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# Catalytic routes for upgrading pyrolysis oil derived from biomass

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The modern energy industry faces the challenge of reducing its carbon footprint, mainly due to fossil fuel use, while satisfying the continuously increasing demand for fuels, electricity, and chemicals. Biomass is one of the six ways to produce renewable energy. It can provide all energy types and become our primary source of chemicals and materials. While energy can also be derived from the other five renewable sources (hydro, solar, wind, ocean, and geothermal), biomass is the only renewable energy source that is further a renewable carbon source. It can potentially complement the production of all C-based raw materials, which are the building blocks of our chemical and biochemical industry. Among the various biomass-conversion technology platforms, 'pyrolysis' is one of the most promising to produce bioenergy and biomaterials, particularly bio-oil. The usefulness of bio-oil in transportation is restricted by its high oxygen concentration. This review summarises the recent progress in catalytically upgrading pyrolysis bio-oils to biofuels and chemicals. The first part of this chapter is on the pyrolysis process itself; it focuses on fast pyrolysis and the resulting bio-oil due to the consensus about this technology's superiority. The second part of this chapter provides an overview of the bio-oil upgrading routes. A comprehensive collection of the results on the type of catalysts used in such processes and their relevant functions are provided. Finally, this chapter closes with a discussion of the challenges and limitations of the bio-oil upgrading processes.

## 1 Introduction

The rapid expansion of energy demands has created an enormous consumption of fossil fuels resulting in the emission of excessive levels of greenhouse gases (GHGs) annually.<sup>1</sup> GHGs generally interfere with natural processes and lead to environmental issues.<sup>2,3</sup> A shift to renewable energy sources is necessary to reduce GHG emissions and reasonably consume fossil fuels. Biomass, a source of organic (biosphere) carbon,<sup>4-6</sup> is the most promising alternative to fossil fuels. It can be processed directly in a combustion furnace to generate heat and electricity and to minimise carbon emissions according to the zero carbon principle.<sup>7-9</sup> Other clean alternatives for biomass utilisation include biofuel production through various biological and thermochemical processes.<sup>10-12</sup> Among the thermochemical processes, pyrolysis is the leading process for converting lignocellulosic feedstocks into added-value products.<sup>13</sup>

Pyrolysis is the thermal decomposition of the biomass macromolecules' polymer chains without oxygen using an external heat source, producing non-condensable gases, liquids (bio-oil), and carbon-rich solids (bio-char). The non-condensable gases are mainly composed of combustible

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hydrocarbons and some inert gas, which can be used to generate heat for endothermic pyrolysis. Biochar is also being studied for various applications, including purifications through adsorption, catalysis, and energy storage.<sup>14–18</sup> This review mainly focuses on bio-oil. In fast pyrolysis, bio-oil represents 70% of the products on average.<sup>19</sup> It is intended for a wide range of applications, including transportation, direct combustion for electricity generation, and as a raw material for biorefineries.<sup>20–24</sup> Bio-oil or crude bio-oil, as a direct pyrolysis product, cannot be directly used as a fuel because of its high oxygen and water content, with the latter rendering it physico-chemically unstable. It is also more viscous and corrosive than the fuel norms permit due to its relatively low pH. It has a lower calorific value than fossil-derived hydrocarbon fuels, averaging  $24 \text{ MJ kg}^{-1}$ , nearly half the average fossil-derived fuel value of  $46 \text{ MJ kg}^{-1}$ . Therefore, bio-oil requires subsequent processing to create a marketable product. Several catalyst-based upgrading processes have been reported to improve the properties of bio-oil as a fuel, such as catalytic cracking,<sup>2</sup> deoxygenation (DO),<sup>25–31</sup> steam reforming,<sup>32–34</sup> electrocatalytic hydrogenation (ECH),<sup>35–38</sup> esterification,<sup>39–43</sup> hydrodeoxygenation (HDO),<sup>2,44</sup> hydrocracking,<sup>45–47</sup> and dry reforming.<sup>48,49</sup>

Steam reforming is a process where bio-oil is upgraded through gasification to generate syngas at 700–1000 °C using a catalyst and upgrading bio-oil by catalytic cracking is typically performed in a fluidized bed or fixed bed reactors with temperatures above 350 °C and at relatively high pressure (up to 14 MPa).<sup>50,51</sup> DO and HDO processes are the most preferred routes to produce upgraded bio-oil with the aid of a catalyst.<sup>2,30,52</sup> HDO of pyrolysis bio-oils tends to be carried out at high hydrogen pressure (up to 300 bar) and moderate temperature,<sup>44</sup> on the other hand, deoxygenation reactions are carried out at high temperature and pressure.<sup>29</sup>

Various catalysts with different precursors, active phases, and support materials have been studied to upgrade bio-oil. Most of these studies used bio-oil surrogate model compounds. This approach is considered necessary because bio-oil is a mixture of hundreds to thousands of compounds, and it is impossible to scientifically study them all simultaneously at a sufficiently deep level. For example, it is impossible to understand the prevailing mechanisms and dependent kinetics of the thermocatalytic processes without focusing on model molecules representing the most important families of the bio-oil content. Nevertheless, studies on real bio-oil are necessary to determine whether the findings apply overall and can be useful in industrial-scale processes. These studies are usually less published and appear as technologies promoted by companies in the marketplace.

Regarding the catalysts used, Wildschut *et al.*<sup>53</sup> tested several heterogeneous noble-metal catalysts, such as Ru/C, Ru/TiO<sub>2</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, Pt/C, and Pd/C, for the hydrotreatment of fast pyrolysis oil. Lin *et al.*<sup>30</sup> studied the direct DO effect of CaO on bio-oil during biomass pyrolysis, proving its significant impact on oxygen content reduction. Kordouli *et al.*<sup>54</sup> investigated phenol hydrodeoxygenation (HDO) using Rh, Ni and Mo–Ni catalysts supported on mesoporous carbon. The catalysts for bio-oil HDO

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must be very selective to produce C–O bond cleavage while maintaining C–C bonds with a minimum of hydrogen consumption for hydrogen formation. Importantly, they must be stable under harsh reaction conditions.<sup>55</sup> Table 1 summarises the different classes of catalysts used in bio-oil upgrading and their advantages and disadvantages.

From the available literature, it can be generally said that transition metal catalysts offer high catalytic activity at a low cost. For example, Carroll *et al.*<sup>37</sup> synthesised Cu/C, Ni/C, and CuNi/C nanoparticles and compared their performance to Pt/C, Ru/C, and PtRu/C for the ECH of hydroxyacetone, a bio-based feedstock surrogate containing carbonyl and hydroxyl functional groups. They found that Ni/C generated propylene glycol with 89% selectivity, while Cu/C catalysed ECH and HDO with 52% and 48% selectivity, respectively. They also confirmed that acid leaching of non-precious metal catalysts did not occur under the reaction conditions, suggesting enhanced stability could be achieved by keeping potentials below the metal's electrodeposition potential.<sup>37</sup> Zhang *et al.*<sup>57</sup> investigated the catalytic performances of transition metal oxides for the catalytic pyrolysis of poplar wood. They found that the metal oxides promoted the formation of alcohols, furan, ketones, acetic acid, and phenolics in bio-oil, except for Fe<sub>2</sub>O<sub>3</sub>.<sup>57</sup> Some active metals such as Ru,<sup>64,65</sup> Pd,<sup>66</sup> Pt,<sup>67</sup> and Ni are effective hydrogenation electrocatalysts, which are used for the cathode compartment.<sup>61</sup> Oxophilic groups, including Fe, W, Re, and Mo, show a stronger affinity for oxygen atoms and are beneficial in the DO pathway.<sup>68</sup> Due to their suitable acidity, zeolite-based catalysts loaded with metals, especially Cu, Ni and Mg, may dramatically enhance the production of hydrocarbon liquids by improving the dehydration/hydrogenation of the intermediate product.<sup>27,69</sup> Metallic species contribute to the decrease in aromatics production, linked to a lower number of Brønsted acid sites.<sup>27</sup> This chapter provides a comprehensive insight into the different catalytic technologies used to upgrade bio-oil to fuel. In addition, it addresses biomass pyrolysis, with a specific emphasis on fast pyrolysis, and subsequent bio-oil properties. Moreover, it discusses some challenges and limitations facing bio-oil upgrading processes.

