

Biofuels

Direct gasoline preblending of bioalcohol mixtures as a means of decreasing separation energy losses

--Manuscript Draft--

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Abstract:	<p>In the context of accelerating climate change, liquid biofuels have become an important source of sustainable energy. However, the energy inefficiency involved in the production of biofuels mitigates many of their benefits. Previous research has shown that gasoline pre-blending can drastically improve the efficiency of bioethanol production by discarding the erroneous assumption that a bio-alcohol must be fully purified before being blended into a fuel. This paper extends that concept into a far broader optimization space by modelling all possible gasoline pre-blending processes incorporating ethanol, butanol or both. It is found that butanol is highly suitable for gasoline pre-blending and that high recovery can be achieved even when starting with dilute concentrations. In addition, the presence of even small amounts of butanol are effective at drawing ethanol into the fuel phase and improving overall alcohol recovery. A graphical design methodology is presented allowing for rapid flowsheet development and performance prediction.</p>

Dear Sir or Madam,

Recent research has demonstrated that bio-alcohols can be recovered with far higher energy efficiencies when one disregards the erroneous assumption that an alcohol must be fully purified before being blended with gasoline. Instead, one can use spontaneous phase separation as a low-energy means of eliminating water. This is an exciting development for the renewable fuels industry, which has thus far struggled to overcome the high-energy cost of purifying bio-alcohols for blending.

Gasoline pre-blending processes are therefore an area of urgent interest for science; this a field of study in which scarcely any research exists, yet it is poised to become a major feature of the renewable fuels industry.

In this paper, we have modelled a comprehensive range of pre-blending processes recovering ethanol, butanol or some combination of the two. In doing the latter, we have disregarded another erroneous assumption underpinning existing industrial processes; that bio-alcohol production should comprise either one molecule or the other, depending on which proves to be most economical. We have discovered that when one takes pre-blending into consideration, there are sound economic reasons to co-produce both molecules for blending.

The simulation results presented graphically in this paper offer designers a means of predicting the performance of any possible pre-blending process with any mix of ethanol and butanol, and we have demonstrated a method of using these results to rapidly design and evaluate new flowsheets. By way of an example, we have used this method to assemble a flowsheet comprised of existing unit operations to recover butanol from ABE fermentation products using 17% less energy than a conventional process. We then extended that same process to take advantage of the butanol-rich

stream to recover ethanol directly from a highly dilute mixture with no separation prior to pre-blending, with a total energy usage 19% less than a conventional approach recovering the same quantity recovering the same quantity of the two alcohols separately.

This result is significant because it demonstrates that butanol can be recovered efficiently with pre-blending, and also proves that co-production of ethanol and butanol has significant advantages in terms of overall economic outlook of the process. This paper has demonstrated simple processes that are more efficient than the industry standards and, more importantly, has demonstrated an incredibly broad optimization space for bio-alcohol production processes. There is therefore a pressing need for scientists to begin examining that optimization space in search of the most efficient possible processes. It follows that there is broad scope and applicability for a means of rapidly designing and evaluating processes of this type.

The paper presented herewith therefore has broad interest within the fields of renewable fuels production and materials separation. Its contents are of direct interest to engineers and designers in industry as well as to researchers in these and associated fields of study. It is our firm conviction that this paper breaks important new ground and has the potential to be a major feature of a rapidly emerging field of research. On behalf of my co-authors, and myself I therefore commend the paper attached herewith for publication in your journal, where we believe it will reach an interested and receptive audience.

Yours Sincerely,

K. Ndlovu

Kudakwashe Ndlovu

Title of manuscript :

Direct gasoline preblending of bioalcohol mixtures as a means of decreasing separation energy losses

Direct gasoline preblending of bioalcohol mixtures as a means of decreasing separation energy losses

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Abstract

In the context of accelerating climate change, liquid biofuels have become an important source of sustainable energy. However, the energy inefficiency involved in the production of biofuels mitigates many of their benefits. Previous research has shown that gasoline pre-blending can drastically improve the efficiency of bioethanol production by discarding the erroneous assumption that a bio-alcohol must be fully purified before being blended into a fuel. This paper extends that concept into a far broader optimization space by modelling all possible gasoline pre-blending processes incorporating ethanol, butanol or both. It is found that butanol is highly suitable for gasoline pre-blending and that high recovery can be achieved even when starting with dilute concentrations. In addition, the presence of even small amounts of butanol are effective at drawing ethanol into the fuel phase and improving overall alcohol recovery. A graphical design methodology is presented allowing for rapid flowsheet development and performance prediction.

Introduction

At the forefront of addressing the question of sustainable development, among others, is the adaptation of renewable fuels to replace the traditional non-renewable ones. To qualify as a replacement, clearly, the essential properties of these two sources need at least to match. In the context of transportation fuels, these essential properties include – high power output, affordability, homogeneity of the fuel, safety, minimal modification to the current engine models,

fast refilling or recharging. Renewable biofuels from various forms of biomass have a potential of approaching this criteria. Biomass fuels are fuels derived from the fermentation of carbohydrates and starches using various microorganisms. The sources of biomass are influenced by geographical and economic considerations and range from edible feedstock like sugarcane, beetroot and wheat to non-edible feedstock like rice stalks, sugarcane bagasse and wheat straw ^{1,2}. Bioethanol is produced through anaerobic fermentation of biomass by microorganisms such as *Saccharomyces cerevisiae* and *Zymomonas mobilis* whilst biobutanol is produced from acetone, butanol and ethanol (ABE) fermentation of sugars using a family of *Clostridia* bacteria³⁻⁶. Butanol has a number of advantages over ethanol in that it has a higher energy density, much less affinity for water and higher energy efficiency⁷. Another area of interest is the production of biofuels from algae ^{2,8}.

The worldwide production of biofuels increased from 1 billion litres in 1981 to over 120 billion litres in 2014 and US Energy Information Administration predicts that figure to reach 200 billion litres by year 2020.⁹ This means biofuels have a role to play in the future. Bioethanol and biobutanol (ethanol and butanol hereafter) are some of the biofuels in current use and are the object of our study. However, at present, neither are regarded as economically favourable, because of the cost and the energy consumption involved in growing and transporting biomass plus subsequent operating fermentation facilities. In general, if 50% of the combustion energy of a biofuel is expended on bioconversion and separation, then economics may not favour any commercial ventures.¹⁰ As an example, calculations based on a corn-to-ethanol production process show that 54% of the energy content per a gallon of ethanol is required to process (that is, purify) the fuel, and a further 24% is spent on growing the biomass, leaving just over 20% as a net gain.¹¹ This net energy value, however, is even questioned¹ and is subject to vigorous debate. We therefore need to find a way to optimise all the production stages to make biofuels commercially competitive.

The product of fermentation is a dilute aqueous solution of alcohol(s). However, water is undesirable in fuel mixtures owing to potential corrosive effects and engine malfunctions and

therefore considerable effort is directed to elimination of water from fuel mixtures. The amount of water in biofuels should not exceed 0.3 wt % for the European Union context and 0.5 wt % for the US market.^{12,13} Distillation is often employed to recover the alcohols from dilute mixtures. While this technique offers high recovery rates, typically 99% of biofuels in the product stream, it has its handicaps. Firstly, distillation of fermentation broths involves evaporation of water, which has a high heat capacity value, making the process energy intensive. Moreover, the presence of azeotropes impedes attainment of fuel-grade dehydration specifications without introducing additional processes such as extractive distillation or pervaporation. These additional processes further raise the cost of production and energy consumption. The overall energy requirements for attaining high purity alcohols from alcohol-water mixtures through distillation are a function of the initial feed and the particular processes used as shown by Vane 2008.⁷ This author shows in his figures 7 (for ethanol) and 8 (for 1-butanol) how the amount of energy required per unit of alcohol recovered increases as the concentration of the alcohol in the feed decreases. This shows that distillation is an area in which optimisation holds some potential. Alternative methods to distillation include gas stripping, pervaporation, adsorption, liquid-liquid extraction^{7,14} and these can help alleviate the issue of energy consumption in biofuels production.

A recent proposal by Stacey et al¹⁵ reduces the energy requirement to separate ethanol from water by making use of a liquid-liquid phase split to eliminate water without separation energy. These authors propose the use of the conventional separation method until the ethanol-water azeotrope is reached, this stream is then blended directly into gasoline which results spontaneously into two phases that can be easily separated in a two-stage counter-current liquid-liquid extraction. In this way, these authors avoid the final purification steps of ethanol distillation, which are energy intensive obtaining a viable fuel mixture with almost complete recovery of ethanol from water. This approach, termed direct gasoline pre-blending, has high recoveries and leads to energy savings of between 17% and 40% in comparison to distillation. The gasoline pre-blending processes presented thus far are limited in scope, focusing only at ethanol and only considering a narrow

range of initial alcohol concentrations. The gasoline pre-blending method is therefore an attractive alternative method because it does not use separation energy. The usual route to fuel blending may be summarised in the following steps - fermentation of biomass using microorganisms to get fermentation broths, which is followed by processing of fermentation broths by filtration and distillation to get dehydrated alcohols and subsequently blending of alcohols with gasoline at pre-distributions sites.^{7,15}

Preblending is not limited to ethanol. Da Silva and Dos Santos¹⁶ show that gasoline pre-blending works for butanol obtained from fermentation as well. It will therefore be possible to use a three-component mixture (water-ethanol-butanol). This paper will evaluate gasoline pre-blending processes far more comprehensively than already demonstrated by Stacey et al¹⁵, i.e., considering all possible combinations of initial feed compositions (water-ethanol-butanol) mixtures to be blended with gasoline. The results shown in this paper will assist the design methodology for future distillation-preblending plants since we offer, in a compact manner, all possible direct pre-blending processes of aqueous ethanol and butanol mixtures that can be useful to rapidly evaluate the performance of the flowsheet in terms of alcohol recovery. Ultimately in this paper, is to present a methodology to check which fuel blends can be achieved that meet specific demands as dictated by regulations from any composition of ethanol, butanol and water.

