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Reconciling the Sustainable Manufacturing of Commodity Chemicals with Feasible Technoeconomic Outcomes

Assessing the investment case for heat integrated aerobic gas fermentation

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The manufacturing industry must diverge from a 'take, make and waste' linear production paradigm towards more circular economies. Truly sustainable, circular economies are intrinsically tied to renewable resource flows, where vast quantities need to be available at a central point of consumption. Abundant, renewable carbon feedstocks are often structurally complex and recalcitrant, requiring costly pretreatment to harness their potential fully. As such, the heat integration of supercritical water gasification (SCWG) and aerobic gas fermentation unlocks the promise of renewable feedstocks such as lignin. This study models the technoeconomics and life cycle assessment (LCA) for the sustainable production of the commodity chemicals, isopropanol and acetone, from gasified Kraft black liquor. The investment case is underpinned by rigorous process modelling informed by published continuous gas fermentation experimental data. Time series analyses support the price forecasts for the solvent products. Furthermore, a Monte Carlo simulation frames an uncertain boundary for the technoeconomic model. The technoeconomic assessment (TEA) demonstrates that production of commodity chemicals priced at ~US$1000 per tonne is within reach of aerobic gas fermentation. In addition, owing to the sequestration of biogenic carbon into the solvent products, negative greenhouse gas (GHG) emissions are achieved within a cradle-to-gate LCA framework. As such, the heat integrated aerobic gas fermentation platform has promise as a best-in-class technology for the production of a broad spectrum of renewable commodity chemicals.

1. Introduction

The development of a sustainable chemical industry requires a transition from the use of finite fossil reserves to renewable carbon feedstocks. Second generation biochemical technologies utilise carbon feedstocks outside the food value chain. Such technologies allow agricultural, industrial and organic municipal solid wastes to be used for chemical production (1). These carbon sources are inexpensive, abundant and renewable, contributing towards the development of a sustainable, circular economy (2). Lignocellulosic biomass typically consists of cellulose, hemicellulose and lignin. However, owing to its recalcitrance, lignin cannot be utilised by conventional fermentation, which accounts for up to 40% of lignocellulosic biomass (3).

Black liquor is a coproduct from Kraft paper and pulp mills, consisting of the residual lignin after recovery of the cellulosic pulp product. In Kraft mills approximately 10 tonnes of weak black liquor is produced per air dried tonne of pulp (4). The combustion of this lignin-rich coproduct in Tomlinson boilers makes modern Kraft mills self-sufficient in steam and electrical energy (4, 5). However, research into Kraft mill heat integration over the last two decades has highlighted the potential to reduce mill energy consumption by up to 40% (6, 7). Such projects would free up a portion of weak black liquor for alternative income generation. Additionally, in mills where the Tomlinson boiler is the bottleneck for the process, diverting a portion of black liquor away from the recovery boiler could allow mills to increase their capacity by 25% (8). Whilst the traditional use for the black liquor coproduct is renewable electricity generation, gasification of this carbon-rich feedstock creates opportunities for biochemical production, expanding the product range of a Kraft mill.

SCWG has emerged as a hydrothermal technology suited to the gasification of wet biomass feedstocks to produce synthesis gas (syngas). SCWG is particularly advantageous for processing feedstocks with moisture contents >30%, where it energetically outcompetes the inherent drying required by conventional gasification (9). It is therefore capable of utilising streams such as black liquor, food waste, sewage sludge and manure which are typically uneconomical as feedstocks for traditional gasification technologies (10). Furthermore, the dissolution of the carbon feedstock in water leads to low tar and coke production in comparison with conventional gasification (11), simplifying purification technologies. Upgrading syngas to fuels and chemicals using metal-based catalysts is an established technology for coal feedstocks. As such, these technologies have been applied to syngas derived from renewable feedstocks, where Johnson Matthey and bp recently licenced their Fischer-Tropsch technology to Fulcrum Bioenergy (12). However, such technologies experience high capital and operating costs due to the utilisation of high operating temperatures and pressures, the prerequisite for specific carbon monoxide to hydrogen ratios and potential catalyst poisoning from gas impurities (13). Moreover, low chemocatalytic selectivity remains a challenge for converting syngas to commodity chemicals. Gas fermentation, on the other hand, circumvents these intrinsic challenges, notably through high selectivity biocatalysis, and has emerged as an alternative technology for syngas upgrading (13). Gas fermentation exploits microbial cell factories able to utilise carbon dioxide and hydrogen as a sole carbon and energy source to produce target chemicals through metabolic engineering (14).

The commercialisation of gas fermentation technology is dominated by anaerobic fermentation, where LanzaTech leads the way in the utilisation of carbon monoxide-rich steel mill off-gas to produce ethanol (15). Their Jintang plant has a 46,000 tonne year^{-1} operating capacity and uses their proprietary anaerobic acetogen, *Clostridium autoethanogenum*, as a microbial cell factory. This microorganism employs the Wood-Ljungdahl pathway, which is a thermodynamically efficient carbon dioxide fixation pathway compared to other biological C1 fixation pathways (16). However, such anaerobic carbon dioxide fixation presents energetic limitations which limit the product scope (17). Also, low value byproducts are common, negatively impacting on the carbon efficiency of the desired product whilst complicating downstream processing (18).

Aerobic cell factories on the other hand, are energetically advantaged compared to anaerobic cell factories (19). Therefore, the use of aerobic bacteria allows for the production of more complex chemicals *via* energy-intensive biochemical pathways (18), broadening the renewable chemical spectrum. However, a disadvantage of aerobic gas fermentation is its reliance on the Calvin-Benson-Bassham cycle. Whilst this cycle achieves favourable kinetics by investing appreciable energy into C1 fixation (20), it is consequently thermodynamically inefficient compared to the Wood-Ljungdahl pathway. Due to the greater heat generation, aerobic bioreactors require the installation of substantial cooling capacity, translating to both capital and operating cost burden (19). In addition, compressors are required to satisfy the oxygen demand and the presence of oxygen necessitates the use of more expensive stainless steel reactors. Historically, aerobic fermentation has been used for high value, low volume products (21). However, for the production of higher volume commodity products, where utility costs dominate (22), aerobic fermentation has been hindered by process economics. This is a result of the aforementioned cooling requirements, associated air compression and reduced economies of scale compared with anaerobic fermentation (23).

The difference between aerobic and anaerobic fermentation's process economics is highlighted in recent work by Dheskali *et al*. who developed an estimation tool for the fixed capital investment (FCI) and utility consumption for large-scale biotransformation processes (24). Their model presented a ~20% increase in unitary FCI and a >1.5 times increase in energy requirement for aerobic fermentation over anaerobic, for a modest aeration rate. This was attributed to the capital and operating costs associated with the air compressors required for aerobic fermentation (24). Gunukula *et al*. also presented an almost 30% increase in the minimum selling price for commodity chemicals produced *via* aerobic compared to anaerobic fermentation (25). Similarly, in a series of technoeconomic studies for cellulosic ethanol production by the National Renewable Energy Laboratory (NREL), the fermentation area was found to be the primary cost for aerobic fermentation, with the fermentation compressors having the greatest power requirement (26). On the other hand, for anaerobic fermentation, the pretreatment section was found to be the largest cost driver with a less pronounced compressor duty (27).

The potential of aerobic fermentation can only be effectively realised by reducing these costs, notably through improved engineering design. This work evaluates the integration of aerobic gas fermentation with SCWG as a solution to economically feasible commodity chemical production as proposed by Bommareddy *et al*. (28). The integration of gas fermentation with SCWG *via* a heat pump allows for the low temperature heat released by gas fermentation to be utilised by the high temperature, endothermic SCWG process. This both removes the cooling water burden required by the bioreactors and reduces the fraction of hydrogen that needs to be combusted to support the endothermic gasification process. Furthermore, the duty released by expanding the high-pressure gas product from SCWG is recovered using a turbo expander and subsequently used to power the air compression, negating the need for external power provision. This integration has the potential to overcome the barriers to cost effective, commercial scale, aerobic gas fermentation for commodity chemical production.

