Challenges and Opportunities for Bio-oil Refining: A Review

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Abstract: Bio-oil derived from fast pyrolysis of lignocellulosic materials is among the most complex and inexpensive raw oils that can be produced today. Although commercial or demonstration scale fast pyrolysis units can readily produce this oil, this industry has not grown to significant commercial impact due to the lack of bio-oil market pull. This paper is a review of the challenges and opportunities for bio-oil upgrading and refining. Pyrolysis oil consists of six major fractions. (water 15-30 wt.%, light oxygenates, 8-26 wt. %, mono-phenols, 2-7 wt.%, water insoluble oligomers derived from lignin 15-25wt.%, and water soluble havey molecules 10-30 wt.%). The composition of water soluble oligomers is relatively poorly studied. In the 1880s bio-oil refining (formally known as wood distillation) targeted the separation and commercialization of C1-C4 light oxygenated compounds to produce methanol, acetic acid and acetone with the commercialization of the lignin derived water insoluble fraction for preserving wooden sailing vessels against rot. More recently Ensyn extracted and commercialized condensed natural smoke as a food additive. Most research efforts in the last twenty years have focused on the two-step hydrotreatment concept for the production of transportation fuels. In spite of major progress this concept remains at the demonstration. In this review, the opportunities and progress to separate bio-oil fractions and chemicals, mainly acetic acid (HAc), hydroxyacetaldehyde (HHA) and acetol, and convert them into value added co-products are thoroughly discussed. In spite of the large number of separation schemes and products tested, very few of them have been studied as part of fully integrated bio-oil refinery concepts. The synthesis, techno-economic and environmental evaluation of novel integrated bio-oil refinery concepts is likely to become a subject of intense research activity in the coming years.

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1. Introduction

The focus of this investigation is the chemistry, refining, fractionation and products of what is generally called fast pyrolysis bio-oil. Fast pyrolysis is a relatively mature thermochemical technology converting between 60 and 70 wt. % of lignocellulosic materials into a liquid called “pyrolysis oil" or "bio-oil”. Besides pyrolysis oil, the products of fast pyrolysis of biomass are gases and char. Liquid pyrolysis oils obtained from fast pyrolysis are generally a dark red to dark brown, acidic, single phase, and relatively low viscocity (50-672 cSt at 20 ºC)[1]. This oil typically contains between 14 and 30 wt. % of water and the remainder (70-86 wt. %) are oxygenated organic compounds (between 38 and 44 wt. % oxygen in dry basis)[2]. The carbon content of the organics is typically around 50 wt. % (dry basis)[2]. Pyrolysis oil is virtually immiscible with hydrocarbons, shows some miscibility with water and is completely soluble in low molecular weight alcohols[3]. According to Ensyn (2017)[4], fast pyrolysis oil production from renewable resources could reach 0.3 billion barrels of bio-oil per day (or 4 % of the current US consumption of 7.26 billion barrels of crude oil per day). The lack of economically viable bio-oil refining technologies is a main hurdle to deploy this technology.

There are excellent reviews on biomass pyrolysis[5–11], bio-oil chemistry[12], bio-oil fuel quality and combustion[13] and bio-oil upgrading and refining[6,9,14–23]. A book chapter on pyrolysis oil biorefinery was recently published by Meier (2017)[1]. Based on our Scopus survey with the key words “pyrolysis oil refining” The number of paper in this area has been steadily growing: 1980-1990 (130 papers), 1990-2000 (204 papers), 2000-2010 (598 papers), 2010-2017 (2,472 papers). The increase in the number of publications in bio-oil chemistry and refining in the last seven years and the lack of critical reviews in this area motivate this work. Thus, the main goal of this paper is to summarize our current understanding of bio-oil chemistry, the state of the art of bio-oil refining schemes described in the literature, the progresses made in bio-oil fractionation, products purification, the new products developed from bio-oil fractions, and the potential to develop new bio-oil refining schemes. In the first section, the overall composition of bio-oil in terms of independent compounds, chemical families and functional groups is presented. In the next section we review existing bio-oil refinery concepts and thoroughly discuss their advantages and disadvantages. The third section is devoted to a review of bio-oil fractionation and purification techniques. Strategies for biofuels production are discussed in section four. Bio-oil derived products are discussed in the last section.

2. Bio-oil Composition

The study of bio-oil chemical composition has been the subject of active research in the last twenty years[2,24–35]. Pyrolysis oil contains numerous oxygenated compounds, which include carboxylic acids, water, alcohols, esthers, anhydrosugars, furanics, phenolics, aldehydes, and ketones covering a wide range of molecular weights and functionalities[2,24,29,30,36–41]. The specific composition is directly related to the feedstock and the conditions used in their production[42–44].

Water is typically quantified by Karl Fischer titration[2] and is the most abundant bio-oil compound accounting between 15 and 30 wt. %[2] (See Figure 1). Water forms mostly from dehydration reactions of carbohydrate depolymerized products in the liquid intermediate[44]. Gas Chromatography/Mass Spectroscopy (GC/MS) is by far the most common technique for the quantification of the pyrolysis oil organic volatile fraction[2,24,27,45]. GC/MS detectable compounds typically account for between 30 and 40 wt. %[2]. Table 2 shows the range of compounds quantified by GC/MS reported in the literature. Only four molecules (glycoaldehyde, acetic acid, acetol and levoglucosan) are found in quantities sufficiently high (>5 wt. %) to justify their separation and commercialization as chemicals. Methanol can also be produced in quantities justifying its commercialization but hardwood has to be used as feedstock. The remainder of the oil if refined is likely to be commercialized as fractions (mono-phenols, pyrolytic lignin, anhydrosugars, pyrolytic humins, and hybrid oligomers).

Because bio-oil consists of hundreds of compounds with concentrations below 0.5 wt. % it is desirable to express their chemical composition in terms of few chemical groups or families[24]. This idea was first proposed by Hallet and Clark[46]. The authors[46] modeled bio-oil evaporation rates using a model based on this characterization scheme[46]. In DTG-FTIR studies with bio-oils doped with pure compounds (butyric acid, syringol, syringaldehyde, levoglucosan), Stankovikj et al.[29] observed that the compound vapor pressures were depressed in pyrolysis oils. The authors described bio-oil composition in several families based on their chemical composition and thermal behavior (see Figure 1). The first family is the C2-C4 compounds (mainly hydroxyacetaldehyde, acetol and acetic acid) typically quantified by GC/MS[2,42,47–49] (see Table

2). This fraction is formed from carbohydrates fragmentation reactions and represents between 8 and 26 wt. % of the oil [2,50] (See Figure 1). The second family is formed by mono-phenols with small quantities of furans (typically 2 to 7 wt. % of bio-oil). These molecules are also typically quantified by GC/MS[2] and are formed from the depolymerization of lignin or its oligomeric products[50]. The compounds not identified by GC/MS are heavy oligomers. The third family is formed by lignin derived oligomers also known as “pyrolytic lignin” which is quantified by cold water precipitation[33]. This fraction is collected in the form of a water insoluble powder at typically between 7 and 24 wt. % of the oil[2]. The lignin oligomers are formed from lignin depolymerization into a liquid intermediate and are removed by thermal ejection[51]. This fraction has been thoroughly characterized[33–35, 52]. The water soluble fraction contains carbohydrates (mono and oligo anhydrosugars) and other poorly characterized oligomers[2,24,45]. The sugars in this fraction are derived from the depolymerization of cellulose and hemicellulose and can be quantified by the sulfuric acid assay[2,44]. Levoglucosan, cellobiosan and cellotriosan are the main carbohydrates found in pyrolysis oils[53] (12 and 17 wt. %[2]). Studies by ICR-MS and UV-Fluorescence of the water soluble fractions and the whole pyrolysis oil[2,29] point to the existence of two other oligomeric fractions soluble in water: pyrolytic humins, and hybrid oligomers (products of carbohydrate and lignin reaction). Standards strategies to separate, quantify and characterize these fractions are lacking[2].

Table 1. Main pyrolysis oil compounds identified and quantified by GC/MS (wt. %)[2, 43]

No.	**Compound**	**Range**
C2-C4 molecules		
1	Glycolaldehyde	1.0-13.7
2	Acetic acid	2.5-8.7
3	Acetol	2.6-8.6
5	Propanoic acid	0.2-2.8
Mono-phenols and mono-furans		
7	2-cyclopenten-1-one	0.1-0.2
8	Furfural	0.1-0.6
11	2(5H)-furanone	0.1-0.8
12	3-methyl-1,2-cyclopentanedione	0.3-0.5
13	Methyl-2(5H)-furanone	0.0-0.2
14	Phenol	0.0-0.9
15	Guaiacol	0.1-0.5
20	Creosol	0.1-0.5
21	2,4-xylenol	0.0-0.0
22	4-ethylguaiacol	0.0-0.1
23	Eugenol	0.1-0.6
25	Catechol	0.2-0.9
26	Syringol	0.0-0.4
27	4-methylcatechol	0.0-0.5
28	Vanillin	0.1-1.5
32	Syringylaldehyde	0.0-0.1
Mono-sugars		
34	Levoglucosan	3.0-6.5

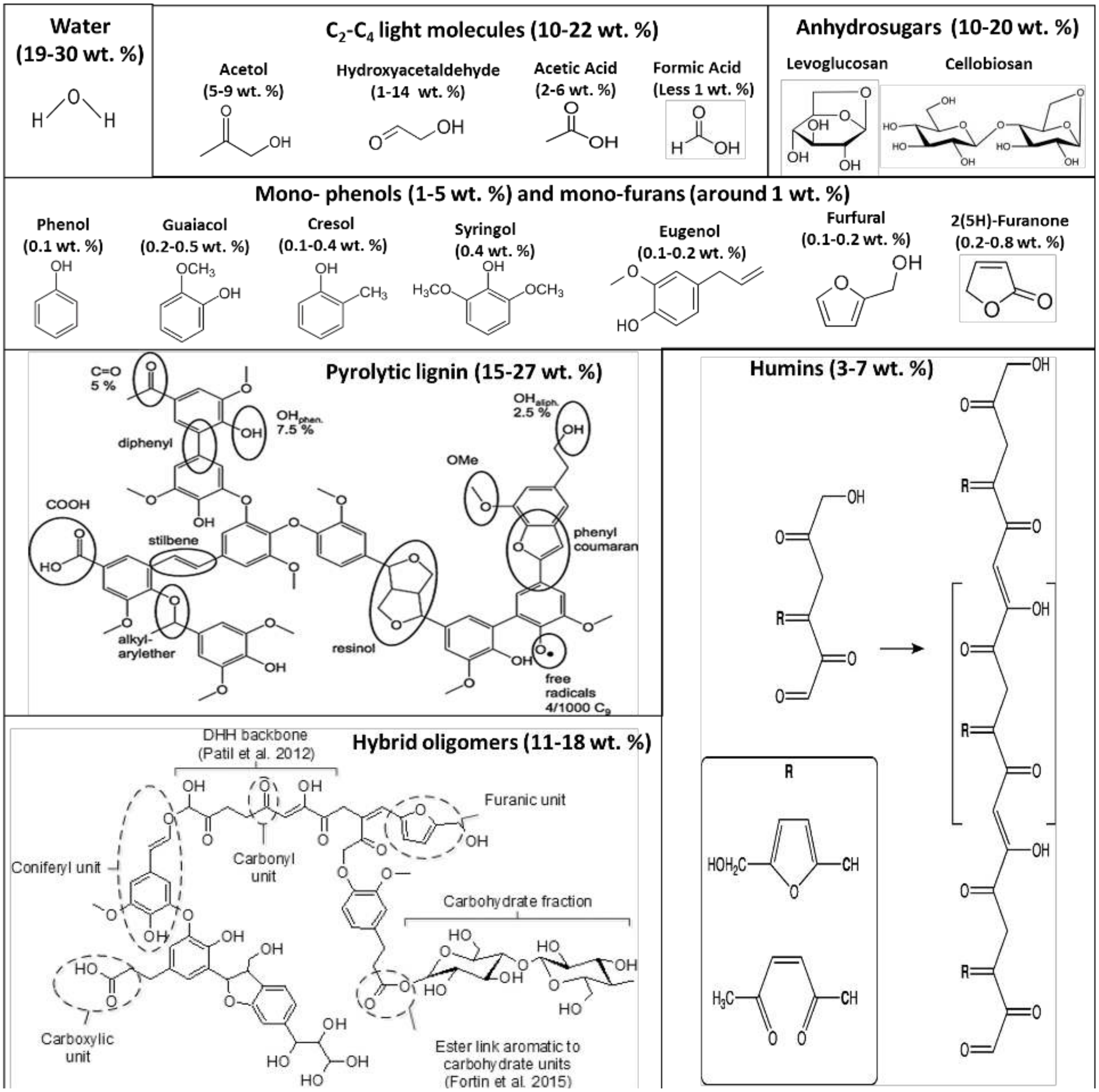


Figure 1. Representative molecules of each of bio-oil fractions

The bio-oil compounds can also be described in terms of functional groups, namely: acids, alcohols, aldehydes, esters, ketones and phenols (see Table 2)[2]. Stankovikj et al.[2] compared the content of functional groups in the whole oil with the content of these groups estimated from GC/MS and concluded that between 85 and 95 % of the phenols, and 33 to 48 wt. % of the acid functional groups in pyrolysis oils are in the form or oligomers Although the GC/MS detectable compounds only represent 30 wt. % of the whole oil, it accounts for half of the very reactive carbonyl and carboxyl functional groups[2].

Table 2. Methods for the quantification of functional groups in pyrolysis oils and range of values[29, 31]

Functional group	[mmol/g]	Quantification Method
Carbonyl	2.8-5.3	Carbonyl titration
Carboxylic acids	0.5-2.6	^{31}P-NMR
Phenolics	0.9-3.9	^{31}P-NMR
Aliphatic alcohols	3.3-5.4	^{31}P-NMR
Total Acid number (mg KOH/g)	181-188	Potentiometric titration

3. Review of Existing Bio-oil Refinery Concepts

3.1. Wood distillation industry

Figure 2 shows is an overview of the historic hardwood distillation industry from the nineteen and early part of the twenty century. This industry produced charcoal, tars, acetone and wood naphtha (C1 to C4 compounds) mostly from hardwoods. When a single condensation step was used, the liquid naturally separates into a decanted tar (formed mostly from lignin derived compounds)[54] and an aqueous phase rich in C1-C4 molecules and dissolved tar (heavy oligomers derived from cellulose and hemicellulose)[54]. Dissolved tar is then obtained via distillation of the aqueous phase (also known as pyrolygneous water). The C2-C4 rich vapors produced in the distillation steps (see Figure 2) were recovered in a limewash vessel as lime acetate and crude wood naphta. The lime acetate was dry-evaporated using drums at temperature up to 180°C. This acetate was known as gray acetate and contained 80 wt. % calcium acetate[55]. When decomposed with sulfuric acid, the gray acetate produced 85 % acetic acid. Acetone could be obtained by heating the gray acetate to 400-500°C and purifying the crude acetone through rectification[55] (see Figure 2). Crude wood naphtha was separated into methanol, water and other organics in a rectification column.

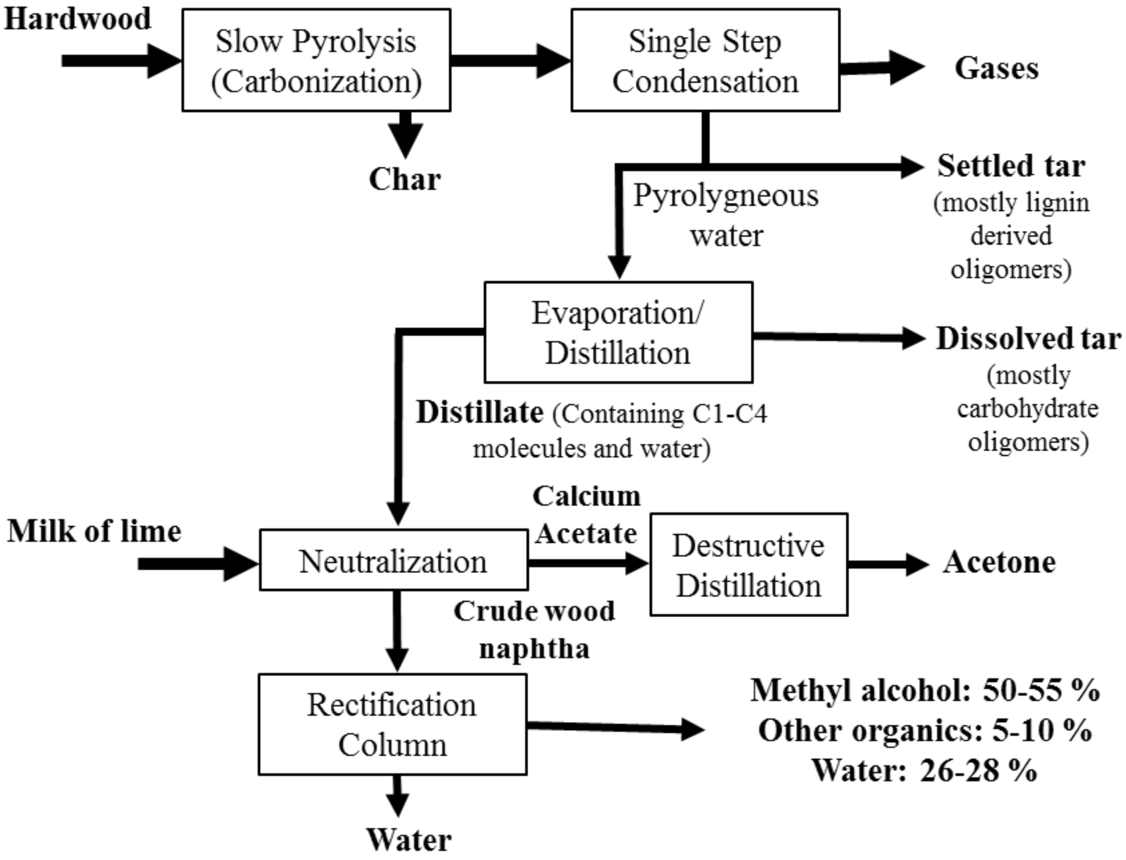


Figure 2. Overview of the old wood distillation industry. The products are in dashed boxes. Adapted from[56]

Acetic acid in the pyrolygneous water could also be recovered by distillation[55]. The first option was a direct method, in which pyroligneous acid was distilled from a weak acid solution and toluene was used to draw off the moisture of the mixture. The second option, slightly more sophisticated, consisted in a two stage process. The solution obtained from the first distillation was mixed with xylene, which formed a low-boiling-point-binary mixture with water. After concentrating acetic acid from the first stage, it undergoes a second distillation with benzene to form a new mixture[55]. Products Chemiques de Clamancy and Lambiotte Brother plant[55] devised a method in which moisture was eliminated either by distilling an azeotrope formed with butyl acetate or by circulating butyl acetate in a counter-current tar reactor with the wood spirit[55].

