

# Biohydrogen Production From Bio-Oil via Hydrothermal Liquefaction

*Mayank Kumar, Adetoyese Olajire Oyedun, Amit Kumar*

Department of Mechanical Engineering, 10-263 Donadeo Innovation Centre for Engineering,  
University of Alberta, Edmonton, AB, Canada

## 29.1 INTRODUCTION

Unlike oil and natural gas, hydrogen gas is not found in nature. Hydrogen is usually obtained from known feedstocks such as coal [1], natural gas [2], water [3], bio-oil [4], and organic molecules like glycerol, butanol, acetic acid, and ethanol [5–8]. In industry, the main technology for hydrogen production relies on a fossil fuel-based source such as natural gas and coal. However, this technology requires high energy and emits considerable greenhouse gases (GHG), which lead to global warming. Hence, there is a great interest in producing hydrogen from renewable feedstocks such as biomass or biomass-derived bio-oil. The two key approaches for biohydrogen production at present are biochemical and thermochemical processes [9, 10]. The biochemical process requires feedstocks rich in sugar/starch and is not feasible for lignocellulosics [10]. Moreover, the process selects biomass type and is time consuming. In contrast, the thermochemical process can handle a wide range of feedstocks and has a high thermal efficiency; the process occurs in minutes [9].

Biomass thermochemical conversion technologies include combustion, gasification, liquefaction, and pyrolysis and are attractive for biohydrogen production [11–16]. Biomass combustion refers to the burning of biomass in air with the intent to convert stored chemical energy into heat, power, and electricity. The process is only feasible for biomass of <50% moisture content. Its main drawback is that it requires pretreatment in the form of grinding, drying, etc., which negatively affect energy consumption and economics [17]. There are considerable challenges in biomass gasification in terms of syngas quality and process operation. Tar accumulation, for instance, fouls equipment [18].

Pyrolysis is the thermochemical conversion of biomass into solid, liquid, and gaseous products in the absence of oxygen [19]. Like combustion, pyrolysis requires drying, which consumes a significant amount of energy. Hydrothermal liquefaction (HTL) is a promising

approach to convert biomass into useful products as it can handle high-moisture containing biomass feedstocks [13]. The process allows the conversion of biomass into a liquid (bio-oil or bio-crude) that can undergo subsequent reforming into syngas [13, 20]. Hence, a key promising method for biomass feedstock is bio-oil reforming to hydrogen production via syngas cleaning [21]. This process has advantages over direct gasification because of its lower operating temperature, which lowers energy inputs [22].

There are a few studies on producing syngas from bio-oil but not solely for hydrogen production [20, 23–29]. The studies have mainly illustrated biohydrogen production via bio-oil steam reforming, which uses catalysts like nickel, Pt/ZrO<sub>2</sub>, zeolites, and noble metals [23, 27, 30–33]. Some studies have only considered the economics of small-scale hydrogen production from biomass [34, 35]. Overall, there is limited information on process modeling and techno-economic analysis, in particular optimum costs for hydrogen production from biomass via bio-oil reforming, from HTL. As biohydrogen production from biomass is yet to be implemented at a commercial scale, it is essential to use simulation tools to assess process feasibility in terms of techno-economic parameters. This study aims to combine two processes for H<sub>2</sub> production from biomass by coupling HTL with bio-oil reforming. The specific objectives of this study are

- To develop a process model for HTL with bio-oil reforming for the production of biohydrogen.
- To assess the capital cost estimations for a 2000-dry tonnes/day biohydrogen production plant using the process model.
- To estimate the product value of biohydrogen using capital cost estimates.
- To conduct a sensitivity analysis to comprehend the impact of parameters influencing process economics.
- To perform an uncertainty analysis with the help of the Monte Carlo approach to determine process uncertainty on the product value of biohydrogen.

### 29.1.1 Biomass and Biomass-Derived Bio-Oil as Feedstock

Biomass refers to organic material produced via photosynthesis from plants such as crops, trees, and algae [17]. The use of biomass feedstock for biohydrogen production has significant environmental benefits as the feedstock is carbon neutral. A variety of biomass feedstocks including lignocellulosics, agricultural products, municipal wastes, industrial wastes, and even animal wastes can be used [36, 37].

Bio-oil is a dark-brown organic liquid obtained from the disintegration of biomass. Bio-oil is a complex mixture of organic molecules such as phenolics, aldehydes, ketones, carboxylic acids, and sugars [38]. It consists of carbon, hydrogen, and oxygen and is usually expressed as C<sub>n</sub>H<sub>m</sub>O<sub>k</sub>·xH<sub>2</sub>O [39]. Its composition is a function of biomass type and processing conditions. Bio-oil refers to the liquid product produced during biomass liquefaction processes, namely fast pyrolysis and HTL [40, 41]. Several studies have focused on the production of bio-oil from feedstocks such as wood and other biomass residues including rice husk, straws, etc., with a wide range of bio-oil yields (from 40% to 83%) [42–56]. Known companies producing bio-oil include BTG Biomass Technology Group (2–6 dry tonnes/day), Ensyn Group Inc. (100 dry tonnes/day), and DynaMotive Energy Systems Corporation (200 dry tonnes/day) [57]. Bio-oil is used to produce heat and electricity in boilers, engines, and turbines and in transportation fuels [58].

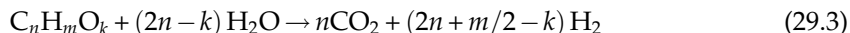
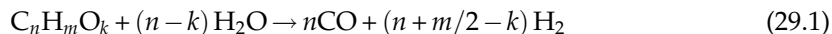
**TABLE 29.1** Typical Physical and Chemical Attributes of Bio-Oil Produced From Biomass

<i>BIO-OIL PHYSICAL PROPERTIES</i>	
C	54–58
H	5.5–7
N	0–0.2
O	35–40
Ash	0–0.2
<i>BIO-OIL CHEMICAL PROPERTIES</i>	
Water (%)	15–30
Specific gravity	1.2
pH	2.5
HHV (MJ/kg)	16–19
Viscosity (cP) @ 500°C	40–100

Biomass feedstocks such as barely, corn stover, saw dust, wood, rice husk, algae, etc., have been used for bio-oil production, as reported by Mohan et al. [59]. The physical and chemical attributes of bio-oil depend on the nature of the biomass. Biohydrogen yield is influenced by the chemical properties of bio-oil, which is in turn dependent on the nature of biomass feedstock. Typical bio-oil physical and chemical properties, as extracted by Mohan et al., are provided in Table 29.1 [59].

## 29.2 STATE-OF-THE-ART TECHNOLOGY

Biohydrogen is widely produced via steam reforming technology, which was introduced by Standard Oil Co., United States, in 1930 [60]. This endothermic process involves the injection of steam in the presence of a catalyst to produce a mixture of gases such as CO, H<sub>2</sub>, and CO<sub>2</sub> [61]. The reactions, shown by Eqs. (29.1), (29.2), occur during the steam reforming process [23]. Eq. (29.1) shows the breakdown of biomolecules into CO, which is used to obtain biohydrogen through a water-gas shift reaction, as shown by Eq. (29.2). The overall reaction network is shown with the help of Eq. (29.3).



The other methods of biohydrogen production from biomass and biomass-derived bio-oil feedstocks are briefly summarized in Table 29.2 [28, 29, 62–75].