Methodology

As stated before, the study of gasoline preblending with mixtures of water-ethanol-butanol with subsequent liquid-liquid separation will be developed here. To that end, we have used ASPEN PLUS V8.6® to model the liquid-liquid equilibrium behaviour of the mixture and used the parameters embedded in the software. These parameters are used for all modelling in this paper, along with an assumption of ambient conditions of 25°C and 1 atm pressure. We chose UNIQUAC (Universal Quasichemical) as the thermodynamic model because it is able to simulate liquid-liquid phase equilibria behaviour in non-ideal systems with partially soluble components.

Data for gasoline, however, is absent in this simulation package and it was decided to opt for isooctane whose liquid-liquid equilibrium closely fits the behaviour of ethanol, water and gasoline.¹⁷

To better understand the concept of phase blending and splitting which is the foundation to this work, it would be very useful to have at our disposal the experimental quaternary liquid-liquid-equilibria (LLE) data corresponding to this system since they set the thermodynamic limitations of phase blending and separation. Unfortunately and to the best of our knowledge these data have not been researched or published. Figure 1 shows the four sides of the tetrahedron for this system obtained through ASPEN and UNIQUAC at 25°C and 1 atm. In this figure we can easily see the miscibility of the six possible pairs: water/isooctane (immiscible), water/1-butanol (partially miscible), isooctane/1-butanol (completely miscible), water/ethanol (completely miscible), ethanol/isooctane (completely miscible), ethanol/1-butanol (completely miscible). In view of the equilibrium data shown in Figure 1, it seems reasonable to blend the product of fermentation (water with low concentration of alcohol) with gasoline so that after settling the gasoline is enriched with alcohols.

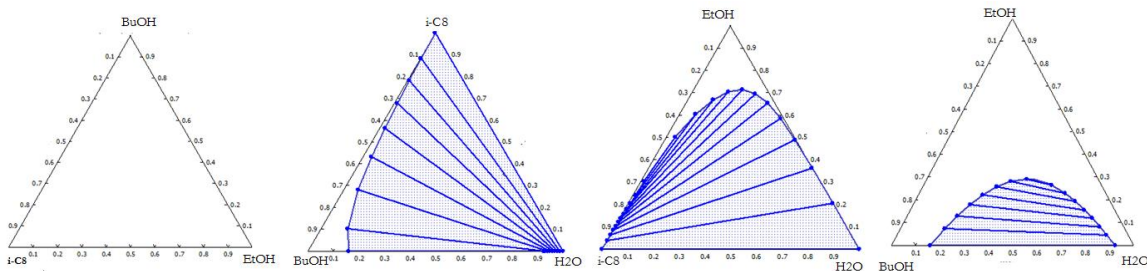


Figure 1. Four sides of the LLE tetrahedron obtained with ASPEN through UNIQUAC at 25°C and 1 atm.

1-BuOH = 1-butanol, EtOH = Ethanol, H₂O=water and i-C8 = isooctane.

Phase equilibrium of any system is a function not only of temperature and pressure but also of the purity of the species involved. One of the species in this quaternary system under study is gasoline, and given that its composition varies since different brands of gasoline have proprietary fuel additives and dyes, it is expected an influence in the phase equilibrium results. Therefore, the

results shown in this paper must be considered to be qualitative descriptions rather than quantitative.

In this paper, all ASPEN simulations are conducted for a two-stage counter-current liquid–liquid extraction set-up as this was the preferred procedure for the ethanol blending in prior research (see Figure 2); hence, it provides an ideal basis of comparison.¹⁵ Multi-stage processes will tend to exhibit the same trends as two-stage processes so, even if the results are not directly applicable in all instances, the qualitative principles will apply.

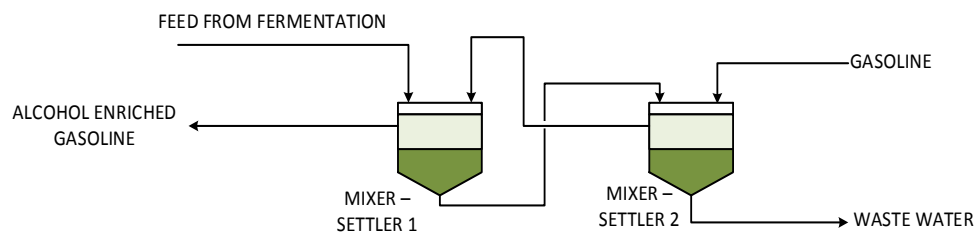


Figure 2. Sketch of the flowsheet used in this study.

We have decided to study three different scenarios classified by the following blending ratios, 1:9, 1:19 and 1:49. The blending ratio states the number of volume units of gasoline blended with one unit of alcohol. The reason to have chosen these three values is that if the recovery of alcohol is 100% or close, then, the volumetric percentages of alcohols in the final product will be 10, 5 and 2 vol % respectively. Each of these compositions represents the target in a particular context, so these values represent real-world process targets.

The way to approach the simulations has been: 1 m³/h of anhydrous alcohol (pure or mixture) is fed to the mixer-settler unit 1 (see Figure 2) in ASPEN. For each of the three blending ratios, we obtained the volumetric flow rate of isooctane to be fed to the unit 2 as shown in Figure 2. Lastly, we fix for each situation under study the volumetric flow rate of water accompanying the alcohol, i.e., we sweep the value of the volumetric flow rate of the water to be fed so that its volumetric percentage in the feed from fermentation stream progresses from 0 to 95%. The alcohol in the

water can be just a single one or a mixture of ethanol/butanol. To state the proportion of individual alcohols in water we refer to them as if no water were present, i.e., we refer to them as if they are a binary mixture and consequently the addition of the two volumetric fractions of alcohols is always equal to 1. Therefore, a volumetric fraction of ethanol equal to 0 (shown in our results as $\text{etOH} = 0$) mean that the $1 \text{ m}^3/\text{h}$ of alcohols is pure butanol; on the contrary, a volumetric fraction of $\text{etOH} = 1$ means that the $1 \text{ m}^3/\text{h}$ is pure ethanol. From the results obtained, the recovery of the alcohols were calculated and then plotted. Recovery is the fraction of alcohol/s from the feed aqueous stream that end up in the fuel phase.

Results and Discussion

After collecting abundant results from various scenarios, three graphs are generated, one for each blending ratio studied. These figures show the recovery of alcohols from different feed mixtures of water, ethanol, and butanol when subjected to two-stage direct blending with gasoline. A single line on the graph is produced by computing the recovery from varying the volume of water whilst keeping alcohol flowrates constant. The complete graphical series is generated by varying the ratios of pure ethanol and pure butanol and computing the recoveries. A movement along a single curve in the direction of decreasing amount of water may be interpreted as a process that dehydrates alcohols.

The analysis of the results shown in Figure 3, Figure 4 and Figure 5 generated from the simulation discloses very important information of this process. Firstly, direct blending of fermentation products with low concentration of alcohols (high concentration of water or right end of any of the three figures) does not offer a high alcohol recovery for any of the three blending ratios. Although feasible, the recoveries are so low that probably are not enough to make the process economically worthwhile. However, blending higher alcohol content mixtures into gasoline (left end of any of the three figures) does yield a gasoline phase with high recoveries of alcohol/s in it.

These three figures clearly confirm the postulate that butanol yields more favourable recoveries to gasoline pre-blending than ethanol does, i.e., the ethanol-only curve (etOH = 1) only achieves near-complete recovery for very high feed concentrations of ethanol, whereas, the butanol-only curve (etOH = 0) shows near-complete recovery even with a dilute butanol concentrations.

It is also relevant to observe how the recovery is influenced by blending ratios. As expected, the higher the blending ratio (higher amount of gasoline), the better the recovery of alcohols as illustrated by comparing Figure 3, Figure 4 and Figure 5. The three graphs follow a similar trend of recovery, nevertheless, with an increase in blending ratio, the steepness of the graphs grows and the lines appear closer together.

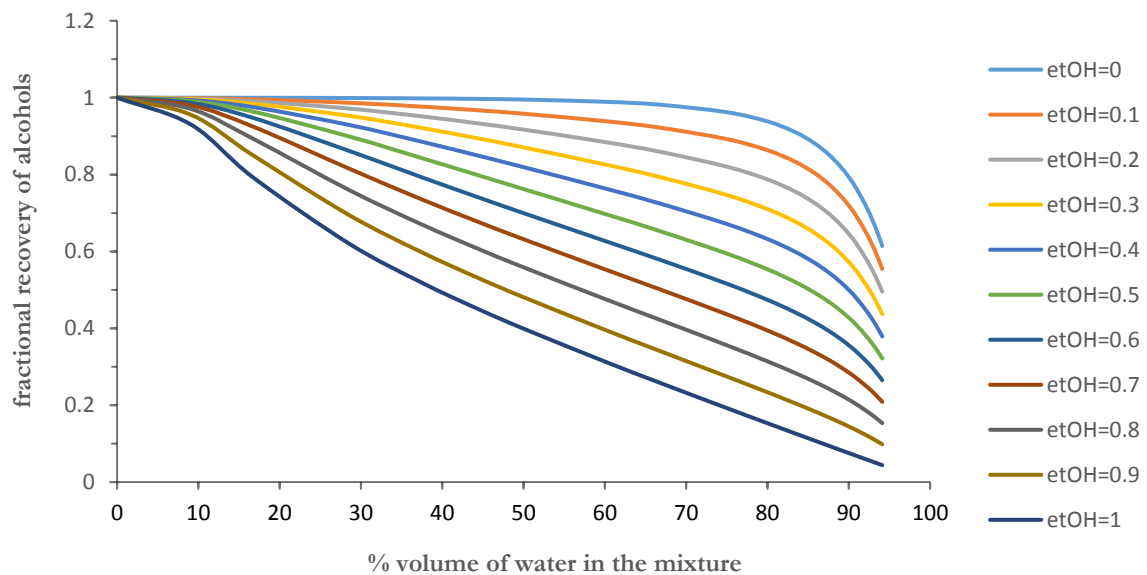


Figure 3. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a feed mixture of butanol, ethanol and water using gasoline at a blending ratio of 1:9. The legend is such that the volume fraction of alcohols is unity, mathematically $etOH + buOH = 1$, therefore if, for example, $etOH=0.3$ then $buOH=0.7$.