3.2. Two steps hydrotreatment

The production of drop-in fuels from pyrolysis oils has received increasing attention in the last thirty years[57,58]. Elliot[59], and, Wang et al.[60], provide a good review of the advances in catalytic hydroprocessing of bio-oils, including the catalysts used on hydrotreating/hydrocracking tests. Early work on bio-oil hydrotreatment was conducted at the Pacific Northwest National Lab (PNNL) using catalysts from petroleum processing (sulfided NiMo/Al_2O_3 and CoMo/Al_2O_3 catalysts)[61] resulting in a hydrocarbon rich product but incurring high hydrogen consumption [4-6 kg H_2 per 100 kg bio-oil]. Supported noble metals, such as Ru, Pd, Pt, and Rh, have recently been investigated as hydrotreating catalysts[60, 62].

The two-stage method was patented by PNNL[63,64] (see Figure 3). The first reactor, or the stabilization reactor, is operated at 150-300 ºC. Although the goal of this step is to convert carbonyl and carboxyl functional groups into alcohols, other reactions such as decarboxylation (CO_2 generation), re-polymerization (water production), and hydrotreating also take place[65,66]. Another important goal of stabilization is to convert sugars into sugar alcohols by hydrogenation, to avoid coking during the deoxygenation and hydrocracking in the second step[67]. Stabilization is challenging because an important fraction of the targeted very reactive functional groups is in the form of heavy oligomeric compounds (40 mol. % of the carboxylic acids, 50 mol. % of the carbonyl and 90 mol. % of the phenols are in oligomeric form)[29]. Deep hydrodeoxygenation and hydrocracking is performed in a second reactor at harsher conditions of 300-500 ºC, and 10-14 MPa[67].

Elliot *et al.*[68, 69] used a Pd on carbon (Pd/C) catalyst at the bench-scale, in a fixed-bed reactor for the hydrotreatment of bio-oils, as a first stabilization step for bio-oil upgrading. The hydrotreatment product was then further processed through hydrodeoxygenation and hydrocracking to achieve final deoxygenation of almost 100%. Wildschut *et al.*[70] compared a range of metal catalysts (Ru/C, Ru/TiO_2, Ru/Al_2O_3, Pt/C and Pd/C) with the classic hydrotreatment catalysts (sulfided NiMo/ Al_2O_3 and CoMo/Al_2O_3), in a batch set-up, at temperatures between 250–350°C and pressures in the range of 100–200 bar. Ru/C catalysts showed to be the most promising. The deoxygenation level was up to 90 wt. %, decreasing the acidity and water content of the oil, while increasing the high heating value from 20.3 MJ/kg to

42.6 MJ/kg. Additional studies involving the use of metal catalysts in bio-oil hydrotreatment can be found elsewhere[71–73]. Another class of catalysts that has been investigated for hydrotreatment of bio-oils are the transition metal phosphides[74,75]. as reviewed elsewhere[74, 76–79].

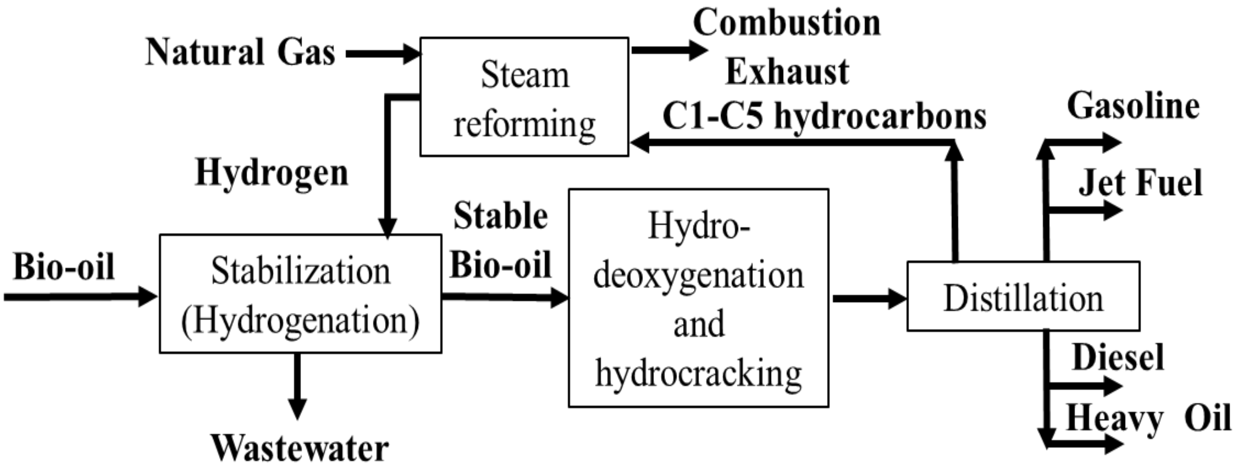


Figure 3. Hydrotreating/hydrocracking of bio-oil process flow[80]

The hydrotreatment of bio-oil consumes 3–5.8 wt. % of hydrogen, and yields approximately 41 wt. % of fuels in the naphtha and diesel range. The remaining products include CO_2, water and volatile compounds[81]. With this technology 33 wt. % of this oil can be converted into hydrocarbons[80–82]. Elliott[83] reported that 121 gallons of hydrocarbons/ton of bone dry wood can be obtained using the hydrotreatment of bio-oil[83, 84].

3.3. Co-processing of bio-oils with petroleum fractions:

Another alternative for bio-oil upgrading is the addition of the whole bio-oil, bio-oil fractions or partially upgraded bio-oil to specific petroleum fractions for further processing in conventional refinery units[85]. This strategy is commonly named co-processing or co-refining, and some examples appearing in literature will be discussed.

The level of deoxygenation of the pyrolysis oils for successful co-processing in refining remains unclear. The NREL thermochemical group[86] recommends that the oxygen content must be reduced to less than 7 wt. % before the oil can be considered stabilized and ready to be co-processed in an existing petroleum refinery. The oil is almost completely miscible with petroleum at these oxygen levels. Stabilized oil with higher oxygen content has been shown[87] to have low acidity, good volatility, and good miscibility. This oil can also be hydrocracked without coking[88]. The hydrodeoxygenated pyrolysis oil was mixed up to 10-20 wt. % with heavy petroleum fractions (i.e. gas oil, vacuum gas oil, VGO spell out) and then co-processed via catalytic cracking in lab-scale reactors using FCC and zeolite-type catalysts[89], and also in a demonstration FCC refinery unit[90]. In general, the amounts of valuable products attained, such as gasoline, naphtha, light cycle-oil (LCO), light gases, and olefins do not differ substantially from those when only a petroleum fraction is processed. The quantity and quality of biogasoline (and naphtha) produced during co-processing of pre-hydrotreated bio-oils with VGO in lab-scale FCC unit can be optimized as a function of the pyrolytic oil/VGO ratio and the severity of hydrotreatment step. The optimum in gasoline/naphtha quality in terms of octane rating was found by mildly hydrotreating bio-oil (H_2 consumption = 202 NL (STP) $kg_{bio\text{-}oil}^{-1}$ = 9 mmol $g_{bio\text{-}oil}^{-1}$) and co-processing hydrotreated-oil/VGO at a 10/90 weight ratio[91, 92]. Nevertheless, the production of aromatics (including phenolic compounds) strongly increased[89], as well as the amount of char and coke formed on the catalyst surface, this leading to the deactivation of the catalyst[88,90]. In fact, studies of catalytic cracking of hydrocarbon fractions with the addition of model oxygenated compounds representative of the bio-oil composition revealed that their presence leads to the rapid formation of carbonaceous deposits (via oxygenated compounds deoxygenation) onto the zeolitic acid active sites of the FCC catalyst[88,91]. Coking deactivates the catalyst by pore blocking of the zeolitic structure and was found to be difficult to reverse.

Similar behavior has been observed by Corma et al.[92] when co-feeding a VGO fraction with glycerol and sorbitol to evaluate the effect of these non-conventional organic compounds in the catalytic cracking of petroleum feedstock at lab-scale by using different catalysts (i.e. FCC catalysts, mesoporous Al_2O_3 and zeolites)[92]. They concluded that oxygen is removed from these compounds as H_2O, CO and CO_2, mainly producing olefins, paraffins and coke, while aromatics are formed in high yields (≈20mol%) via Diels-Alder and condensation reactions of olefins and dehydrated species. More importantly, glycerol can be co-fed with VGO fraction without significantly alteration of the products distribution, resulting in final selectivities better than those calculated by considering a simple additive effect do. Of course, the co-processing of bio-oil + VGO mixtures is more complicated than the co-feeding of only one component, such as glycerol.

Eliminating or replacing the previous hydrodeoxygenation step of bio-oils before co-refining in FCC units by a less energy demanding upgrading step is also another alternative. In this sense, Thegarid et al.[95] have compared the co-processing of both CPO (a bio-oil produced by catalytic pyrolysis of biomass) and Hydrodeoxygenated oil (HDO) with a VGO fraction in a lab-scale FCC unit, concluding that better results in terms of products distribution and final fuel quality favored the co-processing of HDO-oil with the VGO fraction. The observed differences might be overcome with the enhancement of the CPO quality by further catalyst development in the pyrolysis step[95].

Additionally, partially hydrodeoxygenated liquids obtained from both oil fraction (OFWA) and aqueous fraction (AFWA) of pyrolytic oil have been co-processed with Long Residue petroleum fraction in a lab-scale catalytic cracking unit with acceptable results, similar to those attained with the Long Residue alone. The same hydrodeoxygenated liquids have also been co-processed with SRGO fraction in a HDS lab-scale unit, resulting in a competition between HDS and HDO reactions during process without permanent catalyst deactivation[72].

Pinheiro et al.[96] have studied the influence of some selected oxygenated compounds representative of the bio-oils composition in the hydrotreating (simultaneous HDO, HDS and HDN) of a straight-run gas oil (SRGO) fraction over a $CoMo/\gamma\text{-}Al_2O_3$ catalyst under industrial operational conditions. They have observed that the presence of carboxylic group containing compounds strongly inhibit HDS and HDN catalytic functions[96]. Similar behavior was observed when guaiacol was co-processed in an HDS unit together with a straight-run gas oil (SRGO) fraction[97].

4. Major hurdles for bio-oil refining

Although, several fast pyrolysis plants were built and are currently in operation around the world, the lack of bio-oil refining capabilities does not allow the deployment of this technology[2]. The high concentration of oxygen in bio-oil – up to 40 wt. %[98] – associated to the reactivity of these compounds, affects the thermal stability of these oils during storage, handling and upgrading[60,65,99]. Because of the presence of water and the large number of molecules covering a wide range of molecular weights and functionalities will require more separation steps than conventional petroleum, bio-oil refining costs are likely to be higher than for competing sources of organics (molasses and petroleum)[100]. To ensure economic competitiveness, bio-oil price need to be a fraction of those of cheap sugar sources (molasses typically: \$ 300-400 t^{-1}) and petroleum (typically: \$ 206-687 t^{-1}). According to the literature, bio-oil production cost varies between \$ 98 and 860 t^{-1} (\$ 0.41-3.61 $gallons^{-1}$)[67, 101–109]. Thus, efforts are needed to keep bio-oil production costs below \$ 150 t^{-1}.

The published techno-economic analyses on the two step hydrotreatment biorefinery concept estimated minimum selling prices of resulting transportation fuels between \$ 694 and 1455 t^{-1} (\$ 2.1 and 4.4 $gallon^{-1}$)[67,80,82,110-113]. In order to explore how easy will it be to further reduce production costs for the two step bio-oil refinery concept we used the criteria recommended by Lange et al.[100]. In the chemical industry typical conversion costs are between \$ 100-300 t_{feed}^{-1} [100]. Conversion costs depend on complexity and scale and correlate well with the energy transfer duty applied and the number of separation segments[100,114]. A simple calculation supposing an optimistic bio-oil purchasing cost of 150 \$ t^{-1}, an optimistic processing costs of 200 $tfeed^{-1}$ [100] and a very optimistic fuel product yield of 33 wt. %, suggest that a refinery concept with these characteristics will be only viable if the resulting products can be commercialized at least at 1 060 \$ t^{-1} (within the range reported in the literature)[67,80,82,113]. This cost estimation suggest that the two step bio-refinery concept proposed will result in products competitive with chemicals and solvents (\$ 1000 and 2000 t^{-1}) but will have difficulties to be competitive with transportation fuels (gasoline market price: \$ 700-800 t^{-1})[100].

There are fundamental technical challenges to improve fuel yield and reduce production costs in the two step hydrotreatment concept. Bio-oil deoxygenation is fundamentally an emerging, poorly known and very expensive unit operation[100]. In this step, the oxygen purchased as part of the bio-oil is converted into water with high hydrogen and energy consumption[100]. If a fully deoxygenated molecule is the main targeted product (let's suppose benzene), to achieve a 33 wt. % bio-oil conversion (Bio-oil C content: 43 wt. %), overall carbon conversion efficiencies need to be higher than 70 %. Increasing carbon efficiency will require the use of very selective hydrogenation, cracking and hydro-deoxygenation catalysts[100] as well as very efficient separation processes. High hydrogen consumption (5.8 g of H_2/100 g of oil = 2.9 mmol H_2/$g_{bio-oil}$)[82], the lack of high value products, the resulting fuel very rich in aromatics, multiple operational challenges associated with the difficulties to hydrogenate and deoxygenate oligomeric and very reactive oxygenated molecules resulting in frequent catalyst deactivation, coke formation and reactors plugging are other intrinsic weaknesses of this technology[65]. Our analysis clearly shows that the two step hydrotreatment bio-oil refinery concept only targeting the production of hydrocarbon transportation fuels has a very narrow and challenging path to be economically viable.

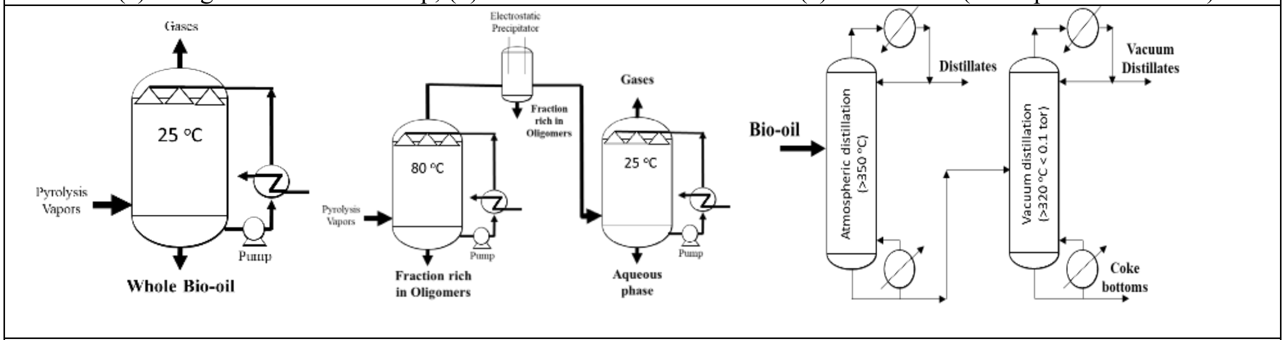
Slightly higher prices than drop in fuels (\$ 700-800 t^{-1}) can be obtained for light olefins (ethylene, propylene, butadiene) (\$ 900-1,500 t^{-1}) used for plastic production. Some small oxygenated molecules (methanol, ethanol, formic acid and acetic acid) have prices below transportation fuels (\$ 400-770 t^{-1}) and markets an order of magnitude smaller however, they are highly oxygenated molecules that at least in theory could be obtained in high yields from these oils. Acetic acid can be produced by biomass pyrolysis[16] but the bulk (65 %) is produced by the carbonylation of methanol. The largest acetic acid uses are in the form of vinyl acetate (4.1 106 t y^{-1}), ethyl acetate (1 million t y^{-1}), peracetic acid (18,000 t y^{-1}), acetic anhydride (1 to 2 106 t y^{-1}), chloroacetic acid (370,000 t y^{-1}), and acetate salts[115]. The fact that the market price of acetic acid (\$ 0.6 kg^{-1}, 2009 level) is significantly higher than pyrolysis oil price estimates (\$ 0.15 – 0.38 kg^{-1}) means that the separation and commercialization of acetic acid likely will continue to increase the economic attractiveness of the pyrolysis oil value chain[15].

