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Techno-economic viability of bio-based methyl ethyl ketone production from sugarcane using integrated fermentative and chemo-catalytic approach: Process integration using pinch technology

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ABSTRACT

Butanediols are versatile platform chemicals that can be transformed into a spectrum of valuable products. This study examines the techno-commercial feasibility of an integrated biorefinery for fermentative production of 2,3-butanediol (BDO) from sucrose of sugarcane (SC), followed by chemo-catalytic upgrading of BDO to a carbon-conservative derivative, methyl ethyl ketone (MEK), with established commercial demand. The techno-economics of three process configurations are compared for downstream MEK separation from water and co-product, isobutyraldehyde (IBA): (I) heterogeneous azeotropic distillation of MEK-water and extractive separation of (II) MEK and (III) MEK-IBA from water using *p*-xylene as a solvent. The thermal efficiency of these manufacturing processes is further improved using pinch technology. The implementation of pinch technology reduces 8% of BDO and 9–10% of MEK production costs. Despite these improvements, raw material and utility costs remain substantial. The capital expenditure is notably higher for MEK production from SC than BDO alone due to additional processing steps. The extraction based MEK separation is the simplest process configuration despite marginally higher capital requirements and utility consumption with slightly higher production costs than MEK-water azeotropic distillation. Economic analysis suggests that bio-based BDO is cost-competitive with its petrochemical counterpart, with a minimum gross unitary selling price of US$ 1.54, assuming a 15% internal rate of return over five-year payback periods. However, renewable MEK is approximately 16–24% costlier than the petrochemical route. Future strategies must focus on reducing feedstock costs, improving BDO fermentation efficacy, and developing a low-cost downstream separation process to make renewable MEK commercially viable.

1. Introduction

We are currently overly dependent on petroleum-based feedstock for industrial manufacturing of broad ranges of bulk, fine, and specialty chemicals to meet the growing demands of commodity products. In the current era, the petrochemical route alone supplies more than 90 % of organic chemicals manufactured industrially [1]. In recent years, the rapid depletion of fossil fuel resources, coupled with an exponential rise in the global population and proliferation of industries, mandates a paradigm shift toward sustainable manufacturing of these chemicals from carbon-neutral renewable resources, such as biomass [2–5]. Biomass is an abundant, renewable, and chemical form of energy resource formed from solar energy through atmospheric carbon fixation. Biomass thus offers a viable alternative to fossil fuels, with reduced carbon emissions to the atmosphere. Besides, the diverse chemical composition of biomass makes it a promising feedstock for sustainable

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Abbreviations: BD, 1,3-Butadiene; BDO, 2,3-Butanediol; IBA, Isobutyraldehyde; IRR, Internal rate of return; MBSP, Minimum BDO selling price; ROI, Return on investment; MEK, Methyl ethyl ketone; MMSP, Minimum MEK selling price; SC, Sugarcane; SCB, Sugarcane bagasse.

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production of functionalized molecules, known as platform chemicals, in a biorefinery [6–9]. These platform chemicals can serve as starting materials for synthesizing a large number of derivatives in an integrated biorefinery approach, analogous to building-block chemicals in the petrochemical industry.

Butanediols have emerged as the new biorefinery platform molecules due to their four isomeric forms with two –OH groups at different positions of the linear carbon backbone [9]. They are derived from carbohydrate fraction of biomass via fermentative route using native or genetically modified microorganisms. These characteristic features make them suitable for the multitude of downstream applications in the production of synthetic rubber, industrial solvents, food, cosmetics, drugs, etc. [9,10]. Among these, 2,3-butanediol (BDO) is the most promising isomer due to being a natural metabolite with high titter (more than 100 g/L), yield, and productivity [9]. Currently, the petrochemical industry is the only source of BDO from 2-butylenes via 2,3-epoxybutane [9]. However, the separation and purification of three BDO stereoisomeric (levo (2R,3R), dextro (2S,3S0), and meso (2R,3S) is a tedious task in the petrochemical route [9,10]. Besides, the prices of BDO are rising due to the short supply of petroleum, its excessive cost, and increasing BDO market demand. Therefore, a sustainable alternative must be established to overcome the challenges associated with the petrochemical route and meet the expanding BDO global market of 3300 thousand metric tons in 2022 [11]. The BDO market is predicted to expand at a compound annual growth rate of 4.38 % till 2030. Consequently, microbial BDO synthesis has emerged as an economical, sustainable, and eco-friendly alternative [5,12–16]. Being a natural metabolite, microbial BDO production technology has advanced considerably in recent decades with high production rates [17–22]. Recently, we published a review article providing state of the art information for BDO production via the microbial route [9].

The BDO derivates, such as methyl ethyl ketone (MEK) and 1,3-butadiene (BD), are prominent petrochemicals and find versatile applications in chemical and polymer sectors [23–25]. At present, MEK is manufactured by dehydrogenation of petroleum-derived 2-butanol and is widely used as a common organic solvent in various process industries [9,26]. The booming industrial landscape and increasing demand for commodities, such as printing inks, paints, coatings, textiles, plastics, and lacquers, ensure significant MEK market growth in the coming years [27]. The global MEK market, valued at US$ 3.36 billion in 2021, is projected to grow annually at a rate of 4.62 % up to 2030 [27]. Furthermore, MEK (33.9 MJ/kg) is recognized as a superior fuel additive compared to ethanol (29.7 MJ/kg) due to its higher heat of combustion [28], lesser emissions of hydrocarbon, reduced oil dilution, and superior cold-start property [29]. However, the present petrochemical MEK synthesis route involves excessive capital investment and poses severe corrosion of the equipment and environmental issues [30]. Alternatively, MEK can be produced by pinacol rearrangement of bio-based BDO with the co-production of isobutyraldehyde (IBA) and accompanied by water. Therefore, an integrated biorefinery approach for fermentative production of BDO from biomass and catalytic dehydration of BDO to MEK is a sustainable solution to tackle both crude oil instability and environmental concerns.

The carbohydrates for BDO fermentation are mainly sourced from sugarcane (SC), starch, and lignocellulose biomass. However, bio-based products derived from lignocellulose biomass are expensive due to the difficulty in the extraction of carbohydrates [31]. Therefore, despite being edible, starch and SC are the commonly used feedstock in 1G biorefinery, such as bioethanol production, due to the ease of extraction of fermentable sugars with simple chemical structures [32]. The SC is still the primary biorefinery feedstock in various countries, such as Brazil, India, etc., due to high SC productivity with economically competitive production costs of biochemicals and biofuels, high sucrose content, and favourable energy input/output ratio [33,34]. The worldwide annual SC production stands at around 1.6 billion metric tons, with the co-generation of about 279 million metric tons of sugarcane bagasse (SCB) [33]. While sucrose syrup is widely used in producing biofuels or biochemicals, the application of SCB, being lignocellulose biomass, is mainly limited to boilers for co-generating electricity and steam [35]. Therefore, in this techno-economic analysis, only sucrose syrup from SC is considered for fermentative BDO production. Nevertheless, the biorefinery facility for BDO production should be near the SC cultivation belt to ensure stable SC supply and avoid expensive SC transportation from far away locations.

The economic feasibility analysis of an end-to-end process is a prerequisite in decision-making for investment in a new commercial venture. This analysis identifies the most economical and simple to operate process configurations, estimates capital investment, identifies principal cost components, and appraises return on investment. Conversely, thermal energy consumption is one of the major operating cost factors in many chemical manufacturing processes [36]. Process integration using pinch technology is an established method for improving thermal efficiency and reducing the operating costs for heating and cooling energy. This technique achieves these objectives by maximizing thermal energy exchange within the process by optimizing a heat exchanger network design. It reduces the external utility demands, thereby improving the overall economics of the process [36]. This work is thus focused on comprehensive process design using Aspen Plus V12.1 for realistic material and energy balance and process integration using pinch methodology to minimize thermal energy demands.

The techno-economic and profitability study for fermentative BDO production from SC and catalytic BDO upgrading to MEK is scarce in the literature. Our recent techno-economic analysis showed that microbial BDO production from brewers' spent grain and SCB is economically feasible [14,15]. A techno-economic study was also reported for BDO production from glucose and catalytic BDO dehydration to MEK [30]. An engineered *Saccharomyces cerevisiae* was employed for producing BDO from glucose using fed-batch fermentation, with almost 109.9 g/L of BDO titter, 1.0 g/L.h productivity, and 0.36 g/g glucose yield [30]. Their economic analysis indicated that the bio-based MEK is cost-competitive with petrochemical MEK [30]. Another study presented an integrated approach for microbial BDO production from crude glycerol using *Klebsiella michiganensis* and catalytic BDO dehydration to MEK [37]. This study considered fed-batch fermentation, with 76.1 g/L BDO titter, 1.38 g/L.h productivity, and 0.41 g/g yield. The minimum bio-based MEK selling price was US$ 1.42/Kg for an annual MEK production capacity of 50,000 metric tons [37].

While few studies reported techno-economic analysis for renewable MEK production, to the best of our knowledge, a comprehensive design of an end-to-end process from biomass using the fundamental principle of Chemical Engineering and pinch technology is still unexplored for integrated biorefinery for BDO biosynthesis from SC and chemo catalytic BDO conversion to MEK. This work is thus dedicated to designing these integrated processes using Aspen Plus to estimate capital and operating expenditures precisely. However, the BDO dehydration reaction co-produces IBA and water. The downstream separation of the MEK-IBA-water following catalytic BDO dehydration is quite complex due to the formation of heterogeneous MEK-water and IBA-water azeotropic mixtures. This work compares three separation strategies to identify the most economical and easy-to-operate process. Likewise, the commercialization perspective of the process is judged by the profitability analysis. Therefore, the profitability of the entire process is investigated to obtain the minimum BDO selling price (MBSP), minimum MEK selling price (MMSP), and return on investment (ROI).

$$C_{12}H_{22}O_{11} + O_2 \rightleftharpoons 2C_4H_{10}O_2\ (\mathrm{BDO}) + H_2O + 4CO_2 \qquad (1)$$

$$\Delta H^0{}_{298\ K} = -962.307\ \mathrm{kJ/mol\ sucrose}$$

Reaction 1. Reaction stoichiometry for aerobic fermentative BDO production from sucrose.

