	TL	Fuel	50	[39]
Spirulina	HTL	Fuel	33	[28]
Spirulina platensis, pre-treated	HTL	Fuel	50	[40]
Switchgrass	TL	Fuel and Chemicals	40	[41]
Walnut shell	HTL	Fuel	-	[18]
Woodchips	TL	Fuel	27	[37]
Woodchips and municipal sewage sludge	TL	Fuel	32	[37]

HTL—hydrothermal liquefaction; TL—thermal liquefaction; CHTL—catalytic hydrothermal liquefaction.

Table 2. Summary of pyrolysis bio-oil references.

Feedstock	Thermochemical Process	Application	Yield (%)	Ref.
Acacia cincinnata	IP	Fuel	53	[42]
Acacia holosericea	IP	Fuel	47	[42]
Acacia mangium	CP	Fuel	45	[43]
Acacia sawdust	P	Fuel	29–45	[44]
Amphiroa fragilissima	P	Fuel	33	[16]
Bamboo	P	Fuel	47	[45]
Bamboo residues	P	Fuel	45	[46]
Brewery residue	Co-P	Fuel and Chemicals	56	[47]
Camellia oleifera shell	MP	Fuel	27	[48]
Cassava peel	P	Chemicals	-	[49]
Cellulose	FP	Chemicals	61–85	[50]
Chlorella vulgaris	CP	Fuel	20	[51]
Chlorella vulgaris	FP	Fuel and Chemicals	-	[52]
Coconut fibers	P	Chemicals	-	[49]
Coconut shells	P	Fuel	50	[46]
Coffee silverskin	P	Chemicals	-	[49]
Corncobs	P	Fuel	44	[46]
Corrugated cardboard	P	Fuel	47	[53]
Cotton seed	FP	Fuel		[54]
Cotton seeds	P	Chemicals	-	[49]
Cotton stalk	CP	Fuel	53–56	[55]
Crambe seeds	P	Chemicals	-	[49]
Crofton weed	P	Fuel and Chemicals	29	[56]
Duckweed	P	Chemicals	-	[49]
Enteromorpha clathrate	P	Fuel	-	[57]
Eucalyptus grandis	CP	Fuel	12–29	[58]
Eucalyptus sawdust	P	Chemicals	-	[49]
Extracted marine *chlorella* sp. residue	MP	Fuel	46	[59]
Food waste	MP	Fuel and Chemicals	30	[60]
Forest residue	Co-P	Fuel	23	[61]
Giant miscanthus	FP	Fuel	50	[62]
Hardwood	P	Fuel	55	[63]
Hemicellulose	FP	Chemicals	34–56	[50]
Imperata cylindrica	P	Fuel and Chemicals	37	[64]
Lactuca scariola	CP	Fuel	34	[65]
Larch sawdust	CP	Chemicals	-	[66]
Lemon myrtle	P	Fuel and Chemicals	39	[67]
Lignin	FP	Fuel	30	[68]
Lignin	FP	Chemicals	27–55	[50]
Mahua seed	P	Fuel	50	[69]
Mango seeds	P	Chemicals	-	[49]
Moso bamboo	MP	Fuel	30	[70]
Municipal solid waste	IP	Chemicals	11	[71]
Napier grass	FP	Fuel	33	[72]
Neem bark	P	Fuel	38	[45]
Oily sludge and rice husk	Co-P	Fuel	72	[73]
Olive pomace	MP	Fuel and Chemicals	30	[74]
Olive pruning residue, *olea europea*	MP	Chemicals	40	[75]
Organosolv lignin	P	Fuel	30	[76]
Palm empty fruit bunch	FP	Fuel	64	[77]
Palm empty fruit bunch	MP	Chemicals	38	[78]
Palm kernel shell and sludge	Co-P	Fuel	41	[79]
Palm shell	P	Fuel	73	[80]
Peach cores	P	Chemicals	-	[49]
Peanut shell	P	Chemicals	-	[49]

