

Techno-Economic and Life Cycle Analysis of Mixalco® Processes For Mixed Alcohol Production From Brown Algae

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Abstract

The need for producing renewable fuels from biomass has increased due to depleting fossil resources and environmental concerns. However, the low fraction of biomass carbon converted to product is an undeniable drawback for most current biofuel productions from fermentation due to undecomposed lignin in biomass composition and carbon loss as CO₂. In this work, two main production routes of the MixAlco® process, the Ketonization route (KR) and Esterification route (ER) are evaluated for the mixed alcohol production by brown algae, third-generation biomass without lignin. A Novel Fermentation process using syntrophic bacteria consortia (SBC) is developed to produce acetic acid from waste gas produced by KR and ER process. The paper investigates the integrated flowsheet for these alternative routes, using techno-economic and life cycle analysis to compare the minimum selling price and environmental impacts. The ER's capital and operating cost combined with the SBC is the highest compared with other routes. The cost of raw materials and utilities are the two major cost factors for all the processing routes examined. ER process performs the best in terms of environmental impacts except in water depletion compared with other processes, while the KR process performs the worst regarding the environmental metrics.

Introduction

World energy demand has multiplied over the past few centuries, along with the human population growth. The increasing production and utilization of these fossil fuels shows an exhausted trend and generates many greenhouse gases like SO₂, NO, and CO₂, which seriously pollute the environment. Therefore, renewable energy sources like sunlight, tides, and biomass have drawn researchers' attention. The production of biochemicals and biofuels makes biomass a more promising renewable energy source that can take the place of fossil fuel resources. In 2016, the International Energy Agency reported biofuels (comprised of solid biofuels, liquid biofuels, biogases, industrial waste, and municipal waste) contributed 1.35 million ktoe (kilotonne of oil equivalent) of energy to the 13.76 million ktoe of world energy demand or about 9.8% of total energy demand^[1]. Meanwhile, a lot of effort on conceptual design, optimization, and other design methodologies has been made to promote biofuel production. The feasibility, sustainability, and environment-friendliness of the designs are determined to increase these designs' possibility to be introduced to an industrial scale^[2-5].

The MixAlco® process is a well-established bio-refining technology that utilizes biomass to produce biofuels^[2-4]. Through biocatalysts and biotransformation processes, carboxylic acids are formed from biomass. Then the process converts these acids into ketones and esters and finally produce mixed alcohol – a renewable gasoline type fuel^[5]. To achieve the first step of alcohol production, non-lignin parts of the biomass are favorable: carboxylate, proteins, and lipids are needed to produce carboxylic acid through fermentation. The ketonization route (KR)^[2,3] and the esterification route (ER)^[4,5] are the two main routes for the MixAlco® process (Fig. 1).

The choice of biomass will affect the feasibility and process economics for different designs. Many of the previous work in this area focused on the first and second generation of biomass. In this work, we use brown algae, which as a third-generation biomass, has the advantage of having a high weight percent of carbohydrates, protein, and liquids and no lignin^[4-6], making it a suitable biomass raw material for the MixAlco® process. The detailed composition of algae is given in the methodology section.

In 2016, the economics of the MixAlco® process using brown algae as a feedstock was evaluated by Peyman et al.^[4]. However, one of the undeniable shortcomings of this biofuel production is that the low fraction of biomass carbon is converted into products while most of the CO₂ and H₂ is directly released to the environment. More specifically, over one-third of biomass carbon is lost to CO₂^[7]. To address this problem, Papoutsakis' lab is developing synthetic syntrophic bacteria consortia of *Clostridium kluyveri* and *Clostridium ljungdahlii*^[8]. The co-existence of these two microbes can enable fast and efficient utilization of carbon and electrons in the substrates by importing additional electrons as needed from H₂. In this work, we designed a Novel Fermentation process using syntrophic bacteria consortia (SBC), taking CO₂, H₂, and ethanol to produce higher carbon carboxylic acids with higher efficiency. Since a large amount of CO₂ and H₂ are generated from the anaerobic

digestion process in KR and ER, the SBC process is being directly integrated into ketonization and esterification routes (KR + SBC and ER + SBC).

Our goal is to develop the flowsheet of the four bio-refining routes: KR, ER, KR + SBC, and ER + SBC for mixed alcohol production from algae and calculate the minimum selling price for each route using techno-economic analysis and predict the environment influence by using life cycle analysis. The rest of the manuscript is structured as follows: Process description is discussed in the next section, and the details of flowsheets for each process. The assumptions required to perform process simulation, economic analysis, and life cycle analysis are discussed. In the last simulation, economic and life cycle results are shown and discussed for all four production routes.

Methodology

Techno-economic and life cycle analysis are the primary tools used in this work to compare the different biofuel production routes' in terms of economic feasibility, sustainability, and environmental performance. The framework constitutes the following:

1. Data Collection: Before starting the simulation, all the information such as chemical formula, structure, and thermodynamic properties for raw materials; detailed reaction pathways; process design, and operating details are collected from either laboratory data or literature.
2. Conceptual Design and Process Simulation: To study process feasibility, a detailed process flowsheet for different scenarios is designed and combined in simulation software. The input information helps the simulation to understand what the user wants to achieve and calculate the desired product.
3. Heat Integration: Heat integration is implemented to generate detailed heat support/exchange designs and energy consumption, which is then integrated with the simulation. This calculation aims to improve the entire process's energy efficiency, reduce energy consumption, and find the bottlenecks of the process.
4. Techno-economic Analysis: Techno-economic is carried out to determine the process's economic sustainability by calculating the capital and operating cost and the product's minimum selling price.
5. Life Cycle Analysis: Life cycle analysis is performed to identify the environmental performance and find essential parameters to commercialize the designed process.

In this work, since the simulation and part of the analysis are designed based on laboratory experiments and not actual pilot plant data from the industry, assumptions are taken, and deviation can arise. The results are used to guide any modifications needed to the base process design. The entire sequence is repeated (if needed) until an efficient production platform is generated with respect to economic and environmental sustainability metrics.

2.1 Process description

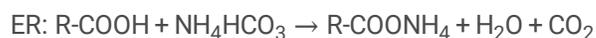
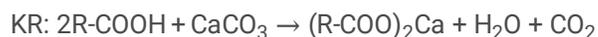
Anaerobic digestion process

This fermentation process is a single-stage process where dry algae are anaerobically fermented to produce mixed acids, including acetic, propionic, and butyric acids, through the following reactions^[4]

Table 1
Anaerobic digestion reactions

Component	Reaction	Conversion
Laminaran & cellulose	$5C_6H_{10}O_5 + 9H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 12H_2$	70%
Mannitol	$5C_6H_{14}O_6 + 4H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 17H_2$	70%
Alginate	$5C_6H_8O_6 + 12H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 10H_2$	56.5%
Fucose	$5C_6H_{12}O_5 + 9H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 17H_2$	70%
Protein	$23C_{13}H_{25}O_7N_3S + 99H_2O + 26H_2 \rightarrow 78C_2H_4O_2 + 26C_3H_6O_2 + 13C_4H_8O_2 + 13CO_2 + 69NH_3 + 23H_2S$	50%
Lipid	$46C_{18}H_{34}O_2 + 294CO_2 + 238H_2O + 102H_2 \rightarrow 306C_2H_4O_2 + 102C_3H_6O_2 + 51C_4H_8O_2$	50%

The anaerobic digestion lasts for five days at 35°C^[9]. The acid concentration is kept at around 5 wt.% by adding water (fresh and recycled). Iodoform is added to prevent the formation of by-products, such as methane^[5]. The mixture acids are then converted to their corresponding carboxylate salts with the help of calcium carbonate (KR)^[4] or ammonium bicarbonate (ER)^[5]:



After the separation of undissolved gases and unreacted biomass, the product is pumped to the drying process for further treatment. 90% of the unreacted biomass is recycled to the fermenter, and the rest are treated as waste.

Dewatering and drying process

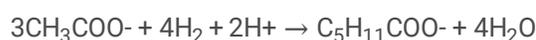
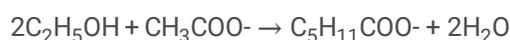
The process of dewatering and drying has been well studied, and our design is based on published studies^[3, 4, 10]. Dry carboxylate salts are the desired product for this process. The dewatering unit consists of 6 stages of evaporators, and 10°C of minimum temperature difference is addressed to the hot and cold streams for each stage. All the heat exchangers are using countercurrent flow. A pressure gradient is imposed on the six stages so that the water steam generated in each stage can be used as the heat source for the next stage. After the dewatering process, the concentrated salts stream achieved a concentration of ~ 50 wt.% and is pumped to a rotary dryer, which uses high temperature to produce dry carboxylate salts.