**TABLE 29.2** Bioprocesses for Biohydrogen Production From Various Feedstocks

Bioprocesses	Key Characteristics/Attributes	References
Partial oxidation	Biomass undergoes partial oxidation in the presence of oxygen (with or without catalyst)	[62, 63]
Autothermal reforming	Biomass undergoes reforming in the presence of air and water; the process involves both partial oxidation and steam reforming. The disadvantage is the lower H <sub>2</sub> yield obtained	[64]
Aqueous-phase reforming	A relatively low temperature (270°C) and high pressure (60bar) process that occurs in liquid phase. The process is advantageous in terms of low CO production	[65, 66]
Supercritical water reforming	The process involves the use of supercritical water (374°C and 22.1 MPa). The supercritical conditions offer favorable transporting properties with high diffusivity	[67–70]
Sequential cracking	Bio-oil undergoes cracking/catalytic reforming in the absence of water followed by catalyst regeneration using oxygen. The key advantage is the ability to regenerate the catalyst through the removal of carbon deposits	[28, 71]
Bio-photolysis	Hydrogen is produced from water that uses sunlight used anaerobically by green algae. The process allows electron flow, resulting in energy synthesis	[72]
Dark fermentation	The use of microorganisms to hydrolyze carbohydrates to obtain hydrogen. A high-energy yield (122kJ/g) of H <sub>2</sub> gas is achieved	[73, 74]
Photo-fermentation	The role of photosynthetic bacteria using solar energy to produce H <sub>2</sub> . Disadvantages include low solar conversion efficiency and the requirement of anaerobic photobioreactors	[75]

## 29.3 PROCESS METHOD

The method used in this study involves process model development followed by techno-economic analysis to estimate the product value of biohydrogen from biomass. A processing plant capacity of 2000 tonnes/day dry biomass is assumed for this analysis.

### 29.3.1 Process Description

A process model for the HTL with bio-oil reforming was developed for biohydrogen production from biomass feedstock. The modeling was carried out using the Aspen Plus process simulator [76]. Fig. 29.1 illustrates a simplified block diagram for biohydrogen production, which includes the HTL of biomass to bio-oil, bio-oil reforming to syngas, syngas cleaning, and purification to biohydrogen.

The biomass is pumped to 18MPa and heated to a temperature of 350°C. The biomass slurry is preheated by incoming hot effluent from the HTL reactor. Under such conditions,

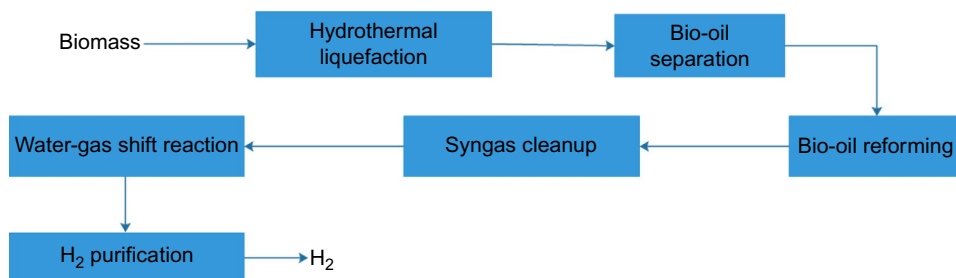


FIG. 29.1 Process flow diagram for the production of biohydrogen through the hydrothermal liquefaction process.

water exists slightly below the supercritical point where dissolution of biomass organics occurs. In the process simulator, RYIELD block is used to model the HTL reactor. The experimental values are used to represent product yield distributions in the HTL reactor, which were based on GC/MS and elemental mass balances [77]. Typically, bio-oil yield ranges from 35 to 65 wt% [54]. The effluent from the HTL reactor is passed through a filter where solids in the form of ash or char are removed. The filtered effluent stream is recycled through a heat exchanger where heat is recovered from the effluent. The cooled effluent is then depressurized and separated into three phases: an organic phase (bio-oil), an aqueous phase, and a gaseous phase [78]. The off-gases from processing areas consist of a mixture of  $\text{CO}_2$ ,  $\text{H}_2$ , and small organics. The aqueous phase, containing water and polar organics, is sent to wastewater treatment [79–81].

The bio-oil from HTL is passed through a pre-reformer in the presence of steam. The steam provides the heat for endothermic reactions during bio-oil reforming in the presence of rhodium as catalyst. Other known catalysts like platinum (Pt) and nickel (Ni) have also been tested for bio-oil reforming [20, 23, 24, 26–28, 82–84]. The gas, devoid of sulfur from bio-oil reforming, is fed to water-gas shift reactors (WGSRs) to increase biohydrogen yield. The process involves the reaction between CO and steam to produce biohydrogen, achieved through a low-temperature shift reactor followed by a high-temperature shift reactor. High-temperature shift uses iron and chromium oxides while low-temperature shift uses copper and zinc oxides as catalysts [85, 86]. The syngas is cleaned and biohydrogen is separated from the mixture of gases and purified in a pressure swing absorption (PSA) column to obtain pure biohydrogen [86–88].

## 29.4 TECHNO-ECONOMIC ASSESSMENT

The techno-economic assessment considers the costs of obtaining biomass feedstock, HTL of biomass for bio-oil production, reforming of bio-crude into syngas, its conversion into biohydrogen via gas cleaning, and purification. The total capital investment and the operating costs for HTL with bio-oil reforming are determined through the Aspen Icarus Process Evaluator [76]. The costs are reported in 2016 US \$, unless stated otherwise. An annual inflation rate of 2% is assumed in this analysis.

### 29.4.1 Capital Cost

The capital cost considers the total purchased equipment costs (TPEC), including the installation factor, and other indirect process costs. The process simulation, which comprises different unit operations and includes equipment sizing and mapping, is exported to the Icarus platform to estimate the purchased equipment costs. An installation factor is applied to the TPEC to determine the total installed costs, which are the costs for electrical fittings, piping, electric insulations, etc. In order to account for the installation costs of process equipment, a factor of 3.02 is used, as suggested by Peters et al. [89]. This factor is typical of solid-liquid plants handling biomass-water mixtures [89]. The cost factors used to determine the total installed cost are listed in Table 29.3. The indirect costs (IC) for the processing plant are the costs associated with engineering and supervision, legal and contractors' fees, and construction expenses [89]. A 10% project contingency was included in total installed (direct) and IC. A 5% location factor was added to the total project investment (TPI) estimate [90]. The location factor considers biomass harvesting at a remote location with relatively little existing infrastructure [90]. The economic assessment assumes an  $n$ th plant design and therefore avoids the costs for financing, long start-up times, and working capital [91]. The other key assumptions in plant economics and the incurred annual operating costs are summarized in Table 29.4.

### 29.4.2 Operating Cost

The operating costs are the raw material, utilities, labor and supervision, maintenance, overhead, and subtotal costs. The forest biomass feedstock cost is assumed to be 46.98 \$/tonnes (dry) for a plant capacity of 2000 dry tonnes/day [90, 92, 93]. The biomass price includes the ash disposal cost, which consists of both transportation and spreading, the details of which have been previously reported [87, 90, 94, 95]. The labor cost includes operator and supervisor wages and is determined based on the 2016 Alberta wage rate [96]. The mean wages for operators and supervisors are 27.30 and 35.10 \$/h, respectively. For a 2000-dry tonnes/day plant capacity, nine personnel (eight operators and one supervisor) are considered per shift and three shifts per day are assumed. The utility cost is based on Alberta's average electricity price at

**TABLE 29.3** Cost Factors Involved in Plant Cost Estimate for Bio-Hydrogen Production

<b>Project Investment Cost Factor Estimates (in 2016 US \$)</b>	
Installation factor	3.02
Total installed cost (TIC)	302% of TPEC
Indirect cost (IC)	89% of TPEC
Total direct and indirect costs (TDIC)	TIC + IC
Contingency	10% of TDIC
Fixed capital investment (FCI)	TDIC + contingency
Location cost	5% of FCI
Total project investment (TPI)	FCI + location cost

**TABLE 29.4** Cost Parameter Assumptions for Biohydrogen Production

Items	Values
Plant life (year)	20
Cost year basis	2016
Capital cost distribution [92, 93]	
Year 1 (%)	20
Year 2 (%)	35
Year 3 (%)	45
Production plant capacity factor	
Year 1	0.7
Year 2	0.8
Year 3 and beyond	0.85
Internal rate of return (%)	10
Maintenance cost (\$)	3% of TPI
Operating charges (\$)	25% of operating labor cost
Plant overhead (\$)	50% of total operating labor and maintenance cost
Subtotal operating cost, SOC (\$)	Sum of all operating costs including raw material and utility cost
G & A cost (\$)	8% of SOC
Solid disposal cost (\$/tonnes) [84]	22.34
Wastewater disposal cost (\$/tonnes) [84]	1.31
Stream factor (%) [91]	90

0.0665 \$/kWh [97]. The maintenance cost, a percentage of the total capital cost ranging from 2% to 8%, is based on previous studies [92, 93, 98]. Operating charges are 25% of operating labor costs, and plant overhead makes up 50% of the operating labor and maintenance costs, which include the charges incurred for facilities and services, payroll, overhead, etc. General and administrative (G&A) expenses account for 8% of operating costs, which include the costs from research and development and product distribution. The reforming catalyst cost is obtained from a study on biohydrogen production from bio-oil [14].