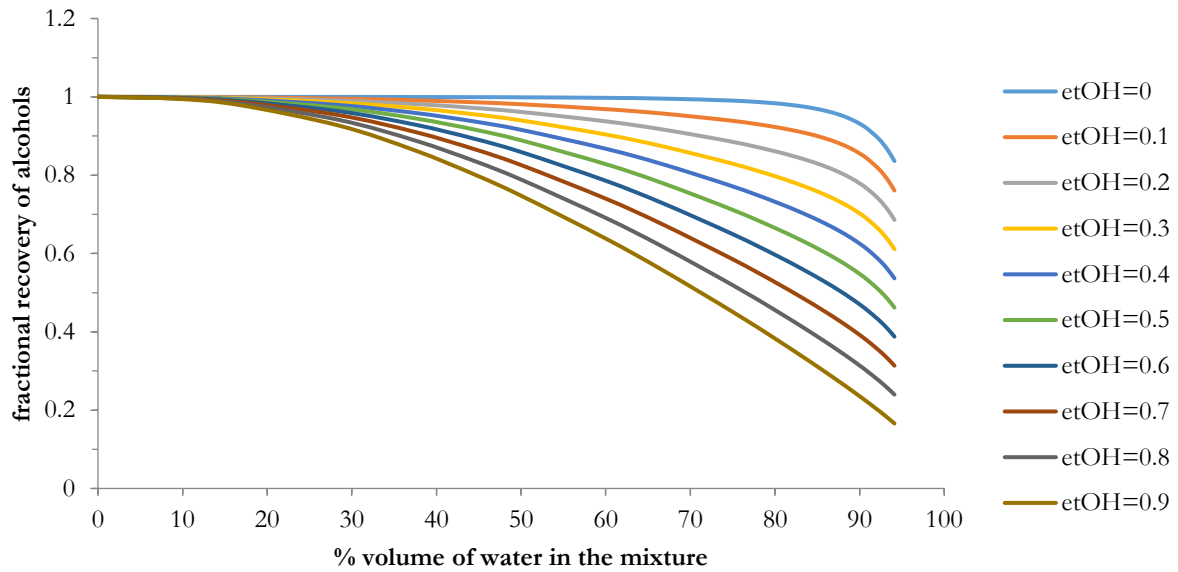


Figure 4. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a mixture of ethanol, butanol and water using gasoline at a blending ratio of 1:19. Refer to Figure 3 for description of legend.

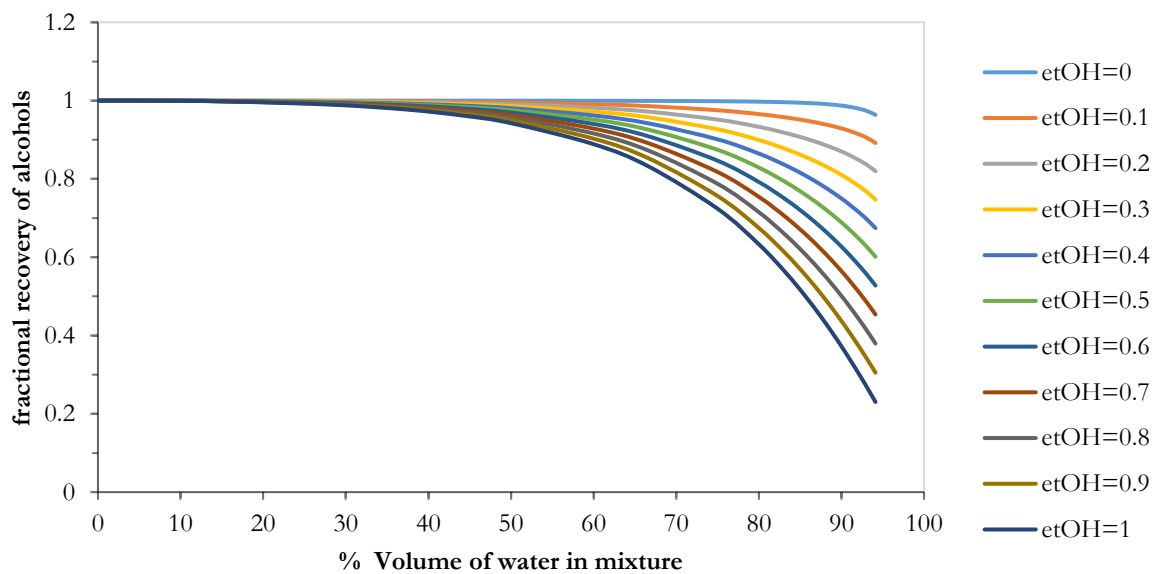


Figure 5. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a mixture of ethanol, butanol and water using gasoline at a blending ratio of 1:49. Refer to Figure 3 for description of legend.

From the data obtained, it is also possible to obtain the recovery of only ethanol, i.e., ethanol present in the gasoline after blending divided by the ethanol present in the water feed stream.

Figure 6 shows, for a water content of 50 vol % in the aqueous feed, how the recovery of ethanol changes with the butanol volume fraction, for the three blending ratios under study. In other words, it shows how the recovery of ethanol specifically is influenced by the presence of butanol. It can be seen that increasing butanol results in better ethanol recovery, so it can be concluded that butanol acts to preferentially draw ethanol into the fuel phase.

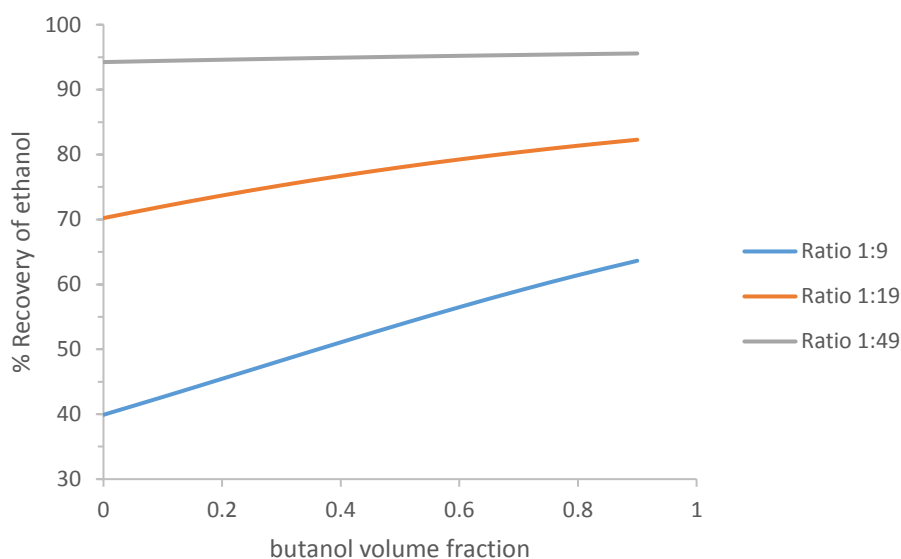


Figure 6. The trend of recovery of ethanol as a function of butanol volume fraction for a stream comprising of 50% water by volume. Refer to Figure 3 for description of butanol volume fraction.

Butanol has several preferable properties as a fuel molecule when compared to ethanol, solving many operational issues associated with ethanol.⁷ However, butanol has proven more costly to produce because of lower product yield resulting in higher feedstock cost, and lower titers resulting in higher energy for complete separation. However, it is apparent from Figures 3 to 5 that this latter constraint becomes less of a concern once gasoline pre-blending processes are considered instead of distillation; even fairly dilute mixtures of butanol achieve high recovery regardless of blending ratio, suggesting that butanol can be easily and efficiently recovered using these processes making unnecessary the purification step by distillation.

Previous research showed that the energy efficiency of ethanol recovery can be significantly improved by gasoline pre-blending.¹⁵ Butanol is more soluble in petrol than ethanol is, and less soluble in water. This suggests that gasoline pre-blending is likely to offer even larger improvements in efficiency for butanol than they do for ethanol. Moreover, the plots demonstrate that using some mixture of butanol and the cheaper ethanol opens up a broad optimization space for finding economical processes. It has been postulated by Stacey¹⁸ that sequential fermentation of butanol and ethanol in the same fermentation broth could result in higher overall alcohol concentrations, resulting in a mixture ideally suited for gasoline pre-blending with minimal separation.

It is readily apparent how one can use this set of Figure 3, Figure 4 and Figure 5 to evaluate a particular gasoline pre-blending process. However, their utility can be extended further as will be illustrated in the next section, where we will demonstrate how to use them as a tool for flowsheeting and process design. These figures will allow us to quickly read off the expected recoveries after a pre-blending process. If the recovery is low, it will be convenient to use a separation method to eliminate water in order to concentrate the alcohol content in the feed mixture. Doing so guarantees that most of the alcohol from the feed stream will be transferred to the fuel phase, otherwise a significant part of the alcohol remains in the water phase and is lost. If the recovery is high, then the preblending can be applied straight away. The treatment or not of the aqueous mixture before blending it with gasoline will depend on the value of the recovery. The particular value where the recovery can be considered high or low must be determined by the designer who can evaluate the economics associated. In summary, a theoretical mixture analysis gives important information regarding the necessity or lack thereof of pre-treatment before preblending.

Another way that these figures can be useful is the following: A stream that has low recovery on the figures, for example a dilute ethanol and water stream, may have its recovery enhanced by

simply mixing it with another stream that has a higher recovery, like a butanol and water stream. The designer can easily calculate the new ethanol/butanol/water concentrations, and refer to in Figure 3, Figure 4 and Figure 5, to ascertain the expected recovery of the resultant stream. Generally, if the stream generated by this combination has a composition whose recovery lies above that of the target stream, then preparing that mixture is a favourable option.

A final consideration is the following: flowsheets for chemical separation systems are designed to show a number of feasible alternative sequences that take certain criteria, for example economics, energy-consumption or physical properties, into account. An optimal flowsheet should address the economic and physical feasibility of the separation techniques employed, so that the best sequence for a given process can be determined. The research work reported in this article focuses on the physical feasibility of the separation systems, and does not dwell on the economic aspects; however reducing energy consumption in biofuels production goes a long way to reducing operation costs.