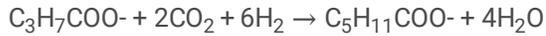
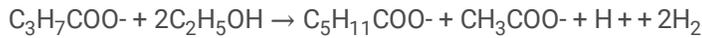
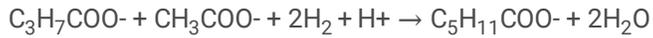
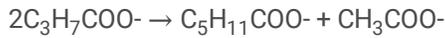
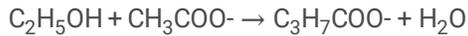
SBC fermentation process

This process is currently developing by the University of Delaware^[8] and is based on synthetic syntrophic consortia of Clostridium organisms for fast and efficient utilization of minimally pretreated biomass for producing targeted metabolites. In this work, we designed a two-stage fermentation process. In the first stage, the gas collected from the anaerobic digestion process ($H_2 + CO_2$) is injected into the fermenter, where Clostridium ljungdahlii (Clj) can produce acetic acid with the help of H_2 and CO_2 by the Wood-Ljungdahl pathway^[11]



This fermentation lasts for 74 hours at 37°C, and carbon dioxide can be fully utilized if enough hydrogen is provided^[7, 8]. In the second stage, acetic acid from the first stage and ethanol that bought from the market are utilized by Clostridium kluyveri (Ckl) to produce higher carbon carboxylic acids and the metabolic pathways below^[12, 13]:

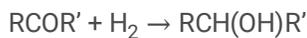




Yin et al.'s work^[12] shows the acetic acid can be fully consumed if a 10:1 mass ratio of ethanol to acetic acid is achieved. Like the anaerobic digestion process, the acids are then converted to the corresponding carboxylate salts with the same reactions.

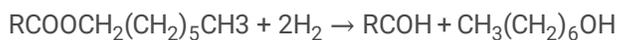
Ketonization and hydrogenation process

Ketonization and hydrogenation process is a two-stage process where the carboxylate salts are first converted into ketones, and then ketones are subsequently converted into their corresponding alcohols. In the first stage, two carboxylate salts are decomposed in the reactor to form ketone and calcium carbonate at a temperature of 430°C and 30 mmHg^[10, 14]. The ketones are in vapor form and easily separated from the solids and are then condensed to liquid at -10°C. The second stage consists of three continually stirred tank reactors (CSTR) operating at 130°C and 55 bar, where the ketones' hydrogenation occurs. Solid Raney-nickel-catalyst is used in the reactors with a 98.4% conversion of the ketones^[2, 15]. The mix-alcohol product is cooled to liquid form, and the unreacted hydrogen is recycled for further utilization. The ketonization and hydrogenation reactions are as following^[3, 14]



Esterification and hydrogenation process

In this process, the dried carboxylate salts are first converted into esters, and then esters are converted to alcohols. In the esterification reactor, the salts are reacted with heptanol to produce mixed esters, water, and ammonia in the presence of a solid acid catalyst^[16, 17]. The reaction occurs at 150°C, with a conversion of 95% of the carboxylate salts^[5]. Alcohols are produced from esters via hydrogenation reaction at 200 psi and 200°C, with a conversion of 97% in the presence of Raney-nickel-catalyst^[5, 18]. The esterification and hydrogenation reactions are as following^[4, 19]



2.2 Simulation analysis

The different processing scenarios are simulated in Aspen Plus V8.8. Most of the components involved in the reactions are directly selected from the Aspen database. For those components that are not included in Aspen databanks (i.e., proteins, high carbon carboxylates), user-defined components are used with chemical formulas, atom structures, and property parameters are taken from the literature^[20]. If the components have no specific information on the structures and properties (i.e., lamina, lipid), surrogates like the components are used. In this work, protein from biomass is user-defined with limited information. High carbon carboxylates are first defined with chemical formulas and structures; the properties are taken from the low carbon carboxylates available in the NRTL databank. Cellulose and oleic acid are used as surrogates for lamina and lipid. Multiple thermodynamic models can be used in Aspen Plus's process simulation, and the proper selection and correct use of the thermodynamic model determine the accuracy, reliability, and success of the simulation. NRTL thermodynamic package is selected for the property method to predict the liquid-liquid and liquid-vapor behavior^[21]. Next, heat integration is carried out

using Aspen Energy Analyzer V8.8 to generate the optimal heat exchanger network designs. The lowest operating cost is the key feature that we selected to choose the design for further research.

To enable process simulation and heat integration, the following assumptions are made:

1. Composition of brown algae is assumed to have 12% protein, 2% lipids, 12% Mannitol, 14% laminarin, 23% alminarin, 6% cellulose, 5% fucoidin and 26% ash (mass fraction) [22].
2. The mixture of components does not affect the conversion and selectivity of any reactions.
3. Bacteria is assumed to be killed after each fermentation reaction is over.
4. For the anaerobic digestion process, the solid filtration processes are assumed to have a full separation fraction, and 90 wt.% of the unreacted biomass is recycled.
5. We assume 95 wt.% of the produced CaCO_3 in the ketonization process is recycled back to the anaerobic digestion process and SBC process.
6. Heptanol is assumed to be separated and recycled[4].
7. Ammonium bicarbonate production using ammonia, water, and carbon dioxide is a well-known process and uses specialized equipment and reaction which cannot be designed in Aspen plus. Assume 99.5 % of the ammonium bicarbonate is produced from ammonia, water, and carbon dioxide produced in the ER process.

2.3 Techno-economic Analysis

Aspen Economic Analyzer® V8.8 is used to perform economic analysis for our four process routes: KR, ER, KR + SBC, and ER + SBC and the minimum product price of the final product, which is defined as the selling price of the product when the net present value (NPV) is zero^[23], is calculated. The capital and operating costs estimated by Aspen Economic Analyzer® V8.8 are based on the first quarter's price in 2014^[21]. The input chemicals' production cost is used to determine the minimum selling price of mixed alcohol^[24]. The plant's capacity is assumed to be 500,000 metric tons/year of brown algae, and the selling price of brown algae is \$80 per metric ton^[4, 25]. Some additional assumptions are necessary to perform the economic analysis:

1. The plant operates in a continuous mode for 8,000 hours per year, and we assume the plant's economic life is 20 years and the recovery period is 10 years. The internal rate of return on investment is assumed to be 15%, and the escalation rate is 3.5%. 35% tax is applied to the profits. The simplest depreciation method – the straight-line method is used as the salvage value is 10% of the original capital cost after 20 years.
2. The cost of ethanol is \$2,850/metric ton, the cost of water is \$1/metric ton, and the cost of hydrogen is \$1,500/metric ton^[4].
3. The market price of calcium carbonate and ammonium carbonate is estimated as \$100/metric ton based on the average prices reported at www.alibaba.com.
4. The solid Raney nickel catalyst is assumed to be 6 g/L of the reactant^[15]. The market price is \$10,000/metric ton. The overall catalyst life is considered to be six months^[24].
5. For the SBC process, the bacteria concentration in the reactor of 0.05 g/L is applied. The bacteria concentration after growing in the culture medium is 0.62 g/L, and 2 g/L of nutrients in the culture medium is assumed. The cost of nutrients needed for growing bacteria is \$0.457/lb.^[7, 12, 13].
6. Reactor capacity is calculated by inlet flow rate and residence time and is shown in supplementary S1. Fermentation reactor is assumed to achieve five times better preference because they are modeled as a standard reactor instead of a big horizontal tank, and the industrial process would have a significantly higher bacterial inoculation^[26].
7. The cost of heat utility and cost of heat exchangers are taken from heat integration.
8. Transportation cost and wastewater treatment have not been included.