## 29.5 RESULTS AND DISCUSSION

The techno-economic model input data obtained from process and economic modeling for biohydrogen production from HTL are discussed in this section along with sensitivity and uncertainty analyses. The reported values are in US \$ and the exchange rate is based on the Bank of Canada rate of 0.78 CAD in September, 2017.

### 29.5.1 Process Modeling Results

The biohydrogen yield obtained from bio-oil in this study was approximately 12.6%, which is in accordance with the values reported in the literature [84, 86, 99, 100]. Czernik et al. [101] reported a yield of 10.3% from bio-oil after reforming. In subsequent studies, authors reported yields of 12.6%–13.8% from bio-oil [99]. Zhang et al. [84] estimated biohydrogen production at 160 tonnes/day for the bio-oil reforming pathway from a 2000-dry tonnes/day biomass plant, for an yield of 12.7%. Kinoshita and Turn [100] studied biohydrogen production from bio-oil using sorbents and reported yields of 0.07–0.08 kg/kg H<sub>2</sub>/bio-oil. Sarkar and Kumar [86] found biohydrogen yields of approximately 196.26 tonnes/day H<sub>2</sub>, which accounted for 14.7 wt% [86]. Theoretically, the maximum biohydrogen yield from bio-oil is usually 17.2 wt% [102], whereas biohydrogen yield from bio-oil reforming could be 12.6 wt% of dry biomass feed [103].

### 29.5.2 Techno-Economics Assessment Results

The plant capital cost was determined by developing cost estimates for various unit operations involved in the production of biohydrogen from HTL. Costs were estimated with an Aspen Process Icarus Evaluator and data from the literature [104–108]. A 2000-dry tonnes/day biomass plant has a TPEC of 86.9M\$ and a fixed capital investment of 411.89M\$, as illustrated in Table 29.5. The HTL cost was found to be 66.25M\$, as shown in Fig. 29.2. Cost estimates of 64.3–75.0M\$ were found in other work for HTL plants processing 2000 dry tonnes/day [77, 109]. The HTL unit has the highest capital cost, attributed to the design of the shell and tube reactor, which can operate at high temperature and pressure [79]. Syngas cleaning and the autothermal reactor (including WGSRs) made up 23.73% of the total cost. Similar cost estimates were found for bio-oil reforming, gas cleaning, and WGSRs in previous studies. Villanueva Perales et al. [110] reported the fixed cost estimates for processing areas, including syngas cleaning using Selexol, the autothermal reactor, the WGS reactor, and heat exchangers at 20%–25% [110]. Dutta et al. [111] reported the cost of syngas cleanup to be 15.06M\$, which included the costs of water-gas shift reactions, tar reforming, cooling, and quenching for a processing plant at 2000 dry tonnes/day for woody biomass. Swanson et al. [112] obtained cost estimates of 16–19M\$ for high- and low-temperature scenarios for a plant processing 2000 tonnes/day of biomass. Overall, Zhang et al. [84] reported 333M\$ in total capital investment for bio-oil reforming for a 2000-dry tonnes/day biomass pyrolysis plant, or approximately 184M\$ of the total installed equipment costs.

The operating costs are the costs of raw materials, utilities, maintenance, labor, disposal, overhead, and administrative charges for bio-oil reforming; the cost break down is provided

**TABLE 29.5** Cost Estimates for Bio-Oil Reforming Plant for Biohydrogen Production

Total purchased equipment cost (M \$)	86.86
Total project investment (M \$)	411.89
Operating cost (M \$)	95.89
Production cost (\$/kg)	2.84 ± 0.10

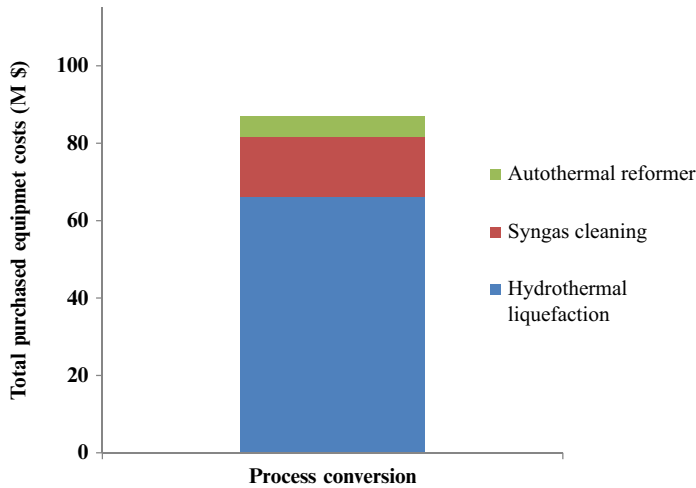


FIG. 29.2 Contribution of unit operations to the plant capital costs.

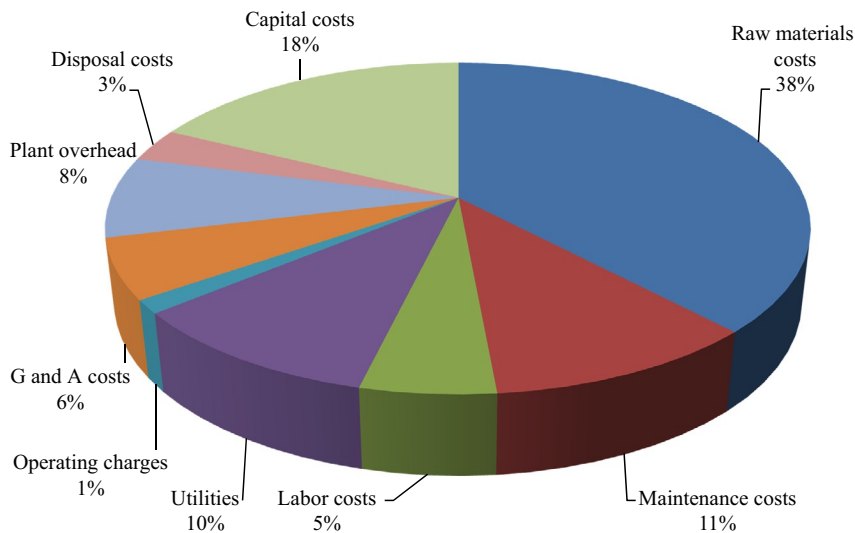


FIG. 29.3 Break down of operating costs for biohydrogen production from biomass.

in Fig. 29.3. The raw material and maintenance costs account for 47% and 12% of the overall operating cost, respectively. Kumar and Sarkar [14] also found that the bio-oil production cost and the operating costs were the key contributors to the cost of biohydrogen production from bio-oil. The solids and wastewater disposal costs contribute 4% to the overall operating cost.