Case Study: ABE Fermentation products

Let us consider a mixture from the biological industrial production of butanol by ABE fermentation of biomass whereby the products are a dilute aqueous mixture of acetone, ethanol and butanol and other trace products.¹⁹ Fermentation broths are sent to beer strippers (C1) that gets rid of 99% of water and 100% biomass as shown in Figure 7. The remaining distillate is fed to an acetone recovery column (C2), which recovers 99.9% of acetone.

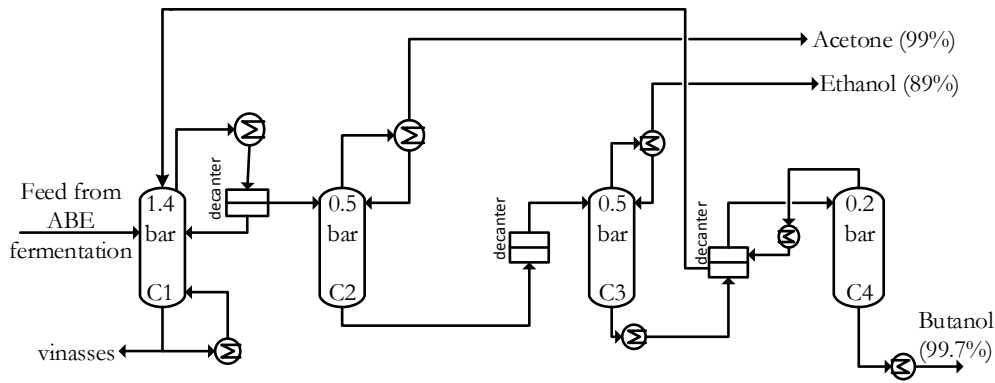


Figure 7. Process flow diagram for producing pure butanol and pure ethanol from ABE fermentation using four distillation columns. All the concentrations depicted here are in wt%.¹⁹

The resultant bottoms from C2 have a chemical composition reported by these authors is shown in Table 1 where for the sake of simplicity, we have ignored the infinitesimal ‘impurities’ in the calculation of the last column.

Table 1. Bottom stream from the acetone recovery column (C2 in Figure 7) from ABE fermentation according to Van Der Merwe.²⁰ The trace compounds have been ignored for the calculation of the last column.

Species	Bottom stream of column C2 (kg/h)	Bottom stream (vol%)
H ₂ O	10967.54	35.3
Butanol	15350.43	61,0
Ethanol	915.53	3.7
Acetone	5.69	-
Butyric Acid	1.77	-
Acetic Acid	3.81	-

CO ₂	0.00	-
H ₂	0.00	-

Referring to Figures 3, 4 and 5 and by extrapolation one can see that little or no further separation of water is necessary for this stream; near-complete recovery is achieved for all three blending ratios. Consequently, one can conclude already that it is possible to achieve this butanol recovery without the use of the final separation steps i.e. columns C3 and C4, that would ordinarily be required to purify the two alcohols. With conventional distillation, at least two further columns would be needed from this point.

Our intention now is to check if direct gasoline pre-blending is suitable for this stream so that the product final composition of gasoline stream contains 2 vol % of alcohols, in line with the South African market demands.²¹ The volume percentage of the bottoms of the acetone recovery column, neglecting minority compounds is 35.3% water, 61.0% butanol and 3.7% ethanol. Since we are aiming for a 2 vol% final mixture, Figure 5 will be used. Before reading off the recovery, we need to choose a particular line. To do that we need to previously calculate the volume fraction of a binary mixture butanol/ethanol. For this particular case it will be etOH = 0.06 and butOH = 0.94. Reading off (by extrapolation) the recovery of alcohols stands at more than 99% and therefore no pre-treatment to concentrate alcohols and eliminate water from the feed stream is necessary.

The exact numerical values of the results after blending and separating the phases for this particular case cannot be read from Figure 5 therefore, they were obtained with ASPEN Plus program and are shown in Figure 8.

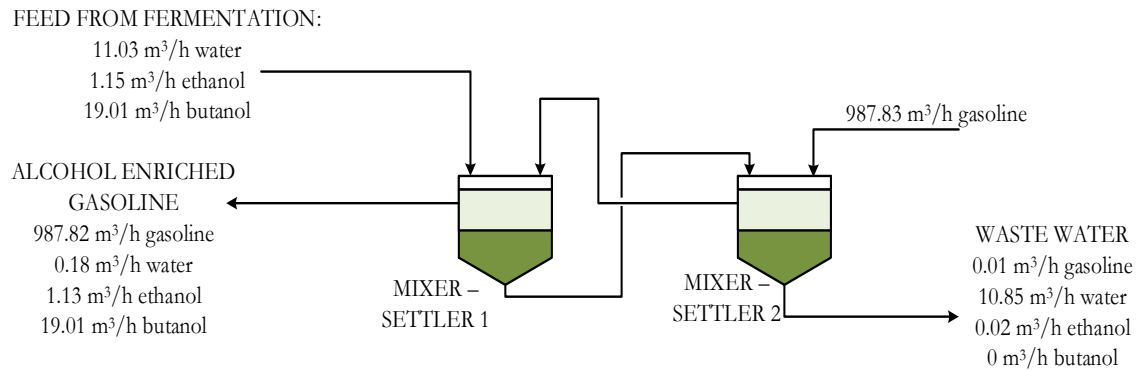


Figure 8. Results of an ASPEN simulation of a two-stage gasoline blending process of the bottom stream from the acetone recovery column (C2 in Figure 7) with gasoline for with a blending ratio of 1:49.

The total amount of alcohols in the biofuels adds up to 2 vol % as stipulated by the South African legislation and the result shows that the direct blending process is highly possible for this market. Water makes up just 0.02 vol % of the mixture and therefore satisfies the requirements of South African regulations. The loss of alcohols although is 0.18 vol % which is enough for environmental concern and ways to properly deal with that stream need to be looked at.

The same can be deduced with respect to the other two blending ratios (1:9 and 1:19) with similar order of magnitude of recoveries achieved. In conclusion, for purposes of obtaining blended fuel as a final product of ABE fermentation process, pre-blending butanol and ethanol directly into gasoline has been confirmed as feasible avoiding the need of two distillation columns. Indeed, in a typical ABE process aiming to obtain pure ethanol and butanol, two additional distillation columns would be required, with the capital and operating costs associated. Here, the same fuel end-product is achieved with considerably reduced expenditure of energy. According to Diaz and Tost¹⁹ a typical 4-distillation column configuration with these targets would consume 16.7MJ per litre of butanol produced, with 2.88MJ of that being used by the final two columns, which are here shown to be replaceable by a gasoline pre-blending step consuming negligible energy. Hence, this very simple modification of a conventional ABE process can result in energy savings of 17.2%. However, particular examination of Figure 5 shows that this process is over-performing, so to speak, because complete recovery of bio-alcohols could be achieved with a more dilute initial

mixture. In this particular case, the composition of this feed stream (bottom stream in Table 1) is dictated by the upstream process recovering the acetone and so it is not necessarily an option to modify the process by using a less strenuous separation process initially. On the other hand, it is possible to exploit this excess of separation capacity in another way; mixing a stream that has excess capacity to transfer to the fuel phase with a stream that is not able to effectively transfer across can serve to achieve the recovery of that second stream without additional separation.

Consider, for example, a 10 vol % ethanol mixture arising from fermentation. To use this stream directly in gasoline pre-blending results in recovery well below 40% (see Figure 5), not a feasible process. However, it was shown earlier in the paper that combining an ethanol-containing stream with a butanol-containing stream tends to improve the overall alcohol recovery in a synergistic manner. For instance, mixing this 10 vol % ethanol-water stream with a concentrated butanol-rich stream with concentration as that reported in Table 1 could result in near-complete recovery of alcohol from both streams. This possibility is investigated in Figure 9 whose process flow diagram is depicted in Figure 10, which shows that the recovery of ethanol can be achieved by mixing it with the butanol-rich stream in suitable proportions. Figure 9 contains 7 marks: 10:0, 8:2, 6:4, 4:6, 3:7, 2:8 and 0:10 referring to the ratio of butanol rich stream to the ethanol diluted stream. In Figure 9, we can observe a relevant outcome: a small ratio of butanol rich stream can vastly improve the recovery of ethanol. For instance, a diluted stream of 10 vol% of ethanol in water has a recovery in gasoline of less than 40%, but if we add a certain amount of butanol rich stream up to a ratio of 2:8 the recovery of ethanol improves to more than 85%.

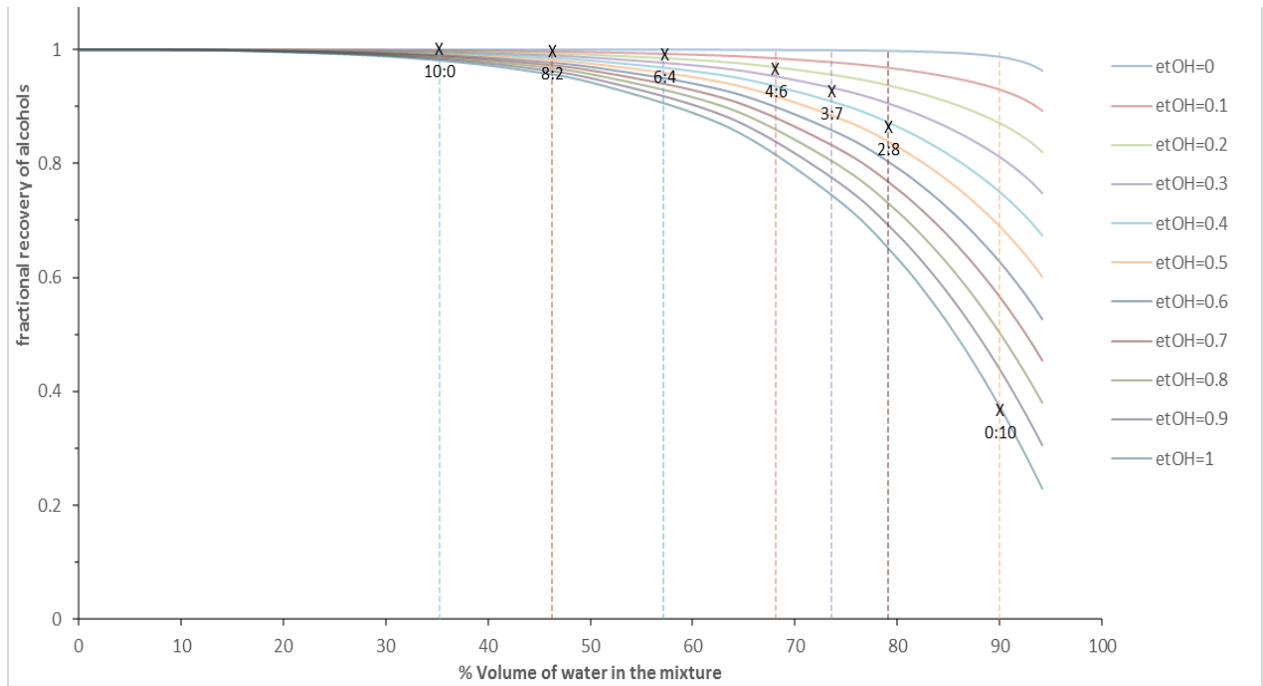


Figure 9. The effect of mixing a butanol rich stream (point 10:0) and an ethanol poor stream (point 0:10) on the fractional recovery of both alcohols in the fuel phase.

