Renewable butadiene: A case for hybrid processing via bio- and chemo-catalysis

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Abstract

1,3-butadiene (butadiene) is a by-product produced during naphtha steam cracking, predominantly used in tyre manufacturing. Recently, steam crackers have converted to using more cost effective, lighter feedstocks such as shale gas, yielding less butadiene. The potential shortfall, coupled with concerns around increasing greenhouse gas emissions, provides a unique opportunity for renewable production. This study investigated the techno-economics and greenhouse gas emissions associated with renewable butadiene production routes within the context of a China located pulp mill. A hybrid bio-catalytic route, utilising black liquor, was compared against two chemo-catalytic routes using forestry residues and pulpwood. The hybrid bio-catalytic route uses a novel aerobic gas fermentation platform, employing heat integrated supercritical water gasification and aerobic gas fermentation to produce acetaldehyde, followed by chemo-catalytic upgrading (Acet-BD). The two chemo-catalytic routes catalytically upgrade biomass derived syngas; where one route (Eth-BD) passes through an ethanol intermediate, and the other (Syn-BD) utilises a series of commercialised catalytic technologies with propene as an intermediate. The hybrid bio/chemo-catalytic route, Acet-BD, was the only route profitable using the nominal techno-economic inputs, producing a Net Present Value of $2.8 million and Minimum Selling Price of $1,367 tn^{-1}. In contrast, the two chemo-catalytic routes produced Minimum Selling Prices of $1,954 tn^{-1} (Eth-BD) and $2,196 tn^{-1} (Syn-BD), demonstrating the competitiveness of this novel platform. Sensitivity analyses highlighted the equipment capital as the main contributor to increased Minimum Selling Price for all cases, and the Acet-BD route presented a 19% probability of achieving a positive net present value. Moreover, owed to the low process emissions and sequestration of biogenic carbon, all routes produced net negative emissions within a cradle-to-gate framework. As such, renewable butadiene production has potential as a net carbon sink for pulp mill residues conventionally destined for energy recovery.

Key words:
1,3-Butadiene, Techno-economic analysis, Life cycle assessment, Renewable chemicals, Biorefinery

Abbreviations:

FCI	Fixed Capital Investment
GHG	Greenhouse Gas
ISBL	Inside Battery Limits
LCA	Life Cycle Assessment
MSP	Minimum Selling Price
MTO	Methanol to Olefins

MTP	Methanol to Propene
NPV	Net Present Value
OSBL	Outside Battery Limits
RBFNN	Radial Basis Function Neural Network
SCWG	Supercritical Water Gasification
TCI	Total Capital Investment
TEA	Techno-economic Analysis

1 Introduction

Currently, the chemical industry is responsible for 7% of anthropogenic greenhouse gas (GHG) emissions and 30% of final industrial energy use (IEA, 2018). However, the carbon content of most chemicals inherently ties the industry to the use of carbon-based feedstocks, making decarbonisation challenging. One approach to reduce emissions is through the replacement of conventional fossil fuel feedstocks with renewable carbon sources. Such resources enable biogenic carbon to be utilised for chemical synthesis, with the potential of achieving negative GHG emissions. Despite the environmental benefit, these sustainable technologies need to be cost competitive with conventional fossil fuel-based processes. Successful implementation of sustainable technologies depends on the identification of opportunistic chemicals based on market trends and technological developments.

Butadiene is an important platform chemical used in synthetic rubber manufacturing, with a global production of 1.5 million tonnes in 2013 (Levi and Cullen, 2018). Currently, 95% of butadiene is produced as a by-product from steam cracking of naphtha to produce ethene (Ren et al., 2006). However, in North America recent technological advances have made shale gas an economically favourable feedstock (Angelici et al., 2013). Consequently, steam crackers have converted operations to cracking this lighter feedstock, yielding less butadiene. Simultaneously, the Methanol To Olefin (MTO) technology is being commercialised in China, which synthesises ethene and propene from coal derived methanol, yielding no butadiene (Tian et al., 2015). These synchronous transitions are projected to reduce global butadiene production (Pomalaza et al., 2020). As such, an on-purpose, selective production method would allow for stable market supply and demand.

In addition to chemical selection, the development of a renewable chemical industry requires renewable resources to be readily available in large quantities. Paper and pulp mills represent an established biomass supply chain. In recent years, interest has grown in developing these facilities into bio-refineries. This increased interest is attributed to decreasing trends in pulp and paper prices and increased competition from low cost paper and pulp suppliers, coupled to the incentives surrounding renewable energy prices and renewable chemical production (Berntsson et al., 2008). Development of existing mills expands the product range of a pulp mill and promotes the full utilisation of woody biomass, making use of residues that are unsuitable for pulp production (Huang et al., 2010). With the existing supply chain infrastructure for biomass delivery, the development of pulp mill bio-refineries can occur using either internal or external (imported) biomass. China is the world’s second largest virgin pulp manufacturer (Food and Agricultural Organization of the United Nations (FAO), 2021; Kong et al., 2013), as well as holding the greatest share of the butadiene market (Mordor Intelligence, 2020). Therefore, China’s pulp mills hold a distinct market opportunity for renewable, on-purpose butadiene production.

There has been increased global interest in renewable butadiene production in recent years. The most notable being production from ethanol. A recent, in depth, review of insights into the reaction pathway and the varying catalysts that have been considered for the reaction can be found in (Pomalaza et al., 2020). There are two different routes from ethanol, the one-step (Lebedev) (Lebedev, 1933) or two-step (Ostromisslensky) process (Toussaint et al., 1947). Both routes were used during

WWII until the 1960s when the processes became economically uncompetitive with naphtha steam cracking (Shylesh et al., 2016). It is important to highlight a major challenge in producing butadiene from ethanol is the intrinsic mass loss owed to the removal of water and hydrogen molecules. This was emphasised in a recent review by Grim et al. (2019) where they demonstrate the theoretical mass yield of butadiene from ethanol is only 60% in comparison to 80% when producing butanol. This unavoidable mass loss significantly reduces the profit margin between ethanol and butadiene.

The primary focus of recent research into this route has been in catalyst development, but more recently, there have been several Techno-economic Analysis (TEA) and Life Cycle Assessment (LCA) studies. Despite this, no existing TEAs have investigated China as a potential location. Notably, in the first LCA of an ethanol route, undertaken by Cespi et al. (2016), the location was dismissed owed to the high ethanol prices. The first LCA was undertaken by Cespi et al. (2016), comparing results of the two production methods for three different locations, the US, Brazil and Europe. Shylesh et al. (2016) later conducted a cradle-to-grave LCA on the one step method using USA Midwest-grown corn grain, USA Midwest- grown corn stover, and Brazilian sugarcane. Farzad et al. (2017) undertook the first TEA, they performed an integrated TEA and LCA on the Two Step process using bagasse derived ethanol. In 2018, the first TEA to evaluate the One Step production method was undertaken by Moncada et al. (2018), who looked at the production of butadiene and ε-caprolactam from C6 sugars. Very recently, the techno economics of the One Step production of butadiene using experimental data under industrial conditions was undertaken (Cabrera Camacho et al., 2020). Finally, the most recent integrated TEA and LCA was undertaken by Dimian et al. (2021). The study evaluated the Two Step process using market ethanol as the feedstock for an undisclosed plant location. Notably, the LCA outcomes have proven to be highly dependent on the feedstock, with some first generation crops yielding poorer outcomes than conventional naphtha cracking (Cespi et al., 2016), highlighting the benefit of integrated studies. Despite the potential of on-purpose routes, and level of interest, no existing studies have demonstrated butadiene's cost-effective production at current market prices. It is thought that the exploitation of China's large pulp industry, substantial share in butadiene market, and lower capital and operating costs may provide a lucrative opportunity to renewable butadiene production.

Butadiene can also be produced through the catalytic dehydrogenation of butane or the oxidative dehydrogenation of butene, both of which are mature industrial technologies (Grub and Löser, 2011). However, these technologies rely on a petroleum derived C4 feedstock. Resultantly, some authors have looked at the renewable production of butene for butadiene production. Hanaoka et al. (2017, 2019, 2021) and Tripathi et al. (2019) evaluated the production of butadiene from lignin via an olefin intermediate. They evaluated three different olefin technologies; the direct production of light olefins, dimethyl ether to light olefins, and methanol to light olefins, all originating from gasification (Hanaoka et al., 2021, 2019, 2017; Tripathi et al., 2019). At present, these olefin technologies are optimised for the production of ethene and propene, meaning butene yields are typically low (Bender, 2014). As a result, these studies have all demonstrated comparatively low butadiene yields.

