REVIEW ARTICLE

A review on catalytic & non-catalytic bio-oil upgrading in supercritical fluids

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Abstract This review article summarizes the key published research on the topic of bio-oil upgrading using catalytic and non-catalytic supercritical fluid (SCF) conditions. The precious metal catalysts Pd, Ru and Pt on various supports are frequently chosen for catalytic bio-oil upgrading in SCFs. This is reportedly due to their favourable catalytic activity during the process including hydrotreating, hydrocracking, and esterification, which leads to improvements in liquid yield, heating value, and pH of the upgraded bio-oil. Due to the costs associated with precious metal catalysts, some researchers have opted for non-precious metal catalysts such as acidic HZSM-5 which can promote esterification in supercritical ethanol. On the other hand, SCFs have been effectively used to upgrade crude bio-oil without a catalyst. Supercritical methanol, ethanol, and water are most commonly used and demonstrate catalyst like activities such as facilitating esterification reactions and reducing solid yield by alcoholysis and hydrolysis, respectively.

Keywords bio-oil, upgrading, supercritical, review

1 Introduction

In recent years, the world has been facing an energy crisis due to a combination of several factors including the depletion of fossil fuels, accelerated population growth, increase in global energy demand, and crude oil price fluctuations. Furthermore, the extensive use of fossil fuels has led to climate change and global warming. These global issues have motivated research into alternative energy technologies, renewable resources, and more sustainable techniques for energy generation.

Biomass can be utilised as a renewable feed for conversion into gaseous, liquid, and solid biofuels [1]. Biomass is any biodegradable material of biological origin excluding fossilized material or peat [2]. Fast pyrolysis is a thermal conversion technique that decomposes biomass in the absence of oxygen [1]. Pyrolysis liquid (bio-oil) is produced under moderate temperature (~500°C) and short vapor residence times (~1 s) [1]. Fast pyrolysis for liquid production is especially interesting as the process directly converts biomass to high yield liquid of up to 75 wt-% whilst keeping gas and char by-products at low yields of 12 wt-% and 13 wt-% [3]. Common feedstocks for pyrolysis oil production include wood, bagasse, rice straw, switchgrass and wheat straw [4]. The liquid biofuel, commonly known as crude bio-oil, has generated growing interest as it can be used for energy, chemicals, or as an energy carrier. However, the properties of crude pyrolysis oil such as high acidity and viscosity and high oxygen and water contents lead to detrimental effects during application including corrosion to metal components, instability during storage and reduced heating value. This affects the direct use of crude bio-oil and its assimilation into existing liquid fuel infrastructures.

Table 1 compares select characteristics of wood-derived crude bio-oil and heavy petroleum fuel oil [1,5,6]. The properties of crude bio-oil such as low heating value, high moisture, and oxygen content lead to unfavourable effects during application including poor stability and immiscibility with hydrocarbons. This inhibits the direct use of crude bio-oil and its assimilation into existing fuel infrastructures. Thus, upgrading the crude bio-oil is necessary. This involves reducing or eliminating one or more of its undesirable properties, ultimately improving its quality before practical application. Among the various upgrading technologies, the use of supercritical fluids (SCFs) has proved promising for bio-oil upgrading.

In the past decade, extensive research has been conducted on bio-oil upgrading in SCFs. However, although several reviews have been done on the topic of bio-oil upgrading; there are no reviews to date,

Table 1 Comparison of wood-derived crude bio-oil and heavy petroleum fuel oil [1,5,6]

Items	Wood-derived crude bio-oil	Heavy petroleum fuel oil
Moisture content /wt-%	0.1	25
pH	–	2.5
Specific gravity	0.94	1.2
C/wt-%	85	56
H/wt-%	11	6
O/wt-%	1	38
N/wt-%	0.3	0–0.1
Higher heating value/(MJ·kg^{-1})	40	17
Viscosity/(mPa·s)	40–100	180
Solids/wt-%	1	0.1

summarizing the research on supercritical fluid (SCF) upgrading of bio-oil. The key words; bio-oil, upgrading, review, were used to identify a total of 19 research papers. When the search terms bio-oil, upgrading, SCFs, review, were used no records were identified. This work aims to review the conducted research and current progress on catalytic and non-catalytic bio-oil upgrading in SCFs.

2 Supercritical fluids

A SCF is defined as the state of a compound, mixture, or element above its critical temperature (T_c) and critical pressure (P_c) but lower than the pressure necessary to condense it into a solid [7]. The critical point marks the end of the liquid-vapour coexistence and only a single homogenous fluid phase can exist in the supercritical region [7]. Thus, the properties of SCFs are frequently described as an intermediate between those of a liquid and a gas, as shown in Table 2 [7,8].

Table 2 compares the selected physical properties of a liquid, gas, and SCF [8]. The density of a SCF approximates to that of a liquid while the viscosity and diffusivity are close to that of a gas. The liquid-like density of SCFs allows many materials to be solubilized to a level significantly greater than that predicted by ideal gas considerations [7]. Due to the high compressibility of fluids near the critical point, their density is highly sensitive to small changes in pressure and temperature

[7,8]. Many solvent properties such as dissolving power and dielectric constant are directly related to bulk density, and therefore exhibit a similar pressure dependence [7]. These characteristics are unique to SCFs and enable the opportunity to tune the reaction environment to optimize the reaction rate and selectivity [7]. The tunable solvent properties are one of the many interesting features associated with SCFs and forms the basis for its application in modern chemical synthesis.

The advantages of using SCFs as reaction media for chemical synthesis rather than liquids have been broadly organised into four categories by Jessop and Leitner and summarised in Table 3.

3 Catalytic bio-oil upgrading in SCFs

The application of catalysts during bio-oil treatment processes improves the reaction rates and bio-oil yield. However, homogenous catalytic reactions lead to expensive and energy-intensive separation processes [9]. Likewise, concerns for heterogeneous catalytic reactions include long reaction times and expensive catalyst [9]. Thus, researchers have developed alternative methods such as the addition of SCFs to overcome the limitations of catalytic bio-oil upgrading processes. Figure 1 illustrates the working principles of the bio-oil upgrading in SCF process.

The ideal catalyst for bio-oil upgrading is highly active, eliminates the oxygen in the bio-oil, promotes high yield, and forms no coke deposits [10]. Studies of bio-oil upgrading by hydrodeoxygenation (HDO) have used sulfided NiMo and CoMo catalysts [10]. However, these catalysts lead to sulfur contamination in the bio-oil and rapid catalyst deactivation [11]. Thus, precious metal catalysts such as supported Pd, Pt, and Ru have been utilised for catalytic upgrading experiments [10,11]. These catalysts promote increased HDO and higher yields compared to traditional hydrotreatment catalysts [10].

3.1 Precious metals catalysts — palladium

Palladium is one of the most frequently used active metal catalysts for bio-oil upgrading due to its high hydrotreating capability [12]. Among the catalysts used for bio-oil upgrading, Pd is highly active during the deoxygenation and hydrogenation of unsaturated carbon-carbon bonds

Table 2 Comparing the properties of liquid, gas, and SCFs [a]

Physical Property	Liquid [b]	SCF	Gas [b]
Density/(kg·m^{-3})	600–1600	200–500	0.6–2
Dynamic viscosity/(mPa·s)	0.2–3	0.01–0.03	0.01–0.3
Diffusion coefficient/($\times 10^6$ m^2·s^{-1})	0.0002–0.002	0.07	10–40

a) Data from [8]; b) ambient conditions.

