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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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ABSTRACT

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 pre-treatment to harness their potential fully. As such, the heat integration of supercritical water gasification and aerobic gas fermentation, unlocks the promise of renewable feedstocks such as lignin. This study models the techno-economics and life cycle assessment 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 techno-economic model. The techno-economic analysis demonstrates that production of commodity chemicals priced at ~\$1000 per ton is within reach of aerobic gas fermentation. In addition, owed to the sequestration of biogenic carbon into the solvent products, negative greenhouse gas emissions are achieved within a cradle-to-gate life cycle assessment 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, owed to its recalcitrance, lignin cannot be utilised by conventional fermentation, which accounts for up to 40% of lignocellulosic biomass (3).

Black liquor is a co-product 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 co-product 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 bottle neck 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 co-product is renewable electricity generation, gasification of this carbon-rich feedstock creates opportunities for biochemical production, expanding the product range of a Kraft mill.

Supercritical water gasification (SCWG) has emerged as a hydrothermal technology suited to the gasification of wet biomass feedstocks to produce 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 owed to: the utilisation of high operating temperatures and pressures, the prerequisite for specific CO/H₂ ratios, and potential

catalyst poisoning from gas impurities (13). Moreover, low chemo-catalytic selectivity remains a challenge for converting syngas to commodity chemicals. Gas fermentation, on the other hand, circumvents these intrinsic challenges, notably through high selectivity bio-catalysis, and has emerged as an alternative technology for syngas upgrading (13). Gas fermentation exploits microbial cell factories able to utilise CO₂ and H₂ 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 [kt/annum] 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 CO₂ fixation pathway compared to other biological C1 fixation pathways (16). However, such anaerobic CO₂ fixation presents energetic limitations which limit the product scope (17). Also, low value by-products 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. Owing 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 Techno-Economic Analyses (TEA) 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 pre-treatment 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 H₂ 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 CO₂ as the sole carbon source, H₂ as electron donor, and O₂ 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 by-products. Bommareddy et al. (28) details the continuous production of isopropanol and acetone using aerobic gas

fermentation. This first generation *Cupriavidus necator* cell factory produces acetone as an overflow co-product 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], 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 Life Cycle Assessment (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 1. 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 Na₂S) are recovered and recycled to the pulping process.

As previously mentioned, investments in heat integration have freed up a portion of the weak black liquor co-product for alternative uses. This study explores the opportunity of utilising this excess co-product, 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.

Table 1: Kraft mill plant capacity.

Parameter	Value	Unit	Reference
Pulp Mill Capacity	130	[Air dried t/h]	
Total weak black liquor production	1300	[t/h]	(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)	

In the proposed solvent plant (Figure 1), weak liquor undergoes SCWG to CO₂ and H₂. A challenge, however, is the efficient recovery of the cooking chemicals from the SCWG reactor and their recycle to the pulp mill digester. 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 in (33).

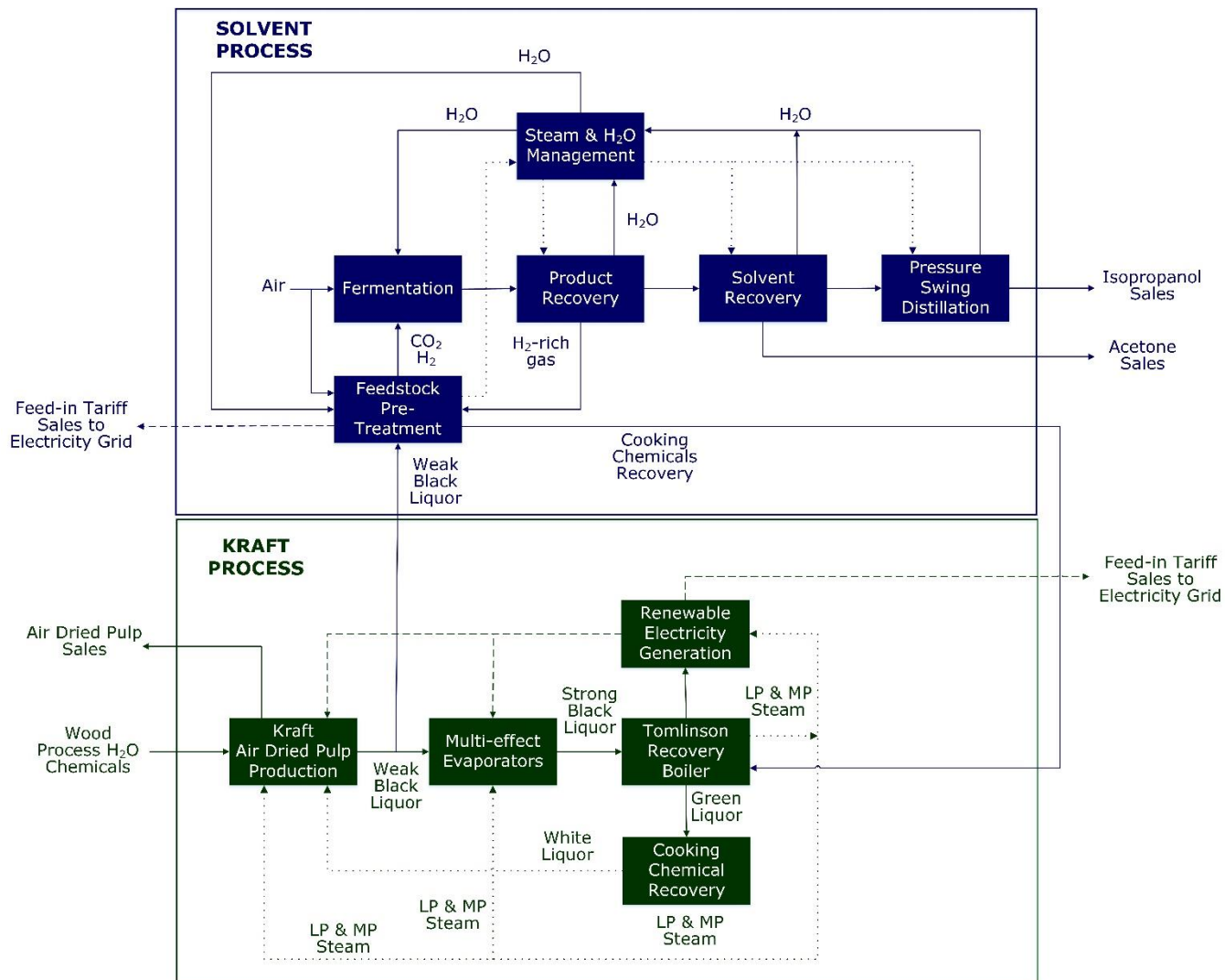


Figure 1: Conceptual solvent process integration with Kraft process, outlining materials (solid lines), power (dashed lines) and steam (dotted lines) flows. Excess weak black liquor is fed to the solvent process from the Kraft process and cooking chemicals are returned to the Tomlinson recovery boiler.

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 published in (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 H₂ and CO₂ 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 2. Table 3 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, detailed in (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

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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 co-product 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 O₂ mass transfer coefficient calculation associated with the solvent plant's mass balance is presented in Table S13, 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 3; 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 9,000 [KPa] and 480 [°C] is used in the steam turbine as outlined (43). The medium pressure steam exiting the turbine (10,000 [KPa]) is used in the multi-effect evaporators to concentrate the excess black liquor to 75% and to pre-heat the

auxiliary air supplied to the Tomlinson boiler. Similarly, the associated electricity demand for the air compressor and pump is provided by the electricity generated. Resultantly, through conventional renewable electricity generation, the excess black liquor produces 138 [GWh/annum] for sale to the grid.

Table 2: 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 3: Summary of scale-up of experimental gas fermentation data for ASPEN HYSYS process simulation.

Sources and sinks	Unit	CO ₂ and H ₂ as sole energy and carbon source
<i>Bioreactors</i>		
Oxygen transfer coefficient	[1/h]	415
O ₂ concentration in off-gas ^a	[%] (mol/mol)	3.35
Vessel Volume	[m ³]	500
Number of bioreactor trains	[-]	4
<i>Gas uptake rates</i>		
O ₂	[mmol/(L·h)]	230
CO ₂	[mmol/(L·h)]	125
H ₂	[mmol/(L·h)]	1006
<i>Isopropanol</i>		
Specific Productivity	[kg/(m ³ ·h)]	1.46
Broth concentration ^b	[g/L]	12.4
<i>Acetone</i>		
Specific Productivity	[kg/(m ³ ·h)]	0.38
Broth concentration	[g/L]	1.7
<i>Biomass</i>		
Growth rate	[h ⁻¹]	0.025
Dry Cell Weight with cell retention	[g/L]	21.5

^a Maintained to ensure oxygen concentration is below hydrogen's Limiting Oxygen Concentration of 4.6 [%] (mol/mol) (44). ^b Controlled via disc stack centrifugation, adding to the capital burden.

