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Steam Reforming of Biomass Pyrolysis Oil: A Review

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Abstract:

The steam reforming of biomass pyrolysis oil is a well-established means of producing the more useful bio-hydrogen. Bio-oil has a comparatively low heating value, incomplete volatility and acidity, hence upgrading to a more useful product is required. Over the years, the experimental conditions of the process have been studied extensively in the domain of catalysis and process variable optimisation. Sorption enhancement is now being applied to the system to improve the purity of the hydrogen stream. Lifecycle analyses has revealed that bio-hydrogen offers considerable reductions in energy consumption compared to fossil fuel-derived hydrogen. Also, green-house-gas savings from the process can also be as high as 54.5%. Unfortunately, techno-economic analyses have elucidated that bio-hydrogen production is still hampered by high production costs. Research endeavours in steam reforming of biomass bio-oil is done with an eye for developing added value products that can complement, substitute (and one day replace) fossil fuels whilst ameliorating the global warming menace.

Keywords: steam reforming, catalyst, biomass, pyrolysis, bio-oil, review

DOI: 10.1515/ijcre-2018-0328

Received: December 20, 2018; **Revised:** February 9, 2019; **Accepted:** March 26, 2019

1 Introduction

The steady rise in fuel consumption with global technological advancement will likely double its current figure before 2050 (Bulushev and Ross 2011). Increasing emissions of greenhouse gases (mainly CO₂) from fossil fuel use is also inducing global warming (Sarkar and Kumar 2010). This has led to the search for alternative and renewable energy sources. Novel techniques of energy recovery to decrease the total global greenhouse gas emissions and combat the impending energy crisis are being investigated: thus resulting in an increasing interest in biofuels (Van Rossum, Kersten, and van Swaaij 2007). Biofuels are produced from biomass sources (Bulushev and Ross 2011). The so-called "First Generation" technologies (edible feedstock) are no longer used. The "Second Generation" technologies for the production of fuels allow the use of a wide range of non-food "cellulosic" biomass feedstock such as agricultural residues, wastes and specially grown energy crops (Bulushev and Ross 2011). Biomass is considered 'clean' for energy recovery because it has negligible content of Sulphur, nitrogen and ash (Zhang et al. 2007b).

Biomass is as hydrocarbon materials consisting mainly of carbon, hydrogen and oxygen (Yaman 2004). It consists of mainly three main polymers; hemicellulose, cellulose and lignin (Demirbas and Balat 2007; Qu et al. 2011). These three essential components form an insoluble three-dimensional network with a sophisticated architecture (Meier and Faix 1999). As presented by Pettersen (1984), components of wood includes: cellulose (Cross and Bevan, holo-, and alpha-), lignin, pentosans, and ash each possessing different thermal behaviours (Asmadi, Kawamoto, and Saka 2011; Collard and Blin 2014). Thermochemical energy conversion processes have been shown to be a viable technique of valorising and exploiting the energetic component of biomass (Arregi et al. 2018).

Over the years, scientific studies have been conducted on the production of bio-oil via pyrolysis of renewable feedstock such as agricultural wastes; bananas residues (Abdullah, Sulaiman, and Taib 2013; Abdullah et al. 2015; Adeniyi, Ighalo, and Amosa 2019; Cheng et al. 2016; Manocha, Bhagat, and Manocha 2001; Navarro-Mtz, Urzua-Valenzuela, and Morelos-Pedro 2017), plantains residues (Abdullah, Sulaiman, and Taib 2013; Ogunjobi and Lajide 2015; Quame 1983) orange residues (Aguilar et al. 2008), maize residues (Encinar et al. 1997; Fu et al. 2009; He et al. 2002; Ioannidou et al. 2009; Jiang and Morey 1992; Naidoo 2018; Trninić 2015; Uzun and Sarioğlu 2009; Wang et al. 2015b; Zabaniotou and Ioannidou 2008; Zheng 2008), rice residues (Ganesh and

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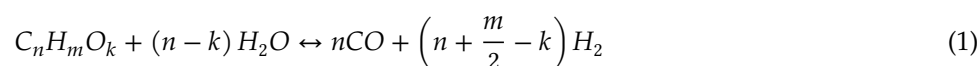
Grover 1992; Ji-Lu 2007; Sharma and Rao 1999; Tsai, Lee, and Chang 2006, 2007), sugar cane residues (Aboyade et al. 2011; Carrier et al. 2012, 2011; Darmstadt et al. 2001; Drummond and Drummond 1996; García-Pérez, Chaala, and Roy 2002; Mancera et al. 2010; Tsai, Lee, and Chang 2006), cassava residues (Farrow, Eterigho, and Snape 2018; Ismadjia et al. 2012; Ki et al. 2013; Moreno-Piraján and Giraldo 2010), and other non-agricultural wastes (Adeniyi, Adewoye, and Ighalo 2018; Adeniyi, Eletta, and Ighalo 2018; Alves and Figueiredo 1989; Encinar et al. 1997; Garcia-Perez et al. 2007; Müller-Hagedorn et al. 2003; Onarheim, Solantausta, and Lehto 2014; Peters and Bruch 2003; Sørum, Grønli, and Hustad 2001). A major product of this process is biomass bio-oil.

Bio-oil is also referred to as pyrolysis oil, bio-fuel oil, pyrolytic oil and liquid wood (Isahak et al. 2012). It is a dark brown organic liquid containing hundreds of organic compounds that belong to alkanes, aromatic hydrocarbons, phenol derivatives and little amounts of ketones, esters, ethers, sugars, amines, alcohols (Isahak et al. 2012) and pyrolytic water. Though much work has been done in improving the biomass pyrolysis bio-oil properties via catalysis (Zarnegar 2018), the presence of water and the diversity of oxygenated organic compounds present in it has hampered its effectiveness in most applications (Chattanathan, Adhikari, and Abdoulmoumine 2012; Trane et al. 2012). The unfavourable properties include low heating value, incomplete volatility and acidity (French and Czernik 2010). Due to these undesirable properties, there is a need to explore alternative techniques of utilising or upgrading the pyrolysis oil to obtain added-value products. The current technologies available for pyrolysis oil upgrading include hydro-deoxygenation, catalytic cracking, emulsification, steam reforming, molecular distillation, esterification and extraction of chemicals from the oil (Gollakota et al. 2016; Trane et al. 2012; Valle et al. 2007; Wildschut et al. 2009; Zhang et al. 2013a; Zhang et al. 2007a). In this review, steam reforming technology was considered.

Hydrogen production from biomass bio-oil can be by steam reforming, partial oxidation, auto-thermal reforming, aqueous phase reforming, super-critical-water reforming, auto-thermal reforming and sequential cracking (Chattanathan, Adhikari, and Abdoulmoumine 2012; Trane et al. 2012). Hydrogen fuel is light, highly flammable, carbon-neutral and possess a very high heating value (Chattanathan, Adhikari, and Abdoulmoumine 2012). It is expected to be the most important energy carrier in a sustainable energy system of future society (Shen, Gao, and Xiao 2008). Over the years, a number of research work has been conducted to study the steam reforming of biomass bio-oil (Chen, Wu, and Liu 2011; Czernik, Evans, and French 2007; Czernik et al. 2002; Kechagiopoulos et al. 2006; Marquovich et al. 1999; Van Rossum, Kersten, and van Swaaij 2007, 2009; Wang, Czernik, and Chornet 1998). They have been from stand-points of catalysis (Remón et al. 2014), novel process design (Bleeker et al. 2010), process optimisation (Goyal, Pant, and Gupta 2013; Remiro et al. 2013a), thermodynamic analysis (Goyal, Pant, and Gupta 2013; Vagia and Lemonidou 2007, 2008; Wang et al. 1997; Xie et al. 2014), techno-economic analysis (Sarkar and Kumar 2010), lifecycle analysis (Heracleous 2011), sorption enhancement (Iordanidis et al. 2006; Xie et al. 2014, 2016), carbon deposition behaviour (Wu and Liu 2010), pyrolysis-steam reforming integration (Arregi et al. 2016; Neumann et al. 2015; Wang et al. 1997; Zhao et al. 2010) and computer simulations (Iordanidis et al. 2006; Kinoshita and Turn 2003; Montero et al. 2015; Peters, Iribarren, and Dufour 2015; Vagia and Lemonidou 2007, 2008; Wright et al. 2010; Zhang et al. 2013b). In view of all these, the current state of knowledge on the steam reforming of biomass pyrolysis oil is herein summarised and catalogue progress made in recent years.

