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Methyl Ethyl Ketone Production through an Intensified Process

Methyl ethyl ketone (MEK) is widely used in the industry and is mainly produced from petroleum. Some works have projected MEK as a possible fuel since its performance in spark engines has overcome the performance of gasoline in certain indexes. Two intensified alternatives to produce MEK are introduced here, consisting of a reactive distillation column, an extractive distillation column, and three conventional distillation columns. The direct alternative resulted as the most promising when it was evaluated based on energy consumption, greenhouse gas emissions, and an environmental index. The obtained energy consumption for MEK production was $11.62 \text{ MJ kg}_{\text{MEK}}^{-1}$ for the entire process. Moreover, those intensified alternatives showed better performance indexes in comparison with a conventional process.

Keywords: Biofuels production, Methyl ethyl ketone, Process intensification

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Supporting Information
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1 Introduction

Methyl ethyl ketone (MEK) is a widely used chemical in the industry [1]. For such chemical versatility, the MEK market is estimated to increase to USD 3.26 billion and its production to 1.754 million tons by 2020 [2]. Most of the MEK uses are directly related to industrial application; however, recent studies suggest the use of MEK as a possible fuel for spark-ignition engines. In the work presented by Hoppe et al. [3], exhaustive research led to the conclusion that MEK offers superior performance over the current gasoline.

The industrial process for the production of MEK is performed through the hydration of butylene and the dehydration of that alcohol. The hydration process is performed at 250 °C, and it requires a 75 wt % H_2SO_4 solution. Butylene is produced from oil cuts. Subsequently, butyl alcohol undergoes dehydration and MEK is produced [1]. However, petroleum is a recognized finite resource and is pointed out as a major cause of environmental issues. So, the production of MEK from a renewable resource may be considered as a relief from these problems. Additionally, high concentrations of H_2SO_4 in the process can cause serious health problems; in addition, continuous exposure to high levels of 2-butanol can cause fatigue, dizziness, and eye irritation [4].

Although the current internal combustion engines run mostly on gasoline or diesel, diversification is projected in the engines of the transport sector. Liquid fuels produced from renewable raw materials keep the promise of closing the carbon cycle.

MEK might be produced by direct fermentation; however, its production is poor, with yields of approximately $0.004 \text{ g}_{\text{MEK}} \text{ g}_{\text{glucose}}^{-1}$ [5]. A promising alternative to produce MEK is by means of 2,3-butanediol (2,3-BD) as intermediate.

The interesting picture of this route is a relatively high yield in the production of 2,3-BD via fermentation near to the theoretical limit of $0.5 \text{ g}_{2,3\text{-BD}}/\text{g}_{\text{glucose}}^{-1}$ [6, 7]. Further, the direct dehydration of 2,3-BD is performed to produce MEK [8].

Regarding the dehydration of 2,3-BD, several catalyst proposals have been studied. There have been reports on the use of zeolites [9, 10], bentonite clay [11], calcium phosphates [12], and so on. Some of these works have reported selectivities of above 90–95 %. Note that there are several works regarding the dehydration of 2,3-BD; however, none of those works have reported the detailed kinetics. In an interesting work reported by Song [1], a set of detailed equations and reaction kinetics were reported for the dehydration of 2,3-BD to 1,3-butadiene (1,3-BD) and MEK over a catalyst of calcium phosphate. In a subsequent work, Song et al. [13] presented an alternative to produce and purify MEK from 2,3-BD. In their proposal, they presented a production scheme based on a reactor followed by a series of separation columns and decanters, making a total of ten separation units and a reactor (Fig. 1, Tab. 1). Most of these separation units are distillation columns.

An alternative to improve a process is process intensification (PI). PI is distinguished by five characteristics: reduced size of the equipment, increased performance of the process, reduced equipment inventory, reductions in using utilities and raw materials, and increased efficiency of the process equipment [14]. This strategy has been successfully proved in many cases where

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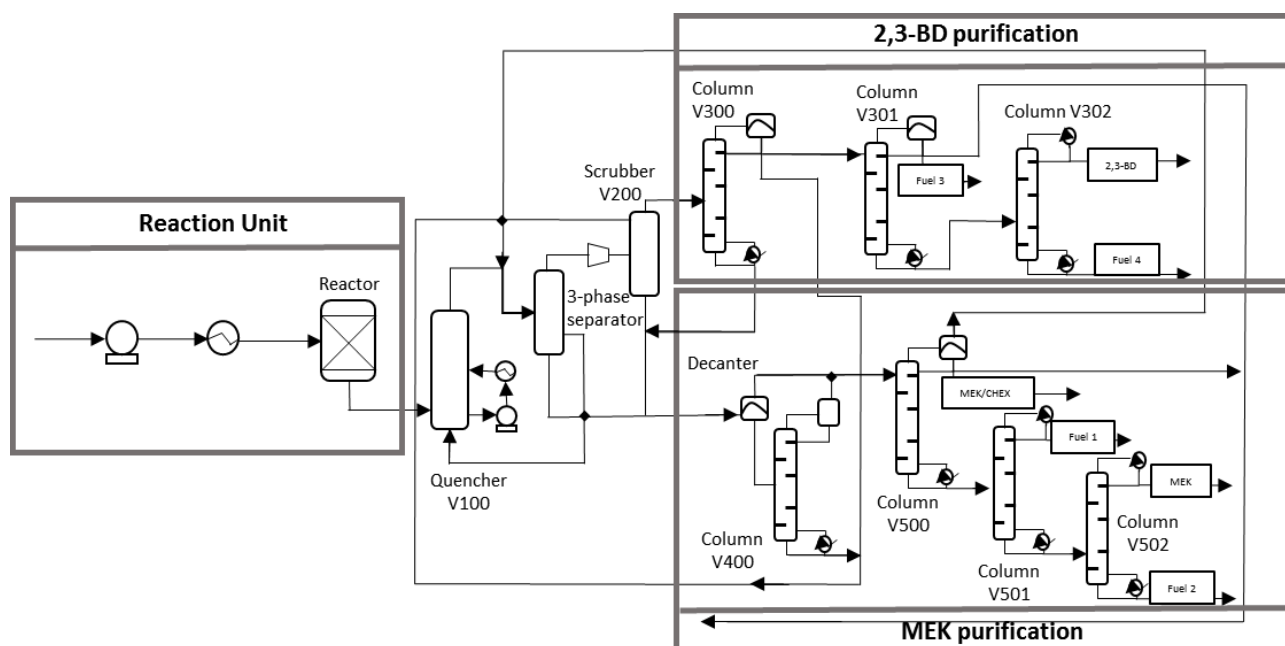


Figure 1. MEK production in a two-step process, design by Song et al. [13].

