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Technical evaluation of Post-combustion CO₂ Capture and hydrogen production industrial symbiosis

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Abstract

The aim of this study is to develop an industrial ecosystem whereby wastes/products from a Postcombustion CO₂ Capture (PCC) plant are utilised in a hydrogen biorefinery. Subsequently, five hydrogen biorefinery models are developed that use PCC's model amine i.e. monoethanolamine (MEA) as a nitrogen source during microbial hydrogen production and CO₂ as a process chemical. Technical evaluations of the five case models are carried out to identify the ones that maximise value by multiproduct generation from biomass and fulfil total/partial parasitic energy demand. The case meeting these criteria, produces 3.1t of succinylated lignin adhesive, 4.9t of dry compost and 2744kWh of electricity from 10t (dry) of sawdust feedstock, daily. Its daily power and heat duties stand at 3906kWh and 52.1GJ respectively. Simulations also demonstrate biohydrogen's potential as an energy storage vector for peak/backup power with an annual 1001.4MWh of power storage capacity from 10t/d feedstock.

Keywords: Biohydrogen; biorefinery; CO₂ capture; industrial ecology; waste

1. Introduction

The 21st conference of the Parties to the United Nations Framework Convention on Climate Change (COP21) culminated with a "save the planet" outcome which necessitates radical changes in global energy and electricity infrastructure. Fossil fuel generated electricity is a major contributing factor to Greenhouse Gases (GHG) emissions (Bruckner et al., 2014). There is intense pressure on coal fired power production due to its contribution to global GHG emissions. Coal has the highest share of electricity generation in the world (40.58%) (Bruckner et al., 2014) and in Australia (61%) (Ball et al., 2015), thereby playing a significant role in the respective economies and energy mixes. The benign utilisation of coal in power plants does require installation of Post-combustion CO₂ Capture (PCC) technologies to scrub CO₂, in addition to SO₂, NO_x and ash from flue gas. Currently, alkanolamines based PCC is the only industrially mature technology. This solution, however, generates its own wastes. The largest waste stream generated in an alkanolamine based PCC process is the degraded amine solution produced by the reclaimer and modelled in this study with monoethanolamine (MEA). Recently, utilisation of PCC waste MEA as a nitrogen source for the fermentative hydrogen production has been proposed (Ghayur et al., 2018).

Hydrogen, as a dense energy carrier, has been a topic of research for many decades now and continues to gain momentum in light of the Climate Change mitigation efforts. Hydrogen is desirable over other biofuels because of its carbon-free conversion into electricity and potential applications in both mobile and stationary domains. Water and biomass are the two competing renewable hydrogen sources.

Electrolytic hydrogen production from water (Kasai, 2014; Kelly, 2014) consuming around 48 kWh electricity per kg hydrogen in today's electrolysers (Gardner, 2009) is an established technology, however, it is energy intensive. Fermentative bio-hydrogen, overcomes this issue but suffers from low yields. Reviews regarding research on bio-hydrogen (Singh et al., 2017) and its production technologies are available and interested readers are referred to the following articles for further information detailing the current status of dark-fermentation (Kumar et al., 2018; Lin et al., 2017; Nagarajan et al., 2017; Urbaniec & Bakker, 2015), photo-fermentation (Khetkorn et al., 2017; Lin et al., 2017; Nagarajan et al., 2017; Zhang et al., 2017) and combined dark-photo-fermentation (Ghosh et al., 2017).

Combined dark-photo-fermentation is a propitious technique, yet to become commercial, overcomes the issue of low hydrogen yield by combining dark- and photo-fermentations. In these systems the carbon-rich by-products of dark fermentation are utilised by the photo fermentative microorganisms thereby increasing the overall hydrogen yield, when compared to individual photo-or dark-fermentation systems. In this study combined dark-photo-fermentation is investigated as this allowed to (1) utilise MEA; (2) generate carbon-free biofuel; and (3) increase the overall hydrogen production.