In this study, three renewable butadiene production routes are compared using renewable resources available within the context of a Kraft paper and pulp mill located in China. The aim of this study is to determine the most promising process through matching an opportune renewable feedstock within the mill's supply chain to a synergetic technology. The study innovatively integrates methods of rigorous process simulation, techno-economic analysis, life cycle assessment, sensitivity, and uncertainty analysis to comprehensively compare impacts of three alternative routes on resources, society and the environment, each exploiting renewable syngas produced via gasification. The principal benefit of gasification is the ability to maximise the recovery of reducing power from the biogenic biomass as syngas for chemical synthesis (Griffin and Schultz, 2012). Furthermore, gasification enables the valorisation of recalcitrant, low value carbon sources. However, to date, the only studies to consider syngas as a feedstock employed chemo-catalytic olefin-based technologies for butadiene production. A hybrid bio/chemo-catalysis route; Acetaldehyde to Butadiene (Acet-BD), is compared against two alternative chemo-catalytic technologies Ethanol to Butadiene (Eth-BD) and Syngas to Butadiene (Syn-BD). The Acet-BD and Eth-BD routes both explore ethanol production methods hitherto investigated for butadiene production, namely heat integrated aerobic gas fermentation (Rodgers et al., 2021), and mixed alcohol synthesis (Dutta et al., 2011). Similarly, the Syn-BD route employs an alternative olefin technology, exploiting the high yield propene fraction obtained from the established Methanol-to-Propene (MTP) technology, as opposed to the low yield butene obtained from the Methanol-to-Olefins (MTO) process. The Syn-BD route therefore represents commercialised technologies that could be integrated to produce renewable butadiene. Overall, our study considers new processing routes with the feedstocks, technologies, and bio-refinery scenario differing from previous studies.

2 Materials and Methods

This study explores three processing routes to butadiene from the renewable resources available within a Kraft paper and pulp mill. The three routes principally exploit aerobic gas fermentation (Acet-BD), mixed alcohol synthesis (Eth-BD) and the Methanol-to-Propene technology (Syn-BD). The hybrid bio-/chemo-catalytic route, Acet-BD, investigates the exploitation of a portion of the pulp mill's black liquor co-product; whilst the two chemo-catalytic routes, Eth-BD and Syn-BD, utilise imported biomass consisting of 80% forestry residues and 20% pulpwood, to limit ash content (Hartley et al., 2020). A block flow diagram of the three conceptual processes is presented in Figure 1. These three routes are rigorously modelled in Aspen HYSYS V11 using the best publicly available data and industrial insights. The conceptual processes are described in detail in the Supplementary Information: Section S1, Detailed Conceptual Process Design. The process models inform the TEA and LCA used to evaluate the economic performance and environmental impact of each route. Single point sensitivity analyses and a Monte Carlo simulation are also undertaken.

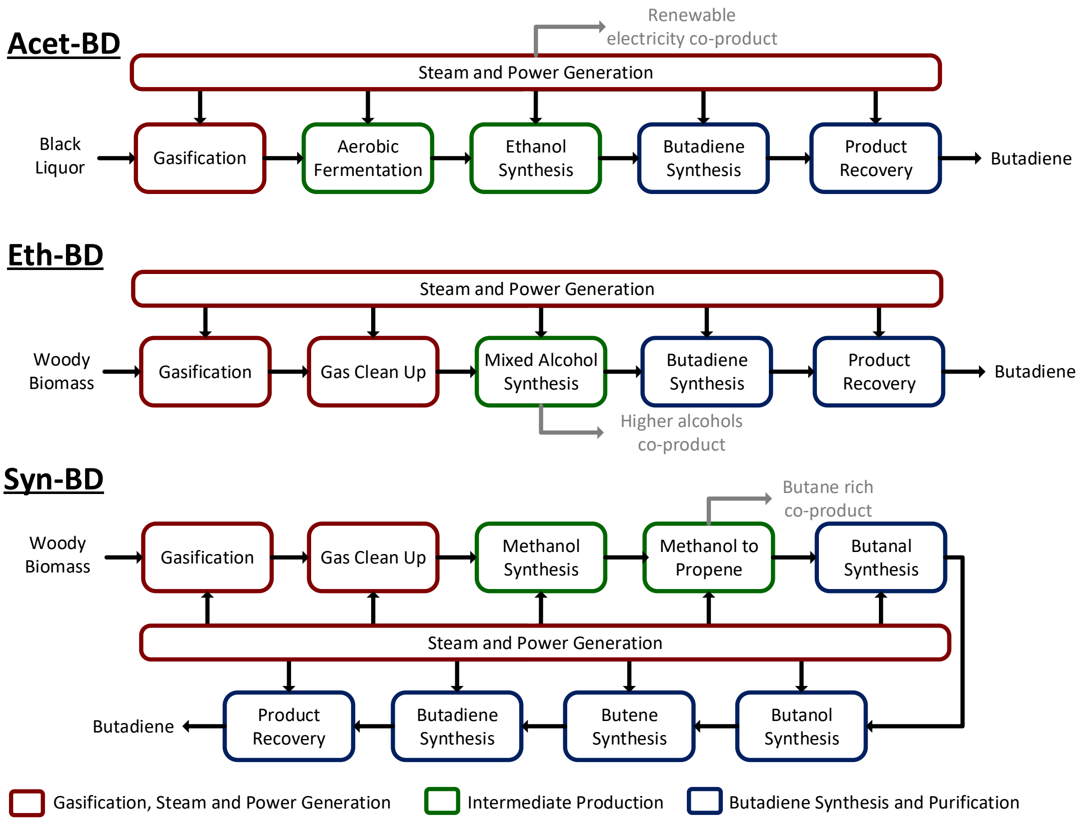


Figure 1: Conceptual Block Flow Diagram of the three green butadiene production routes using renewable resources from a paper and pulp mill as feedstock. The hybrid gas fermentation route through an Acetaldehyde intermediate (Acet-BD) is compared against two chemo-catalysis technologies, Ethanol to Butadiene (Eth-BD) and Syngas to Butadiene (Syn-BD).

The Acet-BD process utilises gasified black liquor as feedstock, followed by gas fermentation to the 2-oxoacid pyruvate, which is decarboxylated to acetaldehyde in a subsequent enzyme plug flow reactor. Acetaldehyde was chosen as the platform intermediate given its high volatility (Eckert et al., 2006), allowing for its low energy intensity recovery from the aqueous media compared to ethanol. The black liquor feedstock is gasified using supercritical water gasification (SCWG), which is heat integrated with the aerobic gas fermentation process using a heat pump, as described by Bommareddy et al. (2020). The novel coupling of technologies provides a synergistic solution which benefits both the endothermic SCWG and exothermic aerobic gas fermentation process, further detail on this technology pairing can be found in Section S1.1, Acet-BD Process Description. This unique pairing also produces renewable electricity for sale to the grid, supplementing the routes income. The acetaldehyde intermediate is hydrogenated to ethanol prior to catalytic upgrading to butadiene. As previously mentioned, two processes exist for butadiene production from ethanol, the one-step Lebedev and the two-step Ostromisslensky process. Currently, there is no consensus which process holds sway. However, it has been previously reported that the Ostromisslensky process has a higher conversion and yield (Corson et al., 1950), where the Lebedev process has been shown to outperform the Ostromisslensky process from an economic and environmental perspective, as only one reactor and catalyst is required (Cespi et al., 2016). In this study, the Lebedev process was investigated due to the presumed economic benefit and the high productivity reported in an experimental study by Dai et al. (2017) using a zeolite-confined bimetallic catalyst.

In the Eth-BD route ethanol is produced via mixed alcohol synthesis of biomass derived syngas, as per the 2011 NREL report (Dutta et al., 2011). The ethanol product is catalytically upgraded to butadiene using the same catalyst as detailed for the Acet-BD route. A detailed description of the process and data used to model the route is outlined in Section S1.2, Eth-BD Process Description.

The Syn-BD route exploits the Methanol-to-Propene process and uses the commercial oxidative dehydrogenation of n-butene to produce butadiene (White, 2007). Though, rather than using a fossil-derived C4 feedstock, this is synthesised from indirect gasification of woody biomass. The produced syngas is upgraded using various industrialised catalytic steps, i.e. (1) syngas to methanol, (2) methanol to propene, (3) propene to butanol via the oxo-alcohols process, (4) dehydration of butanol to butene and (5) oxidative dehydrogenation to butadiene. The MTP process was selected over the MTO process given its enhanced propene selectivity, >70% (Rothaemel and Holtmann, 2002). A detailed description of the process and data used to model the route is outlined in Section S1.3, Syn-BD Process Description.

