Cost-effective routes for Catalytic Biomass Upgrading

W. Jin [1], L. Pastor- Pérez [1], Jie Yu[2], J.A. Odriozola[1,3], S. Gu [1], T. R. Reina[1*]

[1] *Department of Chemical and Process Engineering Department, University of Surrey, Guildford, GU2 7XH United Kingdom.*
[2] *State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, China*
[3] *Departamento de Química Inorgánica e Instituto de Ciencia de Materiales de Sevilla, Avda. Americo Vespucio 49, 41092 Sevilla, Spain.*

Corresponding author: t.ramirezreina@surrey.ac.uk

Abstract

Catalytic hydrodeoxygenation (HDO) is a fundamental and promising route for bio-oil upgrading to produce petroleum-like hydrocarbon fuels or chemical building blocks. One of the main challenges of this technology is the demand of high-pressure H_2, which poses high costs and safety concerns. Accordingly, developing cost-effective routes for biomass or bio-oil upgrading without the supply of commercial H_2 is essential to implement the HDO at commercial scale. This paper critically reviewed the very recent studies relating to the novel strategies for upgrading the bio-feedstocks with 'green' H_2 generated from renewable sources. More precisely, catalytic transfer hydrogenation/hydrogenolysis (CTH), combined reforming and HDO, combined metal hydrolysis and HDO, water-assisted *in-situ* HDO and non-thermal plasma (NTP) technology and self-supported hydrogenolysis (SSH) are reviewed herein. Current challenges and research trends of each strategy are also proposed aiming to motivate further improvement of these novel routes to become competitive alternatives to conventional HDO technology.

Introduction

The increasing energy demand and environmental pollution arise the utilization of sustainable and low-carbon energy to decrease the excessive dependence on limited fossil fuels. In the recent decades, biomass has sparked great interest become among renewable sources considering its distinctive features, such as low price, low-carbon emission, abundant storage and wide distribution [1]. Among all technologies, depolymerization and deoxygenation are two essential processes for biomass valorisation to produce high-valued chemicals and transportation fuels. Hydrodeoxygenation (HDO) technology is typically applied for bio-oil upgrading in which the oxygen will be removed in the form of water. Previous study about the HDO of bio-feedstocks mainly focused on bio-oil model compounds to obtain fundamental mechanistic understanding of bio-oil upgrading process. Recently, the upgrading of crude bio-oil has gained more attention. The 'Achilles Heel' of this technology is demand of high pressure H_2- an expensive resource which could impose security consideration and an economic barrier for its application on commercial scale [2]. Recently, novel strategies are being developed for bio-oil or biomass upgrading with *in-situ* generated hydrogen thus suppressing external H_2 supply. These novel routes include (1) CTH, (2) combined reforming and HDO process, (3) combined metal hydrolysis and HDO process, (4) water-assisted *in-situ* HDO process, (5) NTP and (6) SSH. The hydrogen source of each technology was depicted in Figure 1. Catalytic HDO of bio-oil have been extensively reviewed by Li [3], Besson [4] and Kim et.al [5]. Herein, most recent findings regarding six cost-effective routes for bio-oil or biomass upgrading were selectively overviewed in this work, facilitating the design of

advanced catalysts and motivating the development of potentially economically viable route for catalytic biomass or bio-oil upgrading.
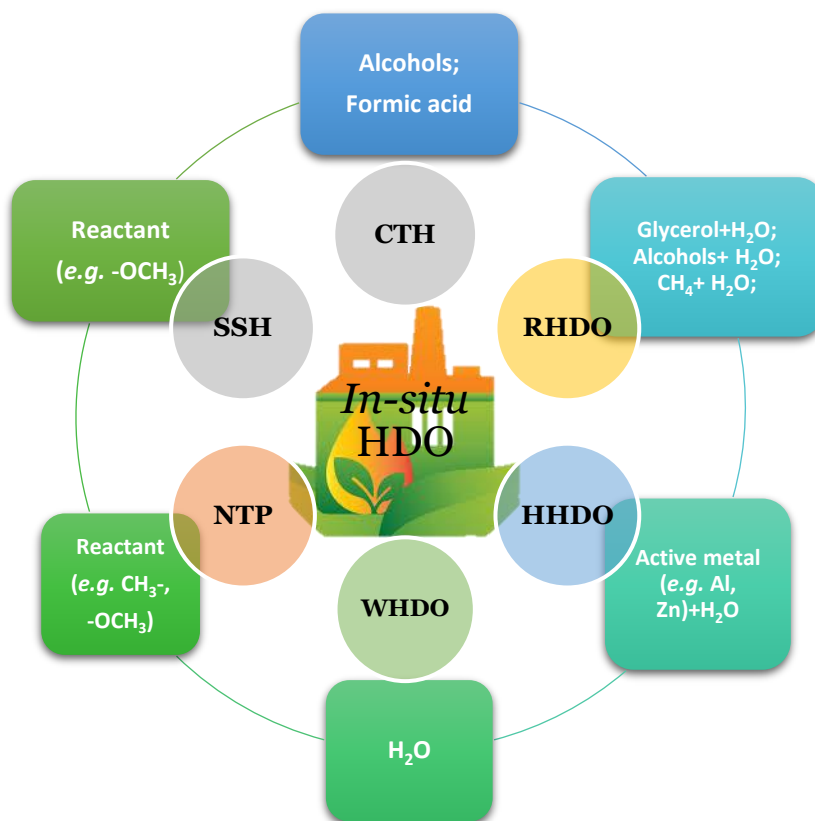

