



## Bioethanol dehydration and mixing by heterogeneous azeotropic distillation

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### ARTICLE INFO

Handling editor: Cecilia Maria Villas Bôas de Almeida

**Keywords:**  
Gasoline additive  
Rigorous simulation  
Enhanced distillation  
Biofuel  
Process intensification

### ABSTRACT

Bioethanol is mixed with gasoline according to many countries' legislation pursuing environmental sustainability by reducing the use of fossil fuels. Bioethanol is produced by fermentation of many organic waste or biomass resources in diluted aqueous media. Unfortunately, bioethanol for fuel use must have a low content of water and its recovery is an energy intensive operation. Heterogeneous azeotropic distillation (HAD) is a well-known suitable option for dehydration of alcohols, e.g. ethanol. Many entrainers for this process are studied in literature and, in this study, is checked and verified that gasoline and gasoline additives present the lowest energy consumption. For this purpose, novel processes are proposed and rigorously simulated using AspenPlus® to verify their performance with respect to conventional processes used currently. Based on the simulation results, the processes are then compared in terms of environmental impact (expressed by the Potential Environmental Impact (PEI) index) and economic cost. Ethanol dehydration is a non-spontaneous process that requires energy to be accomplished and, on the other hand, mixing ethanol with gasoline and additives is a spontaneous process. Combining both processes in synergy in a single unit, energy consumption decreases by 50% and Potential Environmental Impact by 80%. Finally, the economic study indicated the benefits of employing the novel proposed scheme of one distillation column as CAPEX is reduced by 20% and the payback time to 1.5 years. Therefore, a novel viable process is proposed that greatly reduces the environmental impact of nowadays gasoline production.

### 1. Introduction

Transport and vehicles produce large greenhouse emissions. Environmental concerns together with the aim to decrease the fossil fuels dependence have boosted green fuel demand. Many governmental initiatives have been approved to promote the inclusion of biofuels in the existing fuel pool ([Čuček et al., 2012](#)). There are many studies about producing gasoline substitutes from biomass, e.g. [Hancsók et al. \(2019\)](#). Novel processes with low energy consumption have appeared for biodiesel production from oil and ethanol, e.g. [Dimian et al. \(2019\)](#), but not for ethanol dehydration.

Some examples of fermentable raw materials for bioethanol production are (1) pineapple and orange peels ([Tejeda et al., 2010](#)), (2) wood and straw ([Kravanja et al., 2012](#)), (3) sweet sorghum stalks ([Aguilar-Sánchez et al., 2018](#)), (4) lignocellulosic biomass and sugars from crops ([Rodrigues Gurgel da Silva et al., 2018](#)), (5) lignocellulosic residues from fruit pulp, mango and lemon ([Magalón-Micán et al., 2017](#)), (6) wheat straw ([Hasanly et al., 2018](#)), (7) rice straw ([Phuong](#)

[et al., 2017](#)), (8) coffee pulp ([Gurram et al., 2016](#)), (9) cassava plant ([Lyu et al., 2020](#)), (10) palm fruit bunches ([Díaz et al., 2018](#)) etc which are chosen depending on their cost and availability in each region. For lignocellulosic raw materials, the composite nature of lignocellulosic hydroxylates and their low content in sugars produces around four times lower ethanol concentrations than using sugars as raw material. Reviewed values of ethanol production from diverse sources ranges from 0.4 to 7 gCO<sub>2eq</sub>/kg ethanol ([Pacheco and Silva, 2019](#)).

Besides the processes that focus on ethanol production, aqueous ethanol is also obtained as biorefinery by-product, e.g. paper mill sludge ([Zambare and Christopher, 2020](#)). In the production of some organic acids, ethanol is also produced as by-product although the operating conditions focus on minimizing the ethanol production and maximizing the production of the acid, e.g. lactic acid fermentation of *Sophora flavescentis* residues ([Ma et al., 2021](#)). The acid is extracted using triethylamine, i.e. a base, and octanol as solvent while the ethanol remains ([Bonet-Ruiz et al., 2017](#)). The most common technologies produce diluted aqueous bioethanol between 5 and 12 wt% ethanol (EtOH) which must be dehydrated before being blended with gasoline to comply

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## Acronyms and symbols

wt%	Mass percentage [non-dimensional]	NPV	Net Present Value
CAPEX	Capital Expenditure [€]	NRTL	Non-Random Two Liquid
CEPCI	Cost Index Plant [non-dimensional]	OPEX	Operational Expenditure [k€/year]
CFDi	Discounted cash flow [k€/year]	P&L	Profits and Losses
COGS	Cost of Goods Sold [€]	PEI	Potential Environmental Impact
COL1	Distillation 1st Column	PSA	Process Scheme A
COL2	Distillation 2nd Column	PSB	Process Scheme B
COND1	Condenser of 1st distillation column	RCM-LLE	Residue Curve Map - Liquid-Liquid Equilibrium
COND2	Condenser of 2nd distillation column	RD1	Reflux drum of 1st distillation column
DEC	Decanter	RD2	Reflux drum of 2nd distillation column
EBIT	Earnings Before Income Taxes [k€/year]	REB1	Reboiler of 1st distillation column
ETBE	Ethyl tert-butyl ether	REB2	Reboiler of 2nd distillation column
EtOH	Bioethanol	RP1	Reflux pump of 1st distillation column
EU	European Union	RP2	Reflux pump of 2nd distillation column
HAD	Heterogeneous azeotropic distillation	TAME	Tert-amyl methyl ether
MTBE	Methyl tert-butyl ether	UNIFAC	Universal Functional group Activity Coefficient
		WAR	Waste Reduction Algorithm

with European regulations (EN 15376, 2011) that allow a maximum of 0.3 wt% of water in fuels. High purity bioethanol is one of the most valuable biorefinery products (Martínez-Guidos et al., 2016). Ethanol is frequently used in gasoline formulation but also as raw material for some gasoline additives such as ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (Neagu and Cersaru, 2013). A recent literature review by Saini et al. (2020) shows that although there is a great increasing interest on the ethanol production process, this is not the case for the recovery of the diluted aqueous ethanol, although being the step that consumes larger amounts of energy and has a large effect on the economic viability of the process and its environmental impact.

At the contrary of some other fuel alternatives, ethanol is suitable to be added in the formulation of nowadays fuels in use. The usual mixing ratio of ethanol in gasoline is between 5 and 85% (Kiss and Suszalak, 2012). Moreover, the high bioethanol oxygen content of 35% improves the combustion efficiency diminishing the particulate emissions in the exhaust gases (Balat and Balat, 2009). Bioethanol gasoline blends were used before the leaded gasolines to improve gasoline antiknock properties. In Europe, the legislation (Directive 2009/10/EC) regulates a maximum bioethanol in gasoline blend of 10 wt%. Moreover, the maximum content of water is also regulated to 0.3 wt% (EN 15376, 2011). The ethanol, even after being mixed with gasoline, is able to absorb air moisture when stored open to the atmosphere. However, this process is slow enough and E10 gasoline can be safely stored for half year (Wongpromrat et al., 2019). More than five thousand millions liters of fuel ethanol are produced on average every year in the European Union since 2011, this amount corresponds to 85% of its overall production. The blending percentage of ethanol in fuel is set in 5–5.7% (Flach et al., 2018).

An enhanced distillation is required to break the ethanol water azeotrope, e.g. heterogeneous azeotropic distillation (HAD). Distillation is the most widespread industrial technique for bioethanol recovery (Singh and Rangaiah, 2017); although some researchers claim the use of membranes to decrease the energy consumption, e.g. Valentinyi et al. (2018). Besides heterogeneous azeotropic distillation, other enhanced distillation alternatives, such as extractive distillation, are also feasible, e.g. Lara-Montaña et al. (2019). Fuel grade ethanol is produced by dehydration and purification steps consuming large amounts of energy are limiting the viability of lignocellulosic ethanol at industrial level (Saini et al., 2020).

Fig. 1 shows the most common process scheme for bioethanol dehydration. The process is composed by two distillation columns, i.e. a prefractionation distillation column and a azeotropic distillation column with its corresponding decanter. The crude feed stream of ethanol

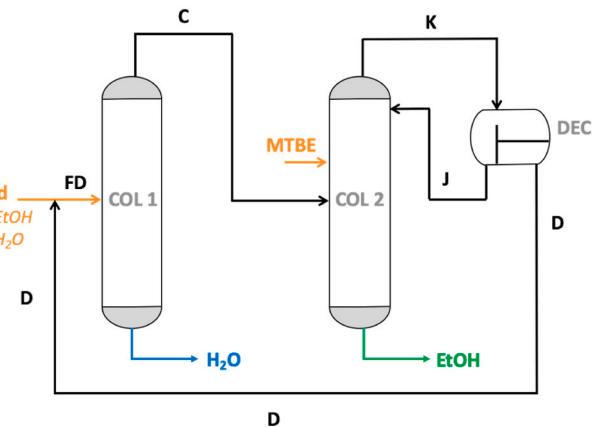


Fig. 1. Conventional process scheme.

diluted in water is introduced in the prefractionation column and the entrainer (i.e. MTBE) is fed at the upper section of the heterogeneous azeotropic distillation column. Ethanol is produced by the bottom of the 2nd heterogeneous azeotropic distillation column and pure water is eliminated from the system by the bottom of the prefractionation distillation column. Approximately 60–80% of process energy to dehydrate the bioethanol from the fermented broth is consumed in the prefractionation distillation column (Galbe et al., 2013).