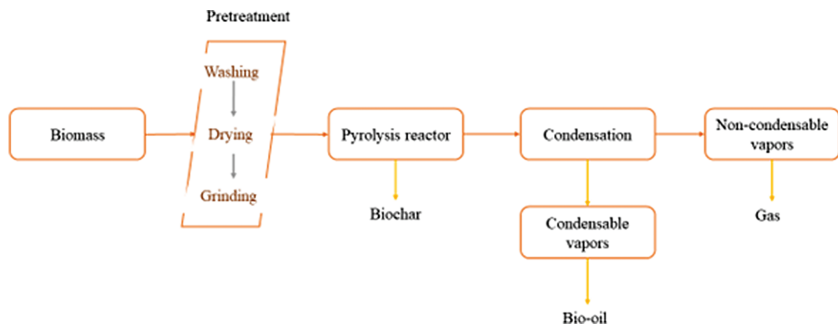
## 2 Pyrolysis of biomass

Raw biomass must typically undergo certain physical, biological, and/or chemical modifications (*e.g.*, size reduction, degradation by microorganisms, or acid and/or alkali treatment) to improve its inherent characteristics before being used in a pyrolysis process.<sup>70,71</sup> Pyrolysis is the thermal degradation of biomass at temperatures of 300–1000 °C without an oxidation medium, while torrefaction is the conversion of biomass to torrefied materials at a mild temperature (200–300 °C).<sup>70,72</sup> A general flow diagram of the pyrolysis process is illustrated in Fig. 1.

The pyrolysis process is classified into three types based on the operating conditions: slow (300–700 °C),<sup>73</sup> fast (600–1000 °C),<sup>74</sup> and flash (800–1000 °C).<sup>75</sup> The first occurs in batches, while the other two are continuous. In addition, the composition and yield of pyrolytic products

**Table 1** Performance of some classes of catalysts used for pyrolysis bio-oil upgrading.

| Performance                          |  | Result  | Advantages  | Disadvantages  | Ref.          |
|--------------------------------------|--|---|---|--|---------------|
| Catalyst                             |  |   |   |  |               |
| Supported transition metal catalysts | TiO <sub>2</sub><br>NiO  | Higher tar yields and lower gas yields                                      | Inexpensive<br>Easily available<br>High catalytic activity                        | Small surface area<br>Easy to sinter and form aggregates                       | 56 and 57     |
| Supported noble metal catalysts      | Ru/C   | Oil efficiency (up to 90% wt) and degree of deoxygenation (up to 90% wt)    | High capacity of hydrogenation<br>Strong catalytic activity and stability         | Expensive and scarce<br>Coke formation<br>Sintering and deactivation           | 53–55 and 58  |
| Metal oxide catalysts                | WO <sub>3</sub> -TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> nanocomposites | Highest ability for deoxygenation during catalytic fast pyrolysis of lignin | Amphoteric properties<br>Easy synthesis   | Low surface area<br>Lack of selectivity  | 29 and 59     |
| Zeolite-based catalysts              | ZnO/HZ 5% wt   | Generate more organic phase and gas with less aqueous phase                 | Large surface area<br>Good thermal stability<br>Bronsted and Lewis active sites   | Coke formation<br>Deactivation by inorganic residues in bio-oil                | 60–62         |
| Zeolite catalysts                    | HZSM-5   | Promote aromatics formation during upgrading processes                      | Strong acidity<br>High specific surface area<br>Adsorption capacity and stability | Low saturated hydrocarbon yield<br>Coke formation<br>Mass transfer limitations | 28, 51 and 63 |



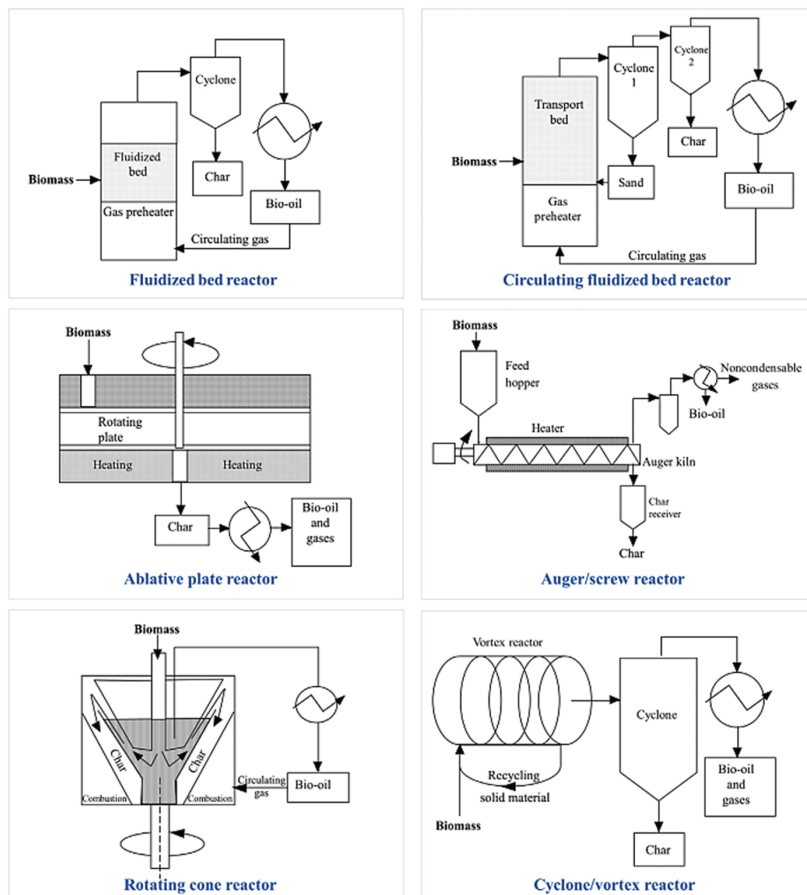
**Fig. 1** General pyrolysis process flow diagram.

depend on the type of the applied process. The pyrolysis process is known to be controlled by parameters such as temperature, heating rate, vapour residence time, particle size, pyrolyser bed height, inert gas flow, pressure, and the presence of a catalyst.<sup>70</sup> Fast pyrolysis is preferred when the target is maximising liquid products.