Table 1. Column specifications for the equipment shown in Fig. 1.

Description	V100	V200	V300	V301	V302	V400	V500	V501	V502
Number of stages	5	5	20	80	56	10	30	62	16
Pressure [$\text{kg cm}^{-2}\text{g}^{-1}$]	1.4	3.9	3.5	3.8	3.5	1.5	1.1	-0.35	-0.3
Feed temperature [$^{\circ}\text{C}$]	180	90	38.5	38	44.4	42.2	56.9	106	72.2
Overhead temperature [$^{\circ}\text{C}$]	51	38	40.6	42.1	40.8	94.1	85	52.8	69
Bottom temperature [$^{\circ}\text{C}$]	80	128	138	44.4	44.1	131.1	106	72.2	175
Heat duty [MMkcal h^{-1}]	-	-	0.76	2.16	0.93	1.72	2.25	2.67	0.65

a chemical reaction is involved, e.g., in reactive distillation (RD) where the reactor also acts as a separation process. Therefore, the intensification of processes allows eliminating conversion and phase equilibrium limitations. Incredibly, the first industrial application of RD was registered in the 1980s, despite the fact that the first patent for the production of methyl *tert*-butyl ether was made in 1921. The commercial success of RD for the production of methyl *tert*-butyl ether was followed immediately by many other applications, from the production of fine chemicals to bulk chemicals. Briefly, RD applications include a wide range of chemical reactions, polymer production, carbonylation, hydration and dehydration, hydrolysis, esterification, alkylation, chlorination, and amination, among others [15].

The improvements reported by the use of RD are quite varied and come in various case studies. For example, Souza et al. [16] report a considerable increase in the purity obtained by producing triacetin compared to the purity obtained in a conventional process. On the other hand, Popken et al. [17] report a decrease in energy requirements, increased selectivity, and conversion when methyl acetate is produced.

In some cases where the use of RD has been reported, savings of 20 % of the capital cost and energy costs have been stated [18].

The use of RD has not been left out of biofuel production; however, its use has been reported mostly for biodiesel production. For example, Kiss et al. [19] proposed the production of biodiesel using several heterogeneous catalysts (niobic acid, sulfated zirconia, sulfated titania, and sulfate tin oxide). Through the use of RD, the reaction time was improved, the productivity was increased and the size of the equipment was reduced, obtaining lower capital costs. In the same way, other authors have reported improvements in productivity and production costs for biodiesel production [20, 21].

On the other hand, the use of RD for other types of biofuels, mainly alcohols as, e.g., bioethanol or biobutanol, has not been investigated, probably because of the nature of the production process. Additionally, there are no reports of MEK production as a biofuel, as far as the authors are aware.

RD is highly attractive in those systems where certain chemical and phase equilibrium conditions exist [22]. According to Shah et al. [23], before a formal proposal of RD, it is necessary

to determine the feasibility of such a process. Following these recommendations, in this case, it should be noted that the following requirements are met: (i) the presence of more than one product, (ii) there is a match between the reaction and separation temperatures, (iii) the operating pressure and temperature are not close to the critical region of the components involved, and (iv) the volatilities of the components.

The reactions that can be performed in an RD process include heterogeneous and homogeneous catalytic reactions and thermal reactions where a catalyst is not needed [24]. Another example of an intensified process is the extractive distillation (ED) column. ED has proven its efficacy in reducing global energy consumption. The main reason for reducing energy requirements lies in the fact that an extractive column, by means of the solvent, helps in breaking the thermodynamic interactions among components and, consequently, the energy requirement is reduced. For example, Errico et al. [25] showed a total annual cost reduction of about 25 %.

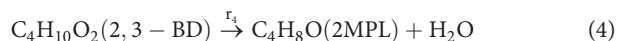
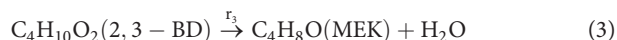
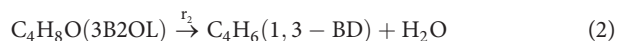
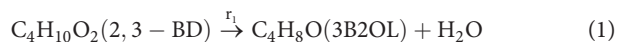
Considering the background mentioned, the aim of this paper is to propose intensified alternatives based on intensified schemes such as RD and ED to produce and purify MEK in order to improve the energy requirements and the number of equipment, having as reference the current technology to produce MEK. As mentioned earlier, this is the first work where MEK production is approached in an intensified process: RD. Additionally, as far as the authors are aware, this is the first work that addresses the production of a biofuel other than biodiesel.

For comparison purposes between the intensified alternatives, the energetic requirements per kilogram of MEK, the CO₂ global emissions, and an environmental index (the eco-indicator 99) will be used. So, the target is to generate a new and feasible technology to improve the current MEK production.