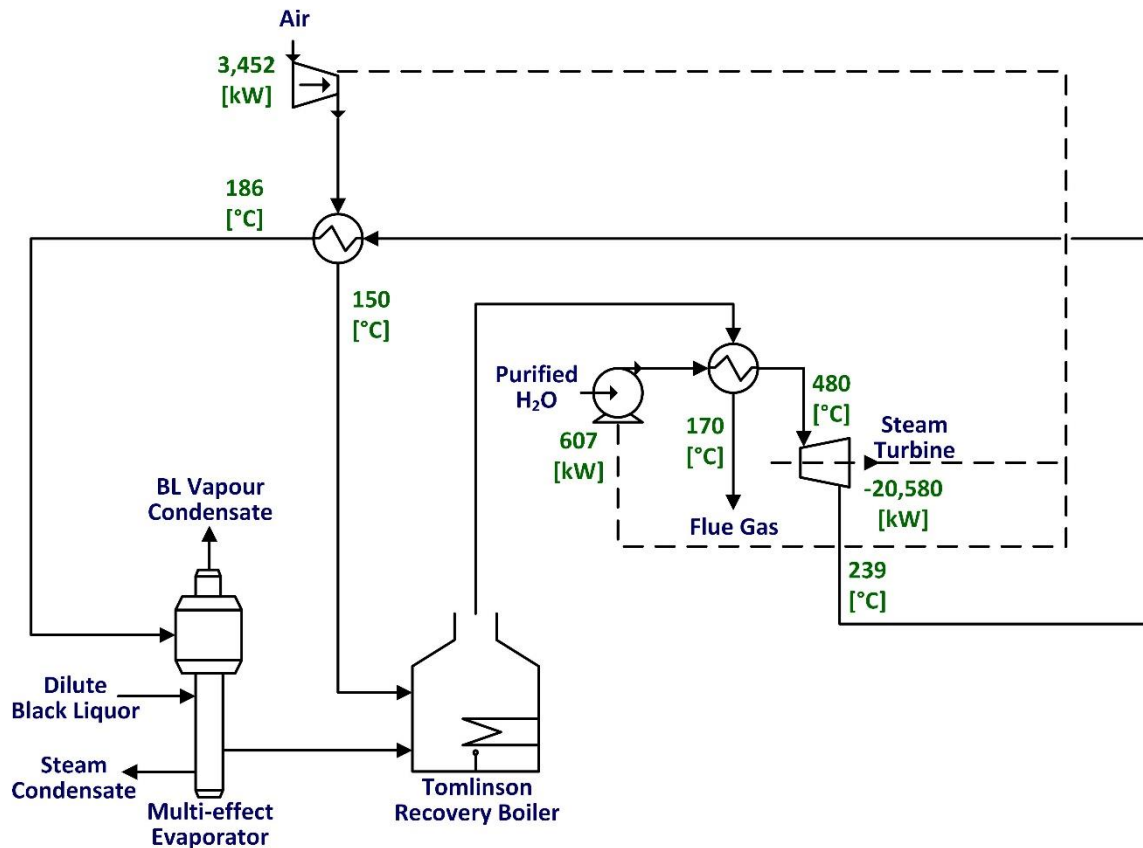


Figure 3: Process flow diagram for black liquor's conventional use, renewable electricity generation.

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 taken from (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 & Sinnott (TS) method taken from

Chemical Engineering 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 4.

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 RMB/\$ exchange rate.

Table 4: Fixed Capital Cost Models.

	NREL	TS	Hand
Year Basis	2019		
Production Year	8110 hours ^a		
Installation Factor (Multiplied by equipment cost) – Inside Battery Limit (ISBL)	Table S1	Table S3	Table S4
Outside Battery Limit (OSBL)	Table S2	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.

Three methods were used to calculate the fixed operating costs as summarised in Table 5. 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 & Richardson Volume 6 (50). Variable operating costs were estimated based on the costs detailed in Table 6, subject to annual inflation as outlined in Table 7.

Table 5: Fixed Operating Cost Models.

Parameters	NREL	TS	Coulson & 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 S5).

Table 6: Variable Operating Cost.

Raw Material	Cost	Unit	Reference	Comments
Ammonia	250	[\$/tonne]	(51)	Average price for 2019.
Cooling water	0.753	[\$/m ³]	(52)	
Electricity	0.06	[\$/kWh]	(52)	
Nutrients	0.75	[\$/(m ³ media water)]		Mineral salt media, containing no complex media or vitamins.
Process water	0.53	[\$/m ³]	(47)	

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 ten 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 8 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 0.109 [\$/kWh] 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 7.

Table 7: 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	

2.6 Sensitivity Analysis

A sensitivity analysis was conducted using a Monte Carlo simulation based on the cost parameters in Table 8, 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, 0.109 [\$/kWh]. 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 8, other than labour and electricity, were varied independently. Two thousand 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.

Table 8: Uncertainty framework for Monte Carlo simulation sensitivity analysis.

Monte Carlo Input Parameter	Lower Limit	Upper Limit
<i>Product Long Term Average Pricing</i>		
Isopropanol Price	0.7	1.3
Acetone Price	0.7	1.3
Renewable Electricity Price	0.7	1
<i>Costing uncertainty factor</i>		
ISBL Capital Cost	0.8	1.3
OSBL Capital Cost	0.8	1.3
Labour Costs	0.8	1.3

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). Greenhouse gas (GHG) emissions were calculated based on the most recent Integrated Pollution Prevention and Control 100-year Global Warming Potential factors to quantify greenhouse gas (GHG) emissions in terms of CO₂ equivalents (CO₂eq) (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 CO₂ 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/acetone products are not considered. These activities are assumed to be identical to those of conventional isopropanol/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 4 is summarised in Figure 4. The underlying capital cost estimation data is detailed in Table S1 – S4. Owing to the close agreement of the NREL and Hand methods, \$64 MM and \$65 MM respectively (Figure 4), and the greater simplicity of the Hand method, this method was used as the capital cost estimation basis. Table S9 details the capital cost estimation for the conventional generation of renewable electricity.

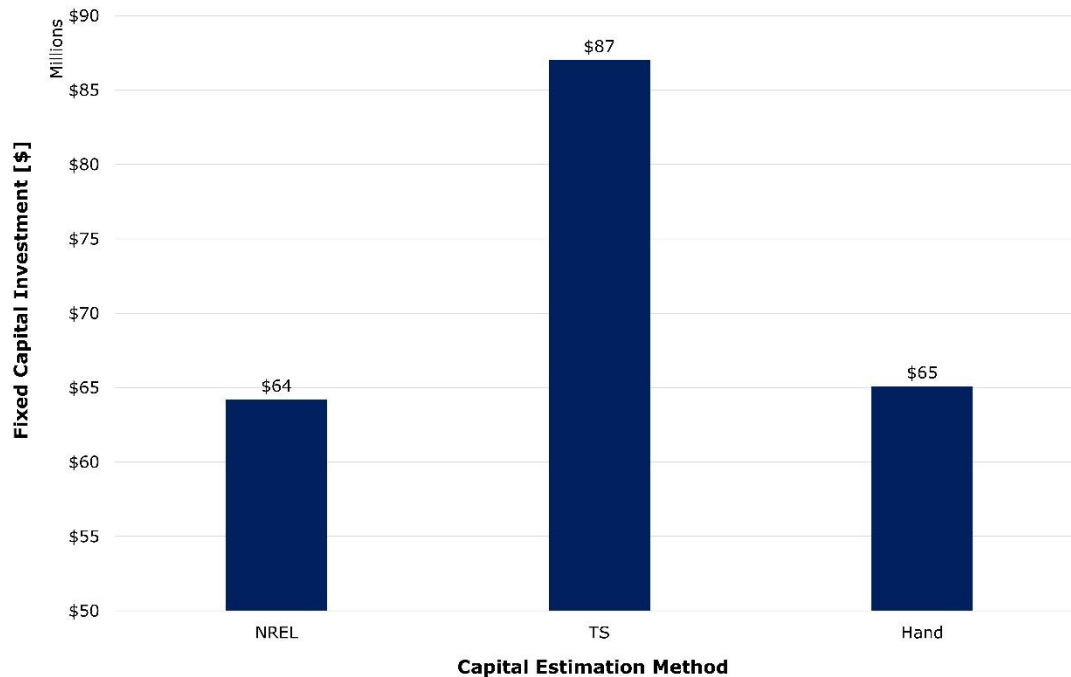


Figure 4: Comparison of three fixed capital investment estimates using the NREL, TS and Hand methods for the solvent plant. The NREL and Hand methods are in close agreement. The Hand method estimate was taken forward into the investment analyses.

Similarly, the three fixed operating cost methods (Table 5) are summarised in Figure 5, where the underlying fixed operating cost data is detailed in Table S5 – S7. Though sharing the same author, the TS and Coulson & Richardson methods have a dissimilar calculation method. However, the results of these two methods are in close agreement, \$4.62 MM and \$5.01 MM respectively (Figure 5). The substantially lower estimate by the NREL method (\$2.48 MM) 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 S10.

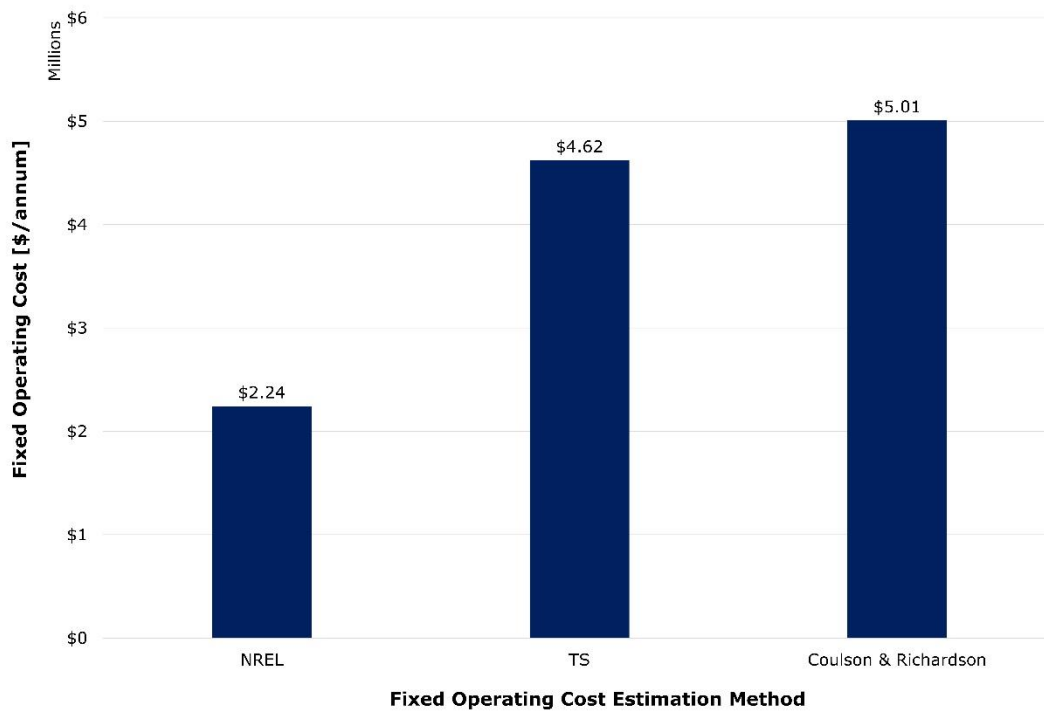


Figure 5: Comparison of three fixed operating cost estimates using the NREL, TS and Coulson & Richardson methods for the solvent plant. Though related, the TS and Coulson & Richardson methods are in close agreement. The TS method estimate was taken forward into the investment analysis.

