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1 comparisons carried out amongst the configurations as well as against standard
2 literature references of similar processes. Finally, a sensitivity analysis was used to
3 assess the impact that changes in key parameters have on the considered metrics. The
4 results show that configurations which import natural gas and electricity as utility
5 sources alongside the macroalgae feedstock offer the lowest MBSP, however they do
6 poorly when cost of CO₂e avoided is considered. On the other hand, the configurations
7 which utilize only macroalgae offer the best potential for cost of CO₂e avoided but have
8 the poorest values for MBSP. In addition, the cost of CO₂e avoided obtained for the best
9 configurations are in line with literature references. However, the MBSP values are
10 higher than literature references for butanol derived from cellulosic feedstock primarily
11 due to the high ash content in seaweed. The sensitivity analyses results show that
12 changes in gasoline prices have a very significant effect on the plant configurations in
13 the South Korean market, but not as significantly in the United States market.

14 **Keywords:** macroalgae; biobutanol; thermochemical; economic analysis; minimum
15 butanol selling price; cost of CO₂e avoided

16 **1. Introduction**

17 Macroalgae or seaweed is a term used to describe non-vascular large aquatic
18 photosynthetic plants, thus they differ from microalgae which are unicellular [1,2].
19 Globally in 2012, seaweed production was estimated to be about 24.9 million wet-
20 metric tonnes (85 - 90 % moisture content) with 96% coming from aquaculture
21 production [3]. Most of the world's farmed macroalgae is produced in Asia, with 99% of
22 the world's production coming from that region [4]. Macroalgae has traditionally been

1 grown for use as edible food, or as a raw material from which hydrocolloids utilized in
2 the pharmaceutical and food industries are extracted.

3 Recently, there has been an increased interest in growing macroalgae for use in
4 biofuel production. This is because macroalgae, which is a feedstock for third
5 generation biofuels, have fast growth rates with up to 4–6 harvest cycles per year.
6 Unlike first and second generation biofuel feedstocks, macroalgae can be grown in the
7 sea thus eliminating issues relating to land use and irrigation water [4]. Furthermore,
8 macroalgae is preferable to microalgae (also a third generation biofuel feedstock) for
9 biofuel production because its plant-like characteristics make it easier to harvest, and its
10 high concentration of carbohydrates in comparison to microalgae make it a potentially
11 better biofuel feedstock [2,5,6].

12 Several studies have been conducted by government research institutes around the
13 world investigating the potential of macroalgae as a biofuel feedstock. One such
14 preliminary study by the Energy Research Center of the Netherlands (ECN) investigated
15 the feasibility of producing biofuels from macroalgae cultivated offshore in the North
16 Sea [7]. The study recommended carrying out a pilot scale seaweed cultivation
17 experiment in the North Sea to improve the technological and ecological know-how of
18 seaweed production, and also endorses the development of biorefinery technologies for
19 seaweed utilization including its conversion to chemicals and fuels. The Sustainable
20 Energy Authority of Ireland also carried out a study which concluded that priority
21 should be given to the large scale cultivation of macroalgae to ensure sufficient
22 feedstock for biofuel production and avoid the negative impact that could occur on
23 marine biodiversity by exploiting wild seaweed [8]. In another study carried out in the
24 United States (U.S.) by the Pacific Northwest National Laboratory, it was concluded

1 that the U.S. has a high potential for producing macroalgae biomass based on the very
2 high surface area of U.S. coastal waters and known rates of macroalgae production in
3 other parts of the world [4]. However, the authors note that additional research into
4 macroalgae cultivation, harvesting and conversion into fuel is needed. In South Korea,
5 research into macroalgae biomass has been funded by the Ministry of Oceans and
6 Fisheries since 2009 and has focused on offshore systems for large scale growth of
7 macroalgae and their conversion to energy [9].

8 In the peer-reviewed literature several recent review studies have been carried out by
9 researchers into the potential of macroalgae use for fuel or chemicals production.
10 Lehamn et. al. [10] used a modeling approach to investigate the global potential for
11 macroalgae growth as identify areas for growth. They estimate that 98 gigatonnes per
12 year dry weight of macroalgae can be grown globally over a surface area of
13 approximately 10^8 km² and conclude that with near-future aquaculture technologies,
14 offshore cultivation of macroalgae has huge potential to significantly provide fuels and
15 chemicals for humans. Another point noted by some of these review studies was that
16 despite the potential for macroalgae based biorefineries, technological improvements in
17 the whole supply chain of macroalgae based biorefineries (such as seaweed cultivation,
18 harvesting and transporting, pretreatment, and fuel conversion technologies) are needed
19 for economically feasible macroalgae fuel and chemical processes [5,11,12].

20 Based on the conclusions from all these studies, there is a high motivation to conduct
21 research into the technological and economical aspects of macroalgae conversion to
22 fuels.

23 Currently, research efforts into biofuels suitable for gasoline replacement have shifted
24 focus to butanol instead of ethanol because of advantages such as lower miscibility with

1 water, higher heating value (HHV), and better compatibility with existing gasoline
2 engines and fuel pipeline infrastructure [13,14]. Similar to first and second generation
3 biofuel feedstocks such as corn and agricultural residue, butanol can be produced from
4 macroalgae using either a biochemical or thermochemical route.

5 The conversion of macroalgae to butanol through the biochemical route is done via
6 the acetone, butanol and ethanol (ABE) process where species of *Clostridium* bacteria
7 are used to convert sugars such as hexoses and pentoses to acetone, butanol and ethanol.
8 Nikolaison et al. [15] fermented the macroalgae *Ulva lactuta* with *Clostridium* strains to
9 produce butanol with a yield of 0.16 g butanol/ g sugars, which was lower than that of
10 ethanol produced under similar conditions. Using *Clostridium beijerinckii* as the
11 fermentation organism Van Der Wal et al. [16] obtained butanol yields of 0.23 g
12 butanol/ g sugars from *Ulva lactuta*. Potts et al. [17] showed through a pilot study in
13 which *Ulva lactuta* grown in Jamaica Bay, New York City was used as a fermentation
14 substrate that a butanol yield of 0.29 g butanol/ g sugars was obtainable. This value
15 corresponds to a 22.4 % deviation from the theoretical yield of 0.37 g butanol/g sugars
16 [18]. Huesemann et al. [19] carried out a study of butanol fermentation from brown
17 algae (*Saccharina*), but obtained very low butanol yields of 0.12 g butanol/g sugars.
18 One challenge of current ABE fermentation strains is the difficulty in effectively
19 converting some glucose-based polysaccharides, such as mannitol which constitutes up
20 to 12 % of brown algae [7], thus leading to slow reaction rates and productivity [6,20],
21 thus progress in the area of metabolic engineering of fermentation organisms is required
22 to improve butanol yields at the laboratory scale [6,11]. This has led to the conclusion
23 that significant improvements at the laboratory scale are still required before
24 economically feasible butanol production from fermentation of seaweed can be

1 achieved on the industrial scale [16,21]. In fact no conceptual studies on the techno-
2 economics of macroalgae-to-butanol processes via the biochemical route have been
3 carried out in the peer reviewed literature.

4 In this regard the thermochemical route might be of considerable interest to study as
5 past research on first and second generation biomass to butanol processes have shown
6 that the thermochemical route has a number of more technologically mature processing
7 steps such as the gasification, syngas cleanup and separation steps [22,23], and thus
8 might be closer to commercial implementation than the biochemical route. However,
9 though past work [24] has shown that economically competitive butanol can be
10 produced from second generation biofuel feedstock using a thermochemical route, no
11 such studies have been carried out on a macroalgae-to-butanol process in the peer
12 reviewed literature to the best of the authors' knowledge.

13 As a first step in building an understanding of the process design and economics of
14 macroalgae to butanol processes, this work will focus on developing a macroalgae-to-
15 butanol process using a thermochemical conversion route and assessing its economics
16 with future work focusing on the biochemical route. The research will aim to develop
17 different design configurations for producing butanol from seaweed and address
18 questions regarding the overall efficiency and butanol yields that are possible from
19 these designs. Furthermore the different configurations will be compared amongst
20 themselves and against other biofuels by using standard metrics such as the cost of CO₂
21 equivalent emissions (CO₂e) avoided as well as the minimum butanol selling price
22 (MBSP). These metrics are also assessed for different market scenarios, and along with
23 sensitivity analyses on key economic parameters help give a robust assessment on the
24 potential for butanol production from seaweed using the thermochemical route.