2 Cases of Study

2.1 Reaction-Separation Scheme

Song et al. [13] presented a proposal for MEK production. This alternative begins with a dehydration reactor, and the effluent is further purified to obtain MEK and all by-products at high concentrations (Fig. 1). In the reaction stage, all reactions can be summarized as follows:



with 2,3-BD, 3B2OL, 1,3-BD, MEK, and 2MPL being 2,3-butanediol, 3-buten-2-ol, 1,3-butadiene, methyl ethyl ketone, and 2-methylpropanal, respectively. In the reference case of Fig. 1, Song et al. [13] considered a reasonable number of decanters which result in many waste streams and, consequently, only 1,3-BD and MEK are partially recovered. The reason for such a design is the thermodynamic complexity of the stream to be purified. In the mixture of five components, there are four azeotropes: three heterogeneous ones between 1,3-BD and H₂O, MEK and H₂O, and 2MPL and H₂O, respectively, and one homogeneous azeotrope between 3B2OL and H₂O (Fig. 2; Supporting Information). For azeotrope separations, conventional columns are not always a suitable option since the energy

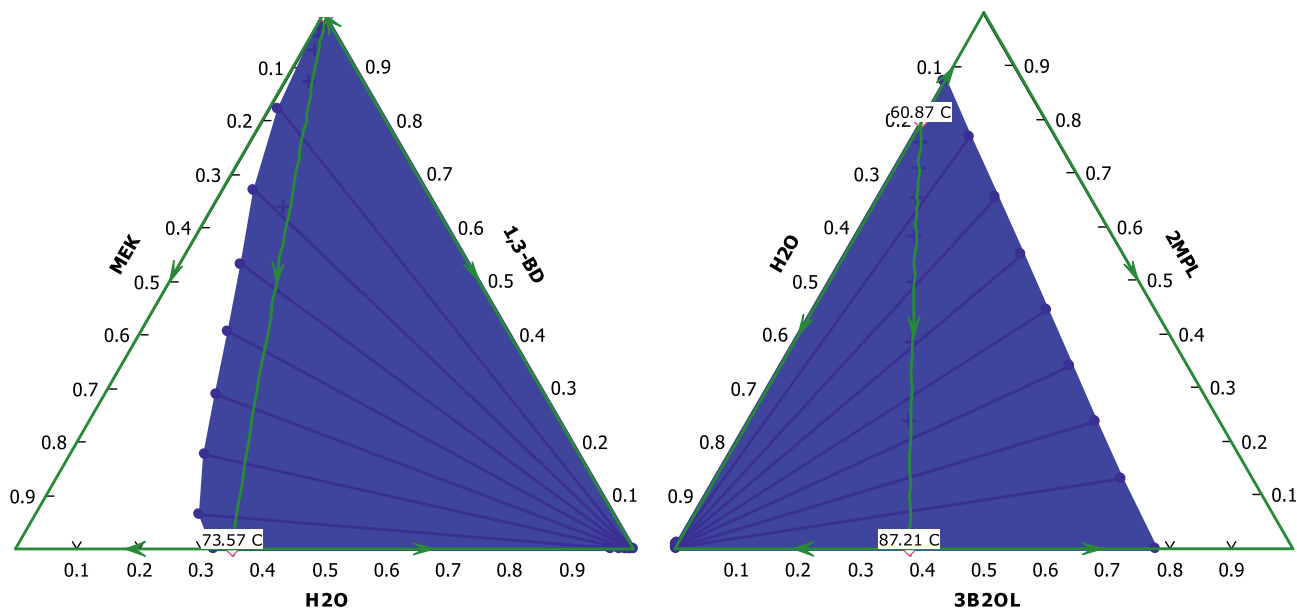


Figure 2. Ternary maps (mole basis) of the components coming from RD.

demand for such a process is considerable. For example, Song et al. [13] reported a selective MEK yield of 33.33 % in a reactor operating at 360 °C and a total energy consumption of 11.14 MMkcal; however, this consumption is only for a set of units. In their report, they did not consider many units like a reactor, a quencher, a three-phase separator, and a scrubber. So, the real energy consumption exceeds the reported one.

2.2 Intensified Alternative

As shown in Fig. 3, the alternative presented in this work is developed from two intensified alternatives, an RD column and an ED column. After an exhaustive revision and several tests, the simulator glycerol resulted as the best candidate for being used as a solvent in the ED column.

Therefore, considering both the RD and an extractive column, Fig. 3 presents two intensified alternatives to produce and separate all the components. Both intensified alternatives accomplish a recovery constraint of at least 98 wt % for all components, and a purity constraint of 99.5 wt % for MEK, 99 wt % for 3B2OL, 99 wt % for 2MPL, 99 % for 1,3-BD, and 99.99 % for glycerol; the purity of MEK is set at this value since 99.5 wt % is the lowest purity for being considered as fuel [26]. Topologically, the only difference between both proposals is that, in scheme A, the purification is carried out in a direct sequence after the ED column, as opposed to scheme B.

3 Methodology to Design the Intensified Alternatives

A feed stream of 1000 kg h⁻¹ of 2,3-BD was defined. The modeling process was performed in the Aspen Plus V10 simulator. Regarding thermodynamic modeling, the NRTL-RK model was chosen due to the formation of water and other organic com-

pounds in the dehydration process. Considering that the majority of compounds are non-electrolyte polar compounds and that the operating pressure is not more than 10 bar, the NRTL-RK model is appropriate [13, 27].

As mentioned before, Eqs. (1)–(4) were considered for the RD column. The kinetic reaction was considered as power-law reaction reduced as follows:¹⁾

$$k_i = k_{T_{ref,i}} \exp\left(\frac{-E_i}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (5)$$

The estimated kinetic parameters of the power-law reaction are shown in Tab. 2.

Table 2. Estimated kinetic parameters of the power-law model [1].

Model parameter	Value
E_1 [J mol ⁻¹]	2.33×10^5
E_2 [J mol ⁻¹]	2.82×10^5
E_3 [J mol ⁻¹]	1.93×10^5
E_4 [J mol ⁻¹]	1.66×10^5
$k_{T_{ref,1}}$ [mol ⁽¹⁻ⁿ¹⁾ m ³⁽ⁿ¹⁻¹⁾ s ⁻¹]	7.45×10^{-4}
$k_{T_{ref,2}}$ [mol ⁽¹⁻ⁿ¹⁾ m ³⁽ⁿ¹⁻¹⁾ s ⁻¹]	4.41×10^{-4}
$k_{T_{ref,3}}$ [mol ⁽¹⁻ⁿ¹⁾ m ³⁽ⁿ¹⁻¹⁾ s ⁻¹]	6.64×10^{-4}
$k_{T_{ref,4}}$ [mol ⁽¹⁻ⁿ¹⁾ m ³⁽ⁿ¹⁻¹⁾ s ⁻¹]	1.27×10^{-4}
n_1, n_3, n_4	1.87×10^{-2}
n_2	1.46×10^{-1}

As highlighted by Huang et al. [28], there is no general and structured methodology for the optimal design of RD columns.