Table 1 shows a literature review of the most common entrainers used for bioethanol dehydration by heterogeneous azeotropic distillation. The overall energy consumption refers to collecting 1 kg of dehydrated ethanol. For all the cases, the crude feed is a mixture of water and ethanol, nevertheless fed ethanol concentration, process scheme and simulation software with the corresponding thermodynamic model differ in each case. The higher the ethanol content in the feed is, the lower the energy consumption is expected.

Many institutions have been promoting the use of bioethanol as a biofuel. Unfortunately, the dehydration process requires substantial amounts of energy and the largest amount allowed in fuel is 10 wt% of ethanol. Minor changes in the global energy consumption in this process could generate great profits in economic and environmental aspects. It is investigated and verified that using a gasoline additive as entrainer, the global energy consumption is reduced significantly. Aqueous diluted alcohols are also a suitable raw material in the synthesis of gasoline

**Table 1**  
Energy consumption review.

Year	Author	Entrainer	Distillation Columns	Product	Energy MJ/kg EtOH
2003	Font et al. (2003) <sup>a</sup>	Isooctane	3	EtOH + Isooctane	19.3
2003	Font et al. (2003) <sup>a</sup>	Isooctane	2	Pure EtOH	12.5
2006	Luyben (2006) <sup>a</sup>	Benzene	3	Pure EtOH	8.6
2011	Sun et al. (2011) <sup>c</sup>	Cyclohexane	2	Pure EtOH	13.7
2012	Sun et al. (2011) <sup>c</sup>	Cyclohexane	1	Pure EtOH	8.0
2012	Luyben (2013) <sup>a</sup>	Benzene	3	Pure EtOH	7.5
2014	Pla-Franco et al. (2014) <sup>b</sup>	Diisopropylether	2	Pure EtOH	54.5
2014	Pla-Franco et al. (2014) <sup>b</sup>	Benzene	2	Pure EtOH	33.0
2015	Li et al. (2015) <sup>a</sup>	MTBE	2	Pure EtOH	12.9
2015	Li et al. (2015) <sup>a</sup>	MTBE	3	Pure EtOH	12.9
2015	Li et al. (2015) <sup>a</sup>	MTBE	2	Pure EtOH	14.7
2015	Gomis et al. (2007) <sup>d</sup>	Isooctane	2	Pure EtOH	14.1
2020	Plesu Popescu et al. (2020) <sup>a</sup>	MTBE	2	EtOH + MTBE	9.3
2020	Plesu Popescu et al. (2020) <sup>a</sup>	ETBE	1	EtOH + ETBE	48.9
2020	Plesu Popescu et al. (2020) <sup>a</sup>	TAME	2	EtOH + TAME	10.5
2020	Plesu Popescu et al. (2020) <sup>a</sup>	MTBE	2	EtOH + MTBE	11.4

<sup>a</sup> Feed stream: 12% EtOH mass composition (5% EtOH molar composition).

<sup>b</sup> Feed stream: 36% EtOH mass composition (18% EtOH molar composition).

<sup>c</sup> Feed stream: 96% EtOH mass composition (90% EtOH molar composition).

<sup>d</sup> Feed stream: 98% EtOH mass composition (95% EtOH molar composition).

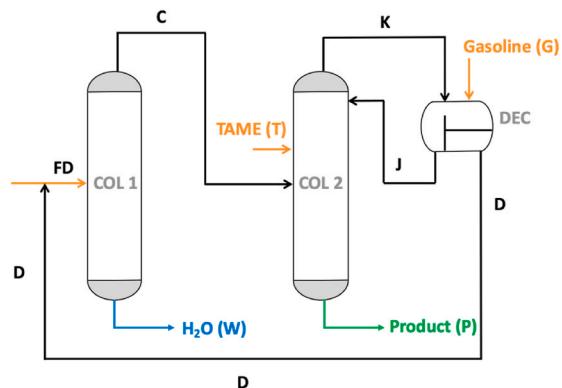
additives, e.g. ETBE (Li and Liu, 2018). In this study, the alcohol dehydration process will be improved using gasoline + gasoline additive as entrainer and producing a blend of gasoline, ethanol and gasoline additive ready to use as fuel. This novel process improves the conventional process scheme that consists of using gasoline additives to obtain pure ethanol, which is further blended with gasoline to be used as a fuel.

## 2. Methodology

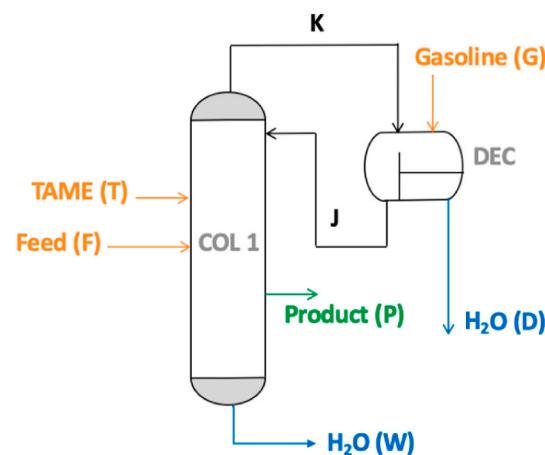
Rigorous simulations have been performed using Aspen Plus ® v10 (AspenPlus, 2020) with the NRTL thermodynamic model estimating the missing parameters by UNIFAC. Moreover, Waste Reduction Algorithm (WAR) is used to determine the potential environmental impact of each process scheme generating the consumed energy with several fuels (WAR, 2020). Finally, an economic assessment is performed to verify the economic viability of each process.

### 2.1. Process schemes

Two process schemes (Figs. 2 and 3) are assessed by rigorous simulation considering energetic, economic and environmental aspects. The



**Fig. 2.** Process Scheme A (PSA) combining ethanol dehydration and mixing with gasoline.



**Fig. 3.** Process Scheme B (PSB) combining ethanol dehydration and mixing with gasoline in a single intensified column.

final product in both process schemes is a mixture of ethanol + gasoline + gasoline additive. For process scheme A, (Fig. 2) the novelty is the final product collected, that is the formulated gasoline instead of pure bioethanol and in process scheme B (Fig. 3), the novelty besides the product is also in a process intensification. Both process schemes are discussed further.

#### 2.1.1. Process scheme A: formulated gasoline product

Fig. 2 shows the process Scheme A (PSA), it is according a classical process scheme for bioethanol dehydration: a prefractionation column (COL 1) to separate the ethanol azeotrope from a large amount of water and a heterogeneous azeotropic distillation column (COL 2) (HAD) to break the water-ethanol azeotrope. The entrainer is composed by a feed stream of additive gasoline, e.g. TAME, and a gasoline stream feed to the decanter. The aqueous crude feed (F) is fed to the 1st distillation column (COL 1). A second feed to this 1st column is an aqueous recycling stream (D) from the decanter of the heterogeneous azeotropic distillation column (COL 2). The aqueous stream (W), water 99.99 wt%, is eliminated at prefractionation column bottom (COL 1). A near azeotropic composition of aqueous ethanol is collected at the distillate stream (C) of the prefractionation column (COL 1). Gasoline additive, stream T used also as entrainer, is fed at the top of the heterogeneous azeotropic distillation column (COL 2) and stream (G), gasoline, is fed in its decanter (DEC). The entrainers are collected mixed with the bioethanol product (stream P). The entrainer rich phase from the decanter (stream J) is refluxed to the distillation column and the aqueous phase from the decanter (stream D)

is recirculated to the prefractionation column to recover its diluted content in ethanol. Notice that stream D is mainly water contaminated with organic compounds and its recycle back to the dehydration process avoids environmental issues related to this stream's processing. Although the output water stream (W) contains only 0.01 wt% of organic compounds (mainly ethanol), this stream must be treated before being discharged into the environment. However, when the fermentation unit to produce ethanol is located near the ethanol dehydration unit, then this water stream (W) should be directly recycled to the fermentation unit, thus saving water and decreasing the load to the wastewater treatment plant. In this way, only the main product stream P is collected.

### 2.1.2. Process scheme B: intensified process to produce formulated gasoline

A novel intensified scheme of a heterogeneous azeotropic distillation (HAD) with a side product stream is proposed and called Process Scheme B (PSB) (Fig. 3). In PSB, the distillation column operates simultaneously as heterogeneous azeotropic distillation and prefractionator. A stream of aqueous diluted bioethanol (stream F) and a stream of gasoline additive stream, e.g. TAME, used as entrainer (stream T) are fed to the column. A gasoline stream (stream G) also used as entrainer is fed to the decanter (DEC) and refluxed to the column with the organic phase from the decanter (stream J). Pure water is collected at the aqueous decanter phase (stream D) and at the column bottom (stream W). The formulated gasoline, i.e. mixture of gasoline, bioethanol and TAME, is collected as a side stream (stream P). Aqueous streams W and D should be mixed and recycled back to the previous fermentation step to produce ethanol; the amount of organic compounds present in this stream is very low and would not interfere with the fermentation process. In this way, water consumption is minimized for the overall process and the main output stream of the dehydration process is the formulated gasoline (stream P).