### 29.5.3 Scale Factor

The effects of scale on biohydrogen production were determined by changing the plant capacity. The biohydrogen production cost decreases with increasing plant capacity (see Fig. 29.4) and declines sharply up to a plant capacity of 2000 dry tonnes/day. Beyond this

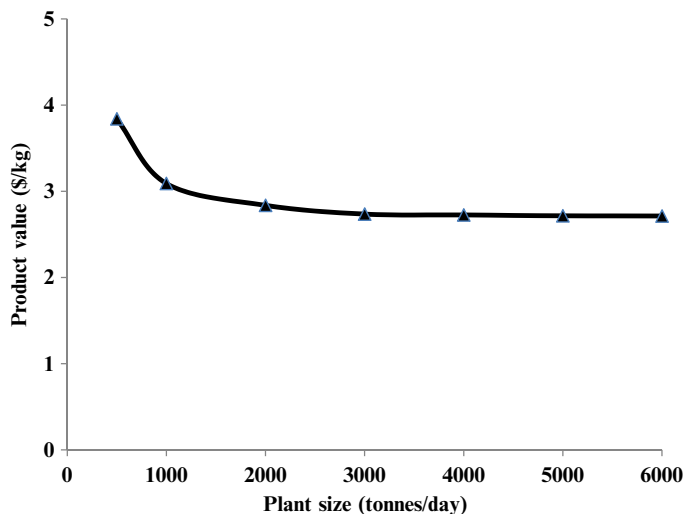


FIG. 29.4 Effect of plant scale factor on the product value of biohydrogen.

capacity, the cost does not change, signifying that there is no appreciable increase in biohydrogen cost with increasing plant capacity. With a plant capacity below 2000 dry tonnes/day, the plant capital cost per unit output decreases with increasing capacity due to economies of scale. However, biomass transportation costs increase with increasing capacity, as a larger collection area is required. Hence, there is a trade-off from the combined effect of decreasing plant capital cost/unit output and increasing biomass transportation cost. Beyond 2000 dry tonnes/day, the curve remains flat, indicating significantly fewer benefits from increased plant capacity vs increased biomass transportation cost. For a biohydrogen plant, Kumar and Sarkar [14] suggested that a 2000-dry tonnes/day plant has considerably low risk with maximum benefits. Other researchers have discussed the optimum plant capacity for other biomass-based conversion pathways [87, 90, 95].

#### 29.5.4 Sensitivity Analysis

A number of technical and economic parameters influence the cost of biohydrogen from biomass. The sensitivity analysis helps understand the effects of techno-economic parameters on the product value of hydrogen. Fig. 29.5 shows the change in the production cost of biohydrogen when key parameters are varied by  $\pm 20\%$ . The biohydrogen yield is the most important parameter influencing the product value of biohydrogen. A 20% increase in biohydrogen yield decreases the product value of biohydrogen by 16.6%. The second important factor affecting the product value of biohydrogen is the capital cost. Biohydrogen produced through HTL with reforming is still at the early stage of development and so there are uncertainties in cost estimates. A 20% increase in total capital investment increases the product value by 6.11%. In the capital cost estimates, HTL contributes the most to the overall project investment; this can be reduced by decreasing the temperature and residence time in

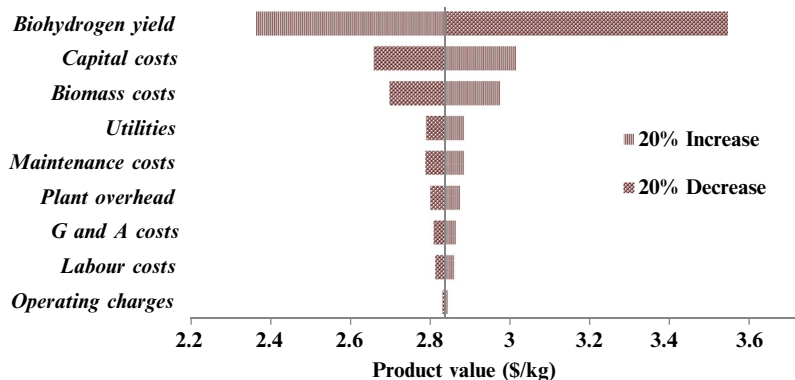


FIG. 29.5 The effect of varying parameters on the product value of biohydrogen.

the high-pressure reactor. A 20% increase in biomass cost increases the biohydrogen product value by approximately 4.99%. The biomass cost depends on biomass availability and plant location, thus high biohydrogen yield is desired to lessen uncertainty risk in procuring biomass. The other cost parameters tested during the sensitivity analysis have little effect on the product value of biohydrogen. The catalyst cost during bio-oil reforming contributes significantly to the overall raw material cost and depends on the nature of the catalyst, its lifetime, and space velocities. The high cost of rhodium catalysts means higher operating costs in the processing plant facility, as described in a study by Villanueva Perales et al. [110]. Market fluctuations in the cost of rhodium catalysts, which depends on the cost of pure rhodium, significantly impact the product value of biohydrogen [110]. Hence, developing active rhodium catalysts would help reduce the influence of catalyst costs on operating costs. Other parameters with little influence on cost include the disposal costs related to solid and wastewater treatment.

## 29.6 UNCERTAINTY ANALYSIS

The considerable knowledge gap and lack of data for advanced HTL with bio-oil reforming leads to uncertainties in cost estimates because assumptions are made in the process study. The sensitivity analysis was performed by varying a single parameter on the product value of biohydrogen. A Monte Carlo simulation was performed on a 2000-dry tonnes/day biomass processing plant through Model Risk software at 10,000 iterations for all parameters influencing product value [113]. The uncertainty analysis considers the costs of procuring raw material, labor and maintenance, utilities, capital costs, operating charges, G&A expenses, overhead, and disposal costs. A range of 80%–125% was considered in the cost parameters. The product values from the uncertainty analysis results are shown in Fig. 29.6. The biohydrogen cost, taking into account the uncertainties, is  $2.84 \pm 0.10$  \$/kg.