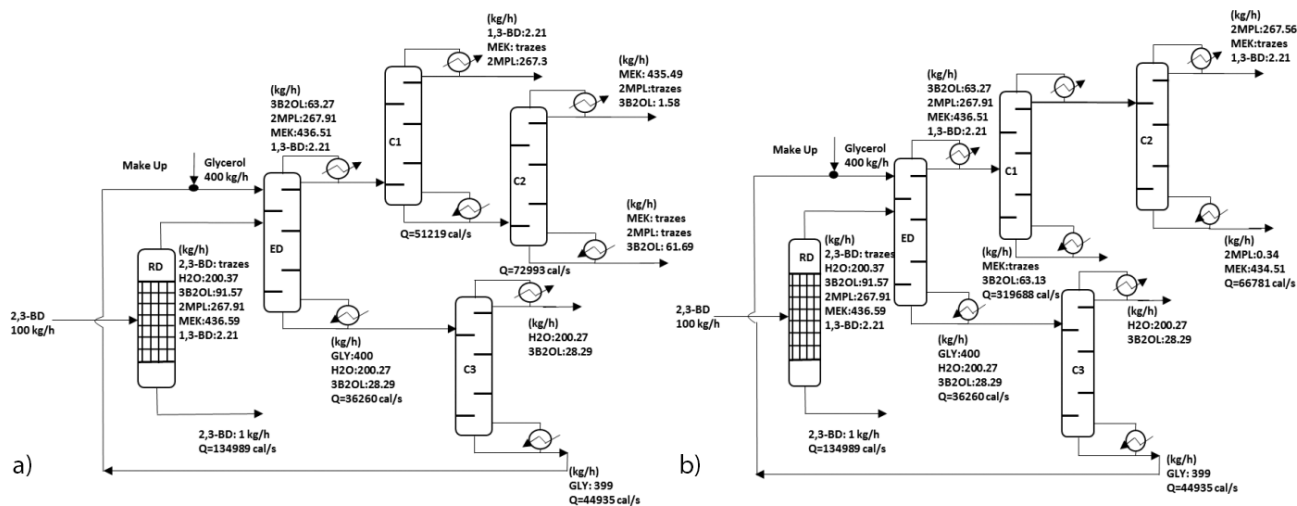


Figure 3. Novel intensified proposals for MEK production.

1) List of symbols at the end of the paper.

Therefore, in this work, the heuristics proposed by Subawalla and Fair [29] were considered. These heuristics are summarized in an algorithm that can be used to estimate parameters such as column pressure, location of the reactive zone, theoretical stages of the column, reflux ratio, column diameter, etc. These variables were varied with the objective of increasing the yield and production of MEK. The size of the holdup was not established arbitrarily; to find an appropriate value, the guide proposed by Barbosa and Doherty [30] was followed. The methodology initially consisted of specifying the compositions of the products and the value of the reflux ratio (obtained with the strategy of Subawalla and Fair [29]); in this way, the volume of the plates could be found so that the chemical reaction was carried out. The implementation of the algorithm proposed by Subawalla and Fair [29] is simple, but does not guarantee the optimal design. Once the procedure was done, it was possible to obtain a design to produce MEK; when the purity of 99.5 wt % was reached, a similar parametric procedure was performed to maximize the productivity of MEK.

For the design of the ED column, the methodology previously proposed by De Figueirêdo et al. [31] was followed. The target is to simultaneously obtain the best values for the variables involved in the design of the ED column, such as the reflux ratio, solvent flow, distillate flow, feed stage, feed stage of the solvent, and the number of theoretical stages.

De Figueirêdo et al. [31] propose a sensitivity analysis where the effect of each variable on a common objective is evaluated. In this study, the minimization of the reboiler duty was considered as an objective, having as a restriction the dragging of the aqueous phase of the fed mixture and the correct distribution of components in the column in order to be able to purify the effluent later. In this study, a solvent-to-feed ratio of 0.4 was employed in both schemes of Fig. 3. Finally, all conventional distillation columns were initially projected by means of short methods using the DSTWU module in Aspen Plus (Winn-Underwood-Gilliland method). Based on the results of the short methods, they were rigorously simulated in compliance with the MESH equations using the Radfrac module of Aspen Plus.

4 Performance Evaluation Indices

A major drawback in the operation of distillation columns is the energy requirement. With this in mind, the first performance index is the energy requirement. The main idea is to realize the amount of energy invested in the process, which is further represented in units like $\text{MJ kg}_{\text{MEK}}^{-1}$. Moreover, since the application of MEK would be in spark-ignition engines, an interesting view would be to compare the amount of energy invested and the amount of energy obtained for the ignition of MEK.

The second performance index is the eco-indicator 99 (EI99). EI99 is calculated as follows [32]:

$$EI99 = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (6)$$

where β_b represents the chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical b released into the environment, ω_d is a weighting factor for damage in category d, and δ_d is the normalization factor for damage of category d [32]. The EI99 methodology considers 11 impact categories aggregated into three major damage categories: human health, ecosystem quality, and resource depletion. In this work, we considered the impact of the steam for heating in reboilers, the steel for building the columns, and the electricity for pumping. Tab. 3 shows the impact values of each category for steel, steam, and electricity.

Table 3. Unit eco-indicator used to measure the eco-indicator 99 in all cases of study [32].