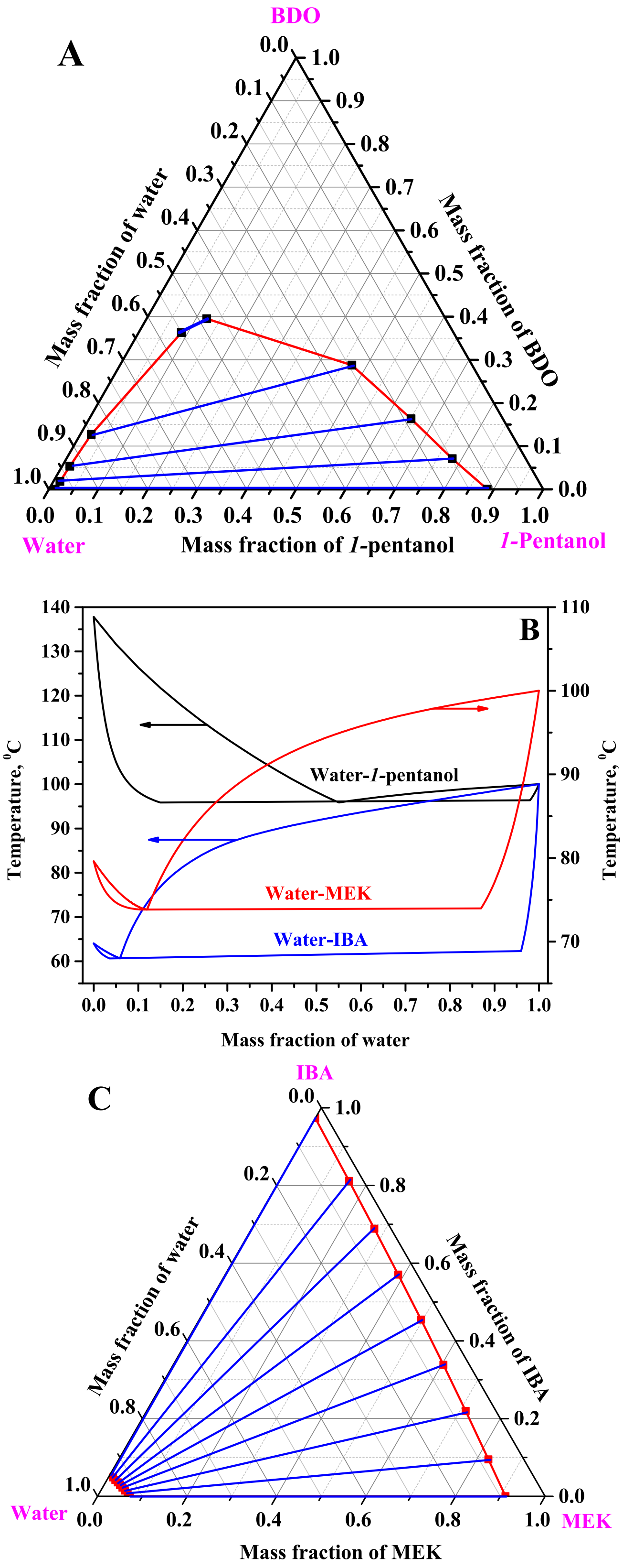


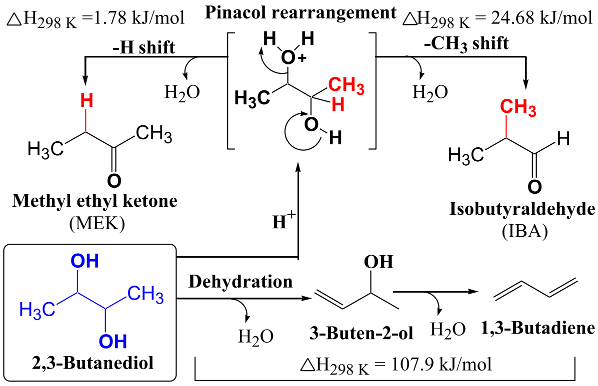
Fig. 1. (A) 2,3-Butanediol (BDO)-water-*1*-pentanol ternary diagram at 30 °C. (B) Txy diagram of water-*1*-pentanol, water-methyl ethyl ketone (MEK), and water-isobutyraldehyde (IBA) at atmospheric pressure. (C) MEK-IBA-water ternary diagram at 30 °C.

2. Process design

In this work, BDO was produced by fermentation of sucrose syrup of SC, which was composed of 13.58 wt% sucrose, 71.12 wt% water, and 15.13 wt% SCB [38]. The SCB was represented as a non-conventional solid with 3.4 % ash and an elemental composition of 45.5 wt% C, 5.6 wt% H, 45.2 wt% O, and 0.3 wt% N [39]. Zhang et al. reported microbial BDO production from sucrose using serrawettin W1-deficient mutant strains of *Serratia marcescens* microbes [40]. They achieved a maximum 152 g/L BDO titer in the fermentation broth using fed-batch fermentation, with a productivity and yield of 2.67 g/L.h and 92.6 %, respectively. The sucrose fermentation to BDO by serrawettin W1-deficient *Serratia marcescens* mutant strain was carried out under aerobic conditions using air at 32 °C with a fermentation time of 72 h [40]. The conversion yield of sucrose to BDO during fermentation was taken as 97 % [40]. The fermentation was performed in a stirred batch reactor that was represented by RStoic and two-phase flash models. The stoichiometry of the reaction for sucrose fermentation to BDO is illustrated in Reaction (1). According to this reaction stoichiometry, the theoretical maximum BDO yield is 0.53 g per g of sucrose. The fermentative production of BDO from sucrose is highly exothermic, and the standard heat of the reaction was calculated using Aspen Plus (Reaction (1)). The process was developed for a SC processing capacity of 2000 metric tons per day.

2.1. BDO separation from fermentation broth

The fermentation broth generally contains unconverted sugars, soluble ingredients added to the fermenter, and various high-boiling metabolites formed during the fermentation, including BDO (around 180 °C). Therefore, unlike bioethanol, BDO cannot be separated as a distillate from heavy soluble components present in the fermentation broth by fractionation. Liquid-liquid extraction is a possible approach to obtain highly pure BDO from fermentation broth and is proposed in this work. Various solvents, such as methyl acetate, ethyl acetate, *1*-pentanol, and oleyl alcohol, were employed to extract BDO from the fermentation broth [41,42]. However, oleyl alcohol is a high-boiling solvent (349.3 °C), and the recovery of oleyl alcohol from BDO is thus energy-intensive. On the other hand, the boiling point of *1*-pentanol (137.8 °C) is much lower than BDO, and the solvent can be easily recovered from BDO. Further, the BDO partition coefficient (mass fraction, x) ($K_{BDO} = x^{org}_{BDO}/x^{aq}_{BDO}$=4.6–3) is very high for *1*-pentanol, with a low distribution coefficient of water ($K_W = x^{org}_{W}/x^{aq}_{W}$=0.1–0.2) and high BDO extraction selectivity (K_{BDO}/K_W=37–16) (Fig. 1A). In this work, *1*-pentanol was thus selected as a solvent for BDO extraction from fermentation broth.



Reaction 2. Reaction network in the conversion of BDO to MEK, BD, and IBA.

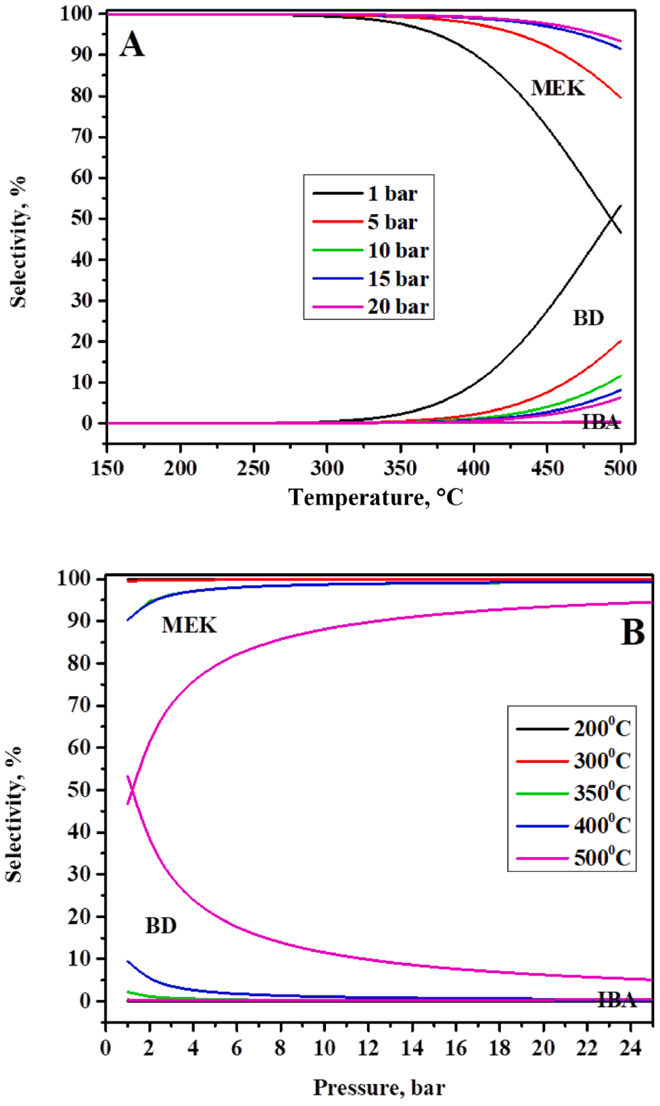


Fig. 2. Thermodynamic equilibrium product selectivity at (A) various reaction temperatures and (B) pressures. Conversion of 2,3-butanediol (BDO) was 100%.