Table 2. *Cont.*

Feedstock	Thermochemical Process	Application	Yield (%)	Ref.
Pine	P	Fuel	48	[81]
Pine needles	CP	Fuel and Chemicals	51	[82]
Pineapple leaves	P	Chemicals	-	[49]
Pinewood sawdust	FCo-P	Fuel	72	[83]
Populus wood	FP	Fuel and Chemicals	63	[84]
Posidonia oceanica	CP	Fuel and Chemicals	51	[85]
Red cedar	FP	Fuel	53	[86]
Rice husk	P	Chemicals	-	[49]
Rice husk	P	Fuel	15	[87]
Rice husk	CFP	Fuel	47	[88]
Rice husk	FP	Fuel	48	[89]
Rice husk	P	Fuel	42	[45]
Rice husk	P	Fuel and Chemicals	75	[90]
Rice straw	MP	Fuel	32	[48]
Rice straw	P	Fuel	33	[91]
Rice straw	MP	Fuel and Chemicals	30	[92]
Sawdust	FP	Fuel	60	[62]
Scrap tire and pinewood sawdust	FCo-P	Fuel	55	[83]
Scrap tire and sugarcane bagasse	Co-P	Fuel	50	[93]
Sewage sludge	MP	Fuel and Chemicals	75	[94]
Softwood	P	Fuel	50	[76]
Softwood	FP	Fuel	31	[95]
Spent coffee grounds	P	Chemicals	-	[49]
Spruce wood	FP	Fuel and Chemicals	65	[84]
Sugarcane bagasse	P	Fuel	39	[45]
Sugarcane bagasse	CP	Fuel	30	[96]
Sugarcane bagasse	P	Chemicals	-	[49]
Sugarcane bagasse	P	Fuel	53	[91]
Sweet lime	P	Fuel	28	[97]
Sweet sorghum bagasse	FP	Chemicals	50	[98]
Switchgrass	P	Fuel	46	[81]
Switchgrass and pine	P	Fuel	45	[81]
Tobacco seeds	P	Chemicals	14–47	[49]
Tobacco wastes	P	Fuel and Chemicals	67	[99]
Tomato peel	P	Fuel	40	[100]
Tulip tree	CP	Fuel	49	[101]
Waste cooking oil	MP	Fuel	40	[102]
Wheat stalk	FP	Fuel	-	[103]
Wheat straw	P	Fuel	37	[91]
Wheat straw	P	Fuel	60	[104]
Wheat straw	P	Fuel	42	[105]
Coffee silverskin	P	Chemicals	15	[106]
Gelidium sesquipedale	P	Fuel and Chemicals	24	[107]

IP—intermediate pyrolysis; CP—catalytic pyrolysis; P—pyrolysis; Co-P—co-pyrolysis; MP—microwave pyrolysis; FP—fast pyrolysis.

3. Thermochemical Conversion Routes of Biomass

Feedstock cellulose, hemicellulose, and lignin contents affect the resulting bio-oil chemical composition as they individually contribute to different chemical groups, as can be seen in Table 3. Cellulose and hemicellulose thermochemical conversion mostly results in anhydrous sugars, furans, pyrans, light oxygenated compounds, and some phenolic species. Lignin, in turn, produces high quantities of phenolic compounds, such as methoxyphenols, aldehydes, ketones, and light oxygenated species [50].

Table 3. Summary of fast pyrolysis products of cellulose, hemicellulose, and lignin. Adapted from [50].

Feedstock	Contents (%)				
	Phenols	**Phenolic Aldehydes and Ketones**	**Furans**	**Anhydro-Sugars**	**Other O Containing**
Cellulose	-	-	11–17	40–77	0–40
Hemicellulose	0–13	-	26–58	6–28	2–67
Lignin	44–65	25–55	-	-	1–10

This is due to the depolymerization of cellulose, hemicellulose, and lignin, with following dehydration, reduction, retro-aldol, decarboxylation and deamination reactions [88,108]. At the end stages of the reaction, oxidation, isomerization, esterification, and aromatization may occur. During pyrolysis, these reactions occur in the gas phase, while during hydrothermal and thermal liquefaction, they take place in the solvent.

A few authors have tried to relate lignocellulosic contents to final bio-oil compositions [18,49,109–111], but correlations seem insufficient to accurately predict the bio-oil composition for a given feedstock [50], with some arriving at the conclusion that even ash content has an influence on final bio-oil compositions [112].

Cellulose affects the thermochemical conversion of lignin and vice versa [10]. Combining various feedstock sources can result in interesting outcomes, either by improving bio-oil yield or by causing changes in composition, as demonstrated in the work of Leng et al. [37]. Authors were able to increase the contents of specific chemical groups beyond the amount obtained from the isolated feedstocks and decrease others through a combination of lignocellulosic matter in varying proportions. However, others who tried similar approaches did not achieve the same results [93]—this further highlights how biomass and bio-oil composition have a more complex than simple correlation.