### 2.2. Rigorous simulation

The process schemes discussed in the previous section are assessed using RADFRAC blocks, for rigorous distillation columns. The number of stages is adjusted by the rule of thumb considering that a near optimal reflux ratio is around 1.3 times the minimum reflux (Bonet et al., 2007). Feed stages minimizing the reboiler duty are chosen according to the sensitivity analysis results. The decanter is adiabatic. The process operates at 1 bar of pressure.

The calculation basis is a production of 18,000 t/year of Ethanol/TAME/Gasoline blend. As shown in Table 1, section 1, our previous publications prove that lower energy consumptions are achievable collecting a mixture entrainer/ethanol instead of pure ethanol. When the final use of the bioethanol is as fuel, collecting a mixture of bioethanol with gasoline additives instead of pure bioethanol is a good choice. The aim of the present study is to perform an assessment when the product stream of the bioethanol dehydration also includes gasoline, i.e. a formulated gasoline as final product consisting of ethanol, gasoline and gasoline additive.

For all scenarios, an aqueous crude feed stream of 12 wt% in ethanol is assumed. TAME is the main gasoline additive used in UE and is mixed with gasoline in concentrations between 12.75 and 17.21 wt%. In order to simplify the gasoline composition, a mixture of hexane, cyclohexane, iso-octane and toluene (all at 25 wt%) is assumed (Gomis et al., 2015). Hence, the desired formulated gasoline has 5.2 wt% ethanol, 15.4 wt% TAME and less than 0.3 wt% of water according to EU requirements (EN 15376, 2011). A near-optimal solution for the distillation columns number of stages, feed stages, reflux ratio is provided.

### 2.3. Utilities & equipment sizing for economic assessment

The utilities for the processes studied are calculated using the empiric equation provided by Ulrich and Vasudevan (2006) assuming a fuel price oil of 7 \$/GJ and a Plant Index Cost set at 581.

The distillation column length is calculated using empiric equation of Luyben (2013) and the diameter of the column with equations of Özçelik (2011). The heat transfer area for condensers and reboilers are calculated with equations proposed by Modi and Westerberg (1992). The volume of the decanter and reflux drum are calculated using the equation proposed by Luyben (2013), where the residence time for decanter is set on 20 min and the reflux drums in 10 min. The reflux pump is calculated using the size factor using the equation proposed by Seider et al. (2015). The sizing is required for the economic viability assessment. For the economic viability study, Cost of Good Sold (COGS), Profit and Losses account (P&L) and Capital Expenditure (CAPEX) are evaluated. A sensitivity analysis highlights the effect of the main factors' variation on the economic viability of each process scheme.

## 3. Results

There are many entrainers useful for bioethanol dehydration, but the present study is focused on compounds that could remain in the gasoline formulation. As previously stated, in Europe, 85% of ethanol production is used in gasoline formulation with a maximum concentration of 10 wt % (Directive 2009/10/EC) and the main gasoline antiknock compound used is TAME. In this section, the residue curve map topology for aqueous ethanol and chemical compounds useful in gasoline formulation is presented. The residue curve maps analysis is a useful tool to propose feasible chemical process schemes that are further rigorously simulated. Based on rigorous simulation results, utilities consumption and units sizing are performed and these results are used for the assessment of the process economic viability and potential environmental impact.

### 3.1. RCM-LLE topologies

A classification of entrainers for ethanol dehydration that could remain in gasoline formulation consists of compounds already present in gasoline (e.g. hexane, cyclohexane, iso-octane and toluene) or compounds that are gasoline additives, (e.g. TAME). All the residue curve maps topologies for TAME (Fig. 4), gasoline linear hydrocarbons (iso-octane and hexane) (Fig. 5) and gasoline cyclic hydrocarbons (toluene and cyclohexane) (Fig. 6) present some common aspects. All entrainers have a low water solubility and present a water-entrainer phase split immiscibility region (water and gasoline are not soluble). All present a common residue curve map topology: three distillation regions where a ternary azeotrope in the phase split region is the

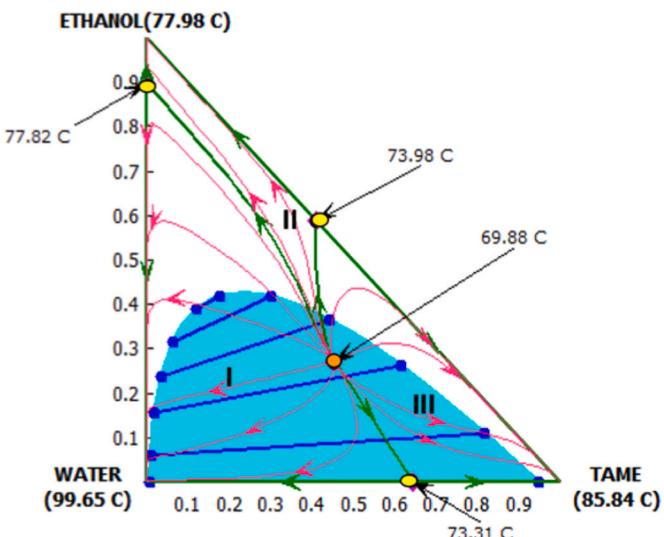


Fig. 4. Residue curve map for TAME.

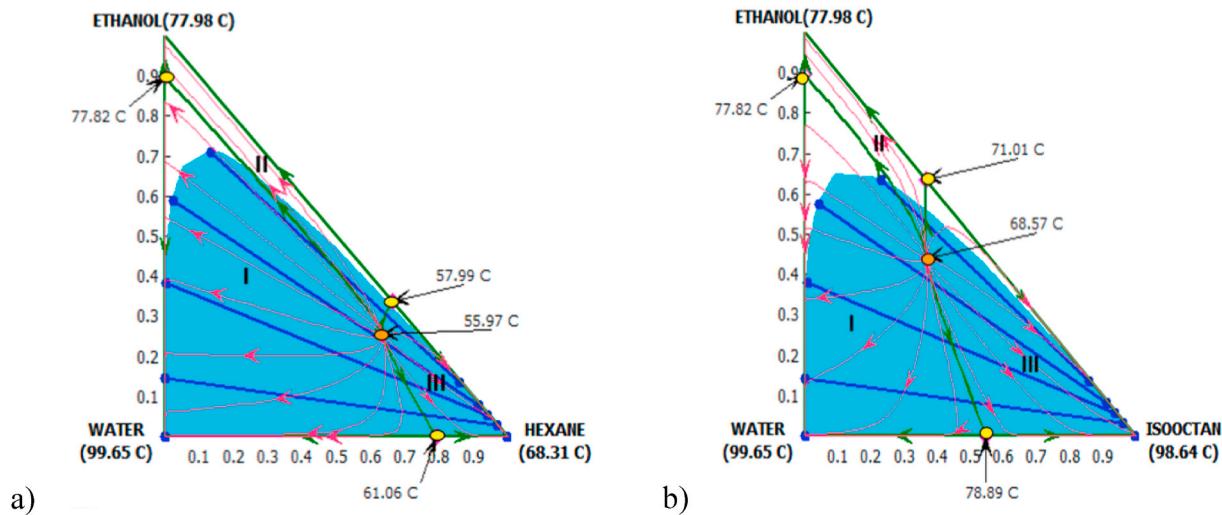


Fig. 5. Residue curve maps for linear compounds of gasoline: a) Hexane, b) Isooctane.

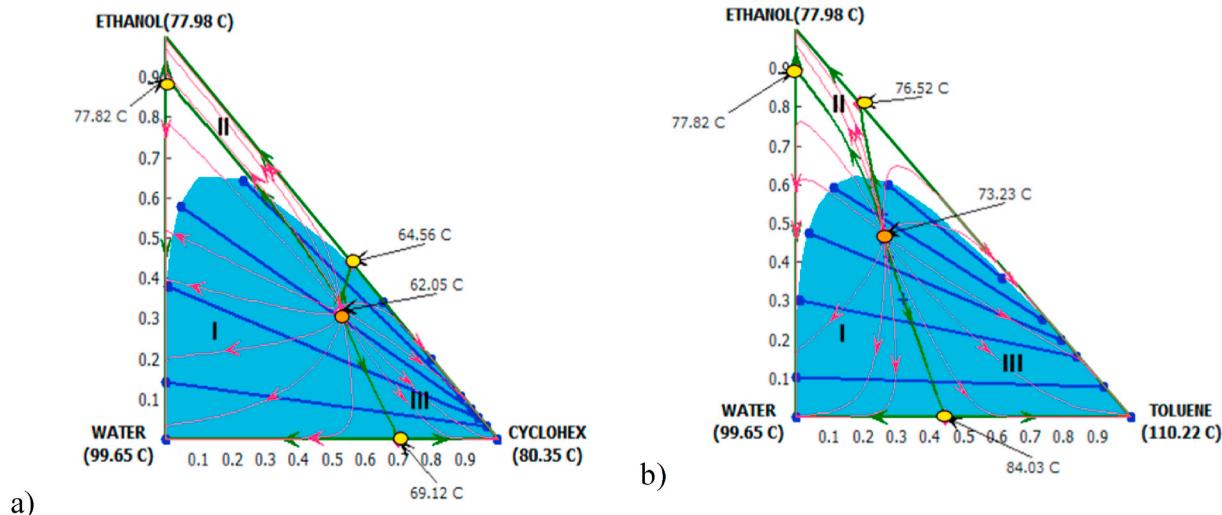


Fig. 6. Residue curve maps for cyclic compounds of gasoline: a) Cyclohexane, b) Toluene.

