Review on Aging of Bio-Oil Derived from Lignocellulosic Biomass Pyrolysis

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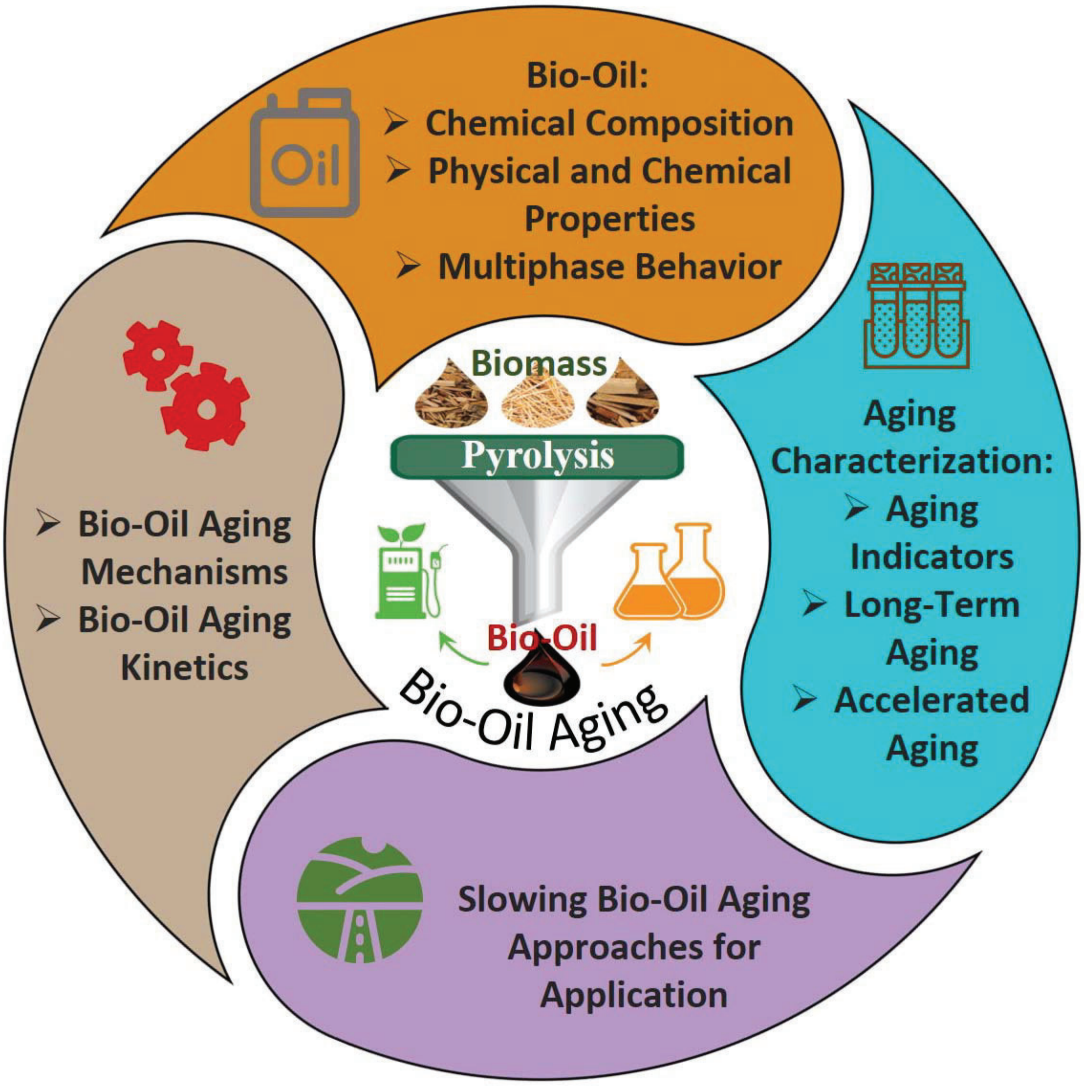
Abstract

Bio-oil from biomass pyrolysis is a promising alternative and clean source of bio-fuels, chemicals, and materials. Its chemical composition, physical and chemical properties and multiphase behavior change over time because of aging, which significantly affects its storage, handling, transportation, upgrading and application. This review focuses on studying bio-oil aging, and its outlook, primarily covering the following four parts: (1) the chemical composition, physical and chemical properties, and multiphase behavior of bio-oil; (2) the indicators for measuring the degree of aging and aging characteristics including physical and chemical properties change during long-term and accelerated aging of bio-oil; (3) the aging mechanisms and kinetics emphasizing the reactions during the aging process and different kinetic models based on different aging indicators; (4) the potential methods for slowing down bio-oil aging rate. This review comes up with highlights in developing aging mechanisms and kinetics that will allow readers' in-depth understanding of the effect of aging on bio-oil properties and the approaches to improve the resistance of bio-oil aging.

Keywords: lignocellulosic biomass; pyrolysis; bio-oil; aging mechanisms; stability

Graphical abstract



1 Introduction

The consumption of fossil energy in the world has been steadily increasing with the development of the world economy and society, especially in the Asia-Pacific region [1]. In recent years, environmental and ecological problems have been resulted from the excessive utilization of nonrenewable fossil fuels, which are currently the world's primary energy source and set to meet over 80% of global energy demand [2]. To address those environmental and ecological problems, low carbon sustainable development has been highly emphasized by most countries [3]. With the increasing demand for energy and growing concerns regarding environmental and ecological issues, the transformation from traditional fossil fuel to renewable energy is an urgent need [4]. China plans to increase the percentage of its energy from renewable resources during the 14th Five-Year Plan (2021-25) period according to the National Energy Administration.

Lignocellulosic biomass is a renewable energy source and an alternative to fossil fuel with rapidly growing interest [5, 6]. It has the potential in terms of low cost, abundance, energy security, and low carbon footprint [7]. Lignocellulosic biomass typically contains three major biopolymer components: cellulose (30-35%), hemicellulose (15-40%), lignin (15-35%), which are associated with each other in a hetero-matrix to different degrees and varying relative contents [8]. There are various biomass conversion technologies, which can be generally categorized into four main types according to the used techniques and principal energy carrier produced in the conversion process: thermal [9], thermochemical [10], biochemical [11] and chemical

[12] conversion technologies (see **Figure 1**). Those technologies exist to convert the energy stored in biomass to more useful forms of energy.

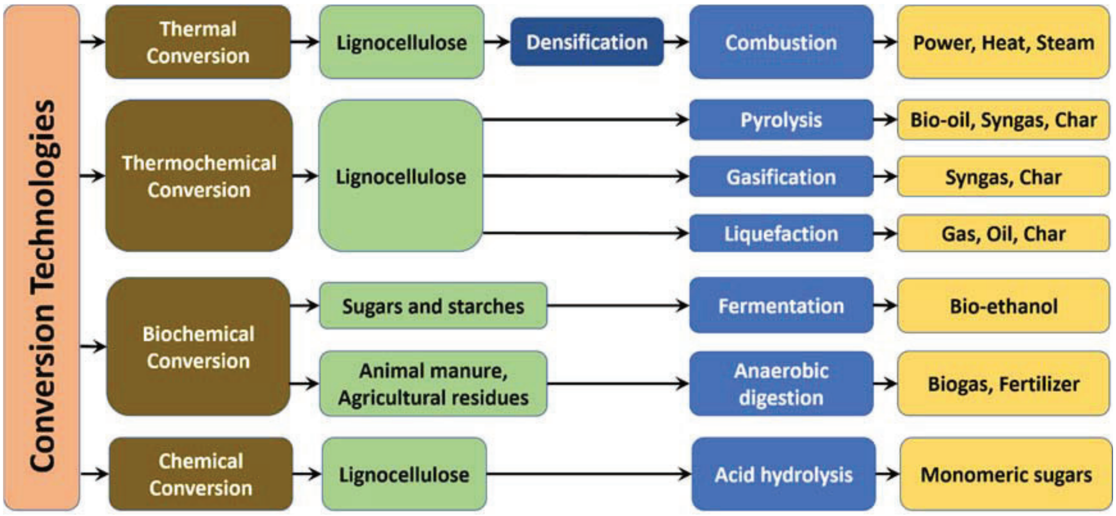


Figure 1. Various conversion technologies of lignocellulosic biomass

Among various conversion technologies, pyrolysis is of particular interest, as it converts solid lignocellulosic biomass into a liquid fuel (bio-oil), which is readily stored, handled, and transported and can be conveniently used in versatile applications [13]. It is the thermal decomposition of biomass in the partial or complete absence of oxygen. The yield and chemical composition of bio-oil are fundamentally determined by feedstock nature [14], pretreatment method [15], catalysts and their structures [16, 17], reactor configurations [18], and process conditions [19, 20].

Bio-oil has a highly promising potential to be widely used considering its advantages of renewability, CO_2 neutrality, transportability, relatively high energy density, and good secondary conversion performance [21-23]. Bio-oil can be utilized in different ways, which are summarized in **Figure 2**. Bio-oil is combustible but requires significant energy for ignition [24], which has been verified by the performance tests of bio-oil combustion in industrial boilers [25, 26], diesel engines [27] and gas turbines [28-30]. It can be burned as a substitute for kerosene in gravity stove for cooking [31], and also transport fuel in combination with diesel fuel by using emulsification [32, 33] or micro-emulsification [34, 35]. Fractioned bio-oil can be upgraded into transportation fuels by using catalytic cracking and hydrotreating [36]. The aqueous fraction of bio-oil can be used to produce hydrogen by catalytic steam reforming [37, 38]. The heavy fractions of bio-oil have similar composition and comparable rheological and adhesion properties as the light fractions of petroleum bitumen [39]. Hence, they can be potentially used as a substitute road material for petroleum-derived bitumen [40, 41] or aged bitumen rejuvenator [42]. Some species rich bio-oil can be used as extracted specific chemicals like sugars, sugar derivatives, carboxylic acids, and aromatic hydrocarbons [43-46]. Some bio-oils can be used as preservatives and pesticides because they contain acid, hexane, ketone, alcohol, and phenolic compounds [47, 48].

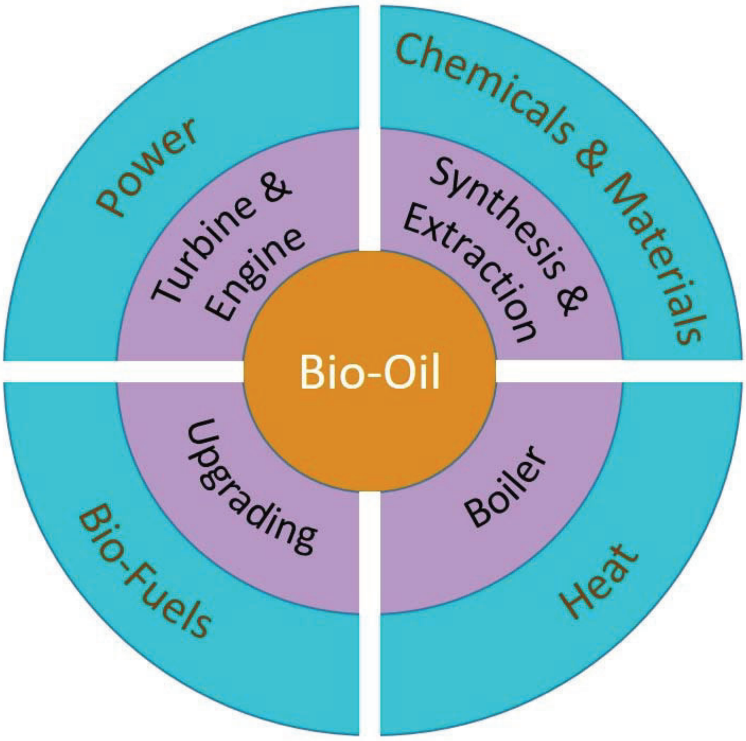


Figure 2. Various applications of bio-oil

The chemical composition of bio-oil is very complicated. It contains a number of mostly oxygen-containing chemical compounds with a wide distribution of physical and chemical properties [49]. Oxygenated compounds in bio-oils includes acids, alcohols, aldehydes, carbohydrates, esters, ethers, furans, ketones, phenols, etc. [50]. Since bio-oil is produced with rapid heating rate, short reaction time and fast cooling rate from the moderate temperature (e.g., 400 – 650 °C), it is not a product of thermodynamic equilibrium during biomass pyrolysis [51]. Chemical compounds, especially those oxygenated compounds, in bio-oil are highly reactive and can lead to undesirable reactions during storage. Therefore, the chemical composition, physical and chemical properties of bio-oil tend to undergo changes. The instability of bio-oil is typically called as ‘aging’, which is defined as the process of irreversibly changing over time [52]. Bio-oil aging would increase its viscosity and molecular weight, and lead to phase separation, delayed ignition during combustion, corrosiveness inside the engine [53], which would make it challenging to bio-oil’s storage, handling, transportation, upgrading and commercialization application [54].

Generally, bio-oil aging is caused by the reactions (e.g., polymerization, esterification, transesterification, hydration, hemiacetal formation, acetalization, dimerization reactions) between bio-oil components under acidic and thermal conditions catalyzed by nano-sized char particles or minerals in bio-oil [55, 56]. To reduce the problems caused by bio-oil aging, some physical and chemical methods are developed to slow aging. These methods include solvent addition, fraction separation, emulsification, removal of solids, water and light volatiles, mild hydrogenation, and so on [57].

Comprehensive reviews have been published on the recent progress of biomass pyrolysis [13, 58], fuel properties [59, 60], chemical characterization [61] and its quantitative analysis [62], upgrading [63-65] and applications [66, 67] of bio-oils, norms and standards for the characterization of bio-oils [68], however, that is not enough to describe characterization and mechanisms of bio-oil aging. Yang et al. [69] conducted a review of strategies applied for improving the storage and transportation stability of bio-oils and discussed economic and environmental issues and challenges. Chen et al. [70] reviewed the testing parameters and technologies used for assessing bio-oil stability. Recently, Oasmaa et al. [71] summarized the phase stability of bio-oils focusing on the bio-oil multiphase structure and behavior. However, aging characteristics, aging mechanisms, aging kinetics as well as approaches to slow bio-oil aging are missing in the literature.

Considering the above concerns, the review aims to provide a comprehensive scenario and possible research approach to bio-oil aging and recent development in technologies for slowing the aging process. The review paper will focus on four main parts: physicochemical characteristics of fresh bio-oil, aging characteristics of bio-oil, bio-oil aging mechanisms and kinetics, and approaches to slowing bio-oil aging.

2 Physicochemical characteristics of fresh bio-oil

The aging processes of bio-oil are strongly dependent on the physicochemical characteristics of fresh bio-oil, including its chemical composition, physical and chemical properties, and multiphase behavior, which are mutually dependent (see **Figure 3**).

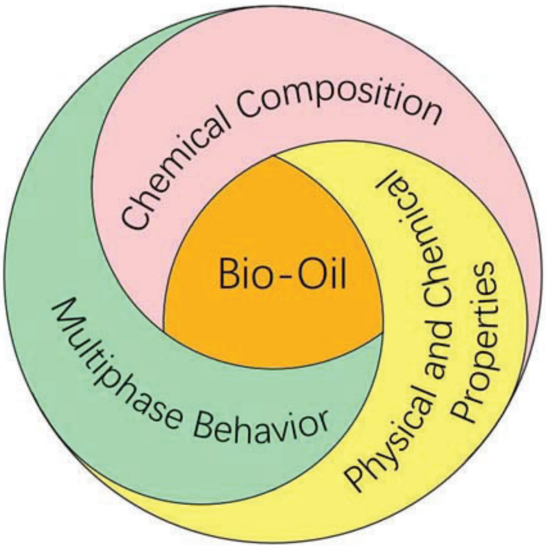


Figure 3. Mutually dependent chemical composition, chemical and physical properties, and multiphase behavior of bio-oil

2.1 Chemical composition

Bio-oil is derived from the depolymerization and fragmentation reactions of structural components of lignocellulosic biomass. The elemental composition of bio-oil correlates strongly with that of original biomass feedstock (see **Table 1**) [72].

Table 1. Typical elemental compositions of bio-oil and biomass

Element	Bio-oil [a] / wt.%	Biomass [b] / wt.%
C	54 – 58	38 – 53
H	5.5 – 7	5 – 7
O	35 – 40	34 – 46
N	0.0 – 0.2	0 – 0.5

ash	0.0 – 0.2	---

[a] Data taken from Ref. [73].

[b] Data taken from Ref. [74]. On dry ash-free basis.

The bio-oil chemical composition is strongly influenced by the nature of lignocellulosic biomass feedstock [75], pyrolysis conditions [76], configuration of pyrolysis reactor and liquid collection systems [77]. Typically, bio-oils contain over 400 chemical compounds with a wide distribution of properties and concentrations, which include (1) water, (2) volatile organic compounds, (3) monolignols, (4) polar compounds with moderate volatility, (5) anhydrosugars, (6) extractive-derived compounds, (7) heavy polar compounds derived from cellulose and hemicellulose decomposition, (8) heavy nonpolar compounds from lignin decomposition, and (9) solid particle including char and ash [78].

In general, the water in bio-oils is mainly derived from the inherent moisture and the dehydration reactions among oxygenated monomers and oligomers of lignocellulosic biomass [79]. The oxygenated compounds contained in bio-oils include carboxylic acids, esters, alcohols, anhydrosugars, furans, phenolics, aldehydes, and ketones, which are related to the lignocellulosic components of biomass (see **Figure 4**) [46, 80]. In general, acetic acid and formic acid are the principal acid components [81], and furfural and furfuralcohol are major furans products [82]. Pyrolysis of cellulose results in the formation of carboxyl, carbonyl and hydroperoxide groups, pyrolysis of hemicellulose produces depolymerization products and monomeric anhydrosugars, and pyrolysis of lignin produces catechols, vanillins, guaicols, propyl guaicols, phenols, aromatic hydrocarbons and others [83, 84]. The chemical compounds in bio-oils can be classified into different chemical families as shown in **Table 2**.

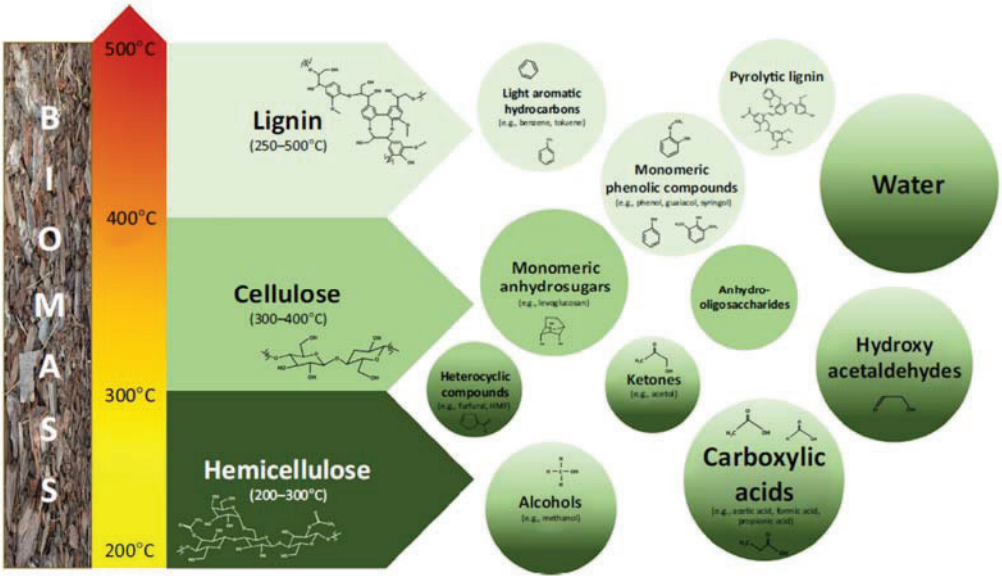


Figure 4. Pyrolysis of biomass and chemical composition of bio-oil (reprinted from Arnold et al. [80] with permission of Elsevier)

Table 2. Chemical families and their contents of bio-oils [a]

Chemical family	**Content / wt.%**
Water	19 – 30
C_2 – C_4 light molecules	10 – 22
Anhydrosugars	10 – 20
Mono-phenols	1 – 5

Mono-furans	~1
Pyrolytic lignin	15 – 17
Humins	3 – 7
Hybrid oligomers	11 – 18

[a] Data taken from Ref. [46].