Table 3 Advantages of using SCFs as reaction media for chemical synthesis [7]

Category	Advantage	SCF type
Environment	Do not contribute to smog	Most
	Do not damage ozone layer	Most
	No acute ecotoxicity	CO_2, H_2O
	No liquid wastes	CO_2 and other volatile SCFs
Health and safety	Noncarcinogenic	Most (but not C_6H_6)
	Nontoxic	Most (but not HCl, HBr, HI, NH_3)
	Non-flammable	CO_2, N_2O, H_2O, Xe, Kr, CHF_3
Process	No solvent residues	CO_2 and other volatile SCFs
	Facile separation of products	CO_2 and other volatile SCFs
	High diffusion rates	All
	Low viscosity	All
	Adjustable solvent power	All
	Adjustable density	All
	Inexpensive	CO_2, H_2O, NH_3, Ar, hydrocarbons
Chemical	High miscibility with gases	All
	Variable dielectric constant	The polar SCFs
	High compressibility	All
	High diffusion rates	All
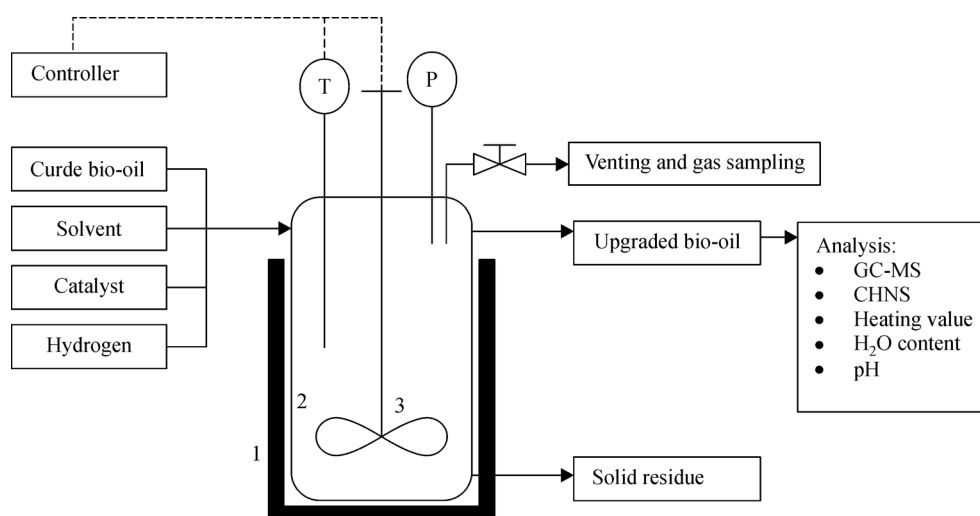
Fig. 1 Schematic diagram of bio-oil upgrading in SCF experiments. (1) heater, (2) autoclave, (3) stirrer, T: temperature detector, P: pressure gauge.

[11]. Pd is also recognised for its effectiveness in converting fatty acids to alkanes, this improves the storage stability of the bio-oil and enhances its energy density [13].

Chen et al. compared and studied the stability of various catalysts (Ru/C, Pd/C, Pt/C, Ru/HZSM-5) in bio-oil upgrading with supercritical ethanol [14]. The results showed the highest heating value, pH value and lowest water content of upgraded bio-oil in supercritical ethanol was achieved over Pd/C. The improvement of these properties in the bio-oil increases its potential for application as an alternative fuel. Similarly, Tang et al. used Pd based catalysts for bio-oil upgrading in supercritical ethanol. In this study, upgrading crude bio-oil in supercritical ethanol using $Pd/SO_4^{2-}/ZrO_2/SBA-15$ (PdSZr) generated a trace amount of tar or coke while with

$SO_4^{2-}/ZrO_2/SBA-15$ (SZr) catalyst, or upgrading without any catalyst, a significant amount of tar and coke was formed [12]. Hence, PdSZr effectively performed as a hydrotreating catalyst and inhibited polymerisation and condensation reactions. Also, the highest heating value, oil yield, and the lowest water content was obtained with the PdSZr catalyst [12].

Zhang et al. investigated bio-oil upgrading over supported Pt and Pd catalysts in supercritical methanol/ ethanol [15]. Like Tang et al., the findings showed Pd, with more dissolved active hydrogen, had a higher hydrogenation activity for large molecular-weight compounds, thus inhibited unstable polymers to form solid products. Moreover, although both Pt and Pd upgraded bio-oils exhibited complete absence of acids, the Pd/HZSM-5

treated oil contained higher esters compared to the Pt/HZSM-5 oil, which may indicate higher esterification was achieved with the former catalyst.

Bai et al. examined the activity of various catalysts on the processing of pre-treated algal oil in supercritical water (SCW) [16]. In this study, Pd/C generated higher oil yield and lower coke yield than Pt/C. Similarly, Zhang et al. examined the effects of several different commercially available catalysts on biocrude in subcritical water [17]. The results showed Pd/C produced bio-oil had a higher H/C content, lower sulfur, and water content than Pt/C as well as lower ash content than both Ru/C and Pt/C. Reduced sulfur, water, and ash content in bio-oil are desirable as these components can lead to catalyst poisoning, reduced heating value, and a phase-separated oil, respectively. However, Duan and Savage suggested Pd/C (5%) and Pt/C (5%) have similar catalytic activity towards upgrading of algal bio-oil in SCW despite their different metal dispersion, specific surface area and micropore volume [13].

3.2 Precious metals catalysts — ruthenium

Ruthenium is a commonly used active metal catalyst for bio-oil upgrading due to its high hydrocracking capabilities [18]. This has several advantages including increasing the oil yield, and heating value whilst limiting solid production. Tang et al. found bio-oil upgraded in supercritical ethanol and Ru catalyst obtained significantly lower solid residue, and higher oil yield and heating value than with ZrO_2/SBA-15, SO_4^{2-}/ZrO_2/SBA-15, or supercritical ethanol alone (i.e., catalyst-free conditions) [18]. Ru based catalysts also provide higher hydrocracking than other commonly used precious metal catalysts. Chen et al. found Ru/C and Ru/HZSM-5 generated an upgraded bio-oil with higher oil content than Pd/C and Pt/C treated oils [14]. Likewise, Bai et al. found among all the single components and precious metal catalysts, Ru/C upgraded oil exhibited the highest oil yield and the highest heating value (45.1 MJ·kg^{-1}); slightly higher than that of petroleum diesel (44.8 MJ·kg^{-1}) [16]. Yao et al. found introducing Ru into acidic catalysts promoted pyrolytic lignin hydrocracking and inhibited polymerization and condensation, this caused the oil yield to increase significantly [19]. Similarly, Duan et al. reported the presence of Ru/C during bio-oil upgrading in SCW led to reduced coke formation due to the catalyst promoting hydrogenation of the coke precursor, and inhibiting polymerisation and condensation reactions [20]. Finally, Ahmadi et al. compared the effects of CoMo and Ru/C catalyst and reported the latter produced the highest oil yield and negligible coke formation (< 1 wt-%) [21].