2.4 Life Cycle Analysis

SimaPro has been widely used for its multiple impact analysis methods and broad international database. In this work, SimaPro V8.4 is used to evaluate the four different routes of mixed alcohol production: KR, ER, KR + SBC process, and ER + SBC process, and the parameter needed is shown in supplementary S2. The ReCiPe midpoint method is used as it contains 18 impact categories at the midpoint level: climate change, ozone depletion, terrestrial acidification, freshwater, and marine eutrophication, human toxicity, photochemical oxidant formation, particulate matter formation, terrestrial ecotoxicity, freshwater, and marine ecotoxicity, ionizing radiation, agricultural and urban land transformation, natural land transformation, water depletion, mineral resource, and fossil fuel depletion^[29]. In this work, we focus on four categories: 1) impacts of climate change (GHG emissions); 2) Land occupation; 3) Water depletion; and 4) Fossil depletion. The functional unit of one metric ton of product is considered for LCA. For inventory analysis, the Ecoinvent® v3.3 database is used for its extensive database^[21, 29, 30]. Furthermore, some assumptions are made to perform LCA, including

1. Brown Algae is considered the biomass for the analysis, and since the algae production is not available in the SimaPro database, the LCA data from Howard's work is introduced^[31].
2. Heptanol is assumed to be fully recycled.
3. The materials used in the manufacturing of mixed alcohol are only considered. The materials used in the construction, other infrastructure, cooling water, and catalysts are supposed to be recycled at the end of the process's life cycle and are not considered.
4. The feedstock is transported by a truck from the local biomass conversion facility and 100 km away from the biorefinery facility.
5. Electricity is supplied by a medium voltage grid based on the average technology and total loss in the US.
6. Cooling is supplied by water, cooling, unspecified natural origin based on the assumption that 99.5% of the total is recycled and waste heat is emitted into the atmosphere.
7. Wastewater is connected to wastewater treatment units.

Process flowsheet

Anaerobic digestion process

Biomass, freshwater, and recycled water from the dewatering and drying process (stream 1) are fed to the fermenter (R1), where brown algae are anaerobically fermented to produce a mixture of VFAs, as shown in Fig. 2. Iodoform and ethanol (stream 2) are added with stream 1 at 30 ppm concentration to avoid by-products like methane. Calcium carbonate is added to the fermentation reactor to produce carboxylate salts. The outlet of the fermenter (stream 3) enters a flash drum (V1) to remove the undissolved Gas (Gas). The product stream (stream 4) is fed to a filter (FIL 1), where the unreacted biomass (stream 5) is separated and recycled to the fermenter for further utilization. The liquid stream (Salts) contains carboxylate salt solution.

Dewatering and drying process

Aqueous solution from the anaerobic digestion process (Fig. 3) is fed to a heat exchanger (HE1) and preheated by the stream (stream 21) from the multistage heat exchangers (Stream 20, 23). The preheated stream (stream 1) from the heat exchanger split into multiple streams and fed to the multistage evaporator. The first stage starts with the inlet stream (Stream 2) entering the pump (P2) to increase the pressure. The pump (Stream 3) outlet passes through a heater (H1) to be adjusted to saturation. The saturated salts solution (Stream 4) enters the evaporator, which consists of a heat exchanger (HE2) and a flash drum (V1). The first stage of the dewatering process is heated by the medium pressure steam (Stream 19) and support Steam. The produced vapors (Stream 22) enter the heat exchanger (HE3) of the next stage. The concentrated salts solution from each stage (Stream 10, 12) is combined and sent to the Drying process, which starts with a high-temperature evaporator consists of a heater (H3) and a flash drum (V3). The vapors (Stream 16) from the high-temperature evaporator and the vapors (Stream 13) from the last stage of the Dewatering process are mixed and cooled to liquid in a flash drum (V5). The outlet (Stream 17) from the cooler is pressurized then vaporized to produce medium pressure steam by a pump (P3) and heater (H5). The outlet of the

flash drum (Stream 14) enters another evaporator (H4, V4) for further drying. The top vapor is treated as waste (Wastewater), and the bottom is the Dry Salts product. Our simulation uses a six-stage evaporator, but we only show a two-stage evaporator to make the flowsheet clearer and easier to understand. Stage three to six are repeated a similar design and flow as stage two.

SBC process

The SBC process is shown in Fig. 4. The Mix Gas from the anaerobic digestion process is fed into the process with Support Hydrogen and recycled hydrogen (Stream 10) from the second fermentation stage. The mixed stream (Stream 1) passes through a heater to adjust to the optimal temperature and goes to the first fermenter (R1). The bacteria *C.lj* in the fermenter consumes carbon dioxide and hydrogen to produce acetic acid and ethanol. The product stream (Stream 3) is fed into a flash drum (V1), where unreacted gases are separated and recycled. The outlet of a flash drum (Stream 4) is combined with the Support Ethanol and unreacted ethanol (Stream 9) and sent to the second fermentation stage. Like the first stage, the flow has first been adjusted to the heater's optimal temperature (H2). Then the outlet of the heater (Stream 5) enters the second fermenter (R2), where the bacteria *C.kl* produce higher carbon carboxylic acids by consuming acetic acid and ethanol. The acids react with Calcium Carbonate and produce the corresponding calcium carboxylate salts. The fermenter's product stream (Stream 6) is fed into a flash drum to separate the produced gas (Stream 7) and cycle back to the first stage as an additional carbon source. The dilute salts solution from the flash drum (Stream 8) then enters a dryer (V3) that removes excess water and ethanol to get a mixture of Dry Salts. Part of the dryer's gas is treated as wastewater, and the rest is recycled to the second stage. The bacteria used in this process are assumed to be fixed that not move with the stream.

Ketonization and hydrogenation process

The flowsheet diagram for the Ketonization and hydrogenation process is shown in Fig. 5. Dry Salts collected from the Anaerobic digestion process and SBC process are preheated by a heater (H1). The heated salts (Stream 1) are introduced to the ketonization reactor (R1) to produce mixed ketones. Ketone stream (Stream 1) is fed into a flash drum (V1). The solid waste from the flash drum (Stream 3) passes through a heat exchanger (H2) and leaves the process. The ketone vapor from the top of V1 (Stream 4) is cooled by a cooler (H3) to liquid form. The outlet of the cooler (Stream 5) enters the pump (P1) to increase the pressure for the hydrogenation reaction. The pressured ketone stream (Stream 6) splits into three streams (Stream 7, 8, 9), and each stream enters a different stage of hydrogenation reactors (R2, 3, 4) to produce mixed alcohol. The inlet stream for the first stage of hydrogenation (Stream 7) is introduced to reactor R2 with hydrogen from pump (P2). The product stream from the first stage (Stream 10) is mixed with the second stage's inlet Stream 8 and the same for product Stream 11. The final alcohol products (Stream 12) are further cooled by a heat exchanger (H3) and introduced to a flash drum (V2), where the excess hydrogen is recycled. The bottom stream from V2 is further flashed to low pressure by a second flash drum (V3) for further purification. The mixed alcohol stream from the bottom of V3 contains C3 to C9 alcohols.

Esterification and hydrogenation process

Figure 6 shows the dry ammonium carboxylate salts are mixed with heptanol and pass through a pump (P1) and heater (H1) to reach the esterification reaction condition. The outlet of H1 (Stream 2) is introduced to the esterification reactor (R1) and produce mix esters. The product stream from R1 (Stream 3) includes esters and side products like water and ammonia, so the stream is introduced into a separation column (DC1) for purification. The vapor stream from the top of DC1 (Stream 4) contains most of the water and ammonia, and some esters. Then the stream passes a condenser (H2) and decanter (D1) to recycle the most esters (Stream 6) and combine with the bottom product of DC1. The purified ester stream is mixed with hydrogen and passes through a pump (P2) and heater (H3) to reach the hydrogenation reaction condition. In the hydrogenation reactor (R2), mixed alcohol (Stream 10) is being produced and goes into a heat exchanger (H4) to condense. The cooled stream enters a flash drum (V1), where the excess hydrogen is recycled (Stream 12). The product stream (Stream 13) is being further depressurized and cooled to room temperature.

Results And Discussion

Simulation: 500,000 metric ton per year brown algae is the input for the four routes [4], and total products produced are calculated for an individual process: 90,100 metric ton of product mixture for KR, 226,310 metric ton of product mixture for KR + SBC, 132,154 metric ton of product mixture for ER and 428,794 metric ton of product mixture for ER + SBC are produced per year. The product mixture contains mixed alcohols from C2 to C9, and the weight percentage of each component varies a lot. The detailed product composition for four routes is listed in Table 2.