It is also apparent that near-complete recovery is achievable if the butanol-rich stream predominates, at a proportion of 8:2. The resulting process therefore achieves butanol recovery with 17.2% less separation energy than conventional processes while also achieving ethanol recovery with no separation energy whatsoever. To recover 1l of butanol along with 0.04l of ethanol would require 17.0MJ of energy but here, the only energy expenditure is that of the initial separation of butanol and hence, the total energy savings are now 19%.

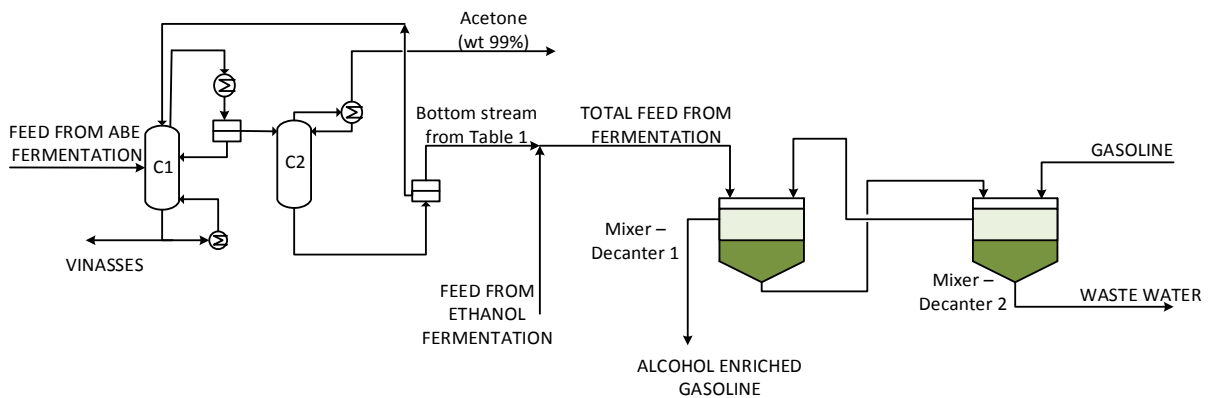


Figure 10: Mixing and subsequent preblending of ABE stream of water, ethanol and butanol and a stream from ethanol fermentation products.

Figure 10 is by no means a refined or optimized process. Instead, it simply takes streams that are present in existing processes and identifies opportunities to utilize them in gasoline pre-blending processes. The distillation columns that are included were designed and optimized for the goal of achieving pure products and not intended for gasoline pre-blending. That it has been possible to achieve energy savings by doing this is indicative firstly of the potential value of combining ethanol- and butanol-producing processes with gasoline pre-blending and, secondly, of the usefulness of these graphs to the process of synthesizing and evaluating such processes.

Conclusions

The graphs displayed in this paper offer a comprehensive summary of gasoline pre-blending processes utilizing both ethanol and butanol, offering a tool for predicting the performance of any process of this type. This approach enables a designer to compare processes from within a radically enlarged optimization space when compared to conventional processes.

It has been demonstrated that even dilute butanol mixtures offer excellent recovery, particularly at high blending ratios, where starting compositions as low as 10% butanol offer almost complete recovery. This suggests that with the benefits offered by gasoline pre-blending, butanol may prove to be more economical than ethanol in a direct comparison. However, it has also been found that the presence of butanol drastically improves the recovery of ethanol in a gasoline pre-blending process. Hence, incorporating both alcohols offers certain synergies taking advantage of the easier production of ethanol coupled with the easier recovery of butanol.

A strong case can therefore be made in favour of both gasoline pre-blending and alcohol co-production. This is a broad class of processes offering many possibilities for process design and significant improvements in energy efficiency. It is not possible at this preliminary stage of analysis to claim that a specific process is optimal; the relative costs and values of feedstocks and products will dictate context-specific solutions. This paper has therefore aimed at offering a tool to enable rapid design in any context despite the complexities posed by the expanded optimization space. A

case studies have been presented, firstly to illustrate the design methodology that has been developed and to present promising flowsheets that offer improvements on existing process.

It has been found that the final two distillation columns in a conventional ABE process can be replaced with a two-stage gasoline pre-blending step, achieving almost complete recovery of alcohols without the separation energy involved in those distillation steps. The resulting process results in a fuel mixture containing both ethanol and butanol with drastically reduced separation energy compared to processes purifying either component.

It has also been shown that the presence of butanol results in drastically improved recovery of ethanol, suggesting that even if ethanol remains economically preferable, and some amount of butanol production could still offer economic advantages.

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Abstract

In the context of accelerating climate change, liquid biofuels have become an important source of sustainable energy. However, the energy inefficiency involved in the production of biofuels mitigates many of their benefits. Previous research has shown that gasoline pre-blending can drastically improve the efficiency of bioethanol production by discarding the erroneous assumption that a bio-alcohol must be fully purified before being blended into a fuel. This paper extends that concept into a far broader optimization space by modelling all possible gasoline pre-blending processes incorporating ethanol, butanol or both. It is found that butanol is highly suitable for gasoline pre-blending and that high recovery can be achieved even when starting with dilute concentrations. In addition, the presence of even small amounts of butanol are effective at drawing ethanol into the fuel phase and improving overall alcohol recovery. A graphical design methodology is presented allowing for rapid flowsheet development and performance prediction.

Introduction

At the forefront of addressing the question of sustainable development, among others, is the adaptation of renewable fuels to replace the traditional non-renewable ones. To qualify as a replacement, clearly, the essential properties of these two sources need at least to match. In the context of transportation fuels, these essential properties include – high power output, affordability, homogeneity of the fuel, safety, minimal modification to the current engine models, fast refilling or recharging. Renewable biofuels from various forms of biomass have a potential of approaching this criteria. Biomass fuels are fuels derived from the fermentation of carbohydrates and starches using various microorganisms. The sources of biomass are influenced by geographical and economic considerations and range from edible feedstock like sugarcane, beetroot and wheat to non-edible feedstock like rice stalks, sugarcane bagasse and wheat straw^{1,2}. Bioethanol is produced through anaerobic fermentation of biomass by microorganisms such as *Saccharomyces cerevisiae* and *Zymomonas mobilis* whilst biobutanol is produced from acetone, butanol and ethanol (ABE) fermentation of sugars using a family of *Clostridia* bacteria³⁻⁶. Butanol has a number of

advantages over ethanol in that it has a higher energy density, much less affinity for water and higher energy efficiency⁷. Another area of interest is the production of biofuels from algae^{2,8}.

The worldwide production of biofuels increased from 1 billion litres in 1981 to over 120 billion litres in 2014 and US Energy Information Administration predicts that figure to reach 200 billion litres by year 2020.⁹ This means biofuels have a role to play in the future. Bioethanol and bio-butanol (ethanol and butanol hereafter) are some of the biofuels in current use and are the object of our study. However, at present, neither are regarded as economically favourable, because of the cost and the energy consumption involved in growing and transporting biomass plus subsequent operating fermentation facilities. In general, if 50% of the combustion energy of a biofuel is expended on bioconversion and separation, then economics may not favour any commercial ventures.¹⁰ As an example, calculations based on a corn-to-ethanol production process show that 54% of the energy content per a gallon of ethanol is required to process (that is, purify) the fuel, and a further 24% is spent on growing the biomass, leaving just over 20% as a net gain.¹¹ This net energy value, however, is even questioned¹ and is subject to vigorous debate. We therefore need to find a way to optimise all the production stages to make biofuels commercially competitive.

The product of fermentation is a dilute aqueous solution of alcohol(s). However, water is undesirable in fuel mixtures owing to potential corrosive effects and engine malfunctions and therefore considerable effort is directed to elimination of water from fuel mixtures. The amount of water in biofuels should not exceed 0.3 wt % for the European Union context and 0.5 wt % for the US market.^{12,13} Distillation is often employed to recover the alcohols from dilute mixtures. While this technique offers high recovery rates, typically 99% of biofuels in the product stream, it has its handicaps. Firstly, distillation of fermentation broths involves evaporation of water, which has a high heat capacity value, making the process energy intensive. Moreover, the presence of azeotropes impedes attainment of fuel-grade dehydration specifications without introducing additional processes such as extractive distillation or pervaporation. These additional processes

further raise the cost of production and energy consumption. The overall energy requirements for attaining high purity alcohols from alcohol-water mixtures through distillation are a function of the initial feed and the particular processes used as shown by Vane 2008.⁷ This author shows in his figures 7 (for ethanol) and 8 (for 1-butanol) how the amount of energy required per unit of alcohol recovered increases as the concentration of the alcohol in the feed decreases. This shows that distillation is an area in which optimisation holds some potential. Alternative methods to distillation include gas stripping, pervaporation, adsorption, liquid-liquid extraction^{7,14} and these can help alleviate the issue of energy consumption in biofuels production.