Other small oxygenated molecules (acetone, butanol, ethylene glycol, propylene glycol) are commercialized at higher prices (\$ 1,100-1,800 t^{-1}). Like in the case of the small molecules, the polymers can also be classified into relatively cheap materials (market price less than \$ 1,000 t^{-1}) (polyester, polyurethane) and those with market price over \$ 1,000 t^{-1} (polyamide, polypropylene, polyether-polyols and hot melt adhesive). Carbon fiber is a very interesting product due to its high market value (more than \$ 50,000 t^{-1}). Agriculture chemicals (insecticides, fungicides, insect-fungicides, herbicides, redentocides, plant growth regulators, repellents, thermicides) are also interesting products have a global market of 215 billion dollars[116] with great potential for pyrolysis products. For example, glyphosate is commercialized today between \$ 4,000 and \$ 6,000 t^{-1}. Today raw wood vinegar (aqueous phase from pyrolysis oils) is commercialized in Asia at \$ 600 t^{-1} for agricultural applications (rosette or green mosaic in wheat, nematode in sweet potato, tobacco mildew in leafy vegetables). A careful analysis of this information and the need to achieve relatively high conversion yields from an oxygenated oil like bio-oil, suggest that a balanced production of materials, oxygenated small molecules and small hydrocarbons is critical to develop viable bio-oil refineries. The production of macro-molecules and polymers from bio-oil fractions should be our priority due to its higher price, but we should be aware of potential market saturation. Our second priority should be the development of small oxygenated molecules to be used as solvents, chemicals or fuel additives. Hydrocarbons for fuel application should only be produced from fractions for which more valuable compounds have saturated their existing markets.

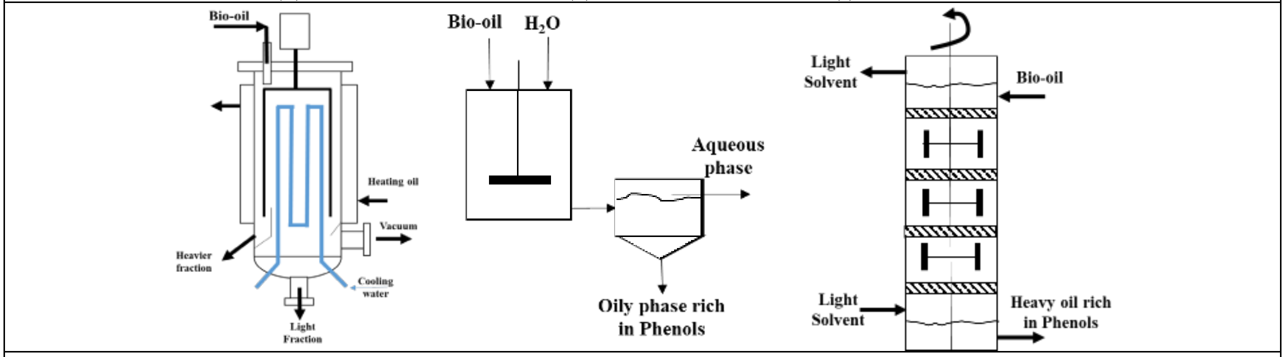
5. Bio-oil Fractionation Strategies

An overview on the importance of separation technologies for the development of bio-oil refineries has been published elsewhere[117]. Diluted aqueous solutions require typically a preconcentration of fractionation before purification. High dilution often results in large reaction processing equipment and expensive operations[117]. The presence of water, small quantities of inorganic compounds and reactive oxygenated compounds forming complex matrices, low thermal stability, azeotropes and low pH are main challenges for the development of bio-oil refineries[117]. In this section we will review processes that result in intermediate enriched fraction critical to reduce overall separation costs in bio-oil refineries. Figure 4 summarizes the stages used in the literature for bio-oil fractionation.

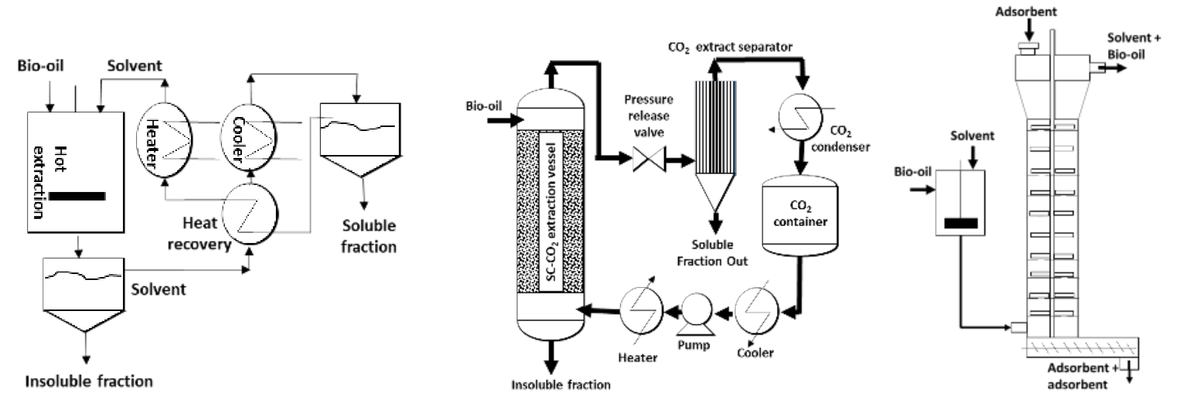
(a) Single condensation Step, (b) Fractional Condensation and (c) Distillation (atmospheric+ vacuum)



(d) Molecular distillation, (e) Water extraction and (f) Solvent extraction



(g) Temperature Swing extraction, (h) supercritical CO_2 extraction, (i) Solid-liquid extraction



(j) Nano-filtration, (k) Pervaporation

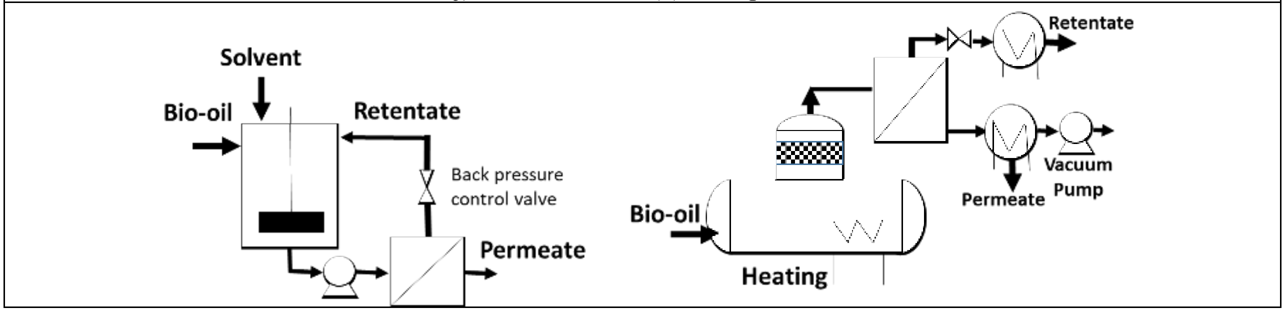


Figure 4. Strategies reported in the literature for bio-oil primary fractionation

5.3. Fractional Condensation Systems

The easiest way to separate bio-oil into light and heavy fractions is using a series of fractional condensation systems operated with decreasing temperature gradient (condensers upstream operating at higher temperatures[118]. Fractional condensation systems were reviewed elsewhere[12]. It is important to highlight that while most of the light fractions (water, C1-C4, mono-phenols and mono-sugars) are in vapor phase, the heavy oligomeric fractions are in the form of aerosols[51]. The temperature, residence time, condensation surfaces and the addition of an electrostatic precipitator, among other factors have a high influence on the final composition of the fractional condensation systems oil fractions[119-134].

Westerhof *et al.*[135] studied the effect of the reactor temperature and the temperature of the first condenser (between 25 and 70 ºC) on the yield and composition of the collected bio-oil. With this system it is possible to separate the bio-oil in an aqueous phase with high content of acetic acid, hydroxyacetaldehyde and acetol, and a heavy oil rich in heavy oligomeric products. The authors[134] developed a mathematical model based on phase equilibrium to describe the yield of products and their composition. The model developed by Westerhof *et al.*[134] considered bio-oils as a mixture of 13 groups representing each of them by a compounds with a well-known vapor pressure (see Table 3). By carefully controlling operational conditions products with up to 10 wt. % acetic acid and 8 wt. % acetol were obtained[135]. Fractional condensation systems with electrostatic precipitators before the cold stage allows the collection of the heavy fractions in the form of aerosols[123,124,126,136].

Table 3. Description of Bio-oil chemical composition in equilibrium model for fractional condenser (Modified from[134])

Group	Normal Boiling point (K)	Components	Representative component	Normal Boiling point (K)
C1-C4 molecules				
1	250-300	Formaldehyde, acetaldehyde	Formaldehyde	253.9
2	300-330	Propionaldehyde, glycolic acid, glyoxal, acetone	Propionaldehdye	322
3	330-360	Methanol, 2-oxobutanoic acid, ethanol, MEK, 2-propanol, (5H)-furan-2-one	Ethanol	351.6
4	360-390	Formic acid, hydroxyacetaldehyde, 5-hydroxymethylfurfural	Formic acid	373.9
5	390-420	Acetic acid, butanol, lactic acid, 4-propylguaiacol, propionic acid, acrylic acid, acetol	Propionic acid	414.2
Mono-phenols and Furans				
1	420-450	Isobutyric acid, 2-hydroxy-2-cyclopentanone-1-one, 2-hydroxy-1-methyl-cyclopentene-3-one, 1-hydroxy-2-butanone, furfural, methacrylic acid, n-butyric acid, coniferylaldehyde	n-butyric acid	436
2	450-500	Phenol, crotonic acid, valeric acid, 3-hydroxypropanoic acid, o-cresol, tiglic acid, 4-methylpentanoic acid, p-cresol, m-cresol, hexanoic acid, guaiacol, 4-hydroxybenzaldehyde, 4-methyl guaiacol, vinylguaiacol	p-cresol	475
3	500-550	4-ethylguaiacol, 1,2-benzendiol, levulic acid, benzaoic acid, eugenol, syringol, vanillin, isoeugenol	Eugenol	526
Sugars				
1	∞	Levoglucosan, glucose, xylose, cellobiosan, hydroquinone,	Hydroquinone	558
2	∞	Other sugars	-	∞
Lignin derived products				
1	∞	Low Molecular Weight Pyrolytic Lignin	-	∞
2	∞	High Molecular Weight Pyrolytic Lignin	-	∞
Extractives				
1	∞	Some compounds identified but not quantitative data on content	-	∞

5.4. Conventional distillation

Conventional distillation typically accounts for atmospheric, vacuum and flash distillation[137]. Bio-oil atmospheric and vacuum distillation is extensively used and well described in the literature[138–145] (see summary of bio-oil distillation studies in Table 4). The results reported for bio-oil direct distillation are not satisfactory due to bio-oil poor thermal stability[117,147].

Table 4. Summary of bio-oil conventional distillation studies

System used	Bio-oil source	Pressures	Temp. range	Observations	Ref.
Lab. batch distillation	Vacuum pyrol. of softwood	Atm.	80-140 ºC	Distillate: 16.5 wt. %.	146
Lab. batch distillation	Vacuum pyrol. sugarcane bagasse	Atm. and vacuum (15 kPa abs.)	Up to 140 ºC	Yield of water: 17 wt. %, yield of organics: 13 wt. %. Very viscous solid residue.	138
Reduced pressure distillation	Fast pyrolysis of rice husk	15 mmHg	80°C	The yield of distilled bio-oil was 61 wt. %	145
Fractional distillation	Pyrolysis of corn stover	Atm. and reduced (approx. 500 mbar)	Up to 250°C (atm. pressure) and up to 230°C (red. pressure)	Atm.pressure: total recovery of 84%. Organic fraction yield: 65%. Vacuum distillation recovery: approx. 73%, with an organic fraction yield of 57.1%	140
Atmospheric distillation and co-pyrolysis process	Pyrol. rice husk	Atm.	Up to 248 ºC	The distillate accounted for 51.86 wt. % of the raw bio-oil	148
Fractional distillation	Tail-gas reactive pyrolysis (TGRP) and regular pyrolysis (switchgrass, horse manure, and *Eucalyptus benthamii*)	Atm. and vacuum	Up to 350°C	Overall yield: 38.9 wt. % with regular pyrol. oil. Yield: up to 56.3 % using TGRP bio-oil	142
Fractionating column or a short-path distilling head	TGRP and regular pyrolysis of switchgrass and horse manure	Atm. and vacuum	Up to 350°C	The yield of pyrolyzate of TGRP-based bottoms was of 20–50%	143
Fractionating column or a short-path distilling head, with devolatilization and calcination	Fast pyrol. of switchgrass, *eucalyptus* and guayule bagasse	Atm. and vacuum	Up to 350°C	Yield of devolatilized bottoms: 50-65%. Yield of calcination was of 85–87%.	149
Atm. Dist., vac. dist., calcination and/or devol. of the dist. Bottoms	Fast pyrol. of switchgrass, *eucalyptus* and guayule bagasse	Atm. dist: 0.9-1 atm. Vac. dist: 0.02 – 0.13 atm.	Atm. Dist.: 50°C to 400°C. Vac.dist: 100 - 400°C. Devol: 400-1000°C. Calcination: 1100-1400°C.	Yields of devolatilized bottoms: 50-65%. Yield of calcination: 85–87%.	150

5.5. Molecular distillation:

Molecular distillation is a process in which the bio-oil is heated under high vacuum in a system in which the distance between the evaporation and the condensation surface is such that the molecules that scape the evaporation surface reach the condensation surface without interacting with other molecules[137]. This method is recommended for the separation of thermally unstable materials[137]. A considerable number of patents and peer reviewed papers on molecular distillation were found in the literature[137,151–159]. Table 5 summarizes the outcome of these papers.

Table 5. Summary of bio-oil molecular distillation studies

System used	Bio-oil source	Pressures	Temperature range (ºC)	Observations	Ref.
KDL5: UIC Corp.	Fast pyr. of Mongolian Scotch pine	60 Pa	70, 100 and 130 ºC	Yield: 83 wt. % of distillate.	137
KDL5: UIC Corp. Bio-oil pretreated by vacuum distillation	Fast pyr.	340-1600 Pa	80°C	Yield: 43 wt.%. of distillate	151
KDL5: UIC Corp.	Fast pyr. of Mongolian pine sawdust	100 Pa	80°C	Yields: 50, 7 and 40 wt.% for light, middle and heavy fractions.	160
KDL5: UIC Corp.	Fast pyr. of pine sawdust	340-1600 Pa	80°C	Yield: 57 wt.% of distillate	161, 162
KDL5: UIC Corp.	Pyrolysis of pine biomass	60 Pa	50°C	Yield: 97 wt. %. Of distillate	163
KDL-5	Fast pyrolysis of rice husk	1000 Pa. Co-cracking of distilled fraction (DF) and Ethanol: 0.1-3 MPa	90°C. Co-cracking of the DF and Ethanol: 340–430°C	The crude-distilled fraction (CDF) yield was 55 wt. %. The total liquid yield varied from 56 wt. % to 78 wt. %, depending on the co-cracking conditions.	163
KDL5 from UIC Corp.	Fast pyrolysis of lauan sawdust	120 Pa	70°C	Yield of heavy fraction: 49.6 wt. %.	164
Short Path Evaporators at two different scales — bench top scale and pilot plant scale	Catalytic Pyr. of southern yellow pine wood chips	1st pass: 0.40 atm, 2nd pass: 0.26 torr 3rd pass: 0.001 atm. .	1st pass: 50°C, 2nd pass: 100°C, 3rd pass at 160°C	The overall yield: 55-92 wt. %.	159
–	Catalytic Pyr. of biomass.	–	Ex.1: Up to 75°C Ex.2: Up to 120°C	Ex. 1: Yields of light and heavy: 12 and 83 wt. %, respectively. Ex 2: Yields of light and heavy: 14 and 38 wt. %, respectively.	154

5.6. *Reactive distillation and condensation*

Some authors[119,139,142,165] have also studied upgraded strategies in which chemical reactions are conducted while the bio-oil is condensed or distilled. These strategies are summarized in table 6.

Table 6. Summary of bio-oil reactive distillation and condensation

System used	Bio-oil source	Operation conditions	Observations	Ref.
Reaction column with diameter of 24 mm and height: 800 mm	Fast pyr. of rice husk	Acid catalysts (SO_4^{2-}, M_xO_y). Temperature: 47-78 ºC.	Important reduction in density and acidity and increase in calorific value and thermal stability. Esters were formed	165
A distillation bottle	Slow pyr. of sawdust pellets and fast pyr. of wheat straw powder	Activated carbon obtained from sawdust pellets was used as catalyst carrier, and p-toluene sulfonic acid was the catalyst. Temperature: 50-80°C	The heat value of both oils increased to 25-29 MJ/kg	60
102 mm i.d. stainless steel tube with a reaction zone length: 457 mm	Slow pyr. of pine wood pellets	Vapors were contacted with atomized ethanol	The linear trend between weight hourly space velocity (WHSV) and the yield. Increasing WHSV, decreases total oily phase yield and increases aqueous phase yield.	119

5.7. *Water extraction*

When water is added to bio-oils (more than 35 wt. % depending on bio-oil composition), a heavy tar-like phase (rich in lignin derived compounds) and an aqueous phase (rich in cellulose and hemicellulose derived compounds) are formed[3]. The water soluble phase is used for the production of liquid smoke for the food industry[3]. In fact, water extraction is often considered the first step for the recovery of chemicals from pyrolysis oils[166]. Vitasari recommends extracting the forest residues at a mass water-to-oil ratio of 0.65-0.7 and the pine-derived oil at 0.5[166]. Upon water addition to the pyrolysis oil, 80-90 % of the oxygenated can be extracted to the aqueous phase, based on their polarity[166]. Oasmaa et al.[26] studied the conditions under which a separated phase was formed when water was added to bio-oil and found that bio-oil phase stability (the formation of an oily and aqueous phases) is controlled by the relative quantities of lignin oligomers (water insoluble materials), water and the sugars and the light C1-C4 molecules that act as solvents. Park et al.[167] studied the separation of bio-oil fractions by adding the oil water, organic solvents (hexadecane and octane) and sodium hydroxide. As pH increases a bi-phase aqueous/organic occurred.