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

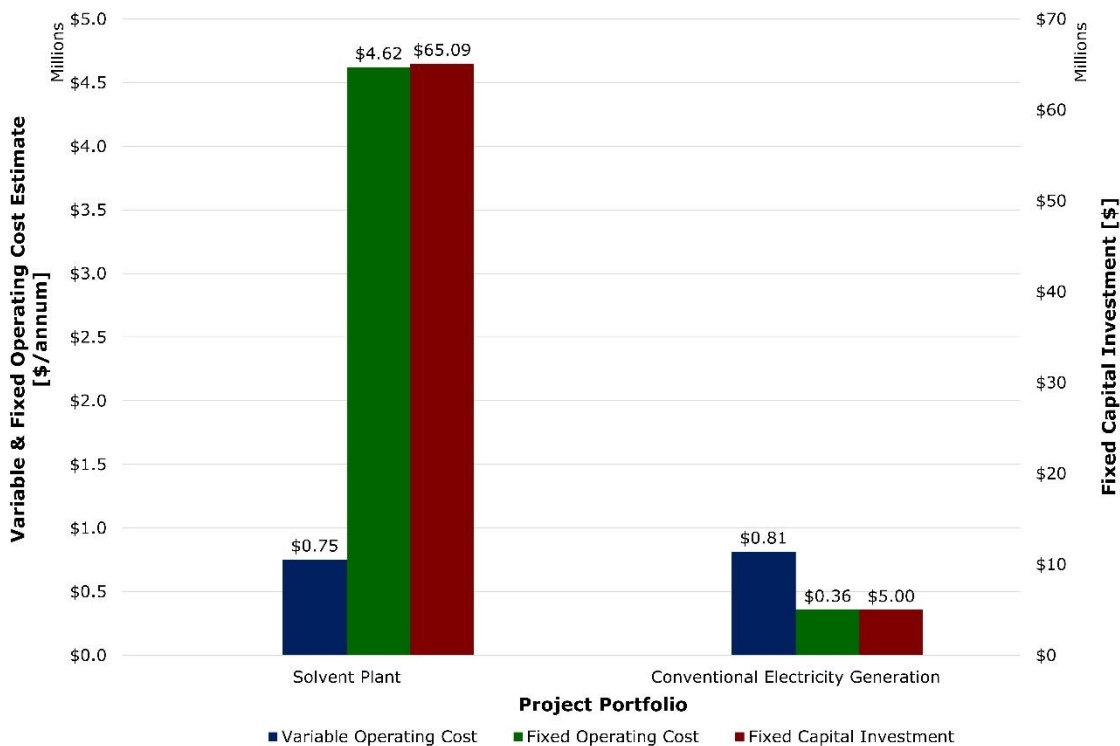


Figure 6: Comparison between production costs and fixed capital investment for the solvent plant and conventional renewable electricity generation.

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.

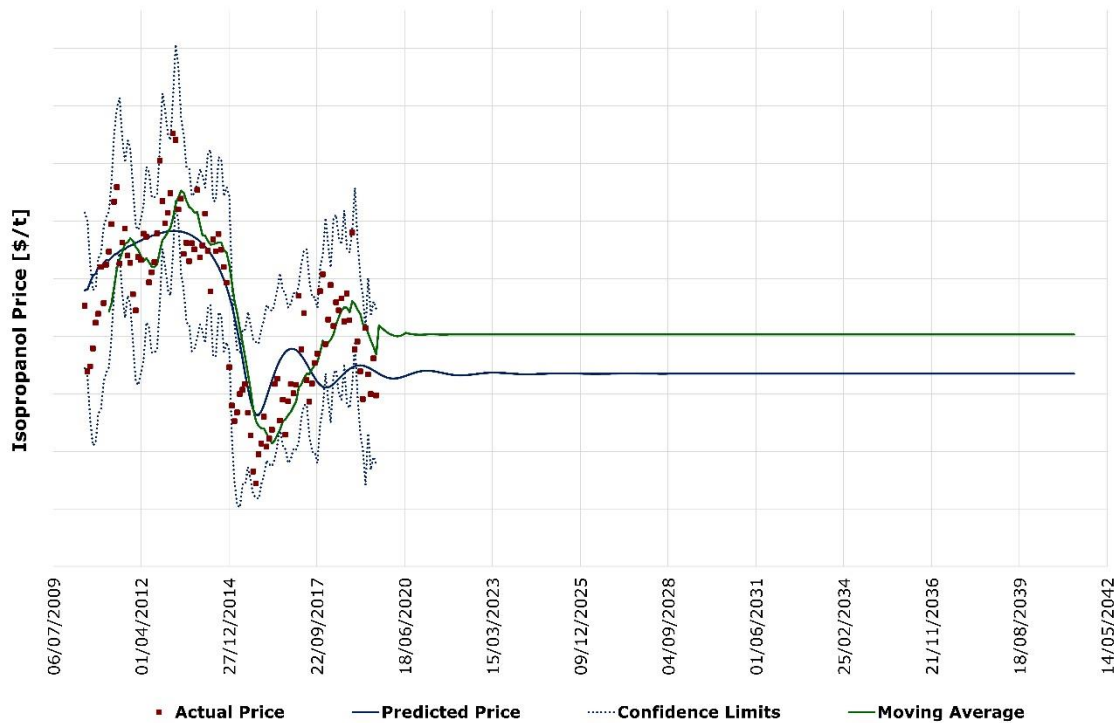


Figure 7: Isopropanol price forecast using a radial basis function time series analysis model in free-run mode. The free-run forecast tracks the historical data appreciably, remaining within the confidence limits for the original one step predictor model fit. The free run prediction settles to a long-term 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.

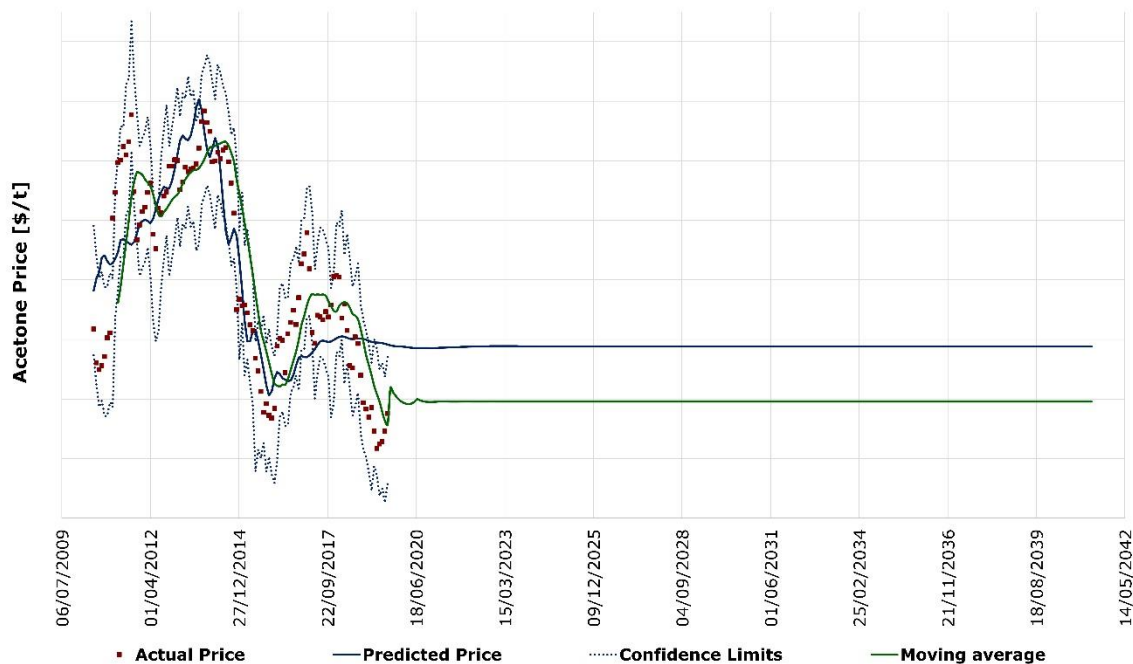


Figure 8: Acetone price forecast using a radial basis function time series analysis model in free-run mode. The free-run prediction tracks the historical data appreciably, remaining within the confidence limits for the original one step predictor model fit. The free run forecast settles to a long-term 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.

3.1 Investment Analysis

The solvent plant (Figure 2) produces three products, summarised in Table 9. 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.

Table 9: Solvent plant production summary.

Product	Production Rates		Product Mass Purity		Contribution to Plant Income [%]
	Value	Unit	Value	Unit	
Isopropanol	13.8	[kt/annum]	99.8	[%] (w/w)	49
Acetone	2.8	[kt/annum]	99.2	[%] (w/w)	6
Total Renewable Electricity	146	[GWh/annum]			45

The investment analyses for the solvent plant and conventional renewable electricity generation are detailed in Table S8 and Table S11, as per the investment analysis parameters presented in Table 7. The NPV for conventional renewable electricity generation represents the utility value of the black liquor, valued at \$73 MM (Table S11). This is subtracted from the NPV of the solvent plant (\$115 MM) to produce the cumulative NPV presented in Figure 9. For the nominal TEA model inputs, the solvent plant's net cumulative NPV is \$42 MM.