2.2. Thermodynamic analysis for conversion of BDO to MEK

The acid catalysed BDO dehydration generally produces two parallel products, MEK and BD, under two different reaction conditions (Reaction (2)). While BDO dehydration to BD proceeds through the 3-buten-2-ol intermediate, the IBA is the competitive product during MEK formation. The equilibrium analysis was thus carried out to identify the thermodynamically favourable reaction conditions for the selective BDO conversion to MEK and BD. MEK and IBA are formed by pinacol rearrangement with hydride and methyl shift, respectively. While pinacol rearrangement reactions are endothermic, the endothermic heat of the reaction for BD formation is much more than that of MEK/IBA. The dehydration of BDO is thus thermodynamically favourable to MEK over BD at relatively lower temperatures (Fig. 2). The reaction equilibrium is highly selective to MEK up to 300 °C for the entire pressure range, with a negligible quantity of co-products. However, BD becomes a prominent product at 350 °C and higher reaction temperatures, and its selectivity further increases at elevated temperatures. On the other hand, the selectivity to MEK was enhanced for increasing pressure up to 12 bars, with a simultaneous reduction in BD selectivity. However, the higher pressure beyond 12 bars has negligible influence on product selectivity. Generally, the pressure has an insignificant impact on the equilibrium product distribution in liquid-phase reactions. The vapor-to-liquid phase transition of the equilibrium product mixture at 350 °C occurs at around 12 bar pressure; equilibrium product composition thus remains unaffected beyond this pressure. However, the equilibrium selectivity to IBA is relatively small compared to MEK, as the hydride shift is much easier than the methyl shift [9]. On the other hand, 3-buten-2-ol was neglected as the product in this reaction due to its negligible quantity. Further, the butylene isomers could be potential products during the BDO dehydration reaction. However, the thermodynamic analysis showed a negligible quantity of butylene isomers in the absence of hydrogen. These results demonstrated that higher pressure and lower temperature are favourable for selective MEK production from BDO, while the elevated temperature and low pressure are suitable for diverting BDO dehydration reaction to BD production.

2.3. BDO dehydration reaction to methyl ethyl ketone (MEK)

The dehydration reaction for selective conversion of BDO to MEK was reported using both homogeneous mineral acid catalysts, such as sulfuric acid, and heterogeneous solid-acid catalysts, such as cation

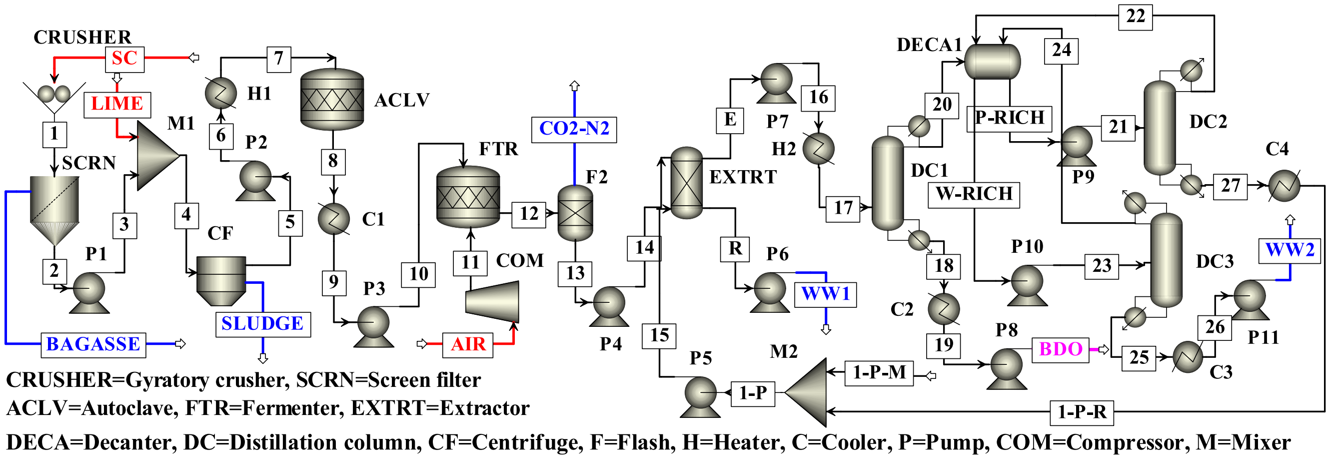


Fig. 3. Process flowsheet without heat exchanger network for the conversion of 2000 metric tons/day of sugarcane (SC) to 2,3-butanediol (BDO).

Table 1
Optimal parameters of the distillation columns.

	SC to BDO			BDO to MEK								
				Common		I			II		III	
	DC1	DC2	DC3	DC4	DC5	DC6	DC7	DC8	DC6	DC7	DC6	DC7
No. of stages	28	30	25	17	10	42	20	20	42	31	17	42
Feed stage	12	2	2	13	2	13	3 (2)	2	13	16	12	17
Reflux ratio (mass)	0.15	2	15	0.079	0.001	22.1	0.01	200	22.1	1.4	5	40

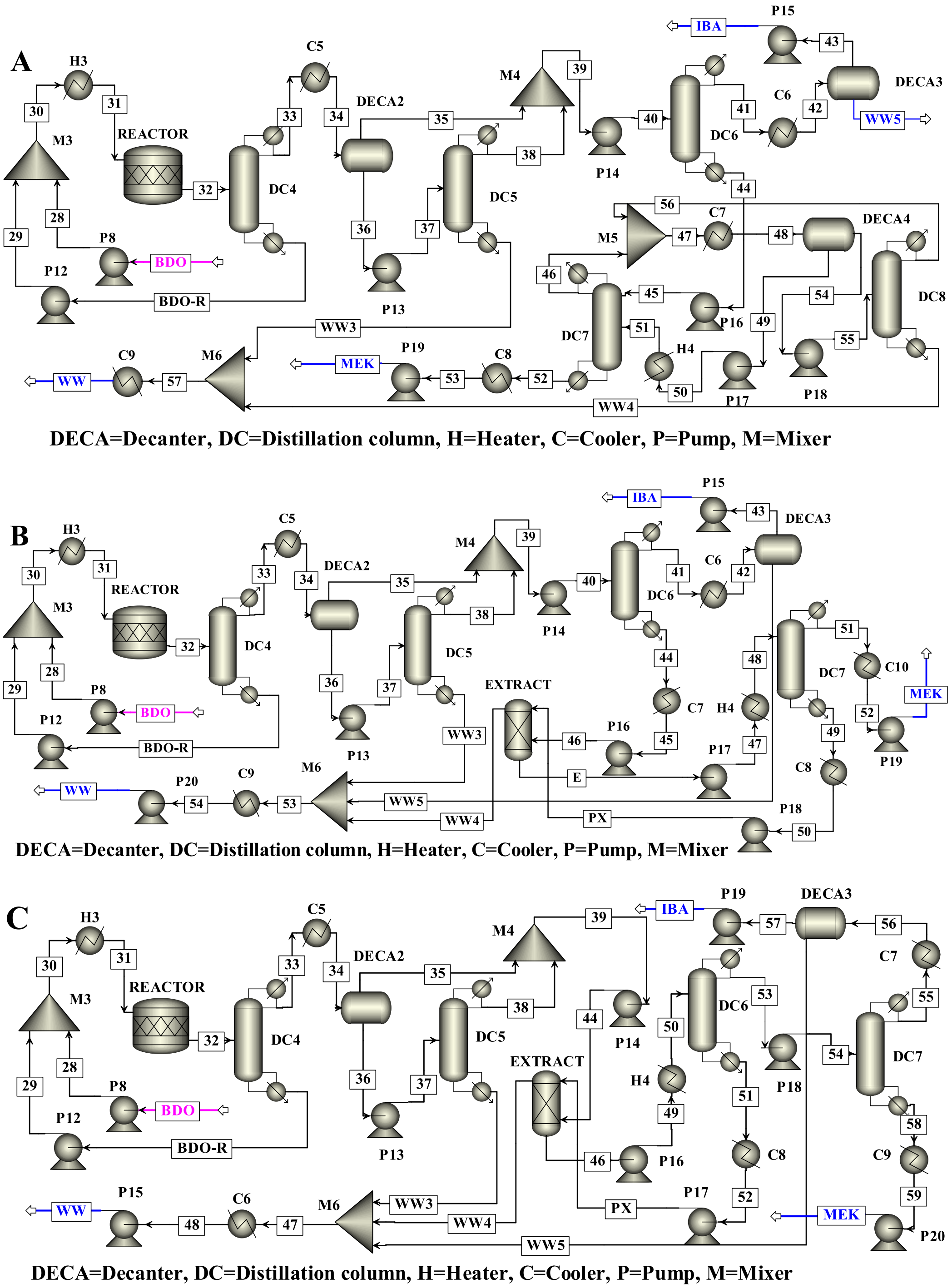


Fig. 4. Process flowsheet for the conversion of 2,3-butanediol (BDO) to methyl ethyl ketone (MEK). Separation of MEK-water using (A) heterogeneous azeotropic distillation (Configuration I), (B) extraction-distillation (Configuration II), and (C) separation of MEK-IBA-water using extraction-distillation (Configuration III).

exchange resin and zeolites [43]. However, the solid-acid catalysts are easy to separate from the reaction mixture and environmentally more benign for industrial applications than the homogeneous counterparts. Among various solid-acid catalysts, γ-Al_2O_3 showed reasonable MEK selectivity at moderate temperatures [24]. However, BDO conversion remained low due to its weak acidity [24]. On the other hand, zeolites are excellent solid-acid catalysts with strong acidity. However, the strong acid sites of zeolites enhance methyl shift, forming a significant amount of IBA by-product (Reaction (2)). The HZSM-5 was thus modified by phosphorous to suppress strong acid sites, with concurrent enhancement of weak and medium acid sites [44]. Phosphorous-modified HZSM-5 thus showed excellent BDO conversion and high MEK selectivity at low temperatures [44]. The process was thus designed in a fixed-bed reactor based on the experimental results reported over the phosphorous-modified HZM-5 catalyst [43]. The reaction was carried out under the liquid phase at 200 °C and 27 bar pressure [43]. The reaction equilibrium is also favourable to MEK at high pressure, as discussed in the previous section. The high pressure also prevents the liquid-to-vapour phase transition of reactant, thereby saving energy consumption for vaporization. Under these reaction conditions, the BDO conversion was 90 %, with 90 % and 10 % selectivity to MEK and IBA, respectively [43]. Penner et al. designed this process using pure BDO as feedstock [43]. However, Maina et al. proposed converting aqueous BDO obtained from fermentation into MEK [37]. However, the fermentation broth contains soluble inorganic nutrients and unconverted sugars. These contaminants may cause catalyst deactivation in the long run. Therefore, in this work, the BDO from the fermentation broth was first separated by liquid–liquid extraction, and pure BDO was then used as feedstock to produce MEK. The fixed-bed reactor was represented by the RStoic model due to the unavailability of reliable kinetics for this reaction.