5.8. *Extraction with organic solvents*

Organic solvent extractions is another strategy extensively studied in the literature[168–173]. Figure 4 shows two of the most common separation strategies used with bio-oil. The first one is based on the polarity of fractions and the second is an acid-base separation (see Figure 5).

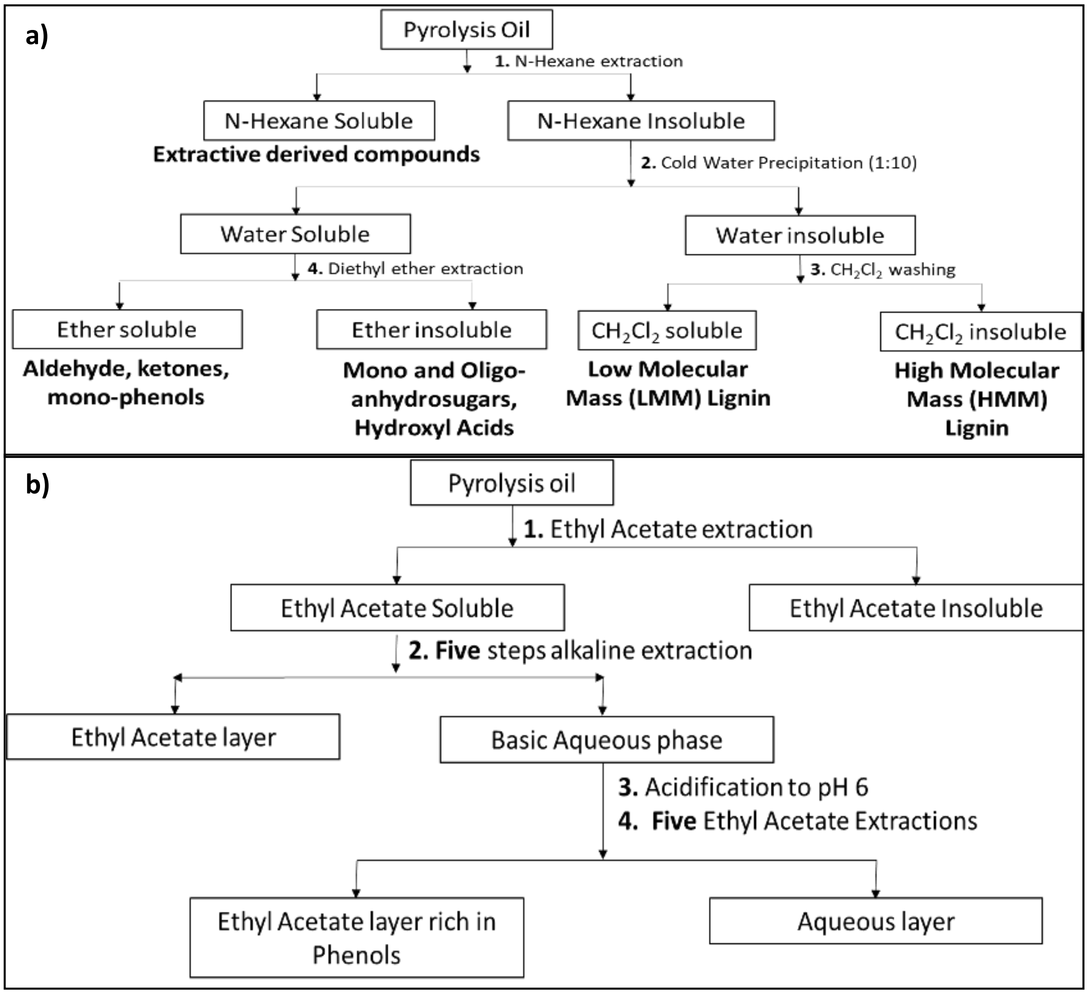


Figure 5. Common schemes used for bio-oil separation (a) based on polarity, (b) acid-base separation[171,174].

To choose a suitable liquid-liquid extraction is important to take into account the boiling point of the solvent used compared with the extractant[117]. We need to avoid the distillation of huge amounts of water or solvent which is very energy intensive[117]. The fraction of the solvent soluble in the pyrolysis oil rich phase is another parameter that need to be carefully considered when developing liquid-liquid extraction strategies[175]. Table 6 summarizes some of the most important liquid-liquid extraction studies reported in the literature.

Table 6. Solvent Extraction method

System used	Variable studied	Observations	Ref.
Fractionation with water and further extraction with diethylether	Physical properties and chemical composition correlations obtained	The presence of volatile acids, water and alcohols like methanol, affects properties like pH, viscosity, pour point ash point and heating value	173
Extraction with ethyl ether and ethyl acetate	Anti-fungal properties of the oil fractions	Anti-fungal properties were stronger in the phenolic-rich fraction	170
Alkali and organic solvents for phenols separation	The effect of pH on the phenols recovery	High pH values (12-13) lead to a complete extraction of phenols from the oil.	174
Steam distillation and extraction of distillate oil fraction obtained at 105°C using organic solvents	The best steam-to-pyrolysis oil ratio for recovery of syringol using steam distillation	88.2% recovery of total phenols was possible with a steam-to-pyrolysis oil ratio of 27. Syringol with 92.3% purity was obtained through pentane and water treatments.	176
Organic solvents for sequential extraction of bio-oil water extract	Optimum solvent and solvent-to-feed ratio	Polar solvents (ethyl acetate and chloroform) are better to recover chemicals from bio-oil aqueous phase. The optimum solvent-to-feed ratio was 2 for hexane, petroleum ether and for ethyl acetate, and 1 for chloroform.	177
Liquid chromatographic separation with silica gel as stationary phase, and hexane and ethyl acetate as solvents. Extraction of the aqueous phase using diethyl ether.	Miscibility of oil with diesel and corrosivity.	Excellent solubility in diesel and very mild corrosivity to copper and stainless steel	172
Acetone followed by extraction with dichloromethane. Extractives were identified as n-hexane-soluble material.	The influence of extractives on phase separation	10 -20 wt. % top phase is formed depending on the content of extractives of feedstock and separation conditions. This phase can be removed y hexane extraction. Besides, the amount of extractives positively affects the proportion of water insoluble fraction of top phase and the solubility of forestry residue liquid.	171

Table 6. Continuation…….

System used	Variable studied	Observations	Ref.
Water wash followed by extraction with organic compounds	Yield and composition of the different bio-oil fractions obtained	Top phase water-insoluble material (60-90 wt. %) includes lignin-based constituents and extractives (35-50 wt. %). The bottom phase chemical composition of forestry residue liquid is similar to that of pine pyrolysis liquid: 8-10 wt. % of volatile acids, 10-15 wt. % aldehydes and ketones, 25-30 wt. % water, 30-35 wt. % of "sugar constituents".	178
Pyrolysis liquids extracted with water. The water-insoluble fraction further extracted with dichloromethane, and the water-soluble fraction with diethyl ether and dichloromethane.	Changes in physical properties and chemical composition of pyrolysis oils during storage	There was an increase in the water-insolubles fraction with storage, with lead to an increase in the average molecular mass and the viscosity of the liquid. In the first 3 months the ether-insolubles decreased and the high-molecular-mass lignin material increased very fast, leveling off afterwards.	179
Reactive Extraction			
Long chain ternary amines (trioctylamine) for acetic acid removal	Type and concentration of amine and co-solvents (THF, octane), T= 20 ºC.	More than 90 % of acetic acid can be extracted in a single step.	175

5.9. Temperature-swing extraction:

Kumar et al.[180] studied bio-oil fractionation by temperature-swing extraction. The method consists on the hot solvent extraction at 70 ºC of the light fraction of the oil with an appropriate solvent followed by cold de-mixing at 25 ºC of the light fraction and the extraction solvent. The authors use the Hansen solubility distance (Ra) which take into account the dispersion forces, dipole forces and hydrogen bonding to explain their results. The light solvent is recovered by the spontaneous liquid/liquid separation upon cooling the extract. The authors[180] screened several solvents: alcohols (methanol, ethanol, 1-butanol, 1-octanol, glycerol), alkanes (n-C_6, n-C_7, n-C_8, n-C_{11}, n-C_{12}, n-C_{16}, cyclo-hexane) and others (acetic acid, furfural, diethylether, toluene, ethylbenzene, water, mixtures of water and methanol). For the regeneration of the extraction solvent immiscibility at room temperature is needed.

5.10. Supercritical fluid extraction

Supercritical fluid extraction (SFE) is typically conducted with CO_2. This technique is suitable for extraction of hydrophobic constituents[117]. The advantage of SFE are speed (no surface tension, low viscosities, fast diffusivity) and selectivity but requires high pressure which increases costs compared with other liquid-liquid extraction methods. Selectivity can be altered by changing pressure and temperature. In many cases SFE is used to avoid water distillation[117]. Notably, the evaporation of water costs in terms of thermal energy 2.26 MJ kg^{-1}, while the CO_2 recompression to supercritical conditions requires up to 0.54 MJ kg^{-1} or 1.3 MJ kg^{-1} equivalent thermal energy when considering electricity generation.

Table 7. Example of bio-oil supercritical fluid extraction methods

System used	Bio-oil source	Operation conditions	Observations	Ref.
SC-CO_2 extraction (EV-3-50-2)	Pyrolysis of palm kernel shell	48 °C, 28 MPa,	Quadratic model developed. Extract enriched with acids and esters.	181
SC-CO_2 unit (Thar Technologies)	Pyrolysis of wheat – wood sawdust biomass	45°C, 25 MPa	Effective water separation. Amount of furanoids, pyranoids and bezenoids improved in the first SC-CO_2 fraction. Later fractions enriched in fatty acids (44 %) and high MW alcohols (5.3%)	182
SC-CO_2 unit (HDT Sigmar Mothes)	Pyrolysis of pine wood biomass	60-80°C, 10- 30 MPa; SiO_2 and activated carbon as carriers. Optimum condition: 60°C, 30 MPa, with SiO_2 as carrier	Soluble Oil yield at 20 MPa - 6-13 wt.%. At 30 MPa: 13-14 wt. %. With exception of levoglucosan, low MW componts in the extracts.	183
SC-CO_2 unit (Thar Technologies)	Fast pyrolysis of wheat-hemlock	40° C, 10, 25 and 30 MPa	10 - 25 MPa: extracted fractions enriched with furanoids, pyranoids and bezenoids. 30 MPa: extracted fractions enriched with fatty acids and alcohols.	184
SC-CO_2 (reservoir, pump, an stirred autoclave extractor, water bath and separator)	Flash pyrolysis of pulverized corn stalk.	45°C, 7-17 MPa, 45°C, 7-30 MPa. Effect of temperature on extraction: Simulated bio-oil: 15 MPa, 35-60°C, Real bio-oil: 30 MPa, 45-65°C	Total ketones, phenols and aldehydes increased, while the acids and water percentage significantly decreased. Maximum extraction efficiency of real bio-oil reached 88.6% at 30.0 MPa and 35°C.	185
Commercial 600 ml SC-CO_2 extraction (HDT Sigmar Mothes, Berlin, Germany)	Slow pyrolysis of beech wood and fast pyrolysis of beech wood	60 ◦C, 15-25 MPa	Yield of extracts from slow pyrolysis oil and fast pyrolysis oil over 50 and 10%, respectively. Extraction significantly reduced water content, and increased carbon content. Extracts lighter than original pyrolysis oil. Residues have higher molecular weight compared with original pyrolysis oils.	186

Table 7. Continuation…….

System used	Bio-oil source		Observations	Ref.
SC-CO_2 unit (640 cm^3, HDT Sigmar Mothes, Berlin, Germany)	Slow pyrolysis of beech wood	60 °C, 20 MPa, SiO_2 as carrier (two weight ratios: 100:80 and 100:40), total extraction time: 6 h, SC-CO_2 flowrate: 500 g h^{-1}	SC-CO_2 extraction gives higher yield than with hexane and acetone. Non-aromatic compounds increased in SC-CO_2.	187
SC-CO_2 unit (MV-10 ASFE, Waters, USA)	Fast pyrolysis of red pine	50°C, Solvent flow rate: 1.0 mL min^{-1}. Step 1: 5 min, 10 MPa, pure SC-CO_2; Step 2: 25 min, 20 MPa, 90% SC-CO_2 and 10% methanol; Step 3: 40 min, 30 MPa, 75% SC-CO_2 and 25% methanol.	Yields of extracted fractions 1, 2 and 3: 13.4 wt. %, 24.8 wt. %, and 32.9 wt. % (A total of 71.1 wt. % of the raw bio-oil). Phenols content increased in fraction 1. Fractions 2 and 3 enriched in carbohydrates. Fraction 1 enriched in lipids, Fraction 3 enriched in lignin and condensed aromatics.	188

5.10. Solid-liquid extraction:

Solid-liquid extraction is based on the affinity of solutes for a solid phase through which the sample is passed. Table 8 summarizes the studies conducted this technique for the separation of pyrolysis oil fractions.

Table 8. Example of bio-oil solid-liquid extraction methods

System used	Bio-oil source	Operation conditions	Observations	Ref.
Sepabeads resin SP207 (Mitsubishi Chemical) and Amberlite XAD4 resin (Rohm and Hass)	Fast pyrolysis of red oak	Room temperature. 1:1 water extraction of the first stage. Kinetic adsorption: 22°C, 500 rpm, 2 hours of sampling;	Adsorption capacity and affinity for phenolic species is higher than for levoglucosan. There might be mass transfer limitation of phenolics in column chromatographic separation.	189
A strong-base anion exchange resin (Amberlyst A26) and a weak-base anion exchange (Amberlite IRA-67).	Model solutions prepared by dissolving phenol in double distilled water.	Flow rate: 10 L h^{-1} and room temperature. Recirculation time: 60 min.	Phenols removal efficiency increased with recirculation time for both resins, and decreased with initial phenol solution concentration.	190

5.11. Membrane separation:

Membrane separation, such as microfiltration (0.05-10 μm), ultrafiltration (1-100 nm) and nanofiltration (< 2 nm) has been bio-oil fractionation[116] (see Table 9).

Table 9. Example of membrane separation studies relevant for bio-oil refining.