2.1 Plant Capacity

The reference pulp mill's capacity, used as the basis for this study, is detailed in Table 1. The Acet-BD route exploits the use of 25% of the mill's black liquor for chemical production (Rodgers et al., 2021). In contrast, the Eth-BD and Syn-BD routes utilise the forestry residues available within the pulp mills collection area, along with a modest collection increase required for the pulpwood fraction. The exploitation of the mill's black liquor co-product or forestry residues within the mills collection area allows mills to generate additional revenue from biochemical production without expanding collection capacity. The capacity of the routes is outlined in Table 1.

Table 1: Reference pulp mill capacity and capacity of proposed routes.

Parameter	Value	Unit	Comment	Reference
Pulp mill capacity	130	Air dried tn.h^{-1}	Capacity of a large pulp and paper mill in China	(Cossalter, 2006)
Black Liquor Feedstock				
Total weak black liquor production	1,300	tn.h^{-1}	10 times pulp production	(Naqvi et al., 2010)
Black liquor solids content	17.5	% (w/w)		
Lignin content in black liquor	7.3	% (w/w)	41.5% lignin content in solids modelled as guaiacol	(Cardoso et al., 2009)
Woody Biomass Feedstock				
Pulpwood removal rate	12	m3.ha^{-1}yr^{-1}	80% of productivity	(Barr and Cossalter, 2004)
Pulp mill collection area	377,650	ha	Based on 4.15 m^{3}. (Air dried tn^{-1})	
Pulpwood mass loss during debark and delimb	10	%		(Jacobson et al., 2014)
Additional collection area required for chemical production	10,154	ha		
Forestry residue removal rate	1.89	m3.ha^{-1}yr^{-1}	0.157 of pulpwood removal rate	(Cossalter and Barr, 2005)
Residue mass loss during clean-up	40	%		(Jacobson et al., 2014)
Total wood chip production	336,388	tn.yr^{-1}	1.63 m3.dry tn^{-1} of chips	(Cossalter and Barr, 2005)

2.2 Feedstock Costs

Black liquor is a by-product from pulp production, conventionally exploited for its energy value (Naqvi et al., 2010; Suhr et al., 2015). New heat integration opportunities have highlighted the potential to reduce mill energy consumption (Ahmetovi and Grossmann, 2020; Keshtkar et al., 2015), freeing up some of this by-product for alternate uses. As black liquor currently has no market value, it is costed at its utility value. As per our previous work, Rodgers et al. (2021), this was calculated as the foregone Net Present Value (NPV) associated with its conventional use for renewable electricity generation. For conventional electricity generation, the weak black liquor with solids concentration 17.5% w/w is used. This is concentrated to 75% w/w in multi-effect evaporators prior to being combusted in the Tomlinson boiler to generate steam. This steam is then used to generate renewable electricity for sale to the grid. The NPV associated with this conventional renewable electricity generation translates to a cost of \$4.19 tn^{-1} of black liquor.

Pulpwood costs were estimated using data from the report prepared for the Guangxi Forestry Bureau on the development of industrial wood demand in the district (Cossalter and Barr, 2005). The mill gate prices presented for labour intensive hill areas were used, as these represent the majority of southern China plantations (Cossalter and Barr, 2006). The average of the three competitive production profiles and locations was taken and updated to a 2020 basis using the Lumber and Wood Products Producer Price Index (U.S. Bureau of Labor Statistics, 2021a) resulting in a cost estimate of \$102.62 tn^{-1}, similar to US pulpwood chip costs, \$109.64 tn^{-1}, as analysed by Idaho National Laboratory (Jacobson et al., 2014). All costs are reported on a dry basis. Whilst there is limited data availability for forestry residue costs in China, detailed cost estimates have been undertaken by the Idaho National Laboratory for delivered forestry residues in the US. Owed to the closeness of the China and US values for pulpwood chips the ratio between these estimates was used to approximate the cost of forestry residues in China, resulting in a cost of \$69.67 tn^{-1}. This price is in line with the range reported by Anttila et al. (2015), who undertook a study on availability of forestry residues for energy production in northern China, and to the prices reported in Gosens (2015) database for Chinese biomass power projects. Anttila et al. (2015) estimated costs of €30-42 tn^{-1} (wet basis), translating to \$51-72 tn^{-1}, whilst the average for facilities using wood residues as part of their feedstock in the Gosens (2015) database was RMB 297 tn^{-1} (wet basis), equivalent to \$65.09 tn^{-1}. Both prices were updated to a dry 2020 basis and assumed a 30% moisture content for delivered chips. Accordingly, using a blend of 20% pulpwood and 80% forestry residues the delivered biomass cost is \$76.26 tn^{-1}.

2.3 Costing Models

Each of the three butadiene process simulations comprise a rigorous mass and energy balance and associated equipment sizing, used to calculate the capital and operating costs. Free on board equipment costs were calculated from cost correlations in Seider et al. (2017) and updated to 2020 prices using the Chemical Engineering Plant Cost Index of 596.2 (Jenkins, 2021).

The Fixed Capital Investment (FCI) was calculated using the Hand method, outlined in Sustainable Design Through Process Integration (El-Halwagi, 2017), where commissioning costs and working capital were calculated as per Table 2.

Table 2: Fixed Capital Cost Model

Economic Parameters	
Free on board equipment purchase cost	Seider et al. (2017)
Installed capital cost	Hand method
Chemical Engineering Plant Cost Index in 2020	596.2 (Jenkins, 2021)
Production Year	8,400[a] or 8,110[b] hours
Installed Cost – Inside Battery Limit (ISBL) Factor	Tables S4-S6
Outside Battery Limit (OSBL)	25% of ISBL
Commissioning Cost	5% of ISBL
Fixed Capital Investment (FCI)	ISBL + OSBL + Commissioning
Working Capital	10% of ISBL + OSBL
Total Capital Investment (TCI)	FCI + Working Capital

[a] Used for Eth-BD and Syn-BD route. [b] Used for Acet-BD route. Based on bioreactor cycle time.

The fixed operating costs were calculated using the methodology proposed by Sinnott & Towler (2009) and Ulrich & Vasudevan (2004) and are outlined in Table 3. The number of plant operators is based on both the methods proposed by Wessel (1952) accounting for the number of processing steps, production capacity, and process complexity, and by Ulrich & Vasudevan (2004) accounting for process equipment. The Acet-BD and Eth-BD routes both have 4 operators. Owing to the greater number of unit operations in the Syn-BD process, 5 operators are required.

Table 3: Fixed Operating Cost Model

Parameters	**Acet-BD**	**Eth-BD**	**Syn-BD**
Operating Labour	Salary estimates in China obtained from salaryexpert.com ($13,373 per year) employing 4 shift teams		
	4 Operators per shift	4 Operators per shift	5 Operators per shift
Supervisory Labour	25% of Operating Labour		
Direct Salary Overhead	50% of Operating and Supervisory Labour		
Maintenance	3% of ISBL		
Property Taxes and Insurance	1% of ISBL		
Rent of Land	1% of FCI		
General Plant Overhead	65% of Total Labour and Maintenance		
Allocated Environmental Charges	1% of FCI		

Variable operating costs were estimated using the respective mass and energy balance and the raw material costs detailed in Table S2. The costs for utilities were taken from Seider et al. (2017). Specialist chemical costs are taken as spot prices and catalyst costs were taken from data available in existing TEA studies or, in the absence of cost data, based on the material composition. Chemical and catalyst costs were updated from their base year using the Chemicals and Allied Products Producer Price Index (U.S. Bureau of Labor Statistics, 2021b). Variable operating costs were subjected to an annual inflation of 2% throughout the life of the project.

2.4 Product Prices

Time series analysis was used to obtain a long-term average price prediction for butadiene based on Takens Theorem (Takens, 1981). An embedding dimension of ten was used to represent approximations for the underlying state variable trajectory, and a Radial Basis Function Neural Network (RBFNN) containing eight neurons was employed to reconstruct an unbiased, one step ahead predictor of the future butadiene price. The historic pricing data for the embedding were obtained from the Intratec database (Intratec, 2020). The confidence limits for the nonlinear RBFNN model were calculated to validate the free-run model prediction (Leonard et al., 1992). Given this predicted long-term price average, the butadiene price lies within an uncertainty framework spanning the project life of 25 years and is therefore subject to sensitivity analysis.