Figure 1. Novel strategies for bio-oil or biomass HDO with *in-situ* hydrogen generation (CTH: Catalytic transfer hydrogenation/hydrogenolysis; RHDO: Combined reforming with hydrodeoxygenation; HHDO: Combined metal hydrolysis with hydrodeoxygenation; WHDO: Water-assisted *in-situ* hydrodeoxygenation; NTP: Non-thermal plasma; SSH: Self-supported hydrogenolysis)

Catalytic Transfer Hydrogenation/Hydrogenolysis (CTH)

Apart from the *in-situ* H_2 generation, the CTH technology owns several advantages such as mild reaction conditions, high atom efficiency and less cost of the experimental setup [6]. Moreover, it is demonstrated that CTH strategy can avoid the excessive hydrogenation and thus favour the production aromatic hydrocarbons compared to conventional HDO route [7,8]. The CTH technology is still in the bud for its application in the HDO of bio-oils, especially for phenolic compounds [8]. The challenge of this strategy remains on the enhancement of deoxygenation rates.

The rational design of catalysts for facilitating synchronous H_2 generation and selective C-O bond cleavage of bio-feedstocks is the key to fulfilling the high HDO efficiency. In most existing investigations, noble catalysts including Ru, Pd and Pt and non-noble catalysts including Ni and Co are among the best candidates for CTH of phenolic compounds. Typically, bimetallic catalysts are superior to monometallic catalyst, due to the introduction of a suitable second metal tuning the metal-H strength on the metal surface, which significantly impacts the decomposition of H-donor and H_2 spillover rates. The optimization of metal-H bonding strength is still a challenge. Most recently, Jin et al. hypothesised the atom H transfer route for mono, bi-metallic admixture showcasing the potential of bimetallic

catalysts in CTH process [6]. For bimetallic catalyst, the CTH reactions involved the atomic H transfer form one metal site to another, while the dehydrogenation of hydrogen donor and the hydrogenolysis is proposed to occur on the same metal site for alloyed bimetallic catalysts [6]. For RANEY Ni catalytic system with 2-proponal as hydrogen donor, the reactivity patterns vary with the position of methoxy group on the substrate. The ATR-IR spectra revealed that the adsorbed guaiacol assumes a parallel orientation to the catalyst surface, which allows a strong interaction between the methoxy C–O bond and the surface of catalyst. Conversely, the adsorption of 3- or 4-methoxyphenol leads to a tilted surface complex in which the methoxy C–O bond establishes no interaction with the catalyst [9].

Formic acid [10, 11] and alcohols (*e.g.* methanol [12], ethanol [13] [14], 2-proponal [15] [16] [17]), have been proved efficient hydrogen donor for CTH process. Generally speaking, small molecules, such as methanol and formic acid are more selective to H_2 generation compared to long chain alcohols. The deteriorated properties for H_2 production could be attributed to the high extent of parallel consumption routes in the upgrading process (*i.e.* dehydration, condensation and etherification) [18]. More recently, researchers are making effort on applying the CTH idea in upgrading of raw feedstocks. Mg-Ni-Mo catalyst supported by KOH treated activated charcoal was demonstrated to be effective for upgrading the bio-tar with supercritical ethanol as the H-donor [14]. The oxygen content decreased from 30.5 wt.% to 11.7 wt.% through series of reactions, such as esterification, hydrogenation, deoxygenation and ring-alkylation. Similarly, methanol was proved to be effective hydrogen donor for the upgrading of pyrolytic oil (degree of deoxygenation= 50-54%) over Pd/C and Pt/C catalyst [19]. Further improvement on enhancing the stability of catalyst is needed considering the obvious deactivation of catalyst caused by the carbon deposition. Recently, the group of McClelland [12] investigated the supercritical methanol depolymerization and hydrogenation (SCM-DHDO) of maple wood and two extracted lignins over reduced porous copper metal oxides using supercritical methanol as hydrogen source. The effective HDO reflects on the decreased O/C ratio of feedstock SCM-DHDO products, in which the O/C ratio decreased from 0.32 in GVL extracted lignin to 0.06 and 0.04 in GVL extracted lignin and maple wood products derived through SCM-DHDO process at 300 °C. Similarly, Regmi and co-workers [13] investigated the CTH of organosolv lignin over B-containing FeNi alloyed catalysts using supercritical ethanol as the hydrogen donor at 320 °C. It is demonstrated that the B-containing FeNi alloys could mediate the selective CTH of ketones to alkanes. The addition of B as promoter could enhance the hydrogenation of C=O bond and C-O hydrogenolysis. By using acetophenone as a model compound in this process, high reactivity (Conversion=74%) and selectivity towards completed deoxygenated product, ethylbenzene (Selectivity=84%) was obtained. Surprisingly, the addition of external H_2 in the catalytic system decreased the monophenols production for the CTH of lignin over PtRe/TiO_2 with 2-propanol as hydrogen source. The competitive adsorption of active sites on catalysts might result in the adverse effect of H_2 on the depolymerization of lignin [17]. Generally, the combination of depolymerization and CTH in one pot simplified the experimental setup and is effective for the lignin monomers production.