Cupriavidus necator (formerly, *Alcaligenes eutrophus* and *Ralstonia eutropha*) is employed as the microbial cell factory in this work. *Cupriavidus necator* is a chemolithoautotrophic bacterium capable of aerobic, autotrophic growth using carbon dioxide as the sole carbon source, hydrogen as electron donor and oxygen as the electron acceptor (29). This cell factory benefits from the kinetic advantage of the Calvin-Benson-Bassham cycle and is strictly respiratory, which compared to anaerobic cell factories results in negligible synthesis of low value, fermentative byproducts. Bommareddy *et al*. (28) detail the continuous production of isopropanol and acetone using aerobic gas fermentation. This first generation *Cupriavidus necator* cell factory produces acetone as an overflow coproduct from the engineered biochemical pathway to isopropanol, which is subject to future optimisation of this carbon flux bottleneck. Further relevant to the process design, this cell factory has not been adapted to be tolerant to concentrations of isopropanol >15 g l^{-1}, necessitating a dilution strategy through an engineering solution. Relying on the sustainable manufacturing paradigm in Bommareddy *et al*. (28), this work presents the TEA and LCA for a solvent plant, that exploits this first generation cell factory, producing isopropanol and acetone *via* aerobic gas fermentation and purifying the solvents *via* a heat and mass integrated separation train network.

2. Materials and Methods

2.1 Conceptual Process

The proposed solvent plant is co-located with a Kraft paper and pulp mill in China with throughput as defined in **Table I**. **Figure 1** outlines the Kraft process, which conventionally directs weak black liquor to multi-effect evaporators, producing strong black liquor which is combusted in a Tomlinson boiler to produce steam (4). This steam makes the mill self-sufficient in steam and electrical energy. Importantly, the cooking chemicals (NaOH and Na_2S) are recovered and recycled to the pulping process.

As previously mentioned, investments in heat integration have freed up a portion of the weak

Table I Kraft Mill Plant Capacity

Parameter	Value	Unit	Reference
Pulp mill capacity	130	Air dried tonne h^{-1}	–
Total weak black liquor production	1300	tonne h^{-1}	(4)
Black liquor solids content	17.5	% (w/w)	(4)
Lignin content in solids	41.5	% (w/w)	(30)
Lignin content in black liquor	7.3	% (w/w)	–

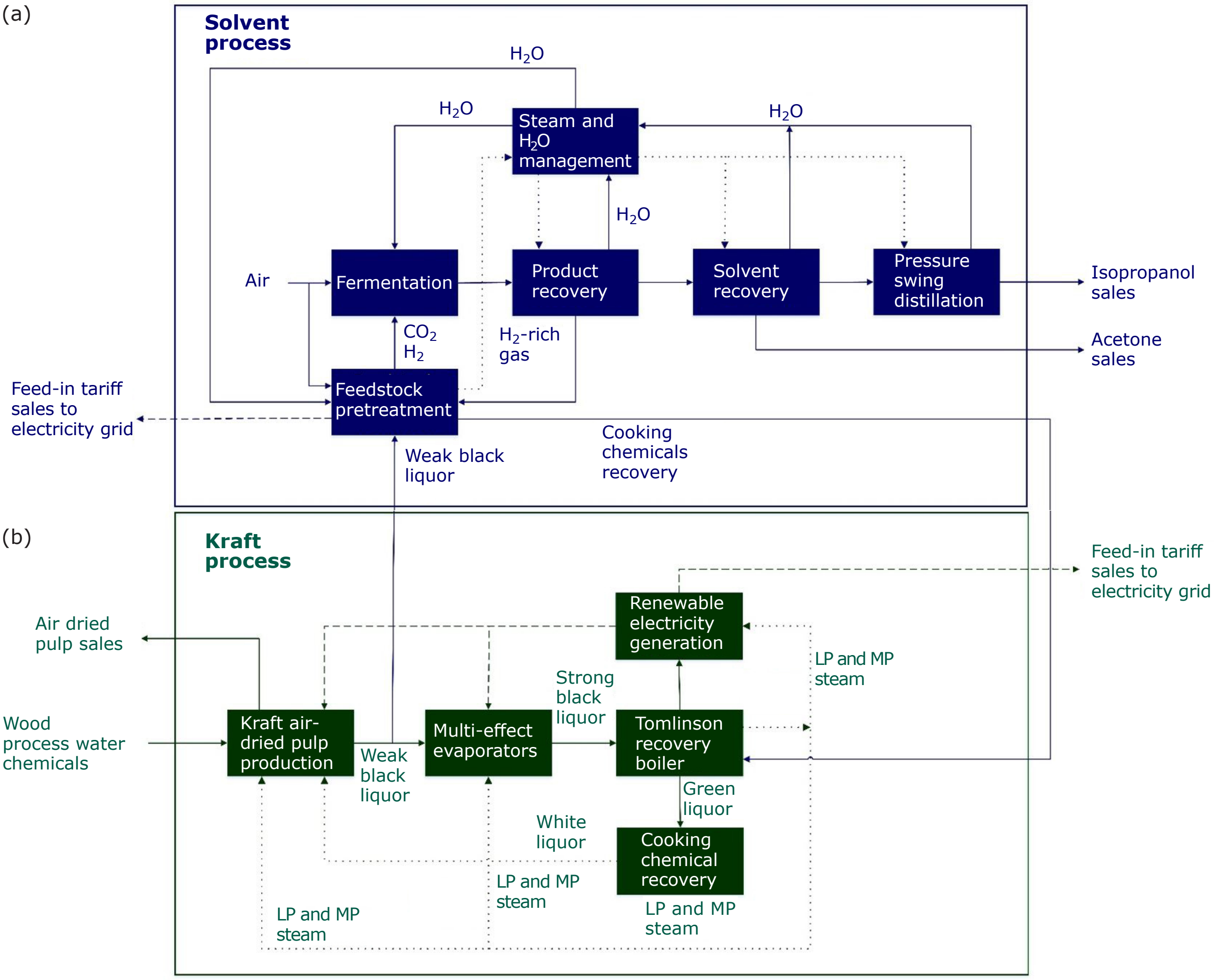

Fig. 1. Conceptual solvent process integration with Kraft process, outlining materials (solid lines), power (dashed lines) and steam (dotted lines) flows. Excess weak black liquor is fed to the solvent process from the Kraft process and cooking chemicals are returned to the Tomlinson recovery boiler. LP = low pressure; MP = medium pressure

black liquor coproduct for alternative uses. This study explores the opportunity of utilising this excess coproduct, taken as 25% of total production, for isopropanol and acetone production through aerobic fermentation in an integrated solvent plant as outlined in **Figure 1**.

Given black liquor has no economic value as a product, it is costed at its utility value. This is calculated based on its conventional use for renewable electricity generation, requiring capital investment in increased steam turbine capacity. The foregone net present value (NPV) associated with this conventional use is used as the utility value for the black liquor feedstock.

In the proposed solvent plant (**Figure 1**), weak liquor undergoes SCWG to carbon dioxide and hydrogen. A challenge, however, is the efficient recovery of the cooking chemicals from the SCWG reactor and their recycle to the pulp mill digestor. Loss of these salts would result in a significant cost to the pulp mill. Under supercritical conditions, the properties of water change from polar to apolar, where the solubility of inorganic salts is very low (31). Cao *et al*. described the precipitation of alkali sodium salts in SCWG, reporting a neutral pH for the reactor effluent, suggesting that under supercritical conditions the salts largely precipitate from the solution (32). However, this precipitation can cause issues with plugging and fouling within the reactor (33). In this study the salts are removed prior to entering the SCWG reactor, in a manner similar to supercritical water desalination (34, 35) and modelled for SCWG of black liquor (33).

2.2 Process Intensification, Heat and Mass Integration

The solvent plant's mass and energy balance was informed by experimental data from continuous gas fermentation (28), and rigorous process simulation using Aspen HYSYS v11. The lignin content in black liquor was modelled as guaiacol, a model compound for lignin (36), as principal feed to the solvent plant. The weak black liquor is further diluted prior to entering the SCWG reactor, as lower biomass concentrations promote superior thermal cracking and yields greater hydrogen and carbon dioxide owed to the increased water concentration favouring the forward water-gas shift reaction (37).