A recent proposal by Stacey et al¹⁵ reduces the energy requirement to separate ethanol from water by making use of a liquid-liquid phase split to eliminate water without separation energy. These authors propose the use of the conventional separation method until the ethanol-water azeotrope is reached, this stream is then blended directly into gasoline which results spontaneously into two phases that can be easily separated in a two-stage counter-current liquid-liquid extraction. In this way, these authors avoid the final purification steps of ethanol distillation, which are energy intensive obtaining a viable fuel mixture with almost complete recovery of ethanol from water. This approach, termed direct gasoline pre-blending, has high recoveries and leads to energy savings of between 17% and 40% in comparison to distillation. The gasoline pre-blending processes presented thus far are limited in scope, focusing only at ethanol and only considering a narrow range of initial alcohol concentrations. The gasoline pre-blending method is therefore an attractive alternative method because it does not use separation energy. The usual route to fuel blending may be summarised in the following steps - fermentation of biomass using microorganisms to get fermentation broths, which is followed by processing of fermentation broths by filtration and distillation to get dehydrated alcohols and subsequently blending of alcohols with gasoline at pre-distributions sites.^{7,15}

Preblending is not limited to ethanol. Da Silva and Dos Santos¹⁶ show that gasoline pre-blending works for butanol obtained from fermentation as well. It will therefore be possible to use a three-component mixture (water-ethanol-butanol). This paper will evaluate gasoline pre-blending processes far more comprehensively than already demonstrated by Stacey et al¹⁵, i.e., considering all possible combinations of initial feed compositions (water-ethanol-butanol) mixtures to be blended with gasoline. The results shown in this paper will assist the design methodology for future distillation-preblending plants since we offer, in a compact manner, all possible direct pre-blending processes of aqueous ethanol and butanol mixtures that can be useful to rapidly evaluate the performance of the flowsheet in terms of alcohol recovery. Ultimately in this paper, is to present a methodology to check which fuel blends can be achieved that meet specific demands as dictated by regulations from any composition of ethanol, butanol and water.

Methodology

As stated before, the study of gasoline preblending with mixtures of water-ethanol-butanol with subsequent liquid-liquid separation will be developed here. To that end, we have used ASPEN PLUS V8.6® to model the liquid-liquid equilibrium behaviour of the mixture and used the parameters embedded in the software. These parameters are used for all modelling in this paper, along with an assumption of ambient conditions of 25°C and 1 atm pressure. We chose UNIQUAC (Universal Quasichemical) as the thermodynamic model because it is able to simulate liquid-liquid phase equilibria behaviour in non-ideal systems with partially soluble components. Data for gasoline, however, is absent in this simulation package and it was decided to opt for isooctane whose liquid-liquid equilibrium closely fits the behaviour of ethanol, water and gasoline.¹⁷

To better understand the concept of phase blending and splitting which is the foundation to this work, it would be very useful to have at our disposal the experimental quaternary liquid-liquid-equilibria (LLE) data corresponding to this system since they set the thermodynamic limitations

of phase blending and separation. Unfortunately and to the best of our knowledge these data have not been researched or published. Figure 1 shows the four sides of the tetrahedron for this system obtained through ASPEN and UNIQUAC at 25°C and 1 atm. In this figure we can easily see the miscibility of the six possible pairs: water/isooctane (immiscible), water/1-butanol (partially miscible), isooctane/1-butanol (completely miscible), water/ethanol (completely miscible), ethanol/isooctane (completely miscible), ethanol/1-butanol (completely miscible). In view of the equilibrium data shown in Figure 1, it seems reasonable to blend the product of fermentation (water with low concentration of alcohol) with gasoline so that after settling the gasoline is enriched with alcohols.

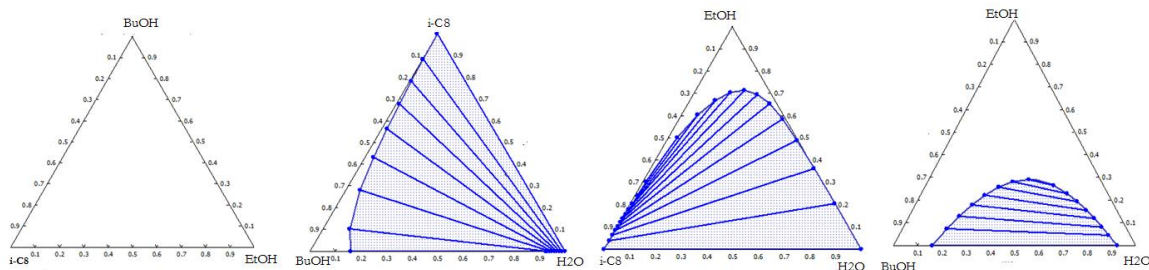


Figure 1. Four sides of the LLE tetrahedron obtained with ASPEN through UNIQUAC at 25°C and 1 atm.

1-BuOH = 1-butanol, EtOH = Ethanol, H₂O=water and i-C8 = isooctane.

Phase equilibrium of any system is a function not only of temperature and pressure but also of the purity of the species involved. One of the species in this quaternary system under study is gasoline, and given that its composition varies since different brands of gasoline have proprietary fuel additives and dyes, it is expected an influence in the phase equilibrium results. Therefore, the results shown in this paper must be considered to be qualitative descriptions rather than quantitative.

In this paper, all ASPEN simulations are conducted for a two-stage counter-current liquid–liquid extraction set-up as this was the preferred procedure for the ethanol blending in prior research (see Figure 2); hence, it provides an ideal basis of comparison.¹⁵ Multi-stage processes will tend to

exhibit the same trends as two-stage processes so, even if the results are not directly applicable in all instances, the qualitative principles will apply.

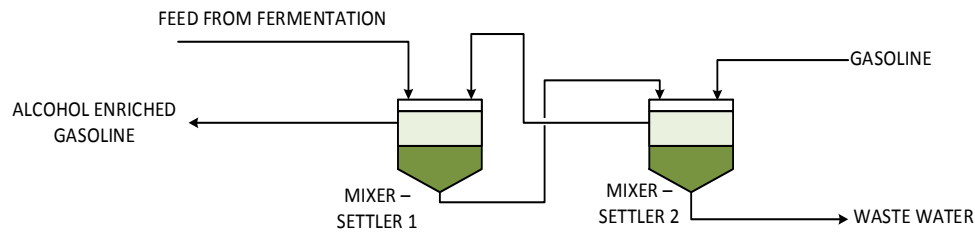


Figure 2. Sketch of the flowsheet used in this study.

We have decided to study three different scenarios classified by the following blending ratios, 1:9, 1:19 and 1:49. The blending ratio states the number of volume units of gasoline blended with one unit of alcohol. The reason to have chosen these three values is that if the recovery of alcohol is 100% or close, then, the volumetric percentages of alcohols in the final product will be 10, 5 and 2 vol % respectively. Each of these compositions represents the target in a particular context, so these values represent real-world process targets.

The way to approach the simulations has been: 1 m³/h of anhydrous alcohol (pure or mixture) is fed to the mixer-settler unit 1 (see Figure 2) in ASPEN. For each of the three blending ratios, we obtained the volumetric flow rate of isooctane to be fed to the unit 2 as shown in Figure 2. Lastly, we fix for each situation under study the volumetric flow rate of water accompanying the alcohol, i.e., we sweep the value of the volumetric flow rate of the water to be fed so that its volumetric percentage in the feed from fermentation stream progresses from 0 to 95%. The alcohol in the water can be just a single one or a mixture of ethanol/butanol. To state the proportion of individual alcohols in water we refer to them as if no water were present, i.e., we refer to them as if they are a binary mixture and consequently the addition of the two volumetric fractions of alcohols is always equal to 1. Therefore, a volumetric fraction of ethanol equal to 0 (shown in our results as etOH = 0) mean that the 1 m³/h of alcohols is pure butanol; on the contrary, a volumetric fraction

of $\text{etOH} = 1$ means that the $1 \text{ m}^3/\text{h}$ is pure ethanol. From the results obtained, the recovery of the alcohols were calculated and then plotted. Recovery is the fraction of alcohol/s from the feed aqueous stream that end up in the fuel phase.

Results and Discussion

After collecting abundant results from various scenarios, three graphs are generated, one for each blending ratio studied. These figures show the recovery of alcohols from different feed mixtures of water, ethanol, and butanol when subjected to two-stage direct blending with gasoline. A single line on the graph is produced by computing the recovery from varying the volume of water whilst keeping alcohol flowrates constant. The complete graphical series is generated by varying the ratios of pure ethanol and pure butanol and computing the recoveries. A movement along a single curve in the direction of decreasing amount of water may be interpreted as a process that dehydrates alcohols.

The analysis of the results shown in Figure 3, Figure 4 and Figure 5 generated from the simulation discloses very important information of this process. Firstly, direct blending of fermentation products with low concentration of alcohols (high concentration of water or right end of any of the three figures) does not offer a high alcohol recovery for any of the three blending ratios. Although feasible, the recoveries are so low that probably are not enough to make the process economically worthwhile. However, blending higher alcohol content mixtures into gasoline (left end of any of the three figures) does yield a gasoline phase with high recoveries of alcohol/s in it. These three figures clearly confirm the postulate that butanol yields more favourable recoveries to gasoline pre-blending than ethanol does, i.e., the ethanol-only curve ($\text{etOH} = 1$) only achieves near-complete recovery for very high feed concentrations of ethanol, whereas, the butanol-only curve ($\text{etOH} = 0$) shows near-complete recovery even with a dilute butanol concentrations.

It is also relevant to observe how the recovery is influenced by blending ratios. As expected, the higher the blending ratio (higher amount of gasoline), the better the recovery of alcohols as illustrated by comparing Figure 3, Figure 4 and Figure 5. The three graphs follow a similar trend of recovery, nevertheless, with an increase in blending ratio, the steepness of the graphs grows and the lines appear closer together.