Glutamate and MEA are generally used as nitrogen sources for biohydrogen production (Ren et al., 2010; Seifert et al., 2012). MEA is a good nitrogen source (Ooshima et al., 1998; Tao et al., 2008; Yang et al., 2014) and in one experiment it was found to be a better option than glutamate for biohydrogen production (Katsuda et al., 2000). Thus, in the biorefinery cases modelled in this study, MEA has been used to fulfil the nitrogen requirements of the microbes generating hydrogen.

Captured CO_2 is the other large stream in PCC plants which is typically intended for capital-intensive underground storage. Given that a typical 500 MW Australian brown coal power plant generates around 1.3 metric tonnes (t) of CO_2 per MWh of electricity (Cottrell et al., 2009), a PCC technology installed on such a plant will capture a large amount of CO_2 . Two processes, discussed below, were modelled in this study to capitalise upon this resource.

The first process is biomass lignocellulose fractionation. This process aims to either release cellulose from the lignocellulose matrix or to separate out its three main components (cellulose, hemicellulose and lignin) for their conversion into fuels and chemicals. By nature, the lignocellulose matrix is recalcitrant to any physical and chemical attack to its structural integrity (Ghayan, 2018a). This necessitates harsh conditions for its fractionation, such as extreme temperature/pressure and high acidic/basic solutions. Contrariwise, low temperature and efficient fractionation technologies are essential for higher biomass to fuel/chemical conversion rates. High temperatures degrade lignocellulose fractions, reducing their conversion rates into fuels/chemicals. Supercritical CO₂ (scCO₂) allows for a low temperature (31.1 °C) and critical pressure (72.9 atm). In literature, effective temperatures from under 100 °C (Zhan et al., 2005) to 200 °C (Lv et al., 2013) and over (Morais & Lukasik, 2017) have been reported for scCO₂ fractionation. Technical complexities of recycling scCO₂ at industrial scale make it economically unattractive. However, in the presence of a large CO₂ source, scCO₂ fractionation is a worthwhile process, and has been used in the design of the multi-product biorefinery cases in this study.

The second process is hemicellulose fermentation to succinic acid. Anaerobic production of succinic acid requires addition of CO_2 to the fermentation process ($3C_5H_{10}O_5 + 5CO_2 \rightarrow 5C_4H_6O_4 + 2.5O_2$).

The lignin fraction of biomass is usually regarded as a waste stream, typically burned for its calorific value. Its thermochemical conversion routes into fuels/chemicals are prohibitively energy intensive while the biochemical processes are still in the early stages of Research and Development (R&D). In this study a comparatively low energy process converting lignin into an adhesive is explored as part of a multi-product biorefinery case. Dry lignin is reacted with succinic anhydride at 28 °C (Xiao et al., 2001) to convert it into succinylated lignin adhesive which is a suitable replacement for formaldehyde based adhesives in the wood industry. Succinic acid from the hemicellulose fermentation is consumed in this process.

Hydrogen from biomass can be produced via a variety of technologies and routes. None of these, however, are commercially attractive. Each of these is in a different stage of R&D and offers unique benefits and challenges. Key questions must be answered before these concepts could reach commercialisation stage. Researchers are using a myriad of tools in their quest for the answers. Process simulations are one such set of tools. They help build theoretical plant details based on existing commercial and experimental data to identify best configurations and parameters. This approach has been used to compare five different case designs of multi-product hydrogen biorefineries and to find the ones that maximise products generation from biomass and fulfil total/partial parasitic energy demand. Case model requirements are compared across electricity, heat, water and CO_2 demands, and quantified for non-food biomass feedstock of 10 metric tonnes (dry) per day (t/d) for a proof-of-concept system. This demonstration biorefinery is designed with the perspective of the Gippsland region of Victoria (Australia). This required due consideration being given to the local brown coal power industry, Forest Value Chain (FVC) and the industrial wastes.

2. Methods and Materials

This study aims to investigate the technical parameters for a demonstration multi-product hydrogen biorefinery as a part of an industrial ecology with a PCC plant.

2.1 Methodology

In the methodology for comparing the five models/cases, the following criteria are considered:

- 1. Utilisation of local organic waste biomass;
- 2. Utilisation of all three fractions of the lignocellulose;
- 3. Minimisation of dry compost production;
- 4. Fulfilment of partial or full parasitic energy demand;
- 5. Utilisation of MEA; and
- 6. Utilisation of CO₂.