System used	Feed	Operation conditions	Observations	Ref.
Laboratory- scale separation unit, with solvent-resistant membranes prepared from polyimides based on PMDA and BPDA by the dry/wet phase-inversion technique	Model mixtures of 1-propanol, acetic acid at concentrations: of 10–90 wt. %	85–135°C, 20–66 kPa (feed) and 4–5 kPa (permeate). The composition of each fraction was determined.	Polyimides with diamine and dianhydride moieties membranes: higher permeability and selectivity. Copolyimide BPDA–50DDS/50ODA and PMDA–50DDS/50ODA membranes: better mechanical and chemical properties.	191
Five dense polyimide membranes (PMDA-50DDS/50ODA, BPDA–50DDS/50ODA, BPDA–DDS, BPDA–ODA, and DSDA-TPER)	Water vapor	Gravimetric method. 85°C, 40kPa (feed) and 1.5-2kPa (permeate). After 6–8 h, the condensed vapors of the permeate samples were collected.	Both the dual-mode sorption model and the GAB model successfully represented the sorption isotherms of water vapor in the polyimides. Water vapor transfer highest for DSDA-TPER and PMDA–50DDS/50ODA (1.6×10^{-13}), and the lowest for BPDA–ODA (2.0×10^{-14}).	192
Polyetherimide/polyvinylpyrrolidone membranes. Prepared by the wet-phase inversion method	Water and n-propanol mixture (1:1 m/m)	85°C, 33kPa (feed) and 7kPa (permeate)	Increasing the total polymer concentration in the casting solution decreased the permeation rates for both water and n-propanol, and increased the membrane selectivity.	193

Table 9. Continuation………

System used	Feed	Operation conditions	Observations	Ref.
Polycrystalline silicalite and ZSM-5 membranes on sintered stainless steel support and on porous alumina support	Aqueous solution of acetic acid or ethanol (2.5-10 vol.%)	Pervaporation experiment: standard pervaporation cell, down stream pressure < 2 Torr.	Silicalite membrane on the sintered stainless steel support permeates acetic acid in preference to water in the region of 5 to 40 vol% of acetic acid in the feed. Porous alumina membrane did not separate acetic acid from the aqueous solution.	194
Poly(vinyl alcohol) (PVA) membranes crosslinked with glutaraldehyde (GA)	70 - 90 wt. % acetic acid in water.	Pervaporation experiment: 35-50°C; permeate pressure < 5mmHg. Liquid nitrogen was used as cooling agent for cold trap.	Swelling behavior controlled by crosslinking density or by the formation of chemical groups such as acetal and aldehyde groups. Separation factor: 120-420 and flux of 29-263 g/m^{2}h (membrane prepared at 5 vol % of GA solution)	195
Acrylonitrile (AN) grafted poly(vinyl alcohol) (PVA) membranes	10–90 wt.% acetic acid	25-50°C; Effective membrane area of 12.5 cm^2; Pressure at downstream side:23 KPa	Increase of downstream pressure improved permeation rate but separation factor decreased. PVA-g-AN membranes have lower permeation and grater separation factors compared to PVA membranes.	196
Two copolyimide dense and asymmetric capillary membranes of PMDA-50DDS/50ODA and BPDA-50DDS/ 50ODA	Pure water, 1-propanol/water and acetic acid/water blends	85–135 ◦C, 20–66 kPa (feed), and 2–5 kPa (permeate)	Skin layer effective thickness was used to simulate the water vapor sorption and transport behavior	197
Polyimide dense membranes (PMDA–50DDS/50ODA, BPDA–50DDS/50ODA, BPDA–DDS, BPDA–ODA, and DSDA–TPER)	1-propanol, H2O, acetic acid and aqueous phase containing 11 wt.% organic compounds as vapor feeds	85–135 ◦C; 20–63 kPa (feed), and 1.5–2 kPa (permeate); Retentate vapor was condensed.	Better separation of water vapor from organics at low temperature in polyimide membranes.	198

Table 9. Continuation………

System used	Feed	Operation conditions	Observations	Ref.
Chemically crosslinked poly (vinyl alcohol) (PVA) membranes	0 to 100% acetic acid solution	30, 45, 60 and 75°C, pressure < 5mmHg at the downstream side.	Separation factor of 13-42 and permeation rate of 79-2285 g/m^{2}h achieved. The strongest permeation was between 50 and 70 wt. % composition.	199
Ge-substituted ZSM-5 membrane on a porous, tubular, stainless steel support	5 wt. % acetic acid	363-303 K, < 0.5 kPa (permeate side). Liquid nitrogen was used as cooling agent for cold trap.	Separation of acetic acid from water was more efficient using Ge-ZSM-5 membrane than silicalite-1 membrane. A total flux of 0.43 kg/(m^{2}h) and an acid/water selectivity of 14 were achieved by Ge-ZSM-5 membrane at 363 K and 5% acetic acid.	200
Two different LiquiCel Membrane Contactors (Membrana, Charlotte, NC): MiniModule 1x5.5 and Extra-Flow 2.5x8, both with polypropylene membranes	Aqueous phase: Pretreated corn stover hydrolysate; Organic phase: octanol and Alamine 336 or octanol and Aliquat 336	-	Over 60% of acetic acid removed using Alamine 336. Extraction rates were lower for Aliquat 336. There is a coextraction of bisulphate anion, which is preferentially extracted at pH values below its pKa.	201

6. Strategies for Purification and Separation of Targeted Compounds

Based on bio-oil composition there are only four compounds that are in concentrations sufficiently high as to explore their separation (acetic acid, hydroxyacetaldehyde, acetol and levoglucosan). Furthermore, there are group of compounds that could be commercialized as fractions (mono and oligo-phenols, sugars and dehydrated sugars). In this section we review how some of these compounds are separated from other aqueous solutions with methods that can be of great value for bio-oil refining.

6.1. Methods for Acetic Acid (HAc) Separation

As discussed above, a fraction rich in acetic acid can be produced using fractional condensation systems[120,122–125,134,135,202–206]. Figure 7 summarizes the methods reported in the literature for acetic acid separation from aqueous solutions.

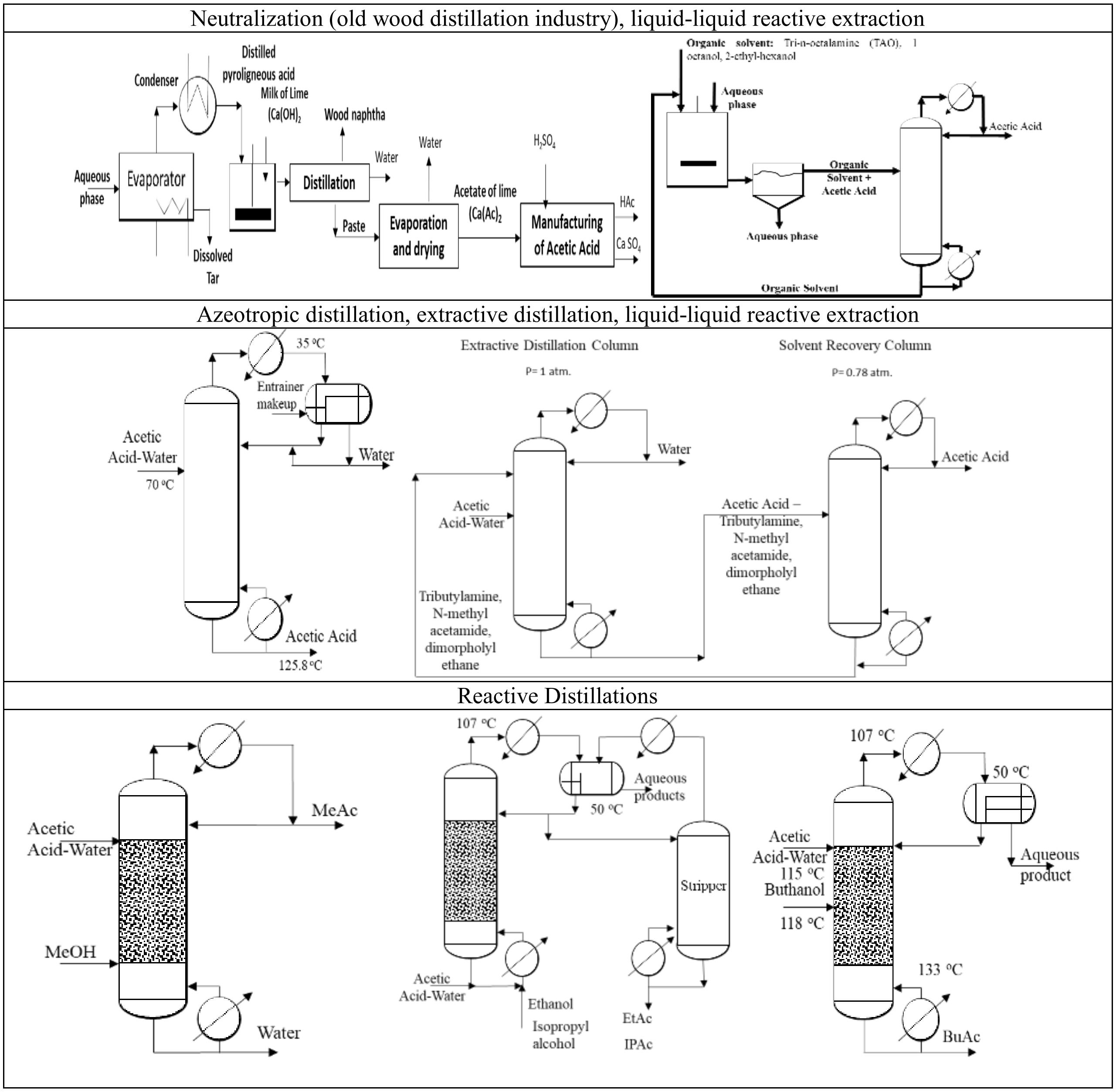


Figure 6. Summary of methods reported in the literature for Acetic Acid separation from aqueous phases

In the old wood distillation industry the acetic acid was separated by precipitation with lime[207]. In this process the aqueous phase (also known as pyrolygneous water) is evaporated to separate the dissolved tar from the light compounds. The distilled pyroligneous acid is then neutralized with milk of lime ($Ca(OH)_2$) and the resulting solution distilled to separate the wood naphata and a paste rich in acetate of lime ($CaAc_2$). This paste is concentrated by evaporation and drying and is and commercialized[207].

Ijmker, *et al.*[208] studied extraction of acetic acid using fatty acids (hexanoic and heptanoic acids). The approach showed promising results. The selectivity of fatty acids over water was 12 for hexanoic acid and 24 for heptanoic acid allowing significant concentration through extraction. This high extraction was explained by the dimerization of carboxylic acid in liner or cyclic forms. The authors[208] developed a mathematical model to describe the extraction with hexanoic acid that take into account the dissociation equilibrium of compounds in the system. Other methods under study to recovery acetic acid can be found elsewhere[18,177,209,210] and are summarized in table 10.

Table 10. Summary of acetic acid separation methods

System used	Operation conditions	Observations	Ref.
Azeotropic distillation			
Simulation with ChemCad, Aspen Plus. Column diameter = 0.3259 m; tray spacing = 0.6096 m. 10 min holdup.	Entrainers used: p-xylene, isobutyl acetate, ethyl acetate, n-butyl acetate. Pressure: 1.1 atm., Reboiler temperature: 125.8 °C, Condenser Temperature: 35 °C. Vapor-liquid-liquid equilibrium calculated from the Nonrandom two-liquid (NRTL) activity coefficient model and second virial coefficient of the Hayden-O'Connell model	Iso-butyl acetate was the best entrainer with total annual cost only about 55% of the system without any entrainer.	211, 212
Extractive distillation			
Two extractive distillation columns and solvent recovery column. Extractive distillation column simulated. Mathematical model of equilibrium stage	Tributylamine was the separating agent. Take advantage of the reversible reaction between acetic acid and tributylamine: $HAC + R_3N{-}R_3NH^+ + OOCCH_3^-$ Number of theoretical plates:25. The solvent recovery column had 20 plates. The extractive distillation column was run at normal pressure, and the solvent recovery column was run at 0.080 MPa. The solvent was recycled from the recovery column to the extractive distillation column.	High-purity of water was obtained at the top of extractive distillation column for small solvent/feed volume ratio and reflux ratio. Therefore, tributylamine seems to be a good separating agent for water and acetic acid mixture. Mathematical model was developed.	213
Continuous experimental system.	Proposed a process for preparing technically pure acetic acid from water-acetic acid mixtures with N-methyl acetamide as an improvement of a process with dimorpholyl ethane	Acetic acid purity vary between 99.8 and 99.9 %. N-methyl acetamide was chemically and thermally stable	214
Reactive Distillations			
Packed reactive distillation column with three sections: non-reactive stripping section; catalytic packed section and non-reactive enriching section	Catalytic section: packed with macroporous Indion 130 ion-exchange resin (catalyst bed), confined in stainless steel wire mesh tea bags. The feeds were injected at room temperature. Several column configurations (A-G) were adopted for recovery of acetic acid. Maximum recovery when acetic acid is inserted from the top and n-butanol/iso-amyl alcohol is introduced from the bottom.	At 1:2 mole ratio of acetic acid to n-butanol: 58% conversion of acetic acid achieved. And 1:2 mole ratio of acetic acid to iso-amyl alcohol, around 51% conversion of acetic acid was achieved. Best result when the column operated in counter-current mode.	215

Table 10. Continuation…....

System used	Operation conditions	Observations	Ref.
Simulation studies	Acetic acid esterifications with five alcohols (C1-C5) were studied in the presence of acidic ion-exchange resins (Amberlyst 15 and Purolite CT179) Reaction: HAc + alcohol = acetate + water	Reaction rate expressed in a Langmuir-Hinshelwood form. Vapor liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) modelled with an NRTL model and UNIQUAC model for activity coefficients.	216
100 mm diameter column installed alternating dualflow tray and a catalyst basket.	Amberlyst 15 was used as a catalyst for the esterification reaction of acetic acid with methanol.	For a feed containing 2.5 to 9.9 wt.% of acetic acid solution, a recovery of methyl acetate over 50 wt.% is possible in the 1.5 meter high test column.	217
Liquid-liquid reactive extractions			
Extraction conducted in vials, stirred by magnetic bar in water bath at 1000 rpm, 25 ºC for 2 h. Followed by centrifugation.	Extraction of acetic acid from succinic acid and from aqueous solutions with tri-n-octylamine (TOA) dissolved in 1-octanol. Concentration of TAO in organic phase (0.25-0.75 mol/kg)	The removal of acetic acid from succinic acid aqueous mixtures take advantage of different degree of dissociation of each acid with pH. The equilibrium data of amine-based extraction was explained by mass action law.	218
Continuous centrifugal contactor separator.	Best extraction results obtained with TOA in 2-ethyl-hexanol (40 wt. %) and room temperature with 84 % acetic acid recovery at equilibrium conditions.	Other organic acids (formic acid and glycolic acid) were also co-extracted at high efficiencies	16
20 mL vial at 20 ºC and 500 rpm for 22 h to ensure equilibrium	TOA/2-ethyl-1-hexanol at 20 ºC, and 120 rpm for 24 h.	Co-extraction of glycoaldehyde and acetic acid. Mixture of TOA. For a combined acetic acid and glucoaldehyde one step extraction 2-ethyl-1-hexanol gave the best results. For a two step extraction, a solvent containing more than 50 wt. % TOA is desired (first acetic acid extracted followed by glycoaldehyde)	18

Table 10. Continuation…....

System used	Operation conditions	Observations	Ref.
Extraction with Ionic liquids			
Three phosphonium ionic liquids (ILs), two imidazolium ILs and a bench mark mixture (40 wt. % TOA/1-octanol)	Phosphonium ILs showed the highest affinities for HAc and glycolaldehyde, and reasonable affinity for acetol. Difficulties to evaporate oxygenates from phosphonium ILs and the reactivity of glycoaldehyde with $P_{666,14}[N(CN)_2]$	Based on the good affinity of imidazolium ILs for acetol, a two step extraction process is proposed where Hmim[B(CN)4 is use to extract acetol and HAc in the first step and P666,14 [Phos] may be applied to extract glycoaldehyde in the second step.	118
Nanofiltration and Reverse Osmosis Membranes			
Polymeric nanofiltration (NF) and reverse osmosis (RO) membranes	Single solute solutions of acetic acid and glucose and a model aqueous fraction of bio-oil containing acetic acid, formic acid, hydroxyacetone, furfural, guaiacol, catechol and glucose. Feed pressure: 40 atm, Temperature: 21 ± 1 ◦C. Transmembrane pressures ranging from 5 to 58 bar. Single solute solutions of 7 wt. % acetic acid and 15 wt. % glucose, binary solute solution of 7 wt. % acetic acid and 15 wt. % glucose and a model Aqueous Fraction of Bio-Oil (AFBO) were used as feed.	At moderate (~40 bar) feed pressures, retention factors of glucose over 90% and negative retention factors of acetic acid can be achieved when using single and binary aqueous solutions of acetic acid and glucose. Fluxes and transmembrane pressure are linearly related. Presence of guaiacol irreversibly damaged all the membranes.	209
Desal-5 DK NF membrane (GE-Osmonics)	A synthetic acetic acid–xylose solution (at the ratio 10:1) was used as the model feed. The solution pH was set to 4.9, 6.9 and 9.1	Retention of xylose and acetic acid was in the range of 28–81% and −6.8%–90%, respectively. Separation factor of 5.4 was achieved at pH 2.9 and 24.5 bar.	219

6.2. *Methods for Acetol Separation*

Acetol is an important compound that can be obtained from bio-oil. It can be used as precursor of many products such as acrolein, acetone, furan derivatives, propylene glycol, among others[220]. The research on acetol recovery from bio-oil is limited (Table 11 and Figure 8 summarizes the results of our literature review).

Table 11. Summary of Acetol separation methods

System used	Operation conditions	Observations	Ref.
Liquid-liquid extraction with 3 phosphonium ionic liquids (ILs) used as solvents: two imidazolium ILs and one benchmark organic mixture (40 wt. % tri-n-octylamine in 1-octanol: TOA/1-octanol)	Feed solutions: 3 single solute solutions — 10 wt. % acetol, 10 wt. % HAc and 5 wt. % glycolaldehyde solution, respectively —, and one mixed solutes solution with 10 wt. % acetol, 10 wt. % HAc and 5 wt. % glycolaldehyde together in milli-Q water. Extraction was conducted by adding 2 g feed solution and 2 g solvent in glass vials. The vials were then introduced in a shaking bath at 200 rpm at the desired temperatures ($25 < T < 60$ C) for 18 hours. IL regeneration: Evaporation of single solutes at 100°C and 20 mbar, or 60°C and 20 mbar for extraction from mixed solutes.	The lowest extraction efficiency for acetol was obtained by TOA/1-octanol, and the highest by the phosphonium ILs. A two-step extraction process was proposed where Hmim[B(CN)$_4$] may be used to extract acetol and HAc in the first step, and P$_{666,14}$[Phos] may be used for glycolaldehyde extraction in a second step.	118,221
Aspen Plus® and Aspen Process Economic Analyzer	Process designed at a capacity of 200 kt pyrolysis oil per year, with an operating time of 8000 h per year, with extraction, distillation, and evaporation.	The process simulated can isolate over 99% of the glycolaldehyde and acetic acid. Approximately two-thirds of the acetol in the bio-oil can be recovered. All three products had high purity (over 98 wt.%)	19
Treatment of distilled phenol containing acetol with an acidic resin at low temperature or at elevated temperature,	A distilled phenol stream containing acetol is contacted with an acidic resin at about 85°C or less. Then phenol is separated from the higher boiling compounds by distillation (preferably flash distillation at low pressure). Treatment times can vary from 5 minutes to 1 hour. Alternatively, the distilled phenol stream containing acetol can be heated in a closed system at high temperature, with or without adding a small amount of caustic. If there's no addition of caustic, the pH of the stream should be more than 2, if possible above 2.5. The phenol is then separated from the higher boiling compounds via distillation. The temperatures of the heat treatment must be at least 175–225°C.	This patent presents several examples at different conditions. 700 ppm of acetol was reduced from phenol stream when the stream is put in contact with an acidic resin at about 85°C for 15 minutes. In another example, the content of acetol was reduced from 1036 to less than 10 ppm when the phenol stream containing acetol was heated to around 198°C for 4 hours without caustic addition.	222

6.3. Methods for Hydroxyacetaldehyde (HHA) Separation

Hydroxyacetaldehyde, also known as glycolaldehyde, is another important oxygenated present in pyrolysis oil. It is used as food browning agent and as a precursor of ethylene glycol[223]. To produce high yields of hydroxyacetaldehyde materials with low nitrogen content has to be used. Hydroxyacetaldehyde reacts with proteins and amines under typical pyrolysis conditions[224]. In the patent of Stradal and Underwood[224] the authors state that in order to precipitate hydroxyacetaldehyde crystals it is necessary to create an homogeneous solution of water with an organic solvent (Methylene chloride) containing at least 2 wt.% of HHA. This solution needs to be cooled to at least 2 ºC for HHA to precipitate. Special care should be made to avoid heating the HHA Basically the method patented consist an evaporation step under reduced pressure to concentrate the hydroxyacetaldehyde, adding the organic solvent and cooling and separating the hydroxyacetaldehyde from the solution[224]. Table 12 summarizes some of the HHA purification procedures reported in the literature [19,118, 224–227].