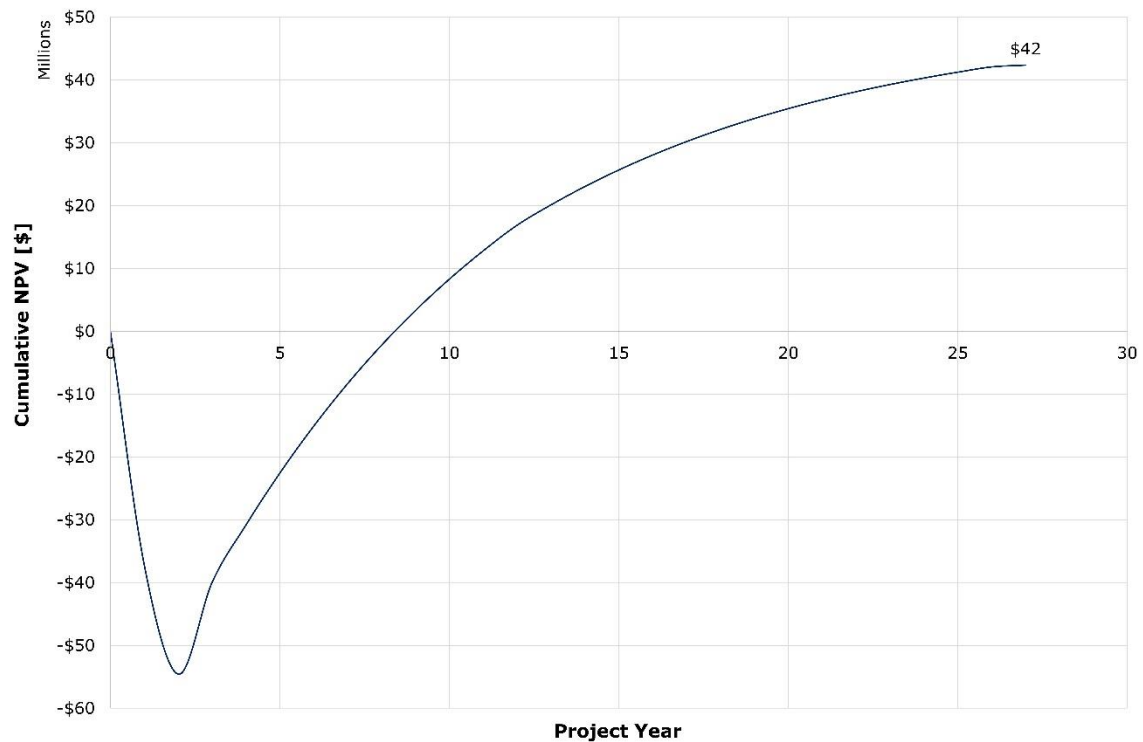


Figure 9: Investment Analysis for the solvent plant including the utility value for black liquor, taken as the NPV for conventional generation of renewable electricity. For the nominal TEA model inputs, the solvent plant presents a net cumulative NPV of \$42 MM.

Given the conceptual stage of the TEA, a Monte Carlo simulation was undertaken as per the uncertainty framework outlined in Table 8. 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 \$35 MM and \$85 MM, noting that no negative outcomes are predicted.

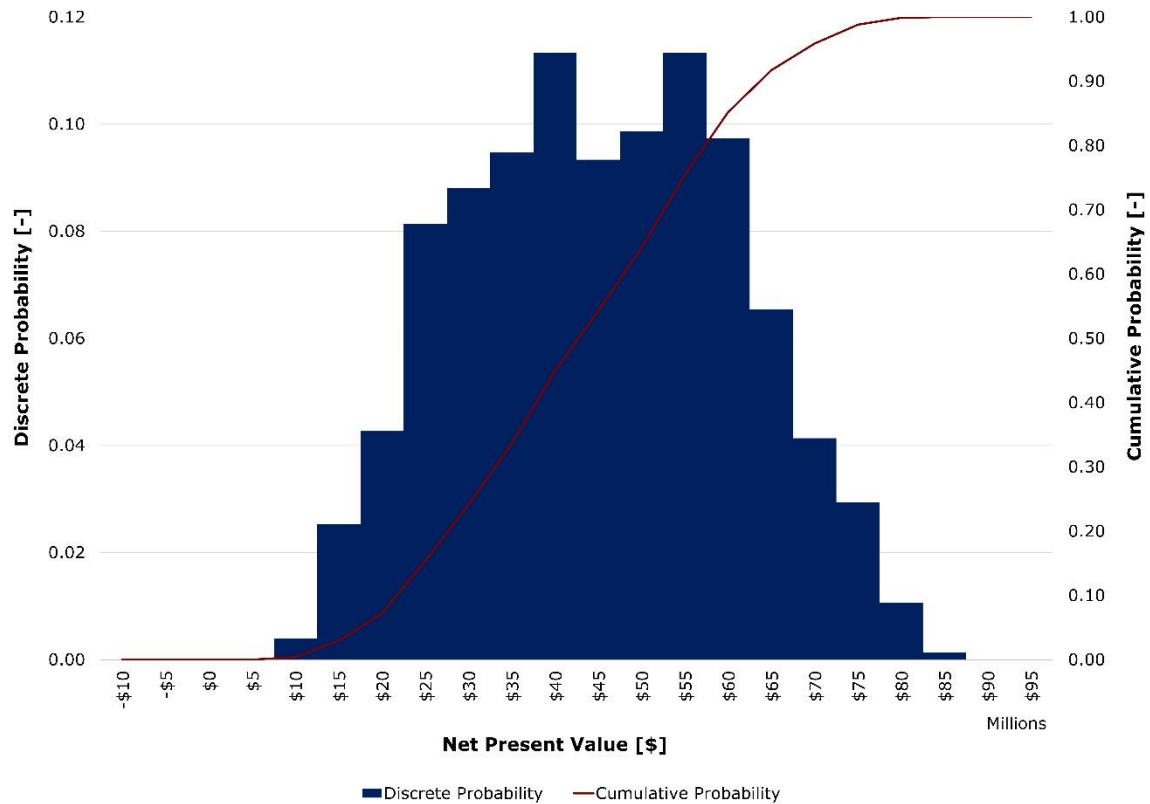


Figure 10: Monte Carlo simulation for the opportunity cost associated with the solvent plant. The cumulative probability curve indicates that the solvent plant has a 70 [%] probability of achieving $\$35 \text{ MM} < \text{net cumulative NPV} < \85 MM .

3.2 Life Cycle Analysis

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 [\$/MJ] 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.

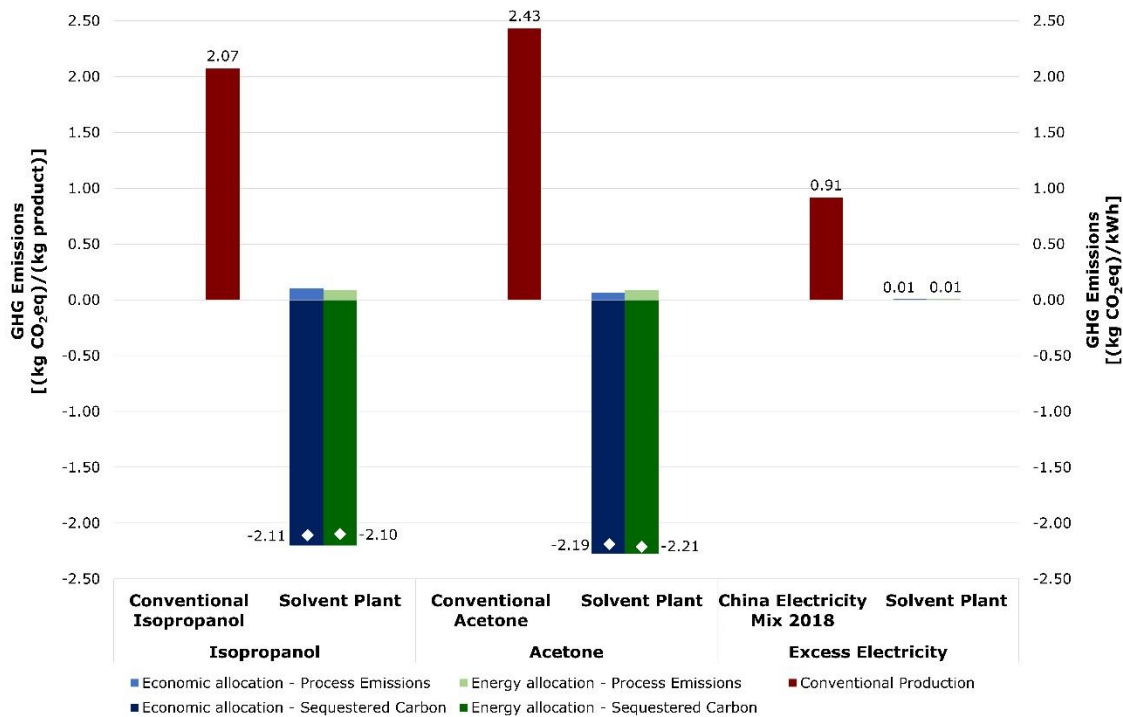


Figure 11: Greenhouse gas (GHG) emissions for the solvent plant compared to the conventional fossil derived processes within a cradle-to-gate life cycle assessment framework. The GHG for the 2018 Electricity Mix in China is also shown, contrasting against near zero net GHG emissions for renewable electricity generation from black liquor.

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 Department of Energy, in

collaboration with Oak Ridge National Laboratory, 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 the process integration outlined in (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 co-produced ethanol at or

below the Department of Energy's 2022 target of 3 [\$/GGE] (66). Therefore, in this study, the [\$/GGE] value for the solvent products as a biofuel mix was calculated, with renewable electricity sold at the current market price. A value of 2.87 [\$/GGE] (Figure 12) was obtained, below the 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.

For LanzaTech's anaerobic process, the cradle-to-gate LCA using energy allocation produced a calculated GHG emission of -1.9 [(kg CO₂eq)/(kg acetone + ethanol)] for a heat integrated scenario (see Table S12 for calculation). In Figure 12, the LCA for the solvent plant is presented, indicating a net GHG emission of -2.04 [(kg CO₂eq)/(kg 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.