The simplified flow diagram (**Figure 1**) outlines the six plant sections of the solvent plant, whilst **Figure 2** presents a detailed process flow diagram and operating conditions for upstream and downstream processing. The unit operations included in each of the six plant sections are summarised in **Table II**. **Table III** summarises the scale-up of the experimental gas fermentation data for the process simulation, which recognises the oxygen mass transfer limitations associated with the safety requirement to maintain non-flammable operating conditions. The heat integration between the low temperature exothermic gas fermentation and the high temperature endothermic SCWG is facilitated using a heat pump with isopentane as the working fluid (28).

Isopropanol and acetone are produced in both the aqueous and vapour phase of the bioreactors. The solvents in the vapour phase are recovered *via* gas absorption through mass integration using internal process streams, i.e. the isopropanol product was utilised to recover acetone, and water to recover isopropanol. For the isopropanol in the aqueous phase, azeotropic distillation is required due to the homogeneous minimum boiling point azeotrope formed between isopropanol and water (38). Conventionally, this azeotrope is broken using an entrainer, historically benzene (39). However, owed to its carcinogenic properties, alternative entrainers such as cyclohexane have been adopted (40). An alternative azeotropic separation technique is pressure swing distillation, taking advantage of the composition differences in the azeotrope at different pressures (41). In this work, pressure swing distillation was employed with the coproduct acetone acting as an unconventional entrainer. Further detail of the separation train is presented in **Figure 2**.

A U-loop bioreactor, similar to the one used by Peterson *et al*., is used in this work (42). The benefit of a U-loop bioreactor is that high mass transfer coefficients can be achieved without the need for mechanical agitation, leading to greater oxygen transfer rate and a reduced power requirement compared to conventional stirred tank reactors (42). The oxygen mass transfer coefficient calculation associated with the solvent plant's mass balance is presented in Table S1 in the Supplementary Information (available with the online version of this article), falling at the lower end of the range of mass transfer coefficients reported by Peterson *et al*. (42). Details of the experimental gas fermentation data is presented in **Table III**; a more detailed explanation of the experimental procedure can be found in Bommareddy *et al*. (28).

Significant heat integration makes the solvent plant self-sufficient in electricity and both low and medium pressure steam. Furthermore, process water recovered from distillation and the steam condensate is recycled to reduce the water make-up burden.

The process flow diagram for conventional renewable electricity generation, used to value the black liquor, is presented in Figure 3. An additional steam turbine is required to produce the renewable electricity for sale, relying upon the existing multi-effect evaporators, air compression and Tomlinson boiler. Superheated steam at 9000 KPa and 480ºC is used in the steam turbine (44). The medium pressure steam exiting the turbine is used in the multi-effect evaporators to concentrate the excess black liquor to 75% and to preheat the auxiliary air supplied to the Tomlinson boiler. Similarly, the associated electricity demand for the air

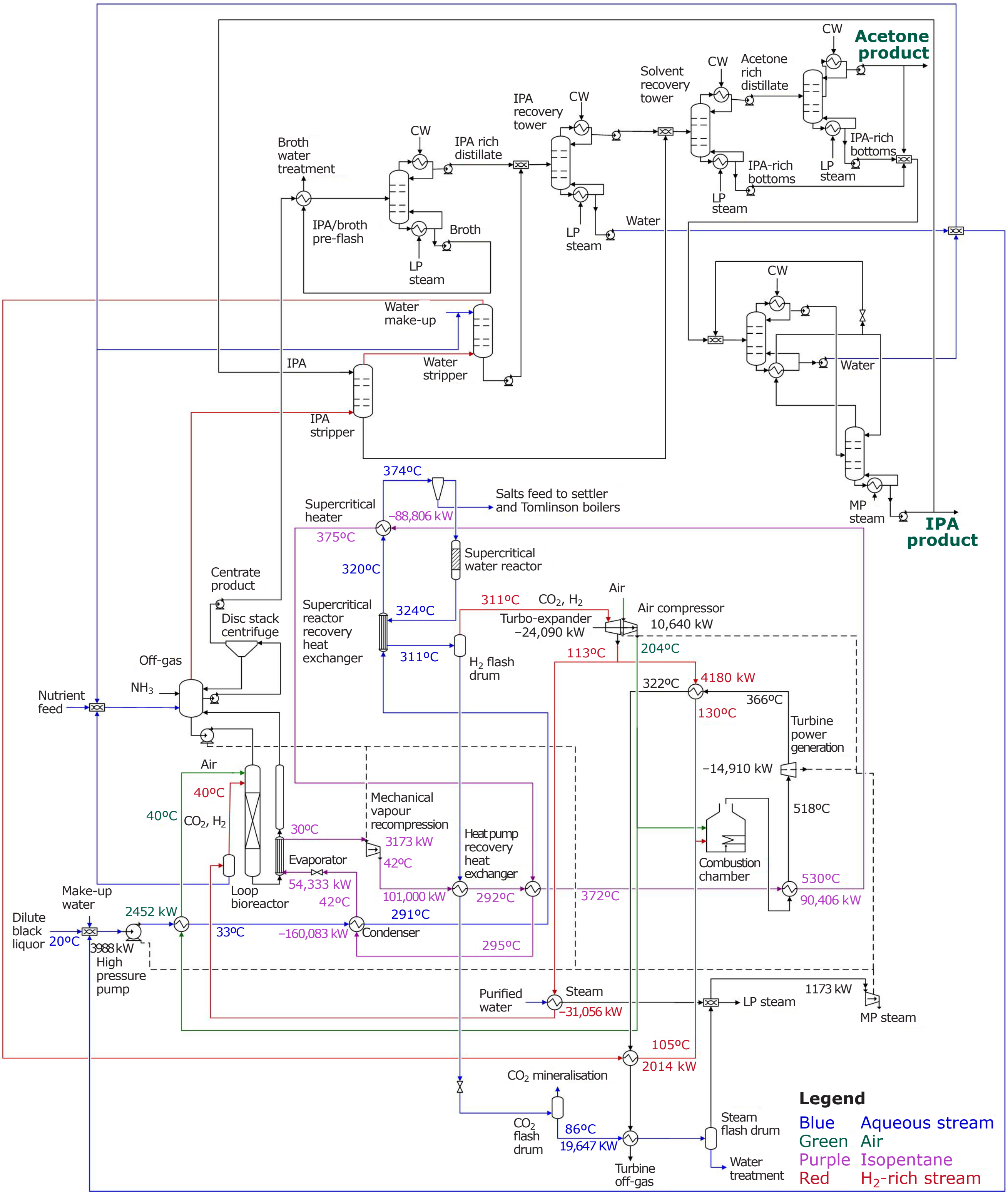

Fig. 2. Solvent plant process flow diagram, detailing the heat integration between gas fermentation and SCWG *via* a heat pump. The heat and mass integrated separation train constitutes the downstream processing, including gas absorption and heat integrated distillation. IPA = isopropanol; LP = low pressure; MP = medium pressure; CW = cooling water

Table II Solvent Plant Section Unit Operations

Plant Section	Unit Operations	Thermodynamic model
Feedstock pre-treatment	SCWG reactor, combustion chamber, combustion turbine, isopentane heat pump cycle	Lee Kesler Plocker
Fermentation	Seed and production bioreactors, pumps, centrifuge	Lee Kesler Plocker
Product recovery	Acetone stripper, water stripper, water removal columns	UNIQUAC
Solvent recovery	Acetone separation and purification columns	UNIQUAC
Isopropanol pressure swing distillation	Low- and high-pressure distillation columns	PSRV
Steam and water management	Mechanical vapour compressor, water and steam heat exchangers	Lee Kesler Plocker

Table III Summary of Scale-Up of Experimental Gas Fermentation Data for ASPEN HYSYS Process Simulation

Sources and sinks	Unit	Carbon dioxide and hydrogen as sole energy and carbon source
Bioreactors		
Oxygen transfer coefficient	1 h^{-1}	415
Oxygen concentration in off-gas[a]	% (mol/mol)	3.35
Vessel volume	m^3	500
Number of bioreactor trains	–	4
Gas uptake rates		
Oxygen	mmol l^{-1} h^{-1}	230
Carbon dioxide	mmol l^{-1} h^{-1}	125
Hydrogen	mmol l^{-1} h^{-1}	1006
Isopropanol		
Specific productivity	kg m^{-3} h^{-1}	1.46
Broth concentration[b]	g l^{-1}	12.4
Acetone		
Specific productivity	kg m^{-3} h^{-1}	0.38
Broth concentration	g l^{-1}	1.7
Biomass		
Growth rate	h^{-1}	0.025
Dry cell weight with cell retention	g l^{-1}	21.5

[a] Maintained to ensure oxygen concentration is below hydrogen's limiting oxygen concentration of 4.6% (mol/mol) (43)
[b] Controlled *via* disc stack centrifugation, adding to the capital burden

compressor and pump is provided by the electricity generated. Resultantly, through conventional renewable electricity generation, the excess black liquor produces 138 GWh $year^{-1}$ for sale to the grid.