## 2.1 Fast pyrolysis

Fast biomass pyrolysis is a thermochemical conversion process at moderate temperature (600–1000 °C), where biomass undergoes heating at a rate  $>1000\text{ °C s}^{-1}$  without any oxidising medium.<sup>76,77</sup> The resulting pyrolysis vapour is condensed to produce a brown liquid with a heating value equivalent to approximately 50% of conventional fuel oil.<sup>76–78</sup> When plastics are used instead of biomass, the bio-oil has heating values equivalent to fossil fuels.<sup>79</sup> The key characteristics for obtaining the highest liquid yields from a fast pyrolysis process are as follows: (i) high heating and transfer rates necessitating a feed of finely milled biomass to minimise mass and heat transfer constraints, (ii) a controlled temperature of 500 °C and a vapour phase temperature of 400–500 °C, (iii) a short vapour residence time of typically  $<2$  s, and (iv) quick cooling of pyrolysis vapours to obtain the bio-oil.<sup>80</sup> This process could be implemented through various reactor designs such as fluidised bed, ablative plate, auger/screw, rotating cone, and cyclone/vortex.<sup>78,81</sup> Various pyrolysis reactor settings are illustrated in Fig. 2.<sup>82</sup>

Pyrolysis can be categorized based on the type of reactor, as the reactor design is a critical element in the pyrolysis process.<sup>83</sup> Among the most used reactors, a fluidised bed reactor have been used by Heidari *et al.*<sup>84</sup> to investigate the fast pyrolysis of eucalyptus wood and a maximum of bio-oil yield with the minimum water content have been obtained at 450 °C. Duanguppama *et al.*<sup>19</sup> utilised a circulating fluidised bed to pyrolyse contaminated sawdust and they found that higher temperatures decrease the water content, increasing the bio-oil's stability, viscosity, and heating value. It is important to note that the circulating fluidised bed reactor is scalable, which allows higher operation rates than competing technologies.<sup>85,86</sup> Moreover, Luo *et al.*<sup>87</sup> developed a lab-scale ablative reactor for fast pyrolysis of whole wood chips and wood rods and achieved a crude bio-oil yield of 60 wt%. They reported that wood chips size had no effect on the ablative process.<sup>87</sup>



**Fig. 2** Pyrolysis reactors.<sup>82</sup> Reproduced from ref. 82 with permission from Elsevier, Copyright 2019.

A major advantage of fast pyrolysis is the potential of co-pyrolysis of biomass with waste polymers, which improves the quality of the bio-oil obtained and offers an environmental gain.<sup>88</sup> Mixing biomass and plastics for co-pyrolysis is favourable since (i) the organic matter in biomass can correct the adverse properties of plastic pyrolysis oil (*e.g.* high oxygen content, moisture, and viscosity), (ii) the plastics can boost the biomass in upgrading the yield and quality of bio-oil and gas through a synergistic effect between raw materials, (iii) the hydrogen requirement during bio-oil hydrotreating is minimised, and (iv) the biomass and plastic waste resource cycles are closed with only one process chain to create biofuels.<sup>79,89,90</sup>

## 2.2 Bio-oil properties

Biomass-derived bio-oils, known as crude bio-oil, are challenging to directly use in engines and transportation because of their higher oxygen content than fossil fuels.<sup>91,92</sup> It generally contains diverse low-carbon organic compounds, including aldehydes, ketones, carboxylic acids,

aromatics, and about 20 wt% of water.<sup>36</sup> This high oxygen amount reduces the products' quality, resulting in many technical challenges such as corrosion, low viscosity and volatility, acidity, lubricant thickening, and carbon deposition.<sup>22,23</sup> In addition, the oxygenated constituents could lead to wasteful carbon losses, reducing the oil and energy recovery percentage.<sup>28</sup> Therefore, upgrading crude bio-oil before introducing them into refineries or other possible usages is imperative. Many features of the bio-oil must be considered for any given application. The principal distinctions between bio-oil and heavy fuel oil are listed in Table 2. Therefore, bio-oil low heating value (LHV) tends to be affected by water content,<sup>93</sup> meaning that high water content results in low bio-oil LHV.

Pyrolysis oil yield and composition are related to biomass components and the operating conditions of the process. Many studies indicate that temperatures between 450 °C and 550 °C achieve higher liquid yields, although this will vary depending on the biomass used and other process parameters.<sup>96–98</sup> Lazzari *et al.*<sup>99</sup> varied the pyrolysis temperature of mango seed kernel from 450 °C to 650 °C with a heating rate of 100 °C min<sup>-1</sup>. A maximum bio-oil yield of 38.8% was obtained at the highest temperature of 650 °C. Huang *et al.*<sup>100</sup> found that bio-oil obtained at low temperatures consisted of alkenes, alkanes, long-chain fatty acids and esters, aliphatic nitriles, and amides. A higher pyrolysis temperature promotes the cracking of aliphatic compounds and the formation of aromatics, leading to a bio-oil with a lower H/C ratio and a higher organo-nitrogen compound content.<sup>100</sup> Several studies have reported that increasing the N<sub>2</sub> flow in pyrolysis enhances bio-oil yield. However, at a very high gas flow rate, the liquid yield is lower because of incomplete condensation of the vapours, resulting in higher gas yields from the process. In addition, some of the biomass may be flushed out of the reactor before the end of pyrolysis.<sup>71</sup> Heidari *et al.*<sup>84</sup> studied the effect of nitrogen flow rate on the fast pyrolysis of eucalyptus wood using a fluidised bed reactor, finding that as the flow rate increased, the bio-oil yield initially increased and then decreased. They hypothesised that as the N<sub>2</sub> flow rate increased considerably, the bubbling became more significant, leading to poor solids mixing and heat transfer, decreasing bio-oil yield.<sup>84</sup>

**Table 2** Exemplary properties of bio-oil derived from wood pyrolysis compared to heavy fuel oil.<sup>94,95</sup>

| Property                                      | Bio-oil | Heavy fuel oil |
|---|---------|----------------|
| pH  | 2.5     | —              |
| Density                                       | 1.2     | 0.94           |
| Water content (wt%)                           | 15–30   | 0.1            |
| Carbon (wt%)                                  | 54–58   | 85             |
| Hydrogen (wt%)                                | 5.5–7.0 | 11             |
| Oxygen (wt%)                                  | 35–40   | 1.0            |
| Nitrogen (wt%)                                | 0–0.2   | 0.3            |
| Sulphur (wt%)                                 | 0.05    | 2.5            |
| Inorganics                                    | 0–0.2   | 0.03           |
| High heating value HHV (MJ kg <sup>-1</sup> ) | 16–19   | 40             |
| Distillation residue (wt%)                    | ≤50     | 1              |
| Solid particles (wt%)                         | 0.2–1.0 | 1              |

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### 3 Bio-oil upgrading

The unstable nature of biomass-derived pyrolysis oil remains a significant challenge to its widespread use as a fuel or chemical product. Bio-oil upgrading of a catalytic pathway involves a complex reaction network because of the large number of compounds in the raw bio-oil. It reduces oxygen compounds *via* DO reactions, including dehydration, decarboxylation, and decarbonylation, by adding catalysts<sup>101</sup> and/or a combination of feedstocks.<sup>102</sup> Three aspects of catalytic pyrolysis/upgrading are critical: the type of catalyst, the heating rate, and the catalyst/feed ratio. Adding a catalyst during and/or after pyrolysis can dramatically enhance the bio-oil's composition.<sup>44</sup>

#### 3.1 Catalytic pyrolysis

Catalytic pyrolysis has recently gained considerable attention due to its advantages of operating at atmospheric pressure and not requiring hydrogen, which have been demonstrated by numerous studies.<sup>11,103–105</sup> The catalytic pyrolysis of biomass has mainly been conducted in a fixed bed reactor<sup>106</sup> or fluidised bed reactor under nitrogen flow with some catalysts, including zeolite,<sup>107</sup> Ni/Ca-promoted Fe,<sup>108</sup> Fe–Ca/SiO<sub>2</sub>,<sup>106</sup> char-supported nanoparticle metals,<sup>109</sup> metal oxides,<sup>57</sup> and sodium carbonate.<sup>110</sup> Coke formation makes catalyst regeneration a critical element in reactor design. The conversion of biomass to fuel using fast *in situ* catalytic pyrolysis with zeolite catalysts allows the production of aromatic compounds such as gasoline. The obtained aromatics' performance depends on the zeolite's acidity, textural, and surface properties.<sup>111</sup> Some studies on catalytic pyrolysis of biomass are listed in Table 3.

