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# Technical evaluation of post-combustion CO<sub>2</sub> capture and hydrogen production industrial symbiosis

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## ARTICLE INFO

### Article history:

Received 30 November 2017

Received in revised form

9 February 2018

Accepted 10 February 2018

Available online xxx

### Keywords:

Biohydrogen

Biorefinery

CO<sub>2</sub> capture

Industrial ecology

Waste

## ABSTRACT

The aim of this study is to develop an industrial ecosystem whereby wastes/products from a Post-combustion CO<sub>2</sub> 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 CO<sub>2</sub> 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 2744 kWh of electricity from 10t (dry) of sawdust feedstock, daily. Its daily power and heat duties stand at 3906 kWh and 52.1 GJ respectively. Simulations also demonstrate biohydrogen's potential as an energy storage vector for peak/backup power with an annual 1001.4 MWh of power storage capacity from 10t/d feedstock.

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## Introduction

The 21st Conference of the Parties (COP21) to the United Nations Framework Convention on Climate Change 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 [3]. 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%) [3] and in Australia (61%) [2], 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 CO<sub>2</sub>

Capture (PCC) technologies to scrub CO<sub>2</sub>, in addition to SO<sub>2</sub>, NO<sub>x</sub> 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 [14].

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

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<https://doi.org/10.1016/j.ijhydene.2018.02.069>

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applications in both mobile and stationary domains. Water and biomass are the two competing renewable hydrogen sources.

Electrolytic hydrogen production from water [17,19] consuming around 48 kWh electricity per kg hydrogen in today's electrolyzers [9] 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 [35] 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 [22,25,30,37], photo-fermentation [20,25,30,41] and combined dark-photo-fermentation [15].

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 [32,34]. MEA is a good nitrogen source [31,36,39] and in one experiment it was found to be a better option than glutamate for bio-hydrogen production [18]. 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<sub>2</sub> 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<sub>2</sub> per MWh of electricity [6], a PCC technology installed on such a plant will capture a large amount of CO<sub>2</sub>. 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 [10]. 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 CO<sub>2</sub> (scCO<sub>2</sub>) allows for a low temperature fractionation of lignocellulose into its three components. scCO<sub>2</sub> is CO<sub>2</sub> above its critical temperature (31.1 °C) and critical pressure (72.9 atm). In literature, effective temperatures from under 100 °C [40] to 200 °C [27] and over [29] have been reported for scCO<sub>2</sub> fractionation. Technical complexities of recycling scCO<sub>2</sub> at industrial scale make it economically unattractive. However, in the presence of a large CO<sub>2</sub> source,

scCO<sub>2</sub> 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<sub>2</sub> 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 [38] 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<sub>2</sub> 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.

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## 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.

### 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 CO<sub>2</sub>.

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