Nevertheless, it could be considered that since lignin decomposes at higher temperatures than cellulose and hemicellulose, increases in processing temperatures result in higher yields of bio-oil as opposed to bio-char yield. Bio-oil portions of phenols, ketones, and aldehydes should also increase, as they are lignin conversion products.

Since biomass such as algae [113], bacteria [114] and food waste [115] are instead rich in proteins and lipids rather than cellulose and lignin, their thermochemical conversion products are mostly N-containing compounds and fatty acids. In Figure 2, a general proposal of the chemical groups that derive from biomass is shown.

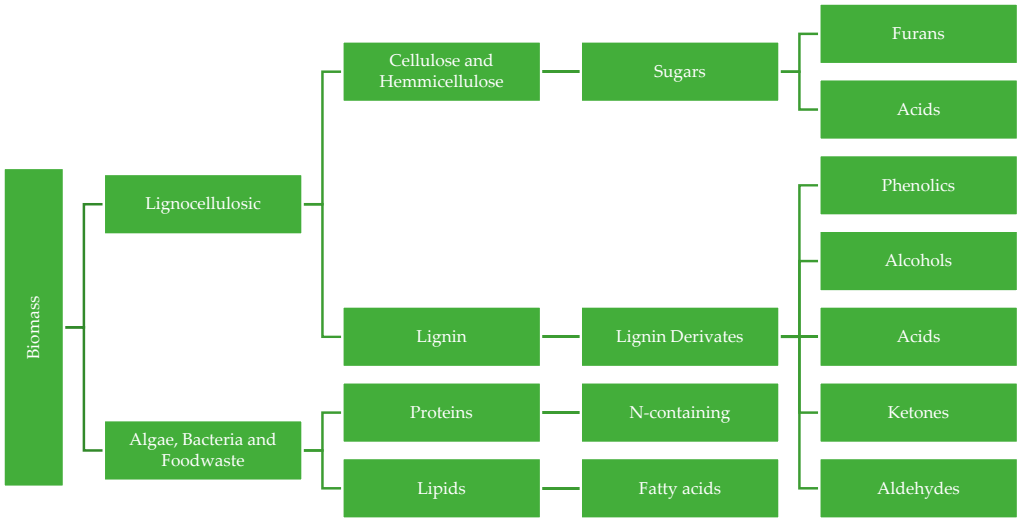

Figure 2. Proposed chemical groups derived from biomass components.

4. Bio-Oil Chemical Composition and Characteristics

4.1. General Traits

Since bio-oil is a product of lignocellulosic thermal conversion, it constitutes a blend of phenols, aldehydes, ketones, furans, alcohols, acids, hydrocarbons, and many others depending on its feedstock [10,116]. Its production process, operating conditions, pre-treatments of the feedstock [117], or later upgrading techniques [118] also determine the final composition. Table 4 summarizes typical bio-oil attributes, even though recent studies have managed to achieve better-performing traits with increased heating values and pH and lower water content and viscosity.

Table 4. Summary of typical bio-oil characteristics. Adapted from [119,120].

					Elemental Composition wt%				
Viscosity	**Relative Density**	**pH**	**Water Content**	**Heating Value**	**O**	**N**	**C**	**H**	**Ash**
25–100 cP	1.1–1.2	2.8–4	15–30 wt%	16–26 MJ/kg	27–40	0.05–1	55–64	5–8	0.03–0.3%

Although naturally rich in N- and O-containing compounds, such values translate into thermal instability and a tendency toward corrosiveness. These traits, together with high viscosity and water content, are suboptimal for fuel applications, and thus, many seek to reduce the amount of N and O compounds in bio-oil, further improving its behavior and efficiency as fuel.

Many of the works in Tables 1 and 2 compare the achieved bio-oil composition with mineral fuels or are concerned with improving thermal capabilities. Naturally, this is of interest if the goal is its application in fuel, cracking, or fractioning processes (such as with petroleum). Nevertheless, bio-oil has proven to have other interesting applications due to its phenolic compounds, for example. In addition, increasing bio-oil fuel performance involves catalysts and upgrading techniques, increasing the production cost. Moreover, currently, bio-oil production as a fuel substitute is not considered to be economically attractive enough to pose a serious alternative to fossil fuels [59].