Ru based catalysts are also recognised for improving the elemental properties of bio-oil through hydrogenation, deoxygenation and denitrogenation reactions. Zhang et al. found Ru/C was the most active catalyst for the upgrading of biocrude compared to 11 different catalysts including Pt/C and Pd/C [17]. Moreover, contrary to findings from Bai et al., Zhang et al. reported Ru/C was the only catalyst capable of promoting denitrogenation [16,17]. Additionally, the oil produced with this catalyst exhibited the lowest sulfur content, highest hydrocarbon content, and the highest heating value. The catalyst screening study by Bai et al. also found Ru/C showed the best performance for deoxygenation by generating an upgraded oil with the lowest O/C molar ratio compared to 15 different catalysts including Pd and Pt [16]. Additionally, the Ru/C produced upgraded oil contained the highest carbon content.

Duan et al. reported on the high performance of Ru/C in hydrogenation reactions, as a result, Ru/C upgraded bio-oil had the lowest unsaturated hydrocarbon content and highest aromatic content [20]. Similarly, Chen et al. found the highest relative content of desired products was achieved over Ru/C and Ru exhibited higher hydrogenation ability than Pd and Pt which might be the reason for the better upgrading performance of Ru/C [14].

Oh et al. investigated the effects of Ru/C and Pt/C catalysts on the HDO of bio-oil [22]. Although both Ru/C and Pt/C treated oils obtained complete removal of acid content, the Total Acid Number (TAN) of the Ru/C upgraded oil decreased by 59% of the original bio-oil whilst Pt/C decreased the TAN by 54%. Similarly, Bai et al. found Ru/C upgraded oil had the lowest TAN compared to several catalysts including Pt/C and Pd/C [16]. Bio-oil with TAN above the American Society of Testing Materials (ASTM) specification (0.50 mg KOH·g^{-1} according to the ASTM D 6751-07a) may lead to operational problems and cause corrosion during storage [23]. Thus, reducing the acidity of bio-oil is essential to enable the storage and transportation of bio-oil.

Interestingly, Bai et al. found a combination of Ru/C and Raney Ni performed better during bio-oil upgrading than either catalyst alone [16]. Likewise, Xu et al. examined the effect of two-component catalyst mixtures, with Ru/C as the baseline catalysts, on the upgrading of pre-treated algal oil in SCW [24]. The authors reported the catalyst mixture provided favourable advantages to bio-oil upgrading such as higher hydrogenation. However, the catalyst mixtures were less effective for deoxygenation compared to Ru/C alone. In addition, ruthenium is very expensive and difficult for regeneration, thus not a viable catalyst for bio-oil upgrading on a large scale.

3.3 Precious metals catalysts — platinum

Among the noble metal catalysts commonly used in bio-oil upgrading, Pt is one of the most active catalysts [25]. Pt is a frequently selected catalyst due to its hydrotreating capability, effectiveness for decarboxylation of fatty acids, enhancing the oil stability, and its high durability

and thermal resistance [22,23]. Bio-oils upgraded in Pt based catalysts have been shown to exhibit a high abundance of hydrocarbons, and lead to a free flowing liquid product oil [23,25].

As previously mentioned, Zhang et al. conducted bio-oil upgrading studies using Pt and Pd catalysts and found Pd/HZSM-5 treated oil contained higher esters compared to the Pt/HZSM-5 oil under supercritical methanol [15]. However, bio-oil upgraded in Pt/SZr and supercritical methanol/ethanol and bio-oil upgraded in Pt/HZSM-5 and supercritical ethanol all exhibited higher ester content than with Pd based catalyst. Similarly, the catalyst screening study by Chen et al. showed bio-oil upgraded over Pt/C exhibited the highest relative content of esters compared to various catalysts including Pd/C and Ru/C [14]. The high presence of esters in upgraded bio-oil is favourable as it corresponds to the reduction in acids due to esterification reactions which leads to less corrosive and more stable bio-oil.

Moreover, the changes in the TAN and pH of the bio-oil can be used to examine the catalysts ability to promote acid decreasing reactions such as esterification during upgrading processes. Bai et al. showed Pt/C upgraded oil had a lower TAN than Pd/C upgraded oil. Hence, the former catalysts proved more effective for reducing the acidity of biocrude oil [16]. However, Chen et al. showed Pd/C upgraded oil exhibited a higher pH than Pt/C treated oil due to the higher relative content of acids in the latter [14]. Nevertheless, Pt based catalysts have been shown to increase the pH of crude bio-oil in many studies. For example, Dang et al. demonstrated Pt/SZr catalyst can increase the pH of crude pyrolysis oil by up to 83% under supercritical ethanol [26]. Likewise, Li et al. demonstrated bio-oil upgraded over PtNi/MgO in supercritical methanol increased in pH value from 2.9 to 6.7 [27]. Overall, these findings may be an indication of Pt based catalyst's ability to catalyse esterification reactions, hence decrease the acidity of crude bio-oil during supercritical upgrading processes.

Several studies have shown Pt catalysts effectiveness for increasing the oil yield. The bio-oil HDO study by Oh et al. found the highest oil yield can be obtained with Pt based catalyst compared to the Ru based catalyst [22]. Similarly, Chen et al. showed Pt/C upgraded oil had a higher oil content than Pd/C upgraded oil [14]. Moreover, both Bai et al. and Zhang et al. showed sulfided Pt/C upgraded oil in supercritical and subcritical water respectively generated higher oil yield than with Pd/C [16,17]. Whereas non-sulfided Pt/C treated oil obtained comparatively lower oil yield. These findings indicated the sulfide form of this catalyst is favourable for realising higher upgraded oil yields [16,17,24]. However, the results from both Bai et al. and Zhang et al. showed the carbon and hydrogen content, and higher heating value (HHV) of the sulfided Pt/C upgraded oil was lower than that of the Pt/C upgraded oil

[16,17]. Hence, the authors concluded pre-sulfiding the Pt/C does not cause any significant variations in the characteristics of the upgraded oil [16,17,28].

Zhang et al. also reported that Pt/C showed the best performance for HDO and biocrude treated with this catalyst exhibited higher heating value, carbon content, and lower nitrogen content than with Pd/C catalyst [17]. Similarly, Bai et al. found Pt/C upgraded oil had lower O/C ratio, nitrogen content, higher H/C ratio, and heating value than several catalysts including Pd/C [16]. Interestingly, Oh et al. found the Pt active sites might accelerate hydrogenation, deoxygenation as well as further decomposition, while hydrogenation and deoxygenation were separated active sites on the Ru catalyst [22]. Moreover, Oh et al. carried out HDO reaction runs with various reaction temperatures and time [22]. The findings showed compared to the Ru/C upgraded oils, the Pt/C upgraded oils exhibited the lowest water, nitrogen, sulfur, and oxygen content, as well as the lowest viscosity, and the highest heating value. However, the studies by Chen et al., Bai et al. and Zhang et al., showed Ru/C upgraded oil exhibited more improvement in properties compared to Pt/C treated oil (e.g., higher heating value) [14,16,17]. Ultimately, the findings from Oh et al. indicate under certain reaction conditions Pt/C can perform better than Ru/C during bio-oil upgrading in supercritical ethanol.