Bio-oil from catalytic pyrolysis shows better quality in terms of high hydrocarbon, less oxygenating and reactive species than that of non-catalytic pyrolysis [10]. The presence of catalyst can promote deoxygenation, oligomerization, and aromatization reaction in pyrolysis and thus, the proportion of oxygenates decrease with increasing catalyst loading [85, 86]. Besides, bio-oil from the co-pyrolysis of biomass and hydrogen-rich substrate (e.g., waste rubber, waste plastics) over catalyst has relatively better quality because of a higher amount of aliphatic and aromatic hydrocarbon, lower fraction of polyaromatic hydrocarbons, oxygenates and nitrogen-containing compounds in bio-oil [87, 88]. In co-pyrolysis, the addition of hydrogen-rich substance donate hydrogen and increase the overall H/C_{eff}, which significantly improves the production of aromatic hydrocarbon in bio-oil [89-92].

There is no standard or widely accepted specification to classify the bio-oil, as the compositions of bio-oil are continuously changed over storage period and conditions.

2.2 Physical and chemical properties

The physical and chemical properties of bio-oil are important to evaluate its quality and potential uses, and to choose proper methods for upgrading [93]. These properties include water content, acidity, density, viscosity, heating value, solubility, char content, carbon residue, ash content, inorganics, pour point, flash point, thermal conductivity, specific heat capacity and refractive index [94, 95].

Usually, the physical and chemical properties of bio-oil are characterized by using the analytical techniques for conventional petroleum-based fuels with/without some minor modifications. Oasmaa and Peacocke [96] tested the applicability of standard methods developed for petroleum-based fuels to bio-oil characterization and presented minor modifications of those standard methods (e.g., avoiding sample preheating and prefiltration during characterization). Staš et al. [61] summarized the chromatographic and spectroscopic methods for bio-oil chemical characterization and presented corresponding analytical procedures. In general, chromatographic techniques allow the analysis of individual components, whereas spectroscopic methods used for the identification of chemical groups. Due to bio-oils' chemical complexity, these analytical techniques face some limitations regarding homogeneity, component separation, and multiple analyses [97]. Although many analytical techniques were more or less successfully applied, only some of them were subjected to round-robin testing. Thus, further research leading to the standardization of analytical techniques for the physical and chemical characterization of bio-oils is necessary. **Table 3** summarizes the analytical standard methods for some physical and chemical properties of bio-oil.

Table 3. Physicochemical characterization of bio-oil

Physical and chemical property	**Standard**	**Apparatus**
Heat of combustion	ASTM D240: Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter	Bomb Calorimeter
Water content	ASTM E203: Standard Test Method for Water using Volumetric Karl Fischer Titration	Karl Fischer Volumetric Titrator
Solids content	ASTM D7579: Standard Test Method for Pyrolysis Solids Content in Pyrolysis Liquids by Filtration of Solids in Methanol	Filter
Kinematic viscosity	ASTM D445: Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids	Viscometers (Glass capillary type)
Density	ASTM D4052: Standard Test Method for Density, Relative Density, and API	Digital Density Analyzer

	Gravity of Liquids by Digital Density Meter	
Ash content	ASTM D482: Standard Test Method for Ash from Petroleum Products	Evaporating Dish or Crucible, Electric Muffle Furnace
pH value	ASTM D70: Standard Test Method for pH of Aqueous Solutions with the Glass Electrode	pH meter
Flash point	ASTM D93: Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester	Pensky-Martens Closed Cup Apparatus
Pour point	ASTM D97: Standard Test Method for Pour Point of Petroleum Products	Test jar, Thermometers, etc.
Carbonyls content	ASTM E3146: Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration	Potentiometric Titrator

The homogeneity of bio-oil is associated with the reactivity and solubility of chemical compounds in bio-oil. Typically, bio-oil is separated into a more dense, more viscous phase and a less dense, less viscous (aqueous) phase depending on storage time and temperature [98]. Bio-oil primarily contains polar compounds, which make it immiscible with petroleum oils. Bio-oil contains more or less solids, mainly solid inorganics and char particles in the range of 1-200 μω [99]. When bio-oil is heated up, evaporation takes place in the temperature range of 100 – 280 °C, and stops at about 320 °C, and a solid residue of 20 – 30 wt.% of the bio-oil sample is formed [100]. The remaining residue consists of heavy molecular weight molecules, ash, and solids, which is considered as a measure of the char in bio-oil [101]. Thermogravimetric analysis (TGA) is usually used to determine the solid residue content of bio-oil [102]. The heating value of bio-oil is 14 – 18 MJ kg^{-1}, which is much lower than that of petroleum fuels (41 – 43 MJ kg^{-1}) [59, 95] because of its relatively high oxygen and water contents. Since bio-oil contains some acids (mainly acetic and formic acids, 8 – 10 wt.%), it has a low pH value of 2 – 4 [43, 103], and hence it is corrosive to carbon steel and aluminum materials [104]. The density of bio-oil is typically 1200 to 1350 kg m^{-3}, and the bio-oil with lower water content has relatively higher density [94]. Generally, bio-oil is Newtonian fluid in the temperature range of 25 – 80 °C and the shear rate range of 0.1 – 1000 s^{-1} [105]. Temperature and water content are major factors affecting bio-oil's viscosity varying from about 25 to 1000 cP at 40 °C [66]. According to our previous study [106], the dependence of bio-oil viscosity on temperature can be described by the William-Landel-Ferry model. The flash and pour points of bio-oils are in the ranges of 40 to 110 °C and -9 to -36 °C, respectively [94]. Unlike petroleum-based fuels, typical bio-oil is non-flammable and non-distillable, and can ignite only at high temperature.

To sum up, bio-oil is a low-grade liquid fuel with high contents of oxygen, water, solids and ash, low heating value and pH, high viscosity, instability, and poor combustion properties. Currently, it is technically suitable for replacing heavy fuel oil without upgrading.

In order to evaluate the applicability of bio-oil in different situations, bio-oil quality should be standardized. Nowadays, there is still only one standard specification for bio-oil: ASTM D7544-12 (Standard Specification for Pyrolysis Liquid Biofuel). Hence, more national or international standards, norms, specifications and guidelines covering a range of applications with different requirements on the physical and chemical properties of bio-oil should be studied and established urgently.

2.3 Multiphase behavior

Bio-oil may be formed by one, two or more phases during pyrolysis, depending on biomass feedstock as well as pyrolysis and condensation operation parameters. Slow pyrolysis generally produces a two-phase bio-oil, while fast pyrolysis result in a single phase bio-oil [71]. Through centrifugation, bio-oil can be separated into two layers. The upper layer shows low water, ash and char contents as well as low acidity and density, high calorific value and viscosity, whereas the bottom layer contains greater contents of water and ash[107]. According to Garcìa-Pérez et al. [108], the complex multiphase behavior of bio-oil is related to the presence of char particles, waxy materials (mainly including fatty acids, fatty alcohols, sterols, hydrocarbons), aqueous and other droplets, micelles which resulted from holocellulose-derived heavy compounds matrix (see **Figure 5**).

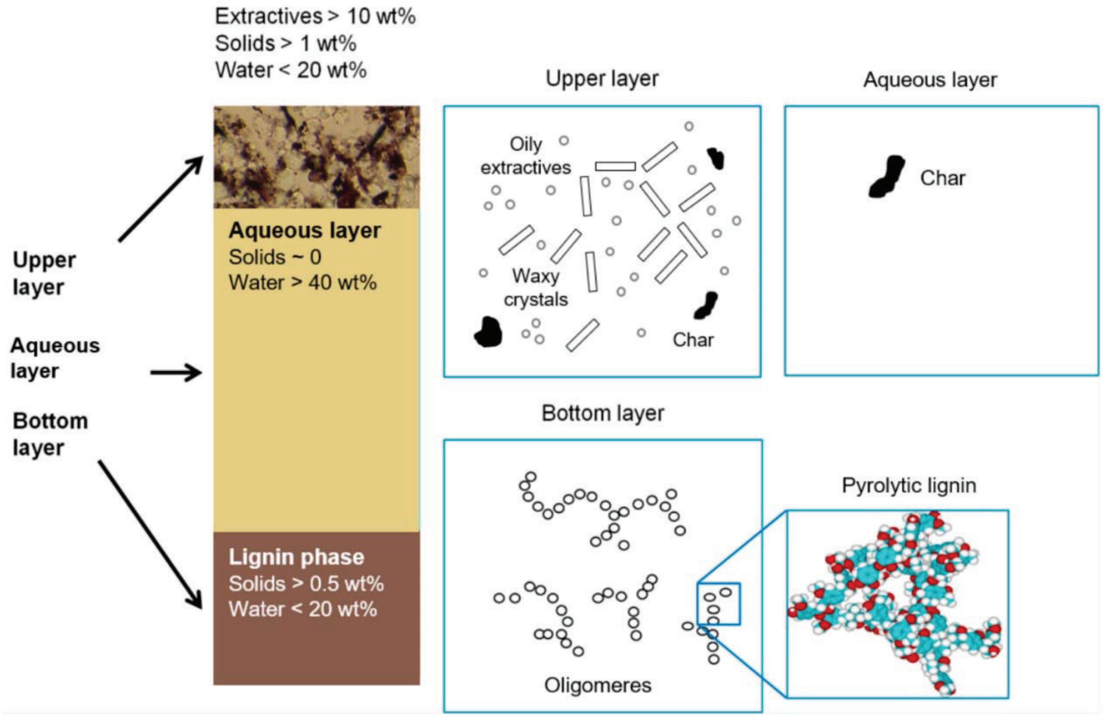


Figure 5. Multiphase structure of bio-oil (reprinted from Oasmaa et al. [71] with permission of American Chemistry Society)

The multiphase behavior of bio-oil is strongly influenced by its complex and ever-changing chemical composition, especially the contents of water, pyrolytic lignin and compounds derived from extractives, and reactions between bio-oil components during aging [71].

Besides, in the micrometre scale, bio-oil shows a nanostructure, which is constituted by a complex continuous phase and nanoparticles mainly formed by the association of units of pyrolytic lignin [109]. These microstructures grow and form relatively heavy oligomeric compounds during aging. The complex multiphase structure of bio-oil is strongly affected by temperature. The temperature effect will terminate when it reaches to melting point of the three-dimensional structures contained in the bio-oil. Aging will lead to the increase in oligomers and the reduction in low-molecular-weight reactive species in bio-oil, which act as solvents influence the growth of microstructure [71].

Although the complex nature of bio-oil multiphase behavior has been studied over the years, more work is still needed to explore its intrinsic mechanisms (e.g., the discrepancy between the dispersed phase and the continuous medium of bio-oil is not apparent due to viscous and multiphase colloidal nature).

3 Aging characteristics of bio-oil

The term "aging" has been used to describe the unstable nature of bio-oil which leads to changes in its chemical composition, physical and chemical properties, and multiphase behavior of bio-oil [57]. Till now, there is no standardized method for measuring the degree of bio-oil aging. In literature, some indicators were used to represent the degree of bio-oil aging. In addition, there were various aging tests at different aging temperatures and over different periods. They can be divided into two types: long-term aging test and accelerated aging test.

3.1 Aging indicators

The simple indicator for bio-oil aging is the phase separation by the visual observation [71]. It is not a quantitative analysis for measuring aging. Thus, the method is usually used in combination with other indicators.

Some researchers directly used an increase in the viscosity of bio-oil as the degree of bio-oil aging [93, 110-112], which was usually called as the aging index [113]:

$$\mathrm{AI} = \frac{v_a - v_i}{v_i} \times 100\% \tag{1}$$

where AI is the aging index, v_a is the viscosity after aging, and v_i is the initial viscosity.

Based on the aging index, a simple viscosity-based test was developed to characterize the aging processes of different bio-oils [111]. In the test, the bio-oil is placed in a container at a fixed temperature for a fixed period of time (e.g., 80 °C for 24 h), to measure the change in viscosity. The viscosity-based test method was verified by an international round-robin test [114].

The change in molecular weight of bio-oil is linearly dependent on the change in its viscosity during aging according to several studies [111, 112, 115]. Therefore, the apparent weight-average molecular weight is served as an approximate measure of the progress of bio-oil aging processes [112]:

$$a = \frac{M - M_0}{M_\infty - M_0} \tag{2}$$

where a is the aging parameter, M_0, M, and M_∞ are the weight-average molecular weight of bio-oil at the initial time of storage, at the time t, and the infinite time of storage, respectively. The above molecular weight-based aging indicator was used to assess the stability of bio-oils from the pyrolysis of biomass biopolymer components [116] and poplar wood [117].

Besides viscosity and molecular weight, an extended aging index was proposed by Meng et al. [118]:

$$\mathrm{AIE} = \frac{P_{\mathrm{AA}} - P_{\mathrm{FH}}}{P_{\mathrm{FH}}} \times 100\% \qquad (3)$$

where AIE is the extended aging index, *P* refers to a particular bio-oil property (e.g., viscosity, molecular weight, water content, acidity), the subscripts FH and AA represent the fresh and aged bio-oils, respectively.

In the study on the polymerization mechanisms of bio-oil water-soluble fraction during accelerated aging by Luo et al. [119], a new aging index based on the yield of the final residue of bio-oil has been proposed:

$$\text{Aging index} = \frac{M_{\text{aged-sample}} - M_{\text{fresh-sample}}}{M_{\text{fresh-sample}}} \times 100\% \qquad (4)$$

where *M* denotes the yield residue of fresh and aged bio-oils.

During aging, the change in carbonyl content of bio-oil would occur because of the reactions between aldehydes and ketones during storage. Oasmaa et al. [120] developed a titration method of identifying carbonyl groups based on the changes in aldehydes and ketones contents to represent the degree of instability during bio-oil aging. The carbonyl titration method is easier to carry out in the laboratory, since the test can be conveniently conducted with standard common laboratory glassware than the viscosity and molecular weight-based methods. Recently, the carbonyl titration method for tracking bio-oil aging was verified by Black and Ferrell [121]. Hence, the change of carbonyl content can be considered as an indicator for bio-oil aging.

According to Sundqvist et al. [122], heat is generated during bio-oil aging, and depends on the temperature, bio-oil reactivity, and addition of alcohol and catalysts, which were verified by the aging experimental results of typically good quality bio-oils in a reaction calorimeter. Therefore, heat generation during aging can also be suggested as an indicator of bio-oil stability.

In addition to the change in viscosity, water content, molecular weight, and carbonyl content, the aging of bio-oil also results in the change in free radicals [116]. Meng et al. [101] investigated the effect of free radicals on bio-oil aging severity with the addition of radical scavengers and found that radical scavengers had negligible effects to control the pyrolytic lignin condensation and only a mild free progressive concentration reduction occurred during bio-oil accelerated aging. According to Kim et al. [116], those free radicals in bio-oil are highly concentrated in bio-oil fractions from lignin pyrolysis. Free radicals in chemical systems can be relatively identified and characterized by electron paramagnetic resonance or electron spin resonance spectroscopy. The relationship between free radicals in bio-oil and its aging is still missing in the literature. Here the authors hypothesize that free radicals in bio-oil could be considered as another indicator for bio-oils propensity to aging.

Table 4 summarizes the above indicators and their analytical methods for bio-oil aging. Currently, there is no specification for the indicators to represent the degree of bio-oil aging. Hence, more work on the bio-oil aging indicators and the corresponding standard test methods for them are needed.

Table 4. Aging indicators and analytical methods for bio-oil aging

Aging indicator	Analytical method	Reference

Viscosity	Rotational rheology test	[56]
Water content	Karl Fischer titration	[56]
Functional group and chemical structure	Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analyses	[56]
Chemical composition of volatiles	Gas chromatography / mass spectrometry (GC/MS) analysis	[56]
Chemical composition of bio-oils (identification of highly reactive oil components)	Liquid chromatographic / mass spectrometric analysis	[123]
Weight-average molecular weight	Gel permeation chromatography (GPC)	[123]
Thermochemical properties (e.g., decomposition temperature)	Thermogravimetric analysis (TGA)	[124]
pH value	pH measurement	[125]
Free radicals	Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy	[101, 116]

3.2 Long-term aging

The purpose of the long-term aging test is to measure the changes in physicochemical properties of bio-oil at ambient temperature during a long period of storage (e.g., several months and even several years), which can simulate bio-oil aging for long time during storage at natural conditions.

The long-term aging of the bio-oil samples from the fast ablative pyrolysis of oak wood at the vortex reactor wall temperature of 625 °C was conducted by Czernik et al. [112]. Seven bio-oil samples were placed in caped glass vessels and stored at thermal chamber at 37 °C for 24 weeks. The results showed that the bio-oil samples remained a single phase, the pH value was not affected by storage, the water content increased with the length of storage because some condensation or dehydration reactions occurred during storage.

Oasmaa and Kuoppala [111] found that the high-molecular-mass (HMM) fraction in bio-oil from forestry residue pyrolysis increased during 6 months of long-term aging because of polymerization and condensation reactions of carbohydrate compounds, aldehydes, and ketones. The increase in HHM fraction resulted in the main physicochemical properties changes, including the increase in viscosity, molecular weight, flash point, pour point and density.

Meng et al. [118] investigated the long-term aging of bio-oils from the pyrolysis of raw and torrefied loblolly pinewood sawdust and found that raw bio-oil completely phase-separated after 6 months, while torrefaction bio-oil maintained a stable uniform oil phase during the even entire 12-month storage, which indicated that the torrefaction pretreatment of bio-oil production raw biomass could potentially slow down the bio-oil aging rate. The reason is that torrefaction mainly removes hemicellulose and reduce the yield of sugar fractions in bio-oil which is the positive effect on bio-oil stability. It can be noted that a high fraction of pyrolytic sugars in bio-oil, including anhydrosugar, oligo/polysaccharide and even aliphatic hydroxyl acid are reactive and increase the viscosity of bio-oil during storage condition.

Bio-oil from the vacuum pyrolysis of mixed hardwood feedstocks were studied for aging at room temperature for 5 months [126] and the results showed that the viscosity of bio-oil increased by approximately a factor of 2.5 and the water decreased by about 4% due to evaporation over 5 months.

The IEA round-robin study on the long-term aging of bio-oils at three temperatures (21, 5, and -17 °C) for one year revealed that a lower temperature can slow down the reaction mechanism to increase the viscosity of the bio-oil [54].

Interestingly, an increase in viscosity was prolonged over the first 6 months of storage at 20 °C, and after that bio-oil's viscosity was found to increase dramatically, the yield of the evaporative residue of bio-oil increased with increasing storage time [102]. However, an increase in evaporative residue started more slowly and picked up after a year of aging (especially for 18 to 24 months) [102].

The aging of the bio-oil samples from Tunisian almond shell fast pyrolysis at room temperature over 5 years investigated by Grioui et al. [127] showed that the methodxylated aromatic compounds were the major compounds in the aged bio-oil samples, and that the viscosity greatly increased due to esterification and decarboxylation reactions while the pH value, water content and higher heating value (HHV) remained unchanged during long-term storage.

Biomass pyrolysis system coupled with fractional condensation systems can yield multi-stage bio-oils, which show different aging behaviors. The bio-oil gathered from higher condensing temperature contains more lignin pyrolytic oligomers and phenols, while the bio-oil collected by lower temperature contains more water and aliphatic compounds [128]. The bio-oil obtained from higher condensing temperature presents fewer changes in physical and chemical properties and chemical composition during long-term storage and is more appropriate for combustion and further processing.

To assess the aging performance of bio-oil heavy factions for potential use as bio-binder, the pre-treated bio-oil samples were tested by using a pressure aging vessel (PAV) procedure, which is commonly adopted to study the long-term aging of petroleum-derived bitumen [129]. Since there are considerable differences between bio-oil and bitumen in compositions and properties, the test conditions (e.g., aging duration in PAV oven, test temperature of degassing container) should be changed to comply with the bio-oil properties. In future research, to measure the long-term aging characteristics, the standardization of the long-term aging test for bio-oil should be investigated.