unstable node (minimum boiling point) and the stable nodes for each regions are water, ethanol and the entrainer. The three binary azeotropes for each binary mixture are the saddle points. The fact that the residue curve maps are qualitatively the same for all these chemical compounds highlights the feasibility of using a mixture of all these categories as entrainers, i.e. gasoline and TAME. The different slope of the liquid-liquid equilibrium tie-lines between the gasoline compounds and TAME shows that the ethanol is more soluble in TAME than in water but is more soluble in water than in gasoline. Therefore, the particularity of the concept presented in this study resides in adding the gasoline directly into the decanter to extract ethanol from the aqueous phase and TAME to the distillation column. The quantitative differences between the gasoline components, e.g. ternary azeotrope boiling point for hexane is lower than for toluene, implies that distillation reflux ratio must be adjusted according to gasoline composition variations.

### 3.2. Rigorous simulation results

Combining in the same process the non-spontaneous ethanol dehydration with the spontaneous process of gasoline mixing, the energy consumption for ethanol dehydration is expected to decrease. However, rigorous simulations are necessary to check the feasibility of the concept

and to quantify the energy savings achieved. The classical process scheme for ethanol dehydration by heterogeneous azeotropic distillation using a prefractionation column is compared to a novel intensified process with a single column and collecting the formulated gasoline as a side stream. The results of the macroscopic mass balance of process scheme A: formulated gasoline product and process scheme B: intensified process to produce formulated gasoline are presented in Tables M.1 and M.2, in the Supplementary Material.

#### 3.2.1. Rigorous simulation of process scheme A: formulated gasoline product

Output streams from process PSA fulfills the desired compositions (Fig. 7). The collected water (stream W) contains solely a 0.1% of ethanol and the formulated gasoline produced (stream P) fulfills the specifications mentioned in section 2.2 with a low content of water.

For the prefractionation distillation column (COL 1), 4.7 is the near optimum reflux ratio and 3.2 for the heterogeneous azeotropic distillation column (COL 2). Around 81% of the energy consumption is in the prefractionator column reboiler (COL1) (Table 2). The bottom and top temperatures of prefractionation column are close to boiling point of water (100 °C) and of azeotrope ethanol/water (78 °C) respectively. The reboiler duty and temperature of COL 2 is lower than the condenser duty

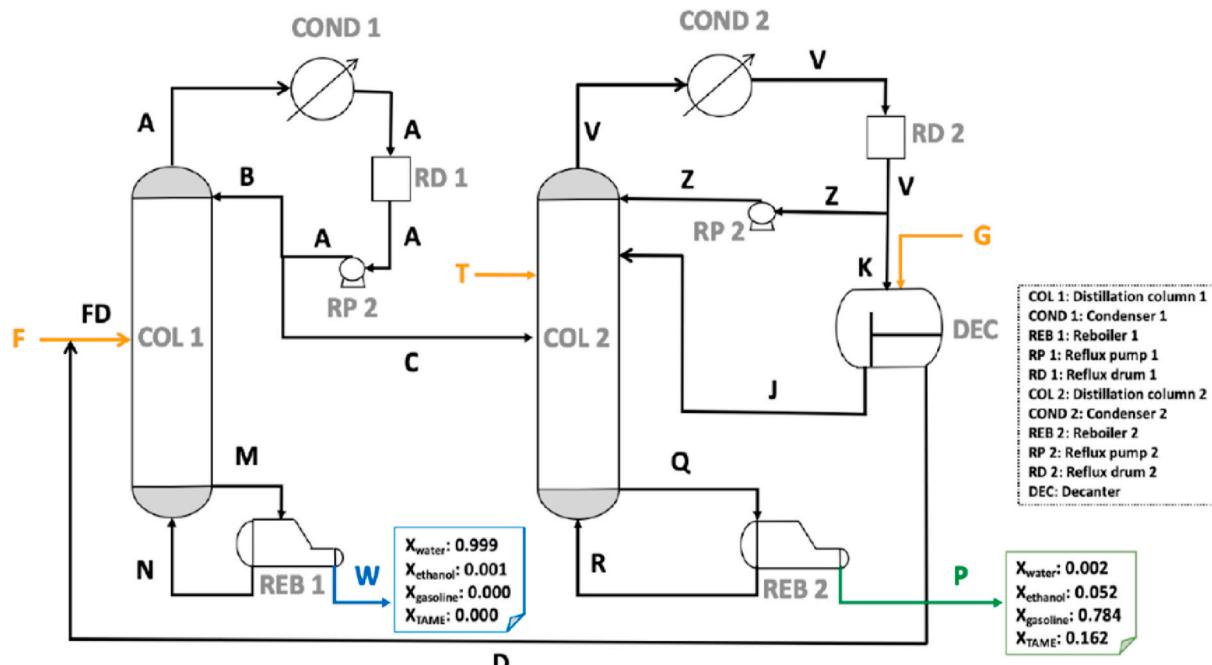


Fig. 7. Process scheme A

**Table 2**  
Condenser and reboiler values for PSA.

	Condenser COL 1	Reboiler COL 1	Condenser COL 2	Reboiler COL 2
Temperature (°C)	78	99	37	65
Distillate flow rate (kg/h)	128	–	839	–
Bottom flow rate (kg/h)	–	866.6	–	2266.4
Heat duty (kW)	−169	181	−67	43

and temperature of COL 1, i.e. the energy eliminated at the condenser of the prefractionation tower is more than 4 times the energy consumed at COL2; its temperature is at 78 °C and COL2 is 65 °C. This situation opens possibilities for heat integration and the energy required for COL2

functioning can be totally retrieved from COL1 condenser. Cooling water is suitable according to the condenser temperature of 37 °C at COL 2. The energy consumption per kilogram of ethanol is 6.8MJ/kgEtOH.

Mass composition column profile for COL 1 shows that water is the main compound at the stripping section and the ethanol increases along the rectifying section towards the azeotropic composition at the top (Fig. 8). The diluted aqueous ethanol feed input, i.e. 12 wt% aqueous ethanol, is located on the 10th stage. The separation of excess water from azeotropic composition is achieved with 14 stages.

The main compound along the heterogeneous azeotropic distillation column (COL 2) is the gasoline (around 80 wt%) and then TAME at a lower extent (around 15 wt%) (Fig. 9). The feed input is located on the 7th stage. Breaking the water-ethanol azeotrope is achieved with 8 stages whose evolution of the compositions profile indicates that ethanol is present with a low fraction of water in the stripping section and water is

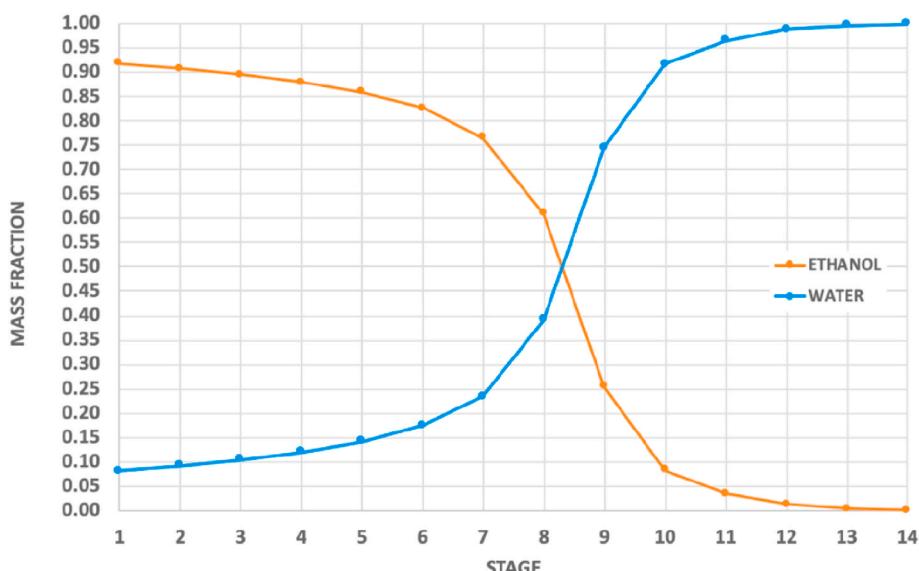


Fig. 8. Column profile for prefractionation column (COL 1)- PSA.