2.3 Costing Models

The mass and energy balance associated with the rigorous process simulation informs the capital cost, fixed operating cost and variable operating cost estimation. For the capital cost estimation, major equipment purchase costs were estimated using the models from Seider *et al*. (45), with the exception of the turbo-expander (46). Three different methods are used to calculate the FCI, owed to differences in the estimation methods. These three methods are designated as: the NREL method outlined in the 2011 NREL report (27), the Towler and Sinnott (TS) method taken from Chemical Engineering

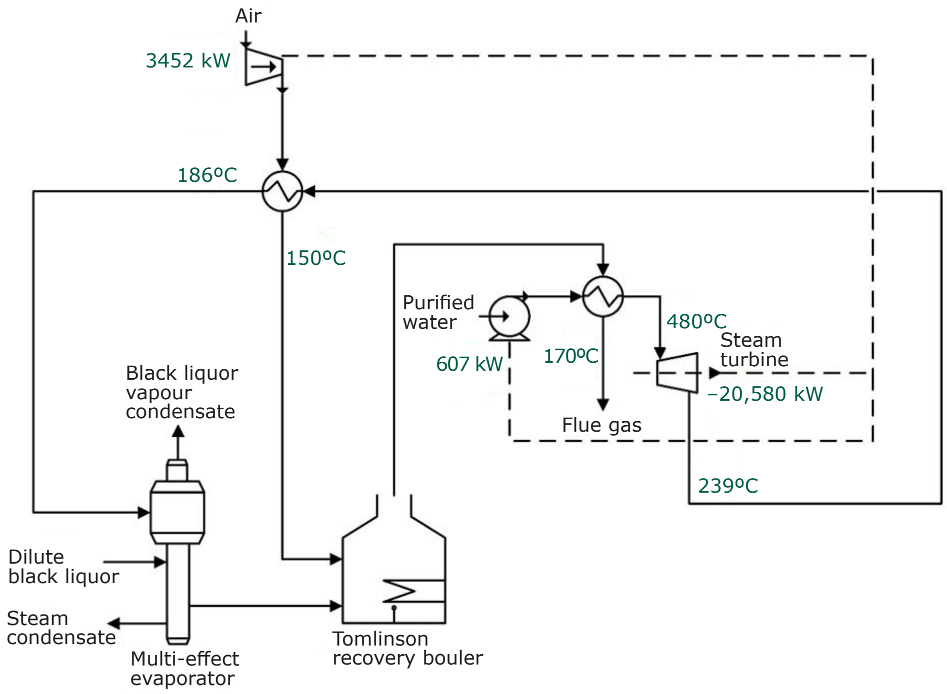

Fig. 3. Process flow diagram for black liquor's conventional use, renewable electricity generation

Table IV Fixed Capital Cost Models

	NREL	TS	Hand
Year basis	2019		
Production year	8110 h[a]		
Installation factor (multiplied by equipment cost) – inside battery limit (ISBL)	Table S2	Table S4	Table S5
Outside battery limit (OSBL)	Table S3	30% of ISBL	25% of ISBL
Contingency	–	10% of ISBL	–
Commissioning cost	5% of ISBL	–	5% of ISBL
Design and engineering cost	–	10% of ISBL	–
Fixed capital investment (FCI)	ISBL + OSBL + commissioning	ISBL + OSBL + contingency + design and engineering	ISBL + OSBL + commissioning
Working capital	10% of FCI		
Total capital investment (TCI)	FCI + working capital		

[a] Based on bioreactor cycle time

Design (47) and the Hand method detailed in Sustainable Design Through Process Integration (48). The calculation basis of the three methods is presented in **Table IV**.

For all three methods, the calculated equipment purchase costs are multiplied by an installation factor to obtain the inside battery limit (ISBL) installed costs. Both the NREL and Hand methods use installation factors dependant on the equipment type, whereas the TS method uses a universal multiplier. All installed equipment costs were adjusted to 2019 costs using the Chemical Engineering Plant Cost Index of 607.5 (49). A location factor of 0.51 was used for China (using indigenous materials), based on the 2003 location factor of 0.61 (47), updated to 2019 *via* the Chinese Yuan to US dollar exchange rate.

Three methods were used to calculate the fixed operating costs as summarised in **Table V**. As before, the NREL method (27) and the TS method (47) were employed. However, as the Hand method is solely for FCI, the third was the taken from Coulson and Richardson Volume 6 (50). Variable operating costs were estimated based on the costs detailed in **Table VI**, subject to annual inflation as outlined in **Table VII**.

Table V Fixed Operating Cost Models

Parameters	NREL	TS	Coulson and Richardson
Operating labour	Salary estimates in China obtained from salaryexpert.com (process operator, engineering and maintenance)[a]	Salary estimates in China obtained from salaryexpert.com 3 process operators per shift 4 shift teams	Salary estimates in China obtained from salaryexpert.com (process operator, engineering and maintenance)
Supervisory labour		25% of operating labour	
Direct salary overhead	90% of operating and supervisory labour	50% of operating and supervisory labour	–
Maintenance	3% of ISBL	3% of ISBL	5% of ISBL + OSBL (conventionally 5% FCI)
Property taxes and insurance	0.7% of FCI	1% of ISBL	2% of ISBL +OSBL (conventionally 2–3% FCI)
Rent of land	–	1% of FCI	–
Royalties	–	–	0% of FCI (conventionally 1% FCI)
General plant overhead	–	65% of total labour and maintenance	50% of operating labour
Allocated environmental charges	–	1% of FCI	–

[a] For a detailed breakdown of operating and supervisory labour for the NREL method see Supplementary Information (Table S6)

Table VI Variable Operating Cost

Raw material	Cost	Unit	Reference	Comments
Ammonia	250	US\$ tonne^{-1}	(51)	Average price for 2019
Cooling water	0.753	US\$ m^{-3}	(52)	–
Electricity	0.06	US\$ kWh^{-1}	(52)	–
Nutrients	0.75	US\$ m^{-3} media water	–	Mineral salt media, containing no complex media or vitamins
Process water	0.53	US\$ m^{-3}	(47)	–

Table VII Investment Analysis Parameters

Parameters	Value	Comments
Discounted rate of return	10%	In line with studies in the BETO Biofuels TEA Database (57)
Corporation tax	25%	Corporation tax in China
Annual inflation	2%	–
Plant life	25 years	–
Depreciation	10 years	Straight line
Plant salvage value	No value	–
Construction period	2 years	–

2.4 Product Price Forecasting

Time series analysis was used to forecast the long-term average price of isopropanol and acetone. Takens' theorem was used as the basis for this analysis (53). Takens' theorem states that for a deterministic system, the underlying state variables that created the time series are embedded within the data. Using this theorem a deterministic, dynamic system can be reconstructed based on the observed time series. Forecast models constructed using the embedded state variables assume that the market drivers underpinning the trajectory of the state variables in phase space remain largely unchanged. An embedding dimension of 10 was used to reconstruct the isopropanol and acetone price models from monthly average price data obtained from the Intratec database (54). In this work, a radial basis function neural network (RBFNN) containing eight neurons was used as a model to predict the future commodity prices. The network was trained as a one step ahead predictor by minimising the mean square error of the difference between the actual and predicted prices. Once trained, the network was evaluated (tested) in free run mode, where successive predicted prices (outputs) become inputs to the RBFNN. The confidence limits corresponding to the trained RBFNN were calculated as a reliability measure of the prediction as per the work undertaken by Leonard, Kramer and Ungar (55). The benefit of using an RBFNN is that the resultant forecast price is an impartial product of the dataset's underlying state variables.