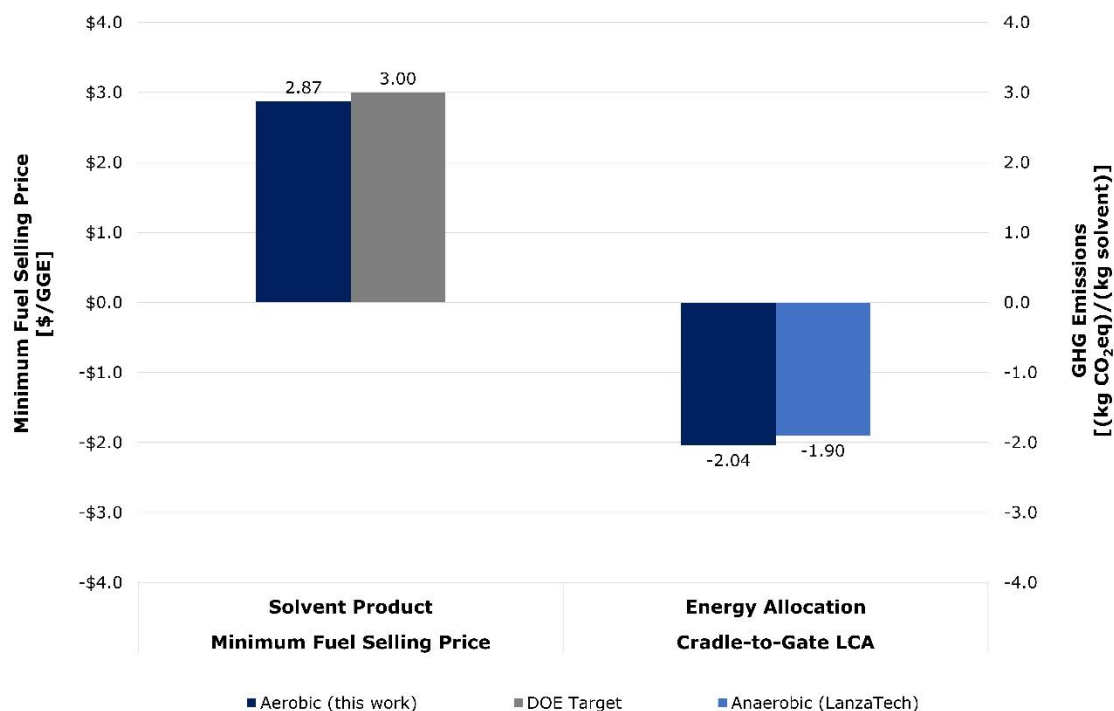


Figure 12: Minimum selling price for the solvent product mix on a [\$/GGE] basis and comparison between aerobic (this work) and anaerobic (LanzaTech) gas fermentation cradle-to-gate GHG emissions. The solvent product is below the DOE's 2022 target of 3 [\$/GGE] and the cradle-to-gate emissions are shown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

4. Conclusions

In exploiting the available excess black liquor, the solvent plant TEA presents a net cumulative NPV of \$42 MM. The solvent plant demonstrates that the sustainable production of commodity chemicals priced near ~\$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 DOE's

2022 target of 3 [\$/GGE]. 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.

Author Contributions

Conceptualisation: A.C. and R.R.B.; Methodology: S.R., A.C., R.K., F.M., J.M.; Software: S.R., A.C., R.K., F.M., J.M.; Formal Analysis: S.R., A.C., R.K., F.M., J.M.; Investigation: S.R., A.C., R.K., F.M., J.M.; Writing – Original Draft: S.R. and A.C.; Writing – Review & Editing: S.R., A.C., R.K., S.P., M.H., R.R.B., F.M., J.M.; Visualisation: S.R., A.C., F.M.; Supervision: A.C. and J.M.; Funding Acquisition: A.C. and J.M.

Nomenclature

Name	Abbreviation
Supercritical Water Gasification	SCWG
Fixed Capital Investment	FCI
Techno-Economic Assessment	TEA
National Renewable Energy Laboratory	NREL
Life Cycle Assessment	LCA
Net Present value	NPV
Towler and Sinnott	TS
Inside Battery Limit	ISBL
Outside battery Limit	OSBL
Total Capital Investment	TCI
Radial Basis Function Neural Network	RBFNN
Greenhouse Gas	GHG

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Reconciling the Sustainable Manufacturing of Commodity Chemicals with Feasible Technoeconomic Outcomes: Supplementary Information

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Table S1: Capital cost estimation for the solvent plant using the NREL method.

Plant section	Major ISBL Equipment item	Quantity	Purchase cost [€]	ISBL Installed Cost Cran factor	Installed cost (2006) [€]	CE cost Index adjustment to 2019 [€]	Location Factor	Total Installed Cost [€]	Total Plant section [€]		
SCWG Thermal Cycle											
Feedstock Pre-treatment	High Pressure Pump	1	86,721	2.30	199,459	242,342	0.51	123,369	21,548,182		
	Heat Pump Condenser	1	618,283	2.20	1,360,223	1,652,671		841,325			
	Heat Pump Compressor	1	1,566,961	1.60	2,507,138	3,046,173		1,550,715			
	SCWG Recovery HE	1	602,795	2.20	1,326,148	1,611,270		820,249			
	SCWG Plug Flow Reactor	1	417,687	1.50	626,531	761,235		387,522			
	Vapour Heater	1	235,313	2.20	517,689	628,993		320,201			
	Heat Pump Recovery HE	1	272,464	2.20	599,420	728,296		370,754			
	Combustion Heater	1	33,243	2.20	73,135	88,859		45,235			
	Supercritical Heater	1	75,606	2.20	166,334	202,096		102,881			
	Turbo-expander	1	3,717,523	1.80	6,691,541	7,737,174		3,938,764			
	Air Compression After Cooler	1	7,281	2.20	16,018	19,462		9,908			
	H ₂ Bioreactor Cooler	1	241,164	2.20	530,561	644,631		328,163			
Combustion											
	H ₂ Combustion Feed Heater	1	26,928	2.20	59,242	71,979	0.51	36,643			
	Bioreactor Off-gas Combustion Feed Heater	1	22,629	2.20	49,783	60,487		30,792			
	Combustion Chamber	1	2,072,893	1.80	3,731,208	4,533,418		2,307,827			
	Combustion Turbine	1	9,281,863	1.80	16,707,353	20,299,434		10,333,834			
Seed Fermenters											
Fermentation	Seed fermenters	1	186,818	2.00	373,637	453,969	0.51	231,102	6,109,348		
	Seed fermenter Recirculation Pumps	1	24,809	2.30	57,060	69,328		35,293			
	Seed fermenter Heat Exchangers	1	26,767	2.20	58,887	71,548		36,423			
	Production Fermenters										
		Production fermenters	4	2,578,892	2.00	5,157,784	6,266,707	0.51		3,190,193	
		Production fermenter Recirculation Pumps	4	516,321	2.30	1,187,539	1,442,860			734,517	
Production Fermenter HE		4	788,587	2.20	1,734,891	2,107,892	1,073,065				
Centrifuge	4	817,228	1.60	1,307,565	1,588,692	808,755					
Absorption											
Product Recovery from Bioreactor Aqueous & Vapour	Acetone Stripper Tower	1	125,436	2.40	301,047	365,772	0.51	186,204	1,853,509		
	Water Stripper Tower	1	106,657	2.40	255,977	311,012		158,327			
	Isopropanol Pre-flash Distillation Tower										
		Pre-flash Bottoms Recovery Heater	1	58,797	2.20	129,354	157,166	0.51		80,008	
		Pre-flash Condensate Recovery Heater	1	8,196	2.20	18,031	21,908			11,153	
		Tower	1	206,398	2.40	495,355	601,857			306,387	
		Reboiler	1	12,468	2.20	27,429	33,326			16,965	
	Condenser	1	8,196	2.20	18,031	21,908	11,153				
	Isopropanol & Acetone Concentration Distillation										
		Column Feed Heater	1	11,033	2.20	24,273	29,492	0.51		15,013	
Tower		1	700,026	2.40	1,680,062	2,041,275	1,039,152				
Reboiler		1	9,476	2.20	20,848	25,330	12,895				
Condenser		1	11,413	2.20	24,866	30,213	15,530				
Acetone Product Distillation											
Solvent Recovery	Tower	1	180,458	2.40	433,099	526,216	0.51	267,881	685,795		
	Reboiler	1	9,772	2.20	21,498	26,120		13,297			
	Condenser	1	7,177	2.20	15,790	19,185		9,767			
	Solvent Distillation										
		Pre-heater	1	7,180	2.20	15,797	19,193	0.51		9,771	
		Tower	1	245,120	2.40	588,287	714,769			363,868	
Reboiler		1	7,225	2.20	15,895	19,313	9,832				
Condenser	1	8,364	2.20	18,400	22,356	11,381					
Low Pressure Swing Distillation											
Isopropanol Pressure Swing Distillation	Feed Condenser	1	7,901	2.20	17,383	21,120	0.51	10,752	1,539,261		
	Tower	1	539,856	2.40	1,295,655	1,574,221		801,389			
	Reboiler	1	7,179	2.20	15,794	19,190		9,769			
	Condenser	1	11,597	2.20	25,513	30,998		15,780			
	High Pressure Swing Distillation										
	First Pre-heater	1	7,917	2.20	17,417	21,162	0.51	10,773			
	Second Pre-heater	1	7,400	2.20	16,280	19,780		10,070			
	Tower	1	447,603	2.40	1,074,247	1,305,211		664,444			
	Reboiler	1	11,968	2.20	26,329	31,990		16,285			
Steam & Water Management											
Steam & Water Management	CO ₂ flash drum steam heater	1	33,438	2.20	73,564	89,380	0.51	45,501	785,217		
	Steam Mechanical Vapour Compressors	1	706,707	1.60	1,130,732	1,373,839		699,380			
	Water Recycle to Fermentation Cooler	1	11,040	2.20	24,287	29,509		15,022			
	Water Recycle to SCWG Gasification	1	11,227	2.20	24,700	30,011		15,278			
	IPA Cooler to Absorber	1	7,376	2.20	16,227	19,716		10,037			

Table S2: Additional capital cost for the solvent plant associated with the NREL method.