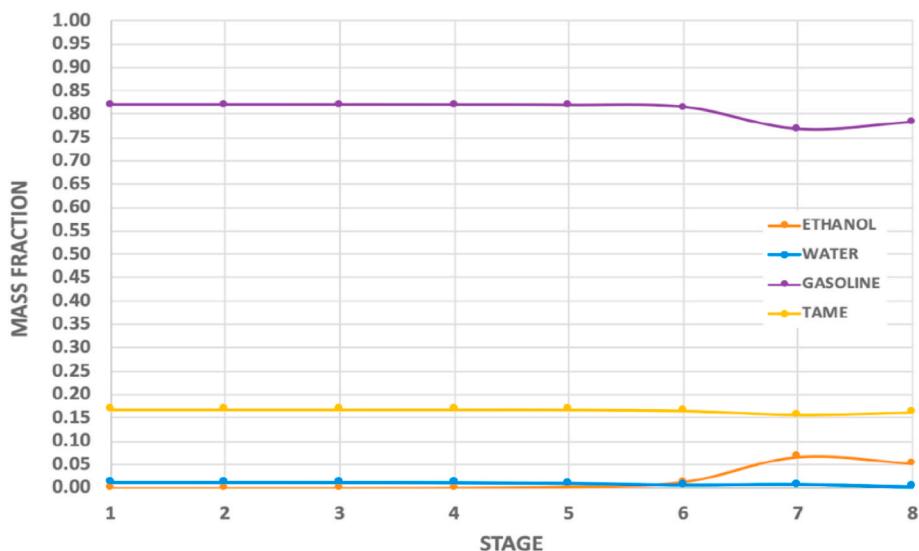


Fig. 9. Column profile for HAD distillation (COL 2)- PSA.

present with a low fraction of ethanol in the rectifying section.

### 3.2.2. Rigorous simulation for process scheme B: intensified process to produce formulated gasoline

In the intensified process scheme, a single distillation column is required (Fig. 10). Stream P, the resulting gasoline formulation final product, is recovered as a side stream, while water is eliminated from the bottom of the distillation column (stream W). The aqueous stream from the decanter, stream D, is essentially pure water and therefore is not recirculated. The flowrate of D is only 6.7% of the overall aqueous output streams. The reflux ratio and stage number for this distillation column (COL 1) are set in 2.25 and 36, respectively. Aqueous 12 wt% ethanol (stream F) is fed on the 24th stage. Stream P, blended gasoline, is produced close to the middle of the distillation column, stage 12. The top of the distillation column operates at 53 °C and the bottom operates close to the water boiling point, i.e. 99 °C versus the 100 °C of the water boiling point (Table 3). The reboiler duty is 193 kW that corresponds to

**Table 3**  
Condenser and reboiler values for PSB.

	Condenser COL 1	Reboiler COL 1
Temperature (°C)	53	99
Distillate flow rate (kg/h)	1155.6	–
Bottom flow rate (kg/h)	–	805.9
Heat duty (kW)	–210.3	193.2

6 MJ/kg ethanol dehydrated.

Water is the main compound at the stripping section below the crude feed stage, 24th stage, increasing its concentration downwards to almost pure water at the bottoms of the distillation column (99.9 wt%) (Fig. 11). Below the feed stage, the main compounds are ethanol and water. Upwards the feed stage, gasoline is the main compound. In between the aqueous ethanol feed stage and the formulated gasoline side stream, the water mass fraction is negligible but increases again at the

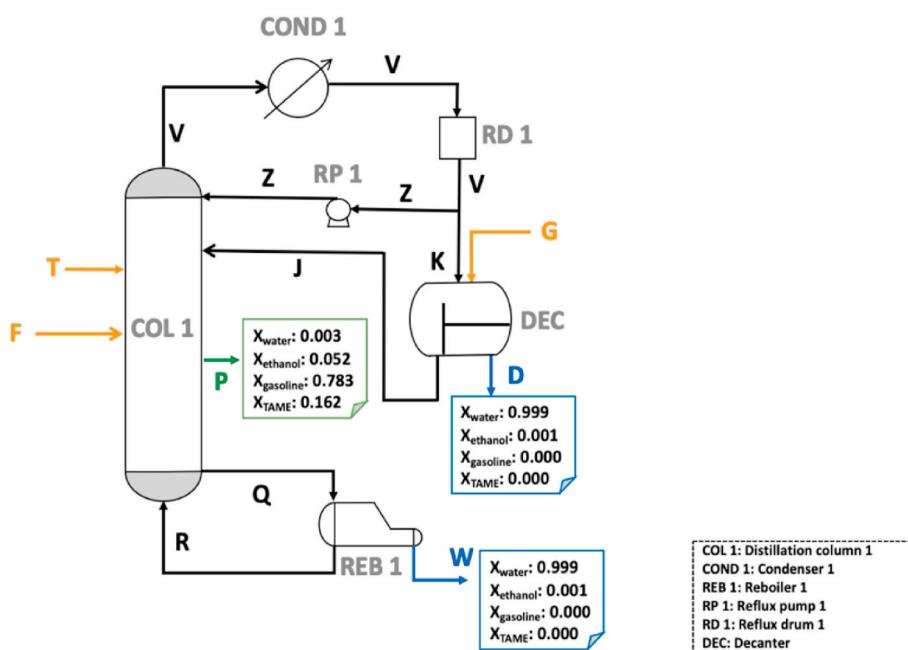
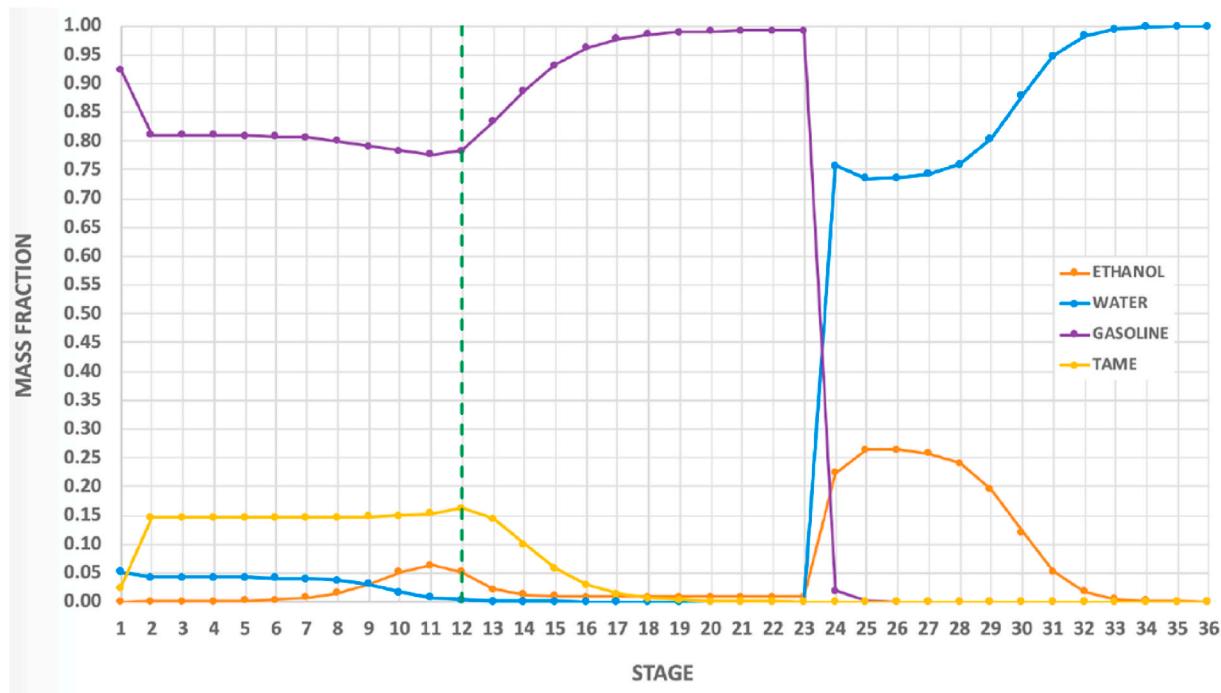


Fig. 10. Process scheme B.