2.4. Process for producing BDO from SC

The SC was first crushed and milled to extract the sucrose syrup (Fig. 3). Filtration was then used to separate SCB from SC juice, which was further treated with lime, maintaining a pH of 5.5. The sludge generated during the lime pretreatment was removed by centrifuge. The purified sugar syrup was heated to 121 °C, sterilized for 20 min at this temperature, brought down to 32 °C, and sent for fermentation. The sucrose was fermented under aerobic conditions using air. The sucrose concentration in the fermenter feed was around 190 g/L without dilution or evaporating water from SC syrup, which resulted in 97 g/L BDO in the fermentation broth.

The BDO was separated from the fermentation broth in two steps. BDO-water-*1*-pentanol ternary mixture shows liquid–liquid two-phase envelop below 40 wt% BDO and 90 wt% *1*-pentanol (Fig. 1A). BDO was thus extracted from the fermentation broth (9.7 wt% BDO) using *1*-pentanol solvent and Extract model. The BDO was then separated from the BDO-rich extract phase using the RadFrac distillation model. The solvent was lighter than fermentation broth, and hence, it was fed from the bottom of the extraction column, which had ten stages. The mass flow rate of *1*-pentanol was around four times of BDO to recover more than 99.9 % of BDO in the extract. The water-rich raffinate was obtained from the bottom of the extractor and composed of unconverted sugars and water (98.28 %), with a small amount of *1*-pentanol (1.2 %). This stream was sent for wastewater treatment.

The BDO-rich extract was obtained from the top of the extractor and composed of 16.4 % BDO, 65 % *1*-pentanol, and 18.6 % water. The extract was fed to a distillation column (DC1) to recover 99.9 % BDO as a bottom product with more than 99.9 % purity. However, the reboiler of this distillation column involved huge heat duty at a high operating temperature of 183.9 °C. Therefore, the extract stream at 30 °C was preheated (H2) to 110 °C before feeding to DC1, which reduced reboiler duty by around 1.01×10^7 kJ/h. Further, the heat duty of the preheater can be obtained from the process hot streams, thereby saving hot utility consumption.

The distillate from DC1 was composed of *1*-pentanol (77.7 wt%) and water (22.3 wt%). However, *1*-pentanol forms heterogeneous azeotrope at around 55 wt% water, with about 14.9 wt% water in the *1*-pentanol-rich phase and 2.4 wt% *1*-pentanol in the water-rich phase (Fig. 1B). *1*-Pentanol was thus separated from water by heterogeneous azeotropic distillation using two distillation columns (DC2-DC3). However, DC1 distillate was directly sent to the decanter as the *1*-pentanol-water composition was within the two-phase region. The water-rich and *1*-pentanol-rich phases were then fed to DC2 and DC3, respectively. The minimum boiling *1*-pentanol-water azeotropic mixture, obtained as a distillate from these distillation columns, was directed to the decanter. *1*-Pentanol and water were obtained as bottom products of DC2 and DC3, respectively. *1*-Pentanol was returned to the extractor after the addition of the makeup amount. The optimum number of stages, reflux ratio, and feed stage of these distillation columns are presented in Table 1.

2.5. Processes for producing MEK from BDO

Fresh BDO obtained from the upstream process (around 138.57 metric tons per day) was mixed with recycled BDO, pressurized to 27 bars by centrifugal pump, heated to 200 °C, and sent to the fixed-bed reactor (Fig. 4). The product stream was composed of around 65 % MEK, 7 % IBA, 18 % water, and 10 % unconverted BDO. The BDO does not form azeotropes with any of the products, and it was thus separated by distillation (DC4) as a bottom product and recycled to the reactor. The distillate from DC4 was composed of 72 % MEK, 20 % water, and 8 % IBA, which was within the liquid–liquid phase envelope (Fig. 1C). The MEK-water-IBA ternary diagram shows the phase separation of this mixture into a water-rich phase containing 6 % MEK and 0.06 % IBA and MEK-rich phase with about 9 % water and IBA each. This stream was cooled to 30 °C for better phase separation and sent to a decanter for liquid–liquid phase separation. The water-rich phase contains a small quantity of MEK and IBA, which was recovered by another distillation column (DC5). The organic phase and distillate from DC5 were mixed, and it was composed mainly of MEK and IBA, with a small quantity of water. However, both MEK and IBA form the heterogeneous azeotropes with water at 12.66 wt% and 8.61 wt% water, respectively (Fig. 1B). The equilibrium water content in the two liquid phases was 10.52 wt% and 86.89 wt% for MEK-water mixture, while it was 3.54 wt% and 95.56 wt % for IBA-water mixture at 30 °C. In this work, three different configurations were compared for separating MEK-IBA-water: (i) distillation of IBA, followed by heterogeneous azeotropic distillation of MEK-water, (ii) distillation of IBA, followed by extraction of MEK from water, and (iii) extraction of MEK and IBA from MEK-IBA-water, followed by distillation. The activity coefficient-based NRTL property model was used for the process design [43]. The number of stages with appropriate feed stage locations and reflux ratios of all distillation columns was optimized, as presented in Table 1.

Configuration I. The IBA-water forms the heterogeneous azeotrope at 5.9 wt% water, with around 3.5 wt% water in the IBA-rich and 95.6 wt% water in the water-rich liquid phases (Fig. 1B). In this configuration, the volatile IBA, accompanied by water corresponding to azeotropic composition, was first separated by a distillation column (DC6) (Fig. 4A). The water was later partially removed in a decanter to get 97 wt% pure IBA. The bottom stream from DC6 was composed of 92 wt% MEK-water, from which pure MEK was obtained using two distillation columns (DC7-DC8). The MEK-water also forms the heterogeneous azeotrope at 11.98 wt% water, with around 10.5 wt% water in the MEK-rich and 86.8 wt% water in the water-rich liquid phases (Fig. 1B). The composition of the MEK-water feed mixture was thus within the single-phase region. Therefore, this stream was directly fed to the DC7, where the minimum boiling MEK-water azeotropic mixture was obtained as distillate with 99.5 % pure MEK as the bottom product. The distillate stream was directed to a decanter for phase separation. The MEK-rich and water-rich phases from the decanter were directed to DC7 and DC8, respectively. The decanter was operated at 30 °C for better phase separation. The MEK-rich phase, which was dominating, was heated to 63 °C before feeding to DC7 to reduce the reboiler duty. The reflux ratio of DC5 and DC7 was quite low due to the subcooled temperature of the feed, which resulted in substantial internal reflux within the column. However, a large number of stages and a high reflux ratio in DC6 were due to the low relative volatility of IBA. On the other hand, the high reflux ratio in DC8 was due to the low distillate rate.

Configuration II. Liquid-liquid extraction is an attractive alternative to heterogeneous azeotropic distillation for separating MEK from the MEK-water mixture. In this configuration, MEK was extracted using *p*-xylene as a solvent [45]. *p*-Xylene has a high partition coefficient (mass fraction, x) for MEK ($K_{MEK} = x_{MEK}^{org}/x_{MEK}^{aq}$=3.9–4.5) and a low distribution coefficient for water ($K_W = x_W^{org}/x_W^{aq}$=0.069–6.5 × 10^{-04}), with high MEK extraction selectivity ($K_{BDO} = x_{BDO}^{org}/x_{BDO}^{aq}$=56–1.7 × 10^{04}) (Fig. S1). The *p*-xylene-MEK-water ternary diagram also showed that water was practically absent in the *p*-xylene-rich phase and vice versa (Fig. S1). Further, the boiling point difference between MEK and *p*-xylene is quite high (around 60 °C), making the separation of *p*-xylene from extract easier by distillation. The MEK-water mixture from DC6, having around 8 wt% water, was fed from the bottom of the liquid–liquid extraction column (Fig. 4B). The column had ten equilibrium stages and was operated using a *p*-xylene/MEK mole ratio of 4.0. In the extraction column, more than 95 % of water was removed as raffinate, with almost complete recovery of MEK in the extract and insignificant loss of solvent with raffinate. The extract, containing 85.44 wt% *p*-xylene, 14.5 wt% MEK, and 0.06 wt% water, was sent to a distillation column, where 99.5 wt% MEK was obtained as distillate, with more than 99.99 % recovery. The *p*-xylene was recovered as a bottom product and recycled to the extractor. The DC7 feed was preheated to 120 °C to reduce the reboiler heat duty.

Configuration III. The *p*-xylene also has a very high partition coefficient for IBA ($K_{IBA} = x_{IBA}^{org}/x_{IBA}^{aq}$=7–9.5), a small distribution coefficient for water ($K_W = x_W^{org}/x_W^{aq}$=0.04–2.4 × 10^{-04}), and a high IBA extraction selectivity (K_{IBA}/K_W=340–2.8 × 10^{04}) (Fig. S1). The *p*-xylene-IBA-water ternary diagram also showed that water was practically absent in the *p*-xylene-rich phase and vice versa (Fig. S1). Therefore, both MEK and IBA were extracted using *p*-xylene as a solvent in this configuration (Fig. 4C). In the extractor, the entire MEK and IBA were extracted into the extract phase, with about 95 wt% removals of water as raffinate. The components in the extract, 84.07 wt% *p*-xylene, 15.87 wt% organics, and 0.06 wt% water, were separated by two distillation columns, DC6-DC7. More than 99.99 % of *p*-xylene was recovered from the bottom of the first distillation column (DC6) and recycled to the extractor. The DC6 feed was preheated to 120 °C to reduce the reboiler heat duty. The distillate from DC6 was further separated in DC7, where 99.95 wt% MEK and IBA were obtained as the bottom product and distillate, respectively. The water was later decanted from the IBA stream to obtain 97 wt% IBA. The reflux ratio in DC7 was quite high due to the lower distillate rate than the bottom product.