Additional Costs for Determining Total Capital Investment (TCI)				
Item	Description	Unit (Basis)	Annual cost [\$/annum]	Comments
Additional Direct Costs				
Warehouse	4	[% of installed cost of ISBL equipment]	1,300,852	On-site storage of equipment and supplies.
Site Development	9	[% of installed cost of ISBL equipment]	2,926,918	Includes fencing, curbing, parking lot, roads, well drainage, rail system, soil borings, and general paving. This factor allows for minimum site development assuming a clear site with no unusual problems such as right-of-way, difficult land clearing, or unusual environmental problems.
Additional piping	5	[% of installed cost of ISBL equipment]	1,463,459	To connect ISBL equipment to storage and utilities outside the battery limits.
Indirect Costs				
Pro-rateable costs	10	[% of TDC]	3,821,254	This includes fringe benefits, burdens, and insurance of the construction contractor.
Field expenses	10	[% of TDC]	3,821,254	Consumables, small tool and equipment rental, field services, temporary construction facilities, and field construction supervision.
Home office and construction	20	[% of TDC]	7,642,508	Engineering plus incidentals, purchasing, and construction.
Project contingency	10	[% of TDC]	3,821,254	Extra cash on hand for unforeseen issues during construction.
Other costs	10	[% of TDC]	3,821,254	Start-up and commissioning costs. Land, rights-of-way, permits, surveys, and fees. Piling, soil compaction/dewatering, unusual foundations. Sales, use, and other taxes. Freight, insurance in transit, and import duties on equipment, piping, steel, instrumentation, etc. Overtime pay during construction. Field insurance. Project team. Transportation equipment, bulk shipping containers, plant vehicles, etc.
TOTAL ADDITIONAL COSTS			28,618,754	

Table S3: Capital cost estimation for the solvent plant using the TS method.

Plant section	Major ISBL Equipment item	Quantity	Purchase cost [€]	ISBL Installed Cost Lang factor	Installed cost (2006) [€]	CE cost Index adjustment to 2019 [€]	Location Factor	Total Installed Cost [€]	Total Plant section [€]		
SCWG Cycle											
Feedstock Pre-treatment	High Pressure Pump	1	86,721	3.3	286,180	347,709	0.51	177,008	38,484,617		
	Heat Pump Condenser	1	618,283		2,040,334	2,479,006		1,261,988			
	Heat Pump Compressor	1	1,566,961		5,170,973	6,282,732		3,198,351			
	SCWG Recovery HE	1	602,795		1,989,222	2,416,905		1,230,374			
	SCWG Plug Flow Reactor	1	417,687		1,378,368	1,674,717		852,548			
	Vapour Heater	1	235,313		776,534	943,489		480,302			
	Heat Pump Recovery HE	1	272,464		899,131	1,092,444		556,130			
	Combustion Heater	1	33,243		109,703	133,289		67,853			
	Supercritical Heater	1	75,606		249,501	303,144		154,321			
	Turbo-expander	1	3,717,523		12,267,826	14,184,819		7,221,067			
	Air Compression After Cooler	1	7,281		24,027	29,193		14,861			
	H ₂ Bioreactor Cooler	1	241,164		795,841	966,947		492,244			
	Combustion										
H ₂ Combustion Feed Heater	1	26,928	3.3	88,863	107,969	0.51	54,964				
Bioreactor Off-gas Combustion Feed Heater	1	22,629		74,675	90,730		46,188				
Combustion Chamber	1	2,072,893		6,840,548	7,329,158		3,731,055				
Combustion Turbine	1	9,281,863		30,630,148	37,215,629		18,945,362				
Seed Fermenters											
Fermentation	Seed fermenters	1	186,818	3.3	616,501	749,048	0.51	381,318	10,081,936		
	Seed fermenter Recirculation Pumps	1	24,809		81,869	99,471		50,638			
	Seed fermenter Heat Exchangers	1	26,767		88,331	107,322		54,635			
	Production Fermenters										
	Production fermenters	4	2,578,892	3.3	8,510,344	10,340,067	0.51	5,263,819			
	Production fermenter Recirculation Pumps	4	516,321		1,703,860	2,070,190		1,053,872			
	Production Fermenter HE	4	788,587		2,602,336	3,161,838		1,609,597			
Centrifuge	4	817,228	2,696,853		3,276,677	1,668,058					
Absorption											
Product Recovery from Bioreactor Aqueous & Vapour	Acetone Stripper Tower	1	125,909	3.3	415,498	504,830	0.51	256,994	2,568,914		
	Water Stripper Tower	1	106,671		352,014	427,697		217,728			
	Isopropanol Pre-flash Distillation Tower										
	Pre-flash Bottoms Recovery Heater	1	58,797	3.3	194,032	235,748	0.51	120,012			
	Pre-flash Condensate Recovery Heater	1	8,196		27,047	32,862		16,729			
	Tower	1	206,398		681,113	827,553		421,282			
	Reboiler	1	12,468		41,144	49,990		25,448			
	Condenser	1	8,196		27,047	32,862		16,729			
	Isopropanol & Acetone Concentration Distillation										
	Column Feed Heater	1	11,033	3.3	36,409	44,237	0.51	22,520			
Tower	1	700,026	2,310,085		2,806,753	1,428,834					
Reboiler	1	9,476	31,272		37,995	19,342					
Condenser	1	11,413	37,663		45,760	23,295					
Acetone Product Distillation											
Solvent Recovery	Tower	1	180,458	3.3	595,512	723,546	0.51	368,336	949,723		
	Reboiler	1	9,772		32,247	39,180		19,945			
	Condenser	1	7,177		23,686	28,778		14,650			
	Solvent Distillation										
	Pre-heater	1	7,180	3.3	23,695	28,789	0.51	14,656			
	Tower	1	245,120		808,895	982,807		500,318			
	Reboiler	1	7,225		23,843	28,969		14,747			
Condenser	1	8,364	27,600		33,534	17,071					
Low Pressure Swing Distillation											
Isopropanol Pressure Swing Distillation	Feed Condenser	1	7,901	3.3	26,074	31,680	0.51	16,127	2,125,662		
	Tower	1	539,856		1,781,526	2,164,554		1,101,910			
	Reboiler	1	7,179		23,691	28,785		14,654			
	Condenser	1	11,597		38,269	46,497		23,670			
	High Pressure Swing Distillation										
	First Pre-heater	1	7,917	3.3	26,126	31,743	0.51	16,159			
	Second Pre-heater	1	7,400		24,420	29,671		15,104			
	Tower	1	447,603		1,477,090	1,794,665		913,610			
Reboiler	1	11,968	39,494		47,985	24,428					
Steam & Water Management											
Steam & Water Management	CO ₂ flash drum steam heater	1	33,438	3.3	110,346	134,070	0.51	68,251	1,571,228		
	Steam Mechanical Vapour Compressors	1	706,707		2,332,134	2,833,543		1,442,472			
	Water Recycle to Fermentation Cooler	1	11,040		36,430	44,263		22,533			
	Water Recycle to SCWG Gasification	1	11,227		37,051	45,016		22,916			
	IPA Cooler to Absorber	1	7,376		24,341	29,574		15,055			

Table S4: Capital cost estimation for the solvent plant using the Hand method.