3.4   Non-precious metal catalysts

Although precious metal catalysts have been predominantly used for bio-oil upgrading in SCFs, non-precious metal catalysts have also been tested and proven effective for improving the quality of crude bio-oil. In two different studies, Peng et al. showed aluminium silicate and the HZSM-5 catalyst played an essential role in upgrading crude bio-oil in supercritical ethanol [29,30]. The acidic aluminium silicate facilitated esterification and cracking reactions and the produced bio-oil exhibited higher pH, heating value, and lower viscosity compared to the crude bio-oil, and the catalyst free upgraded bio-oil. In the second study, Peng et al. showed acidic HZSM-5 also promoted esterification reactions, and stronger acidic HZSM-5 effectively facilitated cracking of heavy components of crude bio-oil. Zhang et al. similarly reported the complete transformation of acetic acid in the supercritical ethanol and HZSM-5 system [31]. Likewise, in the catalytic bio-oil upgrading investigation by Zhang et al., the results showed complete removal of acids in the crude bio-oil after treatment with HZSM-5 supported Ni and supercritical ethanol [32]. However, Chen et al. found at low ethanol to bio-oil ratio less acid was esterified over HZSM-5 supported Ru compared to Ru/C [14]. The authors concluded for non-acidic catalyst should be used at a lower mass ratio of ethanol to bio-oil for higher acid conversion.

Bio-oil treatment with zeolites has been shown to lead to high coke yield and low upgraded oil yield. Both catalyst screening studies by Bai et al. and Zhang et al. reported that HZSM-5 and zeolite treatments led to the highest coke production lowest upgraded oil yield [16,17]. Barreiro et al. also reported a significant increase in the production of solid residue and decrease in upgraded oil yield with HZSM-5 catalyst compared to Pt/Al$_2$O$_3$ [28]. Duan et al. carried out a series of catalytic hydrothermal upgrading experiments of pre-treated algal bio-oil over nine different zeolites [33]. All the zeolite catalysts reduced the production of upgraded bio-oil and most promoted more coke formation relative to the noncatalytic treatment. The results from Cheng et al.'s bio-oil upgrading study in supercritical methanol also demonstrated bio-oil upgrading with HZSM-5 led to the lowest biofuel yield and highest coke yield out of the six varied catalytic conditions [34]. Zhang et al. compared catalytic bio-oil upgrading in supercritical ethanol over various Ni supported catalysts and found the highest coke yield was obtained with Ni/HZSM-5 [32]. Duan et al. suggested the ease of coking and cracking of the zeolites are possible reasons for the reduced production of upgraded bio-oil [33]. In addition, despite the low oil yield, Cheng et al. reported that the content of desirable hydrocarbons in biofuel produced by HZSM-5 based catalysts increased compared to the raw bio-oil [34].

Zhang et al. found processing over HZSM-5-supported catalysts results in less high-molecular-weight components with aromatic groups [15]. Cheng et al. found similar results as HZSM-5 and supercritical methanol upgraded oil exhibited reduced content of phenols compared to raw bio-oil [34]. Similarly, Duan et al. found the presence of HZSM-5 effectively promotes the cracking of macromolecules in the bio-oil and conversion to materials with low-boiling-point fractions [33].

In some cases, zeolite catalysts can provide similar or higher improvement in the elemental composition of bio-oil relative to precious metal catalysts. For example, Zhang et al. showed zeolite upgraded oil had lower nitrogen content than Pt/C and Pd/C upgraded oils [17]. Likewise, Bai et al. found HZSM-5 upgraded oil had lower nitrogen content than all the precious metal catalyst treated oils [16]. Duan et al. also reported HZSM-5 with a low Si/Al molar ratio provided good performance for denitrogenation [33]. Moreover, Barreiro et al. reported HZSM-5 and SCW upgraded biocrude from scenedesmus almeriensis algae obtained the lowest O/C ratios compared to Pt/Al$_2$O$_3$ [28].

The studies by Bai et al. and Zhang et al. found using activated carbon for upgrading biocrude in subcritical and SCW, respectively, produced an upgraded bio-oil with lower nitrogen and oxygen content than the uncatalyzed upgraded oil [16,17]. The authors suggested the carbon might be responsible for denitrogenation (by adsorption rather than catalytic reaction) and deoxygenation. Additionally, both studies showed activated carbon generated

an upgraded oil yield comparable to that of Pt/C upgraded oil. Likewise, the results from Xu et al. showed similar upgraded oil yields were achieved with bio-oil upgraded in Ru mixed with Pt/C and Ru mixed with activated carbon [24]. Zhang et al. also found the activated carbon led to lower coke yield relative to the coke yield with precious metal catalyst treatments [17]. Duan et al. compared the performance of several activated carbons and Ru/C during catalytic bio-oil upgrading in SCW [20]. All the activated carbons exhibited higher desulfurization capability compared to Ru/C, which was confirmed by the lower sulfur content in all the activated carbon upgraded bio-oils relative to the Ru/C upgraded oil. Additionally, four out of the six activated carbons facilitated greater nitrogen removal than Ru/C. Interestingly, the bio-oil upgraded with bamboo stem derived activated carbon obtained a higher heating value and hydrogen content and lower nitrogen and sulfur content than the Ru/C upgraded oil. This demonstrates that activated carbons can be used as an inexpensive alternative to Ru/C to generate a liquid fuel that has similar properties to those of hydrocarbon fuels derived from fossil fuel resources.

Nickel based catalysts are one of the most commonly used non-precious metal catalysts in the bio-oil upgrading studies reviewed in this report. Shi et al. investigated bio-oil upgrading over Ni/ZrO$_2$ in supercritical cyclohexane and reported its stability and effectiveness in catalysing several reactions including hydrogenation, and decarbonylation [35]. Similarly, Zhang et al. utilised Ni/SiO$_2$-ZrO$_2$ catalyst and supercritical ethanol to upgrade bio-oil and reported the catalysts ability to facilitate complete removal of acids and aldehydes and increase the esters, higher heating value, and pH value [32]. In another study by Zhang et al., Ni based catalyst demonstrated excellent resistance to coking and the Ni/MgO catalyst generated an upgraded oil yield over 80% [36]. The author also found the complete removal of organic acids over the 20Ni/MgO catalyst. The results from Bai et al. also showed Ni/SiO$_2$-Al$_2$O$_3$ generated the second-largest upgraded oil yield and the lowest coke yield out of the fifteen catalytic conditions examined [16].