2 Steam reforming theory

The stoichiometry of steam reforming reactions is well understood. The general expressions for the equation of reaction of the steam reforming of any oxygenated organic compound was presented by Czernik et al. (2002) as expressed in eq. (1).



Due to excess steam in the process, the carbon monoxide is oxidised to carbon dioxide leading to the evolution of more hydrogen gas. This is known as the water-gas shift reaction (in eq. (2))



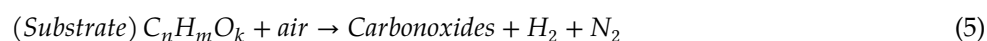
At low temperatures, methanation can occur whereby some of the hydrogen produced recombines with carbon monoxide to give methane in eq. (3).



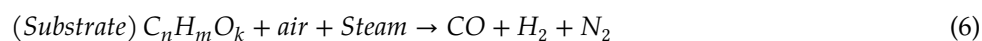
This reaction is exothermic hence will be favoured at low temperatures. On the other hand, steam reforming reactions are endothermic and favoured by higher temperatures (Adeniyi and Ighalo 2018). Similarly, higher molecular weight hydrocarbons can be synthesised during the process especially at low temperatures and for heavier feeds. At high temperatures, coke formation occurs in the system and can lead to depositions on the catalyst surface and subsequent inactivation (eq. (4)).



There are other processes similar to steam reforming. In partial oxidation, the substrate is oxidized with oxygen (in the presence or in the absence of catalyst), resulting in high temperature which in turn balances the energy required for the process (Chattanathan, Adhikari, and Abdoulmoumine 2012).



Auto-thermal reforming is a combination of steam reforming and partial oxidation techniques in which the substrate is reformed in the presence of air and water to produce Hydrogen (Chattanathan, Adhikari, and Abdoulmoumine 2012).



In super critical steam reforming, the steam used is at supercritical conditions. Water when heated and compressed to its critical temperature (374 °C) and pressure (22.1 MPa) becomes supercritical water (Chattanathan, Adhikari, and Abdoulmoumine 2012). Supercritical water possesses characteristics of both liquid water and vapour which includes densities, viscosities, high diffusivity and good transporting properties. For sequential cracking, it involves a two-step process in which the bio-oil is first catalytically cracked/reformed without addition of water followed by subsequent regeneration of the catalyst with oxygen (Chattanathan, Adhikari, and Abdoulmoumine 2012; Davidian et al. 2007; Iojoiu et al. 2007), as presented in eq. (7) and eq. (8).

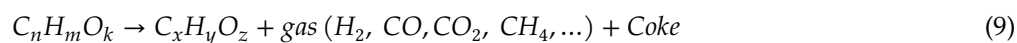
Cracking;



Regeneration;



The organic compounds present in the bio-oil are thermally unstable at the very high temperatures of steam reforming hence while thermally decompose in the system. The steam reforming then has to compete with the cracking reactions. A general form of the thermal decomposition reaction is expressed in eq. (9):



The aqueous fraction of biomass bio-oil is a complex mixture of numerous oxygenated organic compounds and specifying exact reaction stoichiometry to represent its steam reforming process will be impossible. However, for the purpose of research, the major components have been elucidated by researchers so that the bio-oil can be simulated and used in experimental studies (Table 1). This has been an acceptable practice for quite a while (Marquevich et al. 1999; Wang, Montane, and Chornet 1996). The aqueous fraction of biomass bio-oil (Table 2) contains compounds like acetic acid (C₂H₄O₂), acetone (C₃H₆O), acetaldehyde (C₂H₄O), ethylene glycol (C₂H₆O₂), formic acid (CH₂O₂), methanol (CH₄O), formaldehyde (CH₂O), ethanol (C₂H₆O) among others. Of all components in the aqueous fraction, acetic acid usually possesses the highest proportion and has been more keenly studied than the others (Chen et al. 2017). The aqueous fraction can be obtained by adding water to the crude bio-oil, agitating, then carrying out a simple phase separation. Although it may not be necessary or desirable in large scale application, addition of methanol stabilizes bio-oil, reduces viscosity, and facilitates atomization (Rennard et al. 2010).

Table 1: Characteristics of biomass bio-oil and its aqueous fraction (Bimbela et al. 2013).

Bio-Oil	Aqueous Fraction
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pH	2.6	2.5
H ₂ O content (wt%)	36	84
Ultimate Analysis (wt%)		
C	36.07	7.35
H	8.45	10.82
N	0.11	0.00
O ^a	55.37	81.83

^a determined by difference

Table 2: Typical composition of raw bio-oil from pine (*Pinus insignis*) sawdust (Valle et al. 2007).

Component	Amount (wt%)
Acetic acid	15.33
Acetone	5.29
Phenols	6.70
Alcohols	12.34
Ethers	0.84
Levogluconan	3.94
Hydroxyacetaldehyde	10.58
Other ketones	21.74
Other acids and esters	10.84
Other Aldehydes	9.59
Others	1.35
Unidentified	1.43

3 Experimental conditions

The key experimental conditions that affect the steam reforming reaction of biomass bio-oil are temperature, pressure, time, type of catalyst used and the quantity of steam feed. The quantity of steam feed is usually represented as a mass or molar ratio of the steam to the bio-oil feed. In certain cases, CO₂ sorption is included in the process to clean the product steam of the non-combustible by-product. In certain studies, model compounds are used to represent the bio-oil. Model compounds are those compounds that appear in high proportion in the bio-oil and can be study alone. The results are then use to understand and make projections on the actual bio-oil steam reforming process. Catalysis in most cases is not studied under the index of conversion but of hydrogen selectivity. The key parameter is hydrogen gas selectivity (eq. (10)). It is the percentage (%) molar or mass composition of hydrogen in the product stream.

$$\% X \text{ Selectivity} = \frac{\text{amount of } X}{\text{Total amount of syn - gas (dry basis)}} \times 100\% \quad (10)$$

$$\% X \text{ Yield} = \frac{\text{amount of } X}{\text{Total amount of feed}} \times 100\% \quad (11)$$

Where X can be hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄) or any other chemical species present in the product stream. The 'amount' can be in moles or grams depending on the basis of calculations. Hence we have percentage molar selectivity, percentage molar yield, percentage mass selectivity and percentage mass yield. The selectivity of a chemical species in the product stream is in relation to the other competing species is while the yield is a reflection of the outcome based on the amount of feed.

$$S/C = \frac{\text{amount of Steam}}{\text{Total amount of Carbon in the feed (wet basis)}} \quad (12)$$

The steam to carbon ratio (S/C) in mass or moles can be defined as the ration of the amount of steam to the total amount of carbon in the feedstock (including the water content).

3.1 Catalysis of pyrolysis oil steam reforming

Catalyst development is a keenly studied aspect of biomass bio-oil steam reforming. The catalyst are usually noble and transition metals co-precipitated together or impregnated on metal oxides and ores. Among catalyst developed are Ni/La₂O₃- α -Al₂O₃ (Basagiannis and Verykios 2006; Remiro et al. 2013a, 2013b; Valle et al. 2013), Ce-Ni/Co (Xie et al. 2015), Ni (Arregi et al. 2016; Chen, Wu, and Liu 2011; Davidian et al. 2007), Ru/MgO/Al₂O₃ (Basagiannis and Verykios 2007b), co-precipitated Ni/Al modified with Mg and Cu (Bimbela et al. 2012), Ni/Al (Bimbela et al. 2013; Galdámez, García, and Bilbao 2005; Hu, Zhang, and Lu 2012), cobalt promoted nickel and chromium-promoted nickel supported on MgO-La₂O₃- α -Al₂O₃ (Garcia et al. 2000), Pt/Al₂O₃ (Czernik and French 2014), Ni-K/La₂O₃-Al₂O₃ (Davidian et al. 2007), Ni/ZrO₂ (Li et al. 2012a), Ni/Al₂O₃ (Davidian et al. 2007; Goicoechea et al. 2016; Goyal, Pant, and Gupta 2013; Lea-Langton et al. 2012; Valle et al. 2013), Ni-CNT (Hou et al. 2009), Ni/Olivine (Kechagiopoulos et al. 2009), Ni-K-Ca-Mg/Alumina (Magrini-Bair et al. 2002), Ni-Co/Al-Mg (Remón et al. 2014, 2015), Rh-Ce (Rennard et al. 2010), Pt-Pd-Rh/Alumina (Rioche et al. 2005), Pt-Pd-Rh/ceria-zirconia (Rioche et al. 2005), Ni/MgO (Wu et al. 2008; Ceng Wu and Liu 2010; Xu et al. 2010), Ni/cordierite (Zhao et al. 2010), Ni/CeO₂-ZrO₂ (Yan, Cheng, and Hu 2010), zeolite (Vispute et al. 2010; Wang et al. 2013) among others. Table 3 presents a summary of catalyst and process parameters for bio-oil steam reforming.