Biomass is thermochemically converted into bio-oils of varying compositions with the high dispersity of chemical species. If we could control the bio-oil chemical composition, we would be able to manufacture bio-oil with a direct application in mind or as an intermediary to chemicals. This could be achieved via the careful selection of feedstocks, operation conditions and the employment of catalysts. High concentrations of specific chemical species are present in some bio-oils, as shown in Tables 5 and 6. Though, for the same feedstock, some chemical groups are presented in ranges, demonstrating how authors managed to achieve different chemical makeups through variations in methodology alone.

Table 5. Summary of approximate bio-oil compositions from works in Table 1 or others of interest.

Feedstock	Process	Contents (%)									
		Phenols	Esters	Ketones	Acids	Alcohols	Hydrocarbons	Furans	N-Containing	Aldehydes	Ref.
Cellulose	HTL	13	-	21	2	-	-	1	-	24	[18]
Corn straw	HTL	53	-	21	4	1	1	-	3	1	[20]
Hay	HTL	24	1	15	16	-	-	-	-	16	[18]
Nostoc ellipsosporum	HTL	1	3	-	8	-	25	8	-	4	[29]
Oak wood	HTL	38	-	14	5	-	-	-	-	14	[18]
Palm empty fruit bunch	HTL	7	-	16	-	-	-	-	-	-	[121]
Palm kernel shell	HTL	81	3	-	-	3	-	-	-	-	[121]
Palm mesocarp fiber	HTL	89	-	5	-	-	-	-	-	-	[121]
Peanut straw	HTL	28		26	8	1	4		6	1	[20]
Pinus ponderosa	HTL	30	4	-	5	-	-	1	-	-	[1]
Rice straw	CHTL	46	19	7	1	3	11	2	-	-	[35]
Rice straw	CHTL	28–44	-	2–12	-	5–11	-	-	5–16	-	[36]
Rice straw	HTL	45	13	16	7	5	0.5	1	-	0.1	[35]
Rice straw	HTL	25	-	9	6	9	-	-	-	-	[36]
Rice straw	HTL	46–70	-	10–42	-	1–42	-	-	-	1–2	[122]
Rice straw	HTL, heavy oil	0–2	-	4–9	0–0.5	0–13	13–28	-	9–18	-	[13]
Rice straw	HTL, light oil	14–39	0–7	8–24	2–7	0–16	0–12	0–6	0–6	3–23	[13]
Rice straw	CHTL, heavy oil	0–2	-	5–7	8–27	7–11	16–36	-	11–26	-	[13]
Rice straw	CHTL, light oil	14–41	0–1	9–25	3–8	3–27	2–13	0–2	0–0.5	1–19	[13]
Rice straw	HTL	34	-	35	1	1	5	-	4	2	[20]
Soybean straw	HTL	29	-	50	1	-	6	-	8	2	[20]
Spirulina platensis	HTL	6	20	2	1	-	7	5	37	-	[40]
Walnut shell	HTL	50	1	4	2	-	-	-	-	4	[18]

HTL—hydrothermal liquefaction; CHTL—catalytic hydrothermal liquefaction.

Table 6. Summary of approximate bio-oil compositions from works in Table 2 or others of interest.