Impact category	Steel [points kg ⁻¹]	Steam [points kg ⁻¹]	Electricity [points kWh ⁻¹]
Carcinogenics	6.32×10^{-3}	1.18×10^{-4}	4.36×10^{-4}
Climate change	1.31×10^{-2}	1.60×10^{-3}	3.61×10^{-6}
Ionizing radiation	4.51×10^{-4}	1.13×10^{-3}	8.24×10^{-4}
Ozone depletion	4.55×10^{-6}	2.10×10^{-6}	1.21×10^{-4}
Respiratory effects	8.01×10^{-2}	7.87×10^{-7}	1.35×10^{-6}
Acidification	2.71×10^{-3}	1.21×10^{-2}	2.81×10^{-4}
Ecotoxicity	7.45×10^{-2}	2.80×10^{-3}	1.67×10^{-4}
Land occupation	3.73×10^{-3}	8.58×10^{-5}	4.68×10^{-4}
Fossil fuels	5.93×10^{-2}	1.25×10^{-2}	1.20×10^{-3}
Mineral extraction	7.42×10^{-2}	8.82×10^{-6}	5.70×10^{-6}

Finally, the third performance index is the greenhouse gas emission, which is indeed related to the energy requirement. The CO₂ emission is calculated as follows [33]:

$$[CO_2]_{\text{emiss}} = \left(\frac{Q_{\text{fuel}}}{NHV} \right) \left(\frac{C\%}{100} \right) \alpha \quad (7)$$

where $\alpha = 3.67$ is the ratio of the molar masses of CO₂ and C, while NHV (kJ kg⁻¹) represents the net heating value of fuel with a carbon content of C%. For CO₂ emission calculation, we assume that the energy involved in both processes, reaction-separation and the intensified process, comes from burning CH₄ gas. The target is to generate as little CO₂ emissions as possible.

5 Results

Starting with the RD column, as previously reported, one of the advantages of this unit is the improvement in selectivity for certain chemical reactions. In that sense, the RD column of Fig. 3 achieved a conversion (X) of 99.86 % and a selectivity (S) of 44 % according to Eqs. (8) and (9).

$$X_{2,3BD} = \frac{F_{2,3BD,in} - F_{2,3BD,out}}{F_{2,3BD,in}} \times 100 \quad (8)$$

$$S_{MEK} = \frac{F_{MEK,out}}{F_{total} - F_{2,3BD,out}} \times 100 \quad (9)$$

Regarding the two configurations proposed in this work (Fig. 3, Supporting Information), the energy consumption of scheme A was 1 218 797 kcal h⁻¹ (5073 MJ h⁻¹). Thus, considering the total production of MEK, the energy consumption would be 2786 kcal kg_{MEK}⁻¹ (11.6 MJ kg_{MEK}⁻¹). Equally weighting all compounds, MEK, 1,3-BD, and 2MPL, the energy consumption for the entire product would be 1218 kcal kg_{PROD}⁻¹ (5.07 MJ kg_{PROD}⁻¹).

On the other hand, scheme B was less promising in terms of energy consumption. The total energy requirements were 2 313 579 kcal h⁻¹ (9680 MJ kg⁻¹), which is quite high compared to alternative A. However, doing the same exercise for MEK and the entire product gives 5299 kcal kg_{MEK}⁻¹ (22.17 MJ kg_{MEK}⁻¹) and 2313 kcal kg_{PROD}⁻¹ (9.68 MJ kg_{PROD}⁻¹). Moreover, in the hypothetical scenario where all MEK produced as fuel was burned, with 31.45 MJ kg⁻¹ as energy density, the energy profit of scheme A would be 8601 MJ, and 3995 MJ for scheme B.

The main reason for the large difference in energy consumption was generated by the use of a direct and indirect sequence after ED. Although both alternatives have similarities in three columns, the topological difference in the remaining two columns raised the energy consumption dramatically. For example, in Tabs. 4 and 5, the reflux ratios with which the last two columns of scheme B are designed are larger compared to those of scheme A, which produces an increase in reboiler duty.

Table 4. Design parameters for intensified alternative A.

	RD	ED	C1	C2	C3
Number of stages	80	50	80	46	30
Reactive stages	10–80	–	–	–	–
Solvent [kg h ⁻¹]	–	400	–	–	–
Reflux ratio	2.95	0.5	5.488	4.712	0.039
Feed stage	76	5, 46	23	25	14
Operative pressure [kPa]	101.353	101.353	101.353	101.353	101.353
Distillate flow rate [kg h ⁻¹]	999	770	270	437.6	230
Reboiler duty [kcal h ⁻¹]	485 962	130 535	184 390	256 145	161 765
CO ₂ emissions [t h ⁻¹]	7.07				
Eco-Ind [points y ⁻¹]			1.825 × 10 ⁶		

Regarding the greenhouse gas emissions, a panorama can be envisioned based on the energy consumption. Once the greenhouse gas emissions were calculated, the results previously calculated regarding the energy consumption were corroborated.

Table 5. Design parameters for intensified alternative B.

	RD	EC	C1	C2	C3
Number of stages	80	50	56	50	30
Reactive stages	10–80	–	–	–	–
Solvent [kg h ⁻¹]	–	400	–	–	–
Reflux ratio	2.95	0.5	14.1	7.01	0.039
Feed stage	76	5, 46	5	5	23
Operative pressure [kPa]	101.353	101.353	101.353	101.353	101.353
Distillate flow rate [kg h ⁻¹]	999	770	706.65	270.65	230
Reboiler duty [kcal h ⁻¹]	485 962	130 535	1130 280	229 264	161 765
CO ₂ emissions [t h ⁻¹]	13.42				
Eco-Ind [points y ⁻¹]			4.75 × 10 ⁶		

The scheme that showed lower energy consumption turned out to have CO₂ emissions of 7.074 t h⁻¹. On the other hand, scheme B, with its higher energy consumption, showed emissions of 13.43 t h⁻¹ of CO₂. Both kinds of data can be observed more clearly in Fig. 4.

Finally, after calculation of EI99, a wider vision is obtained of the environmental impact. As stated in the methodology, the EI99 evaluates 11 categories. In this way, the evaluation will be of those 11 categories for each component analyzed (steel, steam, and electricity). As a result, Fig. 5 shows the impact of steel, steam, and electricity on each category.