Table 3: Summary of catalysts and process parameters.

Oil Type (Source)	Catalyst	Process parameters				Reference
		Temperature	Pressure	Steam/Carbon molar ratio	Space Time or velocity ⁺	
Bio-oil (Poplar wood)	Ni-Cr ₂ O ₃ -MgO/La ₂ O ₃ -Al ₂ O ₃	700 °C	1 atm	5-35	760-1110 ⁺ hr ⁻¹	Wang, Czernik, and Chornet (1998)
Model compounds (Acetic acid, xylose-sucrose-glucose, m-cresol-dibenzyl ether)	Ni	550-810 °C	1.5-2 bars	3-6	500-11,790 ⁺ hr ⁻¹	Marquevich et al. (1999)
Bio-oil (Pine sawdust)	Ni	800-850 °C	1 atm	7-9	770-1440 ⁺ hr ⁻¹	Czernik et al. (2002)
Bio-oil (Pine wood)	Ni-Mg-K/Al ₂ O ₃	750 °C	-	-	-	Magrini-Bair et al. (2002)
Model compound (Acetic acid)	Pt/ZrO ₂	452 °C	0.1 mbar	5	160,000 ⁺ hr ⁻¹	Takanabe et al. (2004)
Model compound (Acetic acid)	Ni/Al	450-700 °C	-	5.8	62,185-13,061 ⁺ hr ⁻¹	Galdámez, García, and Bilbao (2005)
Model compounds (Acetic acid, phenol, acetone, ethanol)	Pt-Pd-Rh/ceria-zirconia	740-860 °C	-	2-100	43-3090 ⁺ hr ⁻¹	Rioche et al. (2005)
Model compound (Acetic acid)	Pt/ZrO ₂	602 °C	1.7-2.5 kpa	5	320,000-1,600,000 ⁺ hr ⁻¹	Takanabe et al. (2006b)
Model compound (Acetic acid)	Pt/ZrO ₂	502 °C	1.7-2.5 kpa	5	40,000-160,000 ⁺ hr ⁻¹	Takanabe et al. (2006a)
Model compound (Acetic acid)	Fe-Co	250-550 °C	1 atm	2.5-7.5	3.3-9 ⁺ hr ⁻¹	Hu and Lu (2006)
Bio-oil (Beech wood), Model compounds (Acetic acid-acetone-ethylene glycol)	NiO-K ₂ O/CaAl ₂ O ₄	300-1000 °C	1 barg	4-6	300-600, 1500 ⁺ hr ⁻¹	Kechagiopoulos et al. (2006)
Model compound (Acetic acid)	Ni-Co	250-550 °C	1 atm	2.5-7.5	5.1 ⁺ hr ⁻¹	Hu and Lu (2007)
Model compound (Acetic acid)	Ni-Al	550-750 °C	1 atm	5.58	5.81 g _{cat} /min/g _{bio-oil}	Bimbela et al. (2007)
Bio-oil (<i>Pinus insignis</i> sawdust)	HZSM-5 Zeolite (Si/Al = 30)	200-550 °C	-	-	0.12 g _{cat} /h/g _{oxygenates}	Valle et al. (2007)
Model compound (Acetic acid)	Ru/MgO/Al ₂ O ₃	550-800 °C	1 atm	7.2	4880-16,570 ⁺ hr ⁻¹	Basagiannis and Verykios (2007a)

Model compound (Acetic acid)	Rh/Al ₂ O ₃ , Pt/Al ₂ O ₃ , Pd/Al ₂ O ₃ , Ru/Al ₂ O ₃ , Ni/Al ₂ O ₃ , Ru/La ₂ O ₃ /Al ₂ O ₃ , Ru/MgO/Al ₂ O ₃ , Ru/CeO ₂ /Al ₂ O ₃ , Ni/(La ₂ O ₃ /Al ₂ O ₃), Ni/(MgO/Al ₂ O ₃)	550–950 °C	1 atm	3 (steam to feed molar ratio)	–	Basagiannis and Verykios (2007a)
Bio-oil (Beech wood)	Ni/Al ₂ O ₃ and Ni-K/La ₂ O ₃ -Al ₂ O ₃	680–760 °C	–	–	–	Davidian et al. (2007)
Bio-oil (hard wood)	Ni	850 °C	–	5.8	920 ⁺ hr ⁻¹	Czermik, Evans, and French (2007)
Bio-oil (Beech wood chips, pine wood chips)	Ni-K/La-Al ₂ O ₃	523–914 °C	0.1 barg	3.1–3.3	–	Van Rossum, Kersten, and van Swaaij (2007)
Model compound (Acetic acid)	Ni/Al	750 °C	1 atm	5.58	6 $g_{cat}min/g_{bio-oil}$	Medrano et al. (2008)
Model compound (Acetic acid)	Pt/C	320 °C	–	–	–	Güell et al. (2008)
Model compound (Acetic acid)	Co/Al ₂ O ₃ , Co-K/Al ₂ O ₃	300–600 °C	1 atm	7.5	10.1 ⁺ hr ⁻¹	Hu and Lu (2008)
Model compound (Acetic acid)	MgO/Al ₂ O ₃ , Ru/Al ₂ O ₃ , Ru/MgO/Al ₂ O ₃	50–800 °C	≈10 ⁻⁷ mbar	3 (steam to feed molar ratio)	–	Basagiannis and Verykios (2008)
Bio-oil (Sawdust)	NiO/MgO	700–900 °C	1 atm	1–16	0.5–5 ⁺ hr ⁻¹	Wu et al. (2008)
Model compound (Acetic acid)	Ni/Al ₂ O ₃ , Ru/Al ₂ O ₃	400–450 °C	1.5–2.5 bar	10 (steam to feed molar ratio)	–	Basile et al. (2008)
Model compound (Acetic acid)	Ni/Al ₂ O ₃	400 °C	1.5–3.5 bar	10 (steam to feed molar ratio)	–	Iulianelli, Longo, and Basile (2008)
Model compound (Acetic acid)	Ni-M/Al ₂ O ₃ (where M = Li, Na, K, Mg, Fe, Co, Zn, Zr, La and Ce)	0–800 °C	1 atm	1.5–7.5	10.1 ⁺ hr ⁻¹	Hu and Lu (2009a)
Model compounds (Acetic acid, ethylene glycol, acetone, ethyl acetate, m-xylene, glucose)	Ni/Al ₂ O ₃	300–800 °C	1 atm	1–9	12.1 ⁺ hr ⁻¹	Hu and Lu (2009b)
Bio-oil (Beech wood chips, pine wood chips, light sugar waste, heavy sugar waste)	NiO/Al ₂ O ₃	650–850 °C	1 atm	1.6–2.7	50–130 ⁺ hr ⁻¹	Van Rossum, Kersten, and van Swaaij (2009)
Bio-oil (Wood sawdust, rice husk, cotton stalk)	Ni-CNT(Carbon nano-tubes)	350–550 °C	1 atm	2.0–6.1	12,000 ⁺ hr ⁻¹	Hou et al. (2009)
Model compounds (Acetic acid, ethylene glycol)	Ni/Olivine	650–850 °C	1 barg	0–4.6	0.03 – 0.15 $g_{cat}min/cm^3$	Kechagiopoulos et al. (2009)
Model compounds (Ethanol, acetic acid)	Ni-Zn-Al	300–580 °C	–	3–5.5	–	Barattini et al. (2009)
Model compound (Acetic acid)	Ni/Al ₂ O ₃	300–600 °C	1 atm	5.8	5820–11,600 ⁺ hr ⁻¹	Chen et al. (2009a)
Model compound (Acetic acid)	Pt/Al ₂ O ₃ , Pt/SM(Ni), SM(Ni) (SM = Smectite)	200–800 °C	1 atm	–	–	Iwasa et al. (2010)
Bio-oil (Rice husk)	Ni/MgO	500–800 °C	1 atm	8–20	0.2–0.8 ⁺ hr ⁻¹	Xu et al. (2010)