Feedstock	Process	Contents (%)										
		Phenols	Esters	Ketones	Acids	Alcohols	Hydrocarbons	Furans	Anhydro-Sugar	N-Containing	Aldehydes	Author
Acacia mangium	CP	35	-	18	-	13	-	4	45	-	5	[43]
Bamboo residues	P	37	-	17	-	18	-	20	-	-	3	[46]
Cellulose	FP	-	-	-	-	-	-	11–17	40–77	-	-	[50]
Chlorella sp. residue	P	18	18	3	12	6	0.5	6	2	30	-	[59]
Coconut shells	P	43	-	4	-	22	-	1	-	-	6	[46]
Corncobs	P	40	-	6	-	31	-	6	-	-	-	[46]
Crofton weed	P	13	15	-	6	13	2	11	-	-	28	[56]
Hemicellulose	FP	0–13	-	-	-	-	-	26–58	6–28	-	-	[50]
Lignin	FP	44–65	-	-	-	-	-	-	-	-	-	[50]
Palm empty fruit bunch	MFP	59–73	11–16	12–19		8–9	-	-	-	3–8	-	[78]
Palm empty fruit bunch	P	12	-	-	88	-	1	-	-	-	-	[123]
Palm kernel shell	FP	17–25	-	-	19–28	-	-	-	-	-	-	[124]
Palm kernel shell	MP	71	-	-	-	-	-	-	-	-	-	[125]
Palm kernel shell and sludge	CO-P	12–22	-	-	-	-	-	1–5	-	-	-	[79]
Palm shell	P	22	-	-	4	3	-	2	-	47	1	[126]
Pinewood sawdust	CO-FP	11	-	7	6	4	-	6	5	1	8	[83]
Polyhydroxyalkanoate bacteria	P	18	-	10	46		-	-	-	21	-	[114]
Rice husk	P	8	-	6	0.2	1	-	1	-	-	1	[87]
Rice straw	P	8	4	25	-	28	-	17	5	-	-	[91]
Scrap tire and sugarcane bagasse	CO-P	52	-	12	11	11	-	-	-	-	5	[93]
Sugarcane bagasse	P	20	-	-	15	4	-	-	-	-	40	[123]
Sugarcane bagasse	P	23	3	16	-	-	-	23	24	-	-	[91]
Wheat stalk	FP	26–27	-	8	10–11	-	-	-	-	-	-	[103]
Wheat straw	P	19	12	30	-	27	-	7	0.3	-	-	[91]

CP—catalytic pyrolysis; P—pyrolysis; CO-P—co-pyrolysis; MP—microwave pyrolysis; FP—fast pyrolysis.

The following sections further describe the main compounds found in bio-oils from works in Tables 5 and 6, according to their chemical group.

4.2. Phenols

Phenolic compounds frequently make up the major portion of bio-oils since they derive from lignin. Phenol, guaiacol, cresol, eugenol, catechol, and syringol are commonly the principal phenolic compounds found in bio-oil [127,128]. The pyrolysis of bio-oil from palm waste enables the waste to be successfully converted in bio-oil (34% yield) with phenol-derived compounds of up to 90% [121], with some containing phenol as the major entity of the group, up to 65% (25% bio-oil yield) [125].

4.3. Ketones and Aldehydes

Bio-oil from sugarcane bagasse (53% yield) can contain a 40% fraction of aldehydes [123]. One study on pretreated sunflower seed hulls even attained 97% furfural content in bio-oil (33% yield) [129]. Nevertheless, aldehydes usually make up less than below 25%, often in the form of furfural, glycolaldehyde, and hydroxyacetaldehyde [127,128].

Similarly to aldehydes, ketones are often below the 25% range, but there are reports of higher concentrations, such as in the case of a rice husk bio-oil (50% yield) with 40% ketones content [122]. One of the most common ketones is hydroxyacetone [127,128].

4.4. Acids

Acetic acid, propanoic acid, levulinic acid, and fatty acids are acids that are commonly present in the highest proportions in bio-oil [127,128]. The recuperation of acetic acid from bio-oil is described by some as a viable approach to bio-oil valorization besides fuel [130], as is the case for glycolic and formic acids [131].

Bio-oil from olive pomace (30% yield), for example, can be made up of 72% acetic acid alone [74], followed by others such as moso bamboo bio-oil (30% yield), with 47% acetic acid [70], bacteria bio-oil (28% yield), with 41% acetic acid [114], or even Napier grass bio oil (33% yield), with 35% acetic acid [72]. Acids are normally present in lower levels than phenols, ketones, or aldehydes.

4.5. Sugars and Alcohols

The most common alcohols and sugars are acetol, ethylene glycol, levoglucosan, and cellobiosan [127,128]. Although they are mostly found in lower concentrations, it is possible to produce bio-oils with somewhat higher amounts of alcohol or sugar. For instance, bio-oil produced from corrugated cardboard (47% yield) achieved 20% levoglucosan content [53], while there are also reports of alcohol levels around 40% (50% bio-oil yield) [122] and 30% (33% bio-oil yield) [91].

4.6. N-Containing

N-containing compounds typically have a lower concentration in bio-oil, often on a residual level, but when they are present, they can be in somewhat high amounts, mostly when bio-oil is obtained from feedstock with elevated contents of proteins. In bio-oil made from palm residue, amines made up almost 50% of the total content, 47% alone corresponding to trimethylamine [126]. Other bio-oils with elevated levels of N-containing compounds can also be found [40,59], such as the case of food waste bio-oil with 20% 2-ethoxyethylamine and 20% methyl phosphine [60]. The bio-oil yield from these sources is below 50%.