Many studies have incorporated cobalt into catalytic bio-oil upgrading in SCFs [16,17,21,24,37,38]. Cheng et al. used non-sulfided Fe-Co/SiO$_2$ and supercritical methanol to upgrade raw bio-oil and reported that the bimetallic Fe-Co/SiO$_2$ catalysts resulted in better HDO performance than monometallic Fe/SiO$_2$ or Co/SiO$_2$ catalysts due to the synergistic effect of Fe and Co on the SiO$_2$ support [37]. In another study, Cheng et al. used bifunctional Co-Zn/HZSM-5 to upgrade bio-oil and found the bimetallic catalyst increased biofuel yields and hydrocarbons contents in biofuels compared to monometallic Co/HZSM-5 and Zn/HZSM-5 catalysts [38]. Xu et al. reported the Ru/C + Co-Mo/Al$_2$O$_3$ catalyst produced the lowest coke yield compared to eleven other catalytic conditions [24]. Moreover, the combination of Ru/C with

the Co-Mo based catalyst produced higher yields of upgraded oil compared to that obtained with Ru/C alone. Likewise, Zhang et al. found of all the catalysts examined in the catalyst screening study, the Co-Mo/γ-Al$_2$O$_3$ catalyst generated the highest upgraded oil yield, and lower coke yield than C based Ru, Pd and Pt [17]. Similarly, Bai et al. showed the upgraded oil yield with CoMo/γ-Al$_2$O$_3$ exceeded that with Pt/C and Pd/C catalysts and the second-lowest coke yield was observed with this catalyst [16]. Ahmadi et al. investigated the effects of CoMo catalysts on HDO of bio-oil in supercritical ethanol [21]. The results showed CoMo/MCM-41 catalyst produced a high oil fraction which was comparable to Ru/C treatment. Additionally, the composition of the light oil produced from the CoMo catalysts where reportedly comparable to that of the light oil obtained with the Ru/C catalyst.

The catalyst screening studies by Zhang et al. and Bai et al. effectively demonstrate the comparable results of bio-oil upgrading with precious metals and less commonly used ordinary catalysts in sub- and SCW, respectively [16,17]. Zhang et al. showed Mo$_2$C upgraded oils exhibited higher oil yields than all the precious metal catalysts, and MoS$_2$ upgraded bio-oil oil had higher oil yield than Pt/C and Pd/C [17]. In addition, both catalysts generated lower coke yields than C supported Ru, Pd, and Pt. Likewise, Bai et al. demonstrated Mo$_2$C upgraded oils obtained higher oil yield than Pt/C and Pd/C treated oils and lower coke yield than all the precious metal catalysts [16]. Xu et al. showed mixing Ru/C with Mo$_2$C led to the highest oil yield compared to mixing with any other catalyst including various precious metal catalysts [24].

Another less frequently utilised catalyst for bio-oil upgrading in SCFs is alumina. As an active metal catalyst, alumina has repeatedly shown good deoxygenation activity. Bai et al. found alumina upgraded oil exhibited lower oxygen content than Pd/C and Pt/C upgraded oils [16]. Similarly, Xu et al. showed mixing Ru/C with alumina led to deoxygenation and denitrogenation activities equivalent to Ru/C mixed with carbon-supported noble metal catalysts [24]. The authors in this study suggested that carbon or alumina is primarily responsible for the denitrogenation and deoxygenation, whereas noble metals play a smaller role, possibly by adsorption rather than catalytic reaction.

Overall, non-precious metal catalysts have shown activities comparable to that of the precious metal catalysts and they are promising inexpensive catalytic materials for upgrading bio-oils. However, these ordinary catalysts provide limited improvement in the quality of the bio-oil when compared to precious metal catalysts. For example, Tang et al. examined the upgrading of bio-oil and pyrolytic lignin through cracking and hydrotreatment in supercritical ethanol using various catalytic conditions [12,18]. The findings highlighted that although ordinary catalysts such as ZrO$_2$/SBA-15 (Zr) and SO$_4^{2-}$/ZrO$_2$/SBA-15 (SZr)

exhibit high cracking capabilities, these catalysts are prone to promote polymerisation reactions, while the Ru catalysts could promote hydrocracking and inhibit polymerisation [18]. Thus, as stated by Bridgwater, when approaching bio-oil upgrading, it is important to identify which characteristic or characteristics require modification [1]. Consequently, the relevant catalyst can be appropriately selected to meet the product bio-oil specification.

4 Non-catalytic bio-oil upgrading in SCF

Non-catalytic bio-oil upgrading using SCFs has been extensively researched and proved to be a promising alternative to catalytic bio-oil upgrading processes. The challenges associated with catalytic bio-oil upgrading processes (i.e., expensive precious metal catalyst and external H$_2$ addition, the possibility of catalyst deactivation due to contaminants in crude bio-oil and coking on active sites) are not encountered with SCF upgrading [9,21,39]. Thus, SCFs can be effectively used to upgrade crude bio-oil without a catalyst.

4.1 Non-catalytic bio-oil upgrading in supercritical ethanol

Prajitno et al. carried out non-catalytic, non-external H$_2$ bio-oil upgrading in supercritical ethanol [39]. The unique reactivity associated with supercritical ethanol such as hydrogen donation, esterification, alcoholysis, cracking and alkylation, effectively decreased the TAN, water, oxygen contents and increased the bio-oil yield, carbon, hydrogen contents, and HHV. The authors concluded, the bio-oil upgraded at 400°C demonstrated comparable performance to heavy fuel oil in terms of the gas temperature distribution and heat flux produced. Thus, can be considered for utilisation as boiler combustion fuel.

In the bio-oil upgrading study by Dang et al., the distribution of ethers in the product indicated to the participation of supercritical ethanol in aldolization and etherification reactions [26]. Chen et al. also reported that the increase in pH value after upgrading was mainly due to the esterification of acetic acid and ethanol [14]. Similarly, studies by Peng et al. and Kim et al. found supercritical ethanol functioned as both a reaction medium and reactant; as esterification occurred without a catalyst in the supercritical conditions [10,29,30]. Yang et al. also reported on the esterification between acids and ethanol during HDO of bio-oil in supercritical ethanol [40]. Moreover, Peng et al. identified a high relative content of ethanol related compounds in the produced bio-oil, such as 18.53% of 1,1-diethoxy ethane, which suggests ethanol participated in further reactions besides esterification [30]. However, the authors established that although the quality (i.e., higher pH and heating value) of the catalyst-free upgraded bio-oil was higher than that of crude bio-oil, the catalytically upgraded bio-oil generally performed best

[29]. Zhang et al. also showed the role of the supercritical ethanol solvent was extended to reactant [36]. This was confirmed when a part of ethanol was transferred into the upgraded oil via esterification and alkylation. The results also showed that bio-oil esterification with supercritical ethanol is more efficient than with subcritical conditions.

Furthermore, Zhang et al. investigated bio-oil upgrading with supercritical ethanol and found an 11.93% decrease in acid content and a 6.45% increase in ester content after the upgrading process without catalyst addition [32]. These results suggested that organic acids in the bio-oil can be converted into esters via esterification without any catalyst in supercritical ethanol. It should be noted that with the addition of catalysts the esterification reaction was further enhanced and with 20Ni/HZSM-5 catalyst, the acids were completely removed. Moreover, the authors compared upgrading bio-oil without ethanol and found the yield of solid residues and the acid content significantly decreased with the addition of supercritical ethanol. Zhang et al. explained that the coke formation was suppressed due to the excellent dissolubility of supercritical ethanol [32]. Zhang et al. also reported that ethanol has a long alkyl chain which can dissolve higher molecular-weight products, this led to less solid products after bio-oil upgrading [15]. Moreover, ethanol acts as a capping agent which can prevent the re-polymerisation which led to the reduced coke yield [32]. Furthermore, the esterification of bio-oil under supercritical conditions proved more efficient than with liquid or subcritical ethanol. Like Zhang X. et al., Zhang Q. et al. showed carboxylic acids in crude bio-oil can be esterified with supercritical ethanol and 100% conversion of acetic acid was found after 30 min [31,32].