1 2. Materials and Methods

2 2.1 Macroalgae

3 The macroalgae selected for this study is the brown macroalgae *Laminara Japonica. L.*
4 *Japonica* is chosen for this study because it is the most widely produced macroalgae
5 with a production rate of 5 million wet tons per year, making up 33 % of the world's
6 yearly production [6]. Table 1 shows the plant gate characteristics of the *L. Japonica*
7 that is used for this study [25], noting that the chemical composition of brown
8 macroalgae changes somewhat depending on the season, growing habitat, and species
9 [12,20]. In general, carbohydrates are consumed in the dark season and produced in the
10 light season [26]. On a moisture free basis, the biochemical composition of brown
11 macroalgae consist of 30 - 50 % minerals, 30 - 60 % carbohydrates, 10 - 13 % cellulose,
12 6 - 20 % proteins and 1 - 3 % lipids [27].

13 **Table 1.** Ultimate and proximate analysis of *L. Japonica* used in this study [25].

Ultimate analysis	wt % dry basis	Proximate analysis	wt %
Carbon	32.41	Moisture	2.79
Hydrogen	3.37	Volatile matter	70.90
Nitrogen	1.18	Fixed Carbon	3.32
Sulphur	0.31	Ash	22.99
Oxygen	39.74		
Ash	22.99		
HHV (MJ/kg)	14.05		

14

15 2.2 Process simulation and description

16 2.2.1 Process and simulation overview

17 This paper considers and assesses three design configurations for the thermochemical
18 conversion of macroalgae to butanol. All of the design configurations adhere to a

1 similar approach. First, macroalgae is gasified to produce syngas (CO and H₂). The
2 syngas is then cleaned before being sent to the mixed alcohol synthesis reactor for
3 alcohols production, after which the alcohols are separated into the required products in
4 an alcohols separation section. The differences in configurations arise as a result of
5 different criteria for providing high temperature process heat, and power. In
6 configuration 1 (also called the "self-sufficient" configuration), the plant is self-
7 sufficient in terms of high temperature process heat and power, meaning that some of
8 the syngas generated by macroalgae gasification is split and diverted as combustion fuel
9 for the endothermic gasification and tar reforming processes. In other words,
10 configuration 1 is 100% powered by renewable biomass. Configuration 2 or the "natural
11 gas (NG) import" configuration uses NG combustion for high temperature process heat
12 needs instead of bio-syngas combustion because NG is cheaper than seaweed per unit
13 heating value. The disadvantage to this approach is that the use of fossil fuels reduces
14 the "greenness" of the process and the resulting biofuel. Finally, configuration 3 (or the
15 "NG and power import" configuration) utilizes NG for high temperature heat similar to
16 configuration 2, and in addition imports electric power for process use instead of
17 generating power through expansion of hot gases and steam turbines. Past work showed
18 that the steam turbines and gas expanders can contribute up to 25 % of the capital cost
19 of thermochemical biobutanol process [24], thus this configuration is motivated by the
20 idea that it might be better to purchase power from the grid instead and avoid the
21 significant capital costs required for purchasing steam turbines and gas expanders. Even
22 though this could ultimately be somewhat more expensive over the lifetime of the
23 process, the significantly reduced capital may be very desirable in terms of financing
24 and risk, making the process more commercially feasible. The trade-offs between the

- 1 three configurations are the environmental considerations such as CO₂ emissions,
- 2 amount of renewable energy used, capital and operating costs.

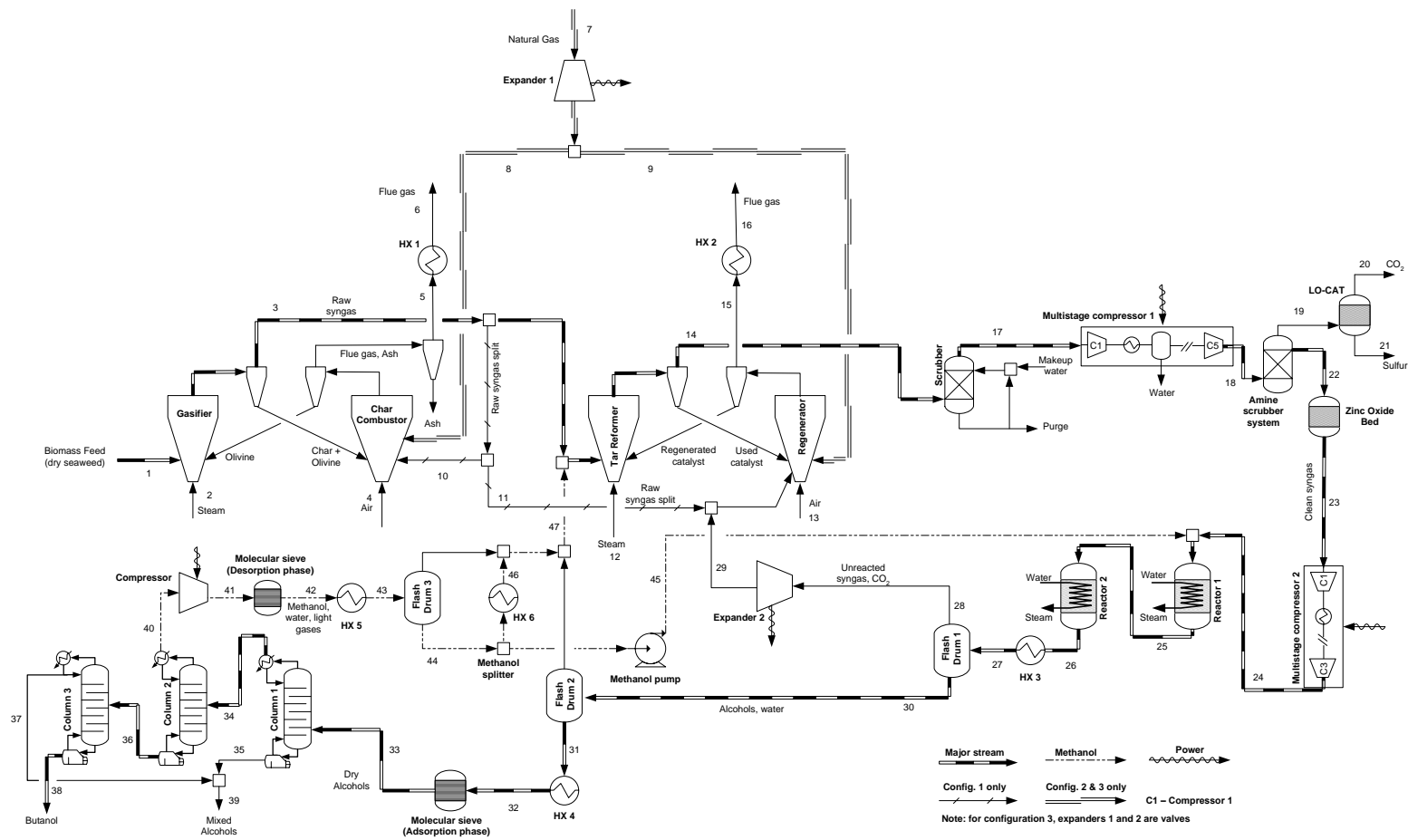


Figure 1: Process flow diagram of the proposed thermochemical biomass (seaweed) to butanol process. Full stream conditions are provided in the Supporting Information

