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Adrian Dawson

A Concentrated Solar Process for the Production of Renewable Hydrogen from Waste Water Streams

Dawson A, Beath A, Hayward J, Sun Y

CSIRO, Newcastle, Australia

E-mail: adrian.dawson@csiro.au

Abstract

The transition to hydrogen as a low carbon fuel source and a solution to energy security has gained renewed interest both locally and overseas, with Australia regarded as having a competitive advantage in the hydrogen supply chain and great export potential. Australian industries with waste water streams are also interested in value adding opportunities that reduce energy use and improve water quality. The CSIRO has investigated a hydrogen production process as a potential solution that utilises concentrated solar thermal heat. Two regional areas, Albury/Wodonga in Victoria and Toowoomba in Queensland were studied to understand the potential resource constraints and how they might affect the levelised cost of hydrogen ($LCOH_2$) with preliminary analysis suggesting the process concept can produce a renewable hydrogen at a competitive cost when compared with other technologies.
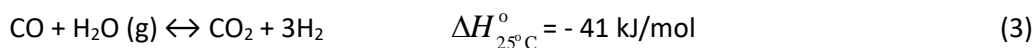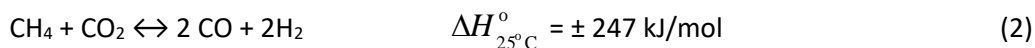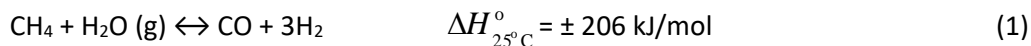
1.   Introduction

With hydrogen being the focus of low emission fuels research, a number of technologies are seeking to utilise waste water resources for its production. Amongst the processes that are proven or in development are are the well-known electrolysis of water to hydrogen but also the biological processes of dark fermentation (Guo, Trably, Latrille, Carrre, & Steyer, 2010) and/or microbial electrolysis (Kadier et al., 2016) amongst others. The National Renewable Energy Laboratories (NREL) estimates that upwards of 4.2 million tonnes/year of hydrogen could be derived from sources of biomethane in the U.S (Saur, 2014) while in Australia, given its smaller quantity of waste water streams the quantity of hydrogen would be expected to be lower. The treatment and disposal of these waste water streams from municipal sewage, abattoirs, intensive agriculture as well as food and beverage represent a significant cost to operators. Increasingly stringent environmental protection and social license put pressure on facilities to ensure minimal impact to catchments from the release of treated wastewaters. The process described in Figure 1 aims to address these waste water issues to produce a truly renewable form of hydrogen using an integrated CST solution at two levels. Firstly lower grade CST heat is used to drive a thermal hydrolysis process (THP) and then higher grade CST heat is used to carry out mixed reforming of methane (MRM) over a CSIRO developed catalyst (MR-24). Also shown are the authors indicative technology readiness levels (TRL's) of components which are either in development or could be further developed to better utilize a CST input as well as the commercial readiness index (CRI) of plant items which have been adopted by industry. The $LCOH_2$ from the two case study locations serves as an indicative starting point. Bio-waste resource data, hydrogen networks and capital costs are all areas that require further work to better understand the economic potential of the process.

1.1. Concentrated solar thermal assisted thermal hydrolysis process

THP is recognised as an effective treatment for enhancing the hydrolysis step in anaerobic digestion (AD), reducing solids retention time (SRT) and increasing biogas yields. Moreover, the inherent process temperature and time can suitably stabilise biosolids to meet Pathogen Grade A end-use classification (Ang, 2000) which can reduce the cost of disposal for waste water utilities. However due to the heat requirement of the THP it has traditionally only been feasible to use when integrated with a combined heat and power plant (CHP) that is fueled with biogas from an AD (Barber, 2016). Typically some amount of supplementary gas (e.g. natural gas) is required to balance the AD + TH + CHP plant energy requirements whereas the process in this study uses a low grade CST source.