The five cases are built incrementally. The first case converts biomass cellulose into hydrogen via dark fermentation. This model was presented previously (Ghayur & Verheyen, 2017a), simulated using COCO-ChemSep and is used as Base Case in this study. In the next iteration – Case 1 – the effluent from dark fermentation undergoes photo fermentation to increase the total hydrogen production. In Case 2, an adhesive is produced from hemicellulose and lignin in addition to hydrogen from cellulose. Case 3 further builds on, converting hydrogen into electricity, in addition to the lignin-adhesive co-product. Case 4 looks at hydrogen generation as a storage vector for peak/backup power demand.

COCO-ChemSep (version 7.21) simulation suite (COCO, 2017) was used for process flow-sheeting and mass-energy calculations. The physical properties of the components were obtained either from its thermodynamic library or from NIST webbook (Mallard & Linstrom, 2017) via COCO-ChemSep's

built-in import function. All five cases are simulated as zero-dimensional energy models. Simulation parameters are listed in the process descriptions in the following section which are based on published literature. All assumptions are duly noted.

2.2 Biorefinery Process Description

10 t/d waste sawdust (dry) from saw-milling of trees grown in Victoria is used as biomass feedstock with cellulose (37.47%), hemicellulose (23.83%), lignin (30.03%) and ash/others (8.67%) composition. This composition is an average of values given in the Commonwealth Scientific and Industrial Research Organisation (CSIRO) studies (Dekker, 1987; Dekker et al., 1987), thus providing a better representation of the heterogeneous nature of sawdust waste in Victoria.

In the following description (figure 1):

- Base Case is denoted by the Dark Fermentation Area (A100);
- Case 1 is comprised of the Dark Fermentation and Photo Fermentation areas (A100, A200);
- Case 2 is defined by the Dark Fermentation, Photo Fermentation and Adhesive areas (A100, A200, A300);
- Case 3 includes Dark Fermentation, Photo Fermentation, Adhesive and Fuel Cell areas (A100, A200, A300, A400); and
- Case 4 includes Dark Fermentation, Photo Fermentation, Adhesive, Fuel Cell and Storage areas (A100, A200, A300, A400, A500).

2.2.1 Dark Fermentation Area (A100)

Hydrogen Area consists of sawdust milling, its scCO₂ Fractionation, De-Lignification, cellulose's conversion to biogas ($H_2 + CO_2$) using dark fermentation and the separation of hydrogen from CO_2 in the Amine Plant. Sawdust is conveyed to the disk mill and grinded to 1 mm size. The milled biomass is sent to screw extruder for $scCO_2$ Fractionation. The screw extruder with water-biomass- CO_2 (2:1:0.4 wt. ratio) stream (Zhan et al., 2006) operates at 90 °C. These parameters help fractionate the lignocellulose matrix. The extruded biomass is mashed with water in the wash tank. Two streams exit the wash tank, namely: solid stream and liquid stream. Solid stream consists of cellulose, lignin, ash and 10% of hemicellulose, all with 30% moisture. Liquid stream consists of 90% of the hemicellulose and sent to succinic acid fermentation (A300). Solid stream is sent to De-Lignification. Here it is washed in ethanol-water-biomass (1:0.8:0.2 wt. ratio) solution to remove lignin. The washing temperature is controlled at about 80 °C (Lv et al., 2013; Schulze et al., 2016). Solid cellulose is separated while lignin solution is sent for distillation. At above 85 °C, ethanol is distilled out and recycled back. 99% of ethanol is recovered via distillation. The recovered stream also contains 4.5% water (wt.). 80% of lignin is recovered and sent for succinylation (A300). Cellulose, ash and the rest of the lignin is sent to dark-fermentation at a total solid content of 10% (wt.). Simultaneous saccharification and fermentation (Li & Chen, 2007) is used to convert cellulose into hydrogen and acetic acid ($C_6H_{12}O_6 + 2H_2O \rightarrow 2CO_2 + 4H_2 + 2C_2H_4O_2$). Butyric acid, propionic acid and ethanol are also generated during the fermentation process. Temperature is kept at 35 °C (Li & Chen, 2007) and the Hydraulic Retention Time (HRT) is 36 hours. MEA demand is calculated as 0.167 kg per kg cellulose consumed (Katsuda et al., 2000). Hydrogen and CO₂ from the fermenter are collected and sent to the Amine Plant operating at 30% MEA concentration. 95% of the CO_2 is assumed to be removed at the Amine Plant, operating at 120 °C.