1 **Table 2.** Major design parameters of process areas

Gasification		Gas cleanup (acid gas removal)	
Feed rate per train (gasifier inlet)	700 dry tonnes/ day	Amine used	Monoethanolamine
Parallel trains required	Two (2)	Amine concentration, wt %	35
Gasifier operating pressure	2.28 bar	Amine temperature in absorber (°C)	43.33
Gasifier operating temp.	800 °C	Absorber pressure (bar)	31
Char combustor pressure	2 bar	Stripper pressure (bar)	4.12
Char combustor temp.	850 °C	Heat duty to remove CO ₂ (kJ/kg)	5337
Gas cleanup (tar reforming)		Alcohol synthesis reactors	
Reformer operating pressure (bar)	1.86	H ₂ /CO ratio (reactor 1 inlet)	1.23
Reformer operating temp. (°C)	910	Gas hourly space velocity (h ⁻¹)	5000
Reformer space velocity (h ⁻¹)	2,476	Reactor 1 temperature (°C)	325
Tar reformer conversions (%)		Reactor 2 temperature (°C)	340
Methane (CH ₄)	80%	Pressure (bar)	76
Ethane (C ₂ H ₆)	99%	CO ₂ concentration (mol %)	5
Ethylene (C ₂ H ₄)	90%	Sulphur concentration (ppmv)	0.1
Tars (C ₁₀₊)	99%	CO conversion per-pass (CO ₂ free basis)	40 mol%
Benzene (C ₆ H ₆)	99%	Total alcohol selectivity	87.27 mol%
Ammonia (NH ₃)	90%	Catalyst alcohol prod. (g/kg-catalyst/hr)	455.26
Alcohol separation (distillation columns)		Steam system and power generation (cases 1 and 2)	
Column 1		Turbine design	Three stage turbine
Butanol recovery in overhead	99.2 mol%	High pressure inlet conditions	58 bar, 482 °C
Pentanol recovery in bottoms	99 mol%	Medium pressure inlet conditions	12 bar, 303 °C
Total number of trays	28	Low pressure inlet conditions	4.5 bar, 210 °C
Column 2		Condenser outlet conditions	0.304 bar, saturated
Methanol recovery in overhead	99 mol%	Cooling water	
Ethanol recovery in bottoms	99 mol%	Supply temperature (°C)	32
Total number of trays	48	Return temperature (°C)	43
Column 3		Alcohol separation (Molecular sieve)	
Propanol recovery in overhead	99.3 mol%	Inlet water content (wt%)	7.93
Butanol purity in bottoms	96 wt%	Outlet water content (wt %)	0.5
Total number of trays	54		

2 This work made use of Aspen Plus V8 software to estimate the mass and energy balance
3 for each design strategy. Physical property packages, and unit operation specifications
4 and design criteria were selected to be consistent with the authors' previous work in
5 which a lignocellulosic biomass to butanol process using a thermochemical route was
6 designed and assessed [24]. In the proceeding process description sub-sections, each

1 plant area that has already been described in the previous work will only be briefly
2 discussed. However, any differences in unit operations design and specification from
3 the previous work will be noted and discussed in more detail.

4 A simplified process flow diagram of the process is shown in Fig. 1. The figure shows
5 the key processing steps for the conversion of seaweed to butanol via gasification,
6 syngas production, and mixed alcohol synthesis. These different areas of the process are
7 further discussed in sections 2.2.2 – 2.2.6. The major design parameters for these
8 process areas are also shown in Table 2.

9 **2.2.2 Gasification**

10 A dried macroalgae feed at 1,200 tonnes per day with characteristics as shown in Table
11 1 is sent to the gasifier in which it is indirectly gasified with low pressure steam. The
12 wet macroalgae after collection is air dried to about 20 - 35 wt% moisture content
13 before being transported to the biobutanol plant [28]. Further drying to the moisture
14 content shown in Table 1 can be done by using waste hot flue gas heat from the
15 biobutanol process (not modeled), using a similar procedure as discussed in Okoli and
16 Adams [24].

17 The composition and higher heating value of syngas produced from biomass
18 gasification is highly variable and is affected by a number of process parameters such
19 as; fuel type and composition, fuel moisture content, gasification temperature,
20 gasification pressure, gasifier bed materials and gasification agent (air, oxygen, steam)
21 [22,29]. Thus the gasifier selection, and its operating conditions are chosen so as to
22 meet specific syngas requirements for downstream operations [30]. For example the

1 syngas H_2/CO ratio for Fischer Tropsch gasoline production is about 0.6, but
2 approximately 2.0 for methanol production [30]. Puig-Arnavat et al. [22] discusses the
3 various types of biomass gasifiers and their syngas outputs in detail.

4 The gasifier design chosen for this work is a low pressure allothermal indirect
5 circulating fluidized bed gasifier that has the product composition of its output modeled
6 with temperature correlations from the Batelle Columbus Laboratory test facility [31].
7 Though this model was not originally developed for seaweed, it has been validated for a
8 wide range of hard and soft woods, as well as for non-woody biomass such as corn
9 stover which have high ash content, low carbon and high oxygen content just like
10 seaweed, thus making the model robust enough to predict the outlet composition of
11 seaweed gasification [31] in the absence of experimental data.

12 The gasification reactions are endothermic; as a result the required heat is supplied by
13 circulating hot olivine from the char combustor through the gasifier. The exit from the
14 gasifier includes the olivine as well as the gasification products (CO , H_2 , CH_4 , tars and
15 solid char). Cyclones are then used to separate the gaseous products (mainly CO , H_2 ,
16 CH_4 and tars) from the solids (olivine and char) which are recycled back to the char
17 combustor. In the char combustor, the char is combusted with air thus heating the
18 olivine. If extra heat is needed, provision is made for extra fuel to be supplied by
19 recycling a fraction of the syngas as in configuration 1 (stream 10 in Fig. 1), or using
20 NG (specifications are shown in Table 3) as in configurations 2 and 3 (stream 8 in Fig.
21 1). Finally, the hot flue gas from the char combustor is used to generate steam in the
22 steam cycle.

23

1 **Table 3.** NG specifications [32]

Component	mol %
Methane	94.9
Ethane	2.5
Propane	0.2
iso-Butane	0.03
n-Butane	0.03
iso-Pentane	0.01
n-Pentane	0.01
Hexanes plus	0.01
Nitrogen	1.6
CO ₂	0.7
Oxygen	0.02
Hydrogen	trace
HHV (MJ/m ³), dry basis	37.8
Density at STP (kg/m ³)	0.585

2 **2.2.3 Gas cleanup**

3 The goal of the gas cleanup section is to remove impurities from the raw syngas such as
4 tars, CO₂ and sulphur that have the potential to foul downstream equipment and poison
5 the mixed alcohol synthesis (MAS) catalyst. There are two steps in the gas cleanup
6 section. First, secondary tar reforming is used to reform the tars, methane, and other
7 hydrocarbons in the syngas from the gasifier. Secondary tar reforming differs from
8 primary tar reforming in that it does not occur internally in the gasifier. Though primary
9 tar reforming has the potential to reduce capital costs by eliminating the extra
10 equipment needed for an external tar reformer, the technology is not commercially
11 mature [33]. The secondary tar reformer is a circulating, heterogeneous, fluidized
12 catalyst bed system which uses separate beds for reforming and catalyst regeneration.
13 The reforming reactions occur between the raw syngas and steam, and are catalyzed by
14 a fluidizable Ni/Mg/K catalyst [31]. The reformer bed is maintained at isothermal
15 conditions by the transfer of heat from the catalyst regenerator which is exothermic. The

1 catalyst is separated from the reformed syngas using cyclones at the reformer exit and
2 then transferred to the catalyst regenerator. The catalyst is regenerated by combusting
3 the coke entrained on the catalyst, after which the heated catalyst is passed through
4 cyclones to separate it from the combustion gases. The loop is completed when the
5 heated catalyst is sent back to the reformer. The hot combustion gases are used to
6 provide heat for steam generation and process heating. If the heat duty supplied from
7 the catalyst regeneration step is insufficient, it can be supplemented by combusting a
8 portion of the raw syngas feed from the gasifier as in configuration 1 (stream 11 in Fig.
9 1) or NG as in configurations 2 and 3 (stream 9 in Fig. 1), as well as unreacted syngas
10 from downstream.

11 In the second step of the gas cleanup process, the hot syngas from the tar reformer is
12 cooled before water quenching and scrubbing to remove any remaining solids, tars, and
13 other impurities. The purge water stream is then sent to a downstream waste water
14 treatment facility (not modeled). The cooled syngas is compressed to 30 bar in a multi-
15 compressor prior to being sent to the amine scrubber system for acid gas removal. The
16 amine scrubbers and the subsequent ZnO bed are used to reduce the H₂S and CO₂
17 concentrations in the syngas to meet the MAS catalyst specifications of < 0.1 ppm H₂S
18 and < 6 % CO₂ [34]. The amine scrubber reduces the H₂S concentration to 10 ppm,
19 before it is further reduced to 0.1 ppm by the ZnO bed. A LO-CAT system then takes
20 the H₂S and CO from the amine scrubber exit, and generates elemental sulphur and
21 CO₂.

22 All the technologies described here for syngas cleanup have been demonstrated
23 commercially. Fluidizable Ni based catalysts for tar reforming have already found wide

1 applications in the petrochemical industry for naphtha and methane reforming to syngas
2 [35]. The LO-CAT system has been commercially implemented with more than 200
3 installations existing around the world for H₂S removal from gas streams as reported by
4 Merichem company [36]. Amine scrubbing with monoethanolamine (MEA) solutions is
5 the leading method for CO₂ and H₂S removal and is used in 75 - 90 % of commercial
6 CO₂ capture processes [37]. Finally ZnO beds have found commercial application in a
7 variety of syngas to chemicals processes where they are used to clean syngas streams to
8 achieve very low H₂S concentrations [38].