Xia *et al.*<sup>118</sup> found that adding a Fe-based catalyst to the pyrolysis process of Chinese chestnut shells successfully reduced the content of oxygen-containing chemical compounds in the bio-oil produced between 400 °C and 800 °C. Ly *et al.*<sup>119</sup> also explored the catalytic pyrolysis of tulip trees in a fluidised bed reactor using a dolomite catalyst. They showed that the oxygen content of pyrolysis vapour was generally reduced by dehydration rather than decarboxylation or decarbonylation with dolomite. In addition, the gaseous products that were released together were found to have a high H<sub>2</sub>/CO ratio.

Naturally occurring alkali and alkaline earth metals (EAMs) are found in lignocellulosic biomass and can affect the pyrolysis reaction process.<sup>120,121</sup> For example, Hu *et al.*<sup>122</sup> examined the effects of the inherent alkali and EAMs on biomass pyrolysis. They reported that these metals improved H<sub>2</sub> and CO<sub>2</sub> production by enhancing the major hydrogen-forming reactions, such as the Boudouard and water-to-gas shift reactions, and favoured levoglucosan production.<sup>122</sup> Wang *et al.*<sup>123</sup> investigated the influences of KCl, CaCl<sub>2</sub>, and FeCl<sub>3</sub> on the pyrolysis performance of alkaline lignin. They found that CaCl<sub>2</sub> and FeCl<sub>3</sub> enhanced the phenol content of the bio-oil. However, KCl was found to inhibit bio-oil production while simultaneously promoting biochar production.<sup>123</sup> Similarly, Shimada *et al.*<sup>124</sup> found that EAM chlorides decreased the decomposition temperature of biomass constituents, while



**Table 3** Catalytic biomass pyrolysis using different catalysts.

| Feedstock                  | Catalyst   | Reactor                | T of pyrolysis | Findings   | Ref. |
|----------------------------|--|------------------------|----------------|--|------|
| Bamboo                     | Iron salts   | Fixed bed              | 850 °C         | Production of ketone-rich oil  | 112  |
| Rice straw                 | P-ZSM-5<br>Alkali (0.4 M ZSM-5)<br>Metal (8 wt% Ni-ZSM-5)                    | Py-GC/MS               | 500 °C         | Maximum aromatic selectivity (47%) with 8 wt% Ni-ZSM-5 followed by P-ZSM-5 (44%) and 0.4 M ZSM-5 (42%)   | 113  |
| Neem seeds                 | Ni-Mo/Al <sub>2</sub> O <sub>3</sub><br>Co-Mo/Al <sub>2</sub> O <sub>3</sub> | Semi-batch             | 450 °C         | Ni-Mo/Al <sub>2</sub> O <sub>3</sub> catalyst showed higher selectivity for cyclic compounds than the Co-Mo/Al <sub>2</sub> O <sub>3</sub> catalyst              | 114  |
| <i>Reutealis trisperma</i> | Dolomite   | Semi batch             | 450 °C         | Dolomite increased liquid yield and reduced solid carbon formation   | 115  |
| Maise straw                | ZSM-11<br>ZSM-5  | Fixed bed              | 500 °C         | ZSM-11, with a silicon-to-aluminium ratio of 40 and slight acidity, showed high performance for hydrocarbon production enhancement and coke formation inhibition | 116  |
| Corn stalks                | ZSM-5<br>USY   | Tubular fixed bed      | 500 °C         | Using synthetic zeolites increased gas yields and decreased liquid yields.   | 117  |
| Chinese chestnut shells    | Iron   | Fixed bed              | 400–600 °C     | Ketone and acid formation  | 118  |
| Tulip trees                | Dolomite   | Bubbling Fluidised bed | 400 °C         | Formation of aromatic compounds (C <sub>5</sub> –C <sub>11</sub> )   | 119  |

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alkali metal chlorides did not meaningfully affect the temperature. Nevertheless, some studies have stressed that such inorganic minerals show a nonsignificant catalytic effect on biomass pyrolysis and marginally impact the performance of bio-oil and biochar.<sup>125,126</sup>

### 3.2 Hydrodeoxygenation

While HDO is a flexible pathway to achieve high-quality hydrocarbon fuels from bio-oils, it requires high H<sub>2</sub> consumption and relatively challenging conditions.<sup>127</sup> The oxygen extracted from the bio-oil's organic compounds is mainly in the form of H<sub>2</sub>O, CO<sub>2</sub>, and CO. HDO enhances the bio-oil's potential as a biofuel and is among the best carbon-saving technologies. The process frequently demands a series of reactions, including hydrolysis, dehydration, and hydrogenation steps, and therefore a catalyst with activity in all these steps.<sup>91</sup> To date, several different types of catalysts have been investigated for the HDO of pyrolysis bio-oils, including metals and metal oxides supported on zeolites,<sup>60,69,128</sup> solid acid-supported noble metal,<sup>129</sup>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported metal and metal phosphide<sup>130</sup> and noble metals supported on carbon.<sup>131</sup> Most catalytic HDO studies have been based on the conversion of model compounds selected to show specific functionalities in the bio-oil. Some catalysts used for bio-oil HDO, and their related results are summarized in Table 4.

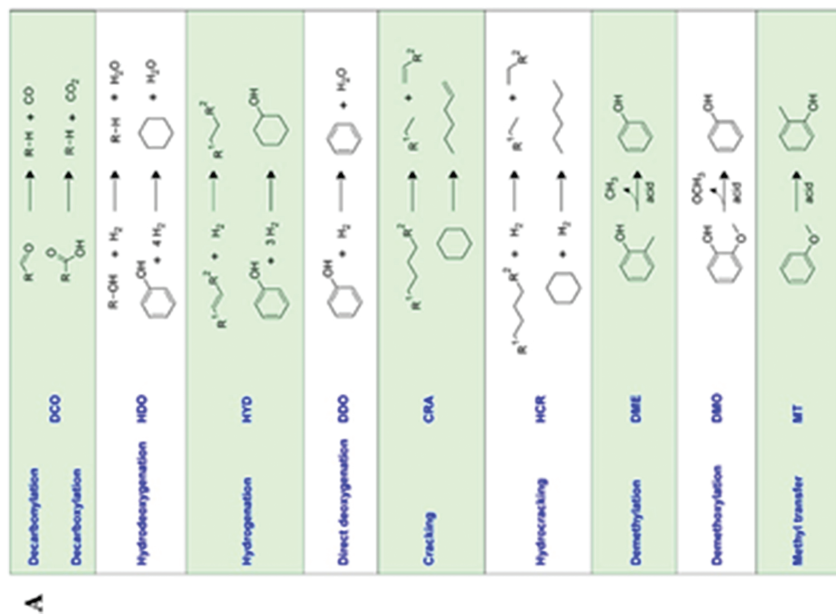
The HDO of phenolic fractions in pyrolysis bio-oil is considered one of the future scenarios for producing sustainable aromatic chemicals. Jiang *et al.*<sup>129</sup> reported the influence of solvents on the HDO of guaiacol, where aromatic compounds were selectively formed in water. They noted that more light alkanes ( $n < 3$ ) were recovered in the product gas when alcohols were used as solvents, suggesting that alcohols were not inert during the reaction.<sup>129</sup> Therefore, they concluded that the quantity of aromatic compounds reaches its maximum value after a 5 h reaction at 240 °C with 1 MPa of H<sub>2</sub>.<sup>129</sup> Fig. 3 shows the reaction process of the controlled HDO of guaiacol. Using 2-furyl methyl ketone (FMK) as a model compound, Ly *et al.*<sup>130</sup> obtained a relatively high conversion of FMK with Ni-based catalysts (Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). However, the HDO was found to be promoted by adding phosphorus, which influences the structural characteristics of the active phase. In addition, a Pt–Pd/ACP catalyst was active and selective for hydrocarbons and, more notably, was stable in the HDO of the crude bio-oil.<sup>127</sup> Similarly, Shafaghat *et al.* used metal/acid bifunctional catalysts for the HDO of a synthetic phenolic bio-oil consisting of phenol (50 wt%), *o*-cresol (25 wt%) and guaiacol (25 wt%).<sup>133</sup> They found that the bi-metallic Ni–Fe/H-beta catalyst had superior HDO activity in converting phenolic compounds to oxygen-free products than the monometallic catalysts.<sup>133</sup>