3.3 Accelerated aging

In natural conditions, bio-oil aging is a slow process [130]. Elevated temperatures can increase the aging rate of bio-oil [56]. It is possible to design the experiment in which aging can reach deep degrees of transformation during a reasonable time. Such technique of aging test is called accelerated aging [131], which is the most common method to measure bio-oil stability. Accelerated aging has usually been performed by storing bio-oil samples at an elevated temperature (e.g., 80 °C) for a specified period of time (from a few hours up to several days). The high temperature in the accelerated aging experiments can increase the bio-oil aging rate [111]. Table 5 summarizes some studies on the accelerated aging of bio-oils.

--- Table 5 ---

According to the results of the IEA round robin on bio-oil aging in 2012 [54], the increase in bio-oils viscosity during the accelerated aging test at 80 °C for 24 h was found to be similar to the rise measured in the natural long-term aging test of 6 months at room temperature. Czernik et al. [112] also found the increase in bio-oil viscosity at 60 °C for 4 days and at 90 °C for 6 h was equivalent to that of bio-oil after 3 months of treatment at 37 °C. Ortega et al. [126] presented that the oils aged at 65 °C showed increases in viscosity similar to the oils aged for 5 months at room temperature.

The effect of accelerated aging at 80 °C on the physical and chemical properties of the bio-oil from the fast pyrolysis of hardwood under different periods of 1, 3, 5, and 7 days in sealed vessels was investigated and analyzed by Alsbou and Helleur [56]. The bio-oils remained a single phase through the first 6 days, while a clear phase separation occurred on day 7. The water content, viscosity, decomposition temperature, and ash content of the bio-oil increased with the increase of aging period (see **Figure 6**). The authors inferred that the esterification, etherification, and olefinic condensation reactions were the main mechanisms of bio-oil accelerated aging.

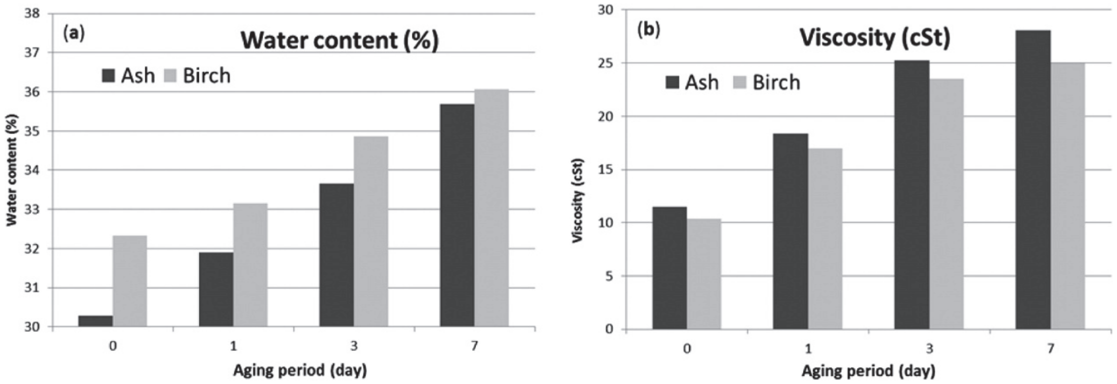


Figure 6. Changes in water content and viscosity of bio-oil from hardwood pyrolysis

(reprinted from Alsbou and Helleur [56] with permission of American Chemistry Society)

To avoid the possible risk of releasing volatiles or from transferring bio-oil samples between the experimental oven and rheometer during aging, a novel method was developed to perform real-time viscosity measurements during bio-oil accelerated aging by using a concentric cylinder rheometer [132]. The aging period of 8, 16, and 24 h with continuous stirring at 90 °C resulted in increased viscosity by 57, 300, and 720 %, respectively. The water content showed a slight decrease, while the average molecular weight showed a slight increase.

The accelerated aging tests of bio-oils produced from the fast pyrolysis of pine wood in the presence of CaO, MgO, and ZSM-5 as *in situ* upgrading catalysts showed that the CaO-catalyzed bio-oil had the lowest aging index compared to other bio-oils [133]. One of the main reasons was that the bio-oil produced using CaO as the catalyst had reduced acidic components, which indicate the presence of organic acids in bio-oil can accelerate the aging of bio-oil.

Char removal before condensation has been found to decrease the rate of bio-oil aging. The impacts of post-condensation filtration on the 3-week accelerated (80 °C) aging of the pine wood derived bio-oil showed that the removal of char particles by post-condensation serial filtration prior to aging could prevent the general trend of viscosity increase during aging [134].

Different bio-oil fractions have different accelerated aging behaviors. The accelerated aging tests of water-soluble and water-insoluble fractions of rice straw pyrolysis bio-oil at different temperatures (80, 90, 100 and 110 °C) for 24 h by Luo et al. [119] showed that the aging rate of the bio-oil water-soluble fraction was higher than that of the bio-oil water-insoluble fraction according to the changes in water content and viscosity before and after aging. Meng et al. [136] also studied the accelerated aging of bio-oil fractions. They revealed that (1) the increased molecular weight was found with increasing aging temperature and the presence of acids for all bio-oil fractions (including water-soluble, ether-soluble and pyrolytic lignin fractions); (2) solid residue was generated when water soluble and ether insoluble fractions were aged; (3) the aging index of water-soluble fraction increased 2-fold at the aging temperature of 110 °C compared to 80 °C.

The aging at elevated temperatures would accelerate phase separation of bio-oil. According to Siriwardhana [135], the bio-oil from the fast pyrolysis of hardwood was phase-separated after 15 h of aging under accelerated aging conditions at 80 °C and the proportion of the viscous bottom phase increased during prolonged aging, which was caused by the polymerization or condensation reactions between the phenolic, sugar, ester, acid, ketone, furan, and aldehyde components in the light fraction with heavy fraction of bio-oil [135].

Due to the compositional and structural complexity of bio-oils, the role of bio-oil's main components to the polymerization reactions has not been well understood yet. Siriwardhana [135] used bio-oil model compounds to investigate the chemical reactions during accelerated aging. Possible reactions have been noted as (1) conversion of carboxylic acids to esters over alcohol and esters is stable at elevated temperatures for prolonged periods of time; (2) decomposition of most of the derivatives from linear ketones and aldehydes into other products or reacted to form components with higher molecular weight, and (3) reactions of furan and aldehydes.

The accelerated aging characteristics of bio-oils from the pyrolysis of hardwood and softwood in a water-saturated environment at 65 °C showed that the water content of the aged bio-oil slightly increased, the pH value decreased, and the viscosity of the aged bio-oil doubled in 3~4 days of aging [126].

Besides, the presence of surfactants has a noticeable effect on the accelerated aging characterization of bio-oil and its fractions. For example, IGEPAL CO890 and soap with high hydrophilic-lipophilic balance (HLB) values have led to phase separation of the bio-oil into dark and bright fractions [137].

Based on the basic assumption that accelerated aging can imitate the natural aging process, the accelerated aging tests were developed for the assessment of the aging performance of bio-oils in a short time. However, the assumption was established on the change in viscosity during aging . There exist some differences between long-term and accelerated aging not only in the aging rate but also in aging reaction mechanisms, which can lead to different chemical composition of aged bio-oils after different aging tests. Accelerated aging tests are conducted at high temperatures, they are unsuitable for simulating in-service aging: the processes induced are relatively different from those observed in utilization. And even for accelerating aging tests, the consistency in oven specification and corresponding operation of accelerating aging should be standardized and normalized [113].

The bio-oil heavy fractions have the potential to use as bio-bitumen [138]. There are standard methods to assess the short-term and long-term aging of bitumen [139]. The Pressure Aging Vessel (PAV) and Rolling Thin-Film Oven (RTFO) procedures provide simulated long- and short-term aged bitumen binder for physical property testing, respectively [140]. The applicability of the conventional aging techniques and equipment of the petroleum-derived bitumen or their modification used for the evaluation of the aging performance of bio-oil can be studied in the future.

4 Bio-oil aging mechanisms and kinetics

To control chemical reactions and assist researchers onwards bio-oil stabilization strategies, understanding of bio-oil aging mechanisms and kinetics are inevitably necessary [56, 57]. Although some reviews have summarized the possible reactions between bio-oil components during aging. Meanwhile, most recent studies of bio-oil aging have been focused on characterizing the aging behavior and seeking methods to slow down the aging rate. [55, 69, 70]. In order to solve the post-processing problems of bio-oil during storage, transportation, handling, feeding and combustion, systematic analysis of the aging mechanisms and kinetics of bio-oil needs to be considered.

4.1 Aging mechanisms

During the storage of bio-oil, the chemical composition change leading to the changes in physical and chemical properties of bio-oil [73, 141]. The whole scenario of bio-oil stability is very intricate, and notably, there is no solo clarification for all the phenomena related to bio-oil aging. Different reactive and unsaturated components undergo through a series of reactions (polymerization, esterification, dimerization/oxidization, and acetalization) during aging to form larger molecules and result in undesirable physical properties of bio-oil like high viscosity [111].

Diebold [55] explained several reactions among compounds of bio-oil during the aging process, and it has been found water, organic acid, aldehyde, alcohol and even phenols are very reactive to form oligomer, ester, acetal, resin, and polyolefin. Furthermore, the air oxidation of bio-oil results in the peroxide formation, which causes polymerization of unsaturated compounds. For instance, phenol and formaldehyde in bio-oil undergo reaction during the aging period to form phenyl hemiformal, which is finally converted to ortho-methyl phenol. Furthermore, the reaction of phenol or substituted phenol and aldehyde hydrate produces resin in bio-oil (see **Figure 7)**.

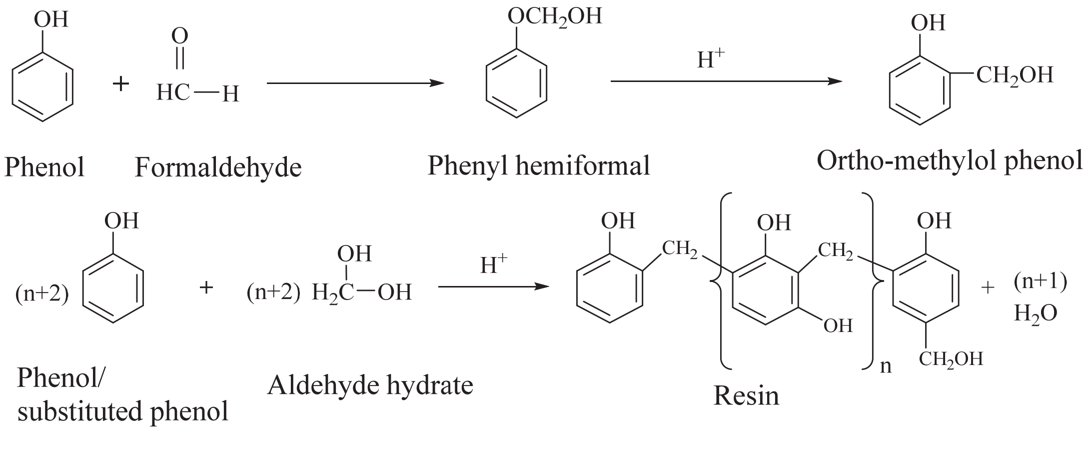


Figure 7. Reactions between phenol and aldehyde compounds in bio-oil during aging [55]

The oxygen-rich compounds such as carboxylic acids and aldehydes undergo several aging reactions such as polymerization, acetalization, oxidation, esterification, and dimerization. Xiong et al. [142] studied the preliminary aging mechanisms of bio-oil. They reported that the aliphatic acids, alcohols, and aldehydes are prone to esterification and acetal reactions, which accompanied by the formation of esters and acetals which involve a small amount of water and some acids (**Figure 8(a)**). The quality impact is not particularly large but may result in stratification due to change in the polarity of the bio-oil molecules. However, the aromatics compounds, as well as sugar derivatives, follow polymerization/self-condensation reactions through acid catalysis or radical polymerization forming polymer compounds (**Figure 8(b)**). This polymer compounds particularly affect the viscosity of bio-oil.

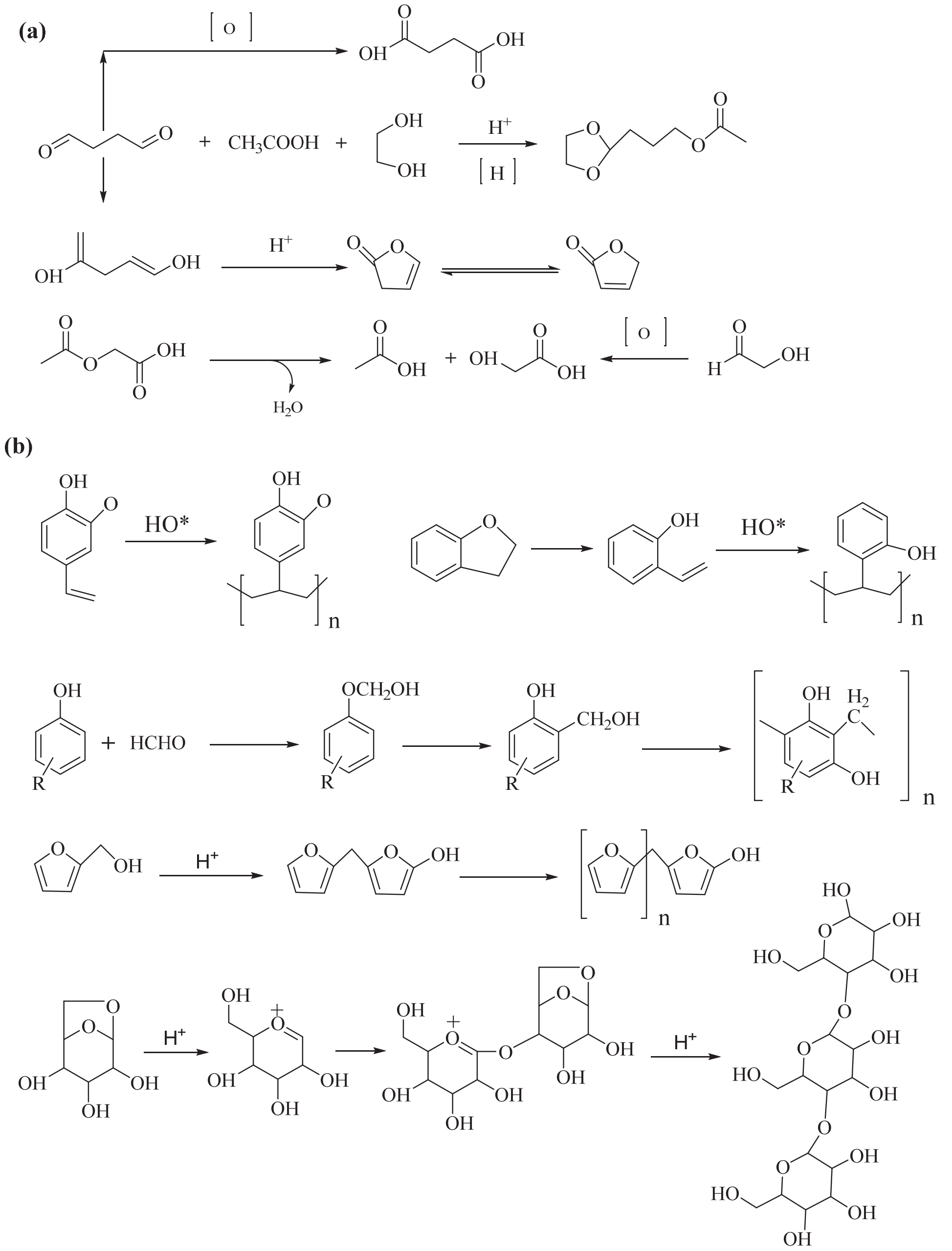


Figure 8. (a) Possible chemical reactions of aliphatic compounds, and (b) polymerization of aromatics and sugar compounds in bio-oil during aging [142]

According to Meng et al. [136], intrinsic reaction mechanisms during accelerated aging of bio-oil include (a) sugar decomposition and condensation to solid humin, (b) aldol condensation of furfural and ketone, (c) acid-catalyzed lignin condensation, (d) free radical lignin condensation, and (e) phenol glycolaldehyde condensation (see **Figure 9**). Phenolic compounds are significant culprits to accelerate the aging rate. To slow down bio-oil aging rate, the fraction of oxygenated aromatics (phenolic compounds) in bio-oil should be low by converting into aromatics.

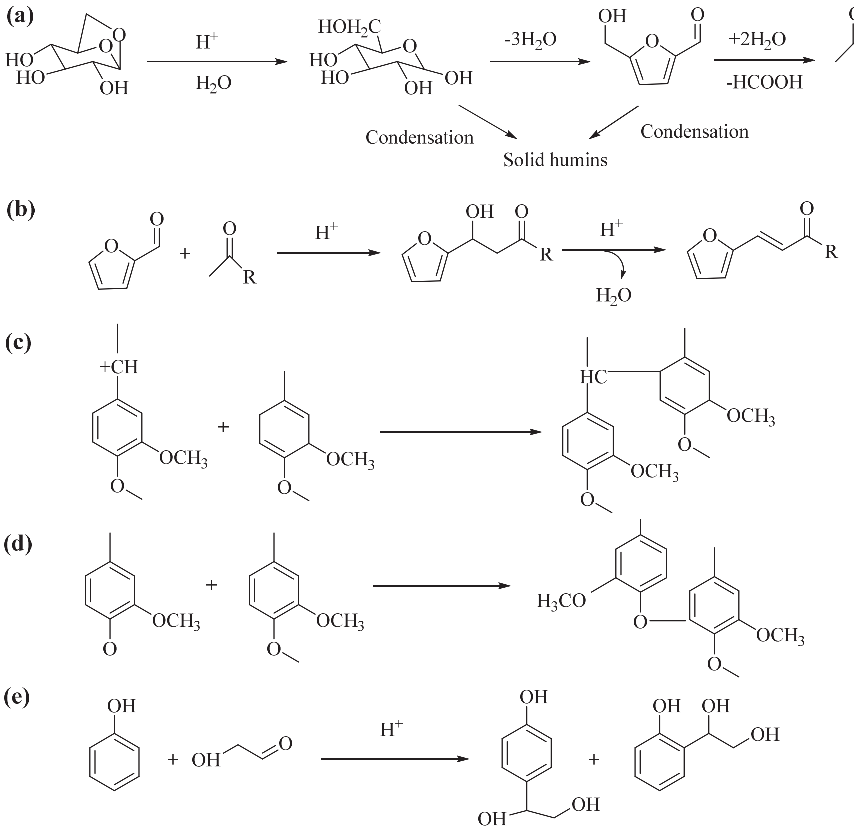


Figure 9. Possible reaction mechanisms during accelerated aging of bio-oil (reprinted from Meng et al. [136] with permission of American Chemistry Society)

Bio-oil contains water and some light-reactive volatiles. Evaporation of volatile components in bio-oil would result in an increase in viscosity and flash point [143], which is another mechanism of bio-oil aging. On the other hand, air oxidation of alcohols and aldehydes in bio-oil may form carboxylic acids, which could easily be esterified with alcohols in bio-oil [134, 144]. During the storage of bio-oil, hydroperoxides and alkyl peroxide can be formed by autoxidation with air [55]. The peroxides are not very stable and decompose to free radicals, which can catalyze the polymerization of olefins and the additional of mercaptans to olefins. Many of these reactions can be catalyzed by the organic acids and char in bio-oil [111]. Therefore, exposure to air would facilitate the formation of polyolefins during storage.

Besides, chemical reactions during bio-oil aging can change the polarity of the bio-oil components [71]: the polarity of the organic components decrease and the content of extremely polar water increases. The difference in polarity among the aged bio-oil components increases and the mutual solubility of the aged bio-oil components decreases because of the formation of larger molecules during aging, which increases the tendency of phase separation [110].

The phase-separation of bio-oil reported between 4 and 6 days of the study period at 85 °C [126] indicates that char-free characteristics and high water content turn to slow polymerization reactions. However, it is quite dreadful to show more stability of bio-oil which has treated hydrothermally compared to fast pyrolysis bio-oil which produced from fixed-bed catalytic hydrotreater [145]. Concerning aging, anhydrosugar is considered as a mostly stable compound. At the same time, significant compositional changes have been reported for xylose, glucose, arabinose as well as other presumed carbohydrate-like compounds especially, hemicellulose-derived sugars and the disappearance of certain furanose-ring sugars. Some of the sugars are assumed to be the result of aging-induced of lignin-carbohydrate oligomers [123].