In addition to butadiene, each route produces a co-product, namely; renewable electricity, higher alcohols and a butane rich co-product for the Acet-BD, Eth-BD and Syn-BD routes respectively. The prices used for these products are detailed in Table S3. For the Acet-BD route, China's renewable electricity price for biomass, 0.109 $\$.kWh^{-1}$ (Ming et al., 2013), was used to value black liquor and the additional electricity sales. For the Eth-BD route, the higher alcohols co-product produced during mixed alcohol synthesis was valued at 90% of its energy value relative to gasoline, using the Energy Information Administration's prediction for wholesale gasoline (EIA, 2021a) as per Dutta et al. (2011). For the Syn-BD route, the butane rich co-product was valued based on its energy content relative to butane. The long-term average price for butane was forecast using the RBFNN methodology, as outlined for butadiene, with historic pricing data taken from EIA (2021b).

2.5 Investment Analysis

The aforementioned cost models informed the investment analysis. The NPV and Minimum Selling Price (MSP) was calculated for each project. The investment analysis parameters are detailed in Table 4.

Table 4: Investment Analysis Parameters

Parameters	Value	Comments
Corporation Tax	25%	Corporation tax in China
Annual Inflation	2%	Long-term average product prices forecast as above. All other costs are subject to annual inflation.
Plant Life (Operational)	25 years	
Discounted rate of return	10%	
Depreciation	10 year	Straight line
Plant Salvage Value	No value	
Construction Period	2 years	

2.6 Sensitivity and Uncertainty Analysis

A sensitivity analysis was conducted using a tornado chart to determine the relative importance of different variables. A Monte Carlo simulation was utilised to determine the probability of achieving a positive NPV. Both analyses were based on the parameters presented in Table 5. The Monte Carlo simulation was run 2,000 times, generating a parameter set for each scenario stochastically using a uniform distribution within the defined lower and upper limits for the parameters.

The lower and upper limit distributions were taken from Sinnott & Towler (2009), with the exception of the renewable electricity price. This was capped at the current biomass subsidy owed to the decreasing trend in renewable electricity subsidies (Reuters, 2019). The lower limit was set to 0.48, translating to an electricity price of 0.052 $\$.kWh^{-1}$. This allows for scenarios where grid parity is met, based on coal electricity prices for 2018 (Lee, 2019).

Table 5: Monte Carlo Simulation Parameters

Monte Carlo Input Parameter	Lower Limit	Upper Limit
Feedstock and Product Pricing		
Butadiene Price	0.8	1.2
Gasoline Price	0.8	1.2
Butane Price	0.8	1.2
Renewable Electricity Price	0.48	1
Woody Biomass Cost	0.7	1.3
Costing uncertainty Factor		
ISBL Capital Cost	0.8	1.5
OSBL Capital Cost	0.8	1.5
Labour Costs	0.8	1.5

2.7 Life Cycle Assessment

A cradle-to-gate LCA model was developed following ISO Standards 14040 (International Organization for Standardization, 2006a) and 14044 (International Organization for Standardization, 2006b). Greenhouse gas (GHG) emissions were calculated based on the most recent Integrated Pollution Prevention and Control 100-year Global Warming Potential factors, thereby quantifying GHG emissions in terms of CO_2 equivalents (CO_2eq) (IPCC Working Group I et al., 2014).

The functional units were defined as 1 kg for butadiene and 1 kg/kWh for the respective co-products. Life cycle environmental impacts were allocated between butadiene and the respective co-products using energy allocation. The co-products are; renewable electricity, higher alcohols, and a butane rich co-product for the Acet-BD, Eth-BD, and Syn-BD routes respectively.

The black liquor feedstock used in the hybrid Acet-BD route is a waste stream from pulp production, moreover it is utilised prior to the conventional multi-effect evaporator process, as such no emissions were assigned to it. Conversely, the two chemo-catalytic routes utilising forestry residues and pulpwood feedstocks have associated emissions. As a by-product from pulpwood harvest, forestry residues constitute 80% of the feedstock and the emissions associated with collection, chipping and loading were taken from McKechnie et al. (2011). The estimated emissions for pulpwood production, excluding land use change, were taken from Bernstad Saraiva et al. (2017) for the pulpwood fraction. For both the residues and pulpwood the transport emissions were updated to correspond to the latest ecoinvent data for EURO 6 freight lorries and a 131 km transport distance, based on the average distance of the Chinese production profiles used for the wood chip cost estimation (Cossalter and Barr, 2005).

The GHG emissions for the utilities used by each butadiene route were calculated using the ecoinvent 3.7 inventory database using the allocation at the point of substitution system model (Wernet et al., 2016). The GHG emissions for grid electricity were taken as the 2018 China electricity mix (Sun et al., 2019). The full life cycle inventory can be found in Table S9.

Renewable butadiene is credited with negative GHG emissions owed to its sequestered biogenic carbon. As the downstream use of butadiene is independent of the production method, the calculated GHG emissions relative to conventional production are valid beyond the employed cradle-to-gate framework.

3 Results and Discussion

The three routes, Acet-BD, utilising black liquor as a feedstock, and the Eth-BD, and Syn-BD routes, using forestry residues and pulpwood, each produce a co-product in addition to butadiene, detailed in Table 6. The energetic conversion efficiency (using lower heating value as the basis) for each route is also displayed. The energetic efficiency is lower for the Acet-BD route than the other two routes, attributed to the enthalpy lost in the supercritical water gasification effluent. The vast quantity of water in the gasification process and feedstock results in a loss in overall efficiency if any residual heat is left unexploited. Further heat integration opportunities could be found to improve the energy efficiency and increase the platforms renewable electricity generation. The carbon yield for butadiene is also lowest for the hybrid Acet-BD route, 6.3% compared to 19% for and 16% for the Eth-BD and Syn-BD routes, respectively. Whilst fermentation displays higher product selectivity with fewer by-products in comparison to catalytic transformation, conversion efficiencies for gas fermentation are typically lower given mass transfer limitations with limited opportunity to cost-effectively recycle feed gases.

The different production capacity between the Acet-BD and the Eth-BD and Syn-BD routes, presented in Table 6, is attributed to the availability of the feedstock as detailed in Section 2.1 Plant Capacity. The production capacity of the Syn-BD and Eth-BD routes are comparable, despite the greater number of catalytic steps involved in the Syn-BD route. This is attributable to the mass loss associated with the upgrading of ethanol and the greater efficiency of the commercial technologies utilised by the Syn-BD route.

Table 6: Production summary for the three butadiene production routes, Acet-BD, Eth-BD and Syn-BD routes.

Route		Conversion	Butadiene		Co-Product		
	Feedstock	Energy efficiency %	Production kt.yr^{-1}	Income contribution %	Co-product	Production	Income contribution %
Acet-BD	Black liquor	20	9.2	39	Renewable electricity	192 Gwh.yr^{-1}	61
Eth-BD	Forestry residues and pulpwood	31	36	88	Higher alcohols	12 kt.yr^{-1}	12
Syn-BD		30	31	92	Butane-rich product	11 kt.yr^{-1}	7.9

3.1 Total Capital Investment

The capital cost estimations for each route are detailed in Tables S4-S6. A breakdown of these costs for the three plant sections; Gasification, Steam and Power Generation, Intermediate Production and Butadiene Production and Recovery are presented in Figure 2. The intermediates for each route are; acetaldehyde, ethanol and propene for the Acet-BD, Eth-BD, and Syn-BD routes respectively. Owed to the heat pump used in the Acet-BD route the capital associated with steam and power generation is grouped with the gasification section for all three routes.

The normalised capital cost breakdown on the basis of tonnes of butadiene produced in Figure 2 highlights the greater capital intensity of the Acet-BD route. The major capital contribution is associated with the Gasification, Steam and Power Generation section, incorporating the SCWG reactor and heat pump cycle. This section contributes 51% of total capital, in contrast to the 35-40% contribution for the Eth-BD and Syn-BD routes, highlighting the capital expense required to heat integrate the bioreactor and SCWG reactor. Conversely, the difference in capital between the routes Intermediate Production and Butadiene Synthesis and Purification plant sections is attributable to the greater economies of scale for the Eth-BD and Syn-BD routes.