2.2.2 Photo Fermentation Area (A200)

The mash from dark fermentation (A100) flows to a rotary drum filter to separate out solids from the aqueous solution. The aqueous stream with the organic acids flows into the photo-fermenters. Liquid streams from Adhesive Area (A300) containing acetic acid joins the aqueous stream in the photo-fermenters. The photo-fermentation is assumed to operate for 10 hours per day, necessitating the storage of liquids from Dark Fermetnation Area (A100) and Adhesive Area (A300) in a tank for 14 hours. The organic acids are fermented into hydrogen with 50% of the theoretical yields. Solids stream is heated and sent to the succinic acid fermenter (A300).

2.2.3 Adhesive Area (A300)

Liquid stream from scCO₂ Fractionation (A100) is assumed to contain 90% of the hemicellulose. This stream is combined with solid stream from Photo Fermentation area (A200) and sent to succinic acid fermentation $(3C_5H_{10}O_5 + 5CO_2 \rightarrow 5C_4H_6O_4 + 2.5O_2)$. CO₂ is also fed to the fermenter. The process produces 0.44kg of succinic acid per kg of hemicellulose at 37 °C (Corona-González et al., 2016; Klein et al., 2017). HRT is kept at 40 hours (Corona-González et al., 2016) and solid to water ratio is 1:6 (wt.) in the fermenter. Broth from fermentation is cooled down to 2-4 °C which crystallises succinic acid (Li et al., 2010; Luque et al., 2009). The broth then undergoes filtration to separate out succinic acid crystals and leftover solids/sugars from liquids. The liquid stream containing acetic acid joins the aqueous stream in the Photo Fermentation area (A200) and fermented into hydrogen.

The solid stream at 30% moisture (wt.) is assumed to retain 90% of the succinic acid crystals. This solid stream is heated to 165 °C to evaporate water and other organic contaminants (e.g. pyruvic acid) from succinic acid. Next it is heated to 185 °C to evaporate succinic acid. Solid residue is recovered as compost. Gaseous succinic acid is heated to over 260 °C to convert it into succinic anhydride ($C_4H_6O_4 \rightarrow C_4H_4O_3 + H_2O$) with an assumed 90% conversion rate. Water and unconverted succinic acid are separated. Succinic anhydride is then reacted with lignin to produce succinylated lignin adhesive. This reaction is carried out in a continuously stirred reactor vessel at 28 °C (Xiao et al., 2001).

2.2.4 Fuel Cell Area (A400)

Clean hydrogen from the Amine Plant (A100) is used to generate electricity $(2H_2 + O_2 \rightarrow 2H_2O)$ via Solid Oxide Fuel Cell (SOFC). It is assumed to operate at 49% efficiency, based on commercially available fuel cells.

2.2.5 Storage Area (A500)

The Storage Area stores hydrogen in a Magnesium Hydride (MgH₂) tank and generates electricity using a SOFC. Heat released during hydrogen absorption is considered lost while heat required during hydrogen desorption is provided by the waste heat from the SOFC (Ghayur & Verheyen, 2018).



Figure 1: Five Areas of the Biorefinery

In the five cases operating parameters are taken as 1 atm of pressure and 25 °C of temperature.

3. Results and Discussion

As stated earlier, the biorefinery is sized for 10t/d of sawdust. Results of the five simulation cases are provided in the following table (1). As is the case with typical biorefinery concepts, all five models have high energy and water demands and a large quantity of biomass ends up as low-value compost.