It can be summarized that bio-oil aging during the storage period is a continuous process due to a number of reactive species produced from the biomass. It is impossible to stop the formation of oxygen-containing species (acid, aldehyde, ketone, alcohol, furan and phenol) which are mostly unstable, react and causes undesirable changes in the physicochemical properties of bio-oil. In addition, the solid content of bio-oil increases the aging process. Therefore, in addition to the treatment of biomass, other process parameters should be optimized to reduce the amount of oxygen-containing species and solid content in bio-oil. In parallel, the storage conditions, like low temperature and the absence of air could be suggested to slow down the aging process of bio-oil. Nonetheless, several upgrading processes can be applied to increase the stability of bio-oil.

To bring in the stabilized method for bio-oil upgrading, it is inevitably crucial to know why and how polymerization reactions take place. Several cabalistic approaches have been taken into account to clarify the reason behind the polymerization and other reactions between alcohol (solvent) and bio-oil. To date, it is unclear that the contribution of parent compounds towards polymerization reactions. To understand the aging mechanism and use of bio-oil and essential features of the bio-oil compound under specific aging temperature, it is inevitably necessary to study the aging kinetics.

4.2 Aging kinetics

The aging kinetics of bio-oil is fundamental for the prediction of the aging rate and the properties of bio-oil over different aging periods, and the estimation of the required time to reach different aging degrees, which is helpful for the application of bio-oil and the validation of various approaches for slowing down bio-oil aging rate.

In literature, there were two kinds of bio-oil aging kinetic models: viscosity-based model and molecular weight-based model.

Nolte and Liberatore [132] used an exponential decay function to fit the experimental data of an oak pyrolysis bio-oil accelerated aging at 90 °C:

$$\eta(t)=\eta_{\infty}\left(1-e^{-bt}\right) \tag{5}$$

where $\eta(t)$ is the viscosity at the time t, η_{∞} is the infinite time steady-state viscosity, and b is the decay constant. **Figure 10** shows the comparison between the experimental data of the oak bio-oil aging and the curve predicted by the model with the parameters η_{∞} = 0.013 Pa s and b = 0.035 h^{-1}.

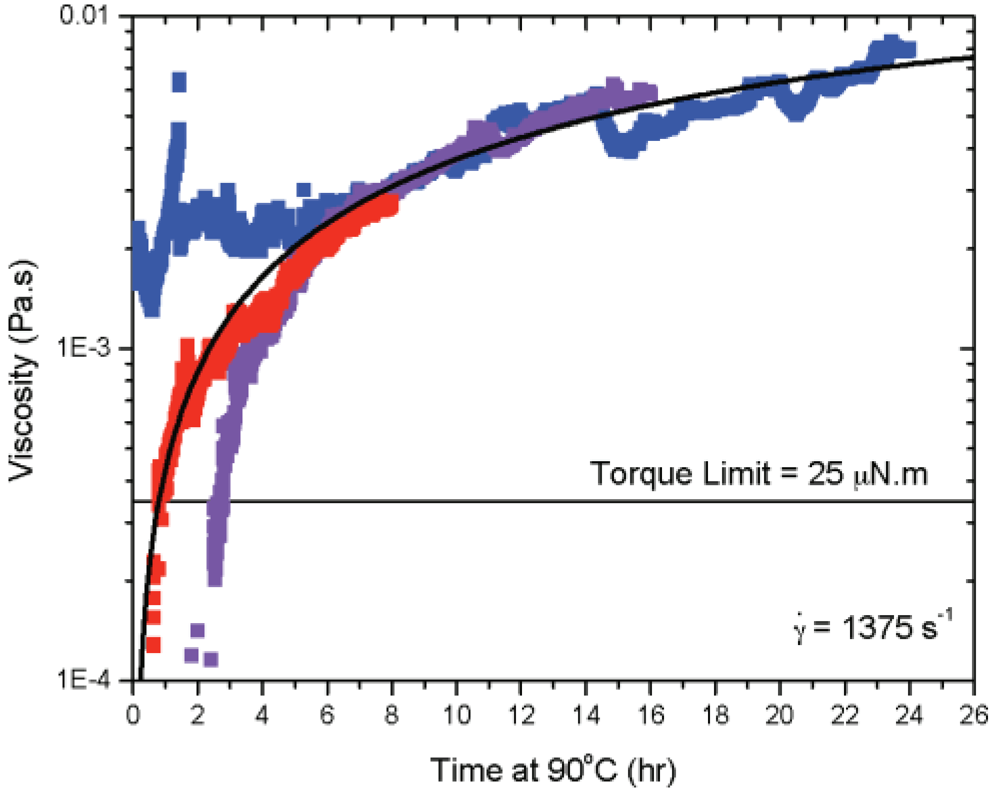


Figure 10. Aging kinetics of oak bio-oil (reprinted from Nolte et al. [132] with permission of American Chemistry Society)

According to the above empirical model (5), when t=0, then η=0. That contradicts the fact that the viscosity of bio-oil is not zero at the beginning of aging. In this aspect, the empirical viscosity-based model has some theoretical drawbacks and has no physical meaning.

Czernik et al. [112] presented a molecular weight-based model for bio-oil aging:

$$-\ln\left[1-\frac{M(t)-M_0}{M_\infty-M_0}\right]=kt \tag{6}$$

where M(t) is the molecular weight at the aging time t, M_0 is initial molecular weight, M is the infinite time steady-state molecular weight, and k is the aging rate constant, which is dependent on the aging temperature.

$$k = A \cdot e^{-E/RT} \tag{7}$$

where T is the aging temperature, A and E are the aging frequency factor and aging activation energy, respectively. From Equations (6) and (7), the following equation can be obtained:

$$M = M_0 + \left(M_{\infty,T} - M_0\right)\left[1 - \exp\left(-A \cdot e^{-E/RT} \cdot t\right)\right] \tag{8}$$

By fitting the aging experimental data of oak pyrolysis bio-oils at three temperatures (37, 60 and 90 °C), Czernik et al. [112] obtained the values of M_∞ at different aging temperatures, and ln$A$ and E: $M_{\infty,\, 37\,°\mathrm{C}} = 930$, $M_{\infty,\, 60\,°\mathrm{C}} = 950$, $M_{\infty,\, 90\,°\mathrm{C}} = 980$, ln$A$ = 35.1, E = 102 kJ mol^{-1}. **Figure 11** shows the change of weight-average molecular weight of bio-oil at different aging temperatures based on the kinetic model with the given parameter values above. From **Figure 11**, it can be observed that the molecular weight of bio-oil increases with increasing aging time, and high temperatures favor the increase of molecular weight.

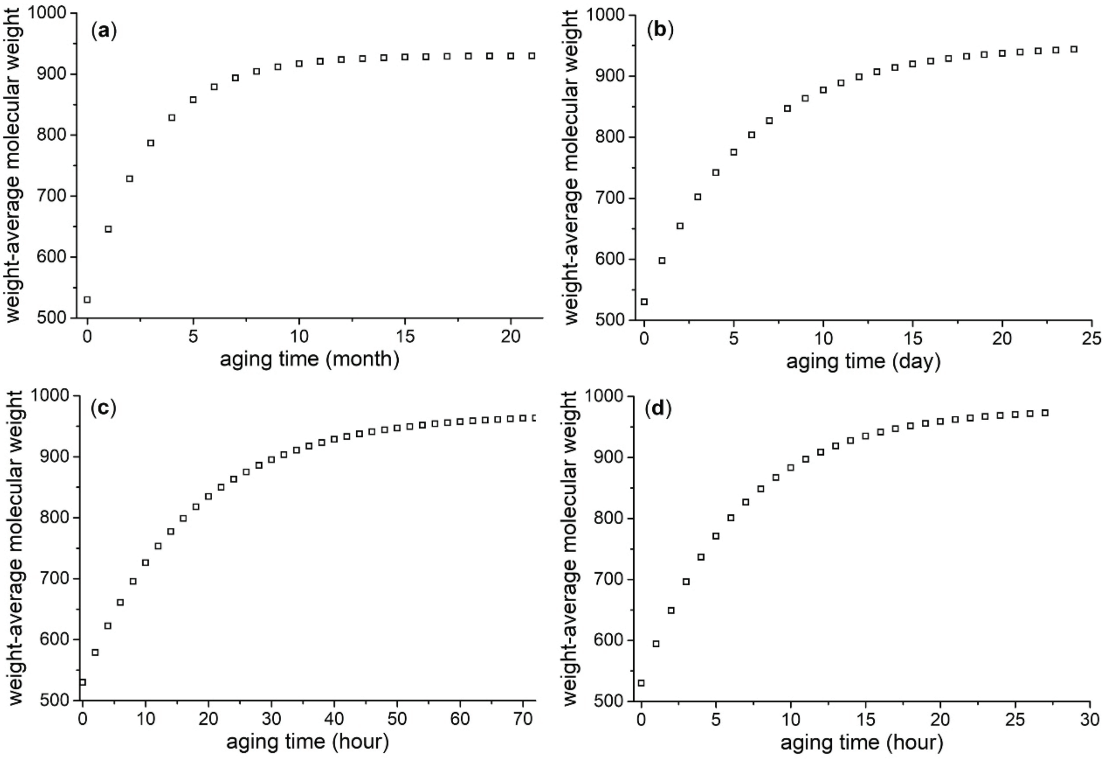


Figure 11. Variation of weight-average molecular weight with aging time at different aging temperatures for oak bio-oil aging (aging model (7) with parameters from Ref. [112])

Zhang et al. [117] successfully employed the above molecular weight-based model to analyze the aging kinetics of bio-oil from poplar wood pyrolysis at different aging temperatures and presented an advanced procedure for bio-oil aging kinetic modeling by simultaneously considering the experimental data at various aging temperatures and using the pattern search method (see **Figure 12**).

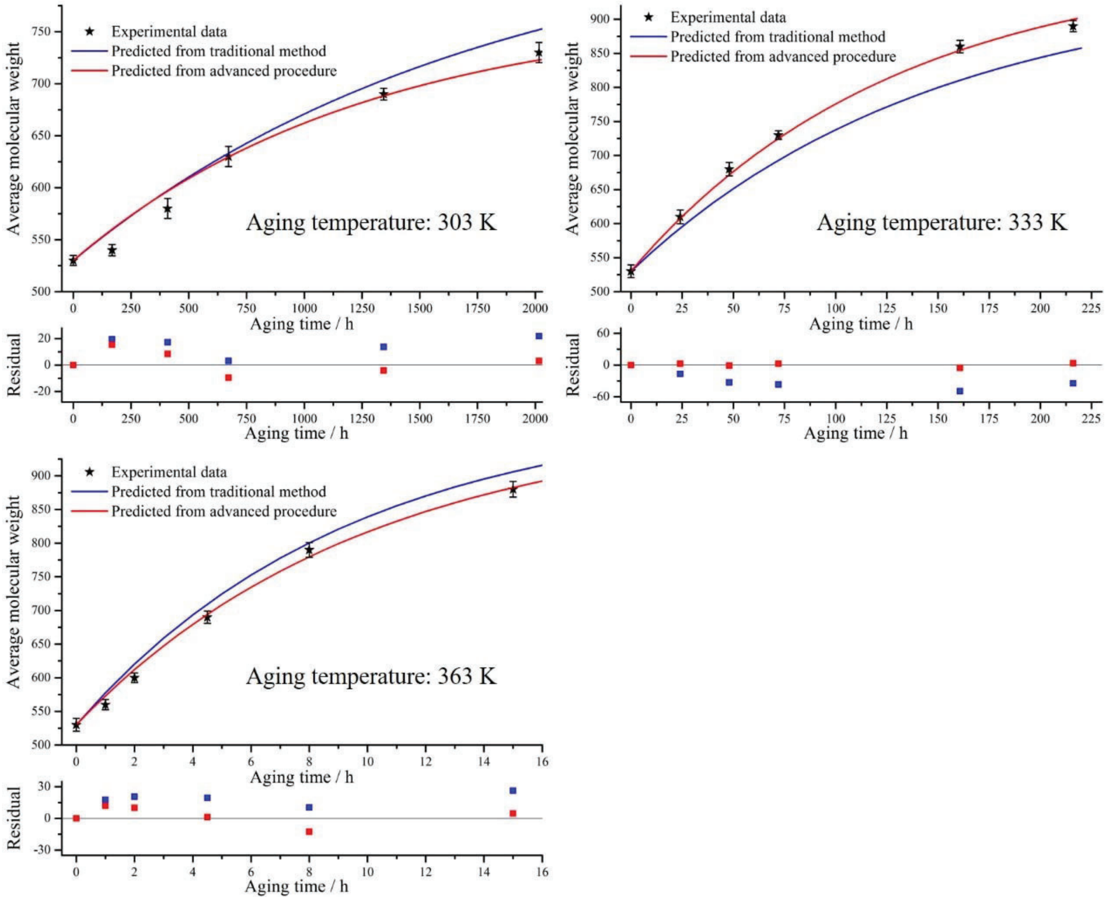


Figure 12. Aging kinetic analysis using molecular weight-based model for bio-oil from poplar wood pyrolysis (reprinted from Zhang et al. [117] with permission of American Chemistry Society)

The carbonyl groups are the most reactive species in bio-oils, but its amount gradually decreased during bio-oil aging which correlates with the increased viscosity and molecular weight [120]. Black and Ferrell [121] considered that the total carbonyl content is a much better metric for tracking bio-oil aging, as it has a significantly lower measurement variability, and can also be applied to samples that have phase separated. However, there is no aging kinetic model to describe the variation of total carbonyl content with time during bio-oil aging. According to the changing trend of the carbonyl content, the following carbonyl-based aging kinetic model has been proposed in this review:

$$C(t) = C_0 - (C_0 - C_\infty)(1 - e^{-mt}) \quad (9)$$

where C is the carbonyl content, C_0 and C_∞ are the initial carbonyl content and the carbonyl content at the aging steady-state, m is the aging rate constant. The curves predicted by the above carbonyl based aging kinetic model are also plotted in **Figure 13**, where it is suffice to verify that the proposed model can fit the experimental data obtained from Oasmaa et al. [120] sufficiently well.

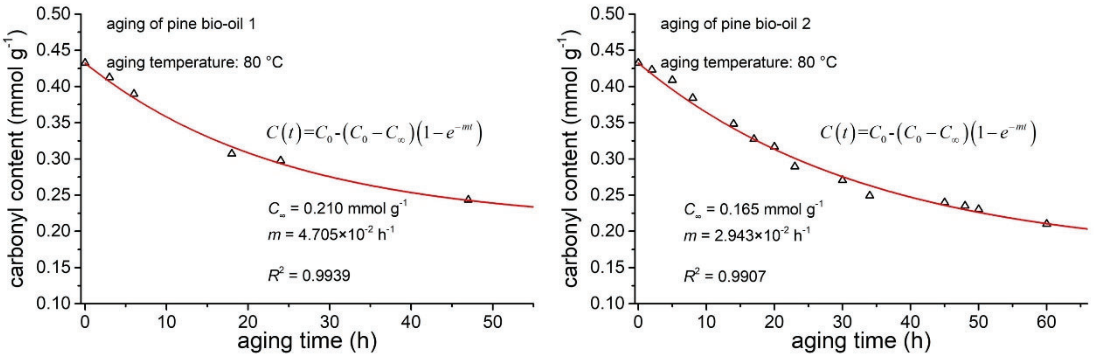


Figure 13. Comparison between aging experimental data of pine bio-oils and carbonyl based aging kinetic modelling (experimental data taken from Oasmaa et al. [120])

There are many aging kinetic models developed to describe the aging kinetics of petroleum-derived bitumen, which consider the effect of the aging time, aging temperature, gas pressure, and diffusion on aging [139]. Some kinetic models for bio-oil aging have been proposed, but most of them are empirical models and only consider the effect of temperature and period on aging. In the future, those bitumen aging kinetic models can be employed to analyze the aging kinetics of bio-oil aging since the heavy fractions of bio-oil has the potential to use as bio-bitumen and has the similar aging kinetic behaviors. And more parameters can be considered in the kinetic modeling of bio-oil aging, for example, water content, solid and char content, and pH value.

5 Approaches to slowing bio-oil aging

Bio-oil aging is one of the key problems that limit its upgrading and application [66, 68, 146, 147]. Slow and unstable combustion has been observed against an increased viscosity and phase separation of bio-oil [93, 94]. The performance and emission results from the use of aged bio-oil in a direct-injection diesel engine showed that it would deteriorate engine performance and increase emission levels at the exhaust [123]. The change in bio-oil properties over time would need adjustments to fuel feeding and to inject system and changes in operational conditions for using in a combustor [148, 149]. The properties of the liquid fuel for commercial energy use should be constant during storage at ambient temperature for at least 6 months [68]. Currently, bio-oils without upgrading can’t meet the above requirement. Besides, the heavy fractions of bio-oils have the potential to substitute some fractions of the bitumen which is the binder in asphalt for road surface construction [40]. Bio-oil aging during storage results in the increased amount of high-molecular-weight fractions, and increase the adhesive properties of bio-oil. After that improve the applicability of those fractions used as bio-binders. Therefore, heat pre-treatment of bio-oils has been used by several researchers to use as a binder [150-153]. It is critical to develop practical approaches to slowing down bio-oil aging rate and maintaining the stability of bio-oil during storage and transportation based on the understanding of bio-oil aging mechanisms and kinetics [154]. The keys to slow down bio-oil aging rate are associated with the following mechanisms [55, 69]: (a) reducing viscosity (e.g., solvent addition), (b) eliminating the highly reactive components (e.g., converting reactive aldehydes into moderate weight and less reactive compounds), (c) mild modifying bio-oil to reduce its reactivity and acidity (e.g., converting organic acids in bio-oil to low molecular weight esters); (d) removing solid char residue [54,157].

5.1 Solvent addition

The addition of less viscous solvents, such as methanol, ethanol, and acetone, combats the polymerization of reactive species and, therefore, retards increasing the viscosity and aging rates of bio-oil [69, 70, 110, 155]. The reactive molecules of bio-oil, like organic acid and aldehyde, react with methanol or ethanol known as esterification and acetalization and are converted to esters and acetals, respectively (see **Figure 14**).

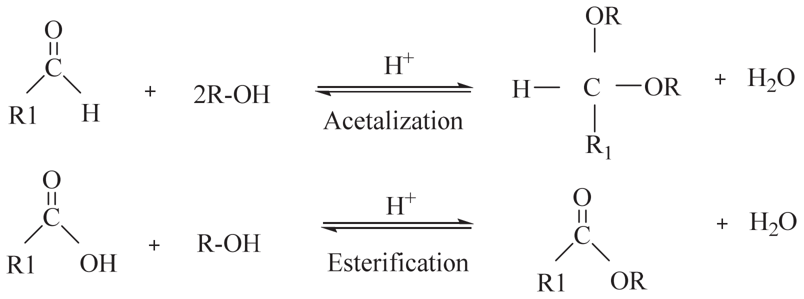


Figure 14. Esterification and acetalization between bio-oil component and alcohol ([156])

Bio-oil from *Calophyllum inophyllum deoiled* seed cake was mixed with 10% (w/w) methanol to reduce the aging rate, and it has been found that the addition of methanol reduces the aging rate to 0.04 and 0.13 cSt h^{-1} for thermal and oxidative aging and improves the stability of bio-oil by decreasing the viscosity [157]. To investigate the impact on the viscosity of bio-oil water contents as high as 30 wt % and methanol as high as 10 wt % were added to a hardwood bio-oil and found that the viscosity was lowered from 76 cP to 12 cP with 30% water and 10% methanol at 25ºC while methanol was slightly more effective than water [158]. Oasmaa et al. [159] investigated 2, 5, 10, and 20 wt % ethanol to a hardwood bio-oil. The bio-oil's initial viscosity decreased from 50 cSt to 10 cSt at 50 ºC with 20% ethanol. After aging at 50 ºC for as long as 7 days, the neat bio-oil's viscosity increase was 3.5 cSt/day compared to 0.4 cSt/day for a mixture of 5 wt % ethanol in bio-oil, for a reduction in the aging rate by a factor of 8.5. Diebold and Czernik [110] investigated bio-oil by adding 10 wt % methanol, ethanol, acetone, ethyl acetate, a 1/1 mixture of acetone and methanol, or a 1/1 mixture of methanol and methyl iso-butyl ketone. The study reported that the initial viscosities decreased from 30 cP to about 15 cP at 40ºC for the bio-oil/solvent mixtures. These experiments were carried out at 90 ºC to investigate the ability to preheat the stabilized bio-oil before combustion and reduce the amount of time required for aging studies. The viscosities for the bio-oil/solvent mixtures and aged neat bio-oil varied linearly with time. Methanol was found as one of the most influential and cheapest organic solvents to reduce the rate of viscosity while the aging rate was reduced by 17 with 10% methanol, compared to the neat bio-oil aged at the same temperature. Among several alcohols, like methanol, ethanol, and isopropanol used in bio-oil stability, methanol is the most effective to reduce the aging rate of bio-oil because methanol has high extractability in compare with ethanol. Additionally, methanol and its polarity work on a vast number of phytochemicals including polar and non-polar compounds [160]. Bio-oil with a compound additive including 1.0 wt.% methanol, 5.1 wt.% dimethyl furan (DMF), and 1.94 wt.% acetone has found with low moisture and viscosity, and high pH after aging at 80 °C for 24h [161]. After aging, the relative proportion of sugars and esters significantly increased, but a number of reactive species, mainly 2-ethoxy-5-(1-propen-1-yl) and 5-hydroxy-2-methylbenzaldehyde were utterly disappeared in bio-oil. The addition of ethanol and ethyl acetate at a mass ratio of 1:1 can significantly improve the stability of the fractional bio-oil from the pyrolysis of rice husk according to Yi et al. [162]. The addition of solvent increases bio-oil stability by the following mechanisms [157, 163]: (1) reaction with active species in bio-oil to produce low molecular weight ester compounds and acetal-based compounds and prevent the generation of large-chain polymers, (2) decreasing the concentration of reactive species or changing the microstructure of reactive components, and (3) physical dilution of bio-oil without affecting any chemical reactions.