9 **2.2.4 Alcohol Synthesis**

10 The cleaned syngas is compressed from 30 bar to 76 bar in a multi-stage compressor,
11 and subsequently heated to 325°C before the reactor inlet. Prior to entering the reactor,
12 the clean syngas is mixed with methanol and water that are recycled from the alcohol
13 separation section. A double bed reactor configuration consisting of two reactors in
14 series is used for the reactor system. Both fixed bed reactors contain equivalent amounts
15 of a modified low pressure methanol synthesis catalyst (Cs/Cu/ZnO/Cr₂O₃ based) with
16 the second reactor operating at 340°C [39,40]. This reactor configuration favors the
17 production of C₁– C₃ alcohols in the first reactor because lower temperatures favor
18 higher equilibrium amounts of methanol, while higher temperature favor the conversion
19 of C₁ – C₃ alcohols to higher alcohols. According to the experimental results of
20 Burcham et al. [40], the double bed reactor configuration produces a higher butanol
21 yield than the single reactor configuration and is thus potentially more favorable. The
22 reactor products consist of C₁ – C₄ alcohols, water, methane, C₅₊ alcohols and other
23 hydrocarbon products. The MAS reactions are highly exothermic, thus a shell and tube

1 configuration is used for the reactors, with the reactions taking place in the tubes while
2 heat removal occurs through steam generation from the shell side. This process helps
3 maintain isothermal conditions in the reaction.

4 The products from the reactor are cooled to 60°C by heat exchange with process streams
5 and cooling water. The unconverted syngas which is still at high pressure is separated
6 from the liquid alcohols by a series of flash drums, and is expanded through a turbine to
7 recover power in configurations 1 and 2, while it is expanded through a flash valve in
8 configuration 3. The expanded syngas is then sent to the gas cleanup section where it is
9 combusted in the catalyst regenerator to help meet the heat requirements of the plant,
10 while the liquid alcohols are sent to the alcohols separation section.

11 **2.2.5 Alcohol Separation**

12 Absorbed gases are removed from the raw alcohols by flashing to 4 bar, with the gases
13 recycled to the tar reformer. The liquid alcohols are superheated prior to being sent for
14 dehydration in a molecular sieve. The alcohols are then separated into final products by
15 three distillation columns in series. The main product for the distillation sequence is
16 isobutanol which is recovered at 96 wt% purity to meet ASTM fuel specification
17 standards [41]. Other products are C₅₊ alcohols recovered from the bottom of column 1,
18 methanol and lighter gases recovered from the top of column 2, and ethanol and
19 propanol recovered from the top of column 3. Methanol recovered from the distillation
20 columns is superheated and recycled as a sweep gas to recover adsorbed water from the
21 molecular sieve. The methanol vapor and recovered water vapor is split and recycled to
22 the MAS reactor to help improve the overall alcohols yield while the rest is recycled to

1 the tar reformer to be reformed back to syngas. The bottoms product of column 1 and
2 the distillate product from column 3 are blended to obtain a mixed alcohol co-product.

3 **2.2.6 Utilities (Steam system, power generation and cooling)**

4 A steam cycle is integrated into the design to produce high pressure (HP) steam for
5 power generation in configurations 1 and 2, and low pressure (LP) steam for direct
6 injection into the biomass gasifier and tar reformer in all the configurations. There is
7 also a requirement for indirect heating using LP steam in the reboilers of the distillation
8 columns and amine system. The steam condensate is then returned to the steam cycle in
9 a loop. HP steam in the steam cycle is generated via heat exchange with hot process
10 streams like the flue gases from the char combustor and catalyst regenerator, and the
11 exothermic heat from the MAS reactors. The steam system design conditions are shown
12 in Table 2.

13 Process power requirements for configurations 1 and 2 are met by the expansion of
14 high pressure steam through steam turbines in series. Extra power is obtained via the
15 expansion of unconverted syngas through a turbine in the alcohol synthesis section. In
16 configuration 3 all power is imported from the grid; this creates a trade-off in
17 eliminating the high cost of capital associated with purchasing and installing turbines
18 and expanders while increasing the operating cost associated with power purchase from
19 the grid.

20 The cooling requirements of all the configurations are met by the use of forced-air
21 heat exchangers and cooling water after process stream to process stream heat exchange
22 has been carried out. Forced-air heat exchangers are used with the aim of reducing the
23 water demand of the process and provide cooling for the multistage compressors,

1 distillation and amine system condensers, as well as for condensing the steam turbine
2 exhaust.

3 2.3 Economic analysis

4 The objective of the economic analysis is to determine the MBSP of the different
5 processes. The MBSP is defined as the unit selling price of butanol over the plant's life
6 such that the net present value (NPV) is zero. It is determined through a discounted cash
7 flow rate of return analysis, which is a useful metric for comparing all the different
8 configurations that are modeled. The economics of a process or product usually depends
9 on the market in which it is to be implemented or assessed. Thus, the economics for the
10 different process designs are considered in both a U.S. market and a South Korean
11 market scenario to reflect the two regions (North America and Asia) of interest for this
12 work.

13 The estimates of capital costs for the processes are based on data from Aspen Capital
14 Cost Estimator software and literature, especially U.S. National Renewable Energy
15 Laboratory (NREL) reports [31,42]. The values which are obtained from the literature
16 are scaled to the required size by using the capacity power law expression shown in
17 equation 1,

$$18 \frac{\text{Cost}_2}{\text{Cost}_1} = \left(\frac{\text{Capacity}_2}{\text{Capacity}_1} \right)^m \quad \text{Equation 1}$$

19 with m varying from 0.48 to 0.87, and adjusted to 2014 US dollars through the
20 Chemical Engineering Plant Cost Index [43]. For the South Korean scenario, the capital
21 cost is adjusted from its corresponding US market value by multiplying with the
22 purchasing power parity (PPP) between US and South Korea, which is 0.78 [44]. The

1 PPP is an economic factor that is used to adjust the exchange rate between countries so
 2 that the exchange rate reflects each country's actual purchasing power or cost of goods
 3 compared to the other country. The assumptions used for the economic analysis are
 4 summarized in Table 4.

5 **Table 4.** Economic parameters and indirect costs basis used in the analysis

Economic Parameter	Basis
Cost year for analysis	2014
Plant financing by equity/debt	50 %/ 50 % [45]
Internal rate of return (IRR)	10 % after tax [46]
Term for debt financing	10 years [46]
Interest rate for debt financing	8 % [46]
Plant life/analysis period	30 years [46]
Depreciation method	Straight Line depreciation 10 years for general plant and utilities
Income tax rate	35% [46]
Plant construction cost schedule	3 years (20% Y1, 45% Y2, 35% Y3) [47]
Plant decommissioning costs	\$0
Plant salvage value	\$0
Start-up period	3 months [46]
Revenue and costs during start-up	Revenue = 50% of normal Variable costs = 75% of normal Fixed costs = 100% of normal [46]
Inflation rate	1.75% [48] U.S., 1.10% [49] South Korea
On-stream percentage	90% (7,884 hours/year)
Land	6.5% of Total Purchased Equipment Cost (TPEC) [50]
Royalties	6.5% of TPEC [50]
Working capital	5% of Fixed Capital Investment (excluding land) [46]
Indirect costs	
Engineering and supervision	32% of TPEC [51]
Construction expenses	34% of TPEC [51]
Contractor's fee and legal expenses	23% of TPEC [51]
Contingencies	20.4% of TPEC [31]

6 The operating costs are broken down into fixed operating costs and variable operating
 7 costs. The correlations used for computing fixed operating costs are obtained from
 8 Seider et al. [50], and consist of items such as maintenance, labour related operations,

1 operating overhead, property tax, and insurance. The variable operating costs which are
 2 used for this study are summarized in Table 5. The values shown are adjusted to U.S.
 3 2014 dollars from their reference values by using an inorganic index obtained from the
 4 U.S. Bureau of Labor Statistics [52]. Besides the sale of butanol as a product, electricity
 5 (for configurations 1 and 2 only) and mixed alcohols are sold as co-products to generate
 6 additional revenue for the plant with the price of mixed alcohols computed as 90% of
 7 the price of gasoline on an HHV equivalent basis (obtained from Aspen Plus
 8 simulations).