Plant section	Major ISBL Equipment item	Quantity	Purchase cost [€]	ISBL Installed Cost Hand factor	Installed cost (2006) [€]	CE cost Index adjustment to 2019 [€]	Location Factor	Total Installed Cost [€]	Total Plant section [€]	
Feedstock Pre-treatment	SCWG Cycle									
	High Pressure Pump	1	86,721	4.00	346,885	421,465	0.51	214,555	30,378,659	
	Heat Pump Condenser	1	618,283	3.50	2,163,991	2,629,249		1,338,472		
	Heat Pump Compressor	1	1,566,961	2.50	3,917,404	4,759,645		2,422,993		
	SCWG Recovery HE	1	602,795	3.50	2,109,781	2,563,384		1,304,942		
	SCWG Plug Flow Reactor	1	417,687	4.00	1,670,749	2,029,961		1,033,392		
	Vapour Heater	1	235,313	3.50	823,597	1,000,670		509,411		
	Heat Pump Recovery HE	1	272,464	3.50	953,623	1,158,653		589,835		
	Combustion Heater	1	33,243	3.50	116,351	141,367		71,966		
	Supercritical Heater	1	75,606	3.50	264,622	321,516		163,674		
	Turbo-expander	1	3,717,523	2.50	9,293,807	10,746,075		5,470,505		
	Air Compression After Cooler	1	7,281	3.50	25,484	30,962		15,762		
	H ₂ Bioreactor Cooler	1	241,164	3.50	844,074	1,025,550		522,077		
	Combustion									
	H ₂ Combustion Feed Heater	1	26,928	3.50	94,249	114,513	58,295	0.51		
	Bioreactor Off-gas Combustion Feed Heater	1	22,629	3.50	79,201	96,229	48,987			
	Fired Heater	1	2,072,893	2.00	4,145,786	4,441,914	2,261,245			
Combustion Turbine	1	9,281,863	2.50	23,204,657	28,193,659	14,352,547				
Fermentation	Seed Fermenters									
	Seed fermenters	1	186,818	4.00	747,274	907,937	0.51	462,204	11,210,164	
	Seed fermenter Recirculation Pumps	1	24,809	4.00	99,236	120,571	61,379			
	Seed fermenter Heat Exchangers	1	26,767	3.50	93,684	113,827	57,946			
	Production Fermenters									
	Production fermenters	4	644,723	4.00	10,315,568	12,533,415	0.51	6,380,386		
	Production fermenter Recirculation Pumps	4	129,080	4.00	2,065,285	2,509,321	1,277,420			
Production Fermenter HE	4	197,147	3.50	2,760,053	3,353,465	1,707,148				
Centrifuge	4	204,307	2.50	2,043,071	2,482,331	1,263,680				
Product Recovery from Bioreactor Aqueous & Vapour	Absorption									
	Acetone Stripper Tower	1	125,909	4.00	503,634	611,916	0.51	311,508	3,076,854	
	Water Stripper Tower	1	106,671	4.00	426,684	518,421	263,913			
	Isopropanol Pre-flash Distillation Tower									
	Pre-flash Bottoms Recovery Heater	1	58,797	3.50	205,791	250,036	0.51	127,286		
	Pre-flash Condensate Recovery Heater	1	8,196	3.50	28,686	34,854		17,743		
	Tower	1	206,398	4.00	825,592	1,003,094		510,645		
	Reboiler	1	12,468	3.50	43,637	53,019		26,991		
	Condenser	1	8,196	3.50	28,686	34,854		17,743		
	Isopropanol & Acetone Concentration Distillation									
	Column Feed Heater	1	11,033	3.50	38,616	46,918	0.51	23,885		
Tower	1	700,026	4.00	2,800,103	3,402,125	1,731,920				
Reboiler	1	9,476	3.50	33,167	40,298	20,514				
Condenser	1	11,413	3.50	39,946	48,534	24,707				
Solvent Recovery	Acetone Product Distillation									
	Tower	1	180,458	4.00	721,832	877,026	0.51	446,468	1,138,897	
	Reboiler	1	9,772	3.50	34,201	41,555	21,154			
	Condenser	1	7,177	3.50	25,121	30,522	15,538			
	Solvent Distillation									
	Pre-heater	1	7,180	3.50	25,131	30,534	0.51	15,544		
	Tower	1	245,120	4.00	980,479	1,191,282	606,446			
Reboiler	1	7,225	3.50	25,288	30,725	15,641				
Condenser	1	8,364	3.50	29,272	35,566	18,106				
Isopropanol Pressure Swing Distillation	Low Pressure Swing Distillation									
	Feed Condenser	1	7,901	3.50	27,655	33,600	0.51	17,105	2,559,872	
	Tower	1	539,856	4.00	2,159,425	2,623,702		1,335,648		
	Reboiler	1	7,179	3.50	25,127	30,530		15,542		
	Condenser	1	11,597	3.50	40,589	49,315		25,105		
	High Pressure Swing Distillation									
	First Pre-heater	1	7,917	3.50	27,709	33,666	0.51	17,139		
	Second Pre-heater	1	7,400	3.50	25,900	31,469		16,020		
Tower	1	447,603	4.00	1,790,412	2,175,351	1,107,406				
Reboiler	1	11,968	3.50	41,887	50,893	25,908				
Steam & Water Management	Steam & Water Management									
	CO ₂ flash drum steam heater	1	33,438	3.50	117,033	142,195	0.51	72,387	1,229,341	
	Steam Mechanical Vapour Compressors	1	706,707	2.50	1,766,768	2,146,623		1,092,782		
	Water Recycle to Fermentation Cooler	1	11,040	3.50	38,638	46,946		23,899		
	Water Recycle to SCWG Gasification	1	11,227	3.50	39,296	47,745		24,305		
IPA Cooler to Absorber	1	7,376	3.50	25,816	31,367	15,968				

Table S5: Fixed Operating Cost for the solvent plant using the NREL method.

Labour & Supervision	Salary [\$] (2020)	Number of personnel	Annual cost [\$/annum]
Plant manager	29,591	1	29,591
Plant engineer	29,977	1	29,977
Maintenance supervisor	20,406	1	20,406
Maintenance technician	14,968	3	44,903
Lab manager	21,569	1	21,569
Lab technician	14,619	1	14,619
Shift supervisor	15,267	4	61,067
Shift operators	13,373	12	160,470
Yard employees	6,184	4	24,735
Clerks and secretaries	11,488	3	34,464
TOTAL SALARIES			441,800
Labour burden	90 [%] of Total Salaries		397,620
TOTAL LABOUR COST			839,421
Other overhead			Annual cost [\$/annum]
Maintenance	3 [%] of ISBL		975,639
Property insurance	0.7 [%] of FCI		427,980
TOTAL FIXED OPERATING COST			2,243,040

Table S6: Fixed Operating Cost for the solvent plant using the TS method.

FIXED OPERATING COST			
Fixed Operational Consideration	Assessment Basis	Unit (Basis)	Annual cost [\$/annum]
Operating Labour	Wage & Salary Cost for shift team members (excl. supervision)	[13,373 [\$/operator], 4 shift teams with 3 operators each]	160,470
Supervisory Labour	25	[% of Operating labour]	40,118
Direct Salary Overhead	50	[% of Operating + Supervisory]	100,294
Maintenance	3	[% of ISBL]	1,673,462
Property taxes & insurance	1	[% of ISBL]	557,821
Rent of land/buildings	1	[% of FCI]	725,167
General plant overhead	65	[% of total labour + maintenance]	1,218,132
Allocated environmental charges	1	[% of FCI]	725,167
Interest charges (capital)	0	[% of total capital investment]	0
TOTAL FIXED OPERATING COST			5,200,631

Table S7: Fixed Operating Cost for the solvent plant using the Coulson & Richardson method.

Labour & Supervision	Salary [\$] (2020)	Number of personnel	Annual cost [\$/annum]
Plant manager	29,591	1	29,591
Plant engineer	29,977	1	29,977
Maintenance supervisor	20,406	1	20,406
Maintenance technician	14,968	3	44,903
Lab manager	21,569	1	21,569
Lab technician	14,619	1	14,619
Shift supervisor	15,267	4	61,067
Shift operators	13,373	12	160,470
Yard employees	6,184	4	24,735
Clerks and secretaries	11,488	3	34,464
TOTAL OPERATING AND SUPERVISORY LABOUR COSTS			441,800
FIXED COSTS			
Fixed Operational Consideration	Assessment Basis	Unit (Basis)	Annual cost [\$/annum]
Maintenance	5	[% of FCI]	3,099,612
Operating Labour			274,703
Laboratory Costs	20	[% Operating Labour]	54,941
Supervisory Labour	20	[% Operating Labour]	167,097
Plant overhead	50	[% Operating Labour]	137,352
Capital charges	10	[% of FCI]	0
Insurance	1	[% of FCI]	619,922
Local taxes	1	[% of FCI]	619,922
Royalties	1	[% of FCI]	0
FIXED COSTS			4,973,549
Sales expense	20	[% of Direct Production Costs]	34,464
General Overheads			
Research & Development			
TOTAL FIXED OPERATING COSTS			5,008,013

Table S8: Investment Analysis for the solvent plant using the Hand method for capital estimation and the TS method for fixed operating cost estimation.

Year	Project Life	Detailed design	Fixed Capital Investment	Working Capital	Fixed OPEX	Variable OPEX	Plant Income	Depreciation	Corporation Tax	Total Cash Flow	NPV	Cumulative NPV	Comments
		[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	
2019	0	-250,000	0	0	0	0	0	0	0	-250,000	-250,000	-250,000	
2020	1	0	-44,262,454	0	0	0	0	0	0	-44,262,454	-40,238,595	-40,488,595	Plant construction & commissioning.
2021	2	0	-22,573,852	0	0	0	0	0	0	-22,573,852	-18,656,076	-59,144,670	
2022	3	0	0	6,578,665	-4,904,838	-798,965	35,292,066	-6,683,631	-5,726,158	30,440,770	22,870,601	-36,274,069	Year 0 for plant operation.
2023	4	0	0	0	-5,002,935	-814,945	35,292,066	-6,683,631	-5,697,639	23,776,548	16,239,702	-20,034,367	
2024	5	0	0	0	-5,102,993	-831,243	35,292,066	-6,683,631	-5,668,550	23,689,280	14,709,179	-5,325,188	
2025	6	0	0	0	-5,205,053	-847,868	35,292,066	-6,683,631	-5,638,879	23,600,266	13,321,735	7,996,547	
2026	7	0	0	0	-5,309,154	-864,826	35,292,066	-6,683,631	-5,608,614	23,509,472	12,064,077	20,060,624	
2027	8	0	0	0	-5,415,337	-882,122	35,292,066	-6,683,631	-5,577,744	23,416,863	10,924,139	30,984,763	
2028	9	0	0	0	-5,523,644	-899,765	35,292,066	-6,683,631	-5,546,257	23,322,401	9,890,975	40,875,738	
2029	10	0	0	0	-5,634,117	-917,760	35,292,066	-6,683,631	-5,514,140	23,226,050	8,954,648	49,830,385	
2030	11	0	0	0	-5,746,799	-936,115	35,292,066	-6,683,631	-5,481,380	23,127,771	8,106,143	57,936,528	
2031	12	0	0	0	-5,861,735	-954,837	35,292,066	-6,683,631	-5,447,966	23,027,528	7,337,280	65,273,808	
2032	13	0	0	0	-5,978,970	-973,934	35,292,066	0	-7,084,791	21,254,372	6,156,634	71,430,442	
2033	14	0	0	0	-6,098,549	-993,413	35,292,066	0	-7,050,026	21,150,078	5,569,477	76,999,919	
2034	15	0	0	0	-6,220,520	-1,013,281	35,292,066	0	-7,014,566	21,043,699	5,037,694	82,037,613	
2035	16	0	0	0	-6,344,931	-1,033,547	35,292,066	0	-6,978,397	20,935,192	4,556,108	86,593,721	
2036	17	0	0	0	-6,471,829	-1,054,218	35,292,066	0	-6,941,505	20,824,514	4,120,019	90,713,740	
2037	18	0	0	0	-6,601,266	-1,075,302	35,292,066	0	-6,903,875	20,711,624	3,725,168	94,438,907	
2038	19	0	0	0	-6,733,291	-1,096,808	35,292,066	0	-6,865,492	20,596,475	3,367,688	97,806,596	
2039	20	0	0	0	-6,867,957	-1,118,744	35,292,066	0	-6,826,341	20,479,024	3,044,076	100,850,672	
2040	21	0	0	0	-7,005,316	-1,141,119	35,292,066	0	-6,786,408	20,359,223	2,751,153	103,601,825	
2041	22	0	0	0	-7,145,422	-1,163,942	35,292,066	0	-6,745,676	20,237,027	2,486,037	106,087,863	
2042	23	0	0	0	-7,288,331	-1,187,220	35,292,066	0	-6,704,129	20,112,386	2,246,114	108,333,977	
2043	24	0	0	0	-7,434,097	-1,210,965	35,292,066	0	-6,661,751	19,985,253	2,029,015	110,362,992	
2044	25	0	0	0	-7,582,779	-1,235,184	35,292,066	0	-6,618,526	19,855,577	1,832,590	112,195,582	
2045	26	0	0	0	-7,734,435	-1,259,888	35,292,066	0	-6,574,436	19,723,307	1,654,893	113,850,475	
2046	27	0	0	-6,578,665	-7,889,124	-1,285,086	35,292,066	0	-6,529,464	13,009,727	992,352	114,842,827	

Table S9: Capital cost estimation for conventional renewable electricity generation using the Hand method.