Moreover, the selection of efficient solvent is the key challenges towards the large implication of bio-oil. It is worth pointing here that the stored oil mustn't be exposed to high temperature for a long duration as it leads to influence the viscosity and acidity of bio-oil. However, based on the above scrutiny, it can be stated that to improve the bio-oil stability, solvent addition is an efficient approach compared to other techniques.

5.2 Fraction separation

Bio-oil is a complex chemical mixture containing various chemical functional groups with different chemical composition and physicochemical properties and can be divided into several fractions (Table 6). Fraction separation is one of the effective mechanism of bio-oil due to its ability to avoid the interaction between those fractions once it is separated into several fractions [46, 164]. Different approaches have been previously used to separate crude bio-oils, of which the standard methods for the separation of bio-oil fractions are liquid-liquid extraction and distillation [46].

Table 6. Major fractions of bio-oil [122]

Fraction of bio-oil	**Chemical composition**	**Typical properties**
Hydrophilic	Water	➢ High oxygen

fraction	Anhydrosugars, polyols, and compounds containing multiple hydroxyl groups	content ➢ Immiscibility with mineral oils
Hydrophobic fraction	Lignin decomposition products along with some extractives (e.g., fatty acids and resin acids)	➢ High density and viscosity ➢ Poor storage stability
Co-solvent fraction	C_1-C_6 oxygenated molecules containing aliphatic and aromatic acids, aldehydes, ketones, alcohols and phenols	➢ Acidity ➢ Poor thermal stability ➢ Solubility

5.2.1 Liquid-Liquid extraction

The addition of water and an organic solvent to bio-oil can enhance the separation and extraction of different fractions [165, 166]. There are two liquid-liquid extraction methods: sequential and combined extractions. The steps of sequential extraction include: 1) adding water into crude bio-oil; 2) centrifuging mixture of crude bio-oil and water to obtain aqueous phase and organic phase; 3) adding selected solvent into organic bio-oil phase; 4) centrifuging mixture of organic bio-oil and selected solvent to obtain solvent-insoluble phase and solvent-soluble phase. For combined extraction, both water and organic solvent are mixed with crude bio-oil, and the mixture is centrifuged to get a water phase, solvent-insoluble phase, and solvent-soluble phase at the same time. The sequential and combined liquid-liquid extractions are presented in **Figure 15**.

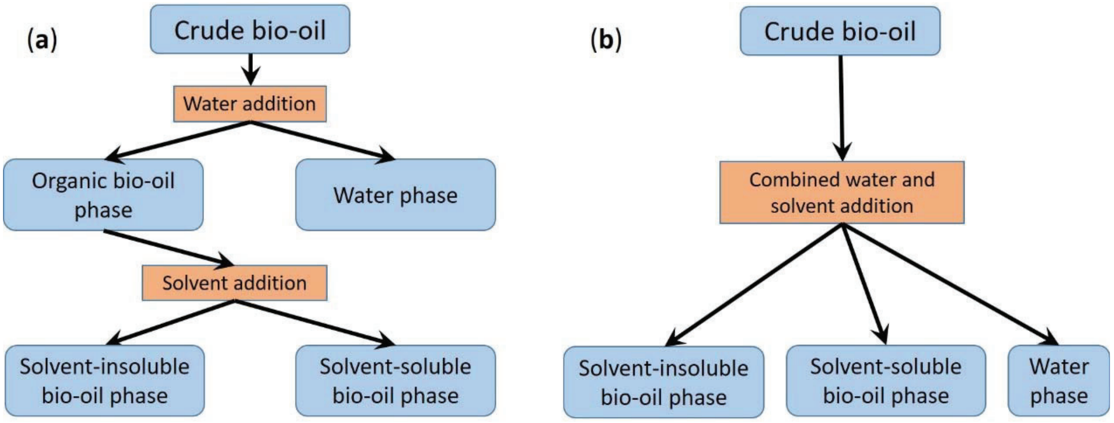


Figure 15. Separation of bio-oil fractions. (a) sequential extraction and (b) combined extraction (reprinted from Park et al. [167] with permission of American Chemistry Society)

Two different types of liquid-liquid extraction of bio-oil based on the polarity and acidity of bio-oil fractions are shown in **Figure 16**. The choice of the organic solvent for liquid-liquid extraction of bio-oil is mainly dependent on its immiscibility with water to facilitate separation and its efficiency in extracting the expected components [167]. The polarity of solvent is an important parameter to consider in selecting appropriate solvents. In general, polar solvents are more suitable for the extraction of bio-oil considering the abundance of polar components in bio-oil [168], which was confirmed by the study on successive extractions of bagasse pyrolysis bio-oil using solvents with different polarity by Garia-Preze et al. [169]. The liquid-liquid extraction of bio-oil and its phase stability is usually investigated by using the ternary phase diagram [71, 170-172], a handy tool to study liquid-liquid phase equilibrium. **Table 7** summaries the studies on the liquid-liquid extraction of bio-oil fractions.

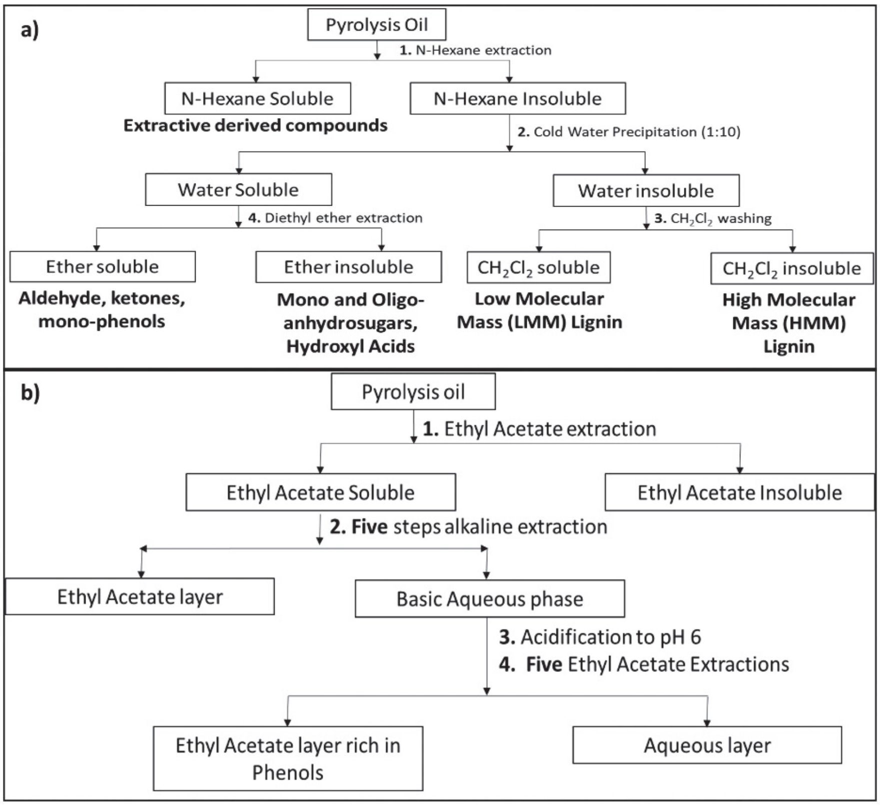


Figure 16. Two common schemes used for liquid-liquid extraction of bio-oil based (a) polarity and (b) acidity (reprinted from Pinheiro et al. [46] with permission of American Chemistry Society)

In general, liquid-liquid extraction can be used for separating bio-oil into an aqueous bio-oil phase and an organic phase. The aqueous bio-oil phase can be used to produce hydrogen by microbial electrolysis [173] or catalytic reforming [174, 175], and to obtain value-added chemicals (e.g., phenols and organic acids) [176, 177]. The organic phase is usually used for obtaining value-added chemicals and fuel additives [178].

Table 7. Studies on Liquid-liquid extractions of bio-oil fractions in literature

Bio-oil sample						
Biomass feedstock	**Pyrolysis reactor**	**Pyrolysis conditions**	**Solvent**	**Target products**	**Year**	**Reference**
Mallee eucalypts wood	Fluidized bed reactor	Pyrolysis temperature: 500 °C	Water / chloroform	Sugar, sugar derivatives and aromatics from aqueous phase	2012	[45]
Douglas fir pellet	Microwave pyrolysis reactor operated in batch mode with 200 g feedstock	Pyrolysis temperature: 500 °C Pyrolysis period: 25 min Microwave	Hexane, petroleum ether, chloroform	Sugar, acid, alcohol from aqueous phase, high concentration 85% of phenols and guaiacols from organic phase	2014	[179]

		power input: 700 W				
Switchgrass	Semi pilot-scaled auger pyrolysis system with biomass feeding rate of 10 kg h^{-1}.	Temperature: 500 °C Residence time: 90 s	Water, Hexadecane, octane	Phenolics and acetic acid from organic phase	2016	[167]
Jatropha Curcas seed cake	Electrically heated fixed bed reactor operated in batch mode with 0.25 kg feedstock	Pyrolysis temperature: 550 °C Pyrolysis period: 30 min	Ethyl acetate, dichloromethane, carbon tetrachloride, diethyl ether, benzene, cyclohexane and hexane for extraction of aqueous	Acidic and basic organic compounds from aqueous phase	2016	[180]

			phase			
Pine wood	Pilot fluidized bed reactor with feedstock feeding rate of 8-10 kg h^{-1}	Pyrolysis temperature: 530 °C Average residence time of pyrolysis vapors: 1.7s	Butyl acetate (1:1, w/w)	Phenolic compounds from aqueous phase	2016	[181]
Air-dried switchgrass			Hexane, petroleum ether, chloroform, and ethyl acetate	Chemical groups including furans, alcohols, ketones, and phenolics from bio-oil aqueous phase	2017	[182]
Debarked	Fluidized bed reactor	Pyrolysis	Diesel and bio-diesel	Phenolic compounds; diesel	2018	[183]

loblolly pine	with feedstock feeding rate of 150 g h^{-1}	temperature: 500 °C Residence time of pyrolysis vapor: 1.5 s		extracts 4.3 wt.% of bio-oil, bio-diesel extracts 26.6 wt.% of bio-oil		
Loblolly pine	**Pilot-scale** bubbling fluidized bed **reactor** with feedstock feeding rate of 1 TPD (ton per day)	Average pyrolysis temperature: 477 °C Pyrolysis over catalyst	Methyl *tert*-butyl ether [MTBE], methyl isobutyl ketone [MIBK], toluene, and isopropanol	Concentration of Monofunctional methoxyphenols > 80 wt.%; Overall separation efficiency > 70 wt.%	2019	[184]
Organosolv lignin	Fixed bed reactor operated in batch	Pyrolysis temperature:	Ionic liquid ([Choline][ntf2])	Phenolic compounds from aqueous phase	2019	[185]

	mode with 475 mg feedstock	500 °C

5.2.2 Distillation

Another method for the separation of bio-oil fractions is distillation, which is also used for the bio-oil chemical characterization and water removal [186]. It is widely used in petroleum refining, which likely makes it an incidental candidate for industrial-scale bio-oil fractionation [168].

Distillation can be ascribed as a heating process of liquid until it boils, then condensing and collecting the resultant hot vapors. There are various methods of distillation: fractional distillation, vacuum distillation, steam distillation, and molecular distillation. Fractional distillation can separate components having different boiling points from each other [168]. Vacuum distillation works under pressure to lower the boiling points separating components at lower temperatures and prevent possible decomposition of some components [187, 188]. Steam distillation uses steam to reduce the partial pressure of substance operating at temperatures lower than the usual boiling points of components [189]. Molecular distillation uses reduced pressures to separate components without the pressure exerted by the gaseous phase, which is used for the separation of thermally unstable substances [190].

Different distillations were used for the separation of bio-oil fractions. For the atmospheric and vacuum distillation of bio-oil derived from corn stover, water, aromatic and oxygenated compounds are concentrated in both light and middle fractions, whereas the phenolic compounds are distributed only in the heavy fraction [191]. For the distillation of microalgae pyrolysis bio-oil at both atmospheric and vacuum pressures, bio-oil was fractionated into three fractions: the light fraction showed a significant reduction in acidity and viscosity and contained most aromatic compounds, and the middle fraction has the highest yield [192]. Vacuum distillation can achieve cleaner separation of bio-oil fractions compared with atmospheric distillation. Continuous and atmospheric distillation was suggested for fractionating chemicals(benzene, toluene, and xylene) from partially deoxygenated pyrolysis oils [193]. Steam distillation can be used to fractionate a phenol-rich fraction from bio-oil derived from woody biomass pyrolysis, resulting in thermally stable fractions [194]. Molecular distillation can efficiently separate the bio-oil fractions at low temperatures to minimize thermal decomposition, and different fractions of bio-oil can be enriched with various chemical families by molecular distillation (see **Figure 17**) [195].

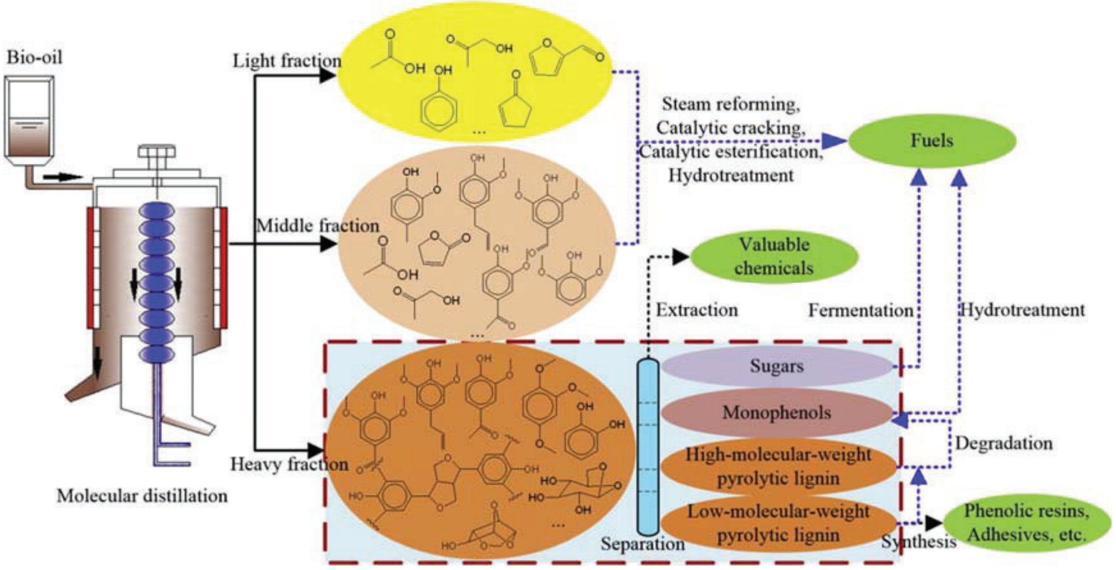


Figure 17. Separation of bio-oil fractions by molecular distillation (reprinted from Wang et al. [195] with permission of Elsevier)

Distillation process is efficient only when the contained compound of bio-oil having different boiling temperature. Implication of this process will not be effective when the bio-oil compound having similar boiling point. And the bio-oil compound is largely influenced by several factors like temperature, heating rate and catalyst. Hence, before chose any upgrading process a regression model including those influencing factors needs to pay utmost attention.

5.3 Emulsification

Emulsification of bio-oil with some chemicals or other fuels (like diesel or bio-diesel) is another efficient, easy, and inexpensive approach to decrease the bio-oil aging rate. In emulsification, two immiscible liquids are subjected to mix in the presence of an emulsifying agent or surfactant, which makes a monolayer interface onto immiscible liquid droplets with sufficient mechanical strength to avoid the phase separation as well coalescence of droplets [33, 196]. However, the quality of mixture largely depends on the ratio of liquid, agitation intensity, surfactant concentration, and operation temperature [197]. The hydrophilic-lipophilic balance (HLB) depends on chemical structure and surfactant properties which is an essential parameter for choosing emulsifier. Lipophilic surfactant is featured by low HLB value, whereas a higher HLB value for hydrophilic surfactant. Usually, surfactants with HLB values of 4-8 are used in water-in-oil emulsification while surfactants with HLB values of 9-12 used in oil-in-water emulsification [198]. According to Zhang et al. [199], direct emulsification of bio-oil and crude glycerol via ultrasound and mechanical agitation can improve the stability of bio-oil, and the aged crude glycerol/bio-oil emulsion fuel showed only minor changes [199]. In recent studies, emulsification of bio-oil with diesel or bio-diesel has been gained much attention in bio-oil stability, and a number of emulsifiers, such as span 20, span 60, span 80, span 80 with n-butanol, n-pentanol, n-hexanol, n-heptanol and n-octanol, and span 100 have been used in the emulsification of bio-oil with diesel [141, 200-202]. Emulsification of bio-oil with 60 vol.% of bio-diesel revealed that viscosity of mixture increased between first 10 and 60 h due to the production of high molecular weight compounds and then gradually decreased up to 180 h [203]. Ultrasonic and ultrasonic-mechanical emulsification was applied to prepare emulsion of bio-oil with conventional diesel with a mass ratio of bio-oil: diesel: emulsifier of 10:85:5. The stability of bio-oil and diesel emulsion was longer rather than an emulsion of different bio-oil fractions [204]. The emulsification mechanism model for bio-oil and diesel has been presented in **Figure 18**.