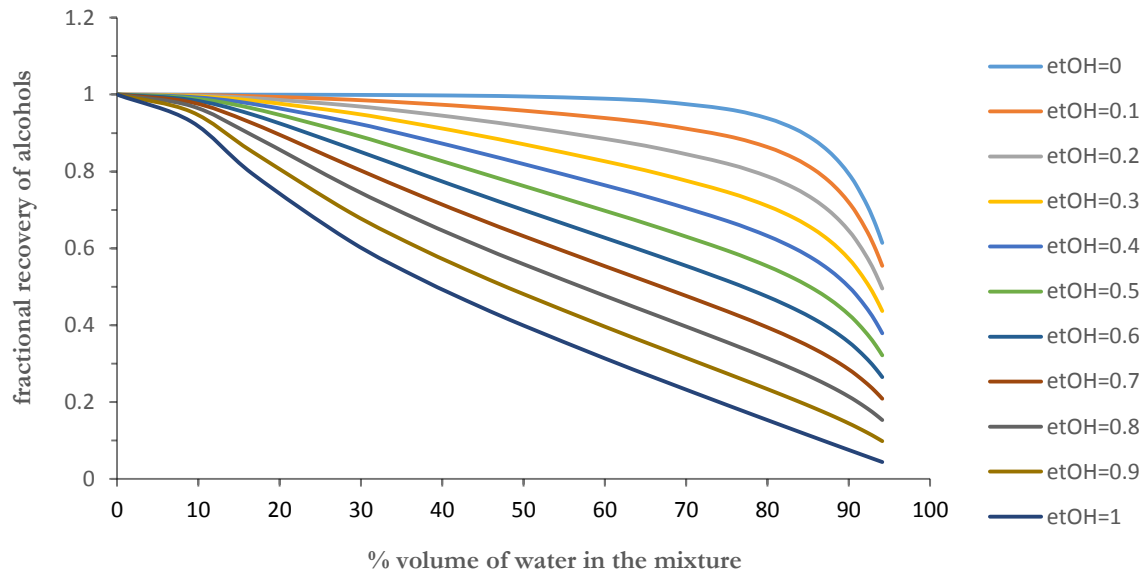


Figure 3. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a feed mixture of butanol, ethanol and water using gasoline at a blending ratio of 1:9. The legend is such that the volume fraction of alcohols is unity, mathematically $etOH + buOH = 1$, therefore if, for example, $etOH=0.3$ then $buOH=0.7$.

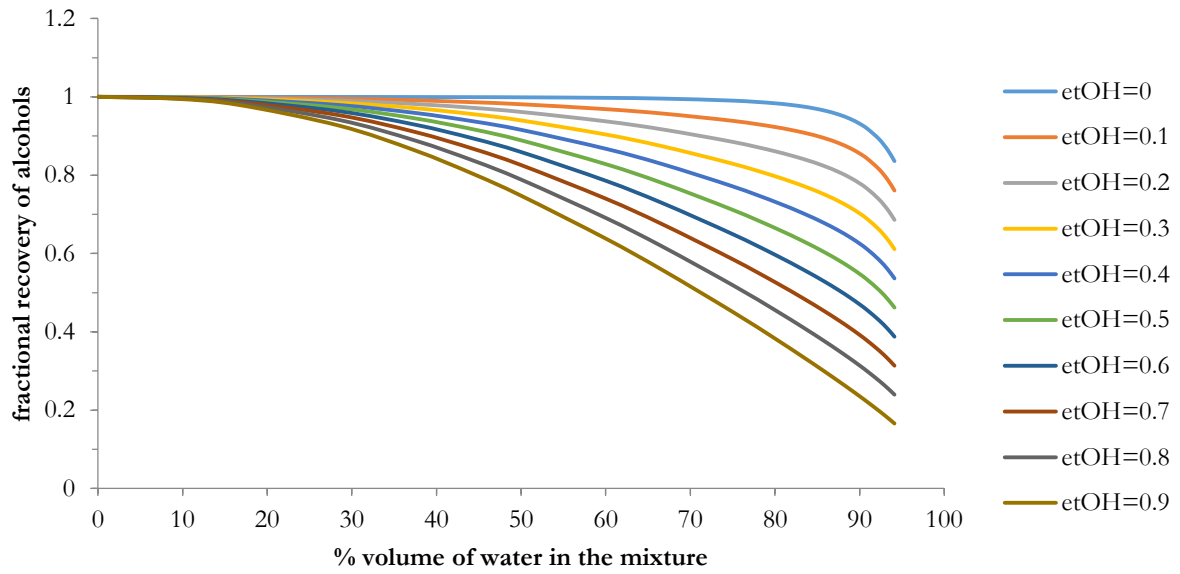


Figure 4. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a mixture of ethanol, butanol and water using gasoline at a blending ratio of 1:19. Refer to Figure 3 for description of legend.

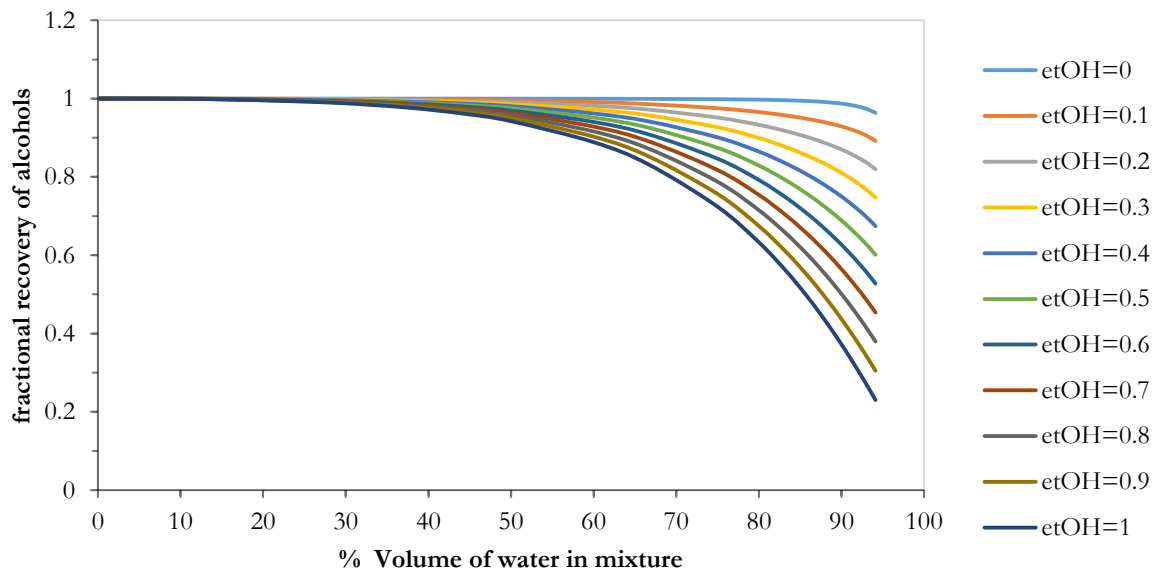


Figure 5. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a mixture of ethanol, butanol and water using gasoline at a blending ratio of 1:49. Refer to Figure 3 for description of legend.

From the data obtained, it is also possible to obtain the recovery of only ethanol, i.e., ethanol present in the gasoline after blending divided by the ethanol present in the water feed stream.

Figure 6 shows, for a water content of 50 vol % in the aqueous feed, how the recovery of ethanol changes with the butanol volume fraction, for the three blending ratios under study. In other words, it shows how the recovery of ethanol specifically is influenced by the presence of butanol. It can be seen that increasing butanol results in better ethanol recovery, so it can be concluded that butanol acts to preferentially draw ethanol into the fuel phase.

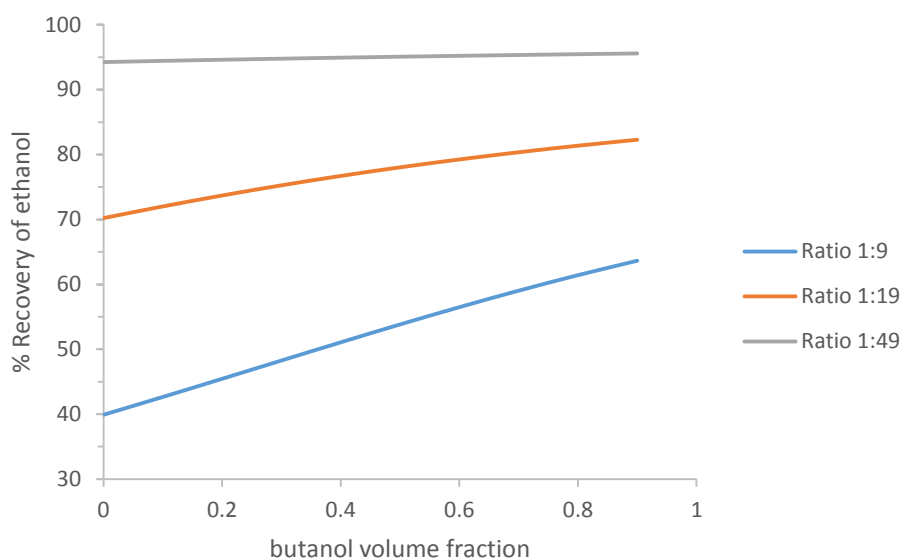


Figure 6. The trend of recovery of ethanol as a function of butanol volume fraction for a stream comprising of 50% water by volume. Refer to Figure 3 for description of butanol volume fraction.

Butanol has several preferable properties as a fuel molecule when compared to ethanol, solving many operational issues associated with ethanol.⁷ However, butanol has proven more costly to produce because of lower product yield resulting in higher feedstock cost, and lower titers resulting in higher energy for complete separation. However, it is apparent from Figures 3 to 5 that this latter constraint becomes less of a concern once gasoline pre-blending processes are considered instead of distillation; even fairly dilute mixtures of butanol achieve high recovery regardless of blending ratio, suggesting that butanol can be easily and efficiently recovered using these processes making unnecessary the purification step by distillation.

Previous research showed that the energy efficiency of ethanol recovery can be significantly improved by gasoline pre-blending.¹⁵ Butanol is more soluble in petrol than ethanol is, and less soluble in water. This suggests that gasoline pre-blending is likely to offer even larger improvements in efficiency for butanol than they do for ethanol. Moreover, the plots demonstrate that using some mixture of butanol and the cheaper ethanol opens up a broad optimization space for finding economical processes. It has been postulated by Stacey¹⁸ that sequential fermentation of butanol and ethanol in the same fermentation broth could result in higher overall alcohol concentrations, resulting in a mixture ideally suited for gasoline pre-blending with minimal separation.