Combined Reforming and HDO Process (RHDO)

The combined reforming and HDO (RHDO) strategy resembles to the CTH strategy discussed in the previous section. Some authors classify the RHDO route to the CTH for liquid phase *in-situ* HDO process probably due to reforming of H-donor (*e.g.* alcohols) might happen with the participation of H_2O produced from the hydrogenolysis process. In this review, the route of RHDO is emphasised since the concept of RHDO route is designed with reforming as the main H_2 generation route instead of the decomposition or dehydrogenation of H-donor. Figure 2 depicts a scheme of the *in-situ* HDO via CTH and RHDO route.
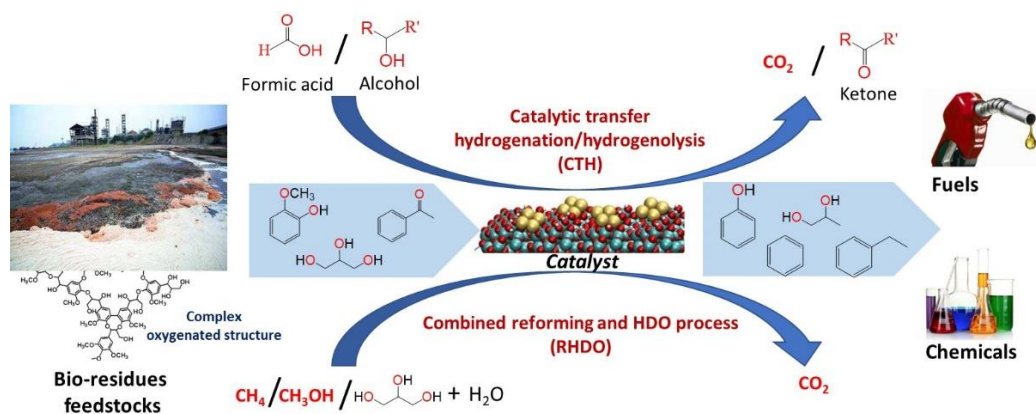
Figure 2. Catalytic biomass upgrading via CTH and RHDO routes

Varma et.al [20] proposed the strategy for bio-oil deoxygenation using *in-situ* hydrogen generated from methane steam reforming. In this process, the multiple reactions including biomass oxygenates dehydration and aromatization together with the methane steam reforming make it realizable for upgrading the bio-oil into aromatic hydrocarbons. Further improvement relating to the deoxygenation degree is urgently needed, however, no new publications for bio-oil upgrading via this route is observed in the recent years.

H_2 formation rate for methanol reforming is higher than the dehydrogenation of other common hydrogen donors (including formic acid, ethylene glycol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and tert-butanol) in catalytic systems with the absence of bio-feedstocks. Moreover, methanol is proved to be the best H-donor for selective production of 1,2-propanediol from glycerol [18]. Glycerol is the one of the main by-products during the biodiesel production. H_2 production from the sacrifice of part of substrates can upgrade the glycerol to deoxygenated products [21] [22]. More recently, attempts about using glycerol APR as the hydrogen source for the bio-oil upgrading process were conducted by researchers. Remón et al. [23] proposed using crude glycerol as the hydrogen source for the valorisation of bio-oil in supercritical water. Results indicated that the synergistic interaction between crude glycerol and bio-oil results in an important decrease in the solid yield [23]. Domínguez-Barroso et. al [24] combined of glycerol-APR and the hydrodeoxygenation of fatty acid over $PtNi/Al_2O_3$ catalysts. However, low deoxygenation conversion of fatty acid (37%) was obtained considering the difference between the optimal condition of glycerol-APR (200 $^\circ$C) and *in-situ* HDO of fatty acid (275 $^\circ$C). Overall, the RHDO route is promising for the non-fossil H_2-based HDO process. The matching of APR and HDO condition should be the key consideration for the design of catalytic upgrading system.

Combined Metal Hydrolysis and HDO Process (HHDO)

Active metals, such as beryllium (Be), aluminium (Al), zinc (Zn), magnesium (Mg), Calcium (Ca), lithium (Li), sodium (Na), and potassium (K) can produce H_2 by reacting with water. Zn and Al excellent candidates. HHDO owns several advantages compared with other novel routes. For example, HDO is favoured since the energy can be released from the exothermal metal hydrolysis process. Besides, metallic oxide, such as ZnO, AlOOH and MgO have catalytic properties [25], which might promote the HDO reaction.