5. Applications of Bio-Oil as Chemical Source and Its Refinement Strategies

While recent works point towards bio-oil as a chemical source of ketones, aldehydes, and acids, most applications are related to the high contents of phenolic compounds. Bio-oils rich in phenols and sugars tend to cross-polymerize over time [132,133], especially

if they contain polymerization promoters in their composition (e.g., furfural) and acids catalysts such as acetic acid [134].

In fact, there are reports of bio-oil being used to produce phenol-formaldehyde resins and adhesives [124,135–138]. Bio-oil is considered suitable by many for phenolic resins due to its high reactivity and low molecular weight [139] and is therefore regarded as a renewable alternative [140]. Sweetgum hardwood bio-oil, for example, was utilized as a partial raw material to produce phenol-formaldehyde resin adhesives with greater bonding strength than ordinary phenol-formaldehyde resin [139].

Other works describe the utilization of bio-oil to produce polyols from which polyurethane foams are later achieved with increased tensile strength and thermal stability and higher biodegradability [141–143]. Bio-oil in bitumen applications is also reported to possibly increase bitumen performance and reduced binder consumption [3,116,144–149].

Many of these more straightforward applications may sometimes still require the preparation of bio-oil to remove water and lower weight acids [136], for example. As sources of various chemical entities, the refinement of bio-oil and separation processes should be applied in other industries in need of platform chemicals. Conveniently, processes such as supercritical extraction, membrane separations, solid–liquid extractions, solvent extraction, and others are described in existing reviews and works [127,150–152], as is also the case for the adequate analytic characterization of bio-oil for chemical applications [153–156].

However, methodologies such as feedstock pre-treatments, the use of catalysts, or process enhancements often enable bio-oils to be produced with improved selectivity.

Pretreatments for feedstock are also described and often result in bio-oils with more defined chemical distribution [129,157–159], which could in turn reduce or even eliminate the need to refine or treat bio-oil after production.

Similarly, other authors obtained more than one bio-oil fraction with different chemical makeups. One study, which describes the hydrothermal liquefaction of rice husks, attained two bio-oil fractions, light and heavy. The light fraction was rich in phenols, ketones, alcohols, and aldehydes, and the heavy presented up to 36% hydrocarbon content but also 26% of N-compounds. Nevertheless, the light and heavy fractions may be deemed suitable for use in the extraction of chemicals and for fuel applications, respectively [13].

Others managed to change pyrolysis-derived bio-oil composition through condensation parameters alone, decreasing water content and increasing phenol and furfural presence [128], or through the separation of bio-oil into different condensing temperature fractions, so-called fractional condensation [90,160–162]. Fractional condensation allows for the separation of different chemically enriched fractions according to their vapor pressure [152], offering the possibility to efficiently utilize the entire biomass liquefaction condensate. Typically, lignin-derived species and sugars are obtained in higher-temperature fractions, as opposed to acids and water, which are abundant in lower-temperature fractions [163].

Heavier fractions with low water content and corrosiveness display higher heating value, thus making them suitable for fuel applications. Mid-range fractions are rich in phenol and aldehyde species, making them suitable for the partial substitution of phenolic raw material in resol resins and the production of polyurethane foams. The recovery of acids such as acetic acid is possible for the lighter, water- and acid-rich fractions [164].

With similar outcomes, there is also the possibility to generate bio-oil fractions through pyrolysis with two or more steps [165], supercritical CO_2 fractioning [166–168], or separations using ionic liquids [169,170].

6. Final Remarks and Prospects

Both pyrolysis and thermal liquefactions present advantages and disadvantages according to the selected feedstock and desired application. Pyrolysis may require previous drying of biomass in the case of less dry feedstocks, but it is possible to employ the processes of fractional condensation later, thus obtaining fractions enriched with different

chemical species and therefore suitable for different applications. This may be an adequate choice for lignocellulosic biomass, which is usually less humid and produces bio-oils with various chemical groups.

On the other hand, hydrothermal liquefactions may be more suitable for feedstocks with elevated water content such as food processing waste, algae, bacteria, or even sewage sludges. Since hydrothermal processes do not produce condensates, it is not possible to employ fractional condensation methods, and as such, the latter separation methods may be necessary. However, non-lignocellulosic feedstock bio-oils are usually rich in either N-containing species or fatty acids and their esters, which may in turn require less complex separation methods.