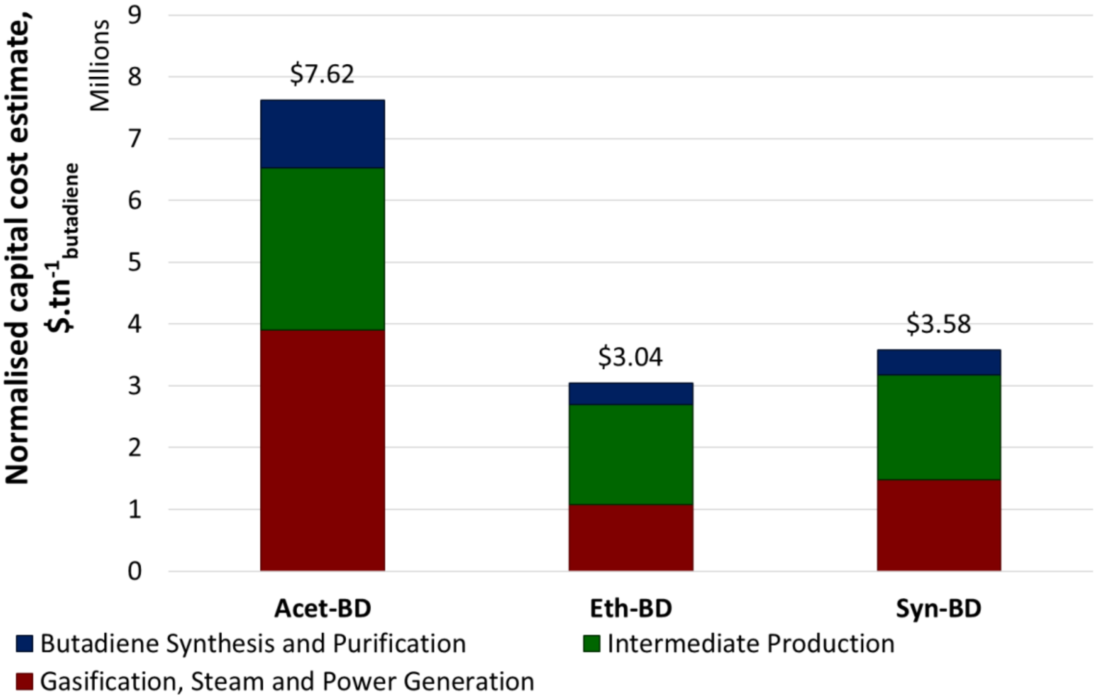


Figure 2: Normalised capital cost estimate for the three butadiene production routes. The intermediate for the three routes are; acetaldehyde, ethanol and propene for the Acet-BD, Eth-BD, and Syn-BD routes respectively.

3.2 Operating Costs

A summary of the fixed and variable operating costs for all three butadiene production routes is presented in Tables S7 and S8. Figure 3 plots the free-run long-term average price for butadiene. For comparative purposes the moving average for the previous 10 time steps is also plotted. The free-run forecast is shown to track the historic prices before settling on the long-term predicted price of $1,421 tn^{-1}, which is used as the nominal value in the investment analysis. The free-run long-term average price forecast for n-butane predicts a nominal price of $376 tn^{-1} and is presented in Figure S4.

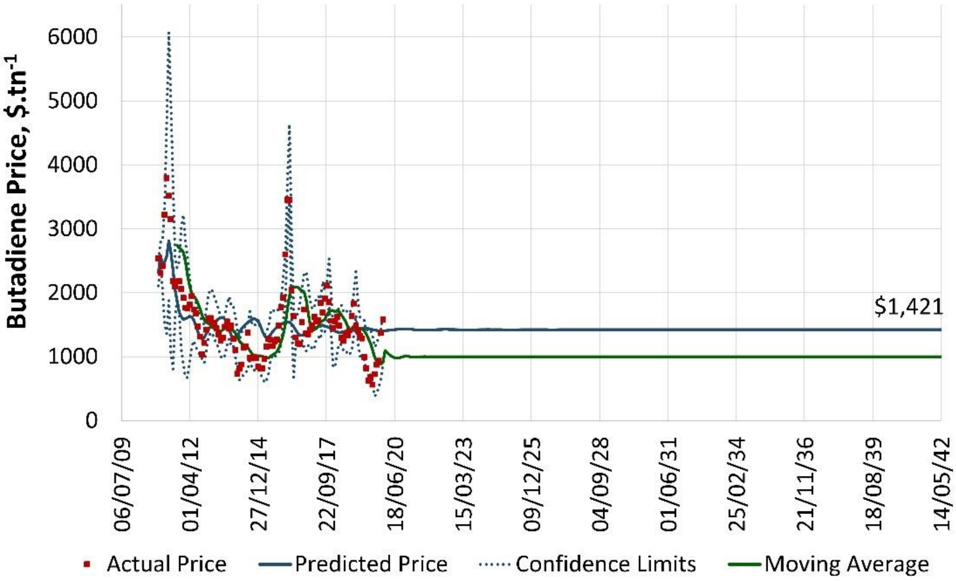


Figure 3: Butadiene long term average price forecast. The free-run radial basis function neural network prediction tracks the historical prices within the confidence limits, before the unbiased, long-term price prediction emerges beyond the historical data.

3.3 Minimum Selling Price

The MSP and the contributing cost breakdown of each butadiene production route is presented in Figure 4. A case considering the catalytic upgrading of market ethanol is also included. The long-term price prediction for ethanol was obtained using the aforementioned RBFNN methodology, yielding a price of $542 tn^{-1} (Figure S5). Despite China being the 4th largest producer of fuel bioethanol, it is still heavily subsidised (USDA Foreign Agricultural Service, 2019), meaning ethanol priced at $542 tn^{-1} would likely be imported from either the US or Brazil.

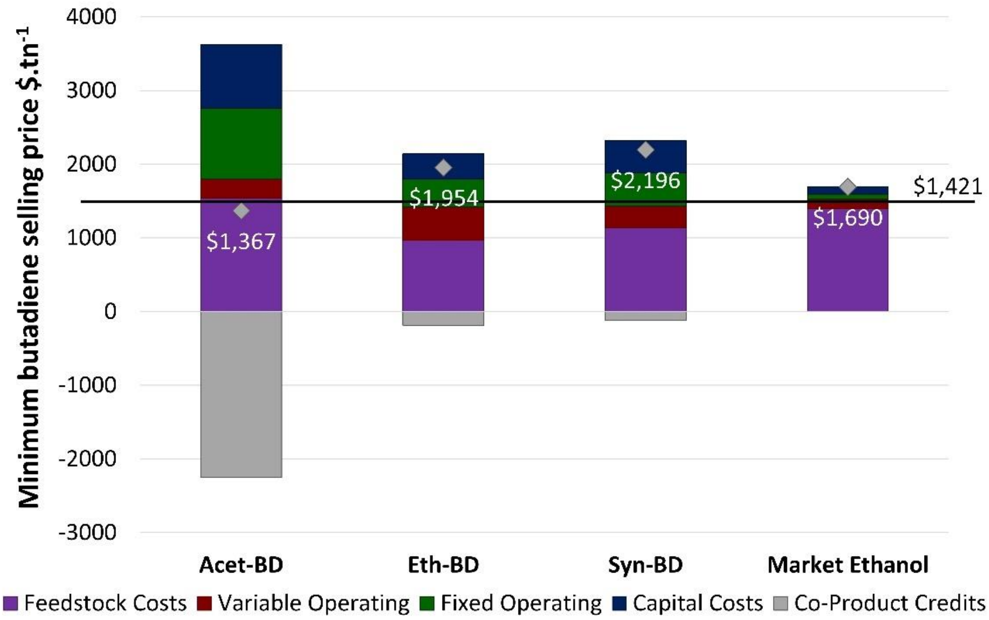


Figure 4: Minimum butadiene selling price breakdown. The hybrid (Acet-BD) route is the only route capable of producing butadiene below the long-term average forecast price. The co-products for each route are; renewable electricity, higher alcohols (sold as gasoline) and a butane rich co-product for the Acet-BD, Eth-BD, and Syn-BD routes respectively. Market Ethanol represents a scenario considering the catalytic upgrading of ethanol purchased at market value using the Eth-BD route.

In all cases the largest MSP contributor is the feedstock cost. The Eth-BD, Syn-BD and market ethanol routes produce MSPs, 1.38, 1.55 and 1.20 times the nominal forecast price respectively. Markedly, despite having a greater capital intensity, the hybrid Acet-BD route is the only route able to produce butadiene below its predicted price, producing a cumulative NPV of $2.8 million, see Figure S6. This demonstrates how the high capital investment of the Acet-BD route preserves the profit margin by making the plant largely self-sufficient in its utility consumption.