The long-term average price for renewable electricity sales was taken as US\$0.109 kWh^{-1} as per the biomass subsidy in China (56). This is used to inform the renewable electricity project to value the black liquor and for the excess electricity generated by the solvent plant.

2.5 Investment Analyses

The cost models from Section 2.3 and the product price forecast models from Section 2.4 inform the investment analyses. The black liquor is costed at its utility value, calculated as the foregone NPV from generating renewable electricity. Resultantly, the NPV for the solvent plant is calculated by subtracting the NPV of renewable electricity generation. The investment analysis parameters used are detailed in **Table VII**.

2.6 Sensitivity Analysis

A sensitivity analysis was conducted using a Monte Carlo simulation based on the cost parameters in **Table VIII**, creating an uncertainty framework. The cost parameters were taken from (47), with the exception of renewable electricity sale price where the upper limit for the long-term average price was capped at the current biomass subsidy in China, US\$0.109 kWh^{-1}. This limit was applied due to the decreasing trend in renewable electricity subsidies (58). In contrast, the long-term average prices for isopropanol and acetone were varied ±30% from the forecast price. This provides a stochastic counter to the assumption used to determine the forecast prices: that the deterministic market drivers underpinning the trajectory of the state variables remain largely unchanged. However, given that market drivers are subject to change, the long-term average price may be banded with an equal likelihood of being higher or lower than the forecast price.

A uniform distribution for these parameters was used and varied for the solvent plant and conventional renewable electricity generation (used to value the black liquor). All the cost parameters in **Table VIII**, other than labour and electricity, were varied independently. 2000 simulations were run, stochastically varying the parameters within the defined lower and upper limits to produce a probability distribution of the solvent plant's NPV.

2.7 Life Cycle Assessment

A cradle-to-gate LCA model was developed using the ecoinvent 3.6 inventory database, following ISO Standards 14040 (59) and 14044 (60). GHG emissions were calculated based on the most recent Integrated Pollution Prevention and Control 100-year global warming potential (GWP) factors

Table VIII Uncertainty Framework for Monte Carlo Simulation Sensitivity Analysis

Monte Carlo input parameter	Lower limit	Upper limit
Product long term average pricing		
Isopropanol price	0.7	1.3
Acetone price	0.7	1.3
Renewable electricity price	0.7	1
Costing uncertainty factor		
ISBL capital cost	0.8	1.3
OSBL capital cost	0.8	1.3
Labour costs	0.8	1.3

to quantify GHG emissions in terms of carbon dioxide equivalents (CO_{2eq}) (61). Functional units were defined as 1 kg isopropanol, 1 kg acetone and 1 kWh of electricity. In line with the investment analysis, the LCA model considers the net electricity output of solvent plant by subtracting the foregone electricity from combustion of black liquor at the pulp mill. Life cycle environmental impacts are allocated between these three products using both economic and energy allocation. The GHG emission rate for the external process inputs: cooling water, process water and ammonia were taken from the ecoinvent 3.6 inventory database using the allocation at the point of substitution system model (62), whereas electricity was taken as the 2018 China electricity mix (63). The bio-based solvents isopropanol and acetone sequester biogenic carbon dioxide and hence are credited with a negative GHG emission based on their carbon content. Downstream activities, including the use and end-of-life of isopropanol and acetone products are not considered. These activities are assumed to be identical to those of conventional isopropanol and acetone, given that they are chemically and functionally identical, and therefore have no influence on the relative GHG emissions of renewable and conventional solvent products.

3. Results and Discussion

The major equipment items were sized using the mass and energy balance from the rigorous HYSYS simulation. The capital cost estimation for the solvent plant using the three methods outlined in **Table IV** is summarised in **Figure 4**. The underlying capital cost estimation data is detailed in Tables S2–S5 in the Supplementary Information. Due to the close agreement of the NREL and Hand methods, US$64 million and US$65 million respectively (**Figure 4**), and the greater simplicity of the Hand method, this method was used as the capital cost estimation basis. Table S10 details the capital cost estimation for the conventional generation of renewable electricity.

Similarly, the three fixed operating cost methods (**Table V**) are summarised in **Figure 5**, where the underlying fixed operating cost data is detailed in Tables S6–S8. Though sharing the same author, the TS and Coulson and Richardson methods have a dissimilar calculation method. However, the results of these two methods are in close agreement, US$4.62 million and US$5.01 million respectively (**Figure 5**). The substantially lower estimate by the NREL method (US$2.48 million) was therefore set aside, and the TS method employed as the fixed operating cost basis. The fixed operating costs for the conventional generation of renewable electricity are detailed in Table S11.

Figure 6 compares the capital estimation, fixed and variable operating cost models for the solvent plant and conventional renewable electricity generation. The large difference between the capital

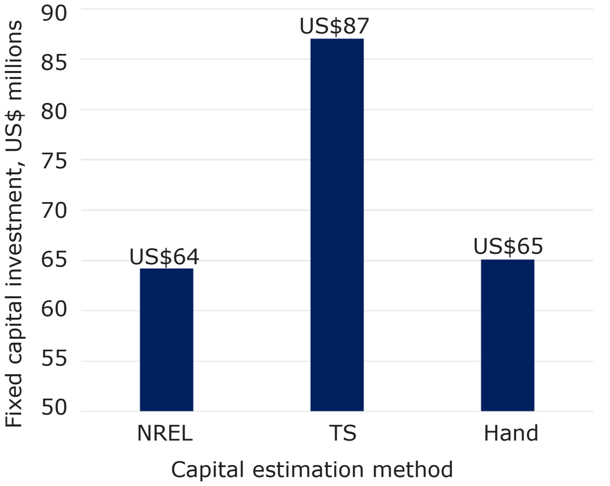

Fig. 4. Comparison of three fixed capital investment estimates using the NREL, TS and Hand methods for the solvent plant. The NREL and Hand methods are in close agreement. The Hand method estimate was taken forward into the investment analyses

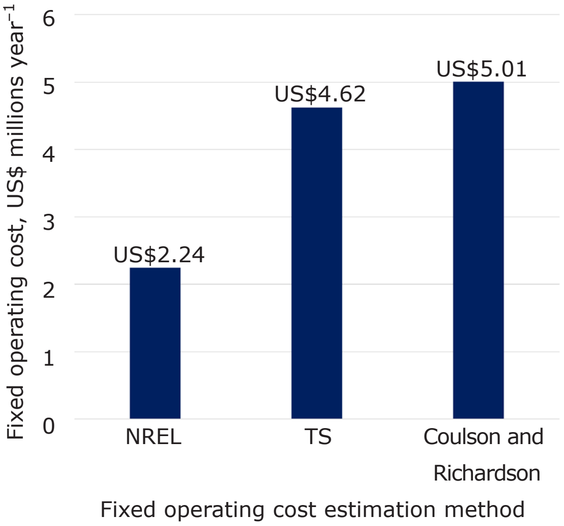

Fig. 5. Comparison of three fixed operating cost estimates using the NREL, TS and Coulson and Richardson methods for the solvent plant. Though related, the TS and Coulson and Richardson methods are in close agreement. The TS method estimate was taken forward into the investment analysis