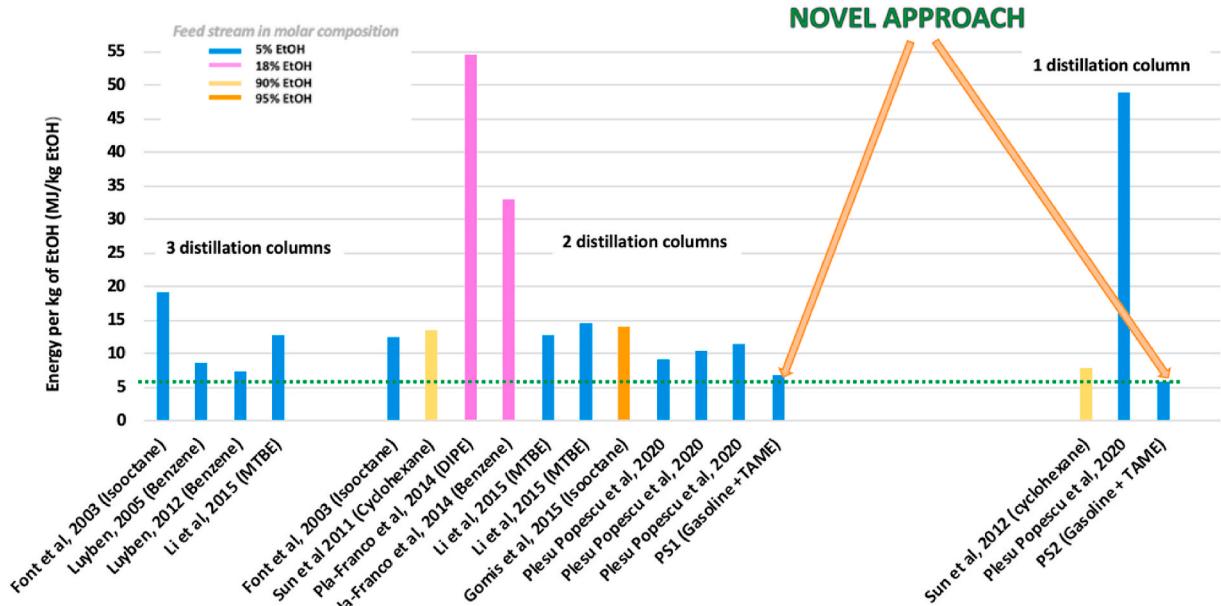
**Fig. 11.** Column profile for distillation column (PSB).

upper part of the column. The ethanol becomes accumulated in two regions: at the stage just below the diluted aqueous ethanol feed and at the stages around the side stream of formulated gasoline. Therefore, the formulated gasoline is withdrawn from stage 12 (dashed green line) as its composition corresponds to the required purity specifications to be used as a fuel. TAME is primarily present in the column profile around the side stream upwards to the top of the column. On stage 1, there is a sudden decrease of TAME and increase of gasoline mass fraction since at this point gasoline is fed to the decanter. Therefore, ethanol dehydration and mixing with gasoline and additives is performed in a single distillation column, obtaining a composition in the column profile fulfilling the formulated gasoline required specifications and almost free of water, i.e. 0.3 wt%.

An accident that affects the column wall is more prone to happen at the lower stages of the column, where the content of the plates is mainly water with a small quantity of ethanol. Therefore, a leakage from the lower stages is not likely to lead to an accident with catastrophic consequences. The column profile indicates an inherently safe operation of the column.

### 3.3. Energy consumption and potential environmental impact results

Fig. 12 reviews the amount of consumed energy to dehydrate 1 kg of ethanol for the literature processes and the two processes proposed in this study. Both processes proposed in this study have a lower energy consumption than the previously proposed processes in the literature.



**Fig. 12.** Energy consumption results comparison.

The energy consumption determines the potential environmental impact (PEI/kg) and therefore the novel approach is also more environmentally sustainable as it is more efficient (Fig. 13). The process scheme selected to dehydrate the bioethanol has a higher effect on the environmental impact than the energy mix used to supply the energy to the process, i.e. coal, natural gas or oil. The conventional process results are calculated from Li et al. (2015) results (pure ethanol as final product). It is appreciated that PSA (2 Distillation columns) and PSB (1 Distillation column), both of them providing a formulated gasoline (mixture of ethanol + gasoline + TAME) as a final product, present the lowest PEI/kg of product in each type of energy and are significantly lower than the processes proposed in literature. The energy consumption is the main factor in the potential environmental impact assessment and therefore both proposed process schemes have a similar impact. The use of coal to generate the energy produces the highest impact.

Assuming that the energy consumed in the process is obtained from natural gas, the calculated carbon dioxide equivalents (EPA, 2018) for the intensified process are 300 g CO<sub>2eq</sub>/kg EtOH produced. Notice that the ethanol production generates less than 7 g CO<sub>2eq</sub>/kg EtOH (Pacheco and Silva, 2019) and that the motor gasoline generates 2.3 kg CO<sub>2eq</sub>/L (EPA, 2018). Most of the carbon equivalent emissions are generated during the gasoline combustion, but besides the combustion, most of the carbon dioxide emissions are produced at the ethanol dehydration step. Any improvement on the energy efficiency of ethanol dehydration produces great reductions on carbon dioxide emissions due to the large amount of gasoline consumed around the world. Nowadays, CO<sub>2</sub> total world emissions are approximately 34 thousand of millions of tons (BP, 2020). Solely in USA are consumed around 1500 million of litres of motor gasoline per day that includes 10% fuel ethanol by volume (EIA, 2020). Hence, an energy consumption reduction of only 1 kJ for each kg of ethanol dehydrated represents approximately 6 tons of CO<sub>2</sub> less emitted at the atmosphere each day solely in USA.

#### 3.4. Economical viability of the process

In this section, the results of the economic viability of the proposed processes are presented. The details of the economic assessment are provided as Supplementary Material. The main parameters to perform the economic viability study are:

- Raw materials price: (1) TAME 0.70 €/kg, (2) Gasoline without additive 0.45 €/kg (3) water 1.12 €/m<sup>3</sup> and (4) ethanol 0.15 €/kg.
- Utilities: (1) electricity 0.13 €/kWh, (2) cooling water 0.06 €/m<sup>3</sup> and (3) steam 27 €/t.
- Sales price: 0.70 €/kg.

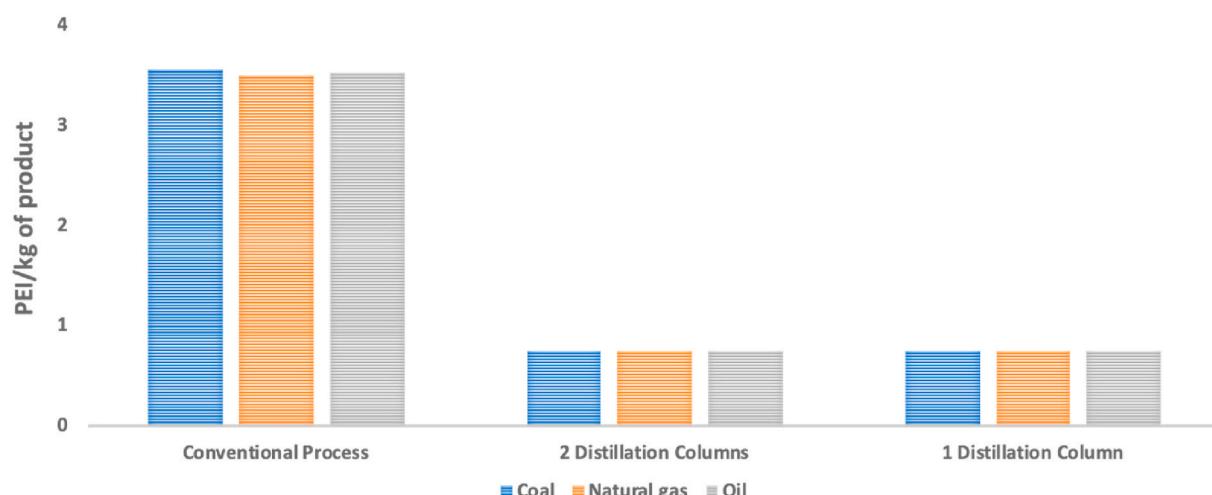


Fig. 13. Environmental impact results.

- CAPEX: 4286 k€ for PSA and 3572 k€ for PSB.

Although the previous sections suggest that the intensified process in a single column (PSB) is slightly better than the process with a pre-fractionation (PSA) from the energy consumption and environmental point of view, the economic results show that the intensified process is preferable. Fig. 14 illustrates that the initial investment is recovered in the classical process (PSA) in 5.7 years while in the intensified process (PSB) is recovered in only 4.2 years.

The sensitivity analysis shows the effect of variations on the cost of utilities, raw material, CAPEX or final product sales prices on the project values. The sensibility analysis is performed according to the Net Present Value (NPV).

As a result, Fig. 15 illustrates how any change affects on each variable in a margin of a ±10%. The results show a low influence of utilities or investment costs (CAPEX) but a substantial influence of the raw material costs or the product selling price. Fig. 15 underlines that a 10% increase on aqueous ethanol cost or a 10% decrease on sales price produces a negative accumulated cash flow. The crucial parameters to set the profitability of the plant are the price of raw materials and the price of the final product. Therefore, the profitability of the process greatly depends on disposing of a cheap fermentable raw material to produce bioethanol. The nowadays intensive research indicated in the Introduction on non-edible, renewable and cheap raw materials useful as substrate for ethanol fermentation is required locally at each region to face the high levels of atmospheric CO<sub>2</sub> globally.