9 **Table 5.** Cost of materials and products used in the analysis

Commodity prices in 2014 U.S. dollars	U.S.	South Korea
Seaweed cost (\$/dry tonne)	71.42 [53]	67.9 [54]
Olivine (\$/tonne)	304.75 [31]	PPP adjusted U.S. price
MgO (\$/tonne)	604.33 [31]	PPP adjusted U.S. price
Tar reformer catalyst (\$/kg)	53.16 [31]	PPP adjusted U.S. price
Alcohol synthesis catalyst (\$/kg)	28.58 [24]	PPP adjusted U.S. price
Solids disposal (Ash) (\$/tonne)	81.28 [31]	PPP adjusted U.S. price
Water makeup (\$/tonne)	0.47 [55]	PPP adjusted U.S. price
Boiler feed water chemicals (\$/kg)	6.79 [31]	PPP adjusted U.S. price
Cooling tower chemicals (\$/kg)	4.08 [31]	PPP adjusted U.S. price
LO-CAT chemicals (\$/tonne sulphur produced)	555.5 [31]	PPP adjusted U.S. price
Amine makeup (\$/ million kg acid gas removed)	44.15 [31]	PPP adjusted U.S. price
Waste water treatment (\$/tonne)	1.12 [31]	PPP adjusted U.S. price
Electricity (cents/kWh)	6.63 [56]	9.98 [57]
Gasoline (\$/L)	0.91 [56]	1.53 [57]
NG (\$/tonne)	397 [56]	1,221 [57]

10 **3. Results and Discussion**

11 **3.1 Process modeling results**

12 The three different design configurations (self-sufficient, NG import, and NG & power
 13 import) were simulated in Aspen Plus so as to be able to quantify the different mass and
 14 energy flows, as well as sizes of processing units. The stream conditions which
 15 correspond to Fig. 1 for the three different configurations are provided in the
 16 Supplementary Material. Table 6 summarizes the process modeling results for the

1 different configurations. The plant energy efficiency shown in the table is computed on
 2 an HHV basis, and is defined as the total HHV of the output products (butanol, mixed
 3 alcohols and electricity) divided by the total HHV of the input feedstocks (seaweed,
 4 NG, and electricity). It shows the major feed and product flows of the processes, as well
 5 as net power and energy efficiency of the processes.

6 **Table 6.** Major flowrates and process energy efficiency

	Case 1- Self-sufficient	Case 2 - NG import	Case 3 - NG & power import
Seaweed flow rate (kg/h)	45,631	45,631	45,631
NG requirement (kg/hr)	-	5,024	5,024
Total Product yields (kg/hr)	5,921	9,730	9,730
Butanol	2,782	4,572	4,572
Mixed alcohols	3,139	5,158	5,158
% products yield per feed (mass basis)	13.0	21.3	21.3
Net Electric Power Exported (MW)	3.24	5.04	-20.4
Power generation	16.04	24.79	-
Power consumption	12.8	19.75	20.4
Biomass HHV (MW)	178.09	178.09	178.09
NG HHV (MW)	-	90.17	90.17
Butanol HHV (MW)	28.85	47.41	47.41
Mixed alcohols HHV (MW)	29.07	47.77	47.77
Total input HHV + electricity import	178.09	268.26	288.66
Total output HHV + electricity export	61.16	100.23	95.19
Plant energy efficiency (% HHV basis)	34.34	37.36	32.98

7 From Table 6 it can be seen that the use of NG as a high temperature heat source leads
 8 to an increase in the liquid product yields in configurations 2 and 3. This is because
 9 more syngas can be diverted to the MAS reactor for conversion to butanol and mixed
 10 alcohols. The table also shows that configuration 2 has a higher net power production
 11 than configuration 1, while a net power import of 20.4 MW is required for configuration
 12 3. As a result of the higher net power production and total liquid product, the plant
 13 thermal efficiency of configuration 2 is higher than configurations 1 and 3. The
 14 requirement for power import reduces the plant thermal efficiency of configuration 3

1 making it have the lowest plant energy efficiency despite the increased liquid products
2 yield. The butanol and mixed alcohols HHVs are computed using Aspen Plus
3 simulations. Note though that the plant energy efficiency of the designed configurations
4 are low in comparison to similar plants which use cellulosic feedstock. For example, the
5 plant energy efficiency of a lignocellulosic biomass-to-butanol self-sufficient process
6 previously published by the authors is 46% on an HHV basis [24]. The main reason
7 behind this disparity is the high ash content in *L. Japonica* seaweed (23%) as compared
8 to the lower ash content ($< 7\%$) in cellulosic biomass. This means that there is much
9 less carbonaceous material in seaweed for conversion to fuel and thus the lower plant
10 energy efficiency values.

11 3.2 Economic analysis results

12 The economic analyses for the different process designs are carried out for a U.S.
13 market scenario and a South Korean scenario with the results summarized in Table 7.
14 Some important points stand out from the results. First of all the total capital investment
15 (TCI) for the different processes follow the same trends for both the US and South
16 Korean scenarios: the NG import configuration has the highest TCI followed by the
17 self-sufficient configuration, with the NG & power import configuration having the
18 lowest TCI. The NG import configuration has the highest TCI because it has the most
19 equipment in comparison to the other configurations, as well as the highest flows of
20 syngas and other process streams downstream of the gasifier. This means larger
21 equipment is needed leading to higher costs. Though the NG & power import case has
22 larger flows through the process in comparison to the self-sufficient case, its TCI is
23 lower because the absence of steam turbines and gas expanders leads to less equipment

1 and significantly lower direct costs in process sections such as the steam system and the
2 power generation section.

3 As for the operating costs, the relative trends remain the same for the U.S. and South
4 Korean scenarios; however the relative scale of the trends has changed. For the U.S.
5 scenario, the NG & power import configuration has the highest total operating costs
6 (TOC), followed by the NG import configuration and finally the self-sufficient
7 configuration. This trend is because the NG & power import configuration has
8 additional costs related to the purchase of NG and electricity, with electricity import not
9 required for the NG import configuration, and import of power and NG not required for
10 the self-sufficient configuration. Note that the scale of the relative differences for the
11 US scenario is much smaller than the South Korean scenario because the cost of energy
12 (NG and electricity) is relatively much higher in South Korea than the US, thus the
13 energy costs dominate the operating costs in the South Korean market scenario. This
14 dominance of the energy costs in the South Korean scenario is clearly shown by the
15 increase in TOC for the NG import and the NG & power import configurations in the
16 South Korean scenario in comparison to their US scenario counterparts.

17 The flipside of the increased energy costs in the South Korean market is that co-
18 products such as mixed alcohols and electricity export have more value (since they are
19 assumed to be proportional to the local gasoline price) and thus bring in more revenue
20 in comparison to the US scenario. Thus the total co-product revenues are the highest in
21 the South Korean scenario.

22 In regards to the MBSP, the lower cost of capital and the higher total co-product
23 revenues for the South Korean cases lead to lower MBSP values for the South Korean

1 cases relative to their equivalent US cases. For each case, the relative difference
2 between the markets is attributable to the TOC. For instance, the self-sufficient plant
3 has the largest magnitude in MBSP difference between markets because the TOC in the
4 South Korean market is 14% lower than in the US market. However, NG & power
5 import case has the smallest MBSP difference between markets because the TOC in the
6 South Korean market is 25% higher than the US market, which is the greatest amongst
7 all the configurations.

8 In general, the total co-product revenue appears to be a good indicator for the MBSP in
9 terms of relative profitability of each case. For instance the South Korean - NG import
10 case has the lowest MBSP because it has the highest total co-product revenue, while the
11 U.S - self-sufficient case has the highest MBSP because it has the lowest total co-
12 product revenue. However there are two exceptions. For the first exception, the MBSP
13 of the US - NG & power import case is lower than that of the US - NG import case.
14 This is because in the US market the cost of capital dominates energy costs, thus the
15 differences in TOC and total co-product revenue for the US market for these two cases
16 are much smaller than in their equivalent South Korean cases leading to a higher MBSP
17 for the US - NG & power import case in comparison to the US - NG case. The second
18 exception is that the MBSP of the US - NG & power import case is lower than that of
19 the South Korean - self-sufficient case. The reason behind this exception is the much
20 lower yield in butanol product in the self-sufficient process design in comparison to the
21 NG & power import design (see butanol yield in Table 6). The much lower butanol
22 yield in the self-sufficient case means that a much higher MBSP is required to make the
23 NPV zero, thus the higher MBSP for the South Korean - self-sufficient case despite its
24 higher total co-product revenue in comparison to the US - NG & power import case.