Bio-oil (Pine wood)	Ni/Al	600–800 °C	1 atm	5.58	9,700–57,000 ⁺ hr ⁻¹	Bimbela et al. (2013)
Bio-oil (Pine sawdust)	Ni/La ₂ O ₃ -αAl ₂ O ₃	500–800 °C	1 atm	12	0.10 –	Remiro et al. (2013a)
Bio-oil (Pine sawdust)	Ni/La ₂ O ₃ -αAl ₂ O ₃	600–800 °C	1 atm	9	0.45 $\frac{h}{g_{cat}}$ / $\frac{h}{g_{bio-oil}}$ 80,000–156,000 ⁺ hr ⁻¹	Remiro et al. (2013b)
Model compound (Acetic acid)	Ni/ZrO ₂ -CeO ₂	550–800 °C	1 atm	3 (steam to feed molar ratio)	–	Hu et al. (2013)
Model compound (Acetic acid)	Ni-Co, Ni-Co/CeO ₂ /ZrO ₂ , Ni/La ₂ O ₃ /Al ₂ O ₃	550–700 °C	1 atm	15–25 wt% Acetic acid in water	28 – 80 $g_{cat} h/mol$	Pant et al. (2013)
Bio-oil (Pine sawdust)	Ni-Mo/Sepiolite	700–800 °C	1 atm	16–18	–	Liu et al. (2013)
Model compounds (Acetic acid, phenol, hydroxyl-acetone)	Ni/γ-Al ₂ O ₃ , Ni/nano-Al ₂ O ₃	500–800 °C	1 atm	1–9.2	3–6 ⁺ hr ⁻¹	Wang et al. (2014)
Bio-oil (Oak, Poplar, Pine)	Pt/Al ₂ O ₃	800–850 °C	1 atm	2.8–4.0	2000 ⁺ hr ⁻¹	Czernik and French (2014)
Bio-oil (Pine sawdust)	Ni-Co/Al-Mg	650 °C (catalytic), 1400 °C (non-catalytic)	1 atm	7.6	4 $g_{cat} min/g_{organics}$	Remón et al. (2014)
Model compound (Acetic acid)	Ni-Co/La ₂ O ₃	500–700 °C	1 atm	–	–	Abdullah et al. (2014)
Model compound (Acetic acid)	Ru-CNT(Carbon nano-tubes)	195–740 °C	225–250 bars	25 wt% Acetic acid in super-critical water	18–448 ⁺ hr ⁻¹	De Vlieger, Lefferts, and Seshan (2014)
Model compound (Acetic acid)	Pd/Ni-Co	475–625 °C	1 atm	3	0.89–17.86 ⁺ hr ⁻¹	Fermoso et al. (2014)
Model compound (Acetic acid)	Ni/MgO/γ-Al ₂ O ₃	500–600 °C	–	2 (steam to feed molar ratio)	–	Nogueira et al. (2014)
Model compounds (Acetic acid-ethanol)	Ru/TiO ₂	200 °C	2.5–3.0 Mpa	10 vol% ethanol, 1 vol% acetic acid in water	–	Nozawa et al. (2014)
Model compound (Acetic acid)	Ni-Co/MgO	600 °C	1 atm	4	3.8 $\frac{g_{acid}}{g_{cat} h}$	Zhang et al. (2014)
Model compound (Acetic acid)	Ni-Fe/Ash	700 °C	–	9.2	4 ⁺ hr ⁻¹	Wang et al. (2015a)
Model compound (Acetic acid)	Ni/ceria-zirconia	100–700 °C	1 atm	5, 14	25.2 ⁺ hr ⁻¹	Hoang et al. (2015)
Bio-oil (Pine sawdust, poplar sawdust)	Ni-Co/Al-Mg	650 °C	1 atm	7.6	–	Remón et al. (2015)
Model compounds (Ethanol, acetic acid, acetone, phenol)	Ce-Ni/Co/Al ₂ O ₃	550–750 °C	–	3–15	0.17–0.68 ⁺ hr ⁻¹	Xie et al. (2015)
Model compound (Acetic acid)	LaNiO ₃ , LaPrNiO ₃ and LaSmNiO ₃	600 °C	1 atm	3 (steam to feed molar ratio)	–	Resende et al. (2015)
Bio-oil (Pine wood)	Ni	550–700 °C	–	2–5 (Steam to biomass ratio)	2.5 –	Arregi et al. (2016)
Bio-oil (Corn Cob)	Ce-Ni/Co/Al ₂ O ₃	600–850 °C	–	9–15	30 $\frac{g_{cat} min}{g_{volatiles}}$	Xie et al. (2016)
Model compound (Acetic acid)	Ru/Mg(Al)O, Rh/Mg(Al)O	700 °C	1 atm	3 (steam to feed molar ratio)	0.08–0.23 ⁺ hr ⁻¹ 6–12 ⁺ hr ⁻¹	Bossola et al. (2016)

Model compounds (Acetic acid-acetone)	Pd/Ni-Co	475–725 °C	1 atm	3–5	0.4423–0.8929 ⁺ hr ⁻¹	Esteban-Díez et al. (2016)
Model compound (Acetic acid)	Pd/Ni-Co	400–900 °C	1–15 atm	0.5–3.5	0.89–2.7 ⁺ hr ⁻¹	Gil et al. (2016)
Model compound (Acetic acid)	Ni-Co/La ₂ O ₃	500–700 °C	1 atm	7.5	5.1 ⁺ hr ⁻¹	Nabgan et al. (2016b)
Model compounds (Acetic acid-phenol)	Ni-Co/ γ -Al ₂ O ₃ -La ₂ O ₃	600–800 °C	1 atm	7.5	5.1 ⁺ hr ⁻¹	Nabgan et al. (2016a)
Model compound (Acetic acid)	NiO/MgO	550–650 °C	1 atm	4–8	–	Yang et al. (2016)
Model compound (Acetic acid)	Ni/La ₂ O ₃ , Co/La ₂ O ₃ , Ni/ γ -Al ₂ O ₃ , Co/ γ -Al ₂ O ₃	500–700 °C	–	1–5	10 ⁺ hr ⁻¹	Zhang et al. (2016)
Bio-oil (Pine sawdust)	La ₂ O ₃ / α -Al ₂ O ₃ , CeO ₂ , CeO ₂ -ZrO ₂	700 °C	1 atm	6	0.3 $\frac{g_{cat}h}{g_{bio-oil}}$	Arandia et al. (2018)
Bio-oil (Pine sawdust)	Ni/Al ₂ O ₃ , Ni/CeO ₂ -Al ₂ O ₃ , Ni/La ₂ O ₃ -Al ₂ O ₃ , Pd-Ni/CeO ₂ -Al ₂ O ₃ , Pt-Ni/CeO ₂ -Al ₂ O ₃ , Rh-Ni/CeO ₂ -Al ₂ O ₃	700–800 °C	1 atm	5	1.45 $\frac{g_{cat}h}{g_{bio-oil}}$	Bizkarra et al. (2018)
Bio-oil (Pine sawdust)	Co-Fe/ZSM-5	500–900 °C	–	10–14	10 $\frac{g_{bio-oil}}{h}$	Chen et al. (2018)
Bio-oil (Pine sawdust)	Ni/La ₂ O ₃ -Al ₂ O ₃	550–700 °C	–	1.5–6.0	0.38 $\frac{g_{cat}h}{g_{bio-oil}}$	Gayubo et al. (2018)
Bio-oil (Pine sawdust)	Rh/CeO ₂ -ZrO ₂	550–700 °C	1 atm	1.5–6.0	0.19 $\frac{g_{cat}h}{g_{bio-oil}}$	Ochoa et al. (2018)
Bio-oil (Pine sawdust)	Ni/Al ₂ O ₃ , Ni/SiO ₂ , Ni/MgO, Ni/TiO ₂ , Ni/ZrO ₂	600–750 °C	–	3–9	0.15 –	Remiro et al. (2018)
Bio-oil (Pine sawdust)	NiO	600 °C	–	7.7	0.6 $\frac{g_{cat}h}{g_{bio-oil}}$	Santamaria et al. (2018)
Bio-oil (Palm empty fruit bunch)	NiO	427–927 °C	1 atm	1–3	10, 20 $\frac{g_{cat}min}{g_{bio-oil}}$	Spragg, Mahmud, and Dupont (2018)
Bio-oil (Pine sawdust)	Ni/La ₂ O ₃ - α -Al ₂ O ₃	550–700 °C	1 atm	1.5–6	–	Valle et al. (2018b)
Bio-oil (Pine sawdust)	Ni/La ₂ O ₃ - α -Al ₂ O ₃	700 °C	1 atm	1.5–6	0.04 –	Valle et al. (2018a)
Model compounds (Acetic acid, Hydroxyacetone, Furfural, Phenol)	Ni/SBA-15, Ni-Cu/SBA-15, Ni-Co/SBA-15, Ni-Cr/SBA 15	600 °C	1 atm	2.67–13.2	0.38 $\frac{g_{cat}h}{g_{bio-oil}}$	Calles et al. (2019)