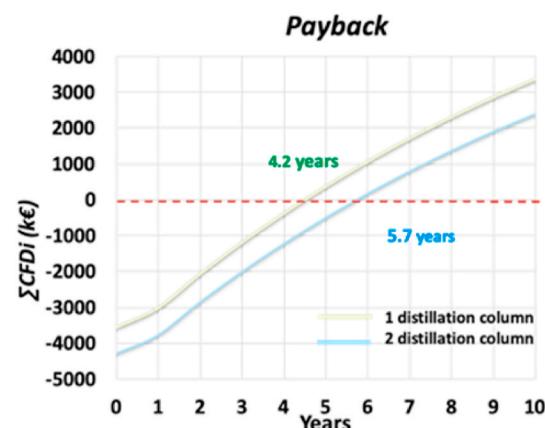
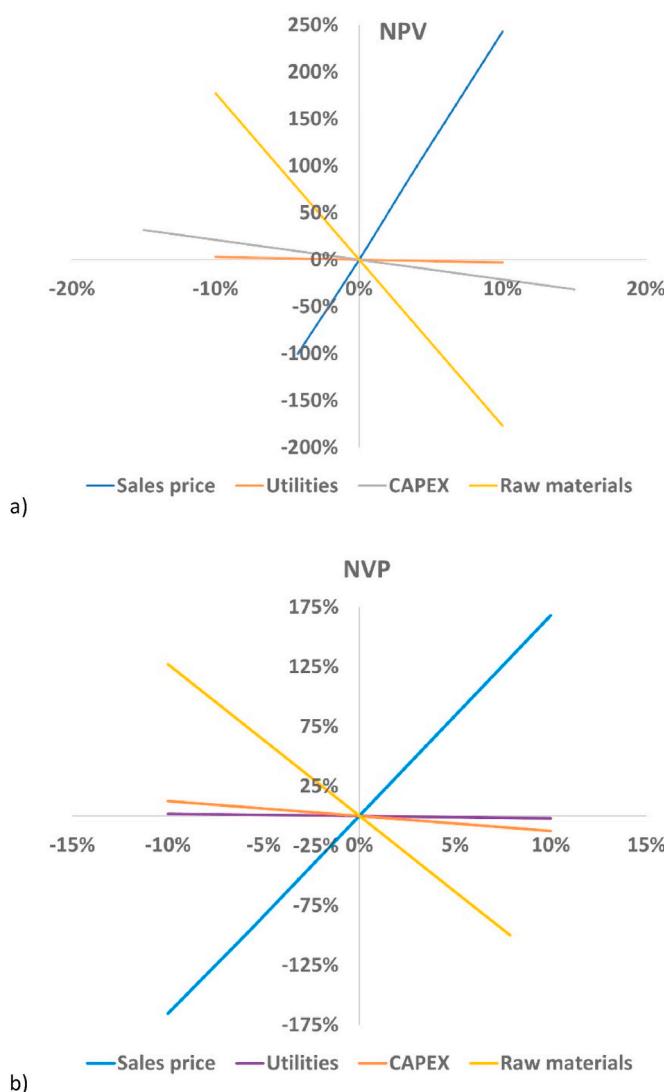


Fig. 14. Payback for classical (PSA) and intensified (PSB) processes.



**Fig. 15.** Sensibility study for a) classical scheme (PSA) and b) intensified scheme (PSB).

Notice that this process does not produce pure ethanol useful to synthetize further compounds, but mixed with gasoline which limits its use as a fuel (its main nowadays use). Further pilot plant experiments are recommended prior the industrial implementation of the proposed process.

#### 4. Conclusions

The bibliographic review shows that the process efficiency increase collecting an entrainer/ethanol mixture instead of only ethanol. The best entrainers are gasoline and the additives that are blended in gasoline. This study shows that the best entrainer is the use of TAME at the top of the column and gasoline in the decanter and produce a blended product of gasoline, TAME and ethanol. Following this strategy, energy savings between 43% and 53% for ethanol dehydration are achieved. In terms of potential environmental impact per kilogram of product is reduced close to 79% from the two novel approaches to the conventional process. In economic terms, the CAPEX needed for the intensified process scheme of one distillation column is 20% less than the conventional process using two distillation columns for a production of 18,000 t/year. When operating with one distillation column instead of two distillation columns, the process is inherently safer and the payback is reduced in 1.5 years, from 5.7 to 4.2 years. The sensibility study shows that the raw

material cost and selling price are of considerable importance. Analysing all the aspects, a single heterogenous azeotropic distillation column collecting a mixture of ethanol, gasoline and TAME as side stream is the best alternative process scheme for ethanol dehydration.

#### CRediT authorship contribution statement

**Alexandra Elena Plesu Popescu:** Conceptualization, Methodology, Formal analysis, Data curation, Writing – review & editing, Visualization. **José Lluis Pellin:** Investigation, Writing – original draft. **Jordi Bonet:** Resources, Supervision. **Joan Llorens:** Project administration.

#### 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.

#### Acknowledgments

Alexandra Elena Plesu Popescu is a Serra Húnter fellow.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2021.128810>.

#### References

- Aguilar-Sánchez, P., Navarro-Pineda, F.S., Sacramento-Rivero, J.C., Barahona-Pérez, L.F., 2018. Life-cycle assessment of bioethanol production from sweet sorghum stalks cultivated in the state of Yucatan. Mexico. Clean. Technol. Environ. Pol. 20, 1685–1696. <https://doi.org/10.1007/s10098-017-1480-4>.
- AspenPlus, 2020. Aspen Plus | leading process simulation software. AspenTech [WWW Document]. <https://www.aspentechn.com/en/products/engineering/aspen-plus>. (Accessed 30 November 2020). accessed.
- Balat, M., Balat, H., 2009. Recent trends in global production and utilization of bioethanol fuel. Appl. Energy 86, 2273–2282. <https://doi.org/10.1016/j.apenergy.2009.03.015>.
- Bonet, J., Galan, M.I., Costa, J., Meyer, X.M., Meyer, M., 2007. Multicomponent rectification: representation of number of stages as function of reflux ratio. In: Proceedings of European Congress of Chemical Engineering (ECCE-6) Copenhagen, 16-20 September 2007. [http://folk.ntnu.no/skoge/prost/proceedings/ecce6\\_sep07/upload/399.pdf](http://folk.ntnu.no/skoge/prost/proceedings/ecce6_sep07/upload/399.pdf). (Accessed 25 March 2021).
- Bonet-Ruiz, A.E., Luna Surinyach, R., Plesu, V., Bonet, J., Iancu, P., Llorens, J., 2017. Distillation sequence efficiency (DSE) for suitable liquid-liquid extraction solvents: acetic acid extraction with TOA. Comput. Aided Chem. Eng. 40, 397–402. <https://doi.org/10.1016/B978-0-444-63965-3.50068-4>.
- BP, British Petrol, 2020. Statistical Review of World Energy, 69<sup>th</sup> edition, p. 13. carbon dioxide emissions. <http://bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-co2-emissions.pdf>. (Accessed 30 November 2020). accessed.
- Čuček, L., Klemes, J.J., Kravanja, Z., 2012. Carbon and nitrogen trade-offs in biomass energy production. Clean Technol. Environ. Policy 14 (3), 389–397. <https://doi.org/10.1007/s10098-012-0468-3>.
- Díaz, S.A., Acosta, M.J.S., Delgado, Á.D.G., 2018. Computer-aided environmental evaluation of bioethanol production from empty palm fruit bunches using oxalic acid pretreatment and molecular sieves. Chem. Eng. Trans. 70, 2113–2118. <https://doi.org/10.3390/CET1870353>.
- Dimian, A.C., Iancu, P., Plesu, V., Bonet-Ruiz, A.-E., Bonet-Ruiz, J., 2019. Castor oil biorefinery: conceptual process design, simulation and economic analysis. Chem. Eng. Res. Des. 141, 198–219. <https://doi.org/10.1016/j.cherd.2018.10.040>.
- Directive 2009/30/EC, 2009. Directive of the European Parliament and of the Council of 23 April 2009 Amending Directive 98/70/EC as Regards the Specification of Petrol, Diesel and Gas-Oil and Introducing a Mechanism to Monitor and Reduce Greenhouse Gas Emissions and Amending Council Directive 1999/32/EC as Regards the Specification of Fuel Used by Inland Waterway Vessels and Repealing Directive 93/12/EEC.
- EIA, US Energy Information Administration, 2020. Gasoline Explained. Use of Gasoline. <http://eia.gov/energyexplained/gasoline/use-of-gasoline.php>. (Accessed 30 November 2020). accessed.
- EPA, 2018. Emission Factors for Greenhouse Gas Inventories, 9 march 2018. [http://epa.gov/sites/production/files/2018-03/documents/emission-factors\\_mar\\_2018\\_0.pdf](http://epa.gov/sites/production/files/2018-03/documents/emission-factors_mar_2018_0.pdf). (Accessed 10 May 2019). accessed.
- Flach, B., Lieberz, S., Lappin, J., Bolla, S., 2018. Biofuels Annual. EU Biofuels Annual 2018, 2018. GAIN Report Number: NL8027.