3. Methodology

3.1. Pinch analysis

The pinch technology efficiently manages thermal energy within the process through process integration via optimal heat exchanger network design. This analysis was carried out based on source and target temperatures, heat duty change, and mass flow rate of the process streams, which were obtained from the designed flowsheets. Additionally, the exothermic or endothermic heat duty of the various unit processes was also considered for pinch analysis. In the case of isothermal unit operations, pinch analysis was performed assuming 1 °C temperature difference between the inflow and outflow. Based on these data, the mass flow rate heat capacity was estimated for the various hot and cold streams, and pinch analysis was then performed using a minimum temperature difference of 10 °C. The T-H diagrams, such as grand composite and composite curves, were used to calculate the minimal (cold and hot) utility demands and pinch point temperatures. The optimal heat exchanger network was then designed for maximum process heat recovery. The cold and hot utilities were taken as cooling water and high-pressure/medium-pressure steam, respectively.

Table 2
Retail price of raw materials, chemicals, and utilities.

Sugarcane (SC)	0.033 US$/kg [38]
Sugarcane bagasse (SCB)	0.04 US$/kg [38]
Lime	0.11 US$/kg [38]
High-pressure steam @400 psi	0.027 US$/kg [14]
Medium-pressure steam @165 psi	0.022 US$/kg [14]
Cooling water	0.032 US$/1000 L [14]
Isobutyraldehyde (IBA)	0.85 US$/kg [52]
Catalysts	0.018 US$/kg BDO [53]
Electricity	0.0775 US$/kW-h

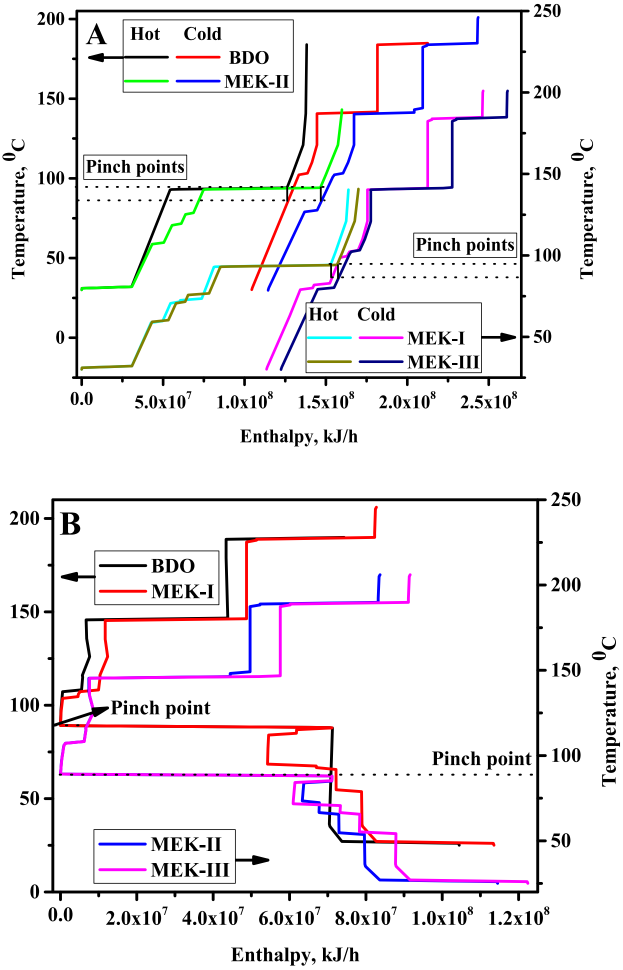


Fig. 5. (A) Composite and (B) grand composite diagram.

3.2. Economic analysis

Process economics involves the estimation of fixed capital investment, operating expenses, production cost, MBSP, and MMSP. The acquired prices of SC, chemicals, and utilities were taken from different sources (Table 2). Lime consumption was taken as 0.01 kg per kg of SC [38]. The BDO dehydration reaction to MEK was performed in a high-

Table 3
Products and co-products produced, and raw materials and utility consumed.

	SC to BDO	SC to MEK		
		I	II	III
BDO, metric tons (MT)/annum	50578.2	–		
Sugarcane bagasse (SCB), MT/annum	111,690	111,690		
MEK, MT/annum	–	36416.3		
IBA, MT/annum	–	4146.6		
Heat duty, kJ/h				
Minimum heating duty, kJ/h	7.43×10^{07}	8.28×10^{07}	8.37×10^{07}	9.16×10^{07}
Actual heating duty, kJ/h	7.49×10^{07}	8.30×10^{07}	8.44×10^{07}	9.24×10^{07}
Percentage of minimum, %	100.78	100.31	100.85	100.85
Minimum cooling duty, kJ/h	1.04×10^{08}	1.14×10^{08}	1.15×10^{08}	1.22×10^{08}
Actual cooling duty, kJ/h	1.05×10^{08}	1.14×10^{08}	1.15×10^{08}	1.23×10^{08}
Percentage of minimum, %	100.56	100.23	100.62	100.64
Utilities consumed after process integration				
Electricity, kW-h/h	813.4	885.4	884.7	895.8
Colling water, MT/annum	4.57×10^{07}	4.96×10^{07}	5.02×10^{07}	5.37×10^{07}
Medium-pressure steam (165 psi)	1.88×10^{05}	2.10×10^{05}	2.16×10^{05}	2.50×10^{05}
High-pressure steam (400 psi)	1.32×10^{05}	1.46×10^{05}	1.46×10^{05}	1.46×10^{05}

pressure fixed-bed continuous reactor, whose operating parameters were practically identical to the reactor used for the hydrotreatment of various petroleum fractions. The capital investment of the BDO dehydration reactor was thus evaluated using the known cost of the hydrotreating facility using the six-tenth rule [46]. In addition, the fermentation reactors were modelled as stirred tanks, and the capital investment of the fermenters was estimated based on the number of 500 m^3 tanks, with 3/4th of the tank as the working volume. The expenses for storage tanks were evaluated based on twelve days of storage provision for raw materials and chemicals and twenty-five days of storage capacity for products and co-products. The capital investment was estimated using the Chemical Engineering Plant Cost Index of 708.0 for 2021 [47].

$$\text{Cost } of\ equipment1 = \text{Cost } of\ equipment2 \times \left(\frac{Capacity\ of\ equipment1}{Capacity\ of\ equipment2}\right)^{n} \tag{1}$$

Twenty years of plant life were considered with three hundred sixty-five working days per annum for economic and profitability analysis. The equipment depreciation cost was computed using the straight-line depreciation method, with 20 % of the initial investment as the salvage value [48]. The operating labour cost was calculated considering four operators and one supervisor for SC conversion to BDO and eight operators and one supervisor for MEK production from SC. The hourly salaries of supervisors and operators were calculated at US$ 35 and US$ 20, respectively [48].

4. Results and discussion

4.1. Pinch analysis

The pinch analysis was carried out for the conversion of SC to BDO and three process configurations for MEK production from SC. The composite and grand composite diagrams for these processes are shown in Fig. 5. These processes exhibited identical pinch point temperatures, i.e., hot and cold pinch point temperatures of 94.13 °C and 84.13 °C, respectively. The minimum heating and cooling duty requirements were

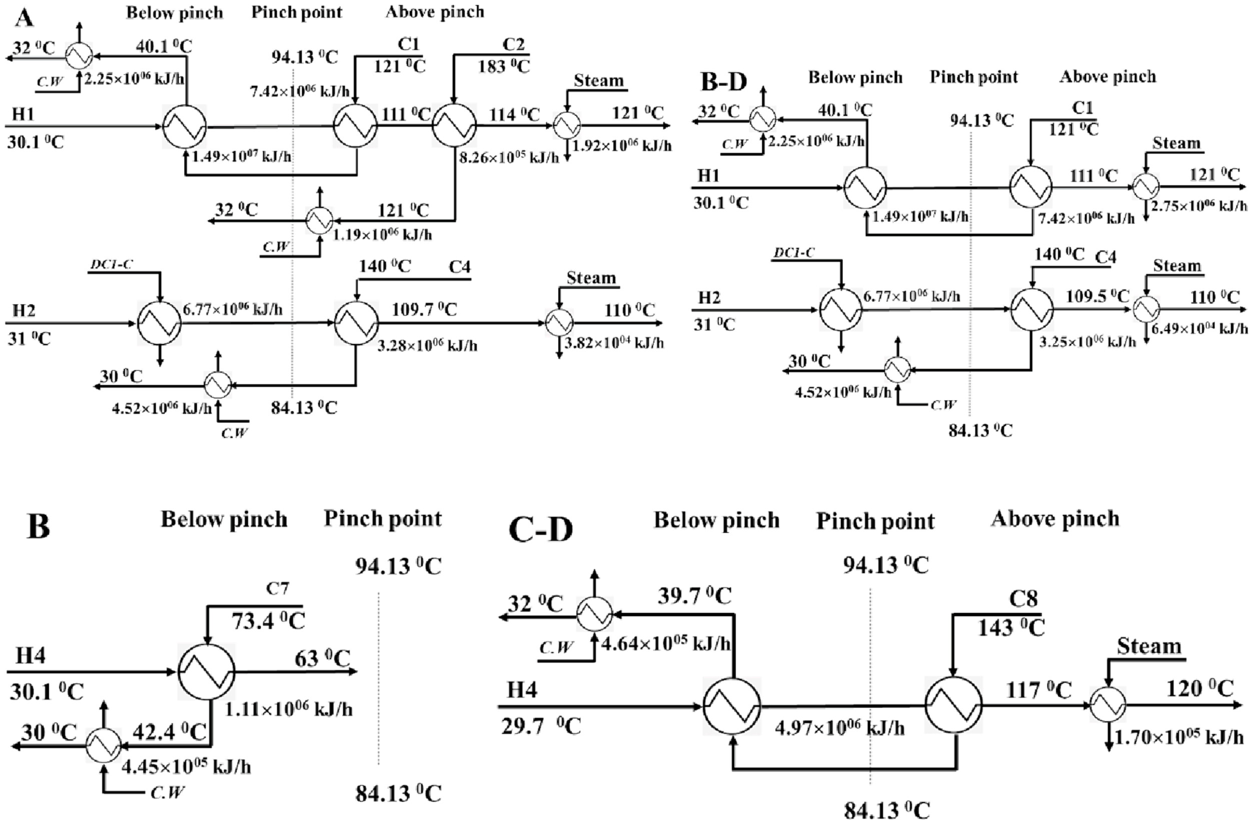


Fig. 6. Heat exchanger network for the conversion of sugarcane (SC) to (A) 2,3-butanediol (BDO) and (B-D) methyl ethyl ketone (MEK) for Configurations I, II, and III.