3.2 Temperature

Increase in temperature will lead to an increase in the hydrogen produced via steam reforming. This because steam reforming is an endothermic reaction. On the other hand, the exothermic methanation reaction recedes with increasing temperature. The yield of hydrogen will experience maxima usually within a threshold of 550–700 °C and then decline gradually from then on. This is as a result of coke forming reaction and competing thermal cracking reactions of the organic compounds at these high temperatures. Remiro et al. (2013b) observed that the optimum temperature is around 700 °C to strike a balance between the severe decrease in bio-oil conversion at low temperature (600 °C) and the high by product yields (CO, CH₄, and HCs) at high temperature (800 °C).

3.3 Pressure

In most of the steam reforming studies, pressure is kept at atmospheric pressure. This is done to maximise hydrogen selectivity in the system as higher pressure leads to drop in hydrogen produced (Vagia and Lemonidou 2007, 2008). Chemical equilibrium shifts in favour of the lighter chemical species when the pressure is reduced and vice versa. Being that hydrogen is the lightest species in the steam reforming system, atmospheric pressure in the system is most often maintained to ensure optimum yield. The effect of pressure has also been reinforced by thermodynamic analysis (Vagia and Lemonidou 2007, 2008). In some reports, pressure is not mentioned altogether as some consider it an insignificant factor in the process.

3.4 S/C ratio

The ratio of steam to carbon in the process system determines the efficiency of the water gas shifts reaction. Higher S/C favours the water gas shift reaction which leads to higher Hydrogen production. Valle et al. (2018a) observed that the increase in S/C ratio shifts the thermodynamic equilibrium of the steam reforming and water gas shift reactions in favour of hydrogen production. The above effect has also been observed by other researchers (Vagia and Lemonidou 2007, 2008; Zhang et al. 2016).

3.5 Space time

Higher space time enhances the steam reforming and water gas shift reactions hence improving the hydrogen yield. Higher velocities mean lesser space time hence the relationship will be inverse. When low space velocities are used, there is a performance of the water gas shift reaction, given by the observation of drop in that CO concentration and rise in CO₂, at the same time as secondary products such as CH₄ and light hydrocarbons produced from mainly cracking reactions disappear (Arregi et al. 2018). Xu et al. (2010) observed an initial hydrogen yield improvement with hourly space velocity and then dropped gradually again for the rest of the study. Zheng et al. (2012) observed steady drop in Hydrogen production with higher space velocities but this time without maxima. The above explained trends for space velocity (Fermoso et al. 2014; Remiro et al. 2013b; Xie et al. 2015, 2016) and space time (Pant et al. 2013; Remiro et al. 2018; Valle et al. 2018a) have also been observed in other studies also. In summary, increasing the contact time of feedstock with catalyst (decrease the weight hourly space velocity or increasing the space time), or using catalysts with high activity will bring the steam reforming performance closer to its thermodynamic equilibrium (Cheng and Dupont 2013).

3.6 Reactor type and process type

In steam reforming systems, a variety of reactor designs have been utilised. However, a major classification is based on catalyst bed. Numerous studies have both been conducted with both fixed bed and fluidised bed reactors and both has been shown to give good yields and selectivity of hydrogen (see Table 4).

Table 4: Summary of feedstock, process and reactor types.

Oil Type (Source)	Process Type	Reactor	Optimal Hydrogen Yield or selectivity	Reference
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Bio-oil (Poplar wood)	Steam reforming	Fixed bed reactor	86 % Stoi yield of H ₂	Wang, Czernik, and Chornet (1998)
Model compounds (Acetic acid, xylose-sucrose-glucose, m-cresol-dibenzyl ether)	Steam reforming	Fixed bed reactor	About 80 % H ₂ yield	Marquevich et al. (1999)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	80–90 mol% H ₂ in product	Czernik et al. (2002)
Bio-oil (Pine wood)	Steam reforming	Fluidised bed reactor	Up to 95 mol% H ₂ yield	Magrini-Bair et al. (2002)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	60 % H ₂ yield	Takanabe et al. (2004)
Model compound (Acetic acid)	Steam reforming	Fluidised bed reactor	0.3 g H ₂ per g of acetic acid	Galdámez, García, and Bilbao (2005)
Model compounds (Acetic acid, phenol, acetone, ethanol)	Steam reforming	Tubular quartz micro-reactor	About 65 % maximum H ₂ yield (acetic acid), about 80 % maximum H ₂ yield (acetone, ethanol), about 100 % maximum H ₂ yield (phenol)	Rioche et al. (2005)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	87 % H ₂ yield	Takanabe et al. (2006b)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	8.2 % H ₂ yield	Takanabe et al. (2006a)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	95.3 % optimum H ₂ selectivity	Hu and Lu (2006)
Bio-oil (Beech wood), Model compounds (Acetic acid-acetone-ethylene glycol)	Steam reforming	Fixed-bed reactor	Up to 80–90 mol% H ₂ in product	Kechagiopoulos et al. (2006)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	96.3 % optimum H ₂ selectivity	Hu and Lu (2007)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	0.146 g H ₂ per g acetic acid	Bimbela et al. (2007)
Bio-oil (<i>Pinus insignis</i> sawdust)	Steam reforming	Fluidised bed reactor	–	Valle et al. (2007)
Model compound (Acetic acid)	Steam reforming	Nozzle-fed reactor	–	Basagiannis and Verykios (2007a)
Model compound (Acetic acid)	Steam reforming	Tubular quartz micro-reactor	83 mol% overall H ₂ yield	Basagiannis and Verykios (2007a)
Bio-oil (Beech wood)	Sequential catalytic cracking	Fixed-bed reactor	45–50 mol% H ₂ in product	Davidian et al. (2007)
Bio-oil (Hardwood)	Steam reforming	Fluidised bed reactor	70 vol% H ₂ in product	Czernik, Evans, and French (2007)
Bio-oil (Beech wood chips, pine wood chips)	Steam gasification	Fluidised bed reactor (with fixed bed freeboard)	Optimal H ₂ selectivity of 62.6 vol% (pine) and 55.5 vol% (beech)	Van Rossum, Kersten, and van Swaaij (2007)
Model compound (Acetic acid)	Steam reforming	Fluidised bed reactor	Optimum H ₂ yield of 0.14 g per g acetic acid	Medrano et al. (2008)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	–	Güell et al. (2008)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	Over 90 % optimum H ₂ selectivity	Hu and Lu (2008)
Model compound (Acetic acid)	Steam reforming	Tubular quartz micro-reactor	Up to 100 % optimum H ₂ selectivity	Basagiannis and Verykios (2008)
Bio-oil (Sawdust)	Steam reforming	Fixed-bed reactor	60 mol% optimum H ₂ yield	Wu et al. (2008)