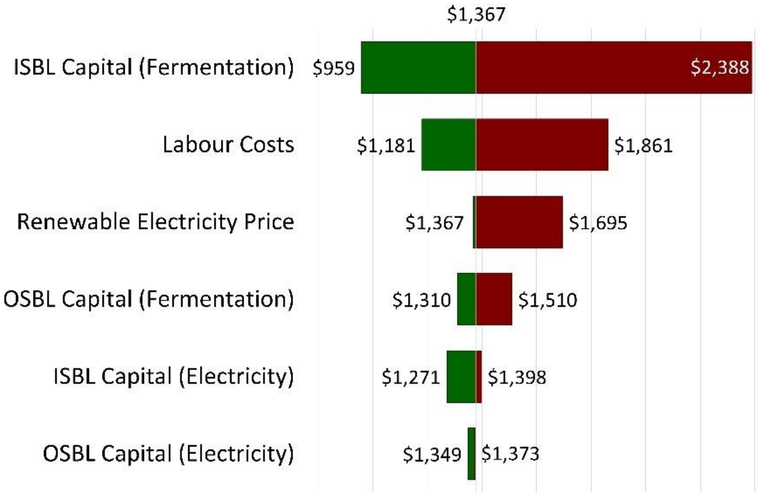
An additional case was considered for the two chemo-catalytic routes (Eth-BD and Syn-BD), whereby the capacity of the facilities was increased to 2,000 tn.day^{-1} as assumed in NREL's U.S based studies (Dutta et al., 2011; Tan et al., 2015). The CAPEX was updated to reflect this capacity increase using a scaling factor of 0.6 (Sinnott & Towler 2009). A 60,555 ha increase in the reference mill's collection area would be required to support the 2,000 tn.day^{-1} capacity. All of the pulpwood from the additional collection area would be directed towards chemical production, resulting in a new feedstock composition of 67% pulpwood and 33% residues, and commanding a higher feedstock cost of $91.73 tn^{-1}. This increase in feedstock cost partially offsets the benefit achieved through economies of scale, emphasising the advantage of exploiting waste, low cost, resources. Using the scaled CAPEX, OPEX, and new feedstock costs the consequent MSP's are $1,907 for the Eth-BD route, and $2,135 for the Syn-BD route. The increased capacity yields a lower MSP for both routes however, the Acet-BD route still produces the lowest nominal MSP. Moreover, the greater capacity necessitates expansion of the mills collection area and the use of a large portion of virgin wood.

The success of the Acet-BD route is largely attributed to the income generated from the renewable electricity. However, as this renewable electricity is inherent to the heat integrated technology platform its generation facilitates butadiene's cost-effective production.

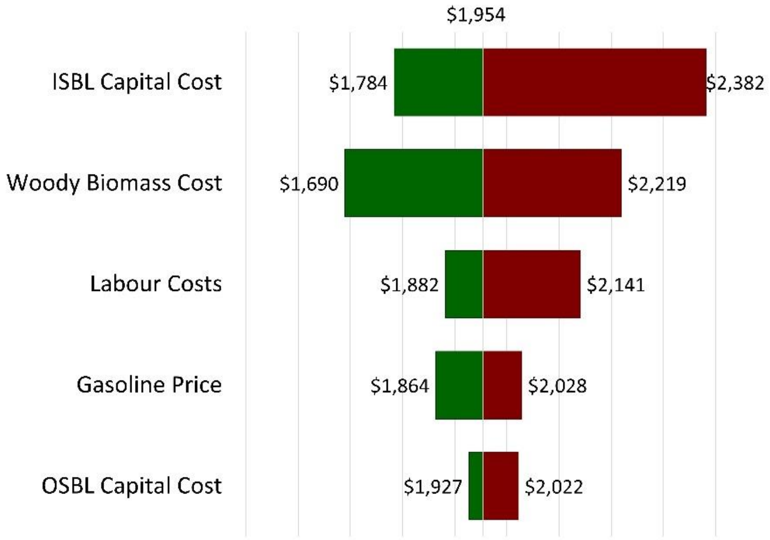
Additionally, mills may receive an additional benefit from utilising black liquor for chemical synthesis. By diverting this co-product away from the recovery boiler, pulp mills have the potential to expand pulp production by up to 25% (Berntsson et al., 2008).

3.4 Sensitivity Analysis

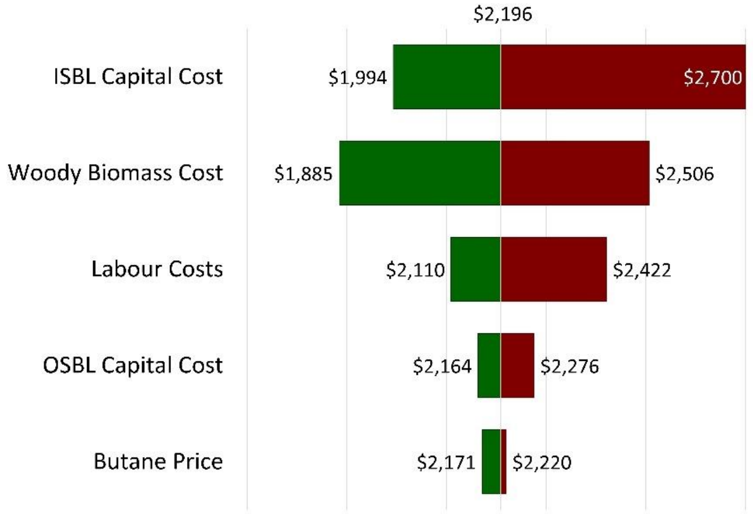
Tornado plots for the MSP of the three butadiene production routes, using the uncertainty framework outlined in Table 5 are presented in Figure 5. In all three cases, ISBL capital costs led to the greatest increase in MSP. Importantly, using the grid parity price for electricity sales, 0.052 $\$.kWh^{-1}$, the Acet-BD route produces an MSP of \$1,695 tn^{-1}, lower than the nominal MSP for the Eth-BD and Syn-BD routes, \$1,954 tn^{-1}, and \$2,196 tn^{-1} respectively. Resultantly, even using a pessimistic electricity price, the Acet-BD route is the most promising renewable production route evaluated. However, the exclusion of renewable electricity subsidies increases the MSP by \$328 tn^{-1}. This price is no longer below butadiene's long term forecast price, highlighting the importance of renewable electricity subsidies in facilitating the success of this technology platform.



Acet-BD



Eth-BD



Syn-BD

Figure 5: Tornado plots for the MSP of the three butadiene production routes. a) Acet-BD route b) Eth-BD route c) Syn-BD Route.

Monte Carlo simulations of all three routes were undertaken using all of the uncertainty parameters in Table 5. As the only route presenting a positive NPV using the nominal inputs, the outcome for the hybrid Acet-BD route is presented in Figure 6, with the results from the Eth-BD, and Syn-BD routes presented in Figures S7 and S8. The Acet-BD route demonstrated a 19% likelihood of producing a positive NPV, presenting a higher probability of producing a negative NPV than positive. There is therefore a greater likelihood of this process losing money over its projected lifetime, making it unlikely to attract investment. However, this was the only route to demonstrate any probability of producing a positive NPV outcome, making it the most promising of the technologies evaluated. Furthermore, these results are based on a long-term forecast price for conventionally produced butadiene. There is potential to attract a higher market price, and thus a more favourable economic outcome, for renewably produced, low carbon butadiene.