Table 4
Capital expenditure in millions of US$.

Equipment	SC to BDO	SC to MEK		
		I	II	III
Crusher	1.481	1.481	1.481	1.481
Screen filter	0.018	0.018	0.018	0.018
Autoclave	0.383	0.383	0.383	0.383
Fermenter	9.602	9.602	9.602	9.602
Extractors	0.330	0.330	0.462	0.462
Decanters	0.026	0.084	0.062	0.062
Reactor	0.000	4.182	4.182	4.182
Distillation columns	2.005	3.211	3.121	3.187
Compressor	0.386	0.386	0.386	0.386
Centrifuge	0.263	0.263	0.263	0.263
Heat exchangers	0.294	0.365	0.379	0.390
Pumps	0.072	0.202	0.208	0.208
Storage tanks	0.235	0.492	0.492	0.492
Total equipment cost (TEC)	**15.095**	**20.999**	**21.040**	**21.117**
Installation, 52 % of TEC	7.849	10.920	10.941	10.981
Instrumentation and controls, 30 % of TEC	4.528	6.300	6.312	6.335
Piping, 75 % of TEC	11.321	15.750	15.780	15.838
Electricals, 12 % of TEC	1.811	2.520	2.525	2.534
Building, 20 % of TEC	3.019	4.200	4.208	4.223
Yard improvements, 11 % of TEC	1.660	2.310	2.314	2.323
Service facilities, 77 % of TEC	11.623	16.170	16.201	16.260
Land, 5 % of TEC	0.755	1.050	1.052	1.056
Direct fixed cost (DFC) (A)	**57.661**	**80.218**	**80.374**	**80.667**
Engineering and supervision, 9 % of DFC	5.190	7.220	7.234	7.260
Construction expenses, 11 % of DFC	6.343	8.824	8.841	8.873
Legal expenses, 1 % of DFC	0.577	0.802	0.804	0.807
Contractor fees, 6 % of DFC	3.460	4.813	4.822	4.840
Contingency, 12 % of DFC	6.919	9.626	9.645	9.680
Indirect fixed cost (B)	**22.488**	**31.285**	**31.346**	**31.460**
Fixed capital cost (FCI) (C = A + B)	80.149	111.503	111.720	112.127
Working capital (D), 5 % of FCI	4.007	5.575	5.586	5.606
Total capital investment (TCI) (C + D)	**84.157**	**117.078**	**117.306**	**117.733**

obtained from the T-H diagrams, as shown in Table 3. Both hot and cold minimum duties were much higher for the processes for converting SC to MEK than BDO alone due to additional processing steps. However, Configuration I of the MEK production processes, which used heterogeneous azeotropic distillation for MEK-water separation, exhibited the lowest heating and cooling duties. The heating (1.29×10^{08} kJ/h) and cooling (1.60×10^{08} kJ/h) duties before process heat exchange were slightly lower for Configuration II involving solvent extraction of MEK compared to Configuration I (heating = 1.33×10^{08} kJ/h and cooling = 1.64×10^{08} kJ/h). However, the process heat exchange was higher for Configuration I than Configuration II, resulting in marginally lower utility consumption. On the other hand, Configuration III involved the highest heating (1.39×10^{08} kJ/h) and cooling (1.70×10^{08} kJ/h) duties without process heat exchange and with maximum utility consumption. The heat exchanger network was designed based on the pinch analysis, as shown in Fig. 6. The grid diagrams are shown in the supplementary information (Fig. S2). The actual duty consumption in all scenarios exceeded by less than 1 % of the minimum requirements (Table 3).

For the SC to BDO conversion process, H1 was heated from the initial temperature to about 111 °C by C1, with the simultaneous cooling of C1 to 40.1 °C. The C1 was further cooled to 32 °C by cooling water. The balance heating duty of H1 was obtained by C2, followed by steam. The remaining cooling duty of C2 was obtained by cooling water. Below the pinch point temperature, the heating duty of H2 was obtained by exchanging heat with the condenser of DC1. However, above pinch point temperature, H2 was heated sequentially by C4 and steam to reach 110 °C. C4 was further cooled by cooling water. The heat-integrated process with the heat exchanger network is shown in Fig. S3.

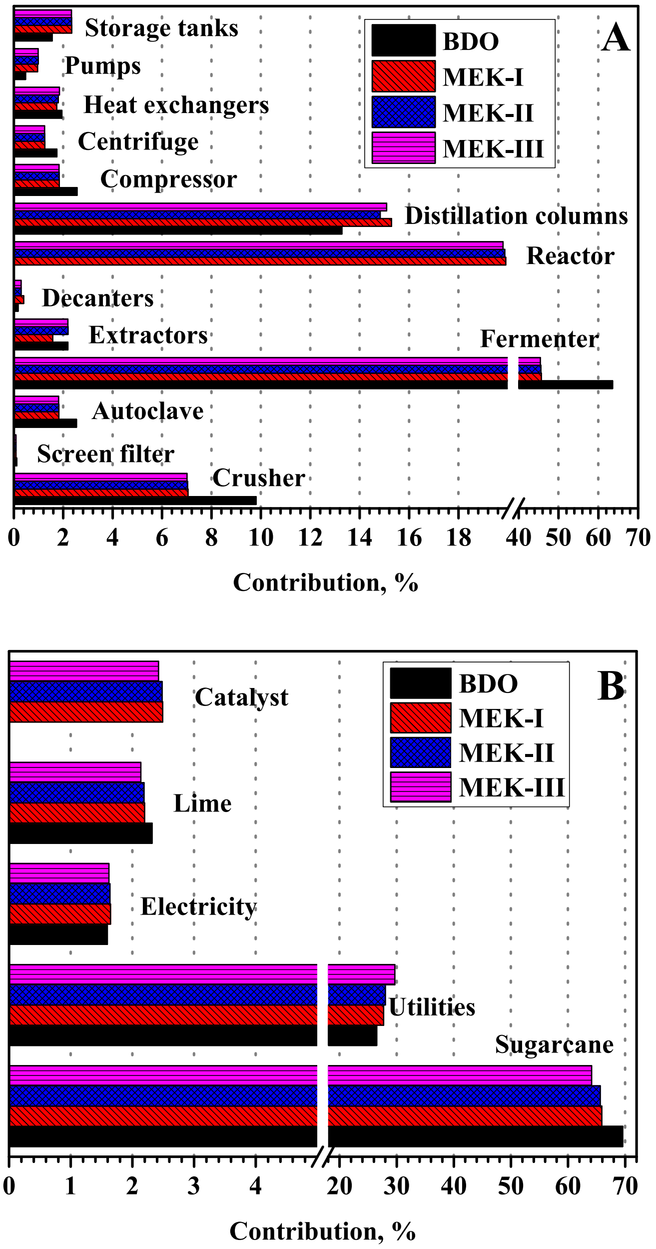


Fig. 7. Contribution of (A) individual equipment and (B) raw materials, utilities, and chemicals to their respective totals.

For MEK production processes from SC, the heat duty of the C1 was utilized for heating H1 from the initial temperature to around 111 °C, which was further heated to 121 °C by steam. During this heat exchange, the temperature of C1 was dropped to 40.1 °C, from which it was cooled to 32 °C by cooling water. Similarly, for all these processes, H2 was heated to the pinch point temperature by process heat exchange with the condenser of DC1, and above the pinch point temperature, it was heated by C4. The balance heating duty of H2 was obtained by steam. In this heat exchanger, the temperature of C4 reached pinch point temperature, from which it was further cooled by cooling water. For Configuration I, the entire heating duty of H4 was accomplished by process heat exchange with C7. In this configuration, the reboiler temperatures of DC6 and DC7 were around 79 °C and 82 °C, respectively. The heating duty of these reboilers was obtained by exchanging heat with the condenser of DC2, whose operating temperature was around 94 °C. Similarly, the reboiler temperature of DC6 in Configuration II and DC7 in Configuration III were below the pinch point temperature, and

Table 5
Operating costs in millions of US$ per annum.

	SC to BDO	SC to MEK		
		I	II	III
Direct costs				
Operating labour	1.007	1.708	1.708	1.708
Maintenance, 6 % of FCI	5.049	7.025	7.038	7.064
Operating charges, 25 % of operating labour	0.252	0.427	0.427	0.427
Plant overhead charges, 50 % of operating labour and maintenance	3.028	4.366	4.373	4.386
Sugarcane (SC)	24.090	24.090	24.090	24.090
Utilities (cooling water and steam)	9.179	10.130	10.282	11.144
Electricity	0.552	0.601	0.601	0.608
Lime	0.803	0.803	0.803	0.803
Catalysts	0.000	0.910	0.910	0.910
Indirect costs				
Insurance & taxes, 1 % of TEC	0.226	0.315	0.316	0.317
Depreciation	0.604	0.840	0.842	0.845
Interest, 5.5 % of TCI	4.629	6.439	6.452	6.475
Other expenses				
General & administration expenses, 8 % of subtotal operating cost	0.747	1.082	1.084	1.087
Total operating cost (A)	**50.167**	**58.737**	**58.926**	**59.864**
Sugarcane bagasse (SCB) credit (B1)	4.468	4.468	4.468	4.468
IBA credit (B2)	0.000	3.525	3.525	3.525
Net production costs (C = A-B1-B2)	45.699	50.745	50.933	51.872
BDO/MEK produced, metric tons/annum (D)	50578.2	36416.3	36416.3	36416.3
Production cost, US$ per kg (C/D)	**0.904**	**1.393**	**1.399**	**1.424**

Table 6
Production costs and selling price of BDO from various feedstocks.