Plant section	Major ISBL Equipment item	Quantity	Purchase cost [\$]	ISBL Installed Cost Hand factor	Installed cost (2006) [\$]	CE cost Index adjustment to 2019 [\$]	Location Factor	Total Installed Cost [\$]	Total Plant section [\$]
Electricity Generation	Steam Turbine	3	2,791,955	2.50	6,979,888	7,478,452	0.51	3,807,056	3,807,056

Table S10: Fixed operating cost estimation for conventional renewable electricity generation using the TS method.

FIXED OPERATING COST			
Fixed Operational Consideration	Assessment Basis	Unit (Basis)	Annual cost [\$/annum]
Operating Labour	Wage & Salary Cost for shift team members (excl. supervision)	[13,373 [\$/operator], 4 shift teams with 3 operators each]	13,373
Supervisory Labour	25	[% of Operating labour]	3,343
Direct Salary Overhead	50	[% of Operating + Supervisory]	8,358
Maintenance	3	[% of ISBL]	114,212
Property taxes & insurance	1	[% of ISBL]	38,071
Rent of land/buildings	1	[% of FCI]	47,588
General plant overhead	65	[% of total labour + maintenance]	85,103
Allocated environmental charges	1	[% of FCI]	47,588
Interest charges (capital)	0	[% of total capital investment]	0
TOTAL FIXED OPERATING COST			357,636

Table S11: Investment Analysis for conventional renewable electricity generation using the Hand method for capital estimation and the TS method for fixed operating cost estimation.

Year	Project Life	Detailed design	Fixed Capital	Working Capital	Fixed OPEX	Variable OPEX	Plant Income	Depreciation	Corporation Tax	Total Cash Flow	NPV	Cumulative NPV	Comments
		[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	[\$]	
2019	0	-25,000	0	0	0	0	0	0	0	-25,000	-25,000	-25,000	
2020	1	0	-3,397,797	0	0	0	0	0	0	-3,397,797	-3,088,907	-3,113,907	Plant construction & commissioning.
2021	2	0	-1,732,877	0	0	0	0	0	0	-1,732,877	-1,432,129	-4,546,036	
2022	3	0	0	505,010	-379,526	-864,501	14,972,100	-513,067	-3,303,751	10,929,331	8,211,368	3,665,332	
2023	4	0	0	0	-387,117	-881,791	14,972,100	-513,067	-3,297,531	10,405,661	7,107,206	10,772,538	
2024	5	0	0	0	-394,859	-899,427	14,972,100	-513,067	-3,291,187	10,386,627	6,449,278	17,221,817	
2025	6	0	0	0	-402,756	-917,415	14,972,100	-513,067	-3,284,715	10,367,213	5,852,021	23,073,838	
2026	7	0	0	0	-410,812	-935,763	14,972,100	-513,067	-3,278,114	10,347,410	5,309,858	28,383,696	
2027	8	0	0	0	-419,028	-954,479	14,972,100	-513,067	-3,271,381	10,327,212	4,817,720	33,201,416	
2028	9	0	0	0	-427,408	-973,568	14,972,100	-513,067	-3,264,514	10,306,609	4,371,008	37,572,425	
2029	10	0	0	0	-435,956	-993,040	14,972,100	-513,067	-3,257,509	10,285,594	3,965,542	41,537,967	
2030	11	0	0	0	-444,676	-1,012,900	14,972,100	-513,067	-3,250,364	10,264,160	3,597,525	45,135,492	
2031	12	0	0	0	-453,569	-1,033,158	14,972,100	-513,067	-3,243,076	10,242,296	3,263,511	48,399,003	
2032	13	0	0	0	-462,640	-1,053,822	14,972,100	0	-3,363,909	10,091,728	2,923,214	51,322,217	
2033	14	0	0	0	-471,893	-1,074,898	14,972,100	0	-3,356,327	10,068,981	2,651,477	53,973,695	
2034	15	0	0	0	-481,331	-1,096,396	14,972,100	0	-3,348,593	10,045,779	2,404,880	56,378,574	
2035	16	0	0	0	-490,958	-1,118,324	14,972,100	0	-3,340,704	10,022,113	2,181,104	58,559,678	
2036	17	0	0	0	-500,777	-1,140,690	14,972,100	0	-3,332,658	9,997,974	1,978,046	60,537,724	
2037	18	0	0	0	-510,792	-1,163,504	14,972,100	0	-3,324,451	9,973,352	1,793,795	62,331,519	
2038	19	0	0	0	-521,008	-1,186,774	14,972,100	0	-3,316,079	9,948,238	1,626,616	63,958,135	
2039	20	0	0	0	-531,428	-1,210,510	14,972,100	0	-3,307,540	9,922,621	1,474,934	65,433,070	
2040	21	0	0	0	-542,057	-1,234,720	14,972,100	0	-3,298,831	9,896,492	1,337,319	66,770,388	
2041	22	0	0	0	-552,898	-1,259,414	14,972,100	0	-3,289,947	9,869,840	1,212,470	67,982,859	
2042	23	0	0	0	-563,956	-1,284,603	14,972,100	0	-3,280,885	9,842,656	1,099,210	69,082,068	
2043	24	0	0	0	-575,235	-1,310,295	14,972,100	0	-3,271,642	9,814,927	996,466	70,078,535	
2044	25	0	0	0	-586,740	-1,336,501	14,972,100	0	-3,262,215	9,786,644	903,268	70,981,803	
2045	26	0	0	0	-598,475	-1,363,231	14,972,100	0	-3,252,599	9,757,796	818,732	71,800,535	
2046	27	0	0	-505,010	-610,444	-1,390,495	14,972,100	0	-3,242,790	9,223,360	703,537	72,504,072	

Table S12: Calculation of greenhouse gas emissions on Cradle-to-Gate basis for LanzaTech's anaerobic gas fermentation technology, producing acetone and ethanol.

Parameter	Value	Unit	Comment
Lower Heating Value for ethanol	26.70	[MJ]/(kg ethanol)]	Lower Heating Value (LHV).
Reported ethanol greenhouse gas (GHG) emissions	8.10	[(g CO ₂ eq)/(MJ ethanol)]	Cradle-to-Grave emissions.
Cradle-to-Grave ethanol GHG emissions	0.22	[(kg CO ₂ eq)/(kg ethanol)]	
Cradle-to-Gate ethanol GHG emissions	-1.69	[(kg CO ₂ eq)/(kg ethanol)]	Stoichiometry of ethanol combustion in excess O ₂ , forming two moles of CO ₂ .
Reported acetone GHG emissions	-2.07	[(kg CO ₂ eq)/(kg acetone)]	Case A.
Cradle-to-Gate GHG emissions for reported solvent mix.	-1.91	[(kg CO ₂ eq)/(kg solvent)]	Reported solvent mix, i.e. 57.3 [%] acetone with balance ethanol on a mass basis.

Table S13: Typical calculation for calculation of required oxygen mass transfer coefficient (k_{LA}) based on Aspen HYSYS mass and energy balance.

Parameter	Value	Unit	Comments
Bioreactor Outlet O ₂ concentration, $C_{g,off-gas}$	3.35	[%] (mol/mol)	
Design O ₂ uptake rate, OUR	230	[(mmol O ₂)/(L·h)]	
Bioreactor headspace back-pressure, P_b	4	[bar] (a)	
Loop reactor downcomer hydrostatic pressure, P_h	2.02	[bar]	Assumes a working volume of 80 [%] (v/v) and a gas hold-up of 25 [%] (v/v).
Inlet O ₂ concentration, $C_{g,air}$	21	[%] (mol/mol)	
Inlet O ₂ saturation in aqueous phase, $C_{L,air}$	1.00	[(mmol O ₂)/L]	Estimated using the Lee Kesler Plocker equation of state.
Outlet O ₂ concentration, $C_{g,off-gas}$	3.35	[%] (mol/mol)	
Outlet O ₂ saturation in aqueous phase, $C_{L,off-gas}$	0.26	[(mmol O ₂)/L]	Estimated using the Lee Kesler Plocker equation of state.
Broth dissolved O ₂ concentration, DO	0	[(mmol O ₂)/L]	Micro-aerobic conditions.
Log mean concentration difference, $LMCD$	0.552	[(mmol O ₂)/L]	$\frac{(C_{L,air} - DO) - (C_{L,off-gas} - DO)}{\ln \frac{(C_{L,air} - DO)}{(C_{L,off-gas} - DO)}}$
Required O ₂ mass transfer coefficient, k_{LA}	415	[1/h]	$\frac{OUR}{LMCD}$
Total ungasged broth volume, V	298	[m ³]	
Air Volumetric Flow Rate, Q	2927	[m ³ /h]	Actual temperature and pressure.
Air superficial gas velocity, u_g	0.075	[m/s]	
Power input to achieve required, k_{LA} (1)	450	[kW]	$\left(\frac{V}{1000}\right) \left(\frac{k_{LA}}{103 \cdot u_g^{0.824}}\right)^{\frac{1}{0.482}}$

References

1. L. A. H. Petersen, J. Villadsen, S. B. Jørgensen and K. V. Gernaey, *Biotechnol. Bioeng.*, 2017, **114**, (2), 344 LINK <https://doi.org/10.1002/bit.26084>