1.2. Concentrated solar thermal mixed-methane reforming

Previous thermodynamic analysis of the mixed reforming of methane (MRM) has shown that the optimal conversion of methane to hydrogen occurs in the temperature range 800 – 850°C (Sun & Edwards, 2015) and is expressed as the following reactions (1) – (3).

$$CH_4 + H_2O\ (g) \leftrightarrow CO + 3H_2 \qquad \Delta H^o_{25^oC} = \pm\ 206\ kJ/mol \qquad (1)$$

$$CH_4 + CO_2 \leftrightarrow 2\ CO + 2H_2 \qquad \Delta H^o_{25^oC} = \pm\ 247\ kJ/mol \qquad (2)$$

$$CO + H_2O\ (g) \leftrightarrow CO_2 + 3H_2 \qquad \Delta H^o_{25^oC} = -\ 41\ kJ/mol \qquad (3)$$

The use of CST as a heat source to promote these reactions represents an effective solar storage mechanism, while MRM has a number of advantages namely;

- Biogas with a wide range of $CH_4/CO_2/H_2O$ molar ratios to match applications (e.g. methanol synthesis)

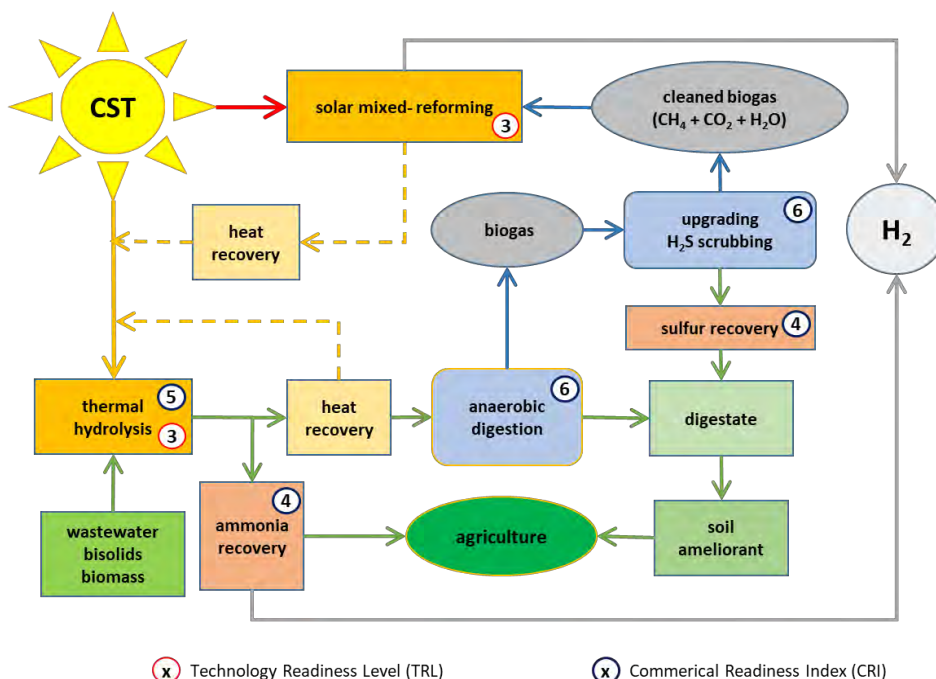- Allows use of "wet" biogas without drying and CO_2 scrubbing.

Figure 1. Schematic of hydrogen production process with indicative TRL and CRI scores for major plant items

2. Methodology

In order to understand the potential to produce hydrogen using the conceptualised process two baseline cases were considered. These cases were required to have a viable population centre of approximately 100,000 people which would provide a feedstock of sewage, a viable source of other waste water resources (dairy/abattoir/industrial food manufacturing/intensive livestock) within a 50 kilometre radius and a viable source of direct normal solar irradiance. These factors were then used to estimate the hydrogen potential for each case site and the approximate levelised cost of hydrogen (LCOH$_2$). It should be noted that the 50 kilometre radius was chosen based on other forms of biomass transport and would need further scrutiny going forward.