Cheng et.al [26] firstly proposed the *in-situ* HDO of bio-oil with hydrogen generated from zinc hydrolysis. However, the deoxygenation degree is not satisfactory, in which oxygen content decreased from 48.78% wt.% to 30.20 wt.% over Pd/C at 250 $^\circ$C [27]. They further investigated the catalytic liquefaction of pine sawdust and *in-situ* hydrogenation of bio-crude over Co-Zn/HZSM-5 catalysts by using zinc hydrolysis as the hydrogen source. The bimetallic Co-Zo/HZSM-5 is superior to monometallic Co/HZSM-5 and Zn/HZSM-5 in terms the production of hydrocarbons considering the synergistic effect of Co and Zn on the support. The oxygen content decreased significantly from original

44.87 wt.% in pine sawdust to 15.29 wt.% for upgraded bio-oil [28]. Following the same strategy, Zero-valent aluminium (ZV-Al) and bio-oil aqueous phase were used as hydrogen source in Yang's study [29]. As a result, the degree of deoxygenation of crude bio-oil reached 76.38%. The higher hydrogen yield derived from the reaction of ZV-Al and bio-oil aqueous phase compared to that of ZV-AL and water can be attributed to the aqueous phase reforming reactions in the catalytic reaction system. In summary, HHDO is effective for deoxygenation of bio-feedstocks. However, the cost of H_2 production from Zn and Al mental hydrolysis is higher than the industrial H_2 and the recovery of zero-valent metal is the main challenging for the commercial application of HHDO strategy. The group of Chen [26] proposed a looped-Zn catalysis for metal recycle and bio-oil HDO process, in which the metallic oxide produced from the metal hydrolysis can be recycled by using solar energy. However, the implementation of this concept requires massive investment on the instruments for chemical industry.

Water assisted *in-situ* HDO Process (WHDO)

Water, is the greenest solvent overall [30] and has the potential to provide hydrogen in HDO process. However, very limited attempts have been made in the HDO by using water as hydrogen source. WHDO route is quite challenging due to the limitations impose by water splitting. Jin et.al proposed for the first time this new route for the *in-situ* HDO using water as the hydrogen source [31]. They investigated the HDO of guaiacol in water-only reaction system using noble metal (Au, Pd, Ru and Rh) [31] and non-noble metal (Ni) [32] as catalysts. They achieved remarkable conversion of guaiacol using Ru/C and no external H_2 supply indicating that water is likely to be the main hydrogen donor in this process [31]. However, the reactant can also supply H_2 in this reaction. According to the study of Zhang's group, the mono-aromatic such as phenol and catechol might be produced from the isomerization of guaiacol, the cracking of the side chains and the rearrangement of the functionalities of the guaiacol [33]. Miyagawa et. al [34] investigated the demethoxylation of hydrogenated derivatives of guaiacol in water-only reaction system. Methanol could be formed from hydrolysis reaction of the reactant. In contrast to Jin's study, the hydrogen applied for the HDO process is generated from the dehydrogenation of cyclohexane and methanol reforming.

The proposed WHDO opens a new way for the biomass upgrading process. However, more investigations relating to the H-transfer route are needed to solidify this new concept. The understanding of the WHDO mechanism could inspire the catalysis community to develop effective catalysts for this economically appealing route.
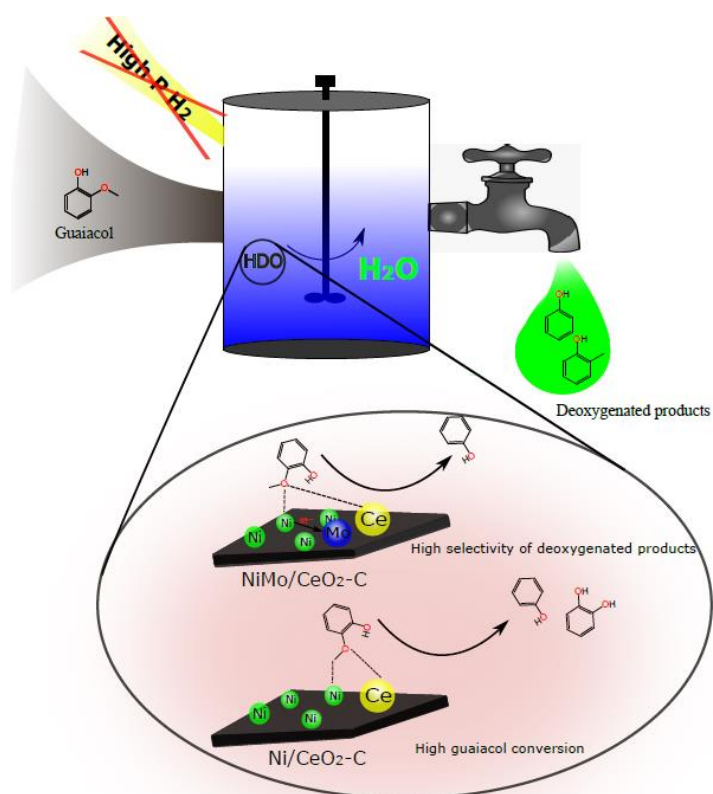
Figure 3. HDO of guaiacol over Ni-based catalyst using water as the H-donor (reprinted from ref.[32]. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