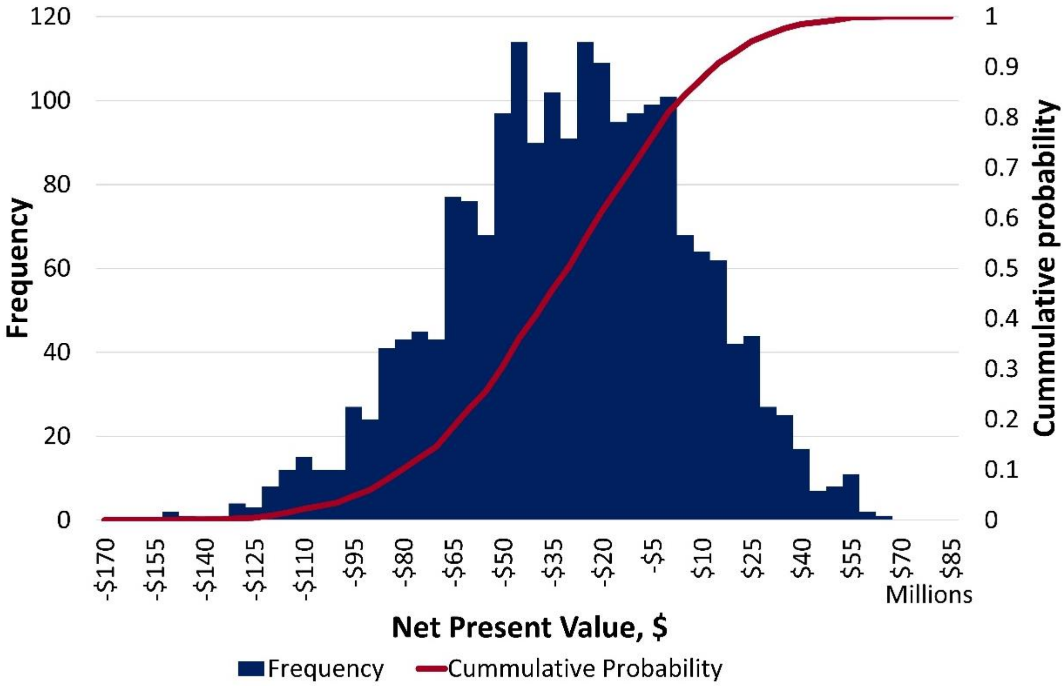


Figure 6: Monte Carlo simulation of the Acet-BD presenting a 19% likelihood of achieving a positive NPV.

3.5 Life Cycle Analysis

All three butadiene production routes produce net negative GHG emissions within a cradle to gate framework (Figure 7). Outcomes are also presented for the use of market ethanol, imported from either the US or Brazil, with US ethanol being corn-based, and Brazil being sugar cane-based. Details of the emissions associated with both ethanol sources are presented in Table S10.

The slightly greater emissions for the Syn-BD route compared to the Eth-BD route are attributed to the energy self-sufficiency and the greater butadiene yield of the Eth-BD route. The Syn-BD route relies on the import of 4.3 GWh.yr^{-1} of electricity, contributing 0.13 kgCO$_{2eq}$ kg^{-1}$_{butadiene}$. The greatest emission contributor for both chemo-catalytic routes is from the feedstock as demonstrated in Figure 7. Despite this, the feedstock emissions are only marginal, 0.33-0.31 kgCO$_{2eq}$ kg^{-1}$_{butadiene}$. The Acet-BD route achieves the lowest emissions, owing to no emissions being attributed to the black liquor feedstock. In comparison to its conventional use, the platform produces a greater amount of renewable electricity to export to the grid, meaning no emissions are associated with the diversion of this feedstock. Furthermore, the energy self-sufficiency of the Acet-BD and Eth-BD routes highlights their efficient biomass utilisation.

Conventionally, black liquor is burned for electricity generation (Naqvi et al., 2010), and forestry residues are seen as an promising feedstock for bio-energy production (Fu et al., 2020), technologies which both ultimately release CO$_2$ into the atmosphere. The net negative emissions achieved through butadiene production demonstrate the carbon sequestration achievable by directing these resources to chemical synthesis. The emission reduction potential of sinking biogenic carbon into ethene was previously highlighted by Zhao et al. (2018) in the context of China's chemical industry. The net negative emissions achieved by all three routes in this study reinforce this claim. However, for this carbon sink to be effective, it needs to be retained over long timescales. Further work is required considering the use of butadiene and the end-of-life management of these products. Nevertheless, the technologies highlight the contribution that Chinese paper and pulp mills can make in reaching China's goal of net neutrality by 2060.

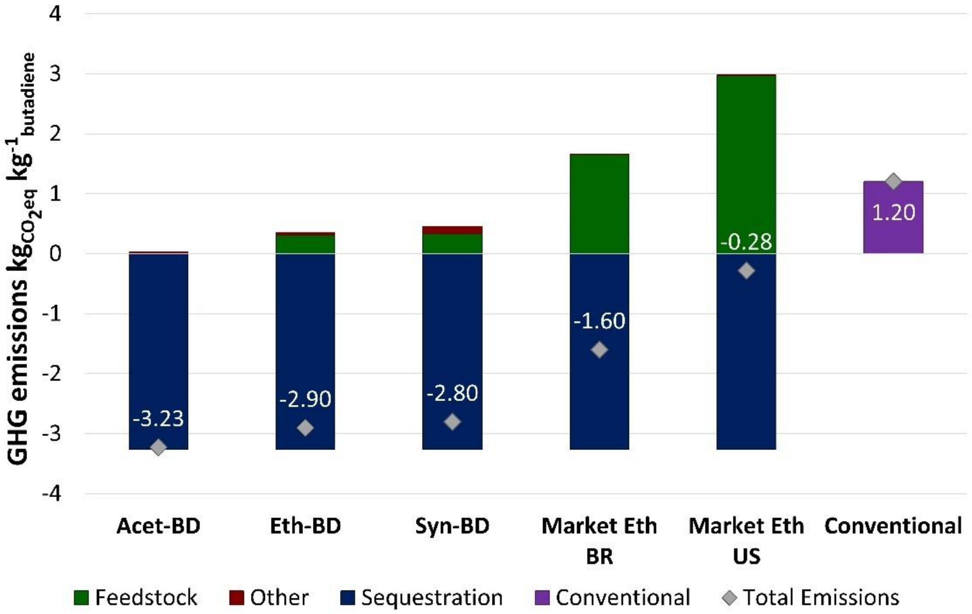


Figure 7: Greenhouse gas emissions attributed to butadiene based on the three butadiene production routes and the Eth-BD route fed with market ethanol. Conventional represents butadiene production from naphtha as in the ecoinvent database.

3.6 Comparison to Existing Work

Studies investigating butadiene production from ethanol and an olefin intermediate have been previously undertaken, but no study has compared these production routes in terms of technical, environmental and financial performances. In this study, the LCA and TEA results of the Acet-BD and Eth-BD routes are compared to existing ethanol studies, and the Syn-BD route is compared to studies evaluating routes via an olefin intermediate.

3.6.1 Ethanol to Butadiene

The MSPs for previous TEA studies investigating butadiene production from ethanol are presented in Table 7. Where necessary prices were converted to US \$ using the € to \$ exchange rate of 1.14 for 2020 (Macrotrends, 2021). The lowest butadiene selling price, achieving a return on investment of 13.25%, was previously reported as \$1,523 tn^{-1}, using an ethanol price of \$500 tn^{-1} (Dimian et al., 2021). All previous studies produce MSPs greater than that achieved by the Acet-BD route in this work, including the much greater facility size considered by Cabrera Camacho et al. (2020). The favourable China location factor, reducing capital costs, likely plays a significant role in this outcome, highlighting the competitive position Chinese paper and pulp mills hold in the potential for market penetration of renewable butadiene.

All existing LCA outcomes are also detailed in Table 7. Notably, in the LCA undertaken by Cespi et al. (2016), emissions were reduced by over a quarter by swapping the wheat portion of the European feed for residual wood chip, thereby highlighting the environmental advantage of utilising lignocellulosic feedstocks. In the cradle-to-grave study by Shylesh et al. (2016), both sugar cane and corn stover achieved net negative emissions, whilst the GHG emissions from corn grain ethanol were too high to be offset by the achieved carbon sequestration. The study by Cabrera Camacho et al. (2020), investigating first generation feedstocks, i.e corn grain and a Europe-centric mix of sugar beet, rye, corn and wheat; also found production emissions were too high to be offset by carbon sequestration. Farzad et al. (2017) found the bio-based production of butadiene from bagasse-derived ethanol to be environmentally advantaged compared to conventional production, further supporting the environmental benefit of utilising lignocellulosic feedstocks. Whilst GHG emissions between studies are not directly comparable, the undivided conclusion of existing studies is the large impact that the ethanol source has on the overall process emissions. This is reinforced by the results of this study, whereby the use of first-generation market ethanol performed worse than the three modelled routes. The favourable emissions for renewable butadiene found in this study can therefore be attributed to the use of second-generation lignocellulosic feedstocks.