Table 12. Summary of glycoaldehyde separation

System used	Operation conditions	Observations	Ref.
Liquid-liquid extraction with 3 phosphonium ionic liquids (ILs): two imidazolium ILs and one organic mixture (40 wt. % TOA/1-octanol)	Feed solutions: 3 single solute solutions — 10 wt. % acetol, 10 wt. % HAc and 5 wt. % glycolaldehyde solution, respectively, and one mixed solutes solution with 10 wt. % acetol, 10 wt. % HAc and 5 wt. % glycolaldehyde together in milli-Q water. Temperatures (25 < T < 60 ºC) for 18 hours. IL regeneration: Evaporation of single solutes at 100°C and 20 mbar, or 60°C and 20 mbar for extraction from mixed solutes.	Phosphonium ILs had the greatest affinities for HAc and HHA, and some affinity for acetol. A two-step extraction process proposed: Hmim[B(CN)$_4$] used to extract acetol and HAc in the first step, P$_{666,14}$[Phos] used for glycolaldehyde extraction in second step.	118
Aspen Plus® and Aspen Process Economic Analyzer	Process designed at a capacity of 200 kt pyrolysis oil per year, with an operating time of 8000 h per year, with extraction, distillation, and evaporation.	Process simulated can isolate over 99% of the glycolaldehyde and acetic acid. Two-thirds of the acetol in the bio-oil can be recovered. All three products had high purity (over 98 wt.%).	19
Rotary evaporator and cooler	Vacuum evaporation to remove water and concentrate hydroxyacetaldehyde. A solution water, methylene chloride with 2 wt. % of HHA is formed. The HHA is precipitated upon cooling below 2 ºC	HHA crystals are produced.	224
Reactive extraction of aldehydes with primary amine Primene JM-T	Organic to aqueous volume phase ratio of 1:25. 24 h at 25°C to achieve equilibrium, and then settle for at least 2 hours. After that, 70 µl samples of the aqueous phase were collected and mixed with 255 µl of ethanol.	Extraction of Primene JM-T decreases in the following order: pentanal > 3-methylbutanal > benzaldehyde > furfural > 2-methyl-2-butenal. Reactive extraction of HHA with primary amines is analogous to that of aldehydes, it is promising in term of yield and selectivity.	226

6.4. *Method for the separation of fermentable sugars*

Bio-oil contains anhydrosugars — mostly levoglucosan and cellobiosan —, monosaccharides and anhydropolysaccharides[228]. Sugars reported at lower concentrations are fucose, arabinose, galactose, fructose, mannose, xylose, ribose[229].

These sugars cause many problems when upgrading the oil through hydrotreatment[229]. Hence, if sugars were removed from bio-oil, it would make the oil hydrotreatment more feasible. Lian *et al.*[229] investigate the isolation, hydrolysis and detoxification of anhydrosugars from pyrolysis oils to produce ethanol and lipids. Ethyl acetate was used for solvent extraction. Two phases were formed, one organic phase, rich in phenolic and furanic, and another aqueous phase, rich in polar compounds such as acetol, acetic acid, and levoglucosan. The aqueous phase was hydrolyzed to produce fermentable sugars and the remaining phenol in the aqueous solution was removed using activated carbon. Besides, $Ba(OH)_2$ was used to neutralize the acids present in the aqueous phase, with a subsequent filtration to remove the precipitate formed.

Rover *et al.*[124] investigate the separation between sugars and phenols from the heavy ends of a fractionated condenser system of bio-oil by a simple washing method. They found out that two consecutive washes were more efficient than a single wash, removing over 90% of the sugars, with 3 to 7% of impurities. For the detoxification, they concluded that NaOH overliming was better than liquid–liquid extraction, ionic liquid and ionic resin extraction methods.

6.5. Methods for the separation of levoglucosan

Levoglucosan, an anhydrosugar, is one of the main degradation products of cellulose and, therefore, encountered in higher amounts in pyrolysis oils[230]. This concentration is likely to increase if the feedstock is pretreated by acid washing prior the pyrolysis[231–234]. Levoglucosan has the potential of being used in the production of many products, such as resins, plastics, plasticizers, explosives, propellants and surfactants[235]. The U.S. patent 3,309,356[235] introduces a method for separation of levoglucosan in its crystalline form. It's done by a series of solvent extractions. Besides, levoglucosan can also be obtained through extraction with ethyl-acetate or with water extraction of the heavy end bio-oil of a fractionation condensation system.

Bennett et al.[230] studied the optimal conditions for the separation of levoglucosan through extraction with water. They found the best conditions are 41 wt. % of water and temperature of 34°C. This allows a final concentration of levoglucosan up to 88 g/L in the aqueous extract. Also, they investigated the optimal conditions for hydrolysis and concluded that at 125°C, with a residence time of 44 minutes in a solution of 0.5 M H_2SO_4 yield to the maximum glucose yield.

Other patent and work describing the recovery of levoglucosan from pyrolysis oil can be found elsewhere[236,237]. Table 13 and Figure 10 summarizes the main papers published on levoglucosan separation.

Table 13. Summary of levoglucosan separation methods found in the literature

System used	Operation conditions	Observations	Ref.
Water extraction	Water and oil were put in contact in 50 mL Erlenmeyer flasks for 24 h at 20° C and 400 rpm. Water-to-oil mass ratio was 0.3–0.8 for forest residue-derived pyrolysis oil, and 0.4–0.9 for pine-derived pyrolysis oils. Then the mixture was let to settle for 3 h for phase separation.	The best water-to-oil ratio for forest residue-derived pyrolysis oil is 0.65–0.7, and for pine-derived pyrolysis oil is at the lowest possible where complete phase separation happens.	166
Simultaneous esterification and acetylation with online solvent extraction (SEAWOSE) in butanol.	Approximately 30 g of aqueous fraction was added into the water knockout trap, while 80 g of butanol and 1 g of sulfuric acid (98 wt. %) were added to the four-necked bottom flask. The temperature in the water knockout trap was about 110 °C.	All aqueous fraction samples had very high saccharide conversions (over 92%). Therefore, with online extraction, the saccharides could be converted into the upgraded oil.	238

6.6. *Methods for the separation of Mono and Oligo-phenols*

Phenols can be used in a wide range of applications: intermediates in the synthesis of pharmaceuticals, raw materials for production of phenol formaldehyde resins, antioxidants, gasoline additives, food additives, polymerization initiators, pesticides, and colorants[239]. Therefore, it is of great interest to efficiently extract the phenols from lignin pyrolysis oil. There are many separation strategies on literature involving phenol separation. Table 14 shows a summary of the methods described in the literature to separate mono and oligo-phenols The reader can find other phenol separations techniques elsewhere[152,174,176,240–248].

Table 14. Summary of mono and oligo-phenols separation

System used	Operation conditions	Observations	Ref.
Sepabeads resin SP207 (Mitsubishi Chemical) and Amberlite XAD4 resin (Rohm and Haas)	Equilibrium adsorption was performed at 22 °C. Over 98% of the phenolic species in the sugar fraction 1 (SF1) were removed by running SF1 solution over SP207 resin.	The adsorption capability for phenolic species of both polymeric resins is greater than for levoglucosan when a mixture of sugars and phenolic species is used as the applied solution.	189
Batch steam distillation, followed by fractional vacuum distillation and a series of liquid-liquid extractions.	Steam injected at 100°C. 100 g of the bio-oil was kept at 130°C in a mineral oil bath during the distillation. The distillate obtained at a temperature of 105°C was condensed, collected, and then decanted. The aqueous phase was extracted with ethyl acetate. The solvent was evaporated under vacuum at 30°C, and this oil further distilled under 0.67 kPa, at temperature up to 135°C. Fraction from vacuum distillation was liquid-liquid extracted to obtain a syringol-rich fraction.	88.2% of the total phenols in the bio-oil are recovered by steam distillation with a steam-to-pyrolytic oil ratio of 27. The successive extractions of the syringol-concentrated fraction using pentane and water yielded high purity syringol (92.3% purity).	176
Multi-step separation procedure	30 g of bio-oil mixed with 30 mL of deionized water. 2.5 mol/L NaOH solution was used to dissolve the water insoluble phase under ultrasonication, at pH 14 followed by an extraction with CH_2Cl_2 to obtain neutral macromolecules. The CH_2Cl_2-insoluble alkaline solution was then acidified to pH 6.4 with HCl. Through filtration, the precipitate was collected and then dried at 40°C. This precipitated was called high-molecular-weight pyrolytic lignin (HMWPL). The chemicals from the acidic solution were recovered by extraction with 100 mL of CH_2Cl_2. The precipitate was named low-molecular-weight pyrolytic lignin (LMWPL).	There was a predomination of polymers with high molecular weight in HMWPL. In LMWPL, the predominant groups were reactive phenolic hydroxyl groups. Overall, the relative contents of total phenolic molecules in fractions B and C summed 94.35% and 54.33%, respectively.	152
Vacuum distillation followed by batch liquid-liquid extraction	Vacuum distillation: 0.40 kPa, temperatures: 230, 190 and 160°C. Volatiles condensed at room temperature, 0°C, -60°C and - 70°C. Liquid-liquid extraction: Oil phase obtained at 160°C was dissolved in ethyl acetate (1:1 weight ratio). Phenols were converted to phenolate ions by the addition of an alkaline solution. A sulfuric acid solution (50 wt. %) was added into the aqueous phase till pH 6 to regenerate the phenols. Phenols are extracted with ethyl acetate	Complete extraction of catechol was achieved at a pH of 11.3 after three stages. The other phenols required five stages. The lower the pH, the harder the phenol extraction. At pH 9.5, no phenol was completely extracted from the primary oil.	174

Table 14. Conclusions……

System used	Operation conditions	Observations	Ref.
Batch aqueous extraction and batch solvent–anti-solvent extraction	Room temperature (23°C). Phase mass ratio of solvent to feed: 1:2.35 up to 2:1 for water extraction Solvent was removed by evaporation. In aqueous extraction, water, aqueous $NaHSO_3$ and alkali solution were tested as solvents. For the solvent–anti-solvent technique, a simultaneous addition of an hydrophobic-polar solvent (e.g. MIBK, toluene, isopropyl ether, ethyl acetate) and either water, aqueous $NaHSO_3$ or alkali solution was used.	Catechol and vanillin had the highest distribution coefficients. Among the aqueous extraction, alkali extraction was the most efficient for phenols recovery. Among the solvent-anti-solvent technique, MIBK is the most effective solvent in combination with NaOH aqueous solution.	240
Small scale extraction with switchable hydrophilicity solvents (SHS)	10 g of pyrolysis oil was mixed with 100 mL of N,N-dimethylcyclohexylamine. The mixture was centrifuged and the insoluble components were removed. The acids from the solution were removed with 50 mL of $NaHCO_3$, after what the remaining amine solution was mixed with distilled water. The mixture was bubbled with CO_2 magnetic stirred for approximately 3 hours until the amine layer and the water layer combined into one single phase. After that, a low-polarity portion of the oil (Fraction #2) detached from the solution, and phenols stayed in the ammonium bicarbonate phase. Ethyl acetate (EtOAc, 6 x 100 mL) was used for phenol extraction. Then this EtOAc solution with phenols was washed sequentially with HCl solution to eliminate residual amine, and with saturated NaCl to remove moisture. The solvent was removed by rotary evaporation, leaving the phenols extract (Fraction #3). The fraction was bubbled with N_2 at 60°C to switch the amine in the solution back to its neutral form.	Phenols were efficiently extracted (72% of guaiacol, 70% of 4-methylguaiacol and 82% of 3-methyl-4-ethylphenol). Overall, 91% of the solvent SHS was recovered and can be reused for next extraction.	247
SG-packed column	A series of extractions were conducted to yield 3 extracts from bio-oil: E_I, E_I and E_{II}). Solvent was used to dissolve the sample followed by solution mixing with 0.5 g of silica gel (SG).	71.2 % of acetophenone was isolated into ES_{a1}, 55.6% of catechol was isolated into ES_{a2}, 95.7% of guaiacols into ES_{a2}, 57.2% of syringol into ES_{c3}, and 52.6% of hydroxycyclopentanones into ES_{c4}.	241

7. Biofuels Production

Bio-oil can be potentially directly used as fuel in burner/furnace and burner/boiler systems, in medium- and slow-speed diesel engines, gas turbines and Stirling engines. However, bio-oils are very corrosive[250], show low thermal stability and low heating value. All these properties hinder their storage and direct use as liquid fuel[2,26]. Therefore, an upgrading process becomes necessary before their use as transportation fuels[251]. The most common upgrading strategies reported in the literature are: production of micro-emulsions[252-257], extraction of fractions with bio-diesel[24, 258], blending with solvents[99, 146, 259-261], acetalization and esterification[78, 165, 262-268], calcium enriched bio-oil[47, 269], co-processing in FCC units[88-92], co-processing in hydrotreating units[72, 93, 94, 96, 97].

Emulsions: Bio-oil can't be directly added to hydrocarbons fuels because they are immiscible. The high amount of water in the bio-oil is responsible for the formation of a separated phase when blending bio-oil with another fuel. This problem is addressed by using surfactants to form emulsions of bio-oil with the fuel[251]. Because emulsion is a mixture of fuels with different characteristics, the final properties will be flanked by the properties of the separated fuels[270]. The cost and energy consumption for emulsions production cannot be disregarded[257].

Lin *et al.*[271] investigated three different emulsifiers (Span 80, Tween 80 and Atlox 4914). Among these three, Atlox 4914 showed the best performance. Moreover, they found that the optimum hydrophilic–lipophilic balance, an important parameter for choosing an emulsifier, is directly proportional to the atomic O/C or H/C ratio, water content and inversely proportional to the high heating value of bio-oil. Other studies on the production of emulsions of bio-oil with diesel can be found elsewhere[252,253,256,272–275].

Mixtures of bio-oils with other fuels: Bio-oils can be used in boilers and engines when blended to conventional fuels[276]. It has been showed that mixtures of bio-oil and alcohols, for instance, improve fuel properties[146,277]. Blending bio-oil with methanol and tetraethylene-glycol dinitrate, a cetane-improving compound, was showed to make bio-oil suitable to use in high speed diesel engines[47].

Zhang and Wu[278] addressed the limitation of blending glycerol with bio-oil by using only the water soluble fraction (WSF) of the oil. This alternative mixture increased the blend rate up to

100%. Besides, the blends between glycerol and the WSF decreased the acidity and water contents, while increasing the density and heating values of the WSF. Finally, they found that adding biochar to this mixture improved even more properties of WSF. Further studies on mixtures of bio-oil and other fuels are available in the literature[258,279–281].

Bio-oil esterification: Bio-oil esterification is another strategy extensively studied to improve bio-oil fuel properties. Table 15 summarizes the studies on bio-oil esterification reported in the literature.