Non-thermal plasma (NTP)

Taghvaei et. al firstly proposed the *in-situ* HDO of bio-oil through NTP technology [35]. The cracking methyl group in the structure of bio-feedstocks could provide hydrogen radicals which is required for HDO reactions. The coaxial cylinder dielectric barrier discharge (DBD) plasma reactor is typically used in bio-oil upgrading process. The investigations of NTP for bio-oil upgrading mainly focus on the optimizing of operation and plasma parameters and the catalyst formula.

The group of Taghvaei did intensive investigations about the HDO of anisole [36], 4-methylanisole [37], guaiacol [38] with *in-situ* hydrogen generation through NTP technology. More recently, they applied the NTP to the upgrading of guaiacol over different Al_2O_3 supported catalyst [39]. Unlike the previous studies in which catechol was the major products, this catalytic system produced high selectivity of aromatic hydrocarbons and phenols. High guaiacol conversion (92%) and deoxygenation degree (65%) were obtained using Pt-Cl/Al_2O_3 and Pt-Re/Al_2O_3 as catalysts, respectively. Fan et. al [40] compared the one-step and two-step plasma-catalytic upgrading of bio-oil to bio-fuel over different HZSM-5 supported catalysts by using DBD plasma reactor. They found that one -step configuration is superior to two-step configuration. The proportion of desired hydrocarbon products reached 68.89% in the bio-oil upgrading process over Ti/HZSM-5 catalyst. Considering the mild reaction condition (ambient temperature and pressure), which could alleviate the catalyst coking, NTP has gain much more attention in the recent few years. Recent progress on the enhancement of the HDO degree makes the NTP technology a comparable approach compared to CTH and WHDO. However, more research about the upgrading of raw bio-oil using NTP is still an open question.
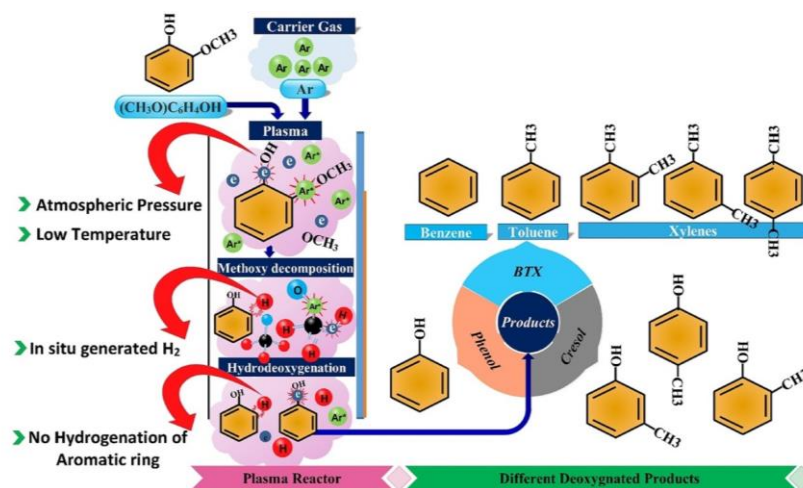
Figure 4. HDO of guaiacol using NTP technology conducted in DBD plasma reactor reproduced from [39].

Self-supported hydrogenolysis (SSH) strategy

Very recently, Meng and co-workers [41] proposed a new strategy, called self-supported hydrogenolysis (SSH), for converting aromatic ethers to arenes without exogenous H_2 and other additional H-donors. The selectivity of an aromatic ether could reach >99.9% at full conversion of the reactant over RuW/SiO_2 bimetallic catalyst. The results of isotope labelling test indicated that the H source in the SSH route is from aliphatic H in methoxy group on the reactant rather than the water solvent. The strategy of SSH open a novel way for the deoxygenation of aromatic ethers to produce arenes without the supply of external H_2 or H-donor solvent.

The typical operation parameters and features of conversional HDO and novel *in-situ* HDO strategies were summarized in Table 1.

Table 1 Conversional HDO and *in-situ* HDO of bio-feedstocks: operation condition and features

	Hydrogen source/mechanism	Typical operation parameters	Pros	Cons
Conversional HDO	H_2	200-400 ºC 40-200 bar	High deoxygenation efficiency	High cost of H_2; Safety concern such as H_2 transportation and storage; Side reactions: hydrogenation of aromatic rings
Catalytic Transfer Hydrogenation/Hydrogenolysis (CTH)	Decomposition or dehydrogenation of H-donors (*e.g.* alcohols, formic acid)	Room temparature-300 ºC Atmospheric pressure -120 bar	Mild reaction condition; Low cost of renewable H-donor; Reduced complexity and cost of the experiment setup; Comparable deoxygenation efficiency	CO_2 production; By-products separation; Low stability of catalysts due to the acidic reaction environment (*i.e.* formic acid as H-donor)