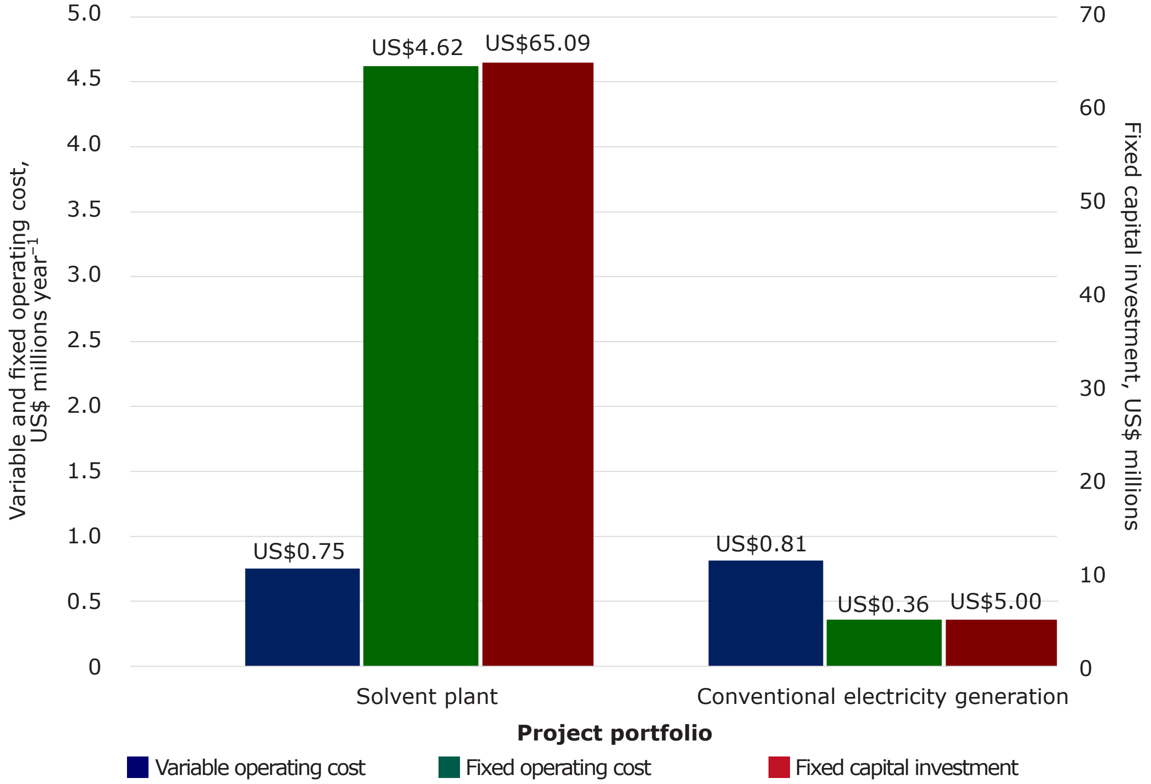

Fig. 6. Comparison between production costs and fixed capital investment for the solvent plant and conventional renewable electricity generation

investment highlights the greater complexity of the proposed solvent plant as an alternate opportunity to conventional renewable electricity generation.

The free-run forecasts for both isopropanol (**Figure 7**) and acetone (**Figure 8**) are shown to track the historical data within the confidence limits of the RBFNN, before settling on a forecast for the long-term average price. For comparative purposes the moving average for the previous ten prices is also plotted in Figures 7 and 8. The difference in the moving average and predicted forecast suggests that the RBFNN has identified pricing dynamics other than the time weighted average, i.e. the underlying state variables within the time series. As such, using this forecast price to inform the investment analysis ensures the nominal TEA inputs and sensitivity analysis are unbiased and centred upon market dynamics, opposed to an artefact of average pricing.

3.1 Investment Analysis

The solvent plant (**Figure 2**) produces three products, summarised in **Table IX**. The contribution of each product to the plant's income is also presented. Whilst isopropanol contributes to almost half the solvent plant income the renewable electricity fraction is the second highest contributor, highlighting the significant amount of renewable electricity generated by the solvent plant.

The investment analyses for the solvent plant and conventional renewable electricity generation are detailed in Tables S9 and S12, as per the investment analysis parameters presented in Table VII. The NPV for conventional renewable electricity generation represents the utility value of the black liquor, valued at US$73 million (Table S12). This is subtracted from the NPV of the solvent plant (US$115 million) to produce the cumulative NPV presented in Figure 9. For the nominal TEA model inputs, the solvent plant's net cumulative NPV is US$42 million.

Given the conceptual stage of the TEA, a Monte Carlo simulation was undertaken as per the uncertainty framework outlined in **Table VIII**. The produced probability distribution in **Figure 10** avoids making an investment decision based solely on nominal TEA inputs. The cumulative probability curve presents a 70% probability that the solvent plant will achieve a net cumulative NPV between

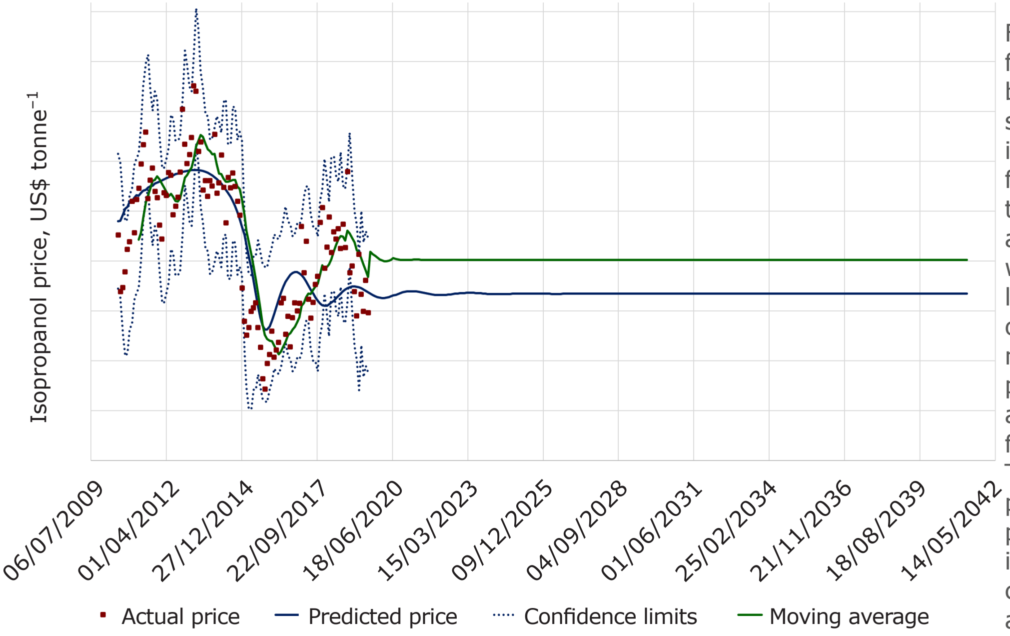

Fig. 7. Isopropanol price forecast using a radial basis function time series analysis model in free-run mode. The free-run forecast tracks the historical data appreciably, remaining within the confidence limits for the original one step predictor model fit. The free run prediction settles to a long-term average forecast for isopropanol. The moving average is plotted for comparative purposes. The y-axis is obscured given copyright restrictions associated with the Intratec database

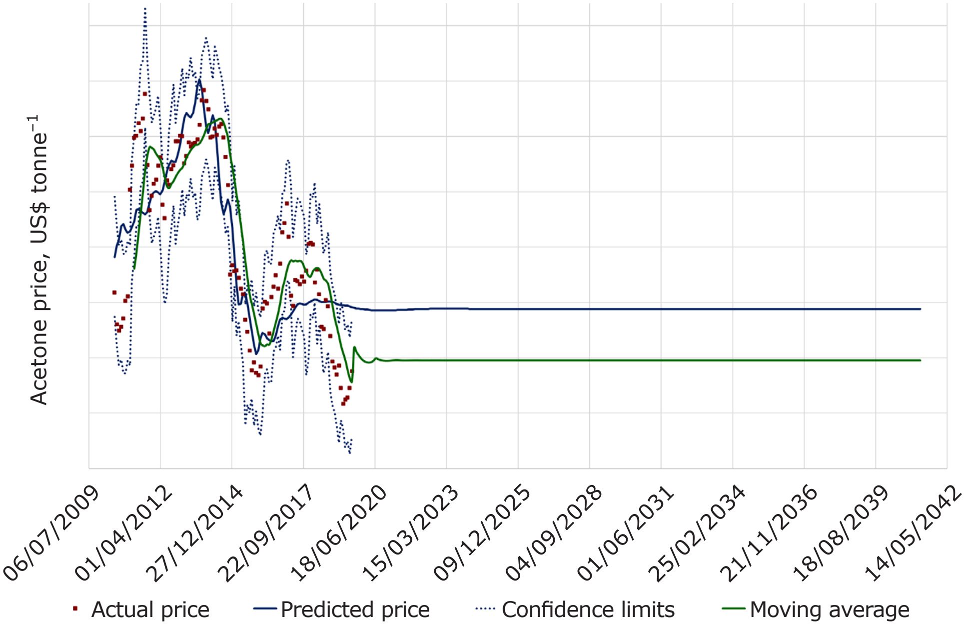

Fig. 8. Acetone price forecast using a radial basis function time series analysis model in free-run mode. The free-run prediction tracks the historical data appreciably, remaining within the confidence limits for the original one step predictor model fit. The free run forecast settles to a long-term average forecast for acetone. The moving average is plotted for comparative purposes. The y-axis is obscured given copyright restrictions associated with the Intratec database