Feedstock	**Titer, g/L**	**Capacity, metric tons/ day**	**BDO price, US$/kg**		**Ref.**
			Production	Selling	
Crude oil	–	–	–	2.8–3.5	[15]
Brewer's spent grain	80	100	1.842	–	[14]
	100		1.764	2.71[a]	
	120		1.736	–	
	100	2000	1.069	1.53	
Glucose	110	–	–	2.52[b]	[30,32]
Sugarcane bagasse (SCB)	–	96	1.13–2.28[c]	1.86–3.99[c]	[15]

[a] 8.5% ROI and nine-year payback period.
[b] Seven-day storage of the high-volume broth.
[c] Cost depends on the disposition of the processing plant.

their heating duties were obtained from the condenser of DC2. For Configuration II and III, the H4 was partially heated to around 117 °C by exchanging heat with C8. The balance heating duty of H4 and C8 was obtained by steam and cooling water, respectively. The process flowsheets for Configurations I, II, and III without and with heat exchanger network are shown in Fig. S4-S6.

4.2. Capital investment

The major equipment involved in producing BDO from SC were fermenters, columns (distillation and extraction), and crusher, contributing around 64 %, 15 %, and 10 % of the equipment costs, respectively (Table 4 and Fig. 7). The long fermentation time was responsible for a large share of the fermenters in the capital investment. On the other hand, the BDO solvent extraction process involved an excessive solvent flow rate in the extractor, coupled with downstream separation of solvent from BDO by distillation, with huge capital investments for columns. The individual contribution of all other equipment was around or less than 2 %. Fermentation was also reported to contribute almost 77 % of total capital investment for microbial BDO production from cellulose fraction of SCB (96 metric tons /day) in a standalone plant [15]. The anaerobic digester, enzymatic hydrolysis, fermenter, and centrifuges together contributed almost 59 % of total equipment costs for BDO production from brewer's spent grain (100 metric tons/day) [14]. However, the capital investment was around 39 % higher for the conversion of SC to MEK compared to producing BDO alone due to additional processing steps (Table 4). The fermenters remained the most capital-intensive equipment in these processes, with around 46 % contribution to the total equipment costs. Further, the high-pressure fixed-bed reactor was the heart of the downstream BDO conversion to MEK, and it contributed around 20 % of the equipment costs. Moreover, the downstream process involved additional columns for purifying products, and their contribution was thus increased to 17 % of the equipment costs. Four decanters were involved in Configuration I compared to only three in Configuration II and III. The decanter cost was thus slightly higher in Configuration I compared to Configurations II and III (Table 4). Similarly, an additional extraction column was involved in Configurations II and III, with higher equipment costs under this head. Though the costs of distillation columns and decanters were slightly lower in the extraction based MEK separation (Configurations II and III), they were compensated by extraction columns, heat exchangers, and pumps. The capital investment was thus slightly higher in Configurations II and III than in Configuration I. Among extraction based MEK separation processes, Configuration III exhibited a marginally higher capital investment due to slightly higher costs for distillation columns and heat exchangers.

4.3. Operating expenditure and production costs

Among raw materials, utilities (cooling water and steam), and chemicals, the SC and utilities were the major operating expenditures, contributing 70–64 % and 27–30 %, respectively (Table 5 and Fig. 7). The high utility expenditure was due to complex BDO extraction from fermentation broth and separation of azeotropic products mixture downstream of BDO dehydration reactor. For SC to MEK conversion processes, the highest utility expenditure was involved in Configuration III, followed by Configuration II and Configuration I (Table 3). The SCB was co-produced in significant quantities with high co-product credit. Similarly, IBA was another co-product in the downstream BDO dehydration to MEK, with a significant co-product credit. The BDO production cost was found to be US$ 0.9 per kg (Table 5). However, without designing the heat exchanger network, extra heating and cooling utilities equivalent to the heat exchange duty were needed, which increased BDO production cost (US$ 0.97 per kg). The pinch analysis thus reduced around 8 % of the BDO production costs. The utilization of SCB for enhanced production of BDO may further affect the process economics. Recently, techno-economics of fermentative BDO production from SCB predicted BDO production costs of US$ 1.13 to US$ 2.28 per kg for 96 metric tons/day plant capacity (Table 6) [15]. Similarly, techno-economic feasibility was evaluated for fermentative BDO production from 100 metric tons/day brewer's spent grain, a by-product in the beer manufacturing industry [14]. The BDO production cost for the heat-integrated process ranged from US$ 1.74 to US$ 1.84 per kg, depending on the BDO titer in fermentation [14]. Scaling up the process to 2000 metric tons/day decreased production cost to merely US$ 1.069 per kg (Table 6) [14]. On the other hand, the production cost of petrochemical BDO is around US$ 1.76 per kg [49]. These results reflect that bio-based

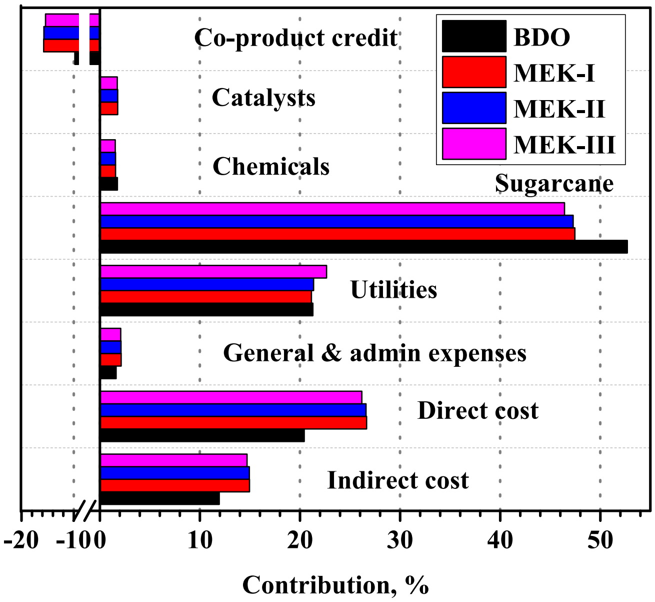


Fig. 8. Cost-contributing factors in the manufacturing of 2,3-butanediol (BDO) and methyl ethyl ketone (MEK) from sugarcane.

BDO is cost-competitive with its petrochemical counterpart.

On the other hand, the MEK production cost was in the range of US$ 1.39 to US$ 1.42 per kg, with the lowest being for Configuration I. The lower MEK production cost for Configuration I was due to lesser capital investment and utility consumption. On the other hand, the marginally higher MEK production cost for Configuration III compared to Configuration II was due to the greater capital expenditure and utility costs. However, the MEK production cost without pinch analysis was US$ 1.54, US$ 1.53, and US$ 1.56 per kg for Configuration I, II, and III, respectively. Therefore, integrating heat energy through pinch analysis saved the MEK production cost by around 9–10 % in these processes. In comparison, the renewable MEK production cost was lower than petroleum based MEK, whose market prices stood at US$ 2.04 per kg in Europe and US$ 1.70 per kg in US regions [50]. The minimum bio-based MEK selling price was reported to be US$ 1.90/Kg for an integrated biorefinery for BDO production from glucose and catalytic BDO dehydration to MEK [30]. It is interesting to note that Configuration II exhibited the lowest MEK production cost without pinch analysis, while Configuration I showed the lowest MEK production cost after pinch analysis. Nevertheless, the MEK production cost after pinch analysis was only marginally higher in extraction based MEK separation processes compared to the heterogeneous azeotropic distillation of MEK-water. However, heterogeneous azeotropic distillation involves a complex loop for MEK-water separation, with associated process operational challenges. Therefore, Configuration II with extraction based MEK separation should be considered for the process development due to the simplicity of process operation. Further, the availability of a more selective low-boiling solvent will enable a lower solvent/MEK mole ratio, with reduced operating costs, especially utility consumption.

4.4. *Cost-contributing factors*

The feedstock, i.e., SC, was the main cost-governing factor in the BDO manufacturing process, with more than 50 % contribution to the production cost (Fig. 8). The SC is edible and highly expensive. Therefore, the availability of cheaper sources of feedstock, for example, industrial or food waste, can ensure BDO production at a lower manufacturing cost. The SCB (96 metric tons/day) was reported to contribute around 30 % of BDO production costs [15]. The utilities were another major operating cost, with around 21 % contribution to the BDO production costs. The indirect costs are linked to capital investment in the form of insurance, taxes, equipment depreciation, and interest on borrowed capital. It contributed around 12 % of the BDO production

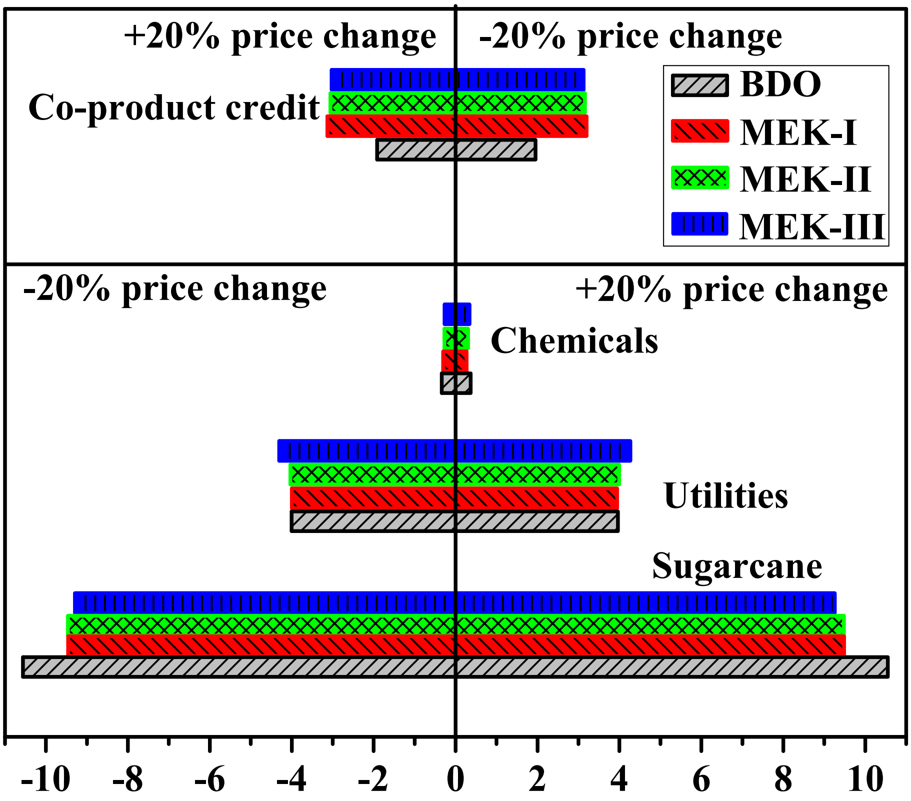


Fig. 9. Effect of ± 20 % variation in feedstock, utilities, and chemical costs and co-product credit on the production cost.