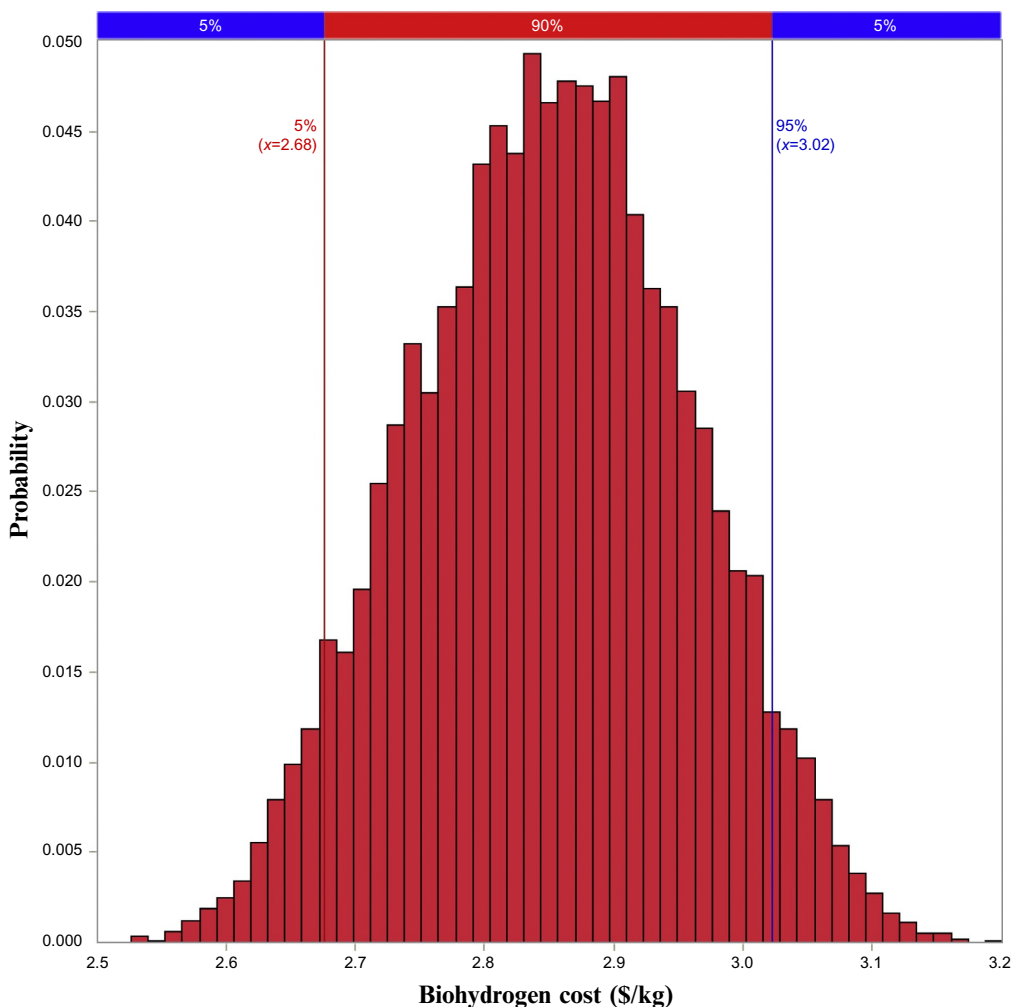


FIG. 29.6 Product value uncertainty analyses for producing biohydrogen through bio-oil reforming.

## 29.7 COST COMPARISON WITH PREVIOUS STUDIES

There have been a few studies on the cost of producing biohydrogen via bio-oil reforming. Sarkar and Kumar studied a 2000-dry tonnes/day biomass plant involving fast pyrolysis coupled with reforming for biohydrogen production from bio-oil obtained from different biomass feedstocks (i.e., whole tree, forest residues, and agricultural residues). They estimated biohydrogen costs at 2.40, 3.00, and 4.55 \$/kg of H<sub>2</sub>, corresponding to 20, 25, and 38 \$/GJ of H<sub>2</sub>, respectively [86]. Kinoshita and Turn [100] performed the techno-economics of the production of biohydrogen from bio-oil obtained from corn stover fast pyrolysis by considering biohydrogen costs from 2.33 to 4.33 \$/kg at 2000 dry tonnes/day. The cost of biohydrogen

**TABLE 29.6** Hydrogen Production Cost From Different Technological Platforms

Process	Cost (\$/kg)	References
Natural gas reforming	1.03	[116]
Natural gas + CO <sub>2</sub> capture	1.22	
Wind electrolysis	6.64	
Nuclear thermal splitting of water	1.63	
Gasoline	0.93	
Coal + CO <sub>2</sub> capture	1.03	
Steam methane reforming	0.75	[117]
Electrolysis	2.56–2.97	
Thermochemical	2.01	
Photocatalytic	4.98	
Biological	5.52	
Partial oxidation	1.39	
Autothermal reforming	1.93	
Coal gasification	0.92–0.96	[116, 117]
Biomass gasification	1.21–4.63	
Biomass pyrolysis	1.21–3.8	

obtained in this study is higher than that obtained from natural gas. Previous studies have indicated costs of biohydrogen from natural gas to be 0.96–3.5 \$/kg; this range is a function of variables such as plant size and natural gas price [86, 95, 114, 115]. Hydrogen production costs by different conversion pathways are listed in Table 29.6 [75, 116, 117]. A previous study indicated more favorable economics of pyrolytic bio-oil reforming than bio-oil gasification for the production of biohydrogen [84].

## 29.8 CONCLUSIONS AND PERSPECTIVES

Biohydrogen has potential both as an energy carrier and source for chemical industry. Because hydrogen production from fossil fuels contributes significantly to greenhouse gas emissions, an alternative and sustainable energy resource for biohydrogen production from biomass is needed. This study addressed the technical and economic feasibility of producing biohydrogen from biomass through the HTL process. The cost of producing biohydrogen from the HTL of biomass is  $2.84 \pm 0.10$  \$/kg. This technology is still at its developmental phase, and hence, as we found in the sensitivity analysis, biohydrogen yield and capital costs have a high impact on the product value of biohydrogen. Other parameters, even with variations of  $\pm 20\%$ , have a relatively small impact on PV. Although process limitations exist,

intensive research is underway to overcome them and make biohydrogen competitive in the market. A considerable effort toward adaptation and commercialization of biomass-based biohydrogen production technology is needed. An interdisciplinary approach with participants from industry and governmental organizations could accelerate the biohydrogen economy at a large scale.

## Acknowledgments

The authors are grateful for the financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC), Alberta Innovates—Bio Solutions (AI-BIO), Climate Change Emissions Management Corporation (CCEMC), and Symbiotic EnviroTek Limited to carry out this research. Astrid Blodgett is thanked for editing this chapter.

## References

- [1] B. Olateju, A. Kumar, Techno-economic assessment of hydrogen production from underground coal gasification (UCG) in Western Canada with carbon capture and sequestration (CCS) for upgrading bitumen from oil sands, *Appl. Energy* 111 (2013) 428–440.
- [2] P.L. Spath, M.K. Mann, *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*, National Renewable Energy Lab, Golden, CO, 2000.
- [3] A. Ursua, L.M. Gandia, P. Sanchis, Hydrogen production from water electrolysis: current status and future trends, *Proc. IEEE* 100 (2) (2012) 410–426.
- [4] A. Renny, V. Santhosh, N. Somkuwar, D. Gokak, P. Sharma, S. Bhargava, Pyrolysis of de-oiled seed cake of *Jatropha Curcas* and catalytic steam reforming of pyrolytic bio-oil to hydrogen, *Bioresour. Technol.* 220 (2016) 151–160.
- [5] E.A. Sanchez, R.A. Comelli, Hydrogen production by glycerol steam-reforming over nickel and nickel-cobalt impregnated on alumina, *Int. J. Hydrog. Energy* 39 (16) (2014) 8650–8655.
- [6] K. Bizkarra, V. Barrio, P. Arias, J. Cambra, Sustainable hydrogen production from bio-oil model compounds (meta-xylene) and mixtures (1-butanol, meta-xylene and furfural), *Bioresour. Technol.* 216 (2016) 287–293.
- [7] V. Nichele, M. Signoretto, F. Menegazzo, I. Rossetti, G. Cruciani, Hydrogen production by ethanol steam reforming: effect of the synthesis parameters on the activity of Ni/TiO<sub>2</sub> catalysts, *Int. J. Hydrog. Energy* 39 (9) (2014) 4252–4258.
- [8] W. Nabgan, T.A.T. Abdullah, R. Mat, B. Nabgan, A.A. Jalil, L. Firmansyah, S. Triwahyono, Production of hydrogen via steam reforming of acetic acid over Ni and Co supported on La<sub>2</sub>O<sub>3</sub> catalyst, *Int. J. Hydrog. Energy* 42 (14) (2017) 8975–8985.
- [9] H. Balat, E. Kirtay, Hydrogen from biomass—present scenario and future prospects, *Int. J. Hydrog. Energy* 35 (14) (2010) 7416–7426.
- [10] P. Basu, *Biomass Gasification and Pyrolysis: Practical Design and Theory*, Academic Press, Elsevier, Burlington, MA, 2010.
- [11] H.L. Chum, R.P. Overend, Biomass and renewable fuels, *Fuel Process. Technol.* 71 (1) (2001) 187–195.
- [12] T. Damartzis, A. Zabaniotou, Thermochemical conversion of biomass to second generation biofuels through integrated process design—a review, *Renew. Sust. Energ. Rev.* 15 (1) (2011) 366–378.
- [13] M. Kumar, A.O. Oyedun, A. Kumar, A review on the current status of various hydrothermal technologies on biomass feedstock, *Renew. Sust. Energ. Rev.* 81 (Part 2) (2018) 1742–1770.
- [14] A. Kumar, S. Sarkar, Biohydrogen production from bio-oil, in: *Biofuels*, Elsevier, Amsterdam, The Netherlands, 2011, pp. 481–497.
- [15] M. Patel, X. Zhang, A. Kumar, Techno-economic and life cycle assessment on lignocellulosic biomass thermochemical conversion technologies: a review, *Renew. Sust. Energ. Rev.* 53 (2016) 1486–1499.
- [16] M. Patel, A. Kumar, Production of renewable diesel through the hydroprocessing of lignocellulosic biomass-derived bio-oil: a review, *Renew. Sust. Energ. Rev.* 58 (2016) 1293–1307.