Combined Reforming and HDO Process (RHDO)	Steam reforming or aqueous phase reforming of H-donors (*e.g.* alcohols, methane and glycerol)	200-400 ºC 5-200 bar	Low cost of renewable H-donor; Comparable deoxygenation efficiency Reduced complexity and cost of the experiment setup	CO_2 production; Low stability of catalysts due to the acidic reaction environment (*i.e.* formic acid as H-donor)
Combined Metal Hydrolysis and HDO Process (HHDO)	Hydrolysis of active metal (*e.g.* Al, Zn).	250-400 ºC 50-300 bar	Comparable deoxygenation efficiency	High energy input in terms of the recovery of active metal
Water assisted *in-situ* HDO Process (WHDO)	Water splitting or hydrogen transfer	200-300 ºC 50-100 bar	Low cost and abundance of water; Reduced complexity and cost of the experiment setup	Relatively low deoxygenation ability
Non-thermal plasma (NTP)	Hydrogen radicals produced from cracking of methyl group in reactant	Room temperature; Atmospheric pressure	Mild reaction condition; Alleviated catalyst deactivation	High cost of experimental setup
Self-supported hydrogenolysis (SSH)	Hydrogen production from methoxy group in the reactant	175-300 ºC; 5 bar	High deoxygenation efficiency; No external H-donor needed.	CO_2 production; Reactant restricted to aromatic ethers

Conclusions and Perspectives

This review critically discussed the novel routes for bio-oil and biomass upgrading to produce value-added chemicals and hydrocarbon oils. Overall, the *in-situ* HDO using CTH and RHDO gain more attention of catalysis community considering relatively sound theoretical basis of these technologies. In contrast, NTP is quite promising even though the investigation of its application in the biomass upgrading field is still in the bud. However, it has the potential to upgrade bio-oil in a non-catalytic process. Finding an economic way for the recycling of zero-valent metal is the main challenging for the hop of HHDO to real-world application. It is worth to emphasizing that the most challenging route, WHDO, would pose tremendous impact on bio-refinery industry if it is successfully proved. The SSH strategy can avoid the addition of H-donor and it is quite promising due to the high deoxygenation efficiency. Overall, the future of bio-compounds upgrading will be linked to these novel approaches where inexpensive, highly effective catalysts and a green solvent are used opening new opportunities in the field of low-carbon technologies. However, the application of these novel technologies in raw biomass feedstocks still need further exploration.

Conflict of interest

The authors declare no conflict of interest.

Reference

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

** outstanding interest

[1] L. Hu, L. Lin, Z. Wu, S. Zhou, S. Liu, Recent advances in catalytic transformation of biomass-derived 5-hydroxymethylfurfural into the innovative fuels and chemicals, Renewable and Sustainable Energy Reviews, 74 (2017) 230-257.

[2] W. Jin, L. Pastor-Pérez, D. Shen, A. Sepúlveda-Escribano, S. Gu, T. Ramirez Reina, Catalytic Upgrading of Biomass Model Compounds: Novel Approaches and Lessons Learnt from Traditional Hydrodeoxygenation–a Review, ChemCatChem, 11 (2019) 924-960.

[3] C. Li, X. Zhao, A. Wang, G.W. Huber, T. Zhang, Catalytic transformation of lignin for the production of chemicals and fuels, Chemical reviews, 115 (2015) 11559-11624.

[4] M.l. Besson, P. Gallezot, C. Pinel, Conversion of biomass into chemicals over metal catalysts, Chemical reviews, 114 (2013) 1827-1870.

[5] S. Kim, E.E. Kwon, Y.T. Kim, S. Jung, H.J. Kim, G.W. Huber, J. Lee, Recent advances in hydrodeoxygenation of biomass-derived oxygenates over heterogeneous catalysts, Green Chemistry, 21 (2019) 3715-3743.

*[6] X. Jin, B. Yin, Q. Xia, T. Fang, J. Shen, L. Kuang, C. Yang, Catalytic Transfer Hydrogenation of Biomass-Derived Substrates to Value-Added Chemicals on Dual-Function Catalysts: Opportunities and Challenges, ChemSusChem, 12 (2019) 71-92.
This review discussed recent studies about the catalytic transfer hydrodegation technology for biomass upgrading and pointed out the opportunities and challenges in this field. It also proposed the H transfer route for bimetallic and alloy catalyst in CTH process.

[7] T. Guo, Q. Xia, Y. Shao, X. Liu, Y. Wang, Direct deoxygenation of lignin model compounds into aromatic hydrocarbons through hydrogen transfer reaction, Applied Catalysis A: General, 547 (2017) 30-36.

[8] M.J. Gilkey, B. Xu, Heterogeneous catalytic transfer hydrogenation as an effective pathway in biomass upgrading, ACS catalysis, 6 (2016) 1420-1436.