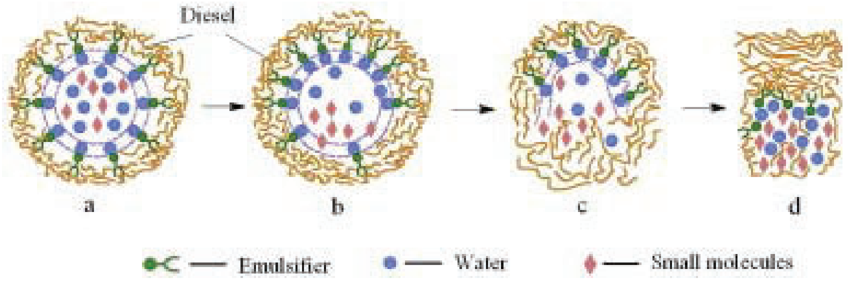


Figure 18. Mechanism of emulsification for bio-oil and diesel (reprinted from Guo et al. [204] with permission of Elsevier)

Typically, bio-oil contains 23.30 wt.% water, small oxygenates, and large molecular sugar derived oxygenates. In the presence of an emulsifier, water in bio-oil exerts strong emulsifying capacity with diesel compared to small molecular oxygenates. Sugar derived oxygenates do not undergo emulsification with diesel alone. Ultrasonic and ultrasonic-mechanical emulsification result in some special structural units from bio-oil components, and the existence of structural units promote the stability of crude bio-oil emulsion. Emulsifying bio-oil from rice husk with diesel using a mixer of emulsifiers of Span 20 (20wt.%), Span 80 (20wt.%) and Span 100 (60wt.%) results in improved anti-wear, friction-reducing, and extreme pressure of emulsion [200]. In the bio-oil stability study through emulsification of ether-extracted bio-oil (EEB) and diesel, it could be observed that EEO/diesel emulsion is stable without phase separation up to 40 days [196]. Similarly, emulsion from wood pyrolysis oil and methyl ester of Jatropha has been suggested to use as the alternative fuel in diesel engine [205]. Therefore, emulsification of bio-oil and other petroleum fuels could be suggested to reduce the aging rate and promote bio-oil stability during the storage, transportation, and application stage.

On the other hand, redundant chemical transformations are not necessarily required for all instance of the emulsification process. Still, energy consumption input and high cost and cannot be neglected. The accompanying corrosiveness and the subassemblies are inevitably serious to the engine. Based on the above findings it is necessary to control the erosion that takes place at certain parts of the diesel engine at the time of operation. Therefore, to solve the key problems associated with bio-oil during feeding, storage, and combustion stage multiphase nature of bio-oil is crucial to take into account for future.

5.4 Removal of solids, water, and light volatiles

The solid content in bio-oil includes incompletely separated coke, char, ash, and impurities from biomass or attained during collection and storage of bio-oil, and the amount is less than 1wt.% [163]. However, a higher fraction of solid is another reason for bio-oil instability because metal ions, like sodium, potassium, calcium, and magnesium present in the solid fraction may catalyze polymerization and condensation of reactive species and consequently increase the viscosity of bio-oil [69, 206]. Besides, char in bio-oil may offer plenty of catalytic sites for promoting some reactions [207]. Ortega et al. [126] also found that bio-oil with char-free characteristics showed slow aging rate. Elliott et al. [54] led the IEA Round Robin study on long-term aging of bio-oils and also found that the storage of a filtered bio-oil can minimize the amount of change in viscosity. However, several approaches, such as cyclone separator, hot gas vapor filtration, microfiltration, and nano-filtration have been studied to separate the solid and reduce its content in bio-oil [208]. Cyclone separator is not practical to trap very fine particles (<10μm). Hot gas filtration can efficiently reduce the solid content in bio-oil and thereafter improve the stability of bio-oil [209]. Generally, two filter elements, namely porous sintered stainless-steel and sintered ceramic power are used in hot gas vapor filtration, and viscosity increase rate of bio-oil is only one-tenth compared to the cyclone system. On the other hand, microfiltration and nano-filtration have been found promising to remove char particles in size less than 10μm from bio-oil [113, 210]. However, a fraction of minerals is solubilized due to high pH of bio-oil, which cannot be removed by filtration, and solubilized minerals might be related to aging-related instability [134].

Also, the quality of bio-oil can be improved by removing water and reducing the light reactive volatiles in bio-oil by evaporation, especially in homogeneity, viscosity, and stability [143].

5.5 Mild hydrogenation

The presence of oxygenated compounds in bio-oil is another influencing factor for bio-oil aging [211, 212]. Therefore, the removal of oxygenated compounds can improve bio-oil stability by mild hydrogenation. Mild hydrogenation is the hydrodeoxygenation (HDO) process of bio-oil at a mild temperature using catalysts under high hydrogen pressure [213-218].

A series of C-C, C-O-C, and C-OH bond cleavage and hydrodeoxygenation reactions expel the oxygen in the form of water during hydrogenation [219, 220]. The produced alcohol undergoes further esterification with carboxylic acid. During hydrogenation of carboxylic acids in bio-oil, it undergoes two major reaction pathways as follows: (1) decarbon(x)ylation with formation of alkanes, and (2) hydro(deoxy)genation to produce aldehyde, alcohol, alkene, and alkanes [221, 222].

In literature, the studies on mild hydrogenation for bio-oil stabilization are focused on (1) hydrogenation of bio-oil model compound, (2) catalytic hydrogenation of bio-oil, and (3) electrocatalytic hydrogenation of bio-oil. To pull in polymerization and following catalyst deactivation stabilization of mild methods are crucial. Homogenous catalytic hydrotreatment of pyrolytic oil at low temperature (e.g., <100 ºC) and low pressure (10-30 bar) of hydrogen has also been scrutinized as a mild stabilization method.

Hydrogenation of propionic acid (a bio-oil model compound) over a Ni-Cu catalyst was studied for bio-oil stabilization [216]. Similar to carboxylic acid, decarbonylation of propionic acid produce ethane. Hydrogenolysis of C-O bond in propionic acid produces propionaldehyde, which followed by hydrogenation to 1-propanol. The dehydration of propanol produces propane, then converts to propene through hydrogenation. The stabilization of woody bio-oil can be achieved by the mild hydrogenation over Ru/TiO_2 catalyst at 120 – 160 °C [217]. Catalytic hydrogenation can remove some reactive species in bio-oil through some reactions, which is an efficient way to stabilize bio-oil (see **Figure 19**). Electrocatalytic hydrogenation was considered a new approach for bio-oil stabilization [218]. After electrocatalytic hydrogenation treatment, aldehydes and ketones in bio-oil are converted to their corresponding alcohols, which can stabilize bio-oil against polymerization. Besides the stabilization of bio-oil, valuable products (such as ethylene glycol and propylene glycol) and hydrogen are produced during electrocatalytic hydrogenation. Electrocatalytic hydrogenation provides a dynamic way of approach to a certain extent of upgrading water-soluble pyrolysis oil into durable fuel intermediates and chemicals.

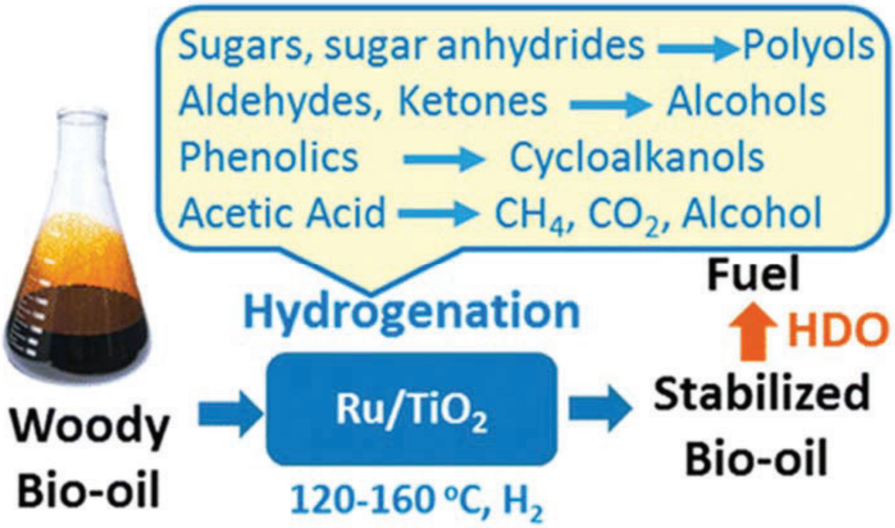


Figure 19. Stabilization of woody bio-oil by catalytic mild hydrogenation (reprinted from Wang et al. [217] with permission of American Chemical Society)

Mild hydrogenation can result in a lower fraction of chemically unstable compounds, oxygenates and water content, and therefore, slow down the aging rate of bio-oil and improve its stability. Despite having an advantage of reducing bio-oil oxygen content, mild hydrogenation may result in a significant decrease of liquid yields and appears to be a cost-effective technique.

5.6 Other approaches

A number of antioxidants, like butylated hydroxyanisole (BHA), and tert-butylhydroquinone (TBHQ) have been studied which improved the stability of bio-diesel [223, 224]. Despite using antioxidants in bio-diesel stability, a few studies on bio-oil stability with antioxidants can be found in past years. The addition of antioxidants to the bio-oil increases the oxidative stability and slow down the aging rate of bio-oil [225]. To improve the overall oxidative stability of bio-oil, three different antioxidants, namely propyl gallate, tert-butyl hydroquinone, and butylatedhydroxyanisole were added to bio-oil in 1000 ppm concentration where the addition of antioxidants was found to slow down the bio-oil aging rate [226]. Several studies have been focused on the antioxidant activity of bio-oil due to a fraction of phenolic compounds [227-230], but that is not enough for its stabilization. The reaction chemistry in bio-oil stabilization upon the addition of antioxidants remains as a scope of study.

Bio-oil comes in contact with air during collection as it is produced in the absence of air. Oxidation of bio-oil produces peroxide that promotes the polymerization of olefins [231]. A small amount of air locates in the headspace of bio-oil jar which does not improve the aging rate [55]. However, access to air to bio-oil should be limited to retard the increase in viscosity as well as the aging process.

In closing, based on above-discussed techniques to slow down the bio-oil aging solvent addition and mild hydrogenation is aroused as practical techniques, although they both have some challenges to overcome. It is necessary pointing here that selection of appropriate and efficient solvent is the key challenge to work. In contrast, mild hydrogenation is the cost-effective approach, while a significant decrease of liquid yield is the main limitation to research on further to overcome these challenges.

6 Conclusions and outlook

Bio-oil from the pyrolysis of lignocellulosic biomass can be used as a liquid fuel to substitute petroleum-derived fuels and a feedstock for the production of chemicals. However, there are challenges in utilizing bio-oil due to its low quality and instability caused by aging. The profound understanding of bio-oil aging is required for its storage, handling, transportation, upgrading and application. The summaries of this review and the recommendations for future research on bio-oil aging are as follows:

- Bio-oil has complex chemical composition, physicochemical properties, and multiphase behavior.
- There are several aging indicators of which the change in viscosity, molecular weight, and carbonyl content are commonly used to characterize the degree of aging during storage. In addition, the change in water content, acidity, heat generation, and free radicals can be considered in future research.
- There are two types of aging test methods: long-term (natural) aging and accelerated aging. The accelerated aging test can quickly determine the change in viscosity during aging. However, it cannot replace long-term aging test because of their different reaction mechanisms. The apparatus and test procedures for aging tests of bio-oil should be standardized and can be referred to the corresponding standard methods for testing the aging behaviors of petroleum-derived bitumen.
- Bio-oil contains reactive chemical functional groups and free radicals. Some reactions, including polymerization, condensation, esterification, and oxidation, likely happen between the chemical compounds in bio-oils. Moreover, air oxidation of alcohols and aldehydes in bio-oil and autoxidation of some bio-oil components to form acids, and hydroperoxides and alkylperoxides are other mechanisms of bio-

oil aging.

- The kinetic behaviors of bio-oil with prolonged aging time can be described by the aging kinetic models based on the form of an exponential function of aging time and temperature. In the future research on the aging kinetics of bio-oil, the kinetic models for bitumen aging are suggested to address more parameters.
- Main approaches to slow bio-oil aging include the reduction of viscosity by solvents addition, fractions separation, and emulsification with bio-diesels, the removal of char by filtration, and microfiltration, the removal of light volatile components by evaporation, and the removal of reactive functional groups by mild hydrogenation. On the recovery of organic solvents and emulsification surfactants is crucial for further research. Although mild hydrogenation for reducing the oxygen content in bio-oil and improving bio-oil stability has been proposed, yet it significantly decreases the yields of target products because of uncontrollable product selectivity, thus it is economically unavailable at the current stage. Future studies might be paid more attention to develop combined processes with catalytic technologies to make the target product more selective and produce more stable bio-oil with controlled components.
- The techno-economic analysis is a timely approach to know the process and product feasibility, and it involves capital cost, operating cost and minimum fuel selling price. Unfortunately, techno-economic analysis research directly involved with bio-oil aging is limited in the available literature. Generally, stabilization or upgrading of bio-oil incurs high capital cost. Aging process of bio-oil will add an

additional cost in the process in order to have stable bio-oil or store the bio-oil for a long period without its quality deterioration as the aging itself an upgrading process. Therefore, it is a matter of urgent to take into account the techno-economic analysis of bio-oil aging for further study.

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References

[1] Ibrahiem DM, Hanafy SA. Dynamic linkages amongst ecological footprints, fossil fuel energy consumption and globalization: an empirical analysis. Management of Environmental Quality: An International Journal. 2020;31:1549-68.

[2] Wu XD, Guo JL, Meng J, Chen GQ. Energy use by globalized economy: Total-consumption-based perspective via multi-region input-output accounting. Science of the Total Environment. 2019;662:65-76.

[3] Kedia S. Approaches to low carbon development in China and India. Advances in Climate Change Research. 2016;7:213-21.

[4] Cao W, Wang Y, Wang C. Fatigue characterization of bio-modified asphalt binders under various laboratory aging conditions. Construction and Building Materials. 2019;208:686-96.

[5] Isikgor FH, Becer CR. Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. Polymer Chemistry. 2015;6:4497-559.

[6] Cai J, He Y, Yu X, Banks SW, Yang Y, Zhang X, et al. Review of physicochemical properties and analytical characterization of lignocellulosic biomass. Renewable and Sustainable Energy Reviews. 2017;76:309-22.

[7] Fatma S, Hameed A, Noman M, Ahmed T, Shahid M, Tariq M, et al. Lignocellulosic biomass: A sustainable bioenergy source for the future. Protein and peptide letters. 2018;25:148-63.

[8] Wang S, Dai G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. Progress in Energy and Combustion Science. 2017;62:33-86.

[9] Sharma S, Meena R, Sharma A, Goyal P. Biomass Conversion Technologies for Renewable Energy and Fuels: A Review Note. IOSR Journal of Mechanical and Civil Engineering. 2014;11:28-35.

[10] Pang S. Advances in thermochemical conversion of woody biomass to energy, fuels and chemicals. Biotechnology Advances. 2019;37:589-97.

[11] Tursi A. A review on biomass: importance, chemistry, classification, and conversion. Biofuel Research Journal. 2019;6:962-79.

[12] Lee YY, Iyer P, Torget RW. Dilute-Acid Hydrolysis of Lignocellulosic Biomass. In: Tsao GT, Brainard AP, Bungay HR, Cao NJ, Cen P, Chen Z, et al., editors. Recent Progress in Bioconversion of Lignocellulosics. Berlin, Heidelberg: Springer Berlin Heidelberg; 1999. p. 93-115.

[13] Sharifzadeh M, Sadeqzadeh M, Guo M, Borhani TN, Murthy Konda NVSN,

Garcia MC, et al. The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions. Progress in Energy and Combustion Science. 2019;71:1-80.

[14] Carpenter D, Westover TL, Czernik S, Jablonski W. Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors. Green Chemistry. 2014;16:384-406.

[15] Dai L, Wang Y, Liu Y, Ruan R, He C, Yu Z, et al. Integrated process of lignocellulosic biomass torrefaction and pyrolysis for upgrading bio-oil production: A state-of-the-art review. Renewable & Sustainable Energy Reviews. 2019;107:20-36.

[16] Rahman MM, Liu R, Cai J. Catalytic fast pyrolysis of biomass over zeolites for high quality bio-oil – A review. Fuel Processing Technology. 2018;180:32-46.

[17] Nishu, Liu R, Rahman MM, Sarker M, Chai M, Li C, et al. A review on the catalytic pyrolysis of biomass for the bio-oil production with ZSM-5: Focus on structure. Fuel Processing Technology. 2020;199:106301.

[18] Griffin MB, Iisa K, Wang H, Dutta A, Orton KA, French RJ, et al. Driving towards cost-competitive biofuels through catalytic fast pyrolysis by rethinking catalyst selection and reactor configuration. Energy & Environmental Science. 2018;11:2904-18.

[19] Guedes RE, Luna AS, Torres AR. Operating parameters for bio-oil production in biomass pyrolysis: A review. Journal of Analytical and Applied Pyrolysis. 2018;129:134-49.

[20] Kan T, Strezov V, Evans TJ. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renewable & Sustainable Energy Reviews. 2016;57:1126-40.

[21] Baloch HA, Nizamuddin S, Siddiqui MTH, Riaz S, Jatoi AS, Dumbre DK, et al. Recent advances in production and upgrading of bio-oil from biomass: A critical overview. Journal of Environmental Chemical Engineering. 2018;6:5101-18.

[22] Balat M, Balat M, Kırtay E, Balat H. Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. Energy Conversion and Management. 2009;50:3147-57.

[23] Chiaramonti D, Oasmaa A, Solantausta Y. Power generation using fast pyrolysis liquids from biomass. Renewable & Sustainable Energy Reviews. 2007;11:1056-86.

[24] Broumand M, Albert-Green S, Yun S, Hong Z, Thomson MJ. Spray combustion of fast pyrolysis bio-oils: Applications, challenges, and potential solutions. Progress in Energy and Combustion Science. 2020;79:100834.

[25] Sippula O, Huttunen K, Hokkinen J, Kärki S, Suhonen H, Kajolinna T, et al. Emissions from a fast-pyrolysis bio-oil fired boiler: Comparison of health-related characteristics of emissions from bio-oil, fossil oil and wood. Environmental Pollution. 2019;248:888-97.

[26] Zheng J-L, Kong Y-P. Spray combustion properties of fast pyrolysis bio-oil produced from rice husk. Energy Conversion and Management. 2010;51:182-8.

[27] Wu S, Wang Z, Yang H, Zhang H, Xiao R. The applicability of catalytic esterified biomass-pyrolysis-oil surrogates in diesel engine. Fuel Processing Technology.

2020;198:106251.

[28] Boucher ME, Chaala A, Roy C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. Biomass and Bioenergy. 2000;19:337-50.

[29] Boucher ME, Chaala A, Pakdel H, Roy C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase. Biomass and Bioenergy. 2000;19:351-61.

[30] Buffi M, Cappelletti A, Rizzo AM, Martelli F, Chiaramonti D. Combustion of fast pyrolysis bio-oil and blends in a micro gas turbine. Biomass and Bioenergy. 2018;115:174-85.

[31] Halder PK, Joardder MUH, Beg MRA, Paul N, Ullah I. Utilization of bio-oil for cooking and lighting. Advances in Mechanical Engineering. 2012;2015:190518.

[32] Lin B-J, Chen W-H, Hsieh T-H, Ong HC, Show PL, Naqvi SR. Oxidative reaction interaction and synergistic index of emulsified pyrolysis bio-oil/diesel fuels. Renewable Energy. 2019;136:223-34.

[33] Calabria R, Chiariello F, Massoli P. Thermal behavior of pyrolysis oil–diesel oil emulsion in evaporating micronic droplets. Combustion Science and Technology. 2019:1-20.

[34] Leng L, Li H, Yuan X, Zhou W, Huang H. Bio-oil upgrading by emulsification/microemulsification: A review. Energy. 2018;161:214-32.

[35] Leng L. Biosurfactant rhamnolipid assisted microemulsification of bio-oil

components in diesel. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2019;41:829-43.

[36] Djandja OS, Wang Z, Chen L, Qin L, Wang F, Xu Y, et al. Progress in hydrothermal liquefaction of algal biomass and hydrothermal upgrading of the subsequent crude bio-oil: A mini review. Energy & Fuels. 2020;34:11723-51.

[37] Setiabudi HD, Aziz MAA, Abdullah S, Teh LP, Jusoh R. Hydrogen production from catalytic steam reforming of biomass pyrolysis oil or bio-oil derivatives: A review. International Journal of Hydrogen Energy. 2020;45:18376-97.

[38] Zhao Z, Situmorang YA, An P, Chaihad N, Wang J, Hao X, et al. Hydrogen production from catalytic steam reforming of bio-oils: A critical review. Chemical Engineering and Technology. 2020;43:625-40.

[39] Al-Sabaeei AM, Napiah MB, Sutanto MH, Alaloul WS, Usman A. A systematic review of bio-asphalt for flexible pavement applications: Coherent taxonomy, motivations, challenges and future directions. Journal of Cleaner Production. 2020;249:119357.