Note that, in general terms, the impact generated by scheme A is less than that generated by scheme B. Once it has been differentiated which design generates a smaller impact, it is important to highlight which evaluated element had a greater impact. Observing Fig. 5, it is easy to note that the steam used for heating the distillation columns represents the greatest impact, especially when it is related to the use of fossil fuels. While the environmental impact of the use of steel and electricity is considerable, the difference in the environmental impact of the use of steam is very large. In the same way as for CO₂, the reflux ratio showed a great impact on the EI99: As long as the reflux ratio increases, the reboiler duty also increases; consequently, the eco-points regarding steam increase as well.

As general observations, it can be seen that scheme A was a better intensified alternative for the production and separation of MEK from 2,3-BD. While it is relatively unfair to make a comparison with the work presented by Song et al. [13], it is clear that the proposal presented in this work may outperform the design previously proposed by Song et al. [13].

Initially, it is clear that, topologically, both intensified schemes involve five columns: one RD column, one ED column, and three conventional columns for the production and separation of MEK, 2MPL, and 3B2OL. On the other hand, the scheme reported by Song et al. [13] involves ten separation units and a reactor. In that sense, the saving in the capital cost is evident.

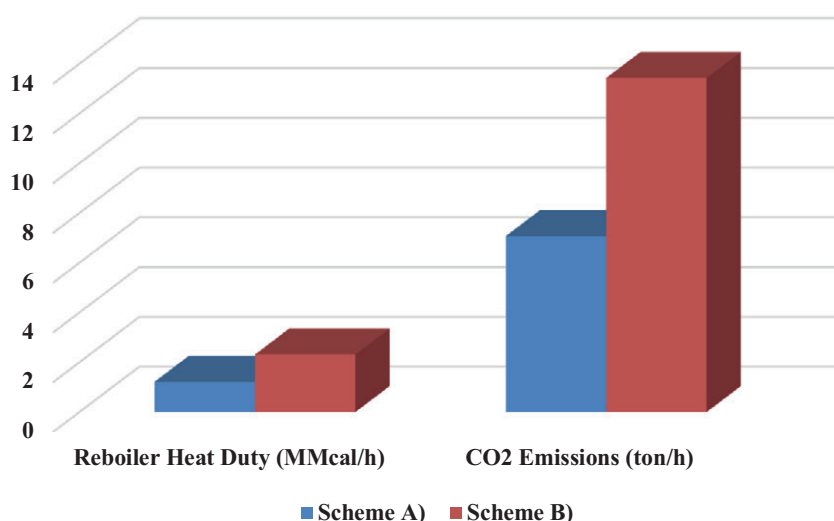


Figure 4. Energy consumption and CO₂ emissions for the intensified alternatives A and B.

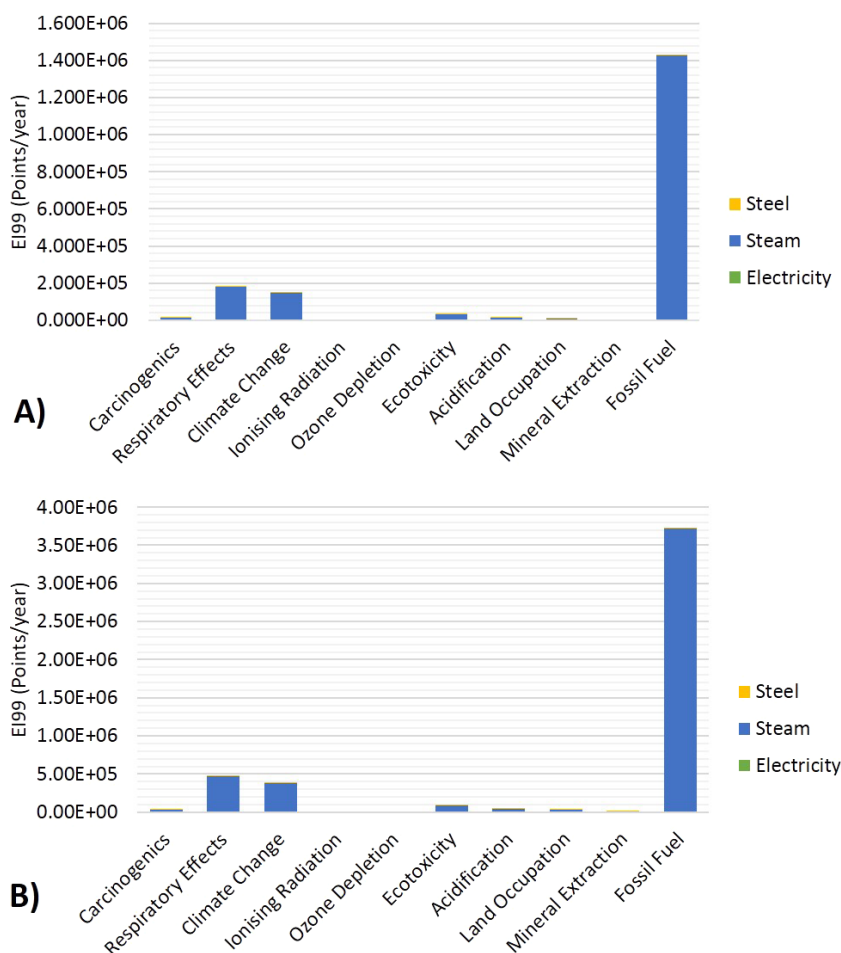


Figure 5. Annualized environmental impact of the intensified alternatives A and B.

Additionally, according to Tab. 1, the energy involved in the upstream process in the scheme reported by Song et al. [13] is 11 140 000 kcal h⁻¹ (46 640.96 MJ h⁻¹) for the production of

4385 kg h⁻¹ of MEK. Thus, the energy consumption per kilogram of MEK is 2540.5 kcal kg_{MEK}⁻¹ (10.64 MJ kg_{MEK}⁻¹). So far, the scheme presented by Song et al. [13] seems interesting; however, when the production of the other purified by-product (3340 kg of 2,3-BD) is considered, the picture changes completely. If the production of MEK and 2,3-BD is considered together, the energy requirements change to 1142.1 kcal kg_{PROD}⁻¹ (6.04 MJ kg_{PROD}⁻¹). In other words, when jointly considering the production of MEK and all the by-products generated in the process, the intensified scheme proposed in this article exceeds that presented by Song et al. [13] by an average amount of 76 kcal kg_{PROD}⁻¹ (0.97 MJ kg_{PROD}⁻¹).