1 The MBSP values obtained for the different case studies range from 1.97 \$/L in the
2 South Korean - NG import case to 3.33 \$/L in the US - self-sufficient plant case. These
3 values are high in comparison to biobutanol obtained from cellulosic biomass sources.
4 For example, Okoli and Adams [24] obtained an MBSP of 0.83 \$/L from a self-
5 sufficient thermochemical lignocellulosic biomass to butanol process which was
6 designed on a similar basis to the designs discussed in this study (albeit at a larger
7 biomass feed rate of 2,000 tonnes per day), while Qureshi et al. [58] obtained an MBSP
8 of 1.05 \$/L for a biochemical wheat straw-to-butanol process.

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- 1 **Table 7.** Economic summary for case studies in US and South Korea scenarios (a more
 2 detailed breakdown is provided in the supporting information)

Plant design	US			South Korea		
	Self-sufficient plant	NG import	NG & power import	Self-sufficient plant	NG import	NG & power import
Capital Investment (\$'000)						
<i>Direct costs breakdown</i>						
Gasification	38,239	38,239	38,239	29,826	29,826	29,826
Gas Cleanup	41,221	51,069	50,269	32,152	39,834	39,210
Mixed Alcohol Synthesis	4,638	6,878	1,484	3,618	5,365	1,157
Alcohol Separation	12,269	13,651	13,651	9,570	10,648	10,648
Steam system & Power Gen.	41,047	54,312	4,613	32,017	42,363	3,598
Cooling Water & Other Utilities	10,448	11,211	11,211	8,150	8,744	8,744
Total Direct Costs	147,863	175,360	119,466	115,333	136,781	93,184
Engineering & Supervision	22,128	26,863	17,055	17,260	20,953	13,303
Construction Expenses	23,511	28,541	18,121	18,339	22,262	14,135
Contractor's Fee & Legal Expenses	15,904	19,307	12,258	12,406	15,060	9,562
Contingency	14,107	17,125	10,873	11,003	13,357	8,481
Royalties	4,470	5,344	3,555	3,487	4,168	2,773
Land	4,470	5,344	3,555	3,487	4,168	2,773
Working Capital	11,399	13,627	9,066	8,891	10,629	7,072
Total Capital Investment	243,852	291,511	193,951	190,205	227,379	151,282
Operating costs (\$'000/year)						
Seaweed	25,693	25,693	25,693	24,428	24,428	24,428
NG	-	13,113	13,113	-	43,942	43,942
Catalysts & Chemicals	1,268	1,695	1,722	989	1,322	1,344
Waste Stream Treatment	7,364	7,425	7,425	5,744	5,791	5,791
Water Makeup	51	35	50	40	27	39
Electricity Import	-	-	8,414	-	-	12,665
Labour Related Costs	22,377	22,377	22,377	18,734	18,734	18,734
Maintenance Costs	15,304	18,150	12,365	11,937	14,157	9,644
Operating Overheads	6,237	6,590	5,873	5,820	6,095	5,536
Property Taxes & Insurance	2,957	3,507	2,389	2,307	2,736	1,864
Total Operating Costs	81,252	98,585	99,422	69,999	117,233	123,988
Co-prod. revenues (\$'000/year)						
Mixed Alcohols	19,459	31,980	31,980	32,849	53,986	53,986
Electricity Export	1,690	2,631	-	2,544	3,961	-
Total co-prod. revenue	21,149	34,612	31,980	35,392	57,947	53,986
MBSP (\$/l)	3.33	2.25	2.07	2.15	1.97	2.01
Butanol Revenue at MBSP (\$'000/year)	89,816	99,618	91,657	57,835	87,326	89,199

1 3.3 Cost of CO₂ equivalent emissions avoided

2 Due to the emission of climate changing greenhouse gases associated with fossil
3 derived fuels, one major objective behind development of biofuels is to minimize
4 greenhouse gas emissions from the transportation sector in a cost effective way. Thus
5 one metric for comparing different biofuel processes is the cost of CO₂e avoided. The
6 cost of CO₂e avoided is defined as the additional cost required to avoid the emission of
7 a unit of CO₂e when a biofuel is combusted in place of a fossil fuel, thus the lower the
8 value the better. This metric is a good indicator for comparing biofuel processes to each
9 other and to non-biofuel processes because it factors in both cost and life cycle impacts.
10 For this work conventional gasoline is used as a baseline for computing the cost of
11 CO₂e, and this is done by using equation 2. Note that this equation is only applicable in
12 cases where the carbon intensity of gasoline is higher than the carbon intensity of the
13 biofuel. This is because if the carbon intensity of the biofuel process is greater than that
14 of gasoline then it is not worth investing in that biofuel process as it does not help offset
15 CO₂e.

16 *CO₂e avoidance cost =*

17
$$\frac{MBSP \left(\frac{\$}{MJ}\right) - \text{wholesale gasoline price} \left(\frac{\$}{MJ}\right)}{\text{Carbon intensity of gasoline} \left(\frac{kgCO_2e}{MJ}\right) - \text{carbon intensity of biobutanol} \left(\frac{kgCO_2e}{MJ}\right)}$$
 Equation 2

18 The carbon intensity of gasoline is the total wells-to-wheels life cycle emissions, made
19 up of the sum of the direct combustion CO₂e of gasoline when used in a vehicle plus the
20 indirect CO₂e of its entire upstream supply chain, including oil drilling, production,
21 refining, and transportation (all greenhouse gas chemicals are considered and expressed
22 in terms of CO₂e using the IPCC 100-year metric [59]).

1 For each butanol process, the carbon intensity is similarly the wells-to-wheels CO₂
2 emissions of the biofuel, including all emissions associated with its production, the
3 indirect emissions of utilities used in the process, and the final combustion of the fuel
4 itself. For NG, this includes indirect emissions related to its production from the well
5 and transportation of NG to the biobutanol plant, as well as direct emissions from its
6 combustion for heating purposes at the plant. More than 90 % of the NG used in South
7 Korea is obtained from liquefied NG (LNG) imports. Thus for this analysis LNG used
8 in South Korea is assumed to be purchased and shipped from the US. The upstream,
9 liquefaction and regasification life cycle inventory (LCI) data are obtained from PACE
10 [60], while the shipping emissions for transportation from US to South Korea is
11 obtained from Abrahams et al. [61].

12 For electricity, the carbon intensity includes indirect emissions related to its generation
13 and transmission to the biobutanol plant, including the production, delivery, and use of
14 all fuels used to produce power for the electric grid, which is different for the United
15 States and South Korea. The indirect and direct gasoline emissions are assumed to be
16 the same for both US and South Korea. Note also that all energy values reported here
17 are assumed to be on a HHV basis with conversion factors for conventional gasoline
18 taken from CTA & ORNL [62].

19 The emissions associated with harvesting seaweed (which include production,
20 mechanical pretreatment, drying and transportation) are assumed to be the same as
21 reported in a study of brown seaweed harvested in Norway (about 176 kg CO₂e/tonne
22 dry seaweed) [63] since data for *L. Japonica* in South Korea and U.S. were not
23 available. Furthermore, it was assumed that all carbon in the seaweed originated from

1 atmospheric CO₂, and thus the biogenic CO₂ uptake can be computed from the ultimate
 2 analysis of the seaweed as shown in Table 1. Finally, an allocation factor computed as
 3 the fraction of butanol product in the total product mix on a HHV basis (see Table 6) is
 4 used to allocate CO₂e from the seaweed-to-biofuel process to butanol. A summary of all
 5 direct and indirect CO₂e along the cradle-to-gate life cycle considered in this analysis
 6 are shown in Table 8.

7 **Table 8.** Indirect and direct CO₂e data used for this analysis

Emissions (kgCO ₂ e/GJ)	US	South Korea
Indirect NG emissions	8.4 [64]	26.63 [60,61]
Indirect electricity emissions	21.26 [65]	18.79 [65]
Indirect seaweed emissions (harvesting, pre-treatment and transportation)	12.53 [63]	12.53 [63]
Indirect gasoline emissions	17.36 [66]	17.36 [66]
Direct gasoline emissions	67.87 [67]	67.87 [67]

8 Very interesting insights are obtained by looking at CO₂e avoided costs, which are
 9 shown in Table 9. The first major insight is the very high values of the CO₂e avoided
 10 cost for the NG & power import cases in comparison to the other cases, despite the NG
 11 & power import cases being amongst the lowest in terms of MBSP. These large values
 12 are directly attributable to the indirect emissions associated with electricity import for
 13 these cases. In fact the CO₂e from the South Korean - NG & power import case are
 14 greater than that of gasoline thus this plant should not be considered for CO₂e avoidance
 15 purposes as it does not help offset CO₂e. Furthermore, the low CO₂e for the self-
 16 sufficient plant cases have led to these cases having some of the lowest CO₂e avoided
 17 costs, with the South Korean - self-sufficient plant having the lowest CO₂e avoided cost.