Table 2
Mixed alcohol composition summary

Composition wt. %	KR	KR + SBC	ER	ER + SBC
Ethanol	0	0	15.65	6.78
Propanol	31.04	3	7.28	3.03
Butanol	43.25	11.95	4.56	7.15
Pentanol	16.02	12.66	0	0
Hexanol	7.62	17.22	0	20.05
Heptanol	1.31	8.45	68.23	57.45
Nonanol	0	22.11	0	0
Octanol	0	23.77	0	0
Impurity	0.77	0.83	4.29	5.55

Economics

The detailed capital and operating costs for KR, ER, KR + SBC, and ER + SBC are calculated by Aspen Economic Analyzer® and listed in the supplementary information. The KR process's capital cost is estimated at \$101.28 million, and the operating cost is estimated at \$108.59 million. The capital cost for the KR + SBC process is estimated at \$117.44 million, and the operating cost is estimated at \$322.56 million. The capital cost is estimated at \$124.48 million for the ER process, and the operating cost is estimated at \$101.42 million. Capital and operating cost for the ER + SBC process are \$212.43 million and \$495.53 million, respectively.

Capital cost for the ER + SBC process is the highest compared to the other three processes. There are several reasons for the considerable difference: 1. SBC process consumes the waste gas from the anaerobic digestion process, which dictates the use of a bigger size reactor, increasing the capital cost. 2. Since more salts solution is produced, more capital cost on the heaters is addressed to fill the necessary drying requirement. 3. Much more initial catalyst is needed for further production in the esterification and hydrogenation process, which increases the capital cost. Although the SBC process only consists of two fermentation reactors, it requires a large amount of ethanol and hydrogen for C.lj and C.kl bacteria to consume and keep ethanol's concentration ratio to acetic acid 10:1 to achieve the best yield and production rate [12]. Therefore, the massive consumption of raw materials like ethanol, hydrogen, and calcium carbonate sharply increases the operating cost, dictating KR + SBC, and ER + SBC processes' highest operational costs. The main contributor to the operating cost for all the four routes is the cost of raw materials at 62%, 82%, 62%, and 80% for KR, KR + SBC, ER, and ER + SBC. The significant fraction of raw material can be further decomposed: 46% from biomass and 18% from calcium carbonate for KR process, 46% from ethanol and 13% from biomass for KR + SBC process, 50% from biomass, and 22% from catalysis for ER process and 56% ethanol and 13% hydrogen for ER + SBC process. The total utility cost contributes 18, 6, 19, and 8% of the overall cost for the KR, KR + SBC, ER, and ER + SBC process. The detailed fractions of the costs are given in Fig. 7, and the contribution of raw material to the MSP is shown in Fig. 8.

The minimum selling price for mixed alcohol of the four production routes is calculated as follows: KR is \$ 4.13/gal, KR + SBC is \$4.46/gal, \$3.52/gal for ER, and \$4.53/gal for ER + SBC. In 2010, Viet [3] performed a hydrocarbon fuel production process via the ketonization process. The base case simulation has 40 dry ton feedstock capacity per hour, and the minimum selling

price is calculated to be \$5.54/gallon of mixed alcohol, which shows an improvement of 25 % and 20% for the KR and KR + SBC process.

Sensitivity Analysis is carried out to estimate the impact of raw materials' cost on mixed alcohol selling price (Fig. 9a) and the relation between plant capacity and minimum selling price (Fig. 9b). From the economic analysis, we know the largest contributor of mixed alcohol price is the cost of raw materials, and the cost of raw materials changes significantly based on geography and source. By changing the price of materials by $\pm 10\%$, the price of mixed alcohol changes by $\pm 5.5\%$, $\pm 7.8\%$, $\pm 5.3\%$, $\pm 7.5\%$ for KR, KR + SBC, ER, and ER + SBC, respectively. Plant capacity needs to be included in sensitivity analysis since the feed amount of raw material (primarily for algae biomass) cannot be determined. The results show that the lower the plant's capacity, the higher the cost of mixed alcohol. It is found that a 50% decrease of biomass capacity raises the minimum price of mixed alcohol by 8.32% for the KR process, 2.65% for the KR + SBC process, 11.23% for ER and process, and 2.28% for the ER + SBC process. Therefore, higher plant capacity is always better. Further information can be extracted from the graph: If the plant's capacity keeps increasing, the curves' slope indicates that mixed alcohol's minimum selling price may not decrease significantly.

Life cycle analysis

The detailed environmental impact information for KR, KR + SBC, ER, and ER + SBC production processes are calculated by applying the ReCiPe midpoint method. Climate change, water depletion, land occupation, and fossil depletion are the impact categories we are interested in and included in this work.

Compared to KR, KR + SBC, and ER + SBC process, ER performs best in all the impact categories except water depletion. ER + SBC is comparable with the ER process. However, ER + SBC produces more products than the ER process. Less electricity is used in ER per ton of mixed alcohol, and it benefits all the categories of life cycle analysis. KR production route has the worst environmental impacts in all categories because it utilizes a large amount of electricity but with relatively low production of mixed alcohol when compared to other processes. Figure 10 shows the details of the life cycle analysis results. The contribution of raw materials for the four routes is also taken into consideration and shown in Fig. 11. Production of electricity is the main contributor for all the impact categories for the case except for water depletion of KR production. Similarly, for the KR + SBC and ER + SBC processes, electricity production is the main contributor to all the impact categories. For the ER process, the algae production and electricity production contribute almost evenly except for water depletion; algae production becomes the main contributor.

Summary

Efforts for developing economically feasible and environmentally friendly designs are made with the increasing interest in bio-based chemicals. This work integrates brown algae –third generation biomass as the raw material for mixed alcohol production to lower the percentage of the inert component of biomass feedstock. A novel fermentation process using C.lj and C.kl is developed and is integrated with the two main routes of the MixAlco® process. Techno-economic and life cycle analysis is carried out for all four production routes. The minimum selling price of mixed alcohol for the KR, KR+SBC, ER, and ER+SBC process is \$ 4.13/gal, \$4.46/gal, \$3.52/gal, and \$4.53/gal, respectively. Economic analysis shows that mixed alcohol cost mainly depends on raw materials' cost, especially the cost of biomass and ethanol. According to the sensitivity analysis, the plant's capacity and raw materials' selling price considerably affect the minimum selling price of mixed alcohol. The ER process's environmental performance is best but comparable to the ER+SBC process from life cycle analysis, and KR performs the worst due to overall less yield of mixed alcohol. For future work, different biomass should be applied to the four production routes and compared.

Declarations

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Ethical Declaration: The current research has no involved human participants and/or animal models.

Competing Interests: The authors declare that they have no competing interests.