Table 7: Published LCA and TEA studies producing butadiene investigating the route to butadiene via ethanol

Study	Route	Carbon Source	Plant Location	Butadiene Produced (kt.yr^{-1})	MSP ($\$.tn^{-1}$)	GHG emissions (kg CO_2eq.kg^{-1} butadiene)	Comments
Cespi et al. (2016)	One Step	Sugar Cane	Brazil	-	-	1.04	Cradle to gate LCA
		Corn, Wheat, Rye, Sugar-beet	Europe			2.04	
		Corn, Residual Wood Chips, Rye, Sugar-beet	Europe			1.49	
		Corn	US			2.30	
	Two Step	Sugar Cane	Brazil	-	-	2.18	
		Corn, Sugarcane, Rye, Sugar-beet	Europe			3.62	
		Corn	US			4.00	
Shylesh et al. (2016)	One Step	Corn Grain	US	-	-	1.81	Cradle to grave LCA
		Sugar Cane				-0.65	
		Corn Stover				-0.52	
Farzad et al. (2017)	Two Step	Bagasse	South Africa	37	2,645	0.08	BD-b (Energy self-sufficient)
					2,385	0.06	BD-c (Coal burning)
Moncada et al. (2018)	One Step	C6 Sugars	Netherlands	24	4,981	-	Case I (base case)
					3,883		Case II (process with possible improvement)
Cabrera Camacho et al. (2020)	One Step	Sugar Cane	Brazil	200	2,197	-0.07	Median Values Scenario B1 Cradle to grave LCA
		Sugar Beet, Rye, Corn and Wheat	Europe			3.19	
		Corn	US			3.98	
		Sugar Cane	Brazil		1,962	-0.05	Median Values Scenario B2 Cradle to grave LCA
		Sugar Beet, Rye, Corn and Wheat	Europe			2.64	
		Corn	US			3.31	
Dimian et al. (2021)	Two Step	-	-	91	1,523	1.6	MSP achieves a return on investment of 13.25% using

							ethanol prices at \$500 tn^{-1} GHG emissions are specific CO_2 emissions
This Work	One Step	Black Liquor	China	9	1,367	-3.23	Cradle to gate LCA
		Woody Biomass		36	1,954	-2.80	
		Sugarcane (BR)			1,690	-1.60	
		Corn (US)				-0.28	

3.6.2 Methanol to Olefins

A number of modelling studies have been undertaken producing butadiene via a renewable olefin intermediate (Hanaoka et al., 2021, 2019, 2017; Tripathi et al., 2019). These studies investigated upgrading the minor C4 fraction, resulting in relatively low butadiene yields. Tripathi et al. (2019) rationalised this low butadiene yield by stating that the production of butadiene through these olefin technologies necessitates the co-production of lower value propene and ethene. Conversely, Hanaoka et al. (2020) recently undertook a study focused on improving the olefin reaction conditions to favour butene production. The produced results represent the highest butadiene yield, 7.0%, higher than the previously reported 3.9% by both (Hanaoka et al., 2017; Tripathi et al., 2019). These studies all use different model compounds for lignin. As such, to ensure the yields are comparable, they are reported based on carbon conversion.

Despite this, the yield is lower than the 16% realised through a propene intermediate in this study, highlighting the inefficiency of C4 production through current olefin technologies. However, even with this greater yield obtained through a propene intermediate, the MSP is still 1.36 times the projected market price. In addition, the route relies on the integration of a vast number of technologies, making for complex commercial implementation. Therefore, our findings are aligned with previous studies and confirm that currently available olefin technologies are inefficient pathways for butadiene production.

3.7 Challenges in Developing the Renewable Chemical Industry

The production of drop-in, or direct replacement, chemicals presents the fewest barriers to introducing biomass-derived chemicals to market (Christensen et al., 2008; Straathof and Bampouli, 2017). Nevertheless, it is important to recognise the challenge in producing these chemicals. Naphtha, used to produce traditional commodity chemicals, has a very low oxygen content in comparison to biogenic feedstocks (Haveren et al., 2008). This higher oxygen content necessitates the use of catalytic technologies to efficiently remove the undesired oxygen. Common catalytic technologies employed to remove oxygen include decarbonylation, dehydration, and hydrodeoxygenation. This oxygen removal inherently lowers the overall mass yield, with butadiene as a leading example. Consequently, the ability to produce these chemicals at market prices is highly dependent on feedstock costs and availability, and technology efficiency. Fundamentally, feedstocks need to be priced at fuel value or below, e.g. utility value such as in the case of black liquor.

Whilst butadiene holds a unique market position, it represents a challenging target chemical owed to its conjugated diene structure and lack of oxygen. Of the technologies evaluated, the hybrid biochemical Acet-BD route was the only economically viable route to butadiene using the nominal TEA inputs. Moreover, this route demonstrates the lowest GHG emissions, reinforcing the platforms efficient biomass utilisation. This builds on our previous work (Rodgers et al., 2021), by demonstrating the novel platform's economic advantage over traditional chemo-catalytic technologies within the context of a pulp mill biorefinery. Moreover, the unique coupling of SCWG with aerobic gas fermentation overcomes the energetic inefficiency of SCWG, one of the major barriers to commercialisation (Lee et al., 2021). This integration of technologies also generates a vast amount of renewable electricity, the income of which facilitates the platforms favourable economics. Whilst SCWG is yet to reach commercial scale, this study highlights heat integrated SCWG and aerobic gas fermentation as an efficient platform to valorise wet, recalcitrant feedstocks for biochemical production.

Importantly, whilst this work investigated the use black liquor as a feedstock, SCWG can be used for a variety of wet feedstocks which are uneconomical for traditional gasification technologies (Kumar et al., 2018). Potential feedstocks include; stillage, produced at a rate of 8-20 L per litre of fuel ethanol (Gebreeyessus et al., 2019), and wastewater residuals, animal and food waste, with an estimated combined availability of 77 million dry tons in the US alone (Bioenergy Technologies Office, 2017). The heat integrated SCWG and aerobic gas fermentation platform's ability to valorise these waste resources demonstrates the technology's importance in the transition to a renewable chemical industry towards carbon neutrality.

4 Conclusion

The hybrid gas fermentation route (Acet-BD) demonstrates marginal techno-economic feasibility of renewable, on-purpose butadiene in the context of Chinese paper and pulp mills. The technology produces a minimum selling price of \$1,367 tn^{-1}, outcompeting the \$1,954 tn^{-1} and \$2,196 tn^{-1} achieved by chemo-catalytic ethanol production (Eth-BD), and via an olefin intermediate (Syn-BD), respectively. Notably, the Acet-BD is the only route capable of producing butadiene below the forecast price, producing a cumulative NPV of \$2.8 million using the nominal TEA inputs. Whilst the co-generation of renewable electricity contributes to the technology's success, its generation does not come at the detriment of butadiene production. The results of the Monte Carlo simulation demonstrate a 19% probability of the Acet-BD route achieving a positive NPV, with a 70% probability of producing an NPV between -\$50 million and \$60 million. Whilst 19% probability is low, the cost-effective production of renewable butadiene has hitherto been demonstrated. Moreover, the analysis is based on a price for conventionally produced butadiene. Renewable, low carbon chemical production has the potential to attract a higher market price, realising a more favourable economic outcome. All three routes evaluated produce net negative GHG emissions within a cradle-to-gate framework, with the Acet-BD producing the lowest emissions overall (-3.23 $kgCO_{2eq}\ kg^{-1}_{butadiene}$ versus 1.2 $kgCO_{2eq}\ kg^{-1}_{butadiene}$ for conventional production). Resultantly, the heat integrated SCWG and aerobic gas fermentation platform can facilitate the decarbonisation of the chemical sector by exploiting wet, previously uneconomical, waste feedstocks in support of developing circular economies.

5 Author Contributions

Sarah Rodgers, Fanran Meng, Alex Conradie, Jon McKechnie: Conceptualization; **Sarah Rodgers:** Data curation; **Sarah Rodgers, Alex Conradie:** Formal analysis; **Alex Conradie, Jon McKechnie:** Funding acquisition; **Sarah Rodgers:** Investigation; **Sarah Rodgers, Fanran Meng, Alex Conradie, Jon McKechnie:** Methodology; **Alex Conradie, Jon McKechnie:** Project administration; **Alex Conradie, Jon McKechnie:** Resources; **Sarah Rodgers, Alex Conradie:** Software; **Fanran Meng, Stephen Poulston, Alex Conradie, Jon McKechnie:** Supervision; **Sarah Rodgers:** Visualization; **Sarah Rodgers:** Writing -

original draft; **Sarah Rodgers, Fanran Meng, Stephen Poulston, Alex Conradie, Jon McKechnie**: Writing - review & editing.

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