- Font, A., Asensi, J.C., Ruiz, F., Gomis, V., 2003. Application of isoctane to the dehydration of ethanol. Design of a column sequence to obtain absolute ethanol y heterogeneous azeotropic distillation. *Ind. Eng. Chem. Res.* 42, 140–144. <https://doi.org/10.1021/ie0204078>.
- European Committee for Standardisation, Automotive Fuels, 2011. Ethanol as a Blending Component for Petrol. Requirements and Test Methods. European Standard EN 15376.**
- Galbe, M., Wallberg, O., Zacchi, G., 2013. Cellulosic bioethanol production. In: John Wiley & Sons, Ltd, Separation and Purification Technologies in Biorefineries, pp. 487–501. <https://doi.org/10.1002/9781118493441.ch18>.
- Gomis, V., Pedraza, R., Francés, O., Font, A., Asensi, J.C., 2007. Dehydration of ethanol using azeotropic distillation with isoctane. *Ind. Eng. Chem. Res.* 46, 4572–4576. <https://doi.org/10.1021/ie0616343>.
- Gomis, V., Pedraza, R., Saquete, M.D., Font, A., García-Cano, J., 2015. Ethanol dehydration via azeotropic distillation with gasoline fractions as entrainers: a pilot-scale study of the manufacture of an ethanol-hydrocarbon fuel blend. *Fuel* 139, 568–574. <https://doi.org/10.1016/j.fuel.2014.09.041>.
- Gurram, R., Al-Shannad, M., Knapp, S., Das, T., Singsaas, E., Alkasrawi, M., 2016. Technical possibilities of bioethanol production from coffee pulp: a renewable feedstock. *Clean Technol. Environ. Policy* 18, 269–278. <https://doi.org/10.1007/s10098-015-1015-9>.
- Hancsók, J., Kasza, T., Visnyei, O., 2019. Isomerization of n-C5/C6 bioparaffins to gasoline components with high octane number. *Chem. Eng. Trans.* 76, 1357–1362. <https://doi.org/10.3303/CET1976227>.
- Hasanly, A., Khajeh Takhoncheh, M., Karimi Alavijeh, M., 2018. Techno-economic assessment of bioethanol production from wheat straw: a case study of Iran. *Clean Technol. Environ. Policy* 20, 357–377. <https://doi.org/10.1007/s10098-017-1476-0>.
- Kiss, A.A., Suszwalak, D.J.P.C., 2012. Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns. *Separ. Purif. Technol.* 86, 70–78. <https://doi.org/10.1016/j.seppur.2011.10.022>.
- Kravanja, P., Könighofer, K., Canella, L., Jungmeier, G., Friedl, A., 2012. Perspectives for the production of bioethanol from wood and straw in Austria: technical, economic, and ecological aspects. *Clean Technol. Environ. Policy* 14 (3), 411–425. <https://doi.org/10.1007/s10098-011-0438-1>.
- Lara-Montaña, O.D., Meléndez-Hernández, P.A., Bautista-Ortega, R.Y., Hernández, S., Delgado, L.A., Hernández-Escoto, H., 2019. Experimental study on the extractive distillation based purification of second-generation bioethanol. *Chem. Eng. Trans.* 74, 67–72. <https://doi.org/10.3303/CET1974012>.
- Li, Y., Liu, G., 2018. Study on coupling separation process of ETBE and absolute ethanol. *Chem. Eng. Trans.* 70, 427–432. <https://doi.org/10.3303/CET1870072>.
- Li, J., You, C., Lyu, Z., Zhang, C., Chen, L., Qi, Z., 2015. Fuel-based ethanol dehydration process directly extracted by gasoline additive. *Separ. Purif. Technol.* 149, 9–15. <https://doi.org/10.1016/j.seppur.2015.05.012>.
- Luyben, W.L., 2006. Control of a multicomponent heterogeneous azeotropic distillation process. *AIChE J.* 2, 623–637. <https://doi.org/10.1002/aiic.10650>.
- Luyben, W.L., 2013. Distillation Design and Control Using Aspen Simulation. Wiley.**
- Lyu, H., Zhang, J., Zhai, Z., Feng, Y., Geng, Z., 2020. Life cycle assessment for bioethanol production from whole plant cassava by integrated process. *J. Clean. Prod.* 269, 121902. <https://doi.org/10.1016/j.jclepro.2020.121902>.
- Ma, X., Wang, J., Gao, M., Wang, N., Li, C., Wang, Q., 2021. Effect of pH regulation mode on byproduct ethanol generated from the lactic acid fermentation of *Sophora flavescens* residues. *J. Clean. Prod.* 279, 123536. <https://doi.org/10.1016/j.jclepro.2020.123536>.
- Magalon-Micán, M.T., Paéz, A.I., Lache-Muñoz, A., Santos-Aguilar, J., Zalaba-García, D. A., 2017. Bioethanol Production from different mixes of organic wastes in a food company. *Rev. Invest.* 10 (1), 47–59.
- Martínez-Guido, S.I., Betzabe González-Campos, J., Ponce-Ortega, J.M., Nápoles-Rivera, F., El-Halwagi, M.M., 2016. Optimal reconfiguration of a sugar cane industry to yield an integrated biorefinery. *Clean Technol. Environ. Policy* 18 (2), 553–562. <https://doi.org/10.1007/s10098-015-1039-1>.
- Modi, A.J., Westerberg, W., 1992. Distillation column sequencing using marginal price. *Ind. Eng. Chem. Res.* 31, 839–848. <https://doi.org/10.1021/ie00003a028>.
- Neagu, M., Cursaru, D., 2013. Bioethanol dehydration by extractive distillation with propylene glycol entrainer. *Rev. Chim. (Bucharest)* 1, 64.
- Özçelik, Y., 2011. Exergetic optimization of distillation sequences using a genetic based algorithm. *J. Therm. Sci. Technol.* 1, 19–25.
- Pacheco, R., Silva, C., 2019. Global warming potential of biomass-to-ethanol: review and sensitivity analysis through a case study. *Energies* 12 (13), 2535. <https://doi.org/10.3390/en1213253>.
- Phuong, N.T.M., Hoang, P.H., Dien, L.Q., Hoa, D.T., 2017. Optimization of sodium sulfide treatment of rice straw to increase the enzymatic hydrolysis in bioethanol production. *Clean Technol. Environ. Policy* 19 (5), 1313–1322. <https://doi.org/10.1007/s10098-016-1329-2>.
- Pla-Franco, J., Llosada, E., Loras, S., Montón, J.B., 2014. Thermodynamic analysis and process simulation of ethanol dehydration via heterogeneous azeotropic distillation. *Ind. Eng. Chem. Res.* 53, 6084–6093. <https://doi.org/10.1021/ie403988c>.
- Plesu Popescu, A.E., Pellin, J.L., Bonet-Ruiz, J., Llorens, J., 2020. Cleaner process and entrainer screening for bioethanol dehydration by heterogeneous azeotropic distillation. *Chem. Eng. Trans.* 81, 829–834. <https://doi.org/10.3303/CET2081139>.
- Rodrigues Gurgel da Silva, A., Errico, M., Rong, B.-G., 2018. Techno-economic analysis of organosolv pretreatment process from lignocellulosic biomass. *Clean Technol. Environ. Policy* 20, 1401–1412. <https://doi.org/10.1007/s10098-017-1389-y>.
- Saini, S., Chandel, A.K., Sharma, K.K., 2020. Past practices and current trends in the recovery and purification of first generation ethanol: a learning curve for lignocellulosic ethanol. *J. Clean. Prod.* 268, 122357. <https://doi.org/10.1016/j.jclepro.2020.122357>.
- Seider, W.D., Seader, J.D., Lewin, D.R., Widagdo, S., 2015. Product and Process Design. Principles Synthesis, Analysis and Evaluation, third ed. Wiley.
- Singh, A., Rangaiah, G.P., 2017. Review of technological Advances in bioethanol recovery and dehydration. *Ind. Eng. Chem. Res.* 56, 5147–5163. <https://doi.org/10.1021/acs.iecr.7b00273>.
- Sun, Y.L., Chang, X.W., Qi, C.X., Li, Q.S., 2011. Implementation of ethanol dehydration using diving-wall heterogeneous azeotropic distillation column. *Separ. Sci. Technol.* 46, 1365–1375. <https://www.tandfonline.com/doi/abs/10.1080/01496395.2011.556099>.
- Tejeda, L.P., Tejada, C., Villabona, A., Alvear, M.R., Castillo, C.R., Henao, D.L., Marimón, W., Madariaga, N., Tarón, A., 2010. Producción de bioetanol a partir de la fermentación alcohólica de jarabes glucosados derivados de cáscaras de naranja y piña. *Revista Educación en Ingeniería* 10, 120–125. <https://doi.org/10.26507/reiv.v5n10.104>.
- Ulrich, G., Vasudevan, P., 2006. How to estimate utility costs. *Chem. Eng.* 113, 66–69.
- Valentini, N., Marton, G., Toth, A.J., Haaz, E., Andre, A., Mizsey, P., 2018. Investigation of process alternatives for the separation of ethanol, N-butanol and water ternary mixture. *Chem. Eng. Trans.* 69, 607–612. <https://doi.org/10.3303/CET1869102>.
- WAR, 2020. Waste Reduction Algorithm. US-EPA. In: <http://epa.gov/chemical-research/waste-reduction-algorithm-chemical-process-simulation-waste-reduction>. (Accessed 30 November 2020). accessed.
- Wongpromrat, P., Rukquan, M., Anantpinijwatna, A., 2019. Experimental and modelling analysis of liquid-liquid formation in alcohol-mixed gasoline fuel. *Chem. Eng. Trans.* 76, 1195–1200. <https://doi.org/10.3303/CET1976200>.
- Zambare, V.P., Christopher, L.P., 2020. Integrated biorefinery approach to utilization of pulp and paper mill sludge for value-added products. *J. Clean. Prod.* 274, 122791. <https://doi.org/10.1016/j.jclepro.2020.122791>.