- [17] P. McKendry, Energy production from biomass (part 1): overview of biomass, *Bioresour. Technol.* 83 (1) (2002) 37–46.
- [18] S. Anis, Z. Zainal, Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: a review, *Renew. Sust. Energ. Rev.* 15 (5) (2011) 2355–2377.
- [19] H.B. Goyal, D. Seal, R.C. Saxena, Bio-fuels from thermochemical conversion of renewable resources: a review, *Renew. Sust. Energ. Rev.* 12 (2) (2008) 504–517.
- [20] C. Rioche, S. Kulkarni, F.C. Meunier, J.P. Breen, R. Burch, Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts, *Appl. Catal. B Environ.* 61 (1) (2005) 130–139.
- [21] R. Trane, S. Dahl, M. Skjøth-Rasmussen, A. Jensen, Catalytic steam reforming of bio-oil, *Int. J. Hydrog. Energy* 37 (8) (2012) 6447–6472.
- [22] A. Lemonidou, P. Kechagiopoulos, E. Heracleous, S. Voutetakis, Steam Reforming of Bio-Oils to Hydrogen, in: *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*, Elsevier, Amsterdam, The Netherlands, 2013, pp. 467–493.
- [23] A.C. Basagiannis, X.E. Verykios, Steam reforming of the aqueous fraction of bio-oil over structured Ru/MgO/Al<sub>2</sub>O<sub>3</sub> catalysts, *Catal. Today* 127 (1) (2007) 256–264.
- [24] F. Bimbela, M. Oliva, J. Ruiz, L. Garcia, J. Arauzo, Hydrogen production by catalytic steam reforming of acetic acid, a model compound of biomass pyrolysis liquids, *J. Anal. Appl. Pyrolysis* 79 (1) (2007) 112–120.
- [25] T. Davidian, N. Guilhaume, C. Daniel, C. Mirodatos, Continuous hydrogen production by sequential catalytic cracking of acetic acid: part I. Investigation of reaction conditions and application to two parallel reactors operated cyclically, *Appl. Catal. A Gen.* 335 (1) (2008) 64–73.
- [26] T. Davidian, N. Guilhaume, H. Provendier, C. Mirodatos, Continuous hydrogen production by sequential catalytic cracking of acetic acid: part II. Mechanistic features and characterisation of catalysts under redox cycling, *Appl. Catal. A Gen.* 337 (2) (2008) 111–120.
- [27] M.E. Domine, E.E. Iojoiu, T. Davidian, N. Guilhaume, C. Mirodatos, Hydrogen production from biomass-derived oil over monolithic Pt-and Rh-based catalysts using steam reforming and sequential cracking processes, *Catal. Today* 133 (2008) 565–573.
- [28] E.E. Iojoiu, M.E. Domine, T. Davidian, N. Guilhaume, C. Mirodatos, Hydrogen production by sequential cracking of biomass-derived pyrolysis oil over noble metal catalysts supported on ceria-zirconia, *Appl. Catal. A Gen.* 323 (2007) 147–161.
- [29] E.C. Vagia, A.A. Lemonidou, Thermodynamic analysis of hydrogen production via steam reforming of selected components of aqueous bio-oil fraction, *Int. J. Hydrog. Energy* 32 (2) (2007) 212–223.
- [30] C.-F. Yan, F.-F. Cheng, R.-R. Hu, Hydrogen production from catalytic steam reforming of bio-oil aqueous fraction over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts, *Int. J. Hydrog. Energy* 35 (21) (2010) 11693–11699.
- [31] T. Hou, L. Yuan, T. Ye, L. Gong, J. Tu, M. Yamamoto, Y. Torimoto, Q. Li, Hydrogen production by low-temperature reforming of organic compounds in bio-oil over a CNT-promoting Ni catalyst, *Int. J. Hydrog. Energy* 34 (22) (2009) 9095–9107.
- [32] F. Seyedeyn-Azad, E. Salehi, J. Abedi, T. Harding, Biomass to hydrogen via catalytic steam reforming of bio-oil over Ni-supported alumina catalysts, *Fuel Process. Technol.* 92 (3) (2011) 563–569.
- [33] S. Thaicharoensutcharittham, V. Meeyoo, B. Kitiyanan, P. Rangsunvigit, T. Rirksomboon, Hydrogen production by steam reforming of acetic acid over Ni-based catalysts, *Catal. Today* 164 (1) (2011) 257–261.
- [34] P.L. Spath, M. Mann, W. Amos, Update of Hydrogen from Biomass—Determination of the Delivered Cost of Hydrogen, National Renewable Energy Lab, Golden, CO, 2003.
- [35] K. McHugh, Hydrogen Production Methods. Report MPR-WP-0001, Revision 0, 2005.
- [36] K. Nath, D. Das, Hydrogen from biomass, *Curr. Sci.* 85 (3) (2003) 265–271.
- [37] M. Ni, D.Y. Leung, M.K. Leung, K. Sumathy, An overview of hydrogen production from biomass, *Fuel Process. Technol.* 87 (5) (2006) 461–472.
- [38] K. Sipilä, E. Kuoppala, L. Fagernäs, A. Oasmaa, Characterization of biomass-based flash pyrolysis oils, *Biomass Bioenergy* 14 (2) (1998) 103–113.
- [39] Z.X. Wang, T. Dong, L.X. Yuan, T. Kan, X.F. Zhu, Y. Torimoto, M. Sadakata, Q.X. Li, Characteristics of bio-oil-syngas and its utilization in Fischer–Tropsch synthesis, *Energy Fuel* 21 (4) (2007) 2421–2432.
- [40] J. Akhtar, N.A.S. Amin, A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, *Renew. Sust. Energ. Rev.* 15 (3) (2011) 1615–1624.
- [41] S. Xiu, A. Shahbazi, Bio-oil production and upgrading research: a review, *Renew. Sust. Energ. Rev.* 16 (7) (2012) 4406–4414.