[40] Yang Y, Zhang Y, Omairey E, Cai J, Gu F, Bridgwater AV. Intermediate pyrolysis of organic fraction of municipal solid waste and rheological study of the pyrolysis oil for potential use as bio-bitumen. Journal of Cleaner Production. 2018;187:390-9.

[41] Wang H, Ma Z, Chen X, Mohd Hasan MR. Preparation process of bio-oil and bio-asphalt, their performance, and the application of bio-asphalt: A comprehensive review. Journal of Traffic and Transportation Engineering (English Edition). 2020;7:137-51.

[42] Zhang X, Zhang K, Wu C, Liu K, Jiang K. Preparation of bio-oil and its application

in asphalt modification and rejuvenation: A review of the properties, practical application and life cycle assessment. Construction and Building Materials. 2020;262:120528.

[43] Pattiya A. 1 - Fast pyrolysis. In: Rosendahl L, editor. Direct Thermochemical Liquefaction for Energy Applications: Woodhead Publishing; 2018. p. 3-28.

[44] Valle B, Remiro A, García-Gómez N, Gayubo AG, Bilbao J. Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review. Journal of Chemical Technology & Biotechnology. 2019;94:670-89.

[45] Hu X, Mourant D, Gunawan R, Wu L, Wang Y, Lievens C, et al. Production of value-added chemicals from bio-oil via acid catalysis coupled with liquid–liquid extraction. RSC Advances. 2012;2:9366-70.

[46] Pinheiro Pires AP, Arauzo J, Fonts I, Domine ME, Fernández Arroyo A, Garcia-Perez ME, et al. Challenges and opportunities for bio-oil refining: A review. Energy & Fuels. 2019:4683–720.

[47] Suqi L, Caceres L, Schieck K, Booker CJ, McGarvey BM, Yeung KKC, et al. Insecticidal activity of bio-oil from the pyrolysis of straw from brassica spp. Journal of Agricultural and Food Chemistry. 2014;62:3610-8.

[48] Bedmutha R, Booker CJ, Ferrante L, Briens C, Berruti F, Yeung KKC, et al. Insecticidal and bactericidal characteristics of the bio-oil from the fast pyrolysis of coffee grounds. Journal of Analytical and Applied Pyrolysis. 2011;90:224-31.

[49] Staš M, Auersvald M, Kejla L, Vrtiška D, Kroufek J, Kubička D. Quantitative analysis of pyrolysis bio-oils: A review. TrAC Trends in Analytical Chemistry.

2020;126:115857.

[50] Bertero M, de la Puente G, Sedran U. Fuels from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning. Fuel. 2012;95:263-71.

[51] Guda VK, Steele PH, Penmetsa VK, Li Q. Chapter 7 - Fast Pyrolysis of Biomass: Recent Advances in Fast Pyrolysis Technology. In: Pandey A, Bhaskar T, Stöcker M, Sukumaran RK, editors. Recent Advances in Thermo-Chemical Conversion of Biomass. Boston: Elsevier; 2015. p. 177-211.

[52] Lødeng R, Bergem H. 7 - Stabilisation of pyrolysis oils. In: Rosendahl L, editor. Direct Thermochemical Liquefaction for Energy Applications: Woodhead Publishing; 2018. p. 193-247.

[53] Mujahid R, Kim J. Aging stability of bio-oil produced from dewatered sewage sludge in subcritical water. The Journal of Supercritical Fluids. 2020;166:105011.

[54] Elliott DC, Oasmaa A, Meier D, Preto F, Bridgwater AV. Results of the IEA round robin on viscosity and aging of fast pyrolysis bio-oils: Long-term tests and repeatability. Energy & Fuels. 2012;26:7362-6.

[55] Diebold JP. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. National Renewable Energy Laboratory; 2000.

[56] Alsbou E, Helleur B. Accelerated aging of bio-oil from fast pyrolysis of hardwood. Energy & Fuels. 2014;28:3224-35.

[57] Oasmaa A, Sundqvist T, Kuoppala E, Garcia-Perez M, Solantausta Y, Lindfors C, et al. Controlling the phase stability of biomass fast pyrolysis bio-oils. Energy & Fuels.

2015;29:4373–81.

[58] Kumar R, Strezov V, Weldekidan H, He J, Singh S, Kan T, et al. Lignocellulose biomass pyrolysis for bio-oil production: A review of biomass pre-treatment methods for production of drop-in fuels. Renewable & Sustainable Energy Reviews. 2020;123:109763.

[59] Lu Q, Li W-Z, Zhu X-F. Overview of fuel properties of biomass fast pyrolysis oils. Energy Conversion and Management. 2009;50:1376-83.

[60] Staš M, Chudoba J, Kubička D, Blažek J, Pospíšil M. Petroleomic characterization of pyrolysis bio-oils: A review. Energy & Fuels. 2017;31:10283-99.

[61] Staš M, Kubička D, Chudoba J, Pospíšil M. Overview of analytical methods used for chemical characterization of pyrolysis bio-oil. Energy & Fuels. 2014;28:385-402.

[62] Staš M, Auersvald M, Kejla L, Vrtiška D, Kroufek J, Kubička D. Quantitative analysis of pyrolysis bio-oils: A review. TrAC Trends in Analytical Chemistry. 2020:115857.

[63] Gollakota ARK, Reddy M, Subramanyam MD, Kishore N. A review on the upgradation techniques of pyrolysis oil. Renewable & Sustainable Energy Reviews. 2016;58:1543-68.

[64] Hansen S, Mirkouei A, Diaz LA. A comprehensive state-of-technology review for upgrading bio-oil to renewable or blended hydrocarbon fuels. Renewable & Sustainable Energy Reviews. 2020;118:109548.

[65] Hu X, Gunawan R, Mourant D, Hasan MDM, Wu L, Song Y, et al. Upgrading of bio-oil via acid-catalyzed reactions in alcohols — A mini review. Fuel Processing

Technology. 2017;155:2-19.

[66] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energy & Fuels. 2004;18:590-8.

[67] Raman NAA, Hainin MR, Hassan NA, Ani FN. A review on the application of bio-oil as an additive for asphalt. Jurnal Teknologi. 2015;72:105-10.

[68] Oasmaa A, Van De Beld B, Saari P, Elliott DC, Solantausta Y. Norms, standards, and legislation for fast pyrolysis bio-oils from lignocellulosic biomass. Energy & Fuels. 2015;29:2471-84.

[69] Yang Z, Kumar A, Huhnke RL. Review of recent developments to improve storage and transportation stability of bio-oil. Renewable & Sustainable Energy Reviews. 2015;50:859-70.

[70] Chen D, Zhou J, Zhang Q, Zhu X. Evaluation methods and research progresses in bio-oil storage stability. Renewable & Sustainable Energy Reviews. 2014;40:69-79.

[71] Oasmaa A, Fonts I, Pelaez-Samaniego MR, Garcia-Perez ME, Garcia-Perez M. Pyrolysis oil multiphase behavior and phase stability: A review. Energy & Fuels. 2016;30:6179-200.

[72] Lin F, Waters CL, Mallinson RG, Lobban LL, Bartley LE. Relationships between biomass composition and liquid products formed via pyrolysis. Frontiers in Energy Research. 2015;3:15.

[73] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy & Fuels. 2006;20:848-89.

[74] Shen J, Zhu S, Liu X, Zhang H, Tan J. The prediction of elemental composition of

biomass based on proximate analysis. Energy Conversion and Management. 2010;51:983-7.

[75] Cheng F, Bayat H, Jena U, Brewer CE. Impact of feedstock composition on pyrolysis of low-cost, protein- and lignin-rich biomass: A review. Journal of Analytical and Applied Pyrolysis. 2020;147:104780.

[76] Mutsengerere S, Chihobo CH, Musademba D, Nhapi I. A review of operating parameters affecting bio-oil yield in microwave pyrolysis of lignocellulosic biomass. Renewable & Sustainable Energy Reviews. 2019;104:328-36.

[77] Papari S, Hawboldt K. A review on condensing system for biomass pyrolysis process. Fuel Processing Technology. 2018;180:1-13.

[78] Lawal A, Farrauto RJ. Chapter 8 - The Convergence of Emission Control and Source of Clean Energy. In: Suib SL, editor. New and Future Developments in Catalysis. Amsterdam: Elsevier; 2013. p. 195-231.

[79] Wang S, Luo Z, Media CSP. Pyrolysis of Biomass: De Gruyter; 2016.

[80] Arnold S, Moss K, Henkel M, Hausmann R. Biotechnological Perspectives of Pyrolysis Oil for a Bio-Based Economy. Trends in Biotechnology. 2017;35:925-36.

[81] Lyu G, Wu S, Zhang H. Estimation and comparison of bio-oil components from different pyrolysis conditions. Frontiers in Energy Research. 2015;3:28.

[82] Zhang L, Xi G, Yu K, Yu H, Wang X. Furfural production from biomass–derived carbohydrates and lignocellulosic residues via heterogeneous acid catalysts. Industrial Crops and Products. 2017;98:68-75.

[83] Banks SW, Bridgwater AV. 14 - Catalytic fast pyrolysis for improved liquid quality.

In: Luque R, Lin CSK, Wilson K, Clark J, editors. Handbook of Biofuels Production (Second Edition): Woodhead Publishing; 2016. p. 391-429.

[84] Carrier M, Windt M, Ziegler B, Appelt J, Saake B, Meier D, et al. Quantitative insights into the fast pyrolysis of extracted cellulose, hemicelluloses, and lignin. ChemSusChem. 2017;10:3212-24.

[85] Zhang X, Lei H, Zhu L, Qian M, Yadavalli G, Wu J, et al. From plastics to jet fuel range alkanes via combined catalytic conversions. Fuel. 2017;188:28-38.

[86] Zhao Y, Wang Y, Duan D, Ruan R, Fan L, Zhou Y, et al. Fast microwave-assisted ex-catalytic co-pyrolysis of bamboo and polypropylene for bio-oil production. Bioresource Technology. 2018;249:69-75.

[87] Uzoejinwa BB, He X, Wang S, El-Fatah Abomohra A, Hu Y, Wang Q. Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: Recent progress and future directions elsewhere worldwide. Energy Conversion and Management. 2018;163:468-92.

[88] Ahmed MHM, Batalha N, Mahmudul HMD, Perkins G, Konarova M. A review on advanced catalytic co-pyrolysis of biomass and hydrogen-rich feedstock: Insights into synergistic effect, catalyst development and reaction mechanism. Bioresource Technology. 2020:123457.

[89] Yu D, Hui H, Li S. Two-step catalytic co-pyrolysis of walnut shell and LDPE for aromatic-rich oil. Energy Conversion and Management. 2019;198:111816.

[90] Zhang H, Nie J, Xiao R, Jin B, Dong C, Xiao G. Catalytic co-pyrolysis of biomass and different plastics (polyethylene, polypropylene, and polystyrene) to improve

hydrocarbon yield in a fluidized-bed reactor. Energy & Fuels. 2014;28:1940-7.

[91] Xie Q, Addy M, Liu S, Zhang B, Cheng Y, Wan Y, et al. Fast microwave-assisted catalytic co-pyrolysis of microalgae and scum for bio-oil production. Fuel. 2015;160:577-82.

[92] Wang L, Chai M, Liu R, Cai J. Synergetic effects during co-pyrolysis of biomass and waste tire: A study on product distribution and reaction kinetics. Bioresource Technology. 2018;268:363-70.

[93] Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils - state of the art for the end users. Energy & Fuels. 1999;13:914-21.

[94] Lehto J, Oasmaa A, Solantausta Y, Kytö M, Chiaramonti D. Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass. Applied Energy. 2014;116:178-90.

[95] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion and Management. 2007;48:87-92.

[96] Oasmaa A, Peacocke C. A guide to physical property characterization of biomass-derived fast pyrolysis liquids: Application of standard fuel oil analyses. Espoo: VTT Technical Research Center of Finland; 2001.

[97] Michailof CM, Kalogiannis KG, Sfetsas T, Patiaka DT, Lappas AA. Advanced analytical techniques for bio-oil characterization. Wiley Interdisciplinary Reviews: Energy and Environment. 2016;5:614-39.

[98] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Organic Geochemistry. 1999;30:1479-93.

[99] Jendoubi N, Broust F, Commandre JM, Mauviel G, Sardin M, Lédé J. Inorganics distribution in bio oils and char produced by biomass fast pyrolysis: The key role of aerosols. Journal of Analytical and Applied Pyrolysis. 2011;92:59-67.

[100] Moloodi S, Tzanetakis T, Nguyen B, Zarghami-Tehran M, Khan U, Thomson MJ. Fuel property effects on the combustion performance and emissions of hardwood-derived fast pyrolysis liquid-ethanol blends in a swirl burner. Energy & Fuels. 2012;26:5452-61.

[101] Meng J, Smirnova TI, Song X, Moore A, Ren X, Kelley S, et al. Identification of free radicals in pyrolysis oil and their impact on bio-oil stability. RSC Advances. 2014;4:29840-6.

[102] Zarghami-Tehran M. Experimental Investigation of the Effects of Fuel Aging on Combustion Performance and Emissions of Biomass Fast Pyrolysis Liquid-Ethanol Blends in a Swirl Burner: University of Toronto; 2012.

[103] Zhang L, Liu R, Yin R, Mei Y. Upgrading of bio-oil from biomass fast pyrolysis in China: A review. Renewable & Sustainable Energy Reviews. 2013;24:66-72.

[104] Lu Q, Zhang J, Zhu X. Corrosion properties of bio-oil and its emulsions with diesel. Chinese Science Bulletin. 2008;53:3726-34.

[105] Nolte MW, Liberatore MW. Viscosity of biomass pyrolysis oils from various feedstocks. Energy & Fuels. 2010;24:6601-8.

[106] Cai J, Banks SW, Yang Y, Darbar S, Bridgwater T. Viscosity of aged bio-oils from fast pyrolysis of beech wood and miscanthus: Shear rate and temperature dependence. Energy & Fuels. 2016;30:4999-5004.

[107] Ba T, Chaala A, Garcia-Perez M, Roy C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. Energy & Fuels. 2004;18:188-201.

[108] Garcìa-Pérez M, Chaala A, Pakdel H, Kretschmer D, Rodrigue D, Roy C. Multiphase structure of bio-oils. Energy & Fuels. 2006;20:364-75.

[109] Fratini E, Bonini M, Oasmaa A, Solantausta Y, Teixeira J, Baglioni P. SANS analysis of the microstructural evolution during the aging of pyrolysis oils from biomass. Langmuir. 2006;22:306-12.

[110] Diebold JP, Czernik S. Additives to lower and stabilize the viscosity of pyrolysis oils during storage. Energy & Fuels. 1997;11:1081-91.

[111] Oasmaa A, Kuoppala E. Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. Energy & Fuels. 2003;17:1075-84.

[112] Czernik S, Johnson DK, Black S. Stability of wood fast pyrolysis oil. Biomass and Bioenergy. 1994;7:187-92.

[113] Elliott DC, Oasmaa A, Preto F, Meier D, Bridgwater AV. Results of the IEA round robin on viscosity and stability of fast pyrolysis bio-oils. Energy & Fuels. 2012;26:3769-76.

[114] Oasmaa A, Meier D. Norms and standards for fast pyrolysis liquids: 1. Round robin test. Journal of Analytical and Applied Pyrolysis. 2005;73:323-34.

[115] Oasmaa A, Elliott DC, Korhonen J. Acidity of biomass fast pyrolysis bio-oils. Energy & Fuels. 2010;24:6548-54.

[116] Kim KH, Bai X, Cady S, Gable P, Brown RC. Quantitative investigation of free

radicals in bio-oil and their potential role in condensed-phase polymerization. ChemSusChem. 2015;8:894-900.

[117] Zhang S, Li C, Guo X, Rahman MM, Zhang X, Yu X, et al. Kinetic analysis of bio-oil aging by using pattern search method. Industrial & Engineering Chemistry Research. 2020;59:1487-94.

[118] Meng J, Moore A, Tilotta DC, Kelley SS, Adhikari S, Park S. Thermal and storage stability of bio-oil from pyrolysis of torrefied wood. Energy & Fuels. 2015;29:5117-26.

[119] Luo D, Yin W, Liu S, Yang N, Xia S, Ma P. Pyrolysis oil polymerization of water-soluble fraction during accelerated aging. Fuel. 2018;230:368-75.

[120] Oasmaa A, Korhonen J, Kuoppala E. An approach for stability measurement of wood-based fast pyrolysis bio-oils. Energy & Fuels. 2011;25:3307-13.

[121] Black S, Ferrell JR. Accelerated aging of fast pyrolysis bio-oil: A new method based on carbonyl titration. RSC Advances. 2020;10:10046-54.

[122] Sundqvist T, Solantausta Y, Oasmaa A, Kokko L, Paasikallio V. Heat generation during the aging of wood-derived fast-pyrolysis bio-oils. Energy & Fuels. 2016;30:465-72.

[123] Joseph J, Rasmussen MJ, Fecteau JP, Kim S, Lee H, Tracy KA, et al. Compositional changes to low water content bio-oils during aging: An NMR, GC/MS, and LC/MS study. Energy & Fuels. 2016;30:4825-40.

[124] Haarlemmer G, Guizani C, Anouti S, Déniel M, Roubaud A, Valin S. Analysis and comparison of bio-oils obtained by hydrothermal liquefaction and fast pyrolysis of beech wood. Fuel. 2016;174:180-8.

[125] Oh SJ, Choi GG, Kim JS. Preparation of calcium magnesium acetate deicer using raw acetic acid-rich bio-oil obtained from continuous two-stage pyrolysis of corncob. ACS Sustainable Chemistry & Engineering. 2018;6:4362-9.

[126] Ortega JV, Renehan AM, Liberatore MW, Herring AM. Physical and chemical characteristics of aging pyrolysis oils produced from hardwood and softwood feedstocks. Journal of Analytical and Applied Pyrolysis. 2011;91:190-8.

[127] Grioui N, Halouani K, Agblevor FA. Bio-oil from pyrolysis of Tunisian almond shell: Comparative study and investigation of aging effect during long storage. Energy for Sustainable Development. 2014;21:100-12.

[128] Wang C, Ding H, Zhang Y, Zhu X. Analysis of property variation and stability on the aging of bio-oil from fractional condensation. Renewable Energy. 2020;148:720-8.

[129] Peralta J, Raouf MA, Tang S, Williams RC. Bio-Renewable Asphalt Modifiers and Asphalt Substitutes. In: Gopalakrishnan K, van Leeuwen J, Brown RC, editors. Sustainable Bioenergy and Bioproducts: Value Added Engineering Applications. London: Springer London; 2012. p. 89-115.

[130] Deroiné M, Le Duigou A, Corre Y-M, Le Gac P-Y, Davies P, César G, et al. Accelerated ageing and lifetime prediction of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) in distilled water. Polymer Testing. 2014;39:70-8.

[131] Hilten RN, Das KC. Comparison of three accelerated aging procedures to assess bio-oil stability. Fuel. 2010;89:2741-9.

[132] Nolte MW, Liberatore MW. Real-time viscosity measurements during the accelerated aging of biomass pyrolysis oil. Energy & Fuels. 2011;25:3314-7.

[133] Mahadevan R, Shakya R, Neupane S, Adhikari S. Physical and chemical properties and accelerated aging test of bio-oil produced from in situ catalytic pyrolysis in a bench-scale fluidized-bed reactor. Energy & Fuels. 2015;29:841-8.

[134] Naske CD, Polk P, Wynne PZ, Speed J, Holmes WE, Walters KB. Postcondensation filtration of pine and cottonwood pyrolysis oil and impacts on accelerated aging reactions. Energy & Fuels. 2012;26:1284-97.

[135] Siriwardhana AGMT. Aging and Stabilization of Pyrolytic Bio-Oils and Model Compounds [Integrated Article]: The University of Western Ontario; 2013.

[136] Meng J, Moore A, Tilotta D, Kelley S, Park S. Toward understanding of bio-oil aging: Accelerated aging of bio-oil fractions. ACS Sustainable Chemistry & Engineering. 2014;2:2011-8.

[137] Zhang M, Li M, Wu H. Ageing of bio-oil and its fractions in presence of surfactants. Fuel. 2019;252:403-7.

[138] Sun Z, Yi J, Feng D, Kasbergen C, Scarpas A, Zhu Y. Preparation of bio-bitumen by bio-oil based on free radical polymerization and production process optimization. Journal of Cleaner Production. 2018;189:21-9.