Model compound (Acetic acid)	Steam reforming	Membrane reactor	36 mol% optimum H ₂ selectivity	Basile et al. (2008)
Model compound (Acetic acid)	Steam reforming	Membrane reactor	70 % CO-Free H ₂ recovery	Iulianelli, Longo, and Basile (2008)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	89.6 mol% optimum H ₂ selectivity	Hu and Lu (2009a)
Model compounds (Acetic acid, ethylene glycol, acetone, ethyl acetate, m-xylene, glucose)	Steam reforming	Fixed-bed reactor	92.8 mol% optimum H ₂ selectivity (acetone)	Hu and Lu (2009b)
Bio-oil (Beech wood chips, pine wood chips, light sugar waste, heavy sugar waste)	Steam gasification	Fluidised bed reactor (with fixed bed freeboard)	Optimal H ₂ selectivity of 62.6 vol% (pine), 61.1 vol% (beech), 50.3 vol% (light sugar) and 51.5 vol% (heavy sugar)	Van Rossum, Kersten, and van Swaaij (2009)
Bio-oil (Wood sawdust, rice husk, cotton stalk)	Steam reforming	Quartz fixed-bed reactor	90 % (% stoi) Hydrogen yield	Hou et al. (2009)
Model compounds (Acetic acid, ethylene glycol)	Steam reforming	Spouted bed reactor	Up to 100 mol% H ₂ in product (for both acetic acid and ethylene glycol)	Kechagiopoulos et al. (2009)
Model compounds (Ethanol, acetic acid)	Steam reforming	Fixed-bed tubular quartz reactor	95 % H ₂ yield	Barattini et al. (2009)
Model compound (Acetic acid)	Electro-chemical steam reforming	Fixed-bed reactor	About 95 mol% H ₂ yield	Chen et al. (2009a)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	–	Iwasa et al. (2010)
Bio-oil (Rice husk)	Steam reforming	Fluidised bed reactor	About 60 mol% optimal H ₂ yield	Xu et al. (2010)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	95.5 % optimal H ₂ selectivity	Hu and Lu (2010a)
Model compounds (Acetic acid, acetone)	Steam reforming	Fixed-bed reactor	Over 90 % optimal H ₂ selectivity	Hu and Lu (2010b)
Model compound (m-cresol)	Steam reforming	Fixed-bed reactor	77.5 mol% H ₂ in product	Wu and Liu (2010)
Bio-oil (Rice husk)	Steam reforming	–	0.63 molar fraction of H ₂ in product	Zhao et al. (2010)
Bio-oil (Poplar wood, pine wood, mixed hardwood), Model compounds (bio-oil-methanol-methane)	Autothermal Partial oxidation	Fixed-bed reactor	94 % maximum H ₂ yield (poplar), 19 % maximum H ₂ yield (pine), 94 % H ₂ yield (mixed hardwood)	Rennard et al. (2010)
Bio-oil (Rice hull)	Steam reforming	Fixed-bed reactor	69.7 vol% H ₂ in product	Yan, Cheng, and Hu (2010)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	Up to 90 % optimal H ₂ yield	Vagia and Lemonidou (2010)
Model compound (Acetic acid)	Steam reforming	Quartz tube micro-reactor	100 % optimal H ₂ yield	Thaicharoensutcharittham et al. (2011)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	–	Iwasa, Yamane, and Arai (2011)
Bio-oil (Rice husk)	Steam reforming	Fixed-bed reactor	61.3 mol% H ₂ in product	Chen, Wu, and Liu (2011)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	30 % H ₂ yield	An et al. (2011)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	About 97 mol% optimal H ₂ selectivity	Zheng et al. (2012)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	93.8 mol% optimal H ₂ selectivity	Li et al. (2012b)

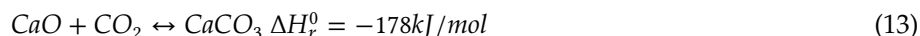
Model compounds (Acetic acid-acetol-butanol)	Steam reforming	Fixed-bed tubular quartz reactor	–	Bimbela et al. (2012)
Bio-oil (Pine wood, empty fruit bunch(EFB))	Chemical looping reforming	Packed-bed quartz reactor	1.3 mol H ₂ per mol C in feed (for both pine wood and EFB)	Lea-Langton et al. (2012)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	Up to 80 mol% optimal H ₂ yield	Mohanty, Patel, and Pant (2012)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	100 % (Stoi %) optimal H ₂ yield	Wang et al. (2012)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	–	Lemonidou, Vagia, and Lercher (2013)
Model compound (Acetic acid)	Steam reforming	Packed bed reactor	Up to 60 mol% optimal H ₂ yield	Cheng and Dupont (2013)
Model compound (Acetic acid)	Steam reforming	Fixed-bed reactor	2.7 mol H ₂ per mol acetic acid	Assaf, Nogueira, and Assaf (2013)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	H ₂ yield of almost 100 mol% (For both catalysts),	Valle et al. (2013)
Model compounds (Ethanol-acetic acid)	Steam reforming	Fixed-bed tubular reactor	3.25 mol H ₂ per mol of bio-oil feed	Goyal, Pant, and Gupta (2013)
Bio-oil (Pine wood)	Steam reforming	Fixed-bed tubular quartz reactor	0.17 g H ₂ per g of organic	Bimbela et al. (2013)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	84 mol% overall H ₂ yield	Remiro et al. (2013a)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	95 mol% overall H ₂ yield	Remiro et al. (2013b)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	Up to 95 mol% optimal H ₂ selectivity	Hu et al. (2013)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	1.4 mol per mol feed	Pant et al. (2013)
Bio-oil (Pine sawdust)	Steam reforming	Fixed bed reactor	67 mol% optimal H ₂ selectivity	Liu et al. (2013)
Model compounds (Acetic acid, phenol, hydroxyl-acetone)	Steam reforming	Fixed bed reactor	About 65 mol% optimal H ₂ selectivity	Wang et al. (2014)
Bio-oil (Oak, Poplar, Pine)	Auto-thermal reforming	Packed bed reactor	9–11 g H ₂ per 100 g of feed	Czernik and French (2014)
Bio-oil (Pine sawdust)	Steam reforming	Entrained flow reactor (EFR), Fluidised bed quartz reactor	H ₂ yield of 0.17 g per g organics (EFR), H ₂ yield of 0.07 g per g organics (FBR)	Remón et al. (2014)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	60 mol% optimal H ₂ selectivity	Abdullah et al. (2014)
Model compound (Acetic acid)	Super-critical steam reforming	–	18.9% optimal H ₂ selectivity	De Vlieger, Lefferts, and Seshan (2014)
Model compound (Acetic acid)	Chemical looping reforming (sorption enhanced)	Fixed bed reactor	100 % optimal H ₂ selectivity	Fermoso et al. (2014)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	90 mol% optimal H ₂ selectivity	Nogueira et al. (2014)
Model compounds (Acetic acid-ethanol)	Steam reforming	–	–	Nozawa et al. (2014)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	80 mol% optimal H ₂ yield	Zhang et al. (2014)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	Up to 90 mol% optimal H ₂ yield	Wang et al. (2015b)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	100 % optimal H ₂ yield	Hoang et al. (2015)