### 3.3 Deoxygenation

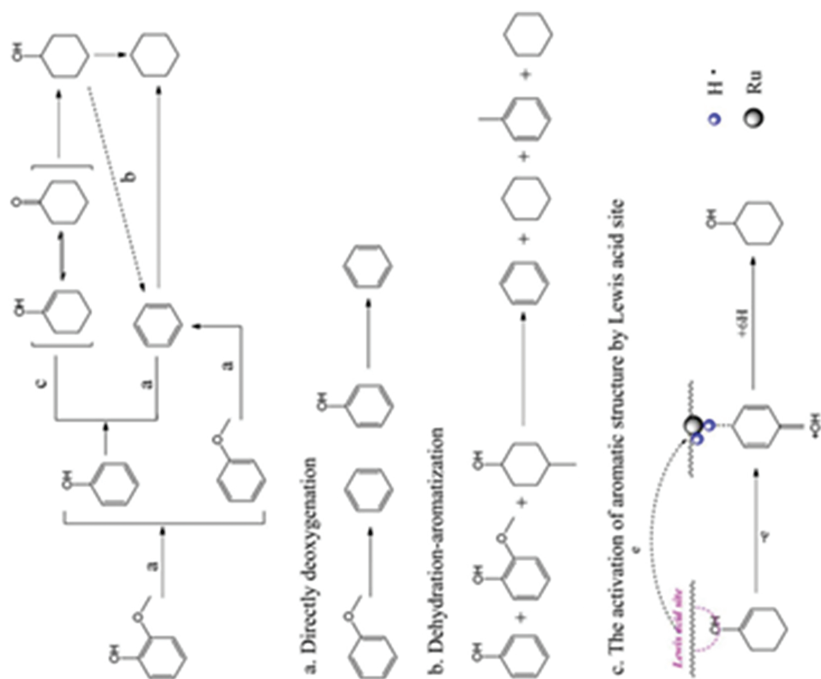
Over the past decade, bio-oil DO has received increasing attention for producing biofuels and environmentally safe chemicals from biomass.<sup>28</sup> It generally operates at high pressures of 1–300 bar.<sup>28</sup> Breaking the C–O bond is challenging and complex without a catalyst.<sup>135</sup> Therefore, catalysts are crucial in biomass DO to facilitate the cleavage of the C–O bond

**Table 4** Some examples of the HDO of pyrolysis bio-oil.

| Feedstock derived bio-oil  | Selected compounds   | Catalyst  | Reaction conditions  | Results  | Ref. |
|--|--|---|--|--|------|
| Flash pyrolysis of rice husk   | Guaiacol, 2-methoxy-4-methylphenol, eugenol, syringols, and eluted bio-oil | Ru-WO <sub>x</sub> /ZrO <sub>2</sub>  | 0.1 g of catalyst, 5 mmol of reactant, 140–240 °C, 10 bar of H <sub>2</sub> , 0.5–5 h  | An increase in hydrogen pressure led to an increase in conversion but a decrease in selectivity for the arenes                           | 129  |
| Fast pyrolysis of black poplar   | Raw bio-oil  | Pt–Pd/ACP<br>Pt–Pd/FCC  | 400–450 °C, 0–10 h, 65 bar, 0.18 g <sub>cat</sub> h g <sub>bio-oil</sub> <sup>-1</sup> | The bifunctional catalyst was pseudo-stable at 450 °C  | 127  |
| Fast pyrolysis of switchgrass, <i>Eucalyptus benthamii</i> , and equine manure | Bio-oil  | Powder charcoal with 5% metal loading (Pt, Ru, or Pd)   | 0.5 g catalyst, 320 °C, 144 bar of H <sub>2</sub> , and 4 h                            | Bio-oil from switchgrass on Pt/C performed best in hydrogen consumption efficacy, DO efficiency, and types of bio-oil compounds upgraded | 131  |
| Fast pyrolysis of <i>Saccharina japonica</i>                                   | Bio-oil  | HZSM-5, Fe, and Co, and metal-phosphide (Fe <sub>2</sub> P, CoP, and CoMoP) supported on $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 350 °C and 3–15 bar  | Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> achieved higher HDO performance than other catalysts  | 132  |



**B**



**Fig. 3** Possible reactions during (A) HDO<sup>134</sup> (reproduced from ref. 134 with permission from Elsevier, Copyright 2018) and (B) the reaction pathway for the controlled HDO<sup>129</sup> (reproduced from ref. 129 with permission from American Chemical Society, Copyright 2018).

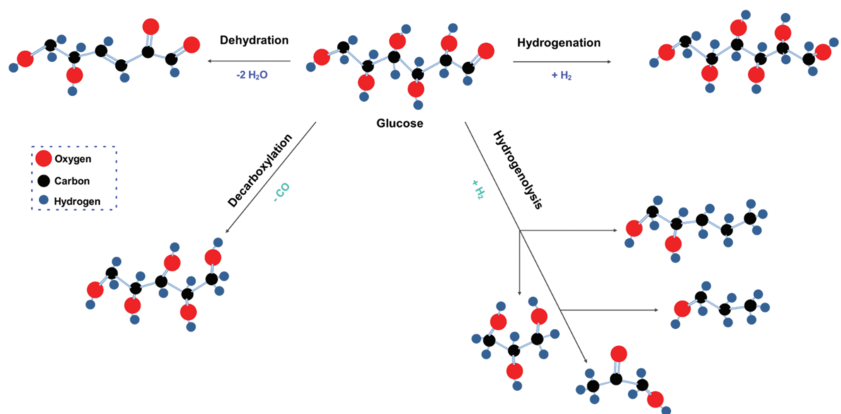


Fig. 4 DO process reactions.

and decrease the oxygen concentration more efficiently.<sup>30,31</sup> It is important to emphasise the distinction between HDO and DO processes: in HDO, a hydrogen source is required, while in DO, hydrogen is generated during the water gas shift reaction.<sup>136,137</sup> The DO process proceeds in four stages (Fig. 4):<sup>52</sup>

1. Hydrogenation, where C–C bonds are split.
2. Hydrogenolysis, where C–C bonds are broken, oxygen atoms are eliminated, and several products are formed.
3. Dehydration, where water molecules are removed, and unsaturated bonds are formed.
4. Decarboxylation (also referred to as decarboxylation), where CO<sub>2</sub> or CO is released.