To estimate the optimum reaction temperature and thus yield of hydrogen from the MRM of biogas, Factsage© was used to predict the hydrogen yield at two temperatures, 700°C to 800°C and a number of $CH_4/CO_2/H_2O$ molar ratios.

2.1. Biogas yield from waste water

Biogas yields were determined using waste water data supplied by the industries surveyed and applying parameters sourced from literature for anaerobic digestion of the various feedstocks. Noting that waste water flows can vary depending on seasonal and process deviations the following parameters for each waste water stream were used to give an approximate rather than exacting measure of biogas yields to better understand the resource scale and ultimately arrive at an indicative LCOH$_2$.

Table 1. Biogas yield parameters

Industry	Biogas yield measure	Reference
Municipal waste water (sewage sludge)	28 L/PE/day PE: population equivalent	(Bachmann, 2015) (Tchobanoglous & Metcalf and Eddy, 1972)
Dairy processing (whey)	213.7 mL CH_4/g VS VS: Volatile solids	(L. B. Moody, R. T. Burns, G. Bishop, S. T. Sell, & R. Spajic, 2011)
Poultry production (broiler)	200 m^3 biogas/tonne litter	(Bijman, 2014)
Abattoirs (slaughterhouse waste water)	VS = 8.6% 600.1 mL CH_4/g VS	(L. B. Moody et al., 2011)

2.2. Levelised cost of hydrogen

For the purpose of this study, the simplified LCOH$_2$ given as $/GJ was calculated using Equation (4).

$$LCOH_2 = \frac{\sum_{t=1}^{n} \frac{CAPEX_t + OPEX_t + Feedstock_t}{(1+r)^t}}{\sum_{t=1}^{n} \frac{Y_t}{(1+r)^t}} \tag{4}$$

Where CAPEX was the sum of all plant costs in dollars ($) including THP, AD, CST and MRM equipment with Engineering, Procurement and Construct (EPC) along with owner costs assumed at 11% of direct capital costs and a 7% contingency. Operational expenditure (OPEX) for the solar component of process covered both fixed and variable costs (Meybodi & Beath, 2016).The Life of project is given as n which was taken as 25 years (Hinkley & et al., 2016), r is the discount rate factor (Campey et al., 2017), Y is the yield of hydrogen generated from the process (GJ/year) and t is the

year of the project. The cost to supply raw bio-solids to the process (Feedstock) was given in $/year. Solar resource for each case site was taken from Australian Renewable Energy Mapping Infrastructure (AREMI, 2018) with cost estimates specific to the solar MRM and CST plant referenced from Concentrating Solar Fuels Roadmap (HInkley, Hayward, McNaughton, & Lovegrove, 2016). Cost estimates for thermal hydrolysis and anaerobic digester plant were taken from a number of biogas case studies and reports (Allan, 2012; Colley Consulting Pty Ltd, 2012; Fachagentur Nachwachsende Rohstoffe e.V., 2012; Murphy et al., 2015) with costs of biogas drying and CO_2 scrubbing excluded. Finally the $LCOH_2$ only covers hydrogen production and does not consider storage or transportation.

3. Results

3.1. Thermodynamic analysis of mixed reforming methane

As Figure 2 shows, thermodynamic analysis using Factsage© software predicted a significant increase in hydrogen yield when the reforming temperature was increased from 700°C to 800°C. This is consistent with results from earlier studies (Ávila-Neto et al., 2009; Sun & Edwards, 2015).
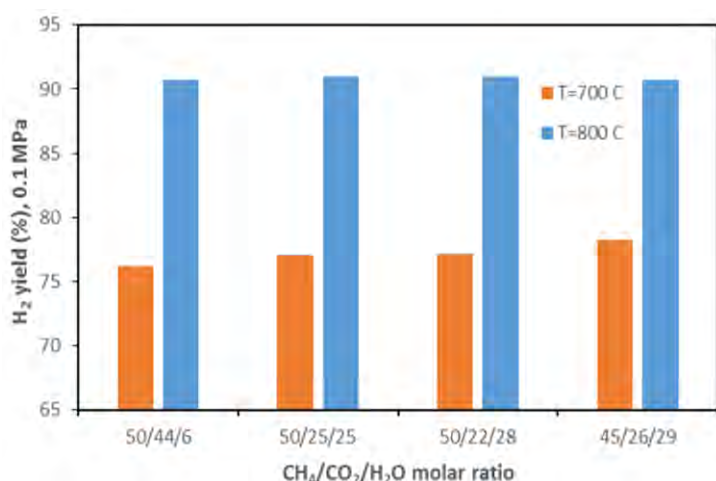