Table IX Solvent Plant Production Summary

Product	Production rates		Product mass purity		Contribution to plant income
	Value	Unit	Value	Unit	%
Isopropanol	13.8	thousand tonnes year^{-1}	99.8	% (w/w)	49
Acetone	2.8	thousand tonnes year^{-1}	99.2	% (w/w)	6
Total renewable electricity	146	GWh year^{-1}	–	–	45

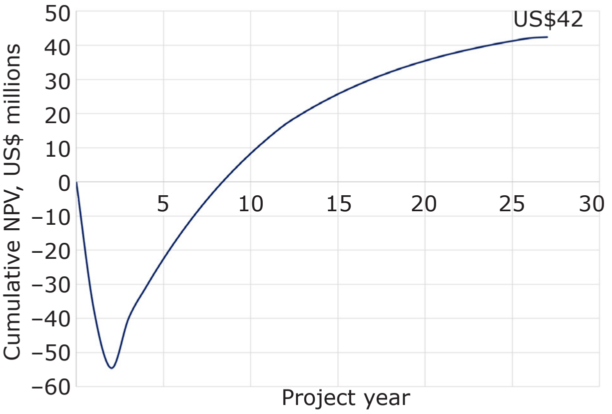

Fig. 9. Investment Analysis for the solvent plant including the utility value for black liquor, taken as the NPV for conventional generation of renewable electricity. For the nominal TEA model inputs, the solvent plant presents a net cumulative NPV of US$42 million

US$35 million and US$85 million, noting that no negative outcomes are predicted.

3.2 Life Cycle Assessment

Figure 11 summarises the outcome of the cradle-to-gate LCA for the solvent plant, compared to the conventional fossil derived processes; using both economic and energy allocation for the isopropanol, acetone and renewable electricity products.

Both solvents achieve negative GHG emissions when produced *via* the solvent plant using economic and energy allocation. The GHG emission for the two allocation methods are comparable, indicating the price per unit energy (US\$ MJ^{-1}) is similar for all three products. The negative emissions are an intrinsic outcome of the cradle-to-gate framework, which excludes the end use for the products. As the total GHG emissions of the solvent plant are lower than the overall biogenic carbon sequestered, negative GHG emissions are achieved for the solvent products.

The negative GHG emissions compare favourably to the conventional isopropanol (hydration of propene) and acetone (oxidation of cumene) processes. Additionally, the GHG emissions associated with the excess renewable electricity from the solvent plant also compare favourably to the electricity mix in China (2018). Furthermore, as the end use for the solvents remains the same regardless of the production method, the relative GHG emissions are valid beyond the cradle-to-gate framework.

3.3 Comparison with Anaerobic Fermentation

As highlighted in the Introduction, the commercial implementation of gas fermentation is largely dominated by anaerobic fermentation. Therefore, it is important to compare the results to a best-in-class technology. In addition to successfully commercialising ethanol production *via* gas fermentation, LanzaTech have also investigated gas fermentation to produce acetone, a precursor to isopropanol (64). As such, LanzaTech's investigation undertaken for the US Department of Energy (US DOE), in collaboration with Oak Ridge National Laboratory, USA, is used as a benchmark anaerobic process (65).

As highlighted previously, the primary differences between anaerobic and aerobic fermentation technologies are inherent to the C1 fixation metabolic pathways. Strictly respiratory (aerobic) cell factories require air to be continuously fed into the bioreactor to facilitate carbon fixation. In addition, owed to the intrinsic thermodynamic inefficiency of the Calvin-Benson-Bassham cycle employed by aerobic bacteria, an excess of low temperature heat is produced. As such, a conventional process flowsheet for aerobic fermentation employs operationally costly compressors and chillers. In contrast, for anaerobic fermentation there is a reduced chiller requirement and the compressor duty is less pronounced. Moreover, owed to the presence of oxygen, aerobic fermentations require the use of more costly stainless steel reactors and more complex process control systems. Whilst the latter is an intrinsic requirement of aerobic fermentations, in this work we have reconciled the increased utility demand of aerobic fermentation through process integration (28). This integration employs a heat pump to utilise the low temperature heat generated by aerobic fermentation to heat the SCWG reactor feed, removing the cooling water burden required by the bioreactors. Additionally, the compressor duty is fully supplied through the electricity generated upon letting down the SCWG reactor's high-pressure gas product. As a result, the economic and LCA outcomes for the solvent plant should be comparable to anaerobic fermentation technology.

LanzaTech's anaerobic study achieved a combined selectivity of 94.7% for ethanol and acetone, of which 57.3% was acetone (65). LanzaTech disclosed that by selling acetone at market prices they are able to sell coproduced ethanol at or below the US DOE's 2022 target of US\$3 GGE^{-1} (GGE

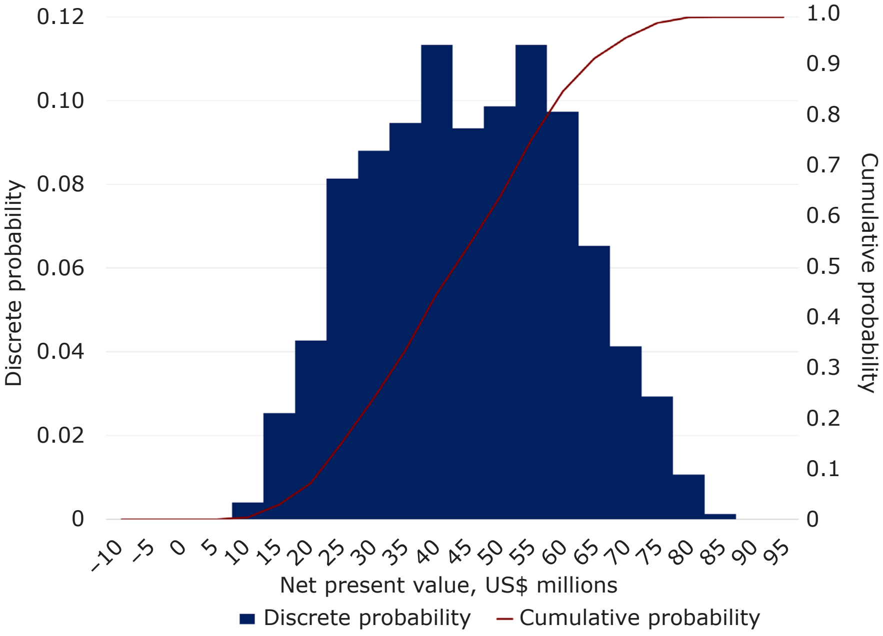

Fig. 10. Monte Carlo simulation for the opportunity cost associated with the solvent plant. The cumulative probability curve indicates that the solvent plant has a 70% probability of achieving US$35 million < net cumulative NPV < US$85 million