[9] I.B.D. de Castro, I. Graça, L. Rodríguez-García, M. Kennema, R. Rinaldi, F. Meemken, Elucidating the reactivity of methoxyphenol positional isomers towards hydrogen-transfer reactions by ATR-IR spectroscopy of the liquid–solid interface of RANEY® Ni, Catalysis Science & Technology, 8 (2018) 3107-3114.

[10] M.J. Hidajat, A. Riaz, J. Kim, A two-step approach for producing oxygen-free aromatics from lignin using formic acid as a hydrogen source, Chemical Engineering Journal, 348 (2018) 799-810.

[11] S. Verma, M.N. Nadagouda, R.S. Varma, Visible light-mediated and water-assisted selective hydrodeoxygenation of lignin-derived guaiacol to cyclohexanol, Green Chemistry, 21 (2019) 1253-1257.

[12] D.J. McClelland, P.H. Galebach, A.H. Motagamwala, A.M. Wittrig, S.D. Karlen, J.S. Buchanan, J.A. Dumesic, G.W. Huber, Supercritical methanol depolymerization and hydrodeoxygenation of lignin and biomass over reduced copper porous metal oxides, Green Chemistry, 21 (2019) 2988-3005.

[13] Y.N. Regmi, J.K. Mann, J.R. McBride, J. Tao, C.E. Barnes, N. Labbé, S.C. Chmely, Catalytic transfer hydrogenolysis of organosolv lignin using B-containing FeNi alloyed catalysts, Catalysis Today, 302 (2018) 190-195.

[14] J.-H. Lee, I.-G. Lee, J.-Y. Park, K.-Y. Lee, In-situ upgrading of bio-tar over Mg-Ni-Mo catalyst supported by KOH treated activated charcoal in supercritical ethanol, Fuel, 247 (2019) 334-343.

[15] M. Kim, J.-M. Ha, K.-Y. Lee, J. Jae, Catalytic transfer hydrogenation/hydrogenolysis of guaiacol to cyclohexane over bimetallic RuRe/C catalysts, Catalysis Communications, 86 (2016) 113-118.

[16] A. Philippov, A. Chibiryaev, O. Martyanov, Raney® nickel-catalyzed hydrodeoxygenation and dearomatization under transfer hydrogenation conditions—Reaction pathways of non-phenolic compounds, Catalysis Today, (2019). https://doi.org/10.1016/j.cattod.2019.05.033.

[17] J. Hu, S. Zhang, R. Xiao, X. Jiang, Y. Wang, Y. Sun, P. Lu, Catalytic transfer hydrogenolysis of lignin into monophenols over platinum-rhenium supported on titanium dioxide using isopropanol as in situ hydrogen source, Bioresource technology, 279 (2019) 228-233.

*[18] V.-L. Yfanti, A. Lemonidou, Effect of hydrogen donor on glycerol hydrodeoxygenation to 1, 2-propanediol, Catalysis Today, (2019). https://doi.org/10.1016/j.cattod.2019.04.080.

In this study, the hydrogen production ablility of common hydrogen donor and their performance in glycerol hydrodeoxygenation were extensively investigated.

[19] I.Y. Mohammed, Y.A. Abakr, R. Mokaya, Catalytic Upgrading of Pyrolytic Oil via In-situ Hydrodeoxygenation, Waste and Biomass Valorization, (2019) 1-13.

[20] S. Fernando, D.A. Gunawardena, Deoxygenation of biomass derived oxygenates to hydrocarbons via direct methane intervention, Google Patents, 2017.

[21] S. Liu, M. Tamura, Z. Shen, Y. Zhang, Y. Nakagawa, K. Tomishige, Hydrogenolysis of glycerol with in-situ produced H2 by aqueous-phase reforming of glycerol using Pt-modified Ir-ReOx/SiO2 catalyst, Catalysis Today, 303 (2018) 106-116.

[22] I.C. Freitas, R.L. Manfro, M.M. Souza, Hydrogenolysis of glycerol to propylene glycol in continuous system without hydrogen addition over Cu-Ni catalysts, Applied Catalysis B: Environmental, 220 (2018) 31-41.

[23] J. Remón, P. Arcelus-Arrillaga, L. García, J. Arauzo, Simultaneous production of gaseous and liquid biofuels from the synergetic co-valorisation of bio-oil and crude glycerol in supercritical water, Applied energy, 228 (2018) 2275-2287.

[24] V. Domínguez-Barroso, C. Herrera, M.Á. Larrubia, L.J. Alemany, Coupling of glycerol-APR and in situ hydrodeoxygenation of fatty acid to produce hydrocarbons, Fuel processing technology, 190 (2019) 21-28.

[25] S.B. Ogale, T.V. Venkatesan, M. Blamire, Functional metal oxides: new science and novel applications, John Wiley & Sons2013.

[26] S. Cheng, L. Wei, J. Julson, K. Muthukumarappan, P.R. Kharel, Y. Cao, E. Boakye, D. Raynie, Z. Gu, Hydrodeoxygenation upgrading of pine sawdust bio-oil using zinc metal with zero valency, Journal of the Taiwan Institute of Chemical Engineers, 74 (2017) 146-153.