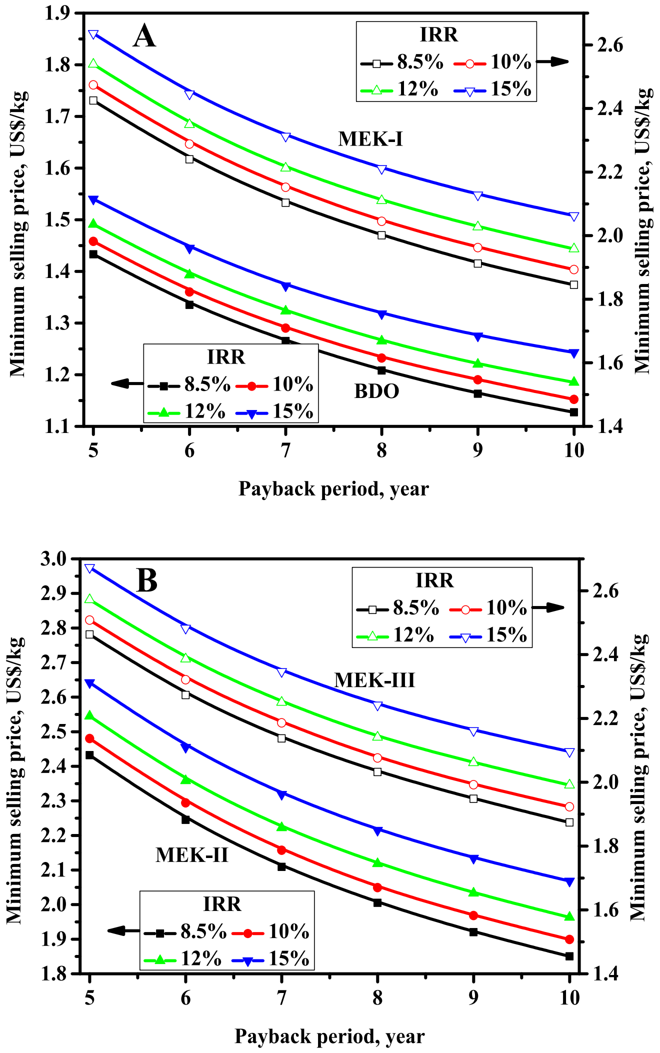


Fig. 10. Minimum product selling price in manufacturing 2,3-butanediol (BDO) and methyl ethyl ketone (MEK) from sugarcane (SC).

cost only, implying nominal capital investment involved in this process. On the other hand, except maintenance, all other components in direct costs were related to manpower and contributed around 20 % of the BDO production cost.

For the MEK manufacturing process, the SC remained as the dominating production cost factor, with around 46–47 % contribution. Utilities (21–23 %), direct costs (26–27 %), and indirect costs (15 %) were the other significant factors in the MEK manufacturing processes. The SCBwas the only co-product in the BDO manufacturing process from SC, and it contributed around 10 % of the production cost. However, IBA was additionally co-produced in the MEK manufacturing processes, with significantly higher co-product credit (15–16 %). The contribution of utilities was increased slightly in the order of Configuration I < Configuration II < Configuration III. The contribution of other operating cost factors thus showed opposite trends.

4.5. *Sensitivity analysis*

The sensitivity analysis was performed for ± 20 % variation in feedstock, utilities, and chemical costs and co-product credit on the production cost (Fig. 9). The feedstock cost is the most sensitive factor and changes BDO/MEK production cost by ± 10.5 %/± 9.3–9.5 % for ± 20 % variation in feedstock cost. The BDO production cost can be reduced to only US$ 0.81 per kg for 20 % reduction in feedstock cost. Similarly, 20 % reduction in feedstock cost results in a drop in MEK production cost to merely US$ 1.26–1.29 per kg. The utilities contributed around ± 4 % variation on BDO or MEK production cost for ± 20 % change in their price. Therefore, efficient product separation methods are needed to reduce utility consumption in these processes. For 20 % reduction in utility consumption, MEK production cost reduces to US$ 1.34–1.36 per kg. The chemicals had a negligible effect on production costs. The co-product credit was another significant sensitive factor, varying around ± 2 % for BDO and ± 3 % for MEK for ± 20 % variation in their prices.

4.6. *Profitability analysis*

The minimum BDO and MEK selling price (MBSP and MMSP) were calculated for 5–10 years payback periods and 8.5–15 % internal rate of returns (IRR) (Fig. 10) [48]. The minimum selling price was taken as the price of the product, for which net present worth became zero for a specified payback period and IRR. However, the sales tax figure is country-specific, and it was thus excluded from the calculation of the selling price. The profitability analysis was performed using a price escalation of 5 % for products, 3 % for utilities, operating labour, and maintenance, and 3.5 % for raw materials. The profitability analysis was performed considering 34 % income tax [48]. The results showed that the MBSP and MMSP were decreased by extending the payback period and reducing IRR. MBSP varied between US$ 1.13 to US$ 1.54, with the lowest being for 8.5 % IRR and ten-year payback period and the highest price being for 15 % IRR and five-year payback period. On the other hand, MBSP was reported to be US$ 2.1–2.9 per kg from glycerol and US $ 2.6–4.8 per kg from SC molasses for 10 % IRR and 30 years of plant life [51]. For the same profitability analysis parameters, MBSP ranged from US$ 1.86 to US$ 3.37 per kg from SCB, depending on the scenarios (Table 6) [15]. The commercial BDO selling price is around US$ 3.23 per kg [14]. Even after adding 30 % sales tax, BDO can be sold at a price of US$ 2.0 per kg, which is much lower than the commercial price. These results demonstrated that microbial production of BDO from SC is economically viable and competitive with the petroleum route. Further, the SC retail price is sensitive to geographic location, and even after a 100 % escalation of SC retail price, both BDO manufacturing cost (US$ 1.35 per kg) and MBSP (US$ 2.0 per kg for five-year payback period and 15 % IRR) remained much lower than the BDO market price. These results demonstrated that this process has a high return on investment potential.

For producing MEK, the MMSP per kg was in the range of US$ 1.85 – 2.64 for Configuration I, US$ 1.85 – 2.64 for Configuration II, and US$ 1.87 – 2.67 for Configuration III. The MMSP was reported as US$ 1.90/ kg for MEK production from glucose and xylose [30]. Currently, the commercial MEK retail price is in the range of US$ 1.5–2.0 [50]. These results demonstrated that the selling price of renewable MEK produced via bio-based BDO dehydration is slightly more expensive than the market price of petroleum derived MEK. Future studies should be directed toward developing novel product separation processes and low-cost feedstock to make renewable MEK commercially viable. For example, if separation processes can slash 20 % utility consumption and capital investment, the renewable MEK becomes commercially competitive, with an MMSP of US$ 1.59 per kg (Configuration II) for ten-year payback period and 8.5 % IRR. The MMSP can be further reduced to US$ 1.54 per kg for 20 % reduction in SC retail price.

5. Conclusions

This study demonstrated the techno-economic feasibility of an integrated biorefinery for the biosynthesis of BDO from sucrose syrup of SC, followed by chemo-catalytic BDO upgrading to MEK. The biorefinery was designed for a daily basis plant capacity of 2000 metric tons SC that produced 138.5 metric tons BDO or 100 metric tons MEK with co-production of 11 metric tons IBA. The thermal energy consumption in the MEK production process was much higher than that of BDO alone due to additional processing steps, with around 40 % more capital investment. Process heat integration reduced about 8 % of BDO and 9–10 % of MEK production cost. The BDO production cost was around US$ 0.9/kg, with an MBSP of US$ 1.54 per kg for 15 % IRR and a five-year payback period, demonstrating the commercial viability of microbial BDO. Though Configuration I, with the heterogeneous azeotropic distillation of MEK-water, involved lower capital investment and utility consumption with marginally lower production cost (US$ 1.39/kg), Configuration II, with extraction based MEK separation (US$ 1.399/kg), was considered most suitable due to the simplicity in process operation. The MMSP was US$ 1.85–US$ 2.64 for Configuration I, US$ 1.85–US$ 2.64 for Configuration II, and US$ 1.87–US$ 2.67 for Configuration III, which was roughly 16–24 % higher than the market price of MEK. The SC (around 50 %), utilities (about 20 %), and direct cost (roughly 25 %) were the major operational cost factors. Therefore, using low-cost lignocellulosic feedstock and improving downstream separation processes are vital in making renewable MEK viable in the future. Future research should be directed towards advanced bioprocessing using various biomass and inhibitor-tolerant strains. More efforts are also needed to integrate microbial BDO production and its chemo-catalytic upgrading to MEK and life-cycle assessment to reckon the sustainability of the bioprocess.

CRediT authorship contribution statement

Abhishek R. Varma: Writing – original draft, Investigation. **Bhushan S. Shrirame:** Methodology, Investigation. **Siddharth Gadkari:** Writing – review & editing. **Kumar Raja Vanapalli:** Writing – review & editing. **Vinod Kumar:** Writing – review & editing, Conceptualization. **Sunil K. Maity:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2024.151297.

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