Tang et al. reported bio-oil upgraded with supercritical ethanol alone exhibited the highest pH value [12]. However, it also possessed higher water content, lower oil yield, and heating value compared to PdSZr and SZr upgraded oil in supercritical ethanol [12]. A further study by Tang et al. achieved similar findings [18]. The supercritical ethanol upgraded oil exhibited improved qualities, e.g., higher oil yield, heating value and lower solid yield than Zr and SZr catalyst treated bio-oils, as well as, lower water content than RuSZr and SZr catalyst treated bio-oils [18]. However, the Ru based catalysts effectively converted the pyrolytic lignin to stable monomers such as esters relative to non-catalytic, Zr or SZr catalytic conditions. In another bio-oil upgrading study, the authors showed similar results, where uncatalyzed upgraded oil exhibited higher oil yield, and lower solid and water yield than SZr upgraded oil [19]. These results indicate that although supercritical ethanol can provide elements of upgrading, the combination of supercritical ethanol and catalyst further enhances the upgrading process. Moreover, precious metal catalysts significantly enhance the bio-oil upgrading in supercritical ethanol whereas ordinary catalysts provide a limited advantage compared to supercritical ethanol alone.

4.2   Non-catalytic bio-oil upgrading in supercritical methanol

The research by Omar et al. included a non-catalytic upgrading of fast pyrolysis bio-oil using supercritical methanol, ethanol and isopropanol conditions, respectively [41]. The results showed supercritical methanol treatment of the crude bio-oil resulted in the complete removal of acids and a significant increase in esters. Consequently, the pH of the crude bio-oil increased from 2.39 to 4.04 after the supercritical methanol reaction. The authors concluded that ester formation could be the main deacidification process for reducing the acidity of the bio-oil.

Cheng et al. found supercritical methanol promoted hydrogenation and esterification reactions over Fe-Co/SiO_2 catalyst during the bio-oil HDO process [37]. This improved the contents of desirable hydrocarbons and esters in the product bio-oil. Moreover, supercritical methanol functioned as a hydrogen donor and promoted the HDO of unsaturated compounds during the upgrading process. In another bio-oil upgrading study by Cheng et al., the results showed a significant reduction in acids in the product oil, the authors predicted the acidic compounds were converted to esters through esterification reactions with alcohol in the supercritical methanol [34].

Li et al. upgraded low-boiling fraction (LBF) of bio-oil in supercritical methanol and reported that after 6 h reaction time the acids were converted into esters without catalyst addition [42]. Supercritical methanol functioned as a reaction medium and reactant by providing an acidic environment for the system and facilitating esterification of LBF of bio-oil without catalyst addition. Moreover, the esterification of LBF in supercritical methanol proceeded under the same reaction mechanism as that of catalytic esterification of LBF using liquid methanol. In another study, Li et al. examined the effects of upgrading high boiling fraction (HBF) of bio-oil under different supercritical media [27]. The findings showed as the polarity of the supercritical media increased (tetrahydrofuran < ethanol < methanol), a corresponding increase in the yield and decrease in the coke formation were observed. Li et al. explained that methanol has the strongest polarity of all monohydric alcohols and in the supercritical phase the polarity of C–O and O–H bonds increase, thus the apparent polarity and acidity are enhanced. This enables supercritical methanol to chemically break acid molecules into methyl esters [42]. The alcoholysis ability and esterification activity of supercritical methanol made it a promising medium for breaking chemical bonds of molecules in HBF and promoting the esterification of high boiling carboxylic acids in HBF.

However, catalytic upgrading with supercritical methanol also demonstrated zero acid content and proved more advantageous for reducing aldehyde and phenol content [27,42]. This is ideal as aldehyde and phenol can form carbonaceous deposits [42]. Likewise, Cheng et al.

concluded that the bio-oil quality improvement after upgrading in supercritical methanol and Co-Zn/HZSM-5 catalyst was partly due to the long contact time of methanol solvent and bio-oil [38]. However, the incorporation of the HZSM-5 based catalysts further promoted the improvement of upgraded bio-oil quality.

Jo et al. investigated the effect of supercritical alcohols (methanol, ethanol, and isopropyl alcohol) on non-catalytic bio-oil upgrading [43]. Despite the absence of a catalyst, the yields of upgraded bio-oil were in the range of 77–85 wt-% and the solid residue yield was in the range of 0.3–0.7 wt-%. Acetic acid esters were the dominant chemical species in the upgraded light-fraction bio-oil. These were predicted to be from esterification reactions between the acetic acid in the LBF bio-oil and the corresponding supercritical alcohols. However, the authors recognised that although the supercritical methanol upgrading process at 400°C resulted in a significant increase in the HHV and a decrease in the TAN, there was a high consumption of methanol at this high temperature. Chen et al. carried out solvent recovery and reutilisation as part of the bio-oil upgrading process to reduce the solvent consumption and costs [14]. The relative content of acids remained stable with the re-utilization of ethanol and the relative content of esters increased gradually. The authors concluded that the recovery and reutilisation of ethanol was an effective method for decreasing the ratio of ethanol to bio-oil.

4.3   Non-catalytic bio-oil upgrading in SCW

Duan and Savage found SCW upgraded bio-oil exhibited lower O/C and N/C molar ratio than bio-oil upgraded in SCW over Pt/C catalyst [23]. Moreover, no sulphur content was detected in SCW-only treated upgraded oil [23]. Thus, deoxygenation, denitrogenation, and desulphurization reactions effectively proceeded without catalyst addition. This phenomenon was also observed in the catalyst screening study by Bai et al. [16]. In this study, bio-oil upgraded in SCW alone exhibited improvement in quality in terms of higher H/C ratio than activated carbon, Mo_2C, Ni/SiO_2-Al_2O_3, and alumina catalysts, as well as, lower O/C ratio and higher heating value than activated carbon catalyst [16]. However, the study by Duan et al. showed the TAN of the uncatalyzed upgraded oil was almost double the Pt/C upgraded oil [23]. This is unfavourable as high acid levels lead to corrosion and hinders consideration for practical application of the oil. In a further report, Duan et al. showed that bio-oil upgraded in SCW without a catalyst exhibited higher TAN, nitrogen and sulphur content, and lower carbon, hydrogen, and HHV than bio-oils treated with various activated carbon catalysts and SCW [20]. Moreover, the bio-oil upgraded with bamboo activated carbon exhibited a higher heating value than Ru/C. Hence, bamboo activated carbon may be considered as an inexpensive alternative that overcomes both

challenges of SCF-only upgrading and precious-metal catalyst upgrading.