[27] S. Cheng, L. Wei, M.R. Alsowij, F. Corbin, J. Julson, E. Boakye, D. Raynie, In situ hydrodeoxygenation upgrading of pine sawdust bio-oil to hydrocarbon biofuel using Pd/C catalyst, Journal of the Energy Institute, 91 (2018) 163-171.

*[28] S. Cheng, L. Wei, M. Rabnawaz, Catalytic liquefaction of pine sawdust and in-situ hydrogenation of bio-crude over bifunctional Co-Zn/HZSM-5 catalysts, Fuel, 223 (2018) 252-260.

This paper first investigated the catalytic liquefaction of biomass and bio-oil upgarding over non-noble catalyst using metal hydrolysis as hydrogen source.

[29] T. Yang, L. Shi, R. Li, B. Li, X. Kai, Hydrodeoxygenation of crude bio-oil in situ in the bio-oil aqueous phase with addition of zero-valent aluminum, Fuel processing technology, 184 (2019) 65-72.

[30] F. Zhou, Z. Hearne, C.-J. Li, Water–the greenest solvent overall, Current Opinion in Green and Sustainable Chemistry, 18 (2019) 118-123.

**[31] W. Jin, J.L. Santos, L. Pastor-Perez, S. Gu, M.A. Centeno, T.R. Reina, Noble metal supported on activated carbon for "hydrogen free" HDO reactions: exploring economically advantageous routes for biomass valorisation, ChemCatChem, (2019). https://doi.org/10.1002/cctc.201900841.

This is the first study to combine water splitting and hydrodeoxygenation of bio-oil model compounds.

[32] W. Jin, L. Pastor-Perez, J.J. Villora-Picó, A. Sepúlveda-Escribano, S. Gu, T. Reina, Investigating New Routes for Biomass Upgrading:"H2-Free" Hydrodeoxygenation Using Ni-Based Catalysts, ACS Sustainable Chemistry & Engineering, (2019). https://doi.org/10.1021/acssuschemeng.9b02712.

[33] Z. Zhang, X. Hu, L. Zhang, Y. Yang, Q. Li, H. Fan, Q. Liu, T. Wei, C.-Z. Li, Steam reforming of guaiacol over Ni/Al2O3 and Ni/SBA-15: Impacts of support on catalytic behaviors of nickel and properties of coke, Fuel Processing Technology, 191 (2019) 138-151.

[34] A. Miyagawa, Y. Nakagawa, M. Tamura, K. Tomishige, Demethoxylation of hydrogenated derivatives of guaiacol without external hydrogen over platinum catalyst, Molecular Catalysis, 471 (2019) 60-70.

[35] H. Taghvaei, M. Kheirollahivash, M. Ghasemi, P. Rostami, B.C. Gates, M.R. Rahimpour, Upgrading of anisole in a dielectric barrier discharge plasma reactor, Energy & Fuels, 28 (2014) 4545-4553.

[36] H. Taghvaei, M. Kheirollahivash, M. Ghasemi, P. Rostami, M.R. Rahimpour, Noncatalytic upgrading of anisole in an atmospheric DBD plasma reactor: effect of carrier gas type, voltage, and frequency, Energy & Fuels, 28 (2014) 2535-2543.

[37] A. Mosallanejad, H. Taghvaei, S.M. Mirsoleimani-azizi, A. Mohammadi, M.R. Rahimpour, Plasma upgrading of 4methylanisole: A novel approach for hydrodeoxygenation of bio oil without using a hydrogen source, Chemical Engineering Research and Design, 121 (2017) 113-124.

[38] H. Taghvaei, M.R. Rahimpour, Plasma upgrading of guaiacol as lignin pyrolytic-oil model compound through a combination of hydrogen production and hydrodeoxygenation reaction, Journal of analytical and applied pyrolysis, 135 (2018) 422-430.

[39] H. Taghvaei, M.R. Rahimpour, Catalytic hydrodeoxygenation of bio-oil using in situ generated hydrogen in plasma reactor: Effects of allumina supported catalysts and plasma parameters, Process Safety and Environmental Protection, 121 (2019) 221-228.

*[40] Y. Fan, Y. Xiong, L. Zhu, L. Fan, L. Jin, Y. Chen, W. Zhao, Comparison of the one-step and two-step plasma-catalytic upgrading of biomass pyrolysis volatiles to bio-fuel, Chemical Engineering and Processing-Process Intensification, 135 (2019) 53-62.

This study compared the one-step and two step bio-oil upgrading via plasma technology. High yield of hydrocarbon products was obtained in one-step configuration.

** [41] Q.L. Meng, J. Yan, H.Z. Liu, C.J. Chen, S.P. Li, X.J. Shen, J.L. Song, L.R. Zheng, B.X. Han, Self-supported hydrogenolysis of aromatic ethers to arenes, Science advances, 5 (2019) eaax6839.

This study first proposed the SSH stratagy to convert aromatic ethers to arenes. High deoxygenation efficiency of reactant was achieved without the supply of H_2 and H-donor solvent.