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Figures

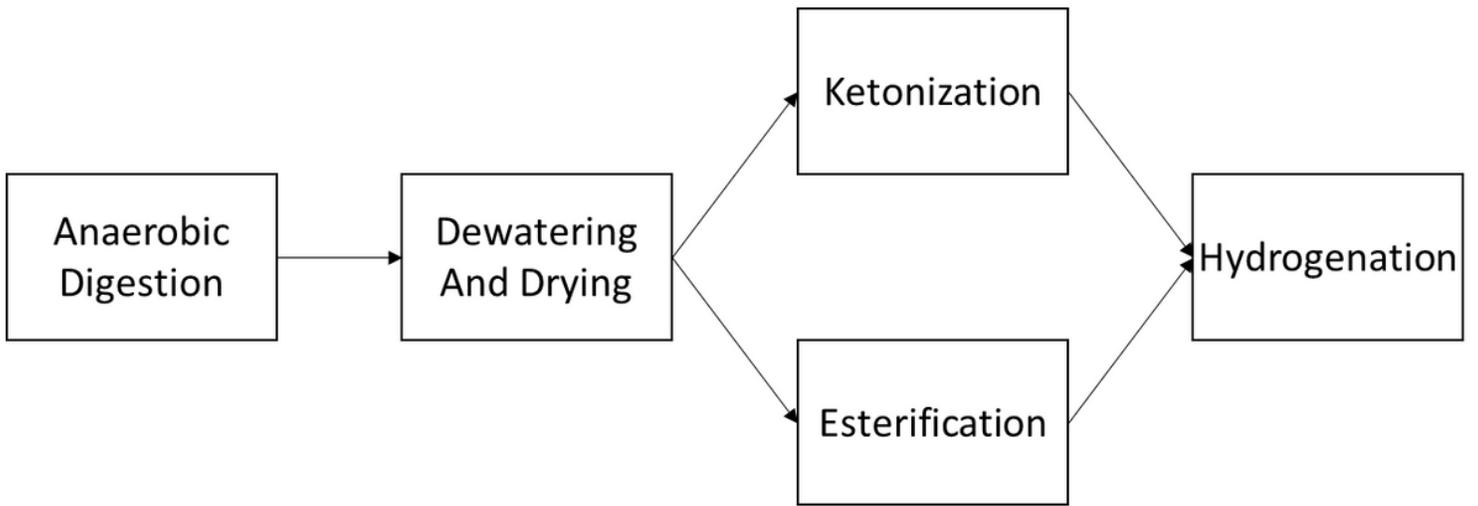


Figure 1

Block Flow diagram for Ketonization and Esterification Routes

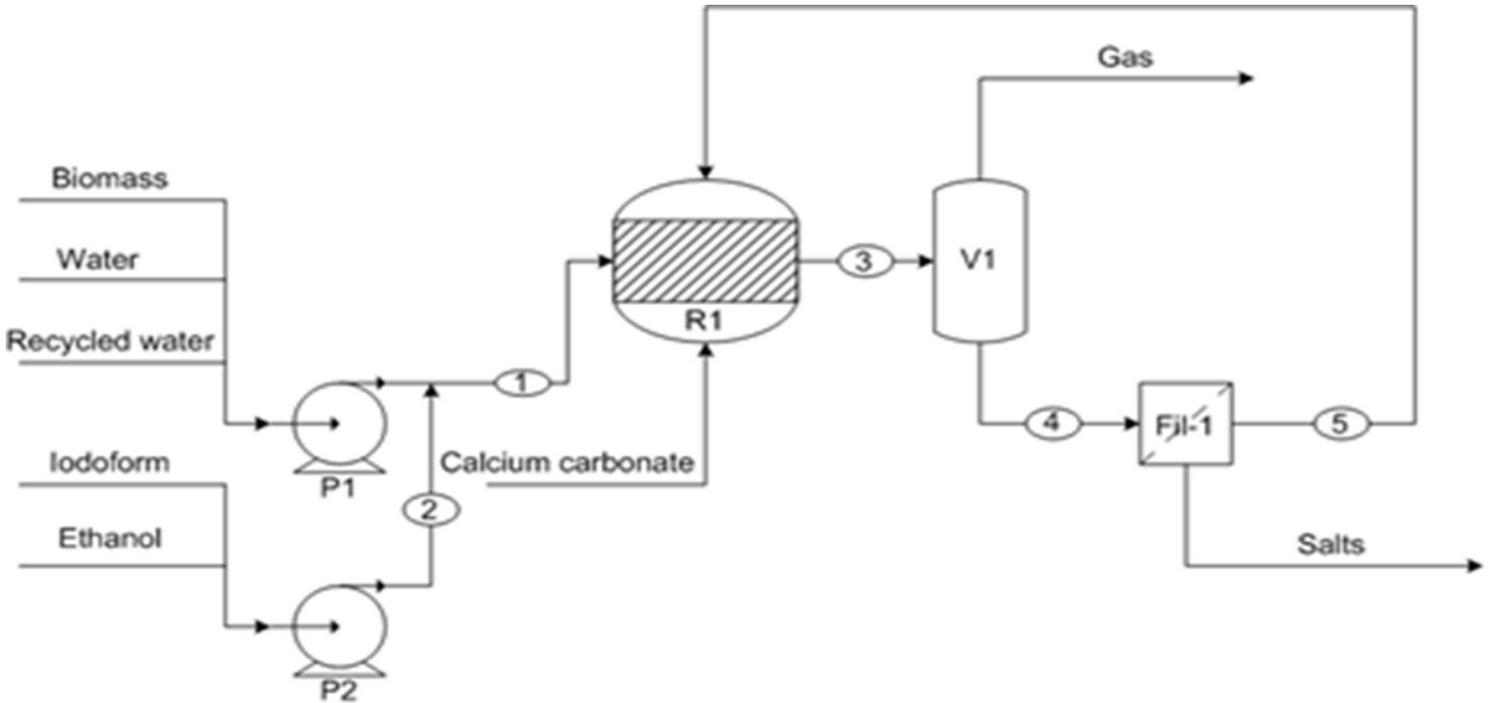


Figure 2

Anaerobic digestion process flowsheet

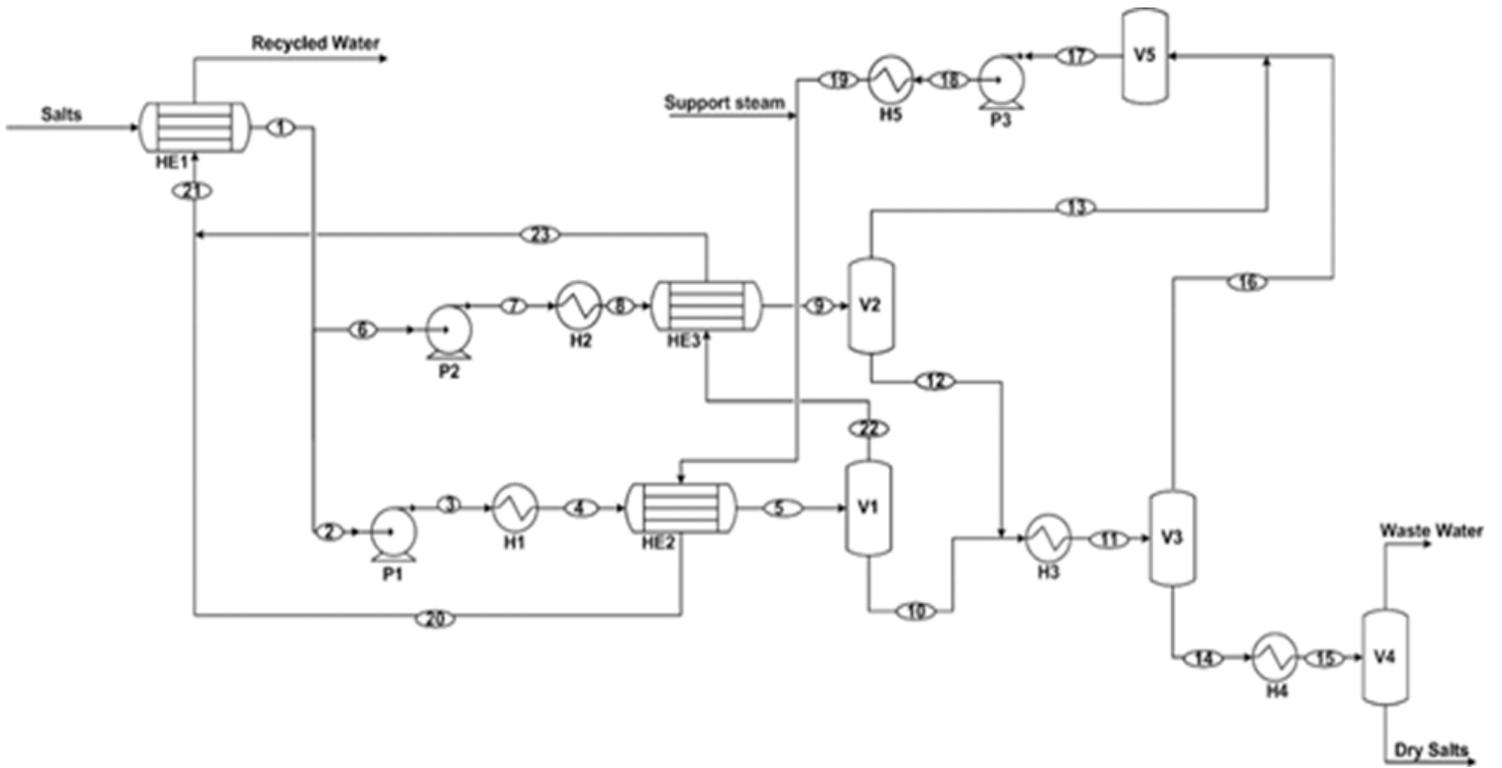


Figure 3

Dewatering and drying process flowsheet