Numerous catalysts have been reported in the literature for HDO of bio-oil, with zeolites having drawn considerably greater attention due to their large specifications.<sup>28</sup> Kurnia *et al.*<sup>138</sup> investigated the selectivity and yield of bio-oil derived from fast pyrolysis of lignin over aluminium-based zeolites (H-ferrierite, H-mordenite, H-ZSM-5, H-beta, and H-USY zeolites). They found that H-beta provided high selectivity, and H-ZSM-5 led to a higher percentage of aromatic compounds. Some studies related to bio-oil DO with zeolite catalysts are listed in Table 5.

Veses *et al.*<sup>27</sup> investigated the catalytic performance of hierarchical metal-loaded ZSM-5 zeolites on biomass-derived pyrolysis oils. They found that when metals such as copper, nickel, magnesium, and tin were added to classified ZSM-5 catalysts, the degree of DO jump from 11.6% to 42.6%. In contrast, adding Mg provided better performance than the other metals for upgrading bio-oil derived from woody biomass.<sup>27</sup> Xu *et al.*<sup>143</sup> used CO<sub>2</sub> as a co-reactant gas to perform *in situ* DO of bio-oil made from microwave pyrolysis of biomass. They reported that a CO<sub>2</sub> atmosphere decreased the oxygen content of the bio-oil by 12.68 wt% and elevated the higher heating value by 26.43% by favouring the migration of oxygen from the bio-oil to the pyrolytic gas. Lin *et al.*<sup>30</sup> examined the effect of CaO on the direct DO of bio-oil during white pine pyrolysis in a

**Table 5** DO of biomass-derived bio-oil using zeolite catalysts.

| Feedstock         | Catalyst                           | Preparation method         | Conditions of reaction  | Result  | Ref. |
|-------------------|------------------------------------|----------------------------|---|---|------|
| Rape straw        | HZSM-5@MCM-41                      | External recrystallisation | 50 mL min <sup>-1</sup> of N <sub>2</sub> , 20 min °C <sup>-1</sup> , 500 °C, 50 min, 15 g of catalyst                          | Maximum yield of monocyclic aromatic hydrocarbons obtained was 11% wt, 2.5 times higher than on HZSM-5.     | 139  |
| Straw stalk       | 3% Zn/20% SiO <sub>2</sub> /HZSM-5 | Wet impregnation           | 400–600 °C, 50 mL min <sup>-1</sup> of N <sub>2</sub> , space velocity of 1 h <sup>-1</sup> , mass ratio 1 : 1 bio-oil/methanol | <i>p</i> -xylene yield of 18.7% with a high <i>p</i> -xylene/xylene ratio of 93.8%                          | 140  |
| Beechwood sawdust | Fe and Zn assisted zeolite         | Wet impregnation           | 2 g of catalyst, 500 °C, 25 °C min <sup>-1</sup>  | It transformed large, oxygenated compounds into smaller units, leading to a better upgrading of raw bio-oil | 141  |
| Wheat straw       | ZSM-5<br>KH-ZSM-5                  | Wet impregnation           | 550 °C, catalyst/biomass ratio of 0.2–0.8 g g <sup>-1</sup>   | KH-ZSM-5 led to a more favourable relationship between the organic oil's oxygen content and yield           | 142  |

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fluidised bed reactor. With a CaO mass ratio of 5, they noted a relative reduction in oxygen content in the bio-oil of up to 21%.<sup>30</sup> Additionally, functional abundances of furfural and furfuryl alcohol, principally derived from the dehydration reactions, were increased, indicating that CaO could also catalyse the dehydration reactions.<sup>30</sup>

Zeolites with different pore sizes and active sites were identified as good candidates for catalysts to enhance the bio-oil yield of DO reactions.<sup>25</sup> Li *et al.* investigated the influences of zeolites modified with three different metals (Fe, Co, and Zr) on pyrolytic oil derived from sawdust.<sup>144</sup> They concluded that ZSM-5 with Fe and Zr favoured the formation of aromatic hydrocarbons, while ZSM-5 with Co promoted better gas yield and coke formation. Naqvi *et al.* examined the DO of pyrolytic bio-oil produced from rice residues using zeolite catalysts with different pore sizes.<sup>145</sup> They found that the degree of DO was highest with medium pore size catalysts such as ZSM-5 (82%) and ITQ-2 (75%) and lowest with ferrierite-based catalysts (56%).

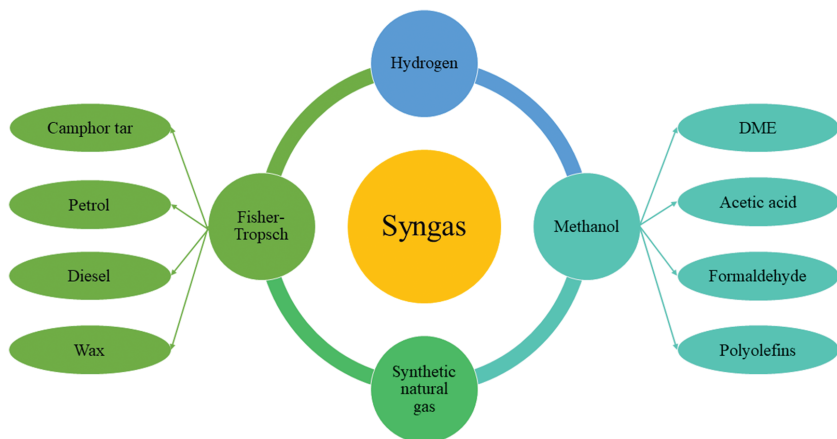
### 3.4 Catalytic cracking and hydrocracking

As their names imply, hydrocracking and catalytic cracking are processes in which large hydrocarbon molecules in bio-oil are broken down into smaller ones with a heterogeneous catalyst at temperatures  $>350$  °C and a hydrogen pressure of 7–210 bar.<sup>2,95,146</sup> The role of catalysts in hydrocracking is twofold: (i) elimination of oxygenates into gases such as water and (ii) cleavage of long-chain hydrocarbons into smaller hydrocarbons. The major products of this process are hydrocarbons, aqueous organics, water, gases, and coke, offering important advantages in processing and economy.<sup>147</sup>

Bio-oil cracking on porous solid catalysts such as zeolite-based catalysts at room pressure is considered one attractive method for bio-oil upgrading, particularly when hydrogen gas is not needed. The main challenge in the catalytic cracking of bio-oils is finding high-performance catalysts.<sup>2</sup> To date, various zeolites have been investigated for bio-oil upgrading, including H-beta zeolite, Y zeolite, and SSZ-55 with large pores; ZSM-5, ZSM-23, ZSM-11, IM-5, TNU-9, and ferrierite with medium pores; and ZK-5 and SAPO-34 with small pores.<sup>148</sup> Most of these zeolites could enhance aromatics generation during process upgrading, with some, particularly protonated ZSM-5 (HZSM-5) and H-beta zeolite, always yielding higher aromatics.<sup>148</sup> For example, Ibarra *et al.*<sup>51</sup> explored the performance of different zeolite-based catalysts (HY, HZSM-5, and H-beta) on the catalytic cracking of bio-oil. They found that the total hydrocarbon yield was higher for the H-beta catalyst (56 wt%), while liquid hydrocarbon yields were similar for all catalysts.<sup>51</sup>

### 3.5 Dry reforming

Dry reforming is typically used to convert CH<sub>4</sub> and CO<sub>2</sub> into syngas, a mixture of H<sub>2</sub> and CO.<sup>149</sup> Syngas is an attractive feedstock to produce alcohols of different chain lengths, ammonia, methanol, hydrogen, and synthetic fuel through Fisher–Tropsch technology.<sup>149,150</sup> Fig. 5 shows the