	Base Case	Case 1	Case 2	Case 3	Case 4						
Area	100	100, 200	100, 200,	100, 200,	100, 200, 300,						
			300	300, 400	400, 500						
Products											
Hydrogen	3.53 kg/h	7.84 kg/h	8 kg/h	-	-						
CO ₂	38.64 kg/h	78.69 kg/h	80.58 kg/h	80.58 kg/h	g/h 80.58 kg/h						
Adhesive	-	-	129.43 kg/h	129.43 kg/h	129.43 kg/h						
Electricity	-	-	-	114.32 kWh	-						
Clean Water	-	-	-	64 kg/h	-						
Compost (dry)	337.65 kg/h	337.65 kg/h	202.79 kg/h	202.79 kg/h	202.79 kg/h						
Consumption											
Water	1326.47 kg/h	1326.47 kg/h	2098.47 kg/h	2098.47 kg/h	2098.47 kg/h						
Heat	407.68 kW	518.9 kW	603.2 kW	603.2 kW	603.2 kW						
Electricity	95.05 kWh	103.63 kWh	155.59 kWh	162.73 kWh	162.73 kWh						
CO ₂	166.67 kg/h	166.67 kg/h	182.58 kg/h	182.58 kg/h	182.58 kg/h						

Table 1: Hourly Consumption and Production of Five Cases

Analysis of simulation results single out Case 3 (table 1), due to its continuous electricity generation, one co-product and smaller compost quantity. Case 4, although, generates similar amount of

electricity over a year, it would not be continuous. This implies, the biorefinery's parasitic power demand could not be fulfilled via the generated electricity. A comparison of the parasitic energy demand of the five cases is provided in the following figure (2).



Figure 2: Hourly Energy Demand (kW) of the Five Cases

Case 2, 3 and 4 generate same quantity of compost and have similar CO_2 , MEA and water demands. Thus, Case 3 has the obvious advantage over the rest of the models. Hourly stream flow rates for the Case 3 are described in the following figure (3).



Stream	S100	S101	S103	S104	S105	S106	S107	S108	S109		
Т (°С)	25	25	25	85	25	25	80	85	25		
P (atm)	1	75	75	1.5	1.5	1.5	1.5	1.5	1.5		
M (kg/h)	541.67	708.33	166.67	1250	424.92	825.09	2973.77	1694.16	294.77		
Stream	S110	S111	S112	S113	S114	S115	S200	S201	S202		
т (°С)	85	25	25	25	25	40	25	25	25		
P (atm)	1.5	1.5	1	1.5	5	1	1.5	1.5	1.5		
M (kg/h)	1279.61	2225.33	42.14	42.14	12.24	76.34	192.05	3227.42	88.58		
Stream	S203	S301	S302	S305	S306	S307	S309	S310	S311		
T (°C)	105	37	25	235	235	260	25	25	25		
P (atm)	1	1.5	1.5	1	1.5	1	1.5	1	1		
M (kg/h)	3159.83	1435.36	302.06	202.79	38.44	9.12	29.32	100.11	129.43		
Figure 2: Case 2 Stream Flows											

Figure 3: Case 3 Stream Flows

A further breakdown of the energy demand of the Case 3 is provided in the following figures (4, 5). Case 3 consumes 603.2kW of heat and 162.73kW of power in one hour (Table 1).



Figure 4: Case 3 Hourly Energy Demand (kW)

Amine plant, scCO₂ Fractionation, De-Lignification and succinic acid heater consume the most energy (figure 5).



Figure 5: Comparison of Process Heat Duties

Utilisation of the generated hydrogen for fulfilling its parasitic electricity demand leaves adhesive as the main product of the Case 3 biorefinery. The succinylated lignin adhesive has immediate application in the Gippsland region as a wood adhesive. A large forest based products industry provides a strong market for an adhesive. Replacing fossil fuel based adhesive with bio-adhesive is an attractive option, however, its success would depend on its selling price. In the large turnover and small profit margin fibre-board market, it can replace urea-formaldehyde adhesive which costs around \$500/ton. Case 3's annual 1139 t production of succinylated lignin adhesive pales in comparison to the global urea-formaldehyde resin production that stands at around one million metric tonnes/annum (Ahamad & Alshehri, 2014). Thus, there is a large scope for green/bio-adhesives to replace urea-formaldehyde resins.