Naturally, it is expected that that cellulose- and hemicellulose-rich feedstocks produce bio-oils abundant in sugars and their derivates, and in turn, lignin-rich biomass produces bio-oil with higher contents of phenols, ketones, and aldehydes. However, there seems to be no direct correlation between feedstock lignocellulosic composition and resulting bio-oil chemical makeup, as the last is also heavily dependent on the chosen process, its conditions, the employment of catalysts, and is even dependent on the chemical interactions between species during thermal processing.

Bio-oil production is mostly approached as an alternative fuel allowing for the reduction in petroleum dependency while making use of organic waste, also making it a strong waste management candidate for biomatter. However, its often-high amounts of oxygenated compounds push the need to employ upgrading methods [171,172]. This need places bio-oil fuel production above the viable economic cost, and this is why much recent research focusses on the co-processing of bio-oil and fossil fuel as a cost-effective way to transition to biofuels made from bio-oil [151,173–175]. It should be noted that bio-oil economics and viability for fuel purposes are usually measured against fossil fuels that, besides being an already established industry, are often subject to government subsidies.

Besides its undeniable potential as biofuel, bio-oil chemical makeup could be so valuable that it is difficult to understand why so little research has been carried out for other applications when compared to that of biofuel, but this is probably due to governments pushing the need to reduce greenhouse gas emissions in fuel and transportation sectors.

While it was previously thought that the extraction of chemicals from bio-oil was not advantageous due to low specific chemical contents and the high economic cost of separation processes [116], recent works suggest that it is possible to obtain more component-specific bio-oils. Additionally, even the co-processing of bio-oil may still require bio-oil to be upgraded [176], thus raising the question whether separation processes are that disadvantageous when compared to upgrading.

It has been shown that bio-oil composition could be somewhat modified and enhanced through the selection of feedstock, the employment of catalysts or pretreatments, or changes in processing parameters. The utilization of bio-oil in resin, foam, and bitumen making also resulted in some better performing products. An application of bio-oil as a successful insecticidal product is also described.

Additionally, via some thermochemical processes, it is also possible to obtain two bio-oil fractions, the light and heavy. The light fraction, abundant in oxygenated compounds, could certainly be further separated and value-added chemicals could be obtained, or it could be utilized as raw material in resin making, allowing bio-based polymers to be produced. The heavy fraction is in turn rich in hydrocarbons and low in the problematic oxygenated compounds and water, thus making it suitable for fuel oil and possibly requiring less upgrading, thus lowering costs. Other similar approaches of bio-oil fractioning through the control of condenser temperatures or two-step conversions were also able to separate bio-oil into fractions with different compositions.

Phenolic species are often the most sought after in the chemical valuing of bio-oil due to their natural high concentration. However, works on bio-oil from feedstock such as algae and food waste can also deliver considerable concentrations of other chemicals species while utilizing waste that is often regarded as less chemically interesting.

Bio-oil is currently produced by a handful of companies or joint ventures such as Ensyn, Chevron, Vyterra, BTG-Bioliquids, Green fuel Nordic Oy, and Secil Group either for fuel application or later co-processing at refineries such as Petrobras in Brazil, also for fuel purposes.

The production of bio-oil-based chemicals appears to still be under investigation by many of above-mentioned companies, with some even open for collaboration on the issue. Nevertheless, Kerry has been refining bio-oil from Ensyn for many years to produce food flavors and aromatics. The absence of bio-oil-based platform chemical industries somewhat mirrors the current state of research on the matter, but the interest of bio-oil producing companies on the subject further confirms the value that resides in it.

Additionally, while either bio-oil fuel or chemicals cannot, at present, be considered economically viable, such an evaluation may not prove true in the near future, as these assessments are tied to the time and place in which they are made. As mentioned, they are also compared to fossil resources and industries that are often still subject to large subsidies as opposed to bio-oils or other fossil alternatives.

There is an overall feeling that bio-oil for fuel and bio-oil for chemical applications are both disconnected faces of the same problem that could greatly benefit from each other if kept in mind together. Indeed, bio-oil appears to be a great alternative to fossil fuels, but it is possible that, as is the case for petrol, it could offer much more and thus become a well-footed competitor to fossil fuels while also acting as a serious form of waste management.

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