Bio-oil (Pine sawdust, poplar sawdust)	Steam reforming	Fixed bed reactor	H ₂ yield of 0.182 g per g organics (Pine bio-oil from fluidised bed pyrolysis), H ₂ yield of 0.129 g per g organics (Poplar bio-oil from fluidised bed pyrolysis)	Remón et al. (2015)
Model compounds (Ethanol, acetic acid, acetone, phenol)	Steam reforming (sorption enhanced)	Packed bed reactor	About 85 mol% optimal H ₂ yield	Xie et al. (2015)
Model compound (Acetic acid)	Steam reforming, oxidative steam reforming	Fixed bed reactor	Up to 50 % H ₂ selectivity	Resende et al. (2015)
Bio-oil (Pine wood)	Steam reforming	Spouted Fluidised bed reactor	107 g per kg of biomass	Arregi et al. (2016)
Bio-oil (Corn Cob)	Steam reforming (sorption enhanced)	Packed bed reactor	About 90 mol% optimal H ₂ yield	Xie et al. (2016)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	75 mol% optimal H ₂ yield	Bossola et al. (2016)
Model compounds (Acetic acid-acetone)	Steam reforming (sorption enhanced)	Fluidised bed reactor	99.4 % optimal H ₂ selectivity	Esteban-Díez et al. (2016)
Model compound (Acetic acid)	Steam reforming (sorption enhanced)	Fixed bed reactor	98.31 % optimal H ₂ selectivity	Gil et al. (2016)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	Up to 0.6 mol fraction H ₂ selectivity	Nabgan et al. (2016b)
Model compounds (Acetic acid-phenol)	Steam reforming	Fixed bed reactor	Up to 40 mol% fraction H ₂ selectivity	Nabgan et al. (2016a)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	3.1 mol/mol H ₂ yield	Yang et al. (2016)
Model compound (Acetic acid)	Steam reforming	Fixed bed reactor	80 mol% optimal H ₂ yield	Zhang et al. (2016)
Bio-oil (Pine sawdust)	Oxidative steam reforming	Fluidised bed reactor	–	Arandia et al. (2018)
Bio-oil (Pine sawdust)	Steam reforming	Fixed bed reactor	About 80 mol% optimal H ₂ yield	Bizkarra et al. (2018)
Bio-oil (Pine sawdust)	Steam reforming	Fixed bed reactor	81 mol% optimal H ₂ yield	Chen et al. (2018)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	–	Gayubo et al. (2018)
Bio-oil (Pine sawdust)	Oxidative steam reforming	Fluidised bed reactor	–	Ochoa et al. (2018)
Bio-oil (Pine sawdust)	Oxidative steam reforming	Fluidised bed reactor	About 0.75 mol fraction optimal H ₂ yield	Remiro et al. (2018)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	About 94 mol% optimal H ₂ yield	Santamaria et al. (2018)
Bio-oil (Palm empty fruit bunch)	Chemical looping reforming	–	11.8 wt% H ₂ yield	Spragg, Mahmud, and Dupont (2018)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	About 95 mol% optimal H ₂ yield	Valle et al. (2018b)
Bio-oil (Pine sawdust)	Steam reforming	Fluidised bed reactor	About 95 mol% optimal H ₂ yield	Valle et al. (2018a)
Model compounds (Acetic acid, Hydroxyacetone, Furfural, Phenol)	Steam reforming	Fixed bed reactor	Up to 65 mol% H ₂ selectivity	Calles et al. (2019)

3.7 Sorption enhancement

In certain processes, sorption enhancement is undertaken to improve the Hydrogen content of the product stream and it has been reported in numerous steam reforming studies (Chen et al. 2009b; Da Silva and Müller

2011; Dou et al. 2009; Esteban-Díez et al. 2016; Gil et al. 2016; Iordanidis et al. 2006; Tzanetis, Martavaltzi, and Lemonidou 2012; Xie et al. 2016, 2016). Iordanidis et al. (2006) and Kinoshita and Turn (2003) implemented CO₂ in computer-aided simulations while others (Esteban-Díez et al. 2016; Xie et al. 2015, 2016) implemented it in experimental studies. Sorption usually encompasses adding a heterogeneous chemical specie in the reacting system to preferentially combine with CO₂ and reduce its concentration in the product stream. In most cases quicklime (CaO) is used (Iordanidis et al. 2006; Kinoshita and Turn 2003; Spragg, Mahmud, and Dupont 2018). Other natural sorbents are dolomite (majorly MgO and CaO), huntite and hydrotalcite. Synthetic sorbents include lithium ortho-silicate (Li₄SiO₄), lithium zirconate (Li₂ZrO₃) and sodium zirconate (Na₂ZrO₃) (Dou et al. 2014). In the case of the more popular quicklime, it reacts reversibly with CO₂ to form calcium tri-oxo-carbonate (CaCO₃) according to the stoichiometry represented in eq. (13):



Generally, hydrogen from steam reforming is difficult to use in energy generation via fuel cells due to its high CO₂ content. Also, carbon monoxide has a poisoning effect on the fuel cell catalyst. This is a key reason for sorption technology to remove these chemical species from the product stream and obtain hydrogen gas of high purity (as revealed in Table 4).

3.8 Carbon deposition behaviour

Carbon deposition is one of the most significant problems in reforming processes, which usually results in gradual deactivation of the catalyst (Montero et al. 2015). Bio-oil oxygenates are considered coke formation precursors, and so oxygenate concentration in the reaction medium is higher as the reforming activity decreases, which contributes to producing more coke (Remiro et al. 2013a). This effect explains the evolution of product distribution with time on stream and is typical in catalytic processes in which deactivation occurs in parallel with the main reaction Remiro et al. (2013a). The deposited carbon on the surface of the catalyst prevents reactants from gaining access to these sites thereby reducing the catalyst activity. At optimum conditions of steam to carbon S/C ratio and temperature, carbon deposition can be minimised in steam reforming systems. The carbon deposits usually take a physical form similar to carbon nano-tubes (Wu and Liu 2010).

Possible reactions leading to carbon deposition in the steam reforming system (Adhikari, Fernando, and Haryanto 2007) are mentioned in eq. (14) to eq. (17).



In a recent study, Ochoa et al. (2018), it has been observed that different types of coke are deposited at different regions of the catalyst. It was revealed that four types of coke were deposited. Firstly, was an encapsulating coke with aliphatic nature placed in the most superficial layers. Secondly was an encapsulating coke with higher aromatic nature in inner layers. Thirdly was the most superficial layers of a filamentous coke, further from active sites and with a more carbonized structure compared to encapsulating coke; and finally was an innermost and mainly poly-aromatic filamentous coke with a low oxygenates content.

4 Thermodynamic analysis

Thermodynamic analysis can be used to predict the composition of the product stream, and to examine the effect of the process factors on the product composition. Key variables are steam to carbon (S/C) ratio, temperature and pressure. Temperature increase favours Hydrogen selectivity until a threshold is exceeded. The best pressure condition for the process is ambient pressure. Higher steam to carbon ratio usually increases the

hydrogen selectivity too. The factors have different ways of interacting as regards the other chemical species. Detailed factor interaction studies for each chemical species has been conducted for steam reforming (Adeniyi and Ighalo 2018). There is a limited number of open literature available on the chemical equilibrium analysis of the steam reforming of mixture of oxygenates. Most studies deal with pure components/model compounds for the sake of simplicity. Thermodynamic analysis of steam reforming was in some cases done with the assistance of softwares (Goyal, Pant, and Gupta 2013; Montero et al. 2015; Vagia and Lemonidou 2007, 2008; Wang et al. 1997; Xie et al. 2014) and in other cases purely theoretical (Xie et al. 2011). The method is usually the minimisation of Gibbs free energy. This method has been explicitly elucidated in open literature (Adeniyi and Ighalo 2018; Adhikari et al. 2007; Adhikari, Fernando, and Haryanto 2007; Ashraf and Kumar 2018; Chen et al. 2009b; Da Silva and Müller 2011; Wang et al. 2008, 2010; Yang et al. 2011). If we keep the temperature and pressure of our system constant, then the equilibrium of the system can be expressed as eq. (18)

$$dG = \sum_{i=1}^K \mu_i n_i dn_i \quad (18)$$

The objective is to find the set of n_i values that will minimise the value of G (Adhikari et al. 2007; Adhikari, Fernando, and Haryanto 2007). This can be done either by a stoichiometric approaches or a non-stoichiometric approach. The non-stoichiometric approach is the more applied technique in open literature haven the advantage that; selecting possible reaction sets is not required; estimation of initial equilibrium composition is not required and divergence do not occur in calculations.

$$G = \sum_{i=1}^K \mu_i n_i \quad (19)$$

To find the value of n_i that will minimize the value of G , then it is important that the value of n_i be in mass balance.

$$\sum_{i=1}^K a_{li} n_i = b_l, \quad l = 1, \dots, M \quad (20)$$

The above expression can then be further expressed as eq. (21):

$$G = \sum_{i=1}^K n_i \Delta G_i^0 + RT \sum_{i=1}^K n_i \ln y_i + RT \sum_{i=1}^K n_i \ln P \quad (21)$$

This is known as the objective function and it can be solved on Process simulation softwares as reportedly used by other researchers (Goyal, Pant, and Gupta 2013; Montero et al. 2015; Vagia and Lemonidou 2007, 2008; Wang et al. 1997; Xie et al. 2014).