[139] Tauste R, Moreno-Navarro F, Sol-Sánchez M, Rubio-Gámez MC. Understanding the bitumen ageing phenomenon: A review. Construction and Building Materials. 2018;192:593-609.

[140] Behnood A, Modiri Gharehveran M. Morphology, rheology, and physical properties of polymer-modified asphalt binders. European Polymer Journal. 2019;112:766-91.

[141] Yang SI, Hsu TC, Wu CY, Chen KH, Hsu YL, Li YH. Application of biomass fast pyrolysis part II: The effects that bio-pyrolysis oil has on the performance of diesel engines. Energy. 2014;66:172-80.

[142] Xiong W, Fu Y, Lu Q, Guo Q. Aging behavior and mechanism of bio-oil (in Chinese with English abstract). Chinese Science Bulletin. 2009;54:2188-95.

[143] Oasmaa A, Sipilä K, Solantausta Y, Kuoppala E. Quality improvement of pyrolysis liquid: Effect of light volatiles on the stability of pyrolysis liquids. Energy & Fuels. 2005;19:2556-61.

[144] Zhang Q, Zhang L, Wang T, Xu Y, Zhang Q, Ma L, et al. Upgrading of bio-oil by removing carboxylic acids in supercritical ethanol. Energy Procedia. 2014;61:1033-6.

[145] Elliott DC, Lee S-J, Hart TR. Stabilization of Fast Pyrolysis Oil: Post Processing Final Report. Pacific Northwest National Lab.(PNNL), Richland, WA (United States); 2012.

[146] Oasmaa A, Peacocke C, Gust S, Meier D, McLellan R. Norms and standards for pyrolysis liquids. End-user requirements and specifications. Energy & Fuels. 2005;19:2155-63.

[147] Srifa A, Chaiwat W, Pitakjakpipop P, Anutrasakda W, Faungnawakij K. Chapter 6 - Advances in bio-oil production and upgrading technologies. In: Rai M, Ingle AP, editors. Sustainable Bioenergy: Elsevier; 2019. p. 167-98.

[148] Hoang AT. Experimental study on spray and emission characteristics of a diesel engine fueled with preheated bio-oils and diesel fuel. Energy. 2019;171:795-808.

[149] Yuan X, Ding X, Leng L, Li H, Shao J, Qian Y, et al. Applications of bio-oil-

based emulsions in a DI diesel engine: The effects of bio-oil compositions on engine performance and emissions. Energy. 2018;154:110-8.

[150] Raouf MA, Williams CR. General rheological properties of fractionated switchgrass bio-oil as a pavement material. Road Materials and Pavement Design. 2010;11:325-53.

[151] Hosseinnezhad S, Zadshir M, Yu X, Yin H, Sharma BK, Fini E. Differential effects of ultraviolet radiation and oxidative aging on bio-modified binders. Fuel. 2019;251:45-56.

[152] Hosseinnezhad S, Fini EH, Sharma BK, Basti M, Kunwar B. Physiochemical characterization of synthetic bio-oils produced from bio-mass: a sustainable source for construction bio-adhesives. RSC Advances. 2015;5:75519-27.

[153] Raouf MA, Williams RC. Temperature and shear susceptibility of a nonpetroleum binder as a pavement material. Transportation Research Record. 2010;2180:9-18.

[154] Alsbou E, Helleur B. Accelerated aging of bio-oil from fast pyrolysis of hardwood. Energy & Fuels. 2014;28:3224-35.

[155] Mei Y, Chai M, Shen C, Liu B, Liu R. Effect of methanol addition on properties and aging reaction mechanism of bio-oil during storage. Fuel. 2019;244:499-507.

[156] Zhang L, Luo Y, Wijayapala R, Walters KB. Alcohol stabilization of low water content pyrolysis oil during high temperature treatment. Energy & Fuels. 2017;31:13666-74.

[157] Rajamohan S, Kasimani R. Studies on the effects of storage stability of bio-oil obtained from pyrolysis of Calophyllum inophyllum deoiled seed cake on the

performance and emission characteristics of a direct-injection diesel engine. Environmental Science and Pollution Research. 2018;25:17749-67.

[158] Diebold J, Scahill J, Czernik S, Phillips S, Feik C. Progress in the production of hot-gas filtered biocrude oil at NREL. National Renewable Energy Lab., Golden, CO (United States); 1995.

[159] Oasmaa A, Leppämäki E, Koponen P, Levander J, Tapola E. Physical characterisation of biomass-based pyrolysis liquids: application of standard fuel oil analyses. VTT publications: VTT, TECHNICAL RESEARCH CENTRE OF FINLAND; 1997. p. 46.

[160] Oasmaa A, Kuoppala E, Selin J-F, Gust S, Solantausta Y. Fast pyrolysis of forestry residue and pine. 4. Improvement of the product quality by solvent addition. Energy & Fuels. 2004;18:1578-83.

[161] Zhu L, Li K, Zhang Y, Zhu X. Upgrading the storage properties of bio-oil by adding a compound additive. Energy & Fuels. 2017;31:6221-7.

[162] Yi W, Wang X, Zeng K, Yang H, Shao J, Zhang S, et al. Improving bio-oil stability by fractional condensation and solvent addition. Fuel. 2021;290:119929.

[163] Xiu S, Shahbazi A. Bio-oil production and upgrading research: A review. Renewable & Sustainable Energy Reviews. 2012;16:4406-14.

[164] Qinjie C, Fan Z, Junhao C, Yuan Z, Lingjun Z. A review on the upgradingof bio-oil based on separation. Science Foundation in China. 2017:57-80.

[165] Li R, Ma Z, Yang T, Li B, Wei L, Sun Y. Sub–supercritical liquefaction of municipal wet sewage sludge to produce bio-oil: Effect of different organic–water

mixed solvents. Journal of Supercritical Fluids. 2018;138:115-23.

[166] Ren S, Ye XP. Stability of crude bio-oil and its water-extracted fractions. Journal of Analytical and Applied Pyrolysis. 2018;132:151-62.

[167] Park LK-E, Ren S, Yiacoumi S, Ye XP, Borole AP, Tsouris C. Separation of switchgrass bio-oil by water/organic solvent addition and pH adjustment. Energy & Fuels. 2016;30:2164-73.

[168] Ramirez JA, Brown RJ, Rainey TJ. A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels. Energies. 2015;8:6765-94.

[169] Garcia-Perez M, Chaala A, Pakdel H, Kretschmer D, Roy C. Characterization of bio-oils in chemical families. Biomass and Bioenergy. 2007;31:222-42.

[170] Li M, Zhang M, Yu Y, Wu H. Ternary system of pyrolytic lignin, mixed solvent, and water: Phase diagram and implications. Energy & Fuels. 2018;32:465-74.

[171] Zhang M, Wu H. Phase behavior and fuel properties of bio-oil/glycerol/methanol blends. Energy & Fuels. 2014;28:4650-6.

[172] Ribeiro LAB, Martins RC, Mesa-Pérez JM, Bizzo WA. Study of bio-oil properties and ageing through fractionation and ternary mixtures with the heavy fraction as the main component. Energy. 2019;169:344-55.

[173] Brooks V, Lewis AJ, Dulin P, Beegle JR, Rodriguez M, Borole AP. Hydrogen production from pine-derived catalytic pyrolysis aqueous phase via microbial electrolysis. Biomass and Bioenergy. 2018;119:1-9.

[174] Kumar A, Chakraborty JP, Singh R. Bio-oil: The future of hydrogen generation.

Biofuels. 2017;8:663-74.

[175] Arandia A, Coronado I, Remiro A, Gayubo AG, Reinikainen M. Aqueous-phase reforming of bio-oil aqueous fraction over nickel-based catalysts. International Journal of Hydrogen Energy. 2019;44:13157-68.

[176] Dong Z, Yang H, Chen P, Liu Z, Chen Y, Wang L, et al. Lignin characterization and catalytic pyrolysis for phenol-rich oil with tio2-based catalysts. Energy & Fuels. 2019;33:9934-41.

[177] Duan D, Lei H, Wang Y, Ruan R, Liu Y, Ding L, et al. Renewable phenol production from lignin with acid pretreatment and ex-situ catalytic pyrolysis. Journal of Cleaner Production. 2019;231:331-40.

[178] del Pozo C, Bartrolí J, Puy N, Fàbregas E. Separation of value-added chemical groups from bio-oil of olive mill waste. Industrial Crops and Products. 2018;125:160-7.

[179] Wei Y, Lei H, Wang L, Zhu L, Zhang X, Liu Y, et al. Liquid–liquid extraction of biomass pyrolysis bio-oil. Energy & Fuels. 2014;28:1207-12.

[180] Kanaujia PK, Naik DV, Tripathi D, Singh R, Poddar MK, Konathala LNSK, et al. Pyrolysis of Jatropha Curcas seed cake followed by optimization of liquid-liquid extraction procedure for the obtained bio-oil. Journal of Analytical and Applied Pyrolysis. 2016;118:202-24.

[181] Müller N, Romero R, Grandón H, Segura C. Selective production of formic acid by wet oxidation of aqueous-phase bio-oil. Energy & Fuels. 2016;30:10417-24.

[182] Ren S, Ye XP, Borole AP. Separation of chemical groups from bio-oil water-

extract via sequential organic solvent extraction. Journal of Analytical and Applied Pyrolysis. 2017;123:30-9.

[183] Kim H, Vinueza NR, Kelley SS, Park S. Correlation between solubility parameters and recovery of phenolic compounds from fast pyrolysis bio-oil by diesel extraction. Carbon Resources Conversion. 2018;1:238-44.

[184] Mante OD, Thompson SJ, Mustapha S, Dayton DC. A selective extraction method for recovery of monofunctional methoxyphenols from biomass pyrolysis liquids. Green Chemistry. 2019;21:2257-65.

[185] Cesari L, Canabady-Rochelle L, Mutelet F. Separation of phenols from lignin pyrolysis oil using ionic liquid. Separation and Purification Technology. 2019;209:528-34.

[186] Qarizada D, Mohammadian E, Alis AB, Yusuf SM, Dollah A, Rahimi HA, et al. Thermo distillation and characterization of bio oil from fast pyrolysis of palm kernel shell (PKS). Key Engineering Materials. 2019;797:359-64.

[187] Torres S, Acien G, García-Cuadra F, Navia R. Direct transesterification of microalgae biomass and biodiesel refining with vacuum distillation. Algal Research. 2017;28:30-8.

[188] Choi JH, Kim S-S, Woo HC. Characteristics of vacuum fractional distillation from pyrolytic macroalgae (Saccharina japonica) bio-oil. Journal of Industrial and Engineering Chemistry. 2017;51:206-15.

[189] Murwanashyaka JN, Pakdel H, Roy C. Seperation of syringol from birch wood-derived vacuum pyrolysis oil. Separation and Purification Technology. 2001;24:155-65.

[190] Wang S, Gu Y, Liu Q, Yao Y, Guo Z, Luo Z, et al. Separation of bio-oil by molecular distillation. Fuel Processing Technology. 2009;90:738-45.

[191] Capunitan JA, Capareda SC. Characterization and separation of corn stover bio-oil by fractional distillation. Fuel. 2013;112:60-73.

[192] Nam H, Choi J, Capareda SC. Comparative study of vacuum and fractional distillation using pyrolytic microalgae (Nannochloropsis oculata) bio-oil. Algal Research. 2016;17:87-96.

[193] McVey M, Elkasabi Y, Ciolkosz D. Separation of BTX chemicals from biomass pyrolysis oils via continuous flash distillation. Biomass Conversion and Biorefinery. 2020;10:15-23.

[194] Murwanashyaka JN, Pakdel H, Roy C. Seperation of syringol from birch wood-derived vacuum pyrolysis oil. Separation and Purification Technology. 2001;24:155-65.

[195] Wang Y, Wang S, Leng F, Chen J, Zhu L, Luo Z. Separation and characterization of pyrolytic lignins from the heavy fraction of bio-oil by molecular distillation. Separation and Purification Technology. 2015;152:123-32.

[196] Farooq A, Shafaghat H, Jae J, Jung S-C, Park Y-K. Enhanced stability of bio-oil and diesel fuel emulsion using Span 80 and Tween 60 emulsifiers. Journal of Environmental Management. 2019;231:694-700.

[197] Martin JA, Mullen CA, Boateng AA. Maximizing the stability of pyrolysis oil/diesel fuel emulsions. Energy & Fuels. 2014;28:5918-29.

[198] Wang X-l, Yuan X-z, Huang H-j, Leng L-j, Li H, Peng X, et al. Study on the solubilization capacity of bio-oil in diesel by microemulsion technology with Span80

as surfactant. Fuel Processing Technology. 2014;118:141-7.

[199] Zhang M, Yewe-Siang Lee Shee We M, Wu H. Direct emulsification of crude glycerol and bio-oil without addition of surfactant via ultrasound and mechanical agitation. Fuel. 2018;227:183-9.

[200] Lu Q, Zhang Z-B, Liao H-T, Yang X-C, Dong C-Q. Lubrication properties of bio-oil and its emulsions with diesel oil. Energies. 2012;5:741-51.

[201] Prakash R, Singh R, Murugan S. Experimental investigation on a diesel engine fueled with bio-oil derived from waste wood–biodiesel emulsions. Energy. 2013;55:610-8.

[202] Lin B-J, Chen W-H, Budzianowski WM, Hsieh C-T, Lin P-H. Emulsification analysis of bio-oil and diesel under various combinations of emulsifiers. Applied Energy. 2016;178:746-57.

[203] Jiang X, Ellis N. Upgrading bio-oil through emulsification with biodiesel: Mixture production. Energy & Fuels. 2010;24:1358-64.

[204] Guo Z, Wang S, Wang X. Stability mechanism investigation of emulsion fuels from biomass pyrolysis oil and diesel. Energy. 2014;66:250-5.

[205] Prakash R, Singh RK, Murugan S. Use of biodiesel and bio-oil emulsions as an alternative fuel for direct injection diesel engine. Waste and Biomass Valorization. 2013;4:475-84.

[206] Moutsoglou A, Lawburgh B, Lawburgh J. Fractional condensation and aging of pyrolysis oil from softwood and organosolv lignin. Journal of Analytical and Applied Pyrolysis. 2018;135:350-60.

[207] Ma Z, Xiao R, Zhang H. Catalytic steam reforming of bio-oil model compounds for hydrogen-rich gas production using bio-char as catalyst. International Journal of Hydrogen Energy. 2017;42:3579-85.

[208] Butler E, Devlin G, Meier D, McDonnell K. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. Renewable & Sustainable Energy Reviews. 2011;15:4171-86.

[209] Baldwin RM, Feik CJ. Bio-oil stabilization and upgrading by hot gas filtration. Energy & Fuels. 2013;27:3224-38.

[210] Javaid A, Ryan T, Berg G, Pan X, Vispute T, Bhatia SR, et al. Removal of char particles from fast pyrolysis bio-oil by microfiltration. Journal of Membrane Science. 2010;363:120-7.

[211] Mante OD, Agblevor FA. Storage stability of biocrude oils from fast pyrolysis of poultry litter. Waste Management. 2012;32:67-76.

[212] Cheng T, Han Y, Zhang Y, Xu C. Molecular composition of oxygenated compounds in fast pyrolysis bio-oil and its supercritical fluid extracts. Fuel. 2016;172:49-57.

[213] Auersvald M, Shumeiko B, Vrtiška D, Straka P, Staš M, Šimáček P, et al. Hydrotreatment of straw bio-oil from ablative fast pyrolysis to produce suitable refinery intermediates. Fuel. 2019;238:98-110.

[214] Zacher AH, Olarte MV, Santosa DM, Elliott DC, Jones SB. A review and perspective of recent bio-oil hydrotreating research. Green Chemistry. 2014;16:491-515.

[215] Schmitt CC, Raffelt K, Zimina A, Krause B, Otto T, Rapp M, et al. Hydrotreatment of fast pyrolysis bio-oil fractions over nickel-based catalyst. Topics in Catalysis. 2018;61:1769-82.

[216] Otyuskaya D, Thybaut JW, Alexiadis V, Alekseeva M, Venderbosch R, Yakovlev V, et al. Fast pyrolysis oil stabilization kinetics over a Ni-Cu catalyst using propionic acid as a model compound. Applied Catalysis B: Environmental. 2018;233:46-57.

[217] Wang H, Lee S-J, Olarte MV, Zacher AH. Bio-oil stabilization by hydrogenation over reduced metal catalysts at low temperatures. ACS Sustainable Chemistry & Engineering. 2016;4:5533-45.

[218] Li Z, Kelkar S, Raycraft L, Garedew M, Jackson JE, Miller DJ, et al. A mild approach for bio-oil stabilization and upgrading: electrocatalytic hydrogenation using ruthenium supported on activated carbon cloth. Green Chemistry. 2014;16:844-52.

[219] Li N, Tompsett GA, Huber GW. Renewable high-octane gasoline by aqueous-phase hydrodeoxygenation of C_5 and C_6 carbohydrates over Pt/zirconium phosphate catalysts. ChemSusChem. 2010;3:1154-7.

[220] Li N, Huber GW. Aqueous-phase hydrodeoxygenation of sorbitol with Pt/SiO_2–Al_2O_3: Identification of reaction intermediates. Journal of Catalysis. 2010;270:48-59.

[221] He Z, Wang X. Required catalytic properties for alkane production from carboxylic acids: Hydrodeoxygenation of acetic acid. Journal of Energy Chemistry. 2013;22:883-94.

[222] Li J, Zhang J, Wang S, Xu G, Wang H, Vlachos DG. Chemoselective hydrodeoxygenation of carboxylic acids to hydrocarbons over nitrogen-doped carbon–

alumina hybrid supported iron catalysts. ACS Catalysis. 2019;9:1564-77.

[223] Nogales-Delgado S, Encinar JM, González JF. Safflower biodiesel: Improvement of its oxidative stability by using BHA and TBHQ. Energies. 2019;12:1940.

[224] van der Westhuizen I, Focke WW. Stabilizing sunflower biodiesel with synthetic antioxidant blends. Fuel. 2018;219:126-31.

[225] Lyckeskog HN, Mattsson C, Olausson L, Andersson S-I, Vamling L, Theliander H. Thermal stability of low and high Mw fractions of bio-oil derived from lignin conversion in subcritical water. Biomass Conversion and Biorefinery. 2017;7:401-14.

[226] Udomsap P, Yapp Hionk Y, Hui JTH, Yoosuk B, Yusuf SB, Sukkasi S. Towards stabilization of bio-oil by addition of antioxidants and solvents, and emulsification with conventional hydrocarbon fuels. 2011 International Conference & Utility Exhibition on Power and Energy Systems: Issues and Prospects for Asia (ICUE)2011. p. 1-5.

[227] Hossain MM, Scott IM, Berruti F, Briens C. Application of novel pyrolysis reactor technology to concentrate bio-oil components with antioxidant activity from tobacco, tomato and coffee ground biomass. Waste and Biomass Valorization. 2018;9:1607-17.

[228] Gil-Lalaguna N, Bautista A, Gonzalo A, Sánchez JL, Arauzo J. Obtaining biodiesel antioxidant additives by hydrothermal treatment of lignocellulosic bio-oil. Fuel Processing Technology. 2017;166:1-7.

[229] García M, Botella L, Gil-Lalaguna N, Arauzo J, Gonzalo A, Sánchez JL. Antioxidants for biodiesel: Additives prepared from extracted fractions of bio-oil. Fuel Processing Technology. 2017;156:407-14.

[230] Patra J, Kim S, Hwang H, Choi J, Baek K-H. Volatile compounds and antioxidant capacity of the bio-oil obtained by pyrolysis of Japanese red pine (pinus densiflora siebold and zucc.). Molecules. 2015;20:3986-4006.

[231] Dahlquist E. Technologies for Converting Biomass to Useful Energy: Combustion, Gasification, Pyrolysis, Torrefaction and Fermentation: CRC Press; 2013.

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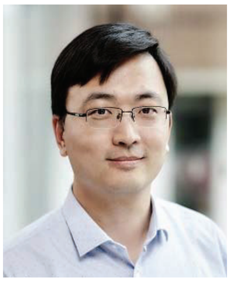

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