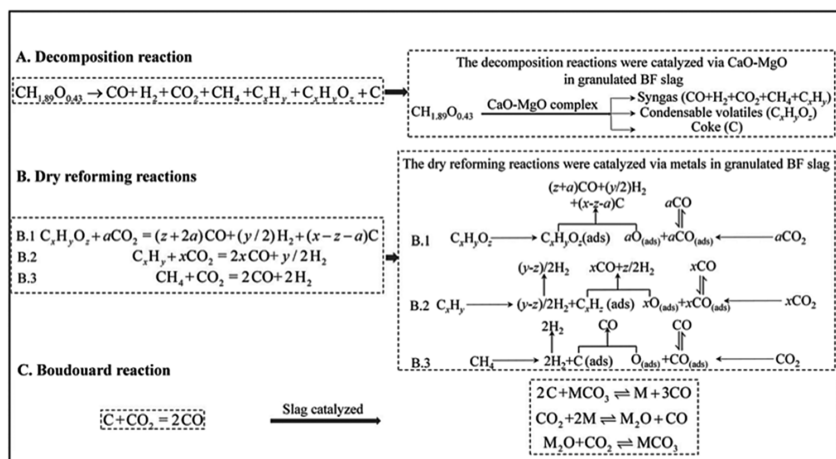
**Fig. 5** Potential syngas applications.

potential syngas applications. The  $H_2/CO$  ratio is highly relevant in these types of uses. With its high quantity and renewable features, biomass has been considered a valuable resource for generating syngas as a substitute for fossil fuels.<sup>48</sup> The bio-oil yielded from the pyrolysis of biomass is commonly represented as  $C_nH_mO_k$ . Due to the complexity of bio-oil composition, the investigation of dry reforming is confined mainly to model bio-oil compounds.<sup>49,50,151</sup>

To date, few studies have examined upgrading bio-oil through dry reforming. For example, Fu *et al.*<sup>151</sup> reported dry reforming of a simulated bio-oil (1 : 1 : 1 : 1) composed of acetic acid, phenol, ethanol, and acetone, in a fixed bed reactor for hydrogen production using a  $Ni/Al_2O_3$  catalyst. They showed that at 700 °C, a  $CO_2$  to bio-oil carbon ratio of 0.75, and weight hourly space velocity of 0.9  $h^{-1}$ , hydrogen yield and compound conversion of the bio-oil model reached 88.19% and 96.87%, respectively. Based on their findings, there are two basic carbon deposit types on the  $Ni/Al_2O_3$  catalyst: filamentous fibres and graphite carbons.<sup>151</sup> Similarly, Yao *et al.* investigated the characteristics of dry reforming ( $CO_2$ ) of a bio-oil model compound in granulated blast-furnace slag (BFS) for syngas production.<sup>152,153</sup> They found that granulated BFS could convert bio-oil into small molecules such as  $H_2$  and  $CO$ , upgrade the conversion of bio-oil and lower heating value, and catalyse the dry reforming process of bio-oil.<sup>153</sup> In addition, Yao *et al.*<sup>152</sup> developed a mechanism for the dry reforming of the bio-oil model compound in granulated BFS based on their experimental results and published literature (Fig. 6).

Xie *et al.*<sup>50</sup> investigated combining dry and steam reforming of bio-oil containing eight typical compounds (15 mol% acetic acid, 15 mol% acetone, 15 mol% acetaldehyde, 15 mol% glycol, 15 mol% formic acid, 10 mol% methanol, 10 mol% formaldehyde, and 5 mol% ethanol) using BFS as the heat carrier to generate syngas with an  $H_2/CO$  ratio of 3 : 1 for subsequent methanation. They reported that the combined bio-oil reforming process might be advantageous since it provided a higher total yield of  $H_2$  and  $CO$  with an extremely low coke yield at a lower reforming temperature.<sup>50</sup> They stated that at a BFS mass of 3.99 times





**Fig. 6** The catalytic mechanism of dry reforming a model bio-oil compound in granulated BFS proposed by Yao *et al.*<sup>152</sup> Reproduced from ref. 152 with permission from Springer Nature, Copyright 2019.



**Fig. 7** Schematic of ECH of bio-oil using two electrodes in separate chambers.

the bio-oil mass, the combined process with a 3.0 steam/carbon ratio and a 0.5  $\text{CO}_2/\text{C}$  ratio could spontaneously produce a 3 : 1  $\text{H}_2/\text{CO}$  syngas.<sup>50</sup>

### 3.6 Electrocatalytic hydrogenation

Electrocatalytic hydrogenation (ECH) is a viable option for safely reducing organic molecules under gentle processing conditions (<80 °C and ambient pressure) without external  $\text{H}_2$ .<sup>36</sup> In addition, the necessary electrical energy for the processing comes from renewable energy sources such as solar and wind energies, making the process entirely separate from fossil energy carriers (Fig. 7). The gentle reaction environment has made electrocatalysis a relevant focus in green chemistry.<sup>154,155</sup>

During ECH, the reduction of protons from the solution creates *in situ* atomic hydrogen on the catalytic electrode surface, which is required to hydrogenate the organic substances.<sup>64</sup> This approach makes processing more efficient and avoids using fossil hydrogen gas from external sources and associated handling facilities. Fig. 7 illustrates the ECH system with

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various electrochemical reactions occurring on the electrodes' surface. In the cathode chamber, both ECH stabilisation of the bio-oil and hydrogen evolution will occur on the cathode surface. In the anode chamber, electrocatalytic oxidation of water or organics will occur on the anode surface to generate the equivalent reductant ( $H^+ + e^-$ ) for the bio-oil ECH in the cathode chamber (Table 6).

A given metal's electrocatalytic activity changes as a function of the substrate employed. For example, Pd performs outstandingly for benzaldehyde ECH but shows minimal performance for phenol ECH.<sup>156</sup> The ECH of bio-oils has been assessed on both Ru<sup>159</sup> and C,<sup>160</sup> showing a reduction in carbonyl content and the elimination of minor acid compounds.<sup>159,160</sup> Some recent studies have found that base metals such as Cu and Ni could be equally active as noble metals in the ECH of biomass-based organic molecules.<sup>35,64,157,161</sup> For example, the activity of Cu for ECH of benzaldehyde was like Pd.<sup>35</sup> Notably, the performance of different metals is not easily predicted when dealing with complex organic streams.<sup>36</sup> Indeed, Andrews *et al.* synthesised and characterised several carbon-supported and noble metal catalysts for the ECH of both selected model compounds, such as furfural and benzaldehyde, and pyrolysis bio-oil.<sup>38</sup> They noted that the most active and efficient catalysts for ECH were Pb and Cu. These two metals appeared selective for bio-oil ECH, with a significant decrease in carbonyl content after ECH.<sup>38</sup>

### 3.7 Esterification

The esterification of bio-oil is a valuable treatment that aims to neutralise its acidity. This process commonly includes the addition of alcohol (30–100 wt%), gentle heating (60–120 °C) under a harsh acid catalyst, and water elimination (20–40 wt%) *via* distillation. For complete conversion, water removal is vital since two types of equilibrium reactions occur between bio-oil and added alcohols: (i) the esterification of carboxylic acids to esters and (ii) the acetalisation of aldehydes, ketones, and sugars to acetals.<sup>162,163</sup> The second product is water, which participates in the opposite reaction, hydrolysing the esters and acetals back into the raw materials. Other than lowering acidity, the principal strengths of this process include an increase in heating value by adding alcohol and removing water, improved stability due to alcohol, and a more stable chemical composition since the catalyst and heat move it toward equilibrium.<sup>40,162,164</sup>