- [42] A.V. Bridgwater, Renewable fuels and chemicals by thermal processing of biomass, *Chem. Eng. J.* 91 (2) (2003) 87–102.
- [43] A.V. Bridgwater, Biomass fast pyrolysis, *Therm. Sci.* 8 (2) (2004) 21–50.
- [44] C. Briens, J. Piskorz, F. Berruti, Biomass valorization for fuel and chemicals production—a review, *Int. J. Chem. React. Eng.* 6 (1) (2008). <https://www.degruyter.com/view/j/ijcre.2008.6.1/ijcre.2008.6.1.1674/ijcre.2008.6.1.1674.xml?format=INT&intcmp=trendmd>.
- [45] S. Czernik, A. Bridgwater, Overview of applications of biomass fast pyrolysis oil, *Energy Fuel* 18 (2) (2004) 590–598.
- [46] H. Darmstadt, M. Garcia-Perez, A. Adnot, A. Chaala, D. Kretschmer, C. Roy, Corrosion of metals by bio-oil obtained by vacuum pyrolysis of softwood bark residues. An X-ray photoelectron spectroscopy and auger electron spectroscopy study, *Energy Fuel* 18 (5) (2004) 1291–1301.
- [47] A. Demirbas, Bio-fuels from agricultural residues, *Energ. Source. Part A* 30 (2) (2007) 101–109.
- [48] M.F. Demirbas, Hydrogen from various biomass species via pyrolysis and steam gasification processes, *Energ. Source. Part A* 28 (3) (2006) 245–252.
- [49] Z. Ji-Lu, Bio-oil from fast pyrolysis of rice husk: yields and related properties and improvement of the pyrolysis system, *J. Anal. Appl. Pyrolysis* 80 (1) (2007) 30–35.
- [50] S.-H. Jung, B.-S. Kang, J.-S. Kim, Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system, *J. Anal. Appl. Pyrolysis* 82 (2) (2008) 240–247.
- [51] R. Liu, C. Deng, J. Wang, Fast pyrolysis of corn straw for bio-oil production in a bench-scale fluidized bed reactor, *Energ. Source. Part A* 32 (1) (2009) 10–19.
- [52] N. Mahinpey, P. Murugan, T. Mani, R. Raina, Analysis of bio-oil, biogas, and biochar from pressurized pyrolysis of wheat straw using a tubular reactor, *Energy Fuel* 23 (5) (2009) 2736–2742.
- [53] W. Tsai, M. Lee, Y. Chang, Fast pyrolysis of rice husk: product yields and compositions, *Bioresour. Technol.* 98 (1) (2007) 22–28.
- [54] T.M. Brown, P. Duan, P.E. Savage, Hydrothermal liquefaction and gasification of *Nannochloropsis* sp, *Energy Fuel* 24 (6) (2010) 3639–3646.
- [55] J.L. Faeth, P.J. Valdez, P.E. Savage, Fast hydrothermal liquefaction of *Nannochloropsis* sp. to produce biocrude, *Energy Fuel* 27 (3) (2013) 1391–1398.
- [56] A. Juneja, G.S. Murthy, Evaluating the potential of renewable diesel production from algae cultured on wastewater: techno-economic analysis and life cycle assessment, *AIMS ENERGY* 5 (2) (2017) 239–257.
- [57] K. Svoboda, M. Pohorelý, M. Hartman, J. Martinec, Pretreatment and feeding of biomass for pressurized entrained flow gasification, *Fuel Process. Technol.* 90 (5) (2009) 629–635.
- [58] A. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, *Org. Geochem.* 30 (12) (1999) 1479–1493.
- [59] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, *Energy Fuel* 20 (3) (2006) 848–889.
- [60] J.R. Rostrup-Nielsen, Catalytic steam reforming, in: *Catalysis*, Springer, Berlin, Heidelberg, 1984, pp. 1–117.
- [61] S. Adhikari, S.D. Fernando, A. Haryanto, Hydrogen production from glycerol: an update, *Energy Convers. Manag.* 50 (10) (2009) 2600–2604.
- [62] J.R. Marda, J. DiBenedetto, S. McKibben, R.J. Evans, S. Czernik, R.J. French, A.M. Dean, Non-catalytic partial oxidation of bio-oil to synthesis gas for distributed hydrogen production, *Int. J. Hydrog. Energy* 34 (20) (2009) 8519–8534.
- [63] D.C. Rennard, P.J. Dauenhauer, S.A. Tupy, L.D. Schmidt, Autothermal catalytic partial oxidation of bio-oil functional groups: esters and acids, *Energy Fuel* 22 (2) (2008) 1318–1327.
- [64] E.C. Vagia, A.A. Lemonidou, Thermodynamic analysis of hydrogen production via autothermal steam reforming of selected components of aqueous bio-oil fraction, *Int. J. Hydrog. Energy* 33 (10) (2008) 2489–2500.
- [65] A. Iriando, V. Barrio, J. Cambra, P. Arias, M. Güemez, R. Navarro, M. Sánchez-Sánchez, J. Fierro, Hydrogen production from glycerol over nickel catalysts supported on  $\text{Al}_2\text{O}_3$  modified by Mg, Zr, Ce or La, *Top. Catal.* 49 (1–2) (2008) 46.
- [66] K. Lehnert, P. Claus, Influence of Pt particle size and support type on the aqueous-phase reforming of glycerol, *Catal. Commun.* 9 (15) (2008) 2543–2546.
- [67] A.J. Byrd, S. Kumar, L. Kong, H. Ramsurn, R.B. Gupta, Hydrogen production from catalytic gasification of switchgrass biocrude in supercritical water, *Int. J. Hydrog. Energy* 36 (5) (2011) 3426–3433.

- [68] A.J. Byrd, K. Pant, R.B. Gupta, Hydrogen production from glycerol by reforming in supercritical water over Ru/Al<sub>2</sub>O<sub>3</sub> catalyst, *Fuel* 87 (13) (2008) 2956–2960.
- [69] A. Loppinet-Serani, C. Aymonier, F. Cansell, Current and foreseeable applications of supercritical water for energy and the environment, *ChemSusChem* 1 (6) (2008) 486–503.
- [70] J.M. Penninger, M. Rep, Reforming of aqueous wood pyrolysis condensate in supercritical water, *Int. J. Hydrog. Energy* 31 (11) (2006) 1597–1606.
- [71] T. Davidian, N. Guilhaume, E. Iojoiu, H. Provendier, C. Mirodatos, Hydrogen production from crude pyrolysis oil by a sequential catalytic process, *Appl. Catal. B Environ.* 73 (1) (2007) 116–127.
- [72] D. Nagarajan, D.-J. Lee, A. Kondo, J.-S. Chang, Recent insights into biohydrogen production by microalgae— from biophotolysis to dark fermentation, *Bioresour. Technol.* 227 (2017) 373–387.
- [73] H. Argun, F. Kargi, Bio-hydrogen production by different operational modes of dark and photo-fermentation: an overview, *Int. J. Hydrog. Energy* 36 (13) (2011) 7443–7459.
- [74] C. Sambusiti, M. Bellucci, A. Zabaniotou, L. Beneduce, F. Monlau, Algae as promising feedstocks for fermentative biohydrogen production according to a biorefinery approach: a comprehensive review, *Renew. Sust. Energ. Rev.* 44 (2015) 20–36.
- [75] W. Nabgan, T.A. Tuan Abdullah, R. Mat, B. Nabgan, Y. Gambo, M. Ibrahim, A. Ahmad, A.A. Jalil, S. Triwahyono, I. Saeh, Renewable hydrogen production from bio-oil derivative via catalytic steam reforming: an overview, *Renew. Sust. Energ. Rev.* 79 (Supplement C) (2017) 347–357.
- [76] AspenTech, Aspen Plus V8.8. Available at, <http://www.aspentech.com/products/Aspen-Plus/V88/> (October 3, 2017).
- [77] I.J. Tews, Y. Zhu, C. Drennan, D.C. Elliott, L.J. Snowden-Swan, K. Onarheim, Y. Solantausta, D. Beckman, Biomass Direct Liquefaction Options. TechnoEconomic and Life Cycle Assessment, Pacific Northwest National Laboratory (PNNL), Richland, WA, 2014.
- [78] M. Kumar, A.O. Oyedun, A. Kumar, Hydrothermal liquefaction of biomass for the production of diluents for bitumen transport, *Biofuels Bioprod. Biorefin.* 11 (5) (2017) 811–829.
- [79] L. Ou, R. Thilakarathne, R.C. Brown, M.M. Wright, Techno-economic analysis of transportation fuels from defatted microalgae via hydrothermal liquefaction and hydroprocessing, *Biomass Bioenergy* 72 (2015) 45–54.
- [80] D.R. Vardon, B.K. Sharma, G.V. Blazina, K. Rajagopalan, T.J. Strathmann, Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis, *Bioresour. Technol.* 109 (2012) 178–187.
- [81] P. Biller, A. Ross, Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content, *Bioresour. Technol.* 102 (1) (2011) 215–225.
- [82] K. Magrini-Bair, S. Czernik, R. French, Y. Parent, M. Ritland, E. Chornet, Fluidizable catalysts for producing hydrogen by steam reforming biomass pyrolysis liquids, in: *Proceedings of the 2002 US DOE Hydrogen Program Review NREL/CP-610, 2002.*
- [83] E.C. Vagia, A.A. Lemonidou, Hydrogen production via steam reforming of bio-oil components over calcium aluminate supported nickel and noble metal catalysts, *Appl. Catal. A Gen.* 351 (1) (2008) 111–121.
- [84] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Comparative techno-economic analysis of biohydrogen production via bio-oil gasification and bio-oil reforming, *Biomass Bioenergy* 51 (Supplement C) (2013) 99–108.
- [85] W.-H. Chen, T.-C. Hsieh, T.L. Jiang, An experimental study on carbon monoxide conversion and hydrogen generation from water gas shift reaction, *Energy Convers. Manag.* 49 (10) (2008) 2801–2808.
- [86] S. Sarkar, A. Kumar, Large-scale biohydrogen production from bio-oil, *Bioresour. Technol.* 101 (19) (2010) 7350–7361.
- [87] S. Sarkar, A. Kumar, Biohydrogen production from forest and agricultural residues for upgrading of bitumen from oil sands, *Energy* 35 (2) (2010) 582–591.
- [88] S. Sircar, T. Golden, Purification of hydrogen by pressure swing adsorption, *Sep. Sci. Technol.* 35 (5) (2000) 667–687.
- [89] M.S. Peters, K.D. Timmerhaus, R.E. West, *Plant Design and Economics for Chemical Engineers*, McGraw-Hill, New York, 2003.
- [90] A. Kumar, J.B. Cameron, P.C. Flynn, Biomass power cost and optimum plant size in western Canada, *Biomass Bioenergy* 24 (6) (2003) 445–464.
- [91] Y. Zhu, K.O. Albrecht, D.C. Elliott, R.T. Hallen, S.B. Jones, Development of hydrothermal liquefaction and upgrading technologies for lipid-extracted algae conversion to liquid fuels, *Algal Res.* 2 (4) (2013) 455–464.
- [92] E. Agbor, A.O. Oyedun, X. Zhang, A. Kumar, Integrated techno-economic and environmental assessments of sixty scenarios for co-firing biomass with coal and natural gas, *Appl. Energy* 169 (2016) 433–449.