It should be noted that, due to the lack of data published by Song et al. [13] in this analysis, the energy consumption of the reactor is not being considered. However, it can be inferred that the energy consumption of the scheme presented by Song et al. [13] would increase since, as discussed by Song et al. [13], the reactor operates at a temperature of 360 °C. On the contrary, in the energy analysis, the energy consumption of the RD column was considered. In this way, we can assume a favorable scenario for the intensified scheme in terms of energy consumption.

Probably one of the reasons why the intensified process energetically exceeds the conventional scheme presented by Song et al. [13] is the number of decanters present in the whole process. Note, for example, that in the scheme presented in Fig. 1, several streams called “fuel” are presented, which can be inferred as a MEK stream but with too low a purity to consider MEK as fuel for ignition purposes. The above is assumed due to the presence of a stream specifically named MEK. Additionally, note that there is at least one waste stream in which MEK is involved (MEK/CHEX stream), which shows that the recovery of MEK may not be high. Unfortunately, in the work of Song et al. [13], a complete mass balance is not presented in order to verify these assumptions.

Finally, please note that the MEK selectivity of the RD column increases by 25 % in comparison with the one reported by Song et al. (33 % and 44 %, respectively).

6 Conclusions

Through the use of intensified technology, in this work, a novel alternative is proposed to produce and purify MEK, 1,2-BD, 2MPL, and water, from 2,3-BD in an RD column using calcium phosphate as catalyst, as previously studied. The RD column resulted in a conversion of 99.86 % and a selectivity for MEK of 44 %. To purify the effluent coming from the reactor, an ED column and three conventional columns (in both direct and indirect arrangement after the extractive column) were used. After evaluation, the direct scheme (scheme A) resulted as the most promising one, with energy requirements of $2790 \text{ kcal kg}_{\text{MEK}}^{-1}$ ($11.6 \text{ MJ kg}_{\text{MEK}}^{-1}$). Regarding the environmental impact, scheme A reported $7.07 \text{ t}_{\text{CO}_2} \text{ h}^{-1}$ of greenhouse gas emissions.

Even though this is not a direct and fair comparison: Previous work has proposed a conceptual design using a reactor and a set of ten separation units accomplishing the purification of MEK and 1,3-BD. In this work, the intensified scheme is able to purify all products obtained in the RD, with less equipment and higher selectivity for MEK.

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Symbols used

E_i	$[\text{J mol}^{-1}]$	activation energy
k_i	$[\text{mol}^{(1-n)} \text{m}^3 \text{s}^{-1}]$	kinetic parameters
$k_{T_{\text{ref}}}$	$[\text{mol}^{(1-n)} \text{m}^3 \text{s}^{-1}]$	kinetic parameters at T_{ref}
S	$[\text{mol mol}^{-1}]$	selectivity
T	$[^\circ\text{C}]$	temperature
T_{ref}	$[^\circ\text{C}]$	reference temperature
X	$[\text{mol mol}^{-1}]$	conversion

Greek symbols

α	$[\text{mol mol}^{-1}]$	ratio of the molar masses of CO_2 and C
$\alpha_{b,k}$	[ecopoints]	damage caused in category k
β_b	$[\text{kg kg}^{-1}]$	chemical b released per unit of reference flow
δ_d	$[\text{ecopoints kg}^{-1}]$	normalization factor for the damage of category d
ω_d	$[\text{ecopoints kg}^{-1}]$	weighting factor for the damage in category d

Abbreviations

1,3-BD	1,3-butadiene
2MPL	2-methylpropanal, $\text{C}_4\text{H}_8\text{O}$
2,3-BD	2,3-butanediol, $\text{C}_4\text{H}_{10}\text{O}_2$
3B2OL	3-buten-2-ol, $\text{C}_4\text{H}_8\text{O}$

ED	extractive distillation
MEK	methyl ethyl ketone, $\text{C}_4\text{H}_8\text{O}$
NHV	net heating value
PI	process intensification
RD	reactive distillation