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1 **Table 9.** Summary of cost of CO₂e avoided calculations

Plant	U.S.			South Korea		
	Self sufficient	NG import	NG + power import	Self sufficient	NG import	NG + power import
Seaweed Growth	-1,189	-1,189	-1,189	-1,189	-1,189	-1,189
Seaweed supply chain	176	176	176	176	176	176
Seaweed to Butanol process	880	981	981	880	981	981
Indirect Emissions from Natural Gas	-	61.47	61.47	-	194.88	194.88
Indirect Emissions from Electricity	-	-	35.20	-	-	31.11
Well to plant exit emissions (kgCO ₂ e/dry tonne seaweed)	-132.83	30.35	65.55	-132.83	163.76	194.87
Well to plant exit emissions allocated to Butanol (kgCO ₂ e/GJ)	-26.76	3.73	8.48	-26.76	20.12	25.21
Direct Emissions from Butanol use (kgCO ₂ e/GJ)	63.32	63.32	63.32	63.32	63.32	63.32
Well to wheel emission for Butanol (kgCO ₂ e/GJ)	36.36	66.85	71.61	36.36	83.25	88.34
CO ₂ e avoided (kgCO ₂ e avoided/GJ)	48.87	18.38	13.62	48.87	1.98	-3.11
MBSP (\$/L)	3.33	2.25	2.07	2.15	1.97	2.01
MBSP (\$/GJ)	110.12	74.40	68.45	71.10	65.14	66.47
Biofuel Marginal cost (\$/GJ)	85.80	50.08	44.13	30.09	24.14	25.46
CO ₂ e avoided cost (\$/t CO ₂ e avoided)	1,756	2,724	3,239	616	12,170	*N/A

2 *N/A - not applicable because the well to wheel emissions for butanol are greater than
3 the well to wheel emissions for gasoline.

4 The CO₂e avoidance costs for these processes are quite high, but are still in the general
5 range of other biofuels. Ryan et al. [68] estimate the cost of CO₂e avoided for European
6 biofuels to be between \$277 - 2,524 per tonne of CO₂e avoided (Euro converted to USD
7 using December 2014 exchange rate) while Fulton et al. [69] puts this cost at \$180 - 874
8 per tonne of CO₂e avoided for ethanol from different biomass sources. The only
9 exception to this is ethanol from sugar cane in Brazil which has a much more practical
10 cost of CO₂e avoided (around \$30/tonne of CO₂e) [69]. This is due to the very high
11 productivity of sugarcane crops in Brazil, and the utilization of its co-products to

1 provide process energy, and also in most cases export electricity resulting in near zero
2 fossil fuel requirements [68,69]. Note that even though the estimated cost of CO₂e
3 avoided for seaweed is in range with other biofuels it is still not competitive with the
4 \$50 per tonne of CO₂e avoided abatement costs recommended by policy makers in most
5 western countries for investment in CO₂ abatement technologies [69].

6 However, it is important to note that the baseline for this analysis is gasoline from
7 conventional crude oil which has lower environmental and economic costs in
8 comparison to unconventional oil from sources such as tar sands and shale oil. In North
9 America, these unconventional oil sources have estimated reserves which are much
10 greater than the estimated reserves of conventional oil, and release much more CO₂e in
11 the production process [70]. It has been noted in some estimates that oil from tar sands
12 releases up to two to six times the amount of CO₂ released per barrel of oil produced
13 from conventional oil [70–72]. Thus if the baseline for computation of CO₂e avoidance
14 costs is changed from conventional gasoline to unconventional gasoline the potential for
15 biobutanol from seaweed improves.

16 3.4 Sensitivity analysis

17 It is important to carry out sensitivity analysis to evaluate the impact that the variations
18 of some of the key parameters used in this study have on MBSP and CO₂e avoided
19 costs. This is because of inherent uncertainties in some of the assumed values for the
20 key costs and parameters. A sensitivity analysis is carried out on the self-sufficient and
21 NG import process designs for US market and the self-sufficient design for the South
22 Korea market, as these options offer the best value on CO₂e avoided cost.

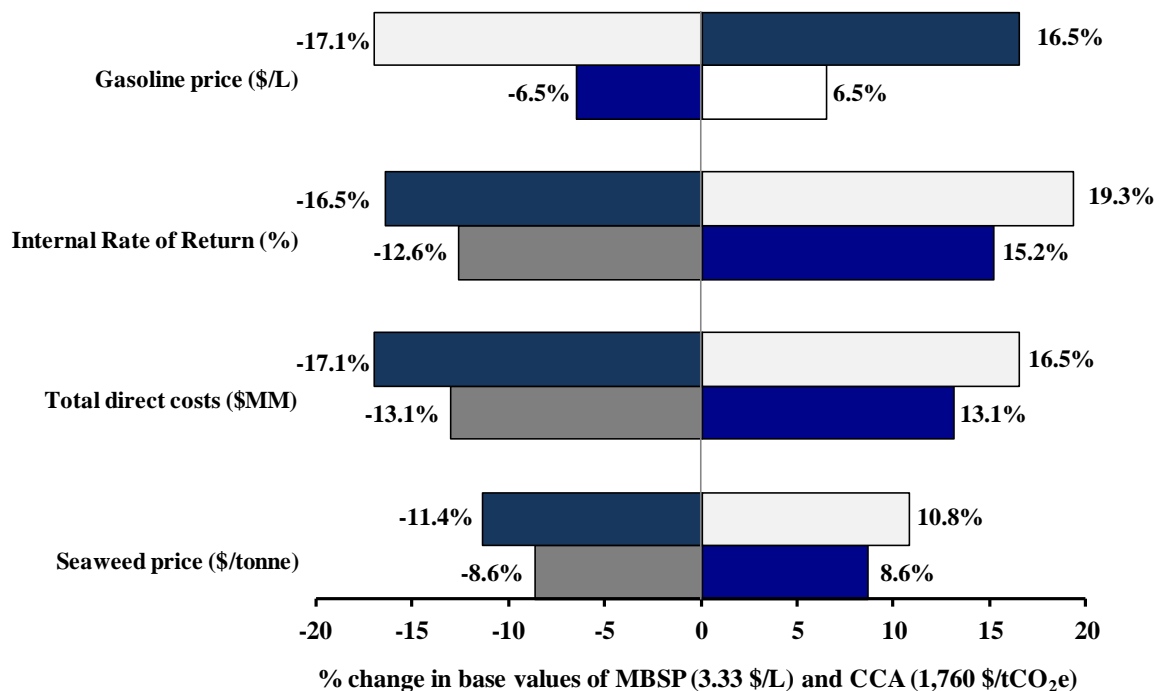
1 **Table 10.** Input parameters for sensitivity analysis

	U.S.	South Korea	deviation amounts
Seaweed price (\$/tonne)	71.42	67.90	+/- 30 % deviation
Total direct costs (\$MM)	175.36	136.78	+/- 30 % deviation
Internal Rate of Return (%)	10	10	+/- 5 units deviation
NG price (\$/tonne)	397.22	1006.38	+/- 30 % deviation
Gasoline price (\$/L)	0.91	1.53	+/- 30 % deviation