- [93] H. Shahrukh, A.O. Oyedun, A. Kumar, B. Ghiasi, L. Kumar, S. Sokhansanj, Techno-economic assessment of pellets produced from steam pretreated biomass feedstock, *Biomass Bioenergy* 87 (2016) 131–143.
- [94] P. Zundel, A. Hovingh, L. Wuest, D. MacElveney, T. Needham, *Silviculture Systems for the Production of Energy Biomass in Conventional Operations in Atlantic Canada*, Fredericton, New Brunswick, 1996.
- [95] S. Sarkar, A. Kumar, Techno-economic assessment of biohydrogen production from forest biomass in Western Canada, *Trans. ASABE* 52 (2) (2009) 519–530.
- [96] Canada-Visa, Canada Salary Wizard, Available from: <http://www.canadavisa.com/canada-salary-wizard.html>, 2014 January 25, 2015.
- [97] EPCOR, Actual Default Prices in Cents per kWh, 2015 [cited 2016 10 February]; Available from: <http://www.epcor.com/power-natural-gas/regulated-rate-option/commercial-customers/Documents/actual-default-supply-rates-2015.pdf>, 2015.
- [98] H. Shahrukh, A.O. Oyedun, A. Kumar, B. Ghiasi, L. Kumar, S. Sokhansanj, Net energy ratio for the production of steam pretreated biomass-based pellets, *Biomass Bioenergy* 80 (2015) 286–297.
- [99] S. Czernik, *Distributed Bio-Oil Reforming*, National Renewable Energy Laboratory, 2013. Available from: [https://www.hydrogen.energy.gov/pdfs/review13/pd004\\_czernik\\_2013\\_p.pdf](https://www.hydrogen.energy.gov/pdfs/review13/pd004_czernik_2013_p.pdf).
- [100] C. Kinoshita, S. Turn, Production of hydrogen from bio-oil using CaO as a CO<sub>2</sub> sorbent, *Int. J. Hydrog. Energy* 28 (10) (2003) 1065–1071.
- [101] S. Czernik, R. French, Penev *Distributed Bio-Oil Reforming*, National Renewable Energy Laboratory, Washington, DC, 2010. Available from: <https://www.nrel.gov/docs/fy10osti/48066.pdf>.
- [102] T.A. Milne, C.C. Elam, R.J. Evans, *Hydrogen From Biomass: State of the Art and Research Challenges*, National Renewable Energy Lab, Golden, CO, 2002.
- [103] D. Wang, S. Czernik, D. Montane, M. Mann, E. Chornet, Biomass to hydrogen via fast pyrolysis and catalytic steam reforming of the pyrolysis oil or its fractions, *Ind. Eng. Chem. Res.* 36 (5) (1997) 1507–1518.
- [104] A. Corradetti, U. Desideri, Should biomass be used for power generation or hydrogen production? *J. Eng. Gas Turbines Power* 129 (3) (2007) 629–636.
- [105] C.N. Hamelinck, R.A. Suurs, A.P. Faaij, International bioenergy transport costs and energy balance, *Biomass Bioenergy* 29 (2) (2005) 114–134.
- [106] T. Kreutz, R. Williams, S. Consonni, P. Chiesa, Co-production of hydrogen, electricity and CO<sub>2</sub> from coal with commercially ready technology. Part B: economic analysis, *Int. J. Hydrog. Energy* 30 (7) (2005) 769–784.
- [107] E.D. Larson, H. Jin, F.E. Celik, *Gasification-Based Fuels and Electricity Production From Biomass, Without and With Carbon Capture and Storage*, Princeton Environmental Institute, Princeton University, 2005.
- [108] P. Spath, A. Aden, T. Eggeman, M. Ringer, B. Wallace, J. Jechura, *Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier*, National Renewable Energy Lab, Golden, CO, 2005.
- [109] Y. Zhu, S.A. Tjokro Rahardjo, C. Valkenburt, L.J. Snowden-Swan, S.B. Jones, M.A. Machinal, *Techno-Economic Analysis for the Thermochemical Conversion of Biomass to Liquid Fuels*, Pacific Northwest National Laboratory (PNNL), Richland, WA, 2011.
- [110] A.L. Villanueva Perales, C. Reyes Valle, P. Ollero, A. Gómez-Barea, Technoeconomic assessment of ethanol production via thermochemical conversion of biomass by entrained flow gasification, *Energy* 36 (7) (2011) 4097–4108.
- [111] A. Dutta, M. Talmadge, J. Hensley, M. Worley, D. Dudgeon, D. Barton, P. Groenendijk, D. Ferrari, B. Stears, E. Searcy, Techno-economics for conversion of lignocellulosic biomass to ethanol by indirect gasification and mixed alcohol synthesis, *Environ. Prog. Sustain. Energy* 31 (2) (2012) 182–190.
- [112] R.M. Swanson, A. Platon, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomass-to-liquids production based on gasification, *Fuel* 89 (Supplement 1) (2010) S11–S19.
- [113] VoseSoftware [Internet], Model Risk-Monte Carlo Simulation [Cited November 28 2017], Available from: <http://www.vosesoftware.com/index.php>.
- [114] M. Balat, Potential importance of hydrogen as a future solution to environmental and transportation problems, *Int. J. Hydrog. Energy* 33 (15) (2008) 4013–4029.
- [115] Z. Chen, S.S. Elnashaie, Development of a novel autothermal reforming process and its economics for clean hydrogen production, *Asia Pac. J. Chem. Eng.* 1 (1–2) (2006) 5–12.
- [116] S.E. Hosseini, M.A. Wahid, Hydrogen production from renewable and sustainable energy resources: promising green energy carrier for clean development, *Renew. Sust. Energ. Rev.* 57 (Supplement C) (2016) 850–866.
- [117] P. Parthasarathy, K.S. Narayanan, Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield—a review, *Renew. Energy* 66 (Supplement C) (2014) 570–579.