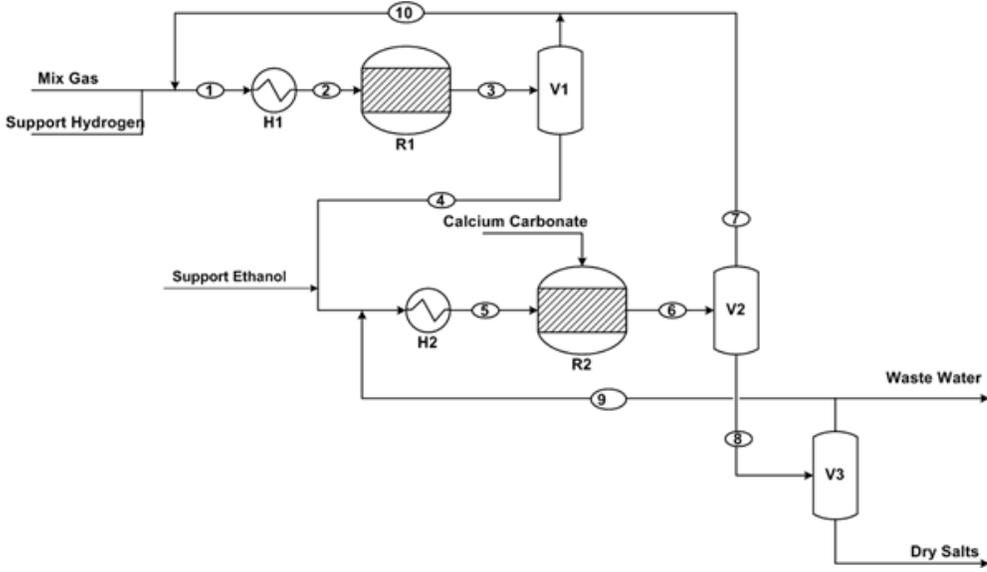


Figure 4

Fermentation using syntrophic bacteria consortia(SBC) process flowsheet

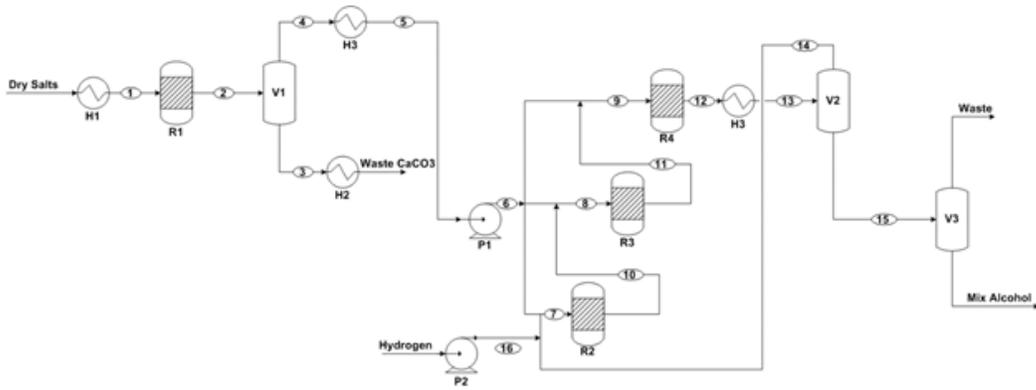


Figure 5

Ketonization and hydrogenation process flowsheet

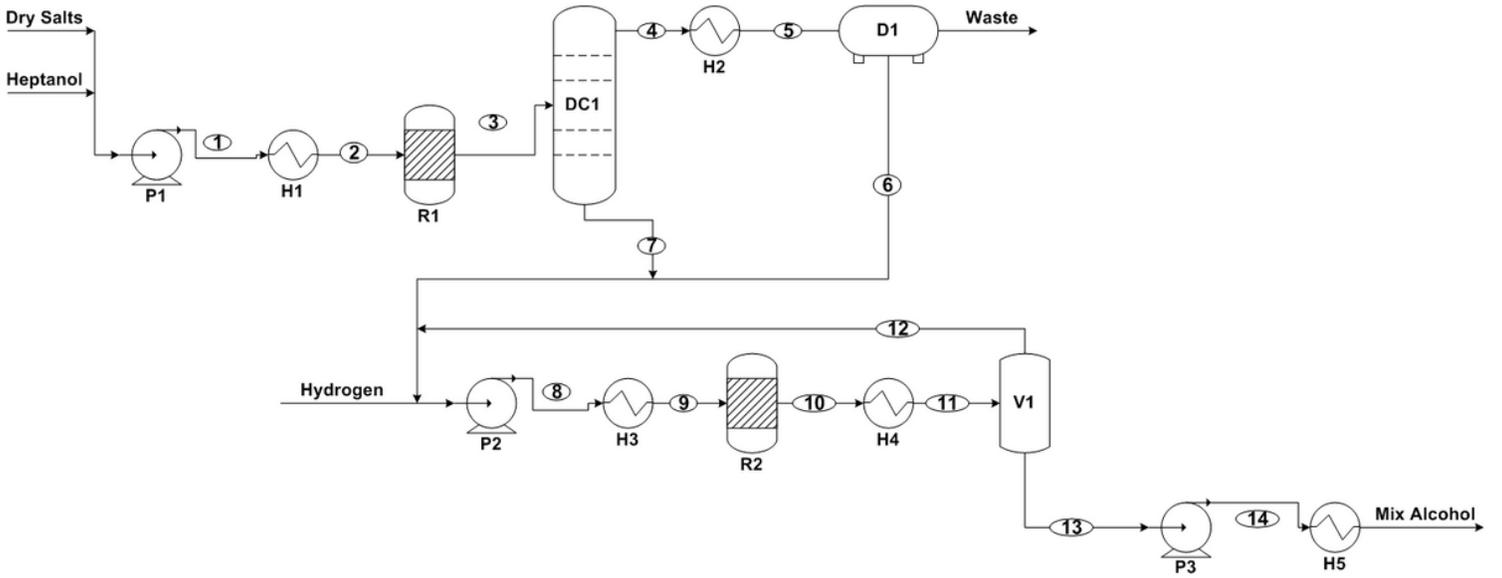


Figure 6

Esterification and hydrogenation process flowsheet

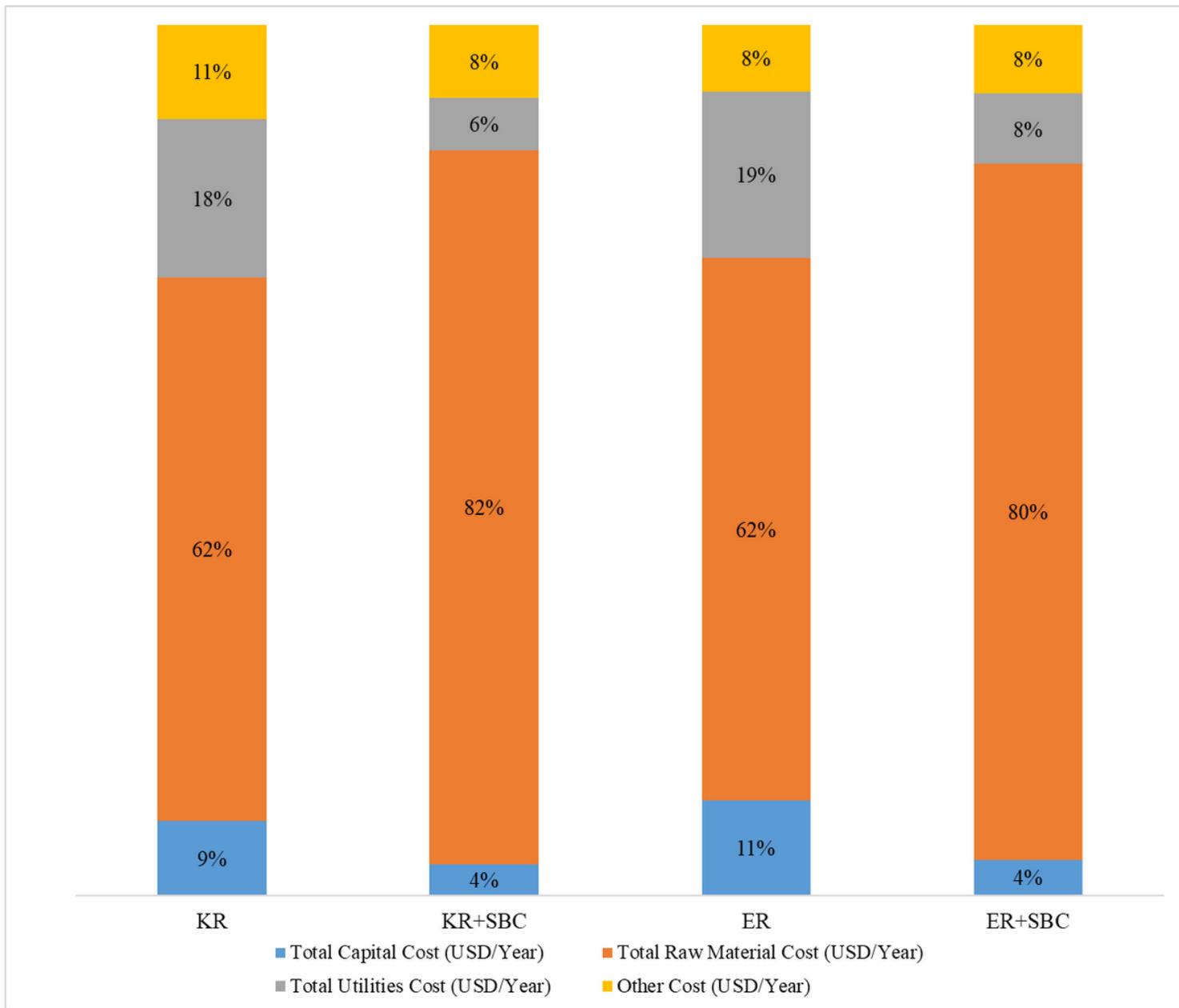