Figure 2. H$_2$ yield for a given CH$_4$/CO$_2$/H$_2$O ratio at 700°C and 800°C.

3.2. Case study locations and their results

Of the chosen case study locations, those that could supply the most complete data were prioritised, with Albury/Wodonga and Toowoomba fulfilling this requirement better than others. This also provided two locations at vastly different latitudes. The main industries and their combined biogas potential for these two locations with appreciable waste water quantities are presented in Table 2.

Table 2. Case study site reference data and results

Case study site	latitude (°)	longitude (°)	DNI average (kWh/y)	Population (approx.)	Industry	H$_2$ yield (tonnes/ year)	CST size (MW$_{th}$)	LCOH$_2$ ($/GJ)
Albury/ Wodonga	-36.100	146.901	2094	90,000	sewage, industrial food manufacturing, abattoir	10682	114	$4.50
Toowoomba	-27.563	151.932	2064	109,000	sewage, intensive agriculture, abattoir	2539	27	$3.18

4. Conclusion

As seen in Table 3, the preliminary investigation into the levelised cost of producing hydrogen in Australia using the process concept of Figure 1 shows promise when compared with other renewable pathways, i.e. solar PV/wind with Proton Exchange Membrane (PEM) electrolyser. It should also be noted that the $LCOH_2$ presented for the MRM via CST + THP +AD process has not taken into account cost savings associated with improved waste water management and the value adding opportunity, indeed the feedstock costs in the $LCOH_2$ could very well be negative, thus further reductions in the $LCOH_2$ could be expected.

Table 3. Levelised cost of hydrogen production in Australia using renewables

Technology	LCOH$_2$ ($/kg)	Calculated as of	Reference
Solar PV with PEM electrolyser, no storage	18.67 9.14	2016 By 2030	(Hinkley & et al., 2016)
Grid based solar PV/wind base case PEM electrolyser	6.08 – 7.43	2018	(Bruce et al., 2018)
Dedicated renewables (solar PV/wind) PEM electrolyser	~ 11	2018	(Bruce et al., 2018)
MRM via CST + THP + AD	~ 3 - 5	2018	(Dawson, 2018)

The potential efficiency gains and monetary savings from removing biogas drying and CO2 scrubbing from conventional biogas production systems is not fully understood. For the purpose of this study, the capital costs for these processes were ignored.

In terms of processes readiness, lower TRL items (solar dedicated thermal hydrolysis and mixed reformer) would require significant engineering to better understand their integration and performance. While the commercially ready plant items would need to be qualified to ensure the suitability of biogas quality for MRM as well as recovery of ammonia and sulfur.

The quantities of the various waste water streams are reasonably indicative of the regions and allowed the initial $LCOH_2$ to be calculated. It is likely there are other sources of waste water and for that matter bio-waste which could also contribute. Much more data on quantities and composition of bio-waste feedstocks and their applicability to the process is needed to better quantify the pathway to hydrogen production in Australia.

Potentially the greatest challenge is the MRM catalysts since the experimental work to date has been of short time duration using a synthesised "biogas" from commercially supplied high purity CH_4, CO_2 sources. In reality, biogas compositions will vary according to feedstocks and treatment variables and will inherently contain other constituents which may lead to deactivation of the catalyst. To this effect laboratory work using real biogas blends would be required to identify shortcomings in biogas scrubbing equipment and the effects of contaminants on the catalyst.

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