Table 15. Summary bio-oil esterification studies reported in the literature

System used	Operation conditions	Observations	Ref.
130 mL Hastelloy batch autoclave reactor	Reaction mixture composed by a methanol: bio-oil ratio of 0.9:1; Solid acid catalyst (1, 3 or 6 wt.% of total mixture); 700 rpm stirring rate; reaction temperature ranging from 70 to 170 °C; nitrogen atmosphere.	Either the increase in temperature, reaction time or catalyst loading lead to a higher conversion of light organic acids and aldehydes to esters and acetals. At temperatures over 110 °C and catalyst loading above 6 wt. %, there could be further decomposition of certain acetals.	282
100 mL stainless steel autoclave	Nitrogen atmosphere, reaction temperature 200 and 250°C, 7 MPa, 500 rpm stirring rate, for 30-180 min. Different ethanol:bio-oil ratios (1:1, 3:1, 5:1, 10:1)	At 250°C and 7 MPa, there was a complete transferal of carboxylic acids in the supercritical ethanol system. Selectivity of ethyl acetate reached 100% at the ethanol/bio-oil ratio of 5:1.	283
Fixed-bed reactor with an HZSM-5 catalyst (Si/Al ¼ 25)	3 groups of reactants: Group A (50 wt.% acetic acid and 50 wt.% deionized water), group B (50 wt.% propanoic acid and 50 wt.% water), and group C (25 wt.% acetic acid, 25 wt.% propanoic acid and 50 wt.% deionized water). Reaction at 330°C, 2 h reaction time.	Conversion degree of acetic acid was lower than propanoic acid. Selectivity for acetic acid increased up to 52% by increasing the Liquid Hourly Space Velocity (LHSV) to 3 h^{-1}. Selectivity for propanoic acid at LSHV=3 h^{-1} was as high as 80%.	284
Round bottom flask in a heating mantle for the reactions under azeotropic water removal and the reactive distillation.	Sulfuric acid was used as catalyst. $CaOH_2$ was added to neutralize the strong acid after the reaction, causing precipitation of calcium sulfate that was then filtered off and washed using methanol. Reactions of bio-oil with alcohols under azeotropic water removal: P-toluenesulfonic acid or Amberlyst-15 were used as catalyst. 81°C, continuous addition of cyclohexane.	High water content in crude bio-oils creates equilibrium limitations in condensation reactions. It wasn't possible to decrease the acid number to a value acceptable by petroleum refinery standards.	264
Custom-built, stirred SUS 316 reactor with an inner volume of 140 mL	Nitrogen atmosphere. 1MPa, 500 rpm stirring rate, heating rate of 15°C/min, various temperatures (300, 350 and 400°C). The produced gas was purged. Liquid and solid products were collected in a beaker and separated through vacuum filtration.	The supercritical ethanol-based upgrading lead to reduced acid number (TAN) and water/oxygen contents. The yield of the upgraded oil was over 80 wt. %.	285

Table 15. Continuation……

System used	Operation conditions	Observations	Ref.
Batch glass reactor equipped with a 200-rpm mixer for ozone oxidation of bio-oil.	Ozone oxidation of bio-oil: Continuous introduction of ozone into the reactor. 20 ± 2°C, 10 h reaction time. Reactions of Bio-Oil with Alcohols under Azeotropic Water Removal: 50g oxidized bio-oil, 50 g of butanol, and 4 g of catalyst ($NaHSO_4$). Temperature maintained at 116°C. The distillate was a two phase liquid. The upper layer (mostly butanol) was returned to the flask, and the lower aqueous layer collected separately.	Acid number of bio-oil was improved, changing from 45.4 to 118.4 mg KOH/g after oxidation. Oxidation also increased the thermal stability in esterification of bio-oil. The oxidized bio-oil had similar molecular weight distribution as the original one. Highest molecular weight of around 19 000 obtained after direct esterification.	286
25 mL round-bottom flask fitted with a condenser and a magnetic stirrer	A dicationic ionic liquid $C_6(mim)_2$-HSO_4 used as catalyst. Typical procedure of Fischer Esterification over $C_6(mim)_2$-HSO_4 Catalysts: Acetic acid, ethanol, and ionic liquid placed under vigorous stirring, at room temperature for 0.5-6 h. Esterification of Bio-oil with Alcohol over IL Catalysts: Bio-oil, ethanol, and ionic liquid, at room temperature for 6 h. After the reaction was complete, the ester and ionic liquid $C_6(mim)_2$-HSO_4 were separated by decanting.	The upgraded bio-oil had a yield of about 48%, and was composed of esters and other low polar components. The upgraded bio-oil had significant better properties compared to the crude bio-oil, as it had less water and acid content.	287
130 mL batch reactor	Reaction mixture composed of methanol and bio-oil at different mass ratios. Acid catalyst Amberlyst-70. Nitrogen atmosphere, 700 rpm stirring rate, 120 min reaction time. Various temperatures (70-170°C).	Simultaneous formation of levoglucosan from the hydrolysis of sugar oligomers and esterification of organic acids to esters occurred. Glycosidation also occurs because levoglucosan is further hydrolyzed into D-glucose, which reacts with methanol producing methyl-a-D-glucopyranoside. Reactions dependent on the catalyst loading and the methanol/bio-oil ratio.	262

8. Bio-Products

In this section we will review existing and potential co-products that can be obtained from the whole bio-oil, its water soluble and insoluble fractions and the main products that can be derived from pyrolysis oils.

Bio-lime: The reaction between bio-oil phenols and the carboxylic acids and lime produce calcium salts that can be applied for the adsorption of acid gas compounds, like SO_x[288]. This product, named BioLime by Dynamotive Corporation, increases the efficiency in capturing acid gases (SO_x) emitted from coal combustors, compared to lime[288].

Slow release nitrogen fertilizers: Amides, imines and Mannich reaction products, are produced from the reaction of bio-oil functional groups (carbonyl, carboxyl, hydroxyl, phenolic and methoxyl) with ammonia, urea, and other amino compounds and can function as slow release organic fertilizers with 10% of nitrogen[266,308]. Fertilizers produced with this method have a lower leachability compared to mineral fertilizers, obtaining then a slow-release nitrogen fertilizer, and thus resulting in less pollution of the groundwater than mineral fertilizers[266]. Typical fertilizer with controlled nitrogen release sells for around \$250-1,250 ton^{-1} [266].

Pesticides and wood preservatives: The development of pesticides from tobacco leaves and dried coffee grounds bio-oil against problematic pests in Canadian agriculture has been studied at the University of Western Ontario[294,295]. Converting tobacco leaves to natural pesticides in the form of bio-oil can be done since tobacco's pesticide properties are well-known[295]. Studies of whole bio-oils and their lignin-rich fractions as potential environmentally friendly wood preservatives have been performed with hopes to replace the metal-based CCA and copper systems that have raised environmental concerns[290]. The lignin-rich fractions showed greater fungal inhibition than whole bio-oils. The synergistic fungicidal properties of bio-oils as a potential substitute for creosote, which also presents environmental concerns, have been demonstrated by several researchers[293]. Pentachlorophenol has been proven to be 10 times more effective with bio-oil[290]. Bio-oil can be used as a green wood preservative due to some terpenoid and phenolic compounds that act as insecticides and fungicides[291,292]. Mohan et al. [290] had some success in initial tests of a polymerization chemical to prevent leaching. Table 16 summarizes some of the studies so far conducted in the use of bio-oil as pesticide in agriculture or as wood preservative.

Table 16. Application of pyrolysis oil fractions in agriculture and as wood preservative

Source and fraction used	Application	Observation	Ref.
Whole bio-oil from coffee grounds and fractions obtained by liquid-liquid extractions	Insecticide (against Colorado Potato Beetle - *Leptinotarsa decemlineata Say*) and bactericide (against bacteria *S. scabies* and *C. michiganensis*)	They showed good insecticide and bactericide effects	294
Bio-oil from tobacco leaves and fractions obtained by liquid-liquid extractions	Insecticide (against Colorado Potato Beetle - *Leptinotarsa decemlineata*), fungicide (against *Pythium ultimum*) and bactericide (against *Streptomyces scabies* and *ClaVibacter michiganensis*)	The Colorado Potato Beetle, *Streptomyces scabies*, *ClaVibacter michiganensis*, and *Pythium ultimum* were all strongly affected by tobacco bio-oils. Good insecticide effect was also observed by the nicotine-free fractions of the tobacco bio-oil, along with inhibited growth for the microorganisms.	295
Wood vinegar obtained from the Gangwon Mokcho Industry Incorporation, Yeongwol, Korea	Insecticide (against *N. lugens* and *L. striatellus*)	When mixed with carbosulfan (an insecticide), wood vinegar enhanced its insecticidal effect. Used alone, wood vinegar had no insecticidal activity. Mixed with other insecticides, wood vinegar had no effect.	296
Wood vinegars from coconut shell (wood vinegar A), coconut shell and coir 1:1 w/w (wood vinegar B)	Termiticide (against *Odontotermes sp*) and pesticide (against *Ferrisia virgate*)	Highest termiticidal activity at a dilution of 1:50 v/v, wood vinegar: sterile water, killing more than 80% of termite workers after the 24 h. Over 95% of striped mealy bugs were killed by wood vinegars A and B at a dilution of 1:10.	297

Table 16. Continuation……

Source and fraction used	Application	Observation	Ref.
Wood vinegar from *Vitex pubescens* at different temperatures	Fungicide (against *Trametes versicolor* and *Fomitopsis palustris*) and termiticide (against *Reticulitermes speratus* and *Coptotermes formosanus*)	Demontrated antifungal activity against *Trametes versicolor* and *Fomitopsis palustris*. Better performance obtained by wood vinegars produced at 450°C. Showed antitermite activity to both termites in the no-choice experiment. In the direct-choice experiment, wood vinegar showed great repellent effect.	298
Wood vinegar produced from fresh wood in a Iwate kiln	Add-on to bio-fertilizer to increase yields and reduce pest infestations on soybean. Six different treatments were tested comparing the effect of wood vinegar with mixtures of well-known insect repellent and pesticide like tobacco, citronella or derris	Average soybean yields of 402 kg/rai were obtained and the yields didn't statistically differ among treatments. The wood vinegar treatment showed the most significant pest control efficiency with an insect damage score of 1.75 compared to 3.29 for the 5 other treatments	299
Wood vinegar produced by burning fresh wood at 120-430°C in a charcoal kiln. Also, extracts from three of the medicinal plants: neem seed (*Azadirachta indica* A. Juss) and yam bean seed *Pachyrhizus erosus* extracts and citronella grass (*Cymbopogon nardus*)	Insecticide (against larvae of mosquito *Culex quinquefasciatus* Say	Using the dropping method, wood vinegar at 2% concentration could kill 73.75 % of mosquito larvae after 24 h, and over 96% after 72 h of test. Using the topical application method, wood vinegar at 20% concentration could kill a maximum of 15 % of mosquito larvae after 72 h of test. Mixed with extract of neem seed, yam bean seed or citronella grass (1:50 mL ratio), the 2% of wood vinegar showed larval mortality of 92.5%, 50.0% and 45.0%, respectively for a 72 h test. And, by dropping method all of the treatments showed 100% mortality of the mosquito larvae after 48 h	300
Wood vinegar (obtained from Energy Ashram, Appropriate Technology Association, Thailand) and fermented bioextracts from plants or animal residues	Enhance growth and yield of tomato	Alone or in combination, slightly increased plant dry weight, fruit number, fruit fresh and weights. Alone, wood vinegar and fermented bioextracts showed similar effects on growth and yield of tomato. Combined, extracts had an additive effect.	301

Table 16. Continuation……

Source and fraction used	Application	Observation	Ref.
Coconut shell vinegar	This review selected over 10 chemical compounds that can be used to develop new products and discussed their applications in different industries	Food industry: anti-microbial, anti-oxidant, flavor. Pharmacy and cosmetics industry: deodorizer, soap, sun screen cream, sterilizing agent, anti-microbial agent for treatment in skin diseases. Chemical industry: latex coagulant and rubber sheet additive, and wood preservative. Agricultural purposes: pesticide, fertilizer and plant growth enhancer, antifungal, feed-stuff, repellent and insecticide	302
Wood vinegar prepared by burning waste wood in a charcoal kiln at 120–430 °C and purified by standing and filtering methods.	Larvicide activity of wood vinegar at different concentrations from 10 to 30% against larvae of housefly *Musca domestica* L.	The feeding method was more efficient than the topical application method. Wood vinegar at 10% concentration showed no effect on mortality of *M. domestica*. Larval mortality increased with increasing concentration of wood vinegar and the duration of exposure. Larval and pupal duration were extended by the treatments	303
Wood vinegar from chips of sugi wood (*Cryptomeria japonica*), hinoki wood (*Chamaecyparis obtusa*), hiba wood (*Thujopsos dolabrata*) and bamboo (*Phyllostachys heterocycla*) obtained at different heating rates (2–8 ºC/min) and temperatures (300–1000 ºC)	Fungicide activity against *Fomitopsis palustris* and *Trametes versicolor* on the agar medium and termiticidal effectiveness using Formosan subterranean termite, *Coptotermes formosanus*	Effective against termite and wood-destroying fungi. The fungicidal efficiency was significantly improved with increasing heating rates, but only slightly with temperature	304
Coconut shell oil supplied by AVT Natural Products, Karnataka, India.	Termiticide compared to wood preservatives currently in use	Coconut shell oil has good termiticidal activity. An 18 month data showed that all the control stakes were 100% destroyed, compared to 34.2% damage in the coconut shell oil brush coated stakes.	305

Table 16. Continuation…….

Source and fraction used	Application	Observation	Ref.
Wood Pyrolysis Liquids	Assessment of pesticide and plant protection activity and comparison with cashew nut shell and Bifenthrin, a termiticide of synthetic origin	The replacement of synthetic pesticides with bio-based ones is likely a slow process, as the chemical composition and mode of action as a pesticide of wood vinegar is still not completely understood.	306
Birch (*Betula sp.*) -derived slow pyrolysis products, birch tar oil, wood vinegar and biochar	Plant protection – mollusk control and herbicide	Birch tar oil and wood vinegar were ineffective in eradicating snails. Birch tar oil and the mixture of birch tar oil and wood vinegar were good in repelling snails and slugs. Soil organisms were more tolerant of wood vinegar than aquatic organisms. Wood vinegar offers negligible risk to soil and aquatic organisms.	307

Production of synthesis gas: Studies about syngas production via gasification can be found in the literature[354]. Due to low ash content, pyrolysis oils potentially can be gasified in the 1000-1250 °C range[354]. Bio-oil to gas conversions as high as 83 wt. % have been reported[354]. Composition of syngas obtained includes 16-36 % CH_4, 19-27 %, and 21-31 % C_2H_4[168].

Asphalt paving substitution: The possibility of using bio-oil as a substitute for petroleum products in asphalt emulsions has been explored by several research groups[369, 370].

Resins and adhesives: Among the several possible applications of bio-oil phenolic compounds maybe the most common is the use as partial substitute of phenol in phenol-formaldehyde resins, such as, novalak and resole resins[21,47,240]. Phenol-formaldehyde resins can be utilized in molded products including billiard balls and laboratory countertops, and as adhesives for example in the manufacturing of wood panels such as plywood, medium density fiberboard (MDF), particle board and oriented strand board (OSB). The manufacture of wood panels such as plywood, MDF, particle board and OSB could employ renewable phenolic resins from bio-oils[406,407]. Resins are prepared by utilizing either the phenolic enriched fraction obtained after fractional condensation, further processing such as solvent extraction, or by utilizing the whole liquid product. None of the phenolic fractions produced allow 100% substitution of the phenol content of the resins without impacting effectiveness, compared to commercial formulations based petroleum-derived phenol. High-quality resins can be produced from the replacement of 30-50% of the phenol with pyrolytic lignin in novolak and resole formations despite the fact that lignin is less reactive than phenol. Further research is required to meet quality requirements and develop a low-cost renewable resin. Areas of concern include the variability of renewable resin properties, odor, and wood panel press times; the potential for increased emissions of volatile organic compounds; and the lack of reactive sites compared to phenol[21,47,168].

There are some papers on the use the phenolic fraction from bio-oils for the development of thermo-responsive with adhesive properties. Extensive work has been done with lignins derived from chemical pulping technologies[164,237,331–339]; however, the phenolic fraction derived from pyrolysis is quite different than chemically-pulped lignins[33,34,341]. Sahaf et al.[343] work showed that pyrolytic lignin can be used in its original uncombined form to produce a thermo-responsive polymer. A stabilized binder that responded to temperature similar to that of a thermoplastic was developed by utilizing a heat-treatment procedure to eliminate water and volatile mono-phenols. This phenolic fraction is likely not a polymer due to its low molecular weight (>950 Mw); however, the thermo-responsive behavior is likely due to interparticle attractions and hydrogen bonding[343]. By thermally treating at differing temperatures, the thermoresponsive behavior can be tailored. A lap-shear test was applied to the glue-line when evaluating the bonding performance of the PRF to wood veneer.

Antioxidants: Bio-oil is a very good source of antioxidants due to the presence of lignin derived compounds[360,361]. Vanillin, identified in bio-oils[29] has an antioxidant effect by protecting mitochondria against protein oxidation and lipid peroxidation induced by photosensitization. This effect is similar to that of the classic antioxidants such as the ascorbic acid and the singlet oxygen quencher, diazabicyclo[2.2.2]octane[362]. Other compounds with antioxidant properties present in bio-oils are the eugenol and hydroquinone[29]. Eugenol inhibits the copper-dependent oxidation of low density lipoproteins[363] and prevents liver damage in rats by reducing the peroxidation indices and protein oxidation[364]. Hydroquinone is recognized as a potent skin lightening agent which also shows a potent 1,1-diphenyl-2-picrylhydrazyl radical scavenging activity[365]. The antioxidant properties of the water-soluble and insoluble fractions derived from pyrolytic oils were investigated applying different assays[360,361]. Results showed that the water-insoluble fraction presented a better capacity to scavenge radicals compared to the water-soluble fraction. It was attributed to the number of phenolic compounds which reached a maximum value 83.1% for ash tree wood[361]. Important improvements in biodiesel oxidative stability has been reported when bio-oil phenolic fractions added to bio-diesel[20,366,367]. In summary, these results suggest that bio-oils could be considered as a source of natural antioxidants to be used for controlling imbalances caused by oxidative stress.