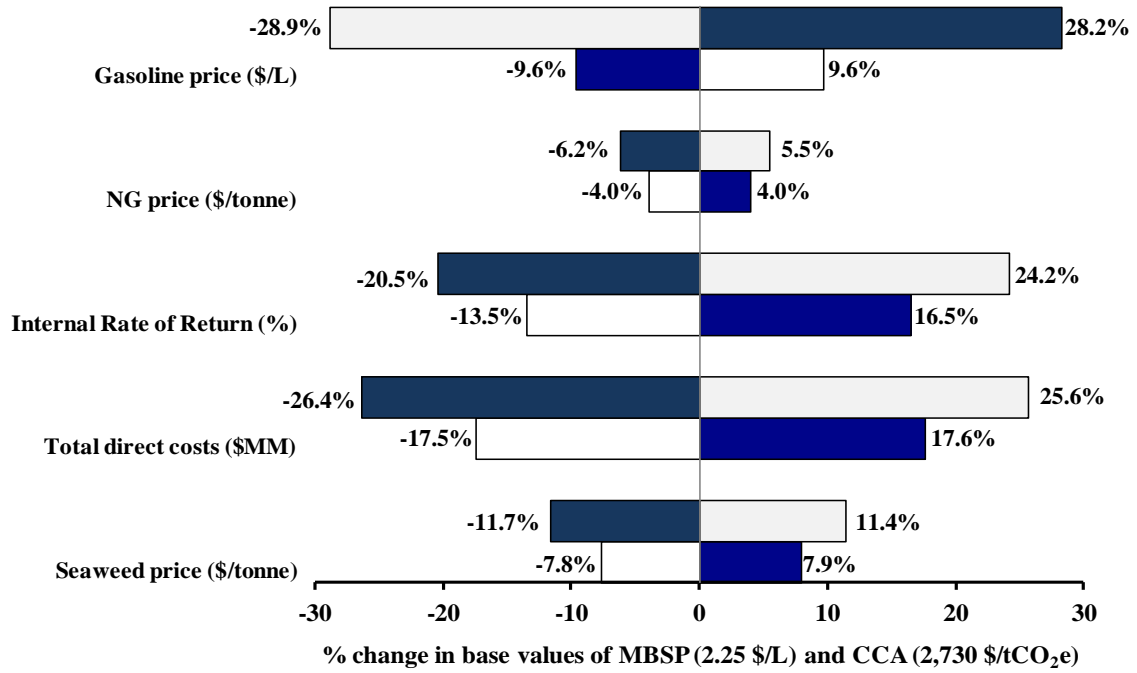
2 Table 10 shows the base case values of the varied parameters and the amounts they are
3 perturbed. The results of the sensitivity analyses for the selected cases are shown in
4 Figs. 2 - 4. The vertical axes show the parameters that are varied while the horizontal
5 axes is the percentage deviation in the response variables, MBSP and cost of CO₂e
6 avoided (CCA), from their base values. The top bars with solid fills represent the
7 percent deviation in the cost of CO₂e as a result of variations in input parameters while
8 the bottom bars with hatched fills represent the percent deviation in the MBSP as a
9 result of input parameters variations. Aside from gasoline price which has an indirect
10 correlation with MBSP and cost of CO₂e, there is a direct correlation between the other
11 sensitivity input parameters and the response variables.

12 Some interesting points can be noted from the sensitivity analysis. First, as can be seen
13 from Figs. 2 - 4, the cost of CO₂e avoided is more sensitive to changes in the input
14 parameters in comparison to the MBSP, with the South Korean market case (Figs. 4)
15 being generally more sensitive. Secondly, deviations in gasoline prices have the most
16 impact on the cost of CO₂e avoided for all the cases. This impact increases from Fig. 2
17 to Fig. 4. For example, in Fig. 4 increasing the gasoline price by 30% results in a 82%
18 reduction in the cost of CO₂e avoided, while reducing the gasoline price by 30% results
19 in a 79% increase in the cost of CO₂e avoided. The increased sensitivity of the cost of
20 CO₂e avoided to gasoline prices for the South Korean cases is because the revenue per

1 unit of mixed alcohols is directly correlated to the unit price of gasoline, thus the higher
 2 gasoline prices in South Korea coupled with the lower cost of capital mean that the
 3 revenue from mixed alcohols have more impact on the MBSP and also cost of CO₂e
 4 avoided. Thus any changes in gasoline price will impact the MBSP and cost of CO₂e
 5 avoided of the South Korean cases more. In general, the South Korean case is more
 6 sensitive to operating cost and revenue items in comparison to the US cases, while the
 7 US cases are more sensitive to capital cost related items such as TDC and IRR. This is
 8 expected, as from the economic analysis results summarized in Table 7 it was shown
 9 that the energy related costs have a more dominant effect on the MBSP and cost of
 10 CO₂e avoided for the South Korean cases while the capital related costs dominate for
 11 the U.S cases.

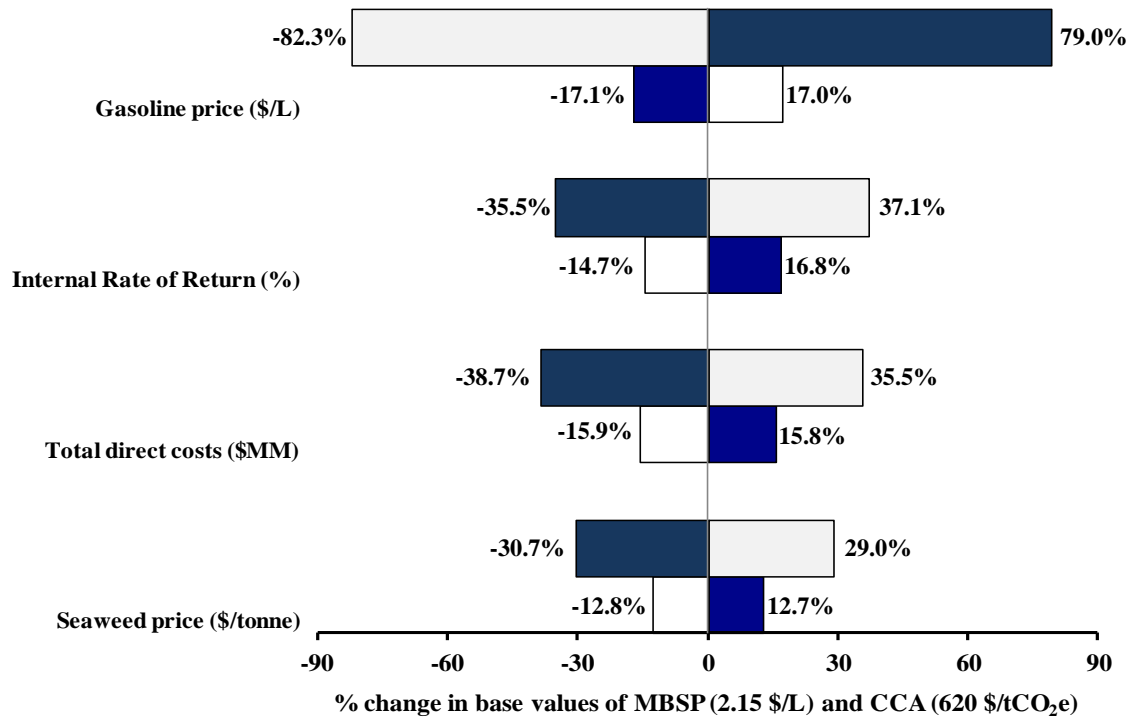


12
 13 Figure 2: The effects of changing key parameters from their base case values on MBSP
 14 (bottom bars with hatched fill) and CCA (top bars with solid fill) of the US - self-
 15 sufficient plant scenario.



1
 2 Figure 3: The effects of changing key parameters from their base case values on MBSP
 3 (bottom bars with hatched fill) and CCA (top bars with solid fill) of the US - NG import
 4 plant scenario.

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1
2 Figure 4: The effects of changing key parameters from their base case values on MBSP
3 (bottom bars with hatched fill) and CCA (top bars with solid fill) of the South Korea -
4 self-sufficient plant scenario.

5 4. Conclusions

6 This work is the first study (to the authors' knowledge) of the techno-economic
7 potential of seaweed-to-biobutanol processes based on a thermochemical route.
8 Different process configurations were designed and simulated, and their economic and
9 environmental feasibility were assessed and quantified using metrics such as the MBSP
10 and cost of CO₂e avoided for different market scenarios.

11 The MBSP results showed that the NG import and NG & power import configurations
12 have the lowest MBSP values in their individual markets. However, when the cost of
13 CO₂e avoided was used as a metric the self-sufficient configurations had the best values
14 in their individual markets with the NG & power import configurations the worst.

1 The most significant result obtained in the sensitivity analysis is that +/- 30% deviations
2 in gasoline prices lead to > +/- 75% deviation in the cost of CO₂e avoided for the South
3 Korean self-sufficient configuration. This is because in comparison to the US market,
4 energy related costs have a more dominant impact in the South Korean market. When
5 MBSP is used as a metric the seaweed biomass-to-butanol process using the
6 thermochemical route, with values ranging from 1.97 \$/L to 3.33 \$/L, is high in
7 comparison to other butanol produced from cellulosic feedstock. However its cost of
8 CO₂e avoided, which ranges from 620 - 2,720 \$/tCO₂e avoided for the best three cases
9 is in line with that of other first and second generation biofuels, but much higher than
10 the break-even value of 50 \$/tCO₂e recommended by policy makers in western
11 countries.

12 These results show that more research on the macroalgae supply chain (harvesting to
13 processing plant) and conversion technologies is required to improve the economic and
14 environmental potential of biobutanol from seaweed.

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