Isa et al. investigated upgrading bio-oil to bio-fuel using sub- and SCW [44]. The SCW conditions gave the highest bio-oil plus water yield and the lowest char yield. Moreover, the non-catalytic SCW treatment reduced the oxygen contents of the bio-oil.

In another study by Duan et al., the treated oil and coke yields with the non-catalytic upgrading process were comparable to the catalytic upgrading process [25]. SCW demonstrated effective coke control due to its ability to extract and transport potential coke precursors from the catalyst pores [25]. Moreover, minimal differences were noted in the H/C ratio between bio-oil upgraded in SCW over Pt/γ-Al_2O_3 and bio-oil upgraded in SCW alone [25]. Thus, SCW alone was capable of promoting hydrogenation of the crude bio-oil. However, significantly higher levels of deoxygenation, denitrogenation, and heating value were achieved with Pt/γ-Al_2O_3 upgraded oil in SCW [25]. Likewise, in a further study, Duan et al. found SCW suppresses coke formation due to its solvation and dilution characteristics, but further reduced coke formation was observed with Ru/C [20]. Another study by Duan et al. showed uncatalyzed bio-oil in SCW generated the highest bio-oil yield and one of the lowest coke yields relative to several different zeolite catalysts [33]. However, bio-oil treated with zeolite catalysts in SCW provided higher levels of hydrogenation, deoxygenation, denitrogenation, desulphurisation, and ultimately higher heating value than SCW upgraded oil alone. Similarly, Remón et al. found the presence of SCW can partially reduce the solid formation and/or favour its removal [45]. The results showed 0% coke yield and the highest liquid yield was obtained without catalyst addition. Moreover, the carboxylic acids were eliminated without catalyst addition at conditions of 450°C 260 bar. However, the HHV without catalyst addition was lower than with the incorporation of Ni-Co/Al-Mg catalyst.

Zhang et al. reported that non-catalytically treated biocrude in subcritical water showed higher oil yield, carbon content, and lower coke yield and water content compared to treatment with several different catalysts [17]. The subcritical water appeared to incorporate into the products fraction and demonstrated some denitrogenation of the biocrude by dissolving the nitrogen-containing compounds [17]. However, uncatalyzed upgraded oil exhibited the lowest HHV and H/C molar ratio, this is unfavourable for considering the fuel for further applications.

In the algal oil upgrading study by Xu et al., the SCW physically decreased the nitrogen content in the upgraded bio-oil [24]. This was indicated by the large number of nitrogen compounds detected in the water-soluble side product. Moreover, the sulphur content was reported as undetectable using a common elemental analyser but was quantified using a coulometric titration method [24].

However, catalytic bio-oil upgrading in SCW achieved a higher H/C ratio, heating value and significantly lower N/C and O/C ratio compared to uncatalyzed upgraded oil [24]. Likewise, Remon et al. found the level of sulphur in the SCW-only treated liquid was the same as the catalytically treated bio-oil [46]. In addition, SCW-only upgraded oil exhibited higher heating value, H/C ratio and lower O/C ratio than NiCo/CNF$_f$-900 catalysed bio-oil in SCW. However, NiCo/CNF$_f$ and NiCo/CNF$_f$-600 catalysts further enhanced the heating value and hydrocarbon content and reduced the carboxylic acids in the bio-oil.

4.4 Non-catalytic bio-oil upgrading in other SCFs

SCFs are recognised for the unique dissolving power which is highly effective during bio-oil upgrading for increasing yield and improving the characteristics of the bio-oil. Shi et al. investigated upgrading bio-oil using supercritical cyclohexane and noted the excellent solubility of hydrogen in the SCF which led to the improvement in yield and quality of liquid hydrocarbons [35]. This was confirmed by the lower liquid hydrocarbon yield and the content of C_8–C_{22} hydrocarbons with non-supercritical cyclohexane, relative to supercritical cyclohexane.

Xu et al. examined bio-oil upgrading using supercritical 1-butanol over Ru/C [47]. The highest hydrogen and carbon content, HHV, pH and the lowest viscosity, moisture and oxygen content was achieved under these conditions relative to subcritical 1-butanol or without solvent addition. More significantly, the solid product decreased from 2.5% without solvent to 0.2% with supercritical 1-butanol which indicated to reduced coke formation in the presence of the supercritical solvent. The study demonstrated that the use of a supercritical solvent particularly enhances the quality of bio-oil. Moreover, like many studies of bio-oil upgrading in supercritical alcohol, Xu et al. reported the carboxylic acids were converted into their corresponding esters via esterification with 1-butanol.

Likewise, Cui et al. examined the effect of scCO$_2$ on the esterification of acids in bio-oil and found the conversion of the acids was higher under the scCO$_2$ conditions compared to atmospheric which indicated the promoting effect of scCO$_2$ [48]. Moreover, scCO$_2$ was used to upgrade the bio-oil by extraction and the scCO$_2$ extract fraction contained higher amounts of esters and lower amounts of water and acids. Additionally, the volatile compounds were enriched into the extract fraction and this oil exhibited improved pH, heating value and stability, thus demonstrated to be a promising fuel for further application.

5 Conclusions

The pro forma Table 4 shows the precious metal catalysts platinum, palladium and ruthenium are the most commonly used in the papers examined in this literature review. Additionally, methanol, ethanol, and water are frequently used as solvents for the SCF upgrading. Majority of the papers highlight the improvement in the properties and characteristics of the bio-oil after upgrading. Moreover, the supercritical solvents are consistently recognised for their active effects on the upgrading process which is more than what is observed in ordinary liquid solvent conditions. The literature review demonstrates that non-precious metal catalysts are a viable and economical alternative to expensive precious metal catalysts for bio-oil upgrading. Particularly when SCFs are used in conjunction which provide some catalyst-like activities.

Most studies of bio-oil upgrading in SCF utilise batch reactors. For future research, continuous flow reactors can be considered to increase bio-oil production efficiency and suitability for commercialisation processes. However, the high viscosity of crude bio-oil presents a technical challenge when feeding into a continuous reactor. This can be solved with SCF treatment, as the literature studies have shown bio-oil treatment with SCFs produces a bio-oil with lower viscosity, as well as higher yield and fuel quality.