Carbon fiber: Polymer composites are materials that are obtained by reinforcing the polymer matrix, often a synthetic polymer, with suitable reinforcement material, generally fibers. Intense efforts are being made to use lignin as a low-cost eco-friendly reinforcement material to prepare high performance composites. Although most of these studies are mainly focused on lignin obtained from pulping or organosolv processes, some researchers have also investigated the use of pyrolytic lignin with this purpose[323]. Carbon fibers from pyrolytic lignin are produced by thermal spinning and carbonization processes, and sometimes involving also other processes, such as, a previous polymerization or a stabilizing treatment by oxidation chemical pre-processing treatment of the pyrolytic lignin, such as, repolymerization[323]. According to these authors, the quality of the carbon fiber produced from pyrolytic lignin could be further improved by process optimization. Qin and Kadla[371] found out that compared to other technical lignins, a lower spinning temperature was required for pyrolytic lignin and also that a thermal treatment before fiber spinning allowed to maintain the fiber integrity during thermostabilization and the following carbonization process. They also determined that the mechanical properties and the yield of the pyrolytic-lignin-based carbon fiber were comparable to those based on other technical lignins, indicating the suitability of pyrolytic lignin as a potential feedstock for low-cost carbon-fiber production. Kadla and Kubo[325] investigated the influence of blending synthetic polymers to enhance the processability and flexibility in the fiber and reported that poly(ethylene oxide) (PEO)/and poly(ethylene terephthalate)(PET)/lignin polymer blends were miscible to produce robust fiber, whereas poly(vinyl alcohol) and polypropylene/lignin polymer blends showed poor miscibility and did not enhance the strength of the fiber.

Production of hydrogen: There are currently no commercial biomass processes for direct hydrogen production[344,345], although some processes, such as, aqueous phase reforming and steam reforming, have been proposed. Aqueous phase reforming approach was developed by Dumesic and co-workers to produce H_2, although the high-energy consumption, the low atom economy and the scarce purity of the H_2 produced make this alternative economically unsuitable[411,412].

Steam reforming can be applied in order to transform aqueous fraction or light oxygenates, such as, acetic acid, ethanol, acetone, acetic acid, acetol or propanal, into H_2, syngas or more valuable compounds. In this sense, acetic acid steam reforming has been largely studied in literature[383,384]. Ni/Al_2O_3 catalyst has been used for H_2 production via steam reforming and sequential cracking process[347]. In addition, Ni/ and Ni-Ce/MgAlOx catalysts have been studied employing light oxygenates (ethanol, acetone, acetic acid, acetol, propanal…) as model compounds of pyrolytic aqueous fractions[385,386]. In general, high-energy consumption and low atom economy of the process are the main drawbacks to overcome.

Aldol condensation and ketonization: The transformation of bio-oil water-soluble compounds by performing "one-pot" C-C bonds formation reactions, such as aldol condensation and ketonization has recently been claimed as a beneficial alternative approach[413–415]. In this way, these short-chain and low value-added oxygenated compounds can be transformed, and further upgraded to generate a mixture of hydrocarbons and aromatics useful for blending with automotive liquid fuels.

Firstly, aldol condensation reactions have been largely studied by different authors employing basic mixed oxides (i.e. Mg-Al derived hydrotalcites, MgO, ZnO) as active materials for acetone-furfural aqueous phase condensation reactions under moderated conditions[416,417]. Moreover, MgO and Mg/Zr oxides have also been used to study acetone gas-phase self-condensation under higher temperature conditions (200-300ºC) [418,419]. The use of amphoteric or acid mixed oxides with well-distributed active sites can as well effectively perform these reactions. In this sense, catalysts based on CeZrO mixed oxides have been widely considered[415] for the gas-phase conversion of small aldehydes at high temperatures (>300 ºC), whereas TiO_2-based materials have been used for the acetone-furfural condensation reaction at moderated conditions[420].

In a similar way, the same oxides can be used as catalysts for ketonic decarboxylation or ketonization reactions of carboxylic acids, where two molecules of short chain acids are transformed in one larger chain ketone via C-C bond formation, also producing CO_2 and H_2O during reaction. This process contributes reducing carboxylic acids content, thus avoiding pH and corrosivity problems of the mixture, while additionally allows hydrocarbon chain growth by means of consecutive C-C bonds formations.

In the last years, both reaction mechanisms have been deeply studied by using acetic acid or propanal as probe molecules with TiO_2 and ZrO_2 as catalysts[421,422]. These studies conclude that the activity of these catalysts is based on their bifunctional character (acid/base sites combination), necessary to assist intermediates formation on the surface of the catalyst. Different strategies even with the incorporation of noble metals on the solid catalyst have been attempted[414].

Most of these studies were performed using single compounds under conditions distant from realistic operation conditions, and not many examples of complex mixtures can be found in literature. Water effect on acetic acid ketonization[414] and furfural, acetol or cresol effects on acetic acid ketonization[423] were studied, meanwhile the effect of acid and water on propanal condensation was carefully considered[415]. In addition, these studies also show CeMOx (Ce, Mn, Al) catalysts to have poor structural stability, while TiO_2, ZrO_2 lose catalytic activity at high temperatures, being this effect enhanced by the presence of water. More recently, hydrothermal niobium oxides and WNbO materials have been claimed as active and stable catalysts when dealing with complex mixtures simulating aqueous effluents obtained by phase separation of pyrolytic bio-oils[424,425]. Based on these considerations, the study of catalytic activity and stability of materials under more realistic operation conditions and employing aqueous complex mixtures is essential to effectively advance in this particular approach.

Food additives: Smoking to preserve food has become less and less important over the course of the last 50 years and today fish and meat are typically smoked only for flavoring reasons. Glucoaldehyde, glyceraldehydes, pyruvaldehyde, dihydroxyacetone, acetone, and diacetyl are effective browning agents[168]. An application that has been commercial for over 10 years uses the water-soluble part of fast pyrolysis bio-oil as browning agent. Both phenolic compounds that provide the smoky flavors and the low-molecular-weight aldehydes that are effective meat browning agents (especially glycolaldehyde) are included in the aqueous extract of bio-oil. Methods for the isolation of glycolaldehyde based on crystallization have been patented by Red Arrow Products and RTI. This compound is susceptible to decomposition at temperatures higher than 100 ºC. If glucose is used instead of wood as the feedstock for fast pyrolysis, the production of glycolaldehyde becomes more attractive[47]. A new method for the separation of glycoaldehyde from pyrolysis oil via physical extraction has been reported by researchers from the Eindhoven

University of Technology[17]. Reactive extraction with the use of tertiary amines for separating acid compounds is incorporated in the conceptual design.

Production of polyethers: We are not aware of any research activity that uses the aqueous fraction of bio-oil to make plastics. However, some studies describe the synthesis of polymers from the anhydrosugars (levoglucosan, cellobiosan, and oligomers) in the water soluble fraction[326–328,330].

Bio-Products from fermentable sugars: Via microbial fermentation, fermentable sugars can produce different chemicals and commodity, such as ethanol, organic acids (e.g., citric acid, fumaric acid, lactic acid, propionic acid, succinic acid, itaconic acid, acetic acid and butyric acid), amino acids, antibiotics, fatty acids, and others (e.g., glycerol, acetone, n-butanol, butanediol, isopropanol, and acetaldehyde) [229,399]. Moreover, it is known that fermentable sugars can be used in the production of second-generation bio-fuels through several different technologies. Huber *et al.*[400] list several pathways to produce hydrocarbons, H_2, CH_4 and above all ethanol from sugars. The sugars can also, through chemical conversion, originate products like furfural, furans, glycols, methyl ethyl ketone, adipic acid, ethylene and propylene[401,402]. This list continues if one assumes that these products can undergo further processing and originate even more products. However, the production of ethanol via fermentation of sugars remains the most commonly used technology[229].

Ethanol is a well-known bio-fuel and an interesting platform chemical since fermentation is already used industrially to produce it from biomass in bulk quantities. The world ethanol production was estimated at 40 billion liters in 2003[115]. The three major uses for ethanol are: fuel and fuel additive (69%), as a solvent and a building block for chemical synthesis (21%), and as an ingredient of alcoholic drinks and a disinfectant and a preserving agent in the food industry (10%)[115]. The production of ethanol from the fermentation of pyrolytic sugars is described in several papers[229,230,355–358].

Bio-carbon electrodes: The production of graphite-like materials using bio-pitch, heaviest fractions obtained by distillation of pyrolysis oils, has been studied by Coutinho et al.[23]. Bio-pitch is compressed with ground solid charcoal and a 120 mm length and 25 mm diameter green, pre-molded electrode is obtained. It is cured using a treatment involving an increasing temperature. Following the curing step, the electrode then undergoes calcinations at 1000 ºC, followed by graphitization at 2700 ºC. The bio-oil derived electrode has comparable properties to the ordinary electrodes[23]. Elliott et al.[373] recently studied the hydroprocessing of bio-oil and the separation of heavy fractions for coke production proposing its use for the manufacture of low-sulfur electrode carbon.

Olefins: Extensive work has been done on ketonization of carboxylic acids (chiefly acetic acid) over both alkali earth metal oxides and transition metal oxides (Mn_2O_3-CeO_2, TiO_2, ZrO_2, and CeO_2)[312–314]. In addition, ketone conversion to olefins has been reported over Brønsted acid sites of zeolites (HZSM5, H-BEA)[315–319]. Not until recently was direct acetic acid conversion to isobutene with a 50% yield achieved. This process used acetic acid ketonization to acetone, followed by acetone aldol condensation to mesityl oxide and mesityl oxide cracking on Zn/Zr catalyst with Brønsted acid active sites prepared by co-precipitation. The group of Co-PI Wang recently found that $Zn_xZr_yO_z$ catalysts with balanced Lewis acid-base pairs convert bio-acetone (acetone/H_2O solution) to isobutene[320,322,372].

Surfactants: Oils to produce surfactants are recovered at various stages of tar distillation and during raw acetic acid refining. They range from transparent to dark brown and have a characteristic smell. More than 10 commercial grades are known and made according to specifications, classified by specific weight, viscosity, calorific value and boiling point. They are widely used in the flotation process for the separation and beneficiation of ores[55]. The price of flotation agents is \$400-2,300 t^{-1}.

Products derived from Acetic Acid: Acetic acid can be transformed in other valuable products by several methods including ketonization, esterification and steam reforming, among others. Firstly, acetic acid ketonization has been previously discussed as one of the principal approaches considered in literature. Ketonic decarboxylation or ketonization consists of two moles of acid transformed in one mol of acetone and one mol of CO_2 and H_2O as the only byproducts. In such a way, acetone can be produced from acetic acid via new C-C bond formation, this process being of great importance. CeO_2, ZrO_2, CeZrO and rare earth metals have been largely studied for C2-C5 organic acid gas-phase ketonization reactions at high temperatures (300-500 ºC)[374–377]. Organic acid and aqueous mixtures containing acetic acid have been considered as model compounds/mixtures when studying this approach. Atom economy of the process and operation conditions traditionally used are the main drawbacks when dealing with this alternative. On the other hand, acetic acid can react with different alcohols via esterification to produce the corresponding ester together with H_2O as byproduct. This reaction pathway has been considered by other authors in order to "catalytic stabilize" aqueous effluents obtained by phase separation of pyrolytic bio-oils or pyrolytic bio-oils themselves. The use of acid catalysts (ionic exchange polymeric resins, such as Amberlyst) together with different alcohols (methanol, ethanol, butanol) under moderated conditions can reduce carboxylic acid contents (TAN/pH reduction), also reducing corrosivity and reactivity concerns when using aqueous effluents derived from pyrolytic bio-oils. Traditional distillation, azeotropic water removal or reactive distillation need to be used in order to increase this process efficiency[121,238,378,379].

Ethanol production from the hydrogenation of acetic acid has been extensively studied[309–311,380,381]. The most common catalysts used are noble metals (Ru, Pd, Pt) on C and TiO_2, and the reaction is typically conducted at temperatures between 150 and 300 ºC[139,310,380]. Ito et al.[309] studied the hydrogenation of acetic acid in the presence of Ru-Sn/TiO_2 for ethanol production. Ru and Sn form alloys and the researchers found that the addition of Sn (2-4 wt. %) improves ethanol selectivity by the suppression of gas production[309]. These authors proposed a mechanism for acetic acid hydrogenation at the Ru-TiO_2 interface in which carbonyl activation through coordination with Ti significantly enhanced hydrogenation[309]. Rachmady and Vannice[382] investigated Pt loaded on SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 for acetic acid hydrogenation to ethanol. The reaction was studied in vapor phase between 150 and 300 ºC. TiO_2 showed the best catalytic performance.

Products derived from Acetol: Due to its high reactivity and usability in organic synthesis, acetol becomes a key intermediate for chemical industry. Acetol has hydroxyl and carbonyl functional groups and, therefore, can promote a lot of reactions, such as dehydration, hydrogenation, oxidation and polymerization[388]. Propylene glycol, acetone, acrolein, furan derivatives and propionaldehyde are examples of products derived from acetol.

Besides, it can be directly used in food, textile and cosmetic industries. In food industry, it can be used to provide aroma to foods and to induce flavor in heated milk. In textile industry, acetol can substitute sodium dithionite, usually used to allow fixation of the dye in the textile by decreasing the dye to a water-soluble compound. And, in cosmetic industry, acetol serves as main constituent of skin tanning agent[392] in addition to provide access to important natural carbohydrates and unnatural polyhydroxylated molecules in medicine[220]. Acetol can promote various reactions (e.g. dehydration, hydrogenation, oxidation) and produce numerous products including propylene glycol, acrolein, acetone, and furan derivatives[220].

Products derived from Hydroxyacetaldehyde: Hydroxyacetaldehyde, also named glycoaldehyde, is a precursor of ethylene glycol through either hydrogenation or fermentation process[223,393]. Ethylene glycol can be used as coolant and antifreeze, as monomer in the production of polyester, as solvent, and as intermediate for chemicals production, among other applications[393]. Besides, hydroxyacetaldehyde is used as food browning agent[395] and for producing flavors when contacting hydroxyacetaldehyde with ammonia or amines[227]. Finally, it has been reported that hydroxyacetaldehyde may also be used to prepare an artificial tanning product to give a brown color to skin[227]. Glycoaldehyde can be used as an effective meat-browning agent[395] or as a fermentation feedstock to produce ethylene glycol[223]. Liquid smoke aroma for the food industry serves for preservation, flavoring and coloring in the treatment of meat, sausages, and cheese to replace the time-consuming and ineffective traditional smoking procedure. In addition, smoke flavoring are increasingly used in soups, sauces, and snacks. Within the EU such liquid flavoring needs to be authorized by the European Food Safety Authority (EFSA)[1]

Ethylene/propylene glycol production: Very few studies mention the heterogeneous catalytic production of ethylene/propylene glycol from hydroxyacetaldehyde and acetol. Most of the reports in the literature consider these compounds as intermediates of cellulose or glycerol hydrogenation[139]. In contrast ethanol production from the hydrogenation of acetic acid has been extensively studied[152,309–311]. Although the electrochemical reduction of various organic molecules has been demonstrated over the past decades, there is very limited information on acetol and hydroxyacetaldehyde electrochemical reduction[152,309–311].

Products derived from levoglucosan: By using demineralized cellulose, high yields of levoglucosan (1,6-anhydro-*a*-D-glucopyranose) (up to 46 wt. %) and levoglucosenone (6,8-dioxabicyclo[3.2.1.]oct-2-en-4-one) (up to 24 wt. %) can be generated[47]. Considerably lower yields (< 10%) of levoglucosan are produced from the pyrolysis of lignocellulosic materials. The efficient isolation of levoglucosan from the pyrolytic liquids is one of the main difficulties involved in its production. Due to the high production price of levoglucosan from lignocellulosic materials, it is unlikely to see extensive use in the near future despite its potential for the manufacturing of pharmaceuticals, surfactants, biodegradable polymers, and others[47]. It is known that levoglucosan can be hydrolyzed to glucose, being a potential route to bio-ethanol production[396,397]. In similar way, it is also a potential route for fatty-acids production[229]. Levoglucosan could serve as chiral synthon to control stereo-selective reactions during synthesis[1]. However, the application of levoglucosan is much more extensive. It has been reported as an important element on the production of antibiotics, antiparasitic agents, and other biologically active compounds[47,188,398]. Levoglucosan could be used as a raw material to produce many materials, such as plasticizers, propellants, explosives, surfactants, resins, plastics, and others[235].

Products derived from pyrolytic humins: Although it was not possible to find products derived from pyrolytic humins there is a growing body of literature on products from humins by products of hydroxyMethyl Furfural/Furfural/FuranDiCarboxylic Acid bio-refinery[426]. These humins are obtained from acid treatment of polysacchairdes and showed very interesting properties as semi-ductile thermoset matrix to impregnate cellulosic fibers with enhanced modulus and tensile strength compared with pure polyfurfurylalcohol resins[426]. Initial ecotoxicity and biodegrability tests of humins did not show any immediate concern[427].

8 Conclusions

The growth of the pyrolysis industry is severely hindered by the lack of commercial bio-oil refineries. Although we do not have a standardized strategy to characterize bio-oil and to separate it in groups or families, the overall chemical makeup of these oils is becoming better known. The four major bio-oil compounds with potential to be commercialized as purified molecules are acetol, hydroxyacetaldehyde, acetic acid, levoglucosan. The rest of the bio-oil needs to be commercialized as fractions. Bio-oil upgrading into a low-quality heavy oil substitute and bio-oil refining to transportation fuels are the two main strategies so far explored for the commercialization of these oils. These concepts remain at demonstration stage due to unsolved operational challenges and high production costs. The increase in the number of papers in bio-oil separation together with the development of equilibrium models to describe the behavior of pyrolysis oils in separation units is encouraging. There are many opportunities to separate bio-oil fractions and convert them into value added co-products in new integrated biorefinery schemes. Despite these progresses, very few fully integrated bio-refinery concepts have been reported in the literature. The synthesis, techno-economic and environmental evaluation of novel integrated bio-oil refinery concepts for fuels and chemicals production is likely to become a subject of intense research activity in the coming years.

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