References

- [1] D. Song, *Ind. Eng. Chem. Res.* **2016**, *55*, 11664–11671. DOI: <https://doi.org/10.1021/acs.iecr.6b02930>
- [2] Z. Liu, W. Huo, H. Ma, K. Qiao, *Chin. J. Chem. Eng.* **2006**, *14*, 676–684. DOI: [https://doi.org/10.1016/S1004-9541\(06\)60134-1](https://doi.org/10.1016/S1004-9541(06)60134-1)
- [3] F. Hoppe, U. Burke, M. Thewes, A. Heufer, F. Kremer, S. Pischinger, *Fuel* **2016**, *167*, 106–117. DOI: <https://doi.org/10.1016/j.fuel.2015.11.039>
- [4] D. Hoell et al., in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, New York **2009**.
- [5] H. Yoneda, D. J. Tantillo, S. Atsumi, *ChemSusChem* **2014**, *7*, 92–95. DOI: <https://doi.org/10.1002/cssc.201300853>
- [6] X. J. Ji, H. Huang, P. K. Ouyang, *Biotechnol. Adv.* **2011**, *29*, 351–364. DOI: <https://doi.org/10.1016/j.biotechadv.2011.01.007>
- [7] M. J. Syu, *Appl. Microbiol. Biotechnol.* **2001**, *55*, 10–18. DOI: <https://doi.org/10.1007/s002530000486>
- [8] R. R. Emerson, M. C. Flickinger, G. T. Tsao, *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 473–477. DOI: <https://doi.org/10.1021/i300007a025>
- [9] A. Molnár, I. Bucsi, M. Bartoók, *Stud. Surf. Sci. Catal.* **1988**, *41*, 203–210. DOI: [https://doi.org/10.1016/S0167-2991\(09\)60816-8](https://doi.org/10.1016/S0167-2991(09)60816-8)
- [10] I. Bucsi, A. Molnár, M. Barók, *Tetrahedron* **1994**, *50*, 8195–8202. DOI: [https://doi.org/10.1016/S0040-4020\(01\)85301-1](https://doi.org/10.1016/S0040-4020(01)85301-1)
- [11] A. N. Bourns, R. V. V. Nicholls, *Can. J. Res.* **1946**, *25*, 80–88. DOI: <https://doi.org/10.1139/cjr47b-010>
- [12] M. A. Nikitina, I. I. Ivanova, *ChemCatChem* **2016**, *8*, 1346–1353. DOI: <https://doi.org/10.1002/cctc.201501399>
- [13] D. Song, Y. Yoon, C. Lee, *Chem. Eng. Res. Des.* **2017**, *123*, 268–276. DOI: <https://doi.org/10.1016/j.cherd.2017.05.019>
- [14] J. M. Ponce-Ortega, M. M. Al-Thubaiti, M. M. El-Halwagi, *Chem. Eng. Process.* **2012**, *53*, 63–75. DOI: <https://doi.org/10.1016/j.ccep.2011.12.010>
- [15] P. Lutze, R. Gani, J. M. Woodley, *Chem. Eng. Process.* **2010**, *49*, 547–558. DOI: <https://doi.org/10.1016/j.ccep.2010.05.002>
- [16] T. F. C. Souza, N. L. Ferreira, M. Marin, R. Guardani, Glycerol Esterification with Acetic Acid by Reactive Distillation Using Hexane as an Entrainer, *Int. J. Chem. Eng. Appl.* **2017**, *8*, 344–350. DOI: <https://doi.org/10.18178/ijcea.2017.8.6.681>
- [17] T. Pöpkén, S. Steinigeweg, J. Gmehling, Synthesis and hydrolysis of methyl acetate by reactive distillation using structured catalytic packings: Experiments and simulation, *Ind. Eng. Chem. Res.* **2001**, *40*, 1566–1574. DOI: <https://doi.org/10.1021/ie0007419>
- [18] P. Lutze, R. Gani, J. M. Woodley, Process intensification: A perspective on process synthesis, *Chem. Eng. Process. Process Intensif.* **2010**, *49*, 547–558. DOI: <https://doi.org/10.1016/j.ccep.2010.05.002>
- [19] A. A. Kiss, A. C. Dimian, G. Rothenberg, Biodiesel by catalytic reactive distillation powered by metal oxides, *Energy*

- and *Fuels*. **2008**, *22*, 598–604. DOI: <https://doi.org/10.1021/ef700265y>
- [20] E. S. Pérez-Cisneros, X. Mena-Espino, V. Rodríguez-López, M. Sales-Cruz, T. Viveros-García, R. Lobo-Oehmichen, An integrated reactive distillation process for biodiesel production, *Comput. Chem. Eng.* **2016**, *91*, 233–246. DOI: <https://doi.org/10.1016/j.compchemeng.2016.01.008>
- [21] T. Poddar, A. Jagannath, A. Almansoori, Use of reactive distillation in biodiesel production: A simulation-based comparison of energy requirements and profitability indicators, *Appl. Energy*. **2017**, *185*, 985–997. DOI: <https://doi.org/10.1016/j.apenergy.2015.12.054>
- [22] W. L. Luyben, C.-C. Yu, *Reactive Distillation Design and Control*, John Wiley & Sons, Hoboken, NJ **2009**. DOI: <https://doi.org/10.1002/9780470377741>
- [23] M. Shah, A. A. Kiss, E. Zondervan, A. B. De Haan, *Chem. Eng. Process.* **2012**, *60*, 55–64. DOI: <https://doi.org/10.1016/j.cep.2012.05.007>
- [24] G. J. Harmsen, *Chem. Eng. Process.* **2007**, *46*, 774–780. DOI: <https://doi.org/10.1016/j.cep.2007.06.005>
- [25] M. Errico, E. Sanchez-Ramirez, J. J. Quiroz-Ramirez, J. G. Segovia-Hernandez, B.-G. Rong, *Comput. Chem. Eng.* **2016**, *84*, 482–492. DOI: <https://doi.org/10.1016/j.compchemeng.2015.10.009>
- [26] D. Penner, C. Redepenning, A. Mitsos, J. Viell, *Ind. Eng. Chem. Res.* **2017**, *56*, 3947–3957. DOI: <https://doi.org/10.1021/acs.iecr.6b03678>
- [27] D. Song, Y. Yoon, C. Lee, *Korean J. Chem. Eng.* **2018**, *35*, 2348–2354. DOI: <https://doi.org/10.1007/s11814-018-0161-2>
- [28] K. Huang, K. Iwakabe, M. Nakaiwa, A. Tsutsumi, *Chem. Eng. Sci.* **2005**, *60*, 4901–4914. DOI: <https://doi.org/10.1016/j.ces.2005.03.052>
- [29] H. Subawalla, J. R. Fair, *Ind. Eng. Chem. Res.* **1999**, *38*, 3696–3709. DOI: <https://doi.org/10.1021/ie990008l>
- [30] D. Barbosa, M. F. Doherty, *Chem. Eng. Sci.* **1988**, *43*, 1523–1537. DOI: [https://doi.org/10.1016/0009-2509\(88\)85144-3](https://doi.org/10.1016/0009-2509(88)85144-3)
- [31] M. F. De Figueirêdo, B. P. Guedes, J. Manzi, M. De Araújo, L. Gonzaga, S. Vasconcelos, R. P. Brito, *Chem. Eng. Res. Des.* **2011**, *89*, 341–346. DOI: <https://doi.org/10.1016/j.cherd.2010.06.011>
- [32] R. Goedkoop, M. Spriensma, *Eco-indicator 99 Manual for Designers*, Pre' Consultants, Amersfoort **2000**.
- [33] M. A. Gadalla, Z. Olujic, P. J. Jansens, M. Jobson, R. Smith, *Environ. Sci. Technol.* **2005**, *39*, 6860–6870. DOI: <https://doi.org/10.1021/es049795q>