Figure 7

Overview of cost for all the four processes

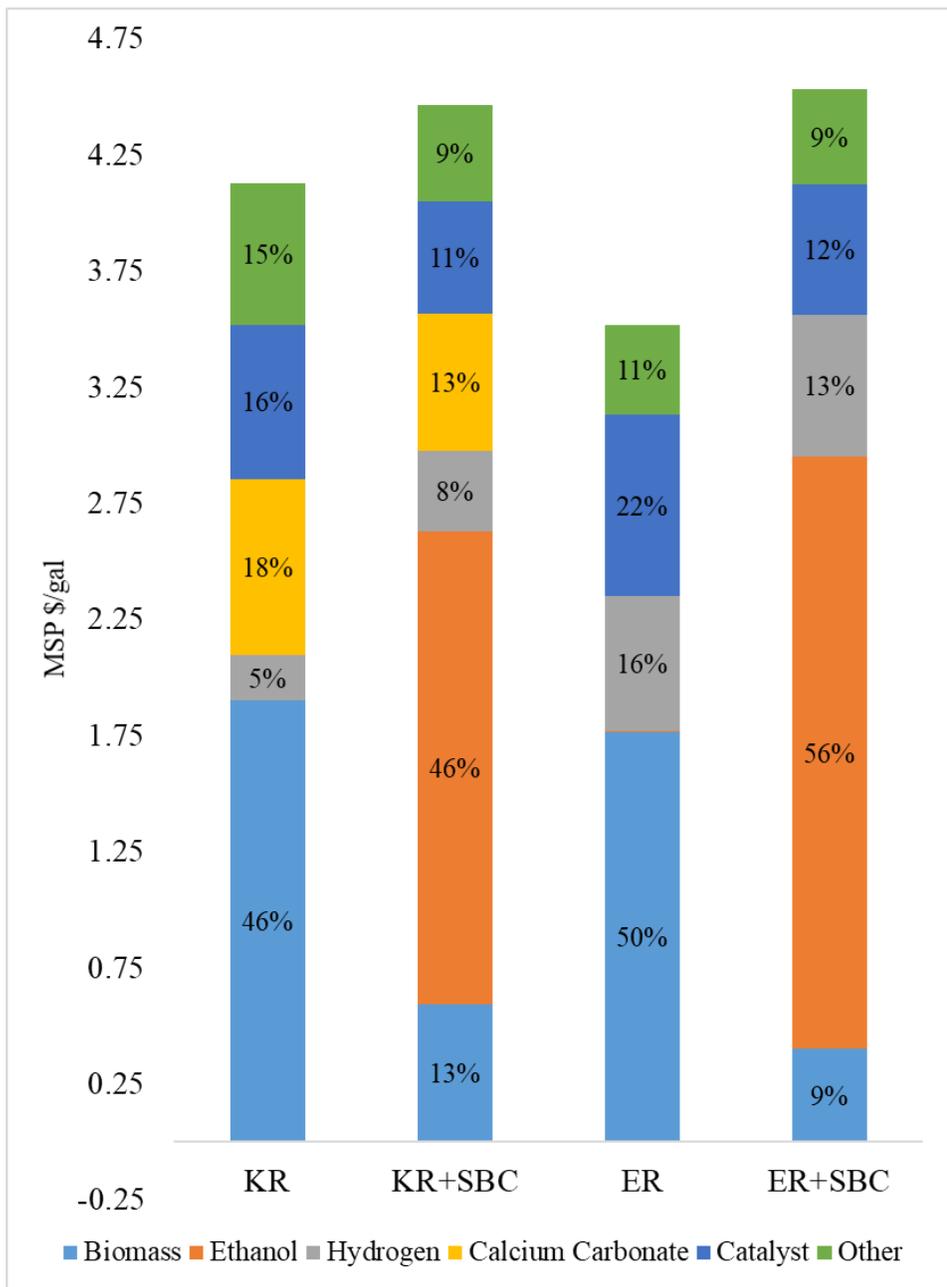


Figure 8

Contributions of raw materials on minimum selling price

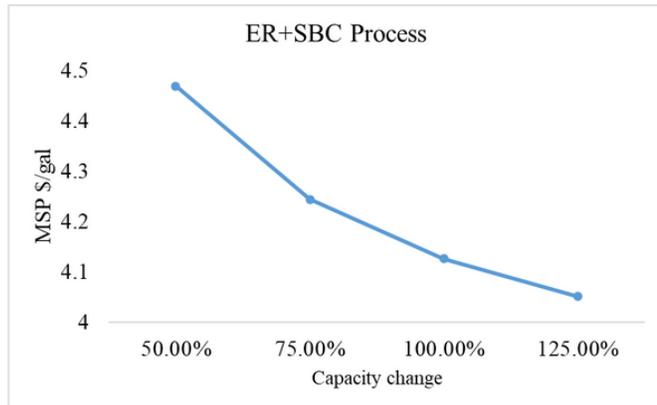
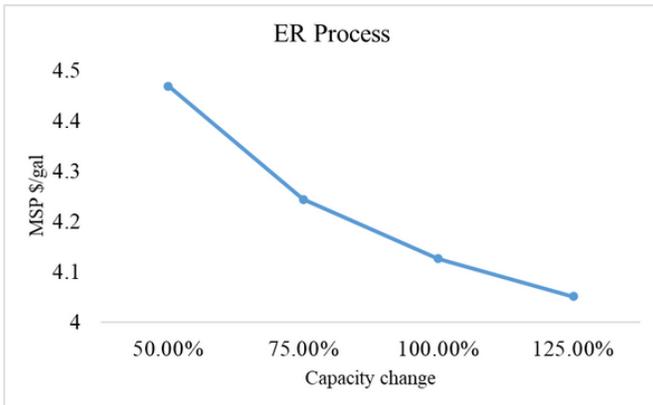
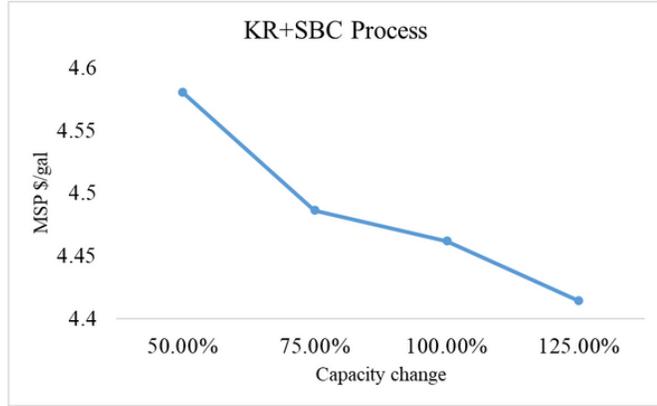
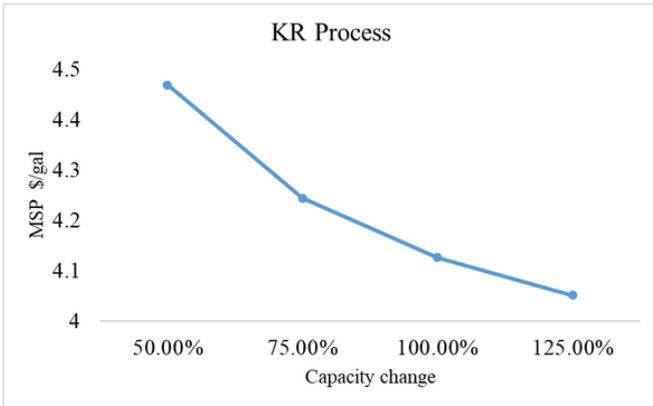
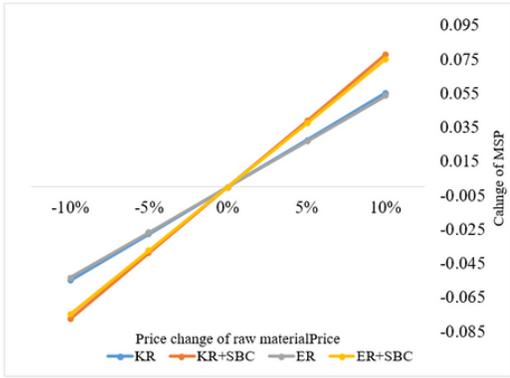