5 Lifecycle analysis

Lifecycle analysis of hydrogen derived from the steam reforming of biomass bio-oil has been conducted both in the experimental (Heracleous 2011) and computer-aided (Peters, Iribarren, and Dufour 2015) domain. Comparison in terms of fossil energy consumption in the lifecycles of bio-derived and fossil fuel-derived hydrogen indicates that bio-hydrogen offers considerable energy reductions compared to conventional hydrogen from natural gas (Heracleous 2011). Also, green-house-gas savings can also be as high as 54.5 % (Peters, Iribarren, and Dufour 2015). This is due to the renewable nature of the feedstock. Prior to combustion, the processes in the case of bio-hydrogen is more energy demanding (Heracleous 2011). The root source of the higher energy consumption is in the bio-oil reforming step This step requires the use of methanol, which is added to stabilize the bio-oil and reduce extensive coking. From an environmental perspective, abiotic depletion potential and non-renewable energy demand for bio-hydrogen are significantly lower than those of fossil gasoline and diesel (Peters, Iribarren, and Dufour 2015). However, higher impacts are obtained in other categories such as acidification and eutrophication, a pattern typical for biofuels (Peters, Iribarren, and Dufour 2015).

6 Techno-economic analysis

A number of studies on techno-economic analysis (Sarkar and Kumar 2010; Wright et al. 2010; Zhang et al. 2013a) of bio-hydrogen production has been conducted and in some aspects softwares have always been utilised. The cost of bio-hydrogen production in-cooperating fast pyrolysis is lowest for whole-tree than for other feedstock like forest residues and straw (Sarkar and Kumar 2010). There is no technical optimum size for bio-oil production plants processing whole-tree and forest residues below a size of 10,000 dry tonnes/day; however, maximum economy of scale benefits in capital cost for fast pyrolysis of whole-tree is observed at 2000 dry tonnes/day (Sarkar and Kumar 2010). Bio-hydrogen produced usually possess a high fuel cost primarily due to the low fuel yield, and about 5 % variations on the bio-oil upgrading yield (Wright et al. 2010). The cost of bio-hydrogen also is highly sensitive to the cost of biomass if to be purchased (Wright et al. 2010). Also, in comparing alternative bio-oil processes, the capital cost investment for bio-oil gasification is greater than for bio-oil reforming pathway (Zhang et al. 2013b). This is mainly because entrained flow gasifiers are much more expensive than reformers. In addition, bio-oil gasification requires air separation equipment and more complicated syngas clean-up system. Sensitivity analysis shows that hydrogen price, hydrogen yield, Fixed Capital Investment (FCI), feedstock cost, and bio-oil yield are key factors in the economic feasibility of bio-hydrogen production via both the bio-oil gasification and bio-oil reforming pathways (Zhang et al. 2013a).

7 Computer simulations

Extensive work has been done to understand biomass pyrolysis in terms of kinetics and reaction sequence (Alves and Figueiredo 1989; Gavin, Stuart, and Emilio 2016; Srivastava and Jalan 1996a, 1996b). Modelling and simulation of biomass pyrolysis (and gasification) using ASPEN Plus in particular (Abdelouahed et al. 2012; Esteban-Díez et al. 2016; Onarheim, Solantausta, and Lehto 2014; Peters, Iribarren, and Dufour 2013; Ramzan et al. 2011; Samson, Shaharin, and Suzana 2011; Tan and Zhong 2010; Wang et al. 1997; Ward, Rasul, and Bhuiya 2014; Yan and Zhang 1999) and other software in general (Goyal, Pant, and Gupta 2013; Iordanidis et al. 2006; Montero et al. 2015; Rennard et al. 2010; Xie et al. 2014; Zhang et al. 2007a) have been conducted. The models have been used to study different aspects of the process which includes concept analysis (Iordanidis et al. 2006), catalysis (Kinoshita and Turn 2003), process optimisation and sorption enhancement (Iordanidis et al. 2006; Kinoshita and Turn 2003), thermodynamic comparison (Goicoechea et al. 2015; Montero et al. 2015; Vagia and Lemonidou 2007, 2008), lifecycle assessment (Peters, Iribarren, and Dufour 2015) and techno-economic analysis (Wright et al. 2010; Zhang et al. 2013a).

Bleeker et al. (2010) undertook a process design study to investigate hydrogen production from bio-oil in an integrated steam-iron process on ASPEN Plus. Their study revealed that an optimum overall energy efficiency of 53 % can be achieved in from the two-step (iron reduction and steam oxidation) process. Iordanidis et al. (2006) modelled sorption-enhanced auto-thermal steam reforming using SIMSCI Pro II simulator. They considered a model compound formulation of acetic acid, acetone, acetaldehyde, ethylene glycol, formic acid, methanol, formaldehyde and ethanol in specified proportions. They elucidated that sorptive removal of the carbon dioxide from the reaction site results in low CO and CO₂ concentrations (< 1 %) in the reformat which gives it an added advantage and better applicability in fuel cells. Goyal, Pant, and Gupta (2013) studied the steam reforming process using PRO-II process simulator. Their work was a thermodynamic investigation of the effects (both singular and combinatorial) of the different process factors on steam reforming.

Kinoshita and Turn (2003) modelled the sorption-enhanced steam reforming using ASPEN Plus 10.2. Theirs were one of the earliest sorption-enhancement simulations in steam bio-oil reforming. Their study revealed that > 95 % purity of hydrogen can be achieved. Montero et al. (2015) carried out a thermodynamic comparison between bio-oil and ethanol steam reforming using Pro II SIMSCI 8.3 software. Their result elucidated the viability of joint valorisation of bio-oil and bio-ethanol by steam reforming. Rennard et al. (2010) performed thermodynamic predictions of product yield and composition in autothermal partial oxidation using Chemkin 4.1.1 software package. Shen, Gao, and Xiao (2008) simulated interconnected fluidized bed for the steam gasification of biomass. Aspen Plus 11.1 was used to perform thermodynamic analysis of steam reforming (Vagia and Lemonidou 2007) and autothermal steam reforming (Vagia and Lemonidou 2008) of bio-oil model compounds (acetic acid, ethylene glycol and acetone). Xie et al. (2014) performed the thermodynamic analysis of the steam reforming of typical bio-oil model compounds (ethanol, acetic acid, acetone, phenol) using HSC Chemistry 5.0. Zhang et al. (2013b) used ASPEN Plus and ASPEN Economic Evaluation to do a comparative study of bio-oil gasification and reforming.

8 Conclusion

The diversity of oxygenated organic compound present in biomass bio-oil has hampered its effectiveness in most applications. The properties that makes it unfavourable includes low heating value, incomplete volatility and acidity. These undesirable properties are as a result of uncharacteristically high proportion of different classes of oxygenated organic compounds as well as moisture content. The steam reforming of biomass pyrolysis oil is a well-established means of converting it into the more useful bio-hydrogen. A lot of work has been done to increase hydrogen yield, hydrogen selectivity and reduce coke deposition in the steam reforming system. Current research trend is in the development of novel catalysts that can simultaneously improve hydrogen yield, hydrogen selectivity, remain stable at high temperatures and maintain its activity over a long period of time. There is still only a very little open literature that pertains to exploration of other biomass feedstock especially those indigenous to Africa. Research endeavours in steam reforming of biomass bio-oil done with an eye for developing added value products that can complement, substitute (and one day replace) fossil fuels whilst ameliorating the global warming menace.

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