Case 3 produces dry compost which might be of value as a feedstock in processes requiring dry biomass. In Case 3, during succinic acid fermentation 2.17 kg/h of acetic acid is also produced which is sent to the photo-fermenter to increase the hydrogen yield. Case 3 consumes 29.92 kg/h of MEA and 182.58 kg/h of CO₂. Although, Case 3 fulfils the required criteria set out in the methodology, a brief discussion on Case 4 is also carried out to explore future research potential of this model.

In Case 4, the generated hydrogen is stored for utilisation as peak/backup power source. In one year the Case 4 generates 70.08 t of hydrogen, necessitating an adequate storage site fulfilling the temporal, spatial and safety requirements. In the simulation MgH₂ tank is used. However, there are other options for hydrogen storage such as above ground gas tanks and underground storage. Salt caverns are a better option for the underground storage. The Chevron-Phillips Clemens Terminal in Texas has a working capacity of 2,500 tonnes and stores hydrogen in a salt cavern (Haratyk & Forsberg 2012). A number of similarly suitable sites in Australia are: Chandler Salt Mine (Titjikala, Northern Territory), Boree site (Adavale, Queensland) and Forme Rocks (Looma, Western Australia). However, there is none in Gippsland. Recently, Gippsland's underground coalbeds have been proposed as storage sites for bio-methane (Ghayur & Verheyen, 2017b) but there is no research on hydrogen storage in coalbeds. This leaves either MgH₂ or above ground gas tank as the storage options. 70.08 t of hydrogen would generate 1001.44 MWh of electricity via 49% design point efficient fuel cells. During power generation, waste heat from SOFC is enough for hydrogen desorption from the MgH₂ (Ghayur & Verheyen, 2018). Heat generated during hydrogen absorption in the MgH₂ tank, however, is lost. This waste heat could be used within the multi-product biorefinery. Due to the intermittent nature of the peak/backup demand, the biorefinery would need to be flexible to use the waste heat when its available.

4. Conclusion

In this study five hydrogen biorefinery models/cases were simulated. The Base Case produced dark fermented hydrogen while the other four cases generated dark-photo fermented hydrogen with lignin adhesive co-product.

Simulation results show Case 3 as the best model suited for further investigation and optimisation. It generates 2743.68 kWh of electricity, 3.12 t of lignin adhesive and 4.87 t of compost (dry) from 10 t of sawdust (dry) in one day. By utilising all the three components of biomass, Case 3 is able to reduce low-value solid compost quantity by 40%, when compared to hydrogen only biorefinery. Case 3's daily demands stand at 50.36 t of water, 52.1 GJ of heat, 3906 kWh of electricity, 0.72 t of MEA and 4.38 t of CO₂. A typical 500 MW Australian brown coal power plant generates 15,600 t of CO₂ and anywhere between 4.68 to 37.44 t of MEA (depending upon process parameters and technology) in one day (Ghayur et al., 2018). Thus, it can sufficiently meet the MEA and CO₂ requirements of the Case 3 for the proposed industrial ecosystem. Energy and water demand reduction and compost value-addition are the next cogent areas of research. Dry compost may be of value as a feedstock in processes requiring dry biomass. Hydrogen produced in Case 4 shows promise as an energy storage vector, however, waste heat utilisation in a multiproduct biorefinery concept is needed to increase the overall system efficiency.

Notwithstanding unforeseeable barriers, hydrogen promises to be the ideal candidate to reduce carbon footprint, help increase renewable energy penetration, enhance grid stability, and improve grid efficiency in Australia and around the world. High energy demand is the biggest hurdle towards commercial hydrogen production. A multiproduct biorefinery such as designed in Case 3 may help either by directly producing biofuel co-products or by valorising co-products that help to meet energy costs. Research, however, is still needed to increase its overall efficiency and to maximise biomass utilisation with the aim of developing a zero-waste (Ghayan, 2018b) biorefinery concept.

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