Table 4 Summary of SCF bio-oil upgrading methods reported in the literature

Feed	Solvent	Performance of SCF	Catalyst	T/°C	P/MPa	t/min	Initial H_2/MPa	Ref.
Flash pyrolysis of pulverized corn stalk	CO$_2$	Higher conversions compared to esterification at atmosphere pressure	p-Toluene sulfonic acid	80	28	180	–	[48]
Heavy residues of fast pyrolysis of rice husk (HBF)	Methanol	Promotes alcoholysis	Pt, PtNi, PdNi on Al$_2$(SiO$_3$)$_3$, SiO$_2$, MgO	290	–	300	2	[27]
Light residues of fast pyrolysis of rice husk (LBF)	Methanol	Facilitates esterification	Pt on Al$_2$(SiO$_3$)$_3$, C and MgO	250	8.6–9.6	180–540	1.5	[42]
Bio-oil from pyrolysis of pine sawdust	Methanol	Hydrogenation and esterification reactions	Co; Zn; Co-Zn on HZSM-5	300	–	300	3.4	[38]
Bio-oil from pine sawdust pyrolysis	Methanol	Functioned as hydrogen donor, promoted HDO	Fe-Co/SiO$_2$ or Co/HZSM-5	300	–	300	3.45	[37]
Bio-oil from pine sawdust pyrolysis	Methanol	Mainly hydrogenation and esterification reactions	Fe-Ni/HZSM-5	300	–	300	3.4	[34]

(*Continued*)

Feed	Solvent	Performance of SCF	Catalyst	T/°C	P/MPa	t/min	Initial H_2/MPa	Ref.
Low boiling fraction of bio-oil from fast pyrolysis of empty palm fruit bunch	Methanol	High esterification and alkylation ability	–	400	22.5–46.7	30	1 MPa N_2	[43]
Pyrolysis oil of *Pinussylvestris* L.	Methanol, Ethanol	Increased variety of esters when processing in ethanol	Pd; Pt on HZSM-5; SO_4^{2-}/ZrO_2/SBA-15	260	7.5–11.5	180	2	[15]
Fast pyrolysis oil of rice husk	Ethanol	Decreased phenols and aldehydes during upgrading	Aluminium silicate	260	7.8	180	–	[29]
Fast pyrolysis oil of rice husk	Ethanol	Effectively removes heavy components in bio-oil	HZSM-5 (Si/Al = 22)	100–238	260	180	–	[30]
Flash pyrolysis oil of rice husk	Ethanol	Facilitates hydrotreatment when used with catalyst	Pd/SO_4^{2-}/ZrO_2/SBA-15	280	8.5–10.5	180	0–2	[12]
Pyrolytic lignin from flash pyrolysis of rice husk	Ethanol	Promotes hydrocracking	Ru/SO_4^{2-}/ZrO_2/SBA-15 or Ru/ZrO_2/SBA-15	260	9.5	480	2	[18]
Fast pyrolysis oil of rice husk	Ethanol	Participation of ethanol in aldolization and etherification reactions	Pt/SO_4^{2-}/ZrO_2/SBA-15	260–300	7–11.8	180	0.5, 2	[26]
Bio-oil from fast pyrolysis of rice husk	Ethanol	Improved bio-oil physical properties and composition of organic compounds	Pt/C; Pd/C; Ru/C; Ru/HZSM-5	300	–	300	2	[14]
Bio-oil from fast pyrolysis of *Miscanthus sinensis* biomass	Ethanol	Decreased viscosity of heavy-oil	Pd/C	250–350	–	30–60	3	[11]
Bio-oil from fast pyrolysis of *Miscanthus sinensis*	Ethanol	Converts acid in bio-oil into ester	Pt/C; Ru/C	250–350	–	30–60	3	[22]
Bio-oil from fast pyrolysis of rice husk	Ethanol	Facilitates catalytic upgrading	Ni/SiO_2-ZrO_2	280	–	300	1.5	[32]
Fast pyrolysis oil of sawdust	Ethanol	Crude bio-oil easily esterified with supercritical ethanol	Zeolite	200–250	7	180	–	[31]
Pyrolytic lignin from fast pyrolysis of rice husk	Ethanol	Enables high hydrocracking activity of supported metal	SBA-15; Zr; RuZr; SZr; RuSZr	260	9.5	480	2	[19]
Bio-oil from fast pyrolysis of yellow poplar wood	Ethanol	Deoxygenation and increased light oil yields	Pd/C	250–370	–	40–120	3	[10]
Bio-oil from fast pyrolysis of empty palm fruit bunch	Ethanol	Hydrogen donation ability	–	300–400	16.8–41.3	30–120	1 MPa N_2	[39]
Bio-oil from hydrothermally liquefied dried cornstalk powder	Ethanol	Promotes esterification reactions	Bimetallic ammonium nickel molybdate	280–370	–	60	4	[40]
Fast pyrolysis of rice husk	Ethanol	Enables esterification of bio-oil	Ni/MgO	280	–	300	1.5	[36]
Pyrolysis oil from hardwood sawdust fast pyrolysis	Ethanol	Effective solvent-reduced the molecular weight of bio-oil	Ru/C	300	–	180	10	[49]
Hardwood sawdust fast pyrolysis oil	Ethanol	Increases H/C ratio and reduces O/C ratio in bio-oil	CoMo catalysts supported on various nanostructured materials; Ru/C	350	22.5	180	5	[21]
Fast pyrolysis of pine sawdust	1-Butanol	Decreases oxygen content, increases heating value in upgraded bio-oil	Ru/C	250–300	8.8–11.5	180	2	[47]
Bio-oil from HTL of cornstalks	Cyclohexane	Improved the yield and the quality of liquid hydrocarbons	Ni/ZrO_2	300	–	240	5	[35]
Crude algal bio-oil from liquefaction of microalga paste	Water	Higher heating value and lower acid number than the crude bio-oil	Pt/C	400	–	240	3.4	[23]
Crude algal bio-oil from liquefaction of microalga paste	Water	Cracking of the longer chain alkanes	Pd/C	400	–	60–480	3.4	[13]

(*Continued*)

Feed	Solvent	Performance of SCF	Catalyst	$T/°C$	P/MPa	t/min	Initial H_2/MPa	Ref.
Crude algal oil from liquefaction of *Chlorella pyrenoidosa* (Alga) powder	Water	Complete desulfurization of crude algal oil	Pt/γ-Al$_2$O$_3$	400	–	60	6	[25]
Duckweed biocrude from liquefaction of duckweed powder	Water	High upgraded oil yield	Ru/C; Pt/C; Pd/C	350	18	240	6	[17]
Pre-treated algal biocrude from liquefaction of *Chlorella pyrenoidosa* algae powder	Water	Improved chemical properties	Ru/C; Pt/C; Pd/C	400	–	240	6	[16]
Pre-treated crude bio-oil from liquefaction of *Chlorella pyrenoidosa* microalga	Water	Decreased the N content in the upgraded oil	Two component catalyst mixtures	400	24	240	6	[24]
Pre-treated crude algal oil from liquefaction of *Chlorella pyrenoidosa* (Alga) powder	Water	Facilitates high oil yield	Zeolites including MCM-41 (100%Si)	400	28	240	6	[33]
Bio-oil from pyrolysis of pine sawdust	Water	Improved physicochemical properties of the bio-oil	Ni-Co supported on carbon nanofibers	380	23	–	–	[46]
Bio-oil from pyrolysis of pine sawdust	Water	Facilitated H$_2$ production from bio-oil	Ni-Co/Al-Mg	310–480	20–26	0–60	–	[45]
Pre-treated crude duckweed bio-oil	Water	Increased alkanes & aromatics & decreased O- and N-compounds	Activated carbon	400	–	60	6	[20]
Pyrolysis oil from biomass	Water	Reduced O content of heavy oils	–	410	32	60	0.2 MPa N$_2$	[44]
Biocrude from HTL of microalgae	Water	Enhanced removal of carbon via decarboxylation or steam reforming	Pt/Al$_2$O$_3$; HZSM-5	400	22.5	240	4	[28]

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