Figure 9

a Sensitivity Analysis of minimum selling price VS. raw material price for the four routes b Sensitivity Analysis of minimum selling price VS. plant capacity for four routes

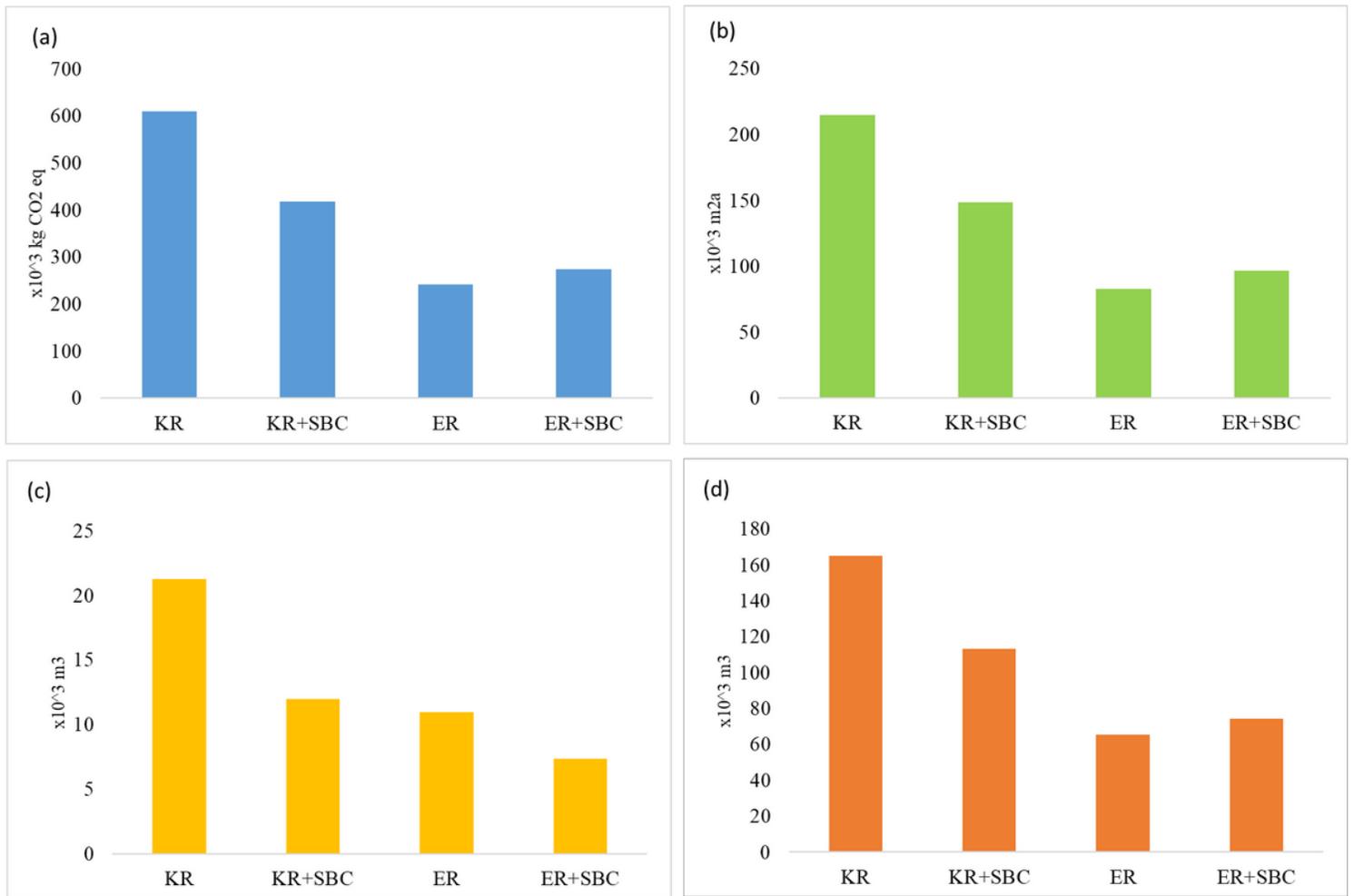


Figure 10

Results of four processes for (a) Climate change, (b) Water depletion, (c) Fossil depletion, (d) Land occupation

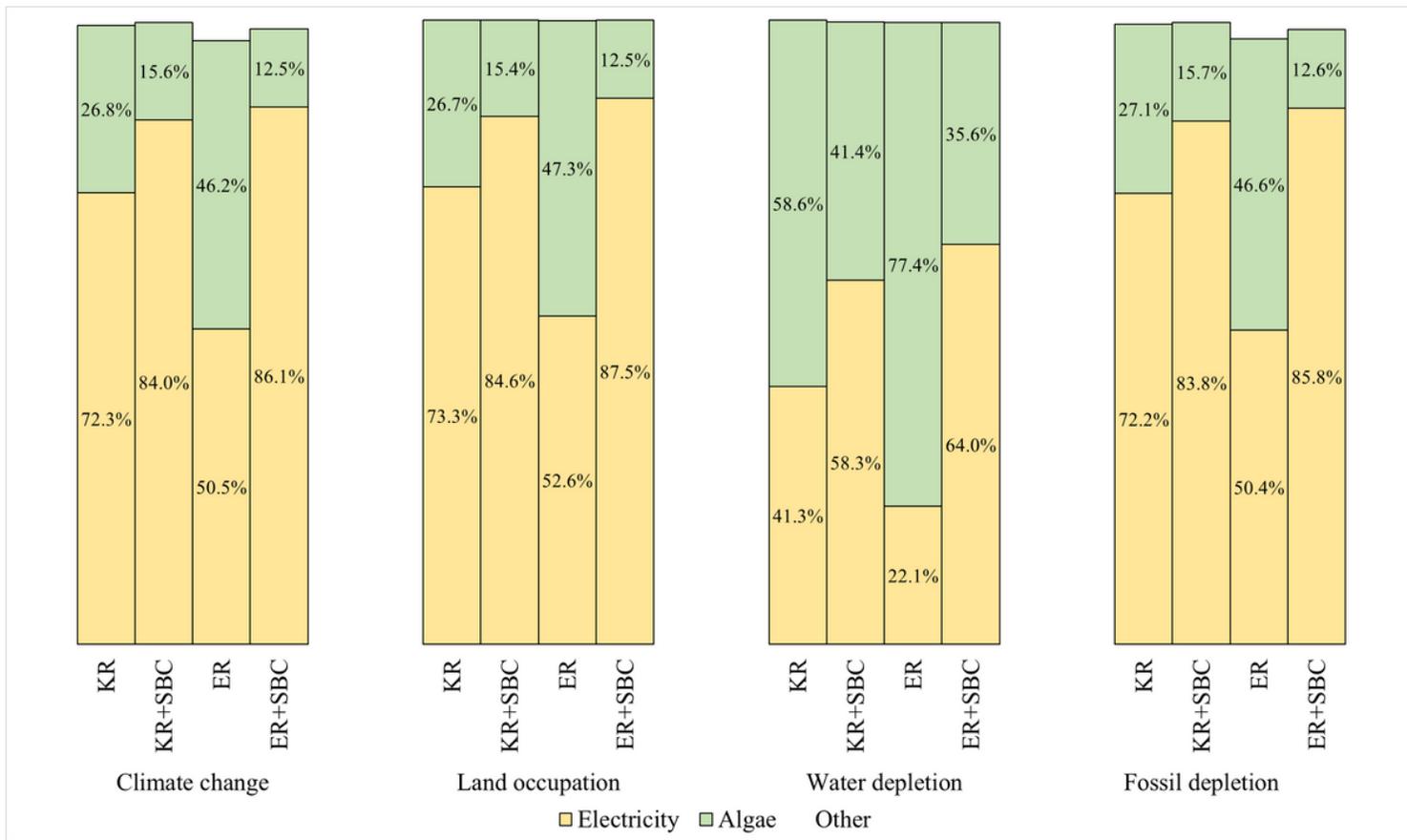


Figure 11

LCA contribution of raw material for all process

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