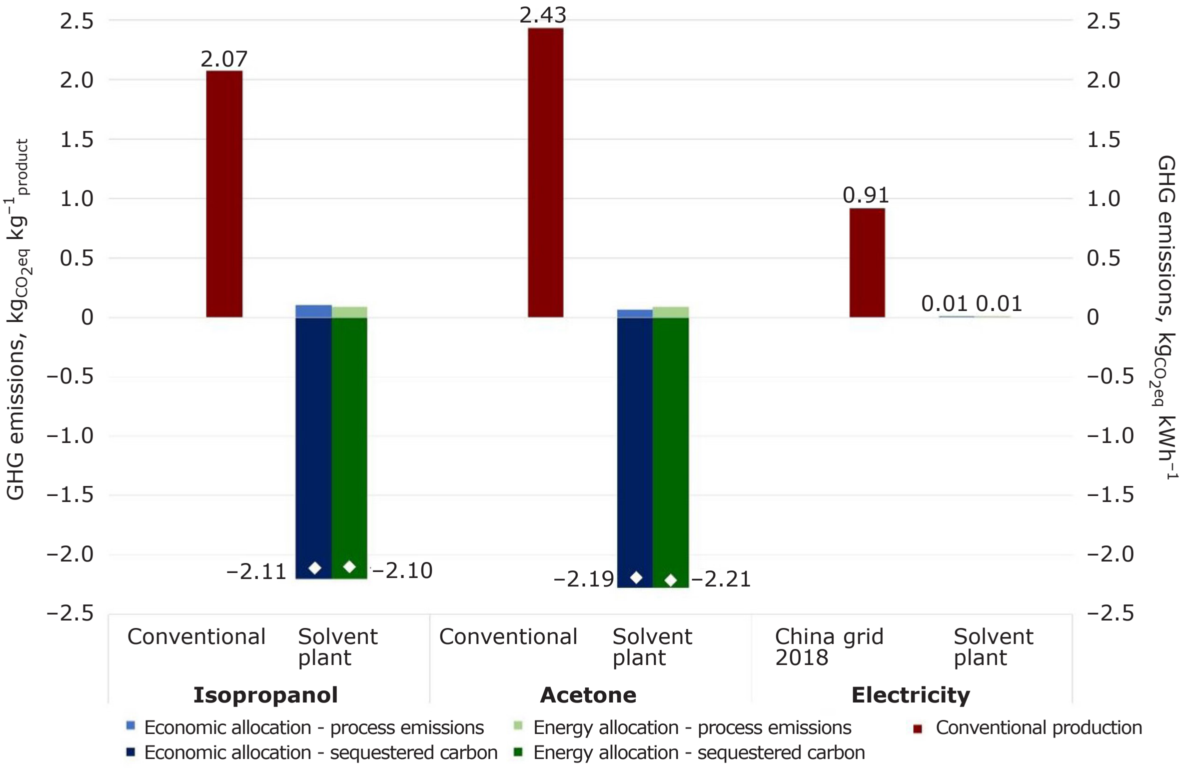

Fig. 11. GHG emissions for the solvent plant compared to the conventional fossil derived processes within a cradle-to-gate LCA framework. The GHG for the 2018 electricity mix in China is also shown, contrasting against near zero net GHG emissions for renewable electricity generation from black liquor

= gallon of gasoline equivalent) (66). Therefore, in this study, the price per GGE was calculated for the solvent products as a biofuel mix, with renewable electricity sold at the current market price. A value of US$2.87 GGE^{-1} (**Figure 12**) was obtained, below the US DOE's target, highlighting the competitiveness of the heat integrated aerobic solvent plant. Notably, neither isopropanol nor acetone are typically used for their fuel value, highlighted by their higher market prices. As such, the solvent plant is profitable as either a biofuel or commodity chemical facility.

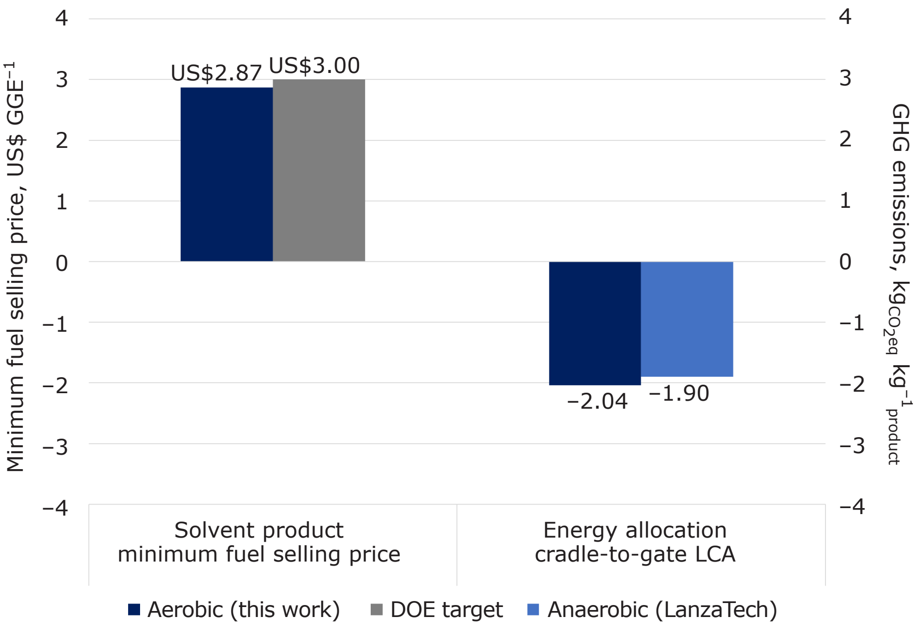

Fig. 12. Minimum selling price for the solvent product mix on a US$ GGE^{-1} basis and comparison between aerobic (this work) and anaerobic (LanzaTech) gas fermentation cradle-to-gate GHG emissions. The solvent product is below the US DOE's 2022 target of US$3 GGE^{-1} and the cradle-to-gate emissions are shown to be comparable to the anaerobic process

For LanzaTech's anaerobic process, the cradle-to-gate LCA using energy allocation produced a calculated GHG emission of −1.9 kg$_{CO_2eq}$ kg$^{-1}_{acetone + ethanol}$ for a heat integrated scenario (see Table S13 for calculation). In **Figure 12**, the LCA for the solvent plant is presented, indicating a net GHG emission of −2.04 kg$_{CO_2eq}$ kg$^{-1}_{isopropanol + acetone}$, which is in line with LanzaTech's study (**Figure 12**). Resultantly, from both the TEA and LCA results, the greater thermodynamic efficiency of the anaerobic Wood-Ljungdahl C1 fixation pathway over the aerobic Calvin-Benson-Bassham Cycle is not evident for the heat integrated solvent plant.

4. Conclusions

In exploiting the available excess black liquor, the solvent plant TEA presents a net cumulative NPV of US$42 million. The solvent plant demonstrates that the sustainable production of commodity chemicals priced near ~US$1000 per tonne is within reach of heat integrated aerobic gas fermentation, whilst achieving an appreciable reduction in GHG emissions compared to conventional production. Moreover, despite having a higher market value, a biofuel mix of the solvent product is able to meet the US DOE's 2022 target of US$3 GGE^{-1}. The heat integration between aerobic gas fermentation and SCWG produces an LCA comparable to a anaerobic gas fermentation technology. The TEA and LCA studies suggest that the intrinsic thermodynamic efficiency of anaerobic fermentation can be attained by aerobic fermentation through process engineering, albeit at a capital expense. Given aerobic cell factories can target a wider product spectrum, the heat integrated aerobic gas fermentation has promise as a best-in-class technology for renewable commodity chemical production.

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Glossary

Abbreviation	Name
FCI	fixed capital investment
GGE	gallon of gasoline equivalent
GHG	greenhouse gas
GWP	global warming potential
ISBL	inside battery limit
LCA	life cycle assessment
NPV	net present value
NREL	National Renewable Energy Laboratory
OSBL	outside battery limit
RBFNN	radial basis function neural network
SCWG	supercritical water gasification
TCI	total capital investment
TEA	technoeconomic assessment
TS	Towler and Sinnott
US DOE	US Department of Energy

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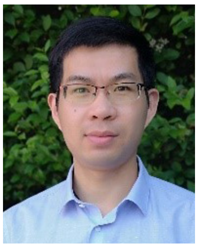

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