Li *et al.* reported simultaneous catalytic esterification and acetalisation of a bio-oil/methanol using a commercial Amberlyst catalyst at 70–170 °C.<sup>43</sup> They found significant increases in the conversion of weak organic acids and aldehydes into esters and acetals with increasing temperature, reaction time, and catalyst loading. Similarly, Gunawan *et al.* used the Amberlyst-70 catalyst to hydrolyse sugars during bio-oil esterification at 70–170 °C.<sup>41</sup> They examined the influence of catalyst loadings on sugar hydrolysis-glycosidation in bio-oil, with levoglucosan production from sugar oligomers and levoglucosan hydrolysis to D-glucose co-occurring with a catalyst loading of 1 wt%.<sup>41</sup>

**Table 6** Some studies investigating ECH on various model compounds.<sup>a</sup>

| Compound                     | Electrolyte   | Catalysts                    | Products   | F.E. % | Ref. |
|------------------------------|---|------------------------------|--|--------|------|
| 20 mM benzaldehyde           | Acetate buffer  | 5% Ni/C                      | Benzyl alcohol   | 35     | 156  |
|                              |   | 5% Pt/C                      |  | ~39    |      |
|                              |   | 5% Rh/C                      |  | ~65    |      |
|                              |   | 5% Pd/C                      |  | 99     |      |
| 50 mM hydroxyacetone         | 0.5 M Na <sub>2</sub> SO <sub>4</sub>                     | 1 mg cm <sup>-2</sup> Cu/C   | Propylene glycol   | 11     | 37   |
|                              |   | 1 mg cm <sup>-2</sup> Ni/C   |  | 17     |      |
|                              |   | 1 mg cm <sup>-2</sup> CuNi/C |  | 16     |      |
|                              |   | 1 mg cm <sup>-2</sup> Pt/C   |  | 20     |      |
|                              |   | 1 mg cm <sup>-2</sup> Ru/C   |  | 22     |      |
| 1 mg cm <sup>-2</sup> PtRu/C | 22  |                              |  |        |      |
| 5 wt% furfural               | 0.5 M of H <sub>2</sub> SO <sub>4</sub>                   | 1 mg cm <sup>-2</sup> Pd/C   | Furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, and 2-methyltetrahydrofuran | 54     | 157  |
| 100 mM furfural              | 20% acetonitrile and 0.5 M H <sub>2</sub> SO <sub>4</sub> | Cu                           | Furfuryl alcohol and 2-methylfuran   | 52.2   | 158  |

<sup>a</sup> F.E.%, faradaic efficiency.

## 4 Challenges and limitations

Bio-oils produced *via* the fast pyrolysis of biomass are significantly limited in their direct uses due to their high oxygen content and, thus, poor quality. Therefore, pyrolysis bio-oil upgrading is commonly undertaken by hydrogenation at elevated temperatures and pressures. However, the rapid generation of carbonaceous substances *via* condensation of reactive compounds (*e.g.*, sugars, phenols, aldehydes, and ketones) makes the hydrogenation of bio-oil challenging due to catalyst deactivation and eventual metal leaching during reactions and reactor fouling. Moreover, H<sub>2</sub> production under high pressure and bio-oil hydrogenation are the most energetic and expensive operations in converting bioliquids into biofuels and bioproducts.<sup>38</sup> Therefore, ECH was considered a promising option for the sustainable reduction of organic molecules under gentle processing conditions.<sup>65,66</sup> Despite the complexity of the organic streams produced by pyrolysis, most published studies have focused on using ECH in dilute aqueous solutions for only selected model molecules. Moreover, electrocatalysts are usually investigated under ideal, controlled conditions and are seldom evaluated in real bio-oil.

Regardless of the unique characteristics of zeolite catalysts, several obstacles challenge and prevent their application in the catalytic DO of pyrolysis bio-oil. For example, inorganic residues in bio-oils can block zeolite micropores, resulting in the catalyst's rapid deactivation.<sup>165</sup> In addition, zeolite catalyst recovery and regeneration after the reaction is also a critical issue because repeated regeneration stages frequently lead to dealumination and acidic site loss, resulting in their irreversible deactivation.<sup>166</sup>

Nevertheless, a hydrogen source is needed to convert bio-oil into a suitable fuel grade (*i.e.*, HDO). However, this route is also far from being industrially implemented. A major concern in this process is the catalyst's durability since carbon deposition on such systems is an issue that must be overcome before regular production can be realised. Further research is required to understand the chemical reactions controlling coke formation and to find appropriate technological solutions in the upgrading process, such as reducing the coke production or regenerating the catalysts. The most critical research challenge is to develop catalysts that effectively remove oxygen from bio-oil at moderate conditions with low hydrogen consumption. Table 7 summarises some advantages and disadvantages of bio-oil upgrading processes with catalysts.

**Table 7** Some advantages and disadvantages of bio-oil upgrading processes.<sup>2,95,167</sup>

|                    | Characteristics  | Limitations  |
|--------------------|--|--|
| Catalytic cracking | <ul style="list-style-type: none"><li>• H<sub>2</sub> not required</li><li>• Reaction conditions like the pyrolysis reaction</li></ul>           | <ul style="list-style-type: none"><li>• Poor hydrocarbon yields</li><li>• High coke yields</li><li>• Short catalyst life</li></ul> |
| HDO                | <ul style="list-style-type: none"><li>• Prevents coke deposition on the catalyst's surface</li><li>• Increases the bio-oil's H/C ratio</li></ul> | <ul style="list-style-type: none"><li>• High H<sub>2</sub> pressure</li><li>• High cost</li></ul>                                  |
| Esterification     | <ul style="list-style-type: none"><li>• Ester formation</li><li>• Improved stability</li></ul>   | <ul style="list-style-type: none"><li>• Low oil production</li><li>• Poor performance</li></ul>                                    |

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Developing and using upgrading technologies in the industrial production of bio-oil from biomass pyrolysis is a significant challenge. Future efforts are expected to focus on the following aspects to address this:

1. Developing more suitable catalysts and reliable, robust, and well-designed reactor systems is needed.
2. The catalyst deactivation mechanism requires a better explanation when upgrading bio-oil using various catalysts.
3. Greater efforts are needed to build large-scale, high-efficiency experimental plants to promote the industrialisation of bio-oil upgrading.
4. Upgrading bio-oil using co-processing approach could be a smart route to overcome the limitations of each process and obtain a high-quality biofuel.<sup>168</sup>

## 5 Conclusions

Given the increasing demand for fuels, the increasing accumulation of CO<sub>2</sub> in the atmosphere, and the exhaustion of oil reserves, the necessity of renewable fuels is becoming apparent. Biomass-derived fuels offer a potential route in this context since they are the only renewable carbon resource with a relatively short life cycle.

Bio-oils are complex mixtures of oxygenated compounds that undergo different thermic and catalytic pathways during their chemical transformation depending on the process conditions and catalysts. Various technologies exist for processing/upgrading bio-oil, including catalytic cracking, HDO, DO, and esterification. Since no single-step conversion process can offer an ideal solution, a series of processes in an integrated biorefinery, analogous to conventional oil refineries, is the ultimate solution. In addition, the commercialisation of bio-oil upgrading technology still needs further development.

## Conflicts of interest

The authors declare no competing interests.

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