It is readily apparent how one can use this set of Figure 3, Figure 4 and Figure 5 to evaluate a particular gasoline pre-blending process. However, their utility can be extended further as will be illustrated in the next section, where we will demonstrate how to use them as a tool for flowsheeting and process design. These figures will allow us to quickly read off the expected recoveries after a pre-blending process. If the recovery is low, it will be convenient to use a separation method to eliminate water in order to concentrate the alcohol content in the feed mixture. Doing so guarantees that most of the alcohol from the feed stream will be transferred to the fuel phase, otherwise a significant part of the alcohol remains in the water phase and is lost. If the recovery is high, then the preblending can be applied straight away. The treatment or not of the aqueous mixture before blending it with gasoline will depend on the value of the recovery. The particular value where the recovery can be considered high or low must be determined by the designer who can evaluate the economics associated. In summary, a theoretical mixture analysis gives important information regarding the necessity or lack thereof of pre-treatment before preblending.

Another way that these figures can be useful is the following: A stream that has low recovery on the figures, for example a dilute ethanol and water stream, may have its recovery enhanced by

simply mixing it with another stream that has a higher recovery, like a butanol and water stream. The designer can easily calculate the new ethanol/butanol/water concentrations, and refer to in Figure 3, Figure 4 and Figure 5, to ascertain the expected recovery of the resultant stream. Generally, if the stream generated by this combination has a composition whose recovery lies above that of the target stream, then preparing that mixture is a favourable option.

A final consideration is the following: flowsheets for chemical separation systems are designed to show a number of feasible alternative sequences that take certain criteria, for example economics, energy-consumption or physical properties, into account. An optimal flowsheet should address the economic and physical feasibility of the separation techniques employed, so that the best sequence for a given process can be determined. The research work reported in this article focuses on the physical feasibility of the separation systems, and does not dwell on the economic aspects; however reducing energy consumption in biofuels production goes a long way to reducing operation costs.

Case Study: ABE Fermentation products

Let us consider a mixture from the biological industrial production of butanol by ABE fermentation of biomass whereby the products are a dilute aqueous mixture of acetone, ethanol and butanol and other trace products.¹⁹ Fermentation broths are sent to beer strippers (C1) that gets rid of 99% of water and 100% biomass as shown in Figure 7. The remaining distillate is fed to an acetone recovery column (C2), which recovers 99.9% of acetone.

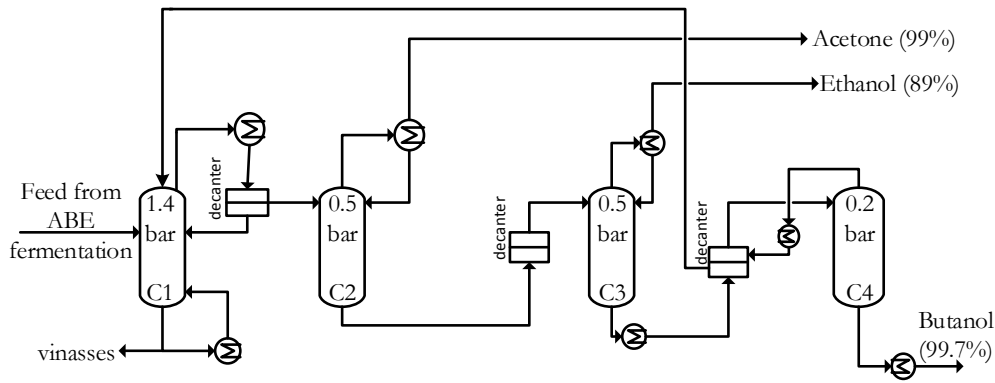


Figure 7. Process flow diagram for producing pure butanol and pure ethanol from ABE fermentation using four distillation columns. All the concentrations depicted here are in wt%.¹⁹

The resultant bottoms from C2 have a chemical composition reported by these authors is shown in Table 1 where for the sake of simplicity, we have ignored the infinitesimal ‘impurities’ in the calculation of the last column.

Table 1. Bottom stream from the acetone recovery column (C2 in Figure 7) from ABE fermentation according to Van Der Merwe.²⁰ The trace compounds have been ignored for the calculation of the last column.

Species	Bottom stream of column C2 (kg/h)	Bottom stream (vol%)
H ₂ O	10967.54	35.3
Butanol	15350.43	61,0
Ethanol	915.53	3.7
Acetone	5.69	-
Butyric Acid	1.77	-
Acetic Acid	3.81	-

CO ₂	0.00	-
H ₂	0.00	-

Referring to Figures 3, 4 and 5 and by extrapolation one can see that little or no further separation of water is necessary for this stream; near-complete recovery is achieved for all three blending ratios. Consequently, one can conclude already that it is possible to achieve this butanol recovery without the use of the final separation steps i.e. columns C3 and C4, that would ordinarily be required to purify the two alcohols. With conventional distillation, at least two further columns would be needed from this point.

Our intention now is to check if direct gasoline pre-blending is suitable for this stream so that the product final composition of gasoline stream contains 2 vol % of alcohols, in line with the South African market demands.²¹ The volume percentage of the bottoms of the acetone recovery column, neglecting minority compounds is 35.3% water, 61.0% butanol and 3.7% ethanol. Since we are aiming for a 2 vol% final mixture, Figure 5 will be used. Before reading off the recovery, we need to choose a particular line. To do that we need to previously calculate the volume fraction of a binary mixture butanol/ethanol. For this particular case it will be etOH = 0.06 and butOH = 0.94. Reading off (by extrapolation) the recovery of alcohols stands at more than 99% and therefore no pre-treatment to concentrate alcohols and eliminate water from the feed stream is necessary.

The exact numerical values of the results after blending and separating the phases for this particular case cannot be read from Figure 5 therefore, they were obtained with ASPEN Plus program and are shown in Figure 8.

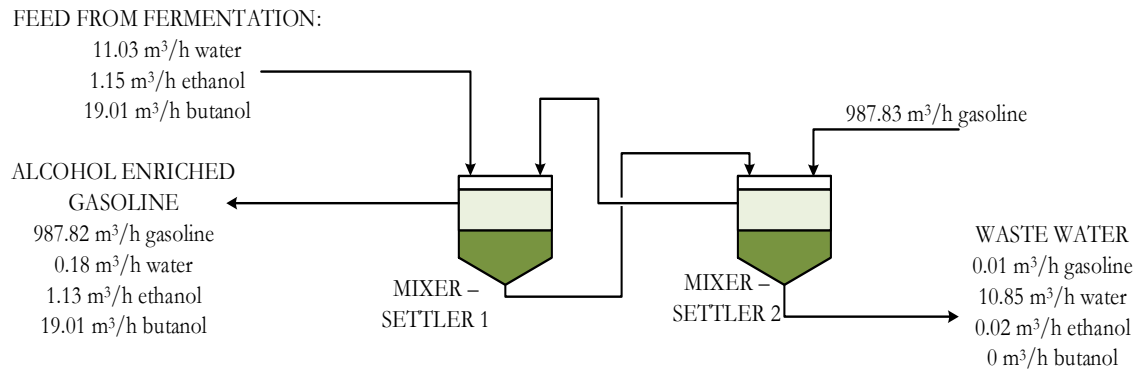


Figure 8. Results of an ASPEN simulation of a two-stage gasoline blending process of the bottom stream from the acetone recovery column (C2 in Figure 7) with gasoline for with a blending ratio of 1:49.

The total amount of alcohols in the biofuels adds up to 2 vol % as stipulated by the South African legislation and the result shows that the direct blending process is highly possible for this market. Water makes up just 0.02 vol % of the mixture and therefore satisfies the requirements of South African regulations. The loss of alcohols although is 0.18 vol % which is enough for environmental concern and ways to properly deal with that stream need to be looked at.

The same can be deduced with respect to the other two blending ratios (1:9 and 1:19) with similar order of magnitude of recoveries achieved. In conclusion, for purposes of obtaining blended fuel as a final product of ABE fermentation process, pre-blending butanol and ethanol directly into gasoline has been confirmed as feasible avoiding the need of two distillation columns. Indeed, in a typical ABE process aiming to obtain pure ethanol and butanol, two additional distillation columns would be required, with the capital and operating costs associated. Here, the same fuel end-product is achieved with considerably reduced expenditure of energy. According to Diaz and Tost¹⁹ a typical 4-distillation column configuration with these targets would consume 16.7MJ per litre of butanol produced, with 2.88MJ of that being used by the final two columns, which are here shown to be replaceable by a gasoline pre-blending step consuming negligible energy. Hence, this very simple modification of a conventional ABE process can result in energy savings of 17.2%. However, particular examination of Figure 5 shows that this process is over-performing, so to

speak, because complete recovery of bio-alcohols could be achieved with a more dilute initial mixture. In this particular case, the composition of this feed stream (bottom stream in Table 1) is dictated by the upstream process recovering the acetone and so it is not necessarily an option to modify the process by using a less strenuous separation process initially. On the other hand, it is possible to exploit this excess of separation capacity in another way; mixing a stream that has excess capacity to transfer to the fuel phase with a stream that is not able to effectively transfer across can serve to achieve the recovery of that second stream without additional separation.

Consider, for example, a 10 vol % ethanol mixture arising from fermentation. To use this stream directly in gasoline pre-blending results in recovery well below 40% (see Figure 5), not a feasible process. However, it was shown earlier in the paper that combining an ethanol-containing stream with a butanol-containing stream tends to improve the overall alcohol recovery in a synergistic manner. For instance, mixing this 10 vol % ethanol-water stream with a concentrated butanol-rich stream with concentration as that reported in Table 1 could result in near-complete recovery of alcohol from both streams. This possibility is investigated in Figure 9 whose process flow diagram is depicted in Figure 10, which shows that the recovery of ethanol can be achieved by mixing it with the butanol-rich stream in suitable proportions. Figure 9 contains 7 marks: 10:0, 8:2, 6:4, 4:6, 3:7, 2:8 and 0:10 referring to the ratio of butanol rich stream to the ethanol diluted stream. In Figure 9, we can observe a relevant outcome: a small ratio of butanol rich stream can vastly improve the recovery of ethanol. For instance, a diluted stream of 10 vol% of ethanol in water has a recovery in gasoline of less than 40%, but if we add a certain amount of butanol rich stream up to a ratio of 2:8 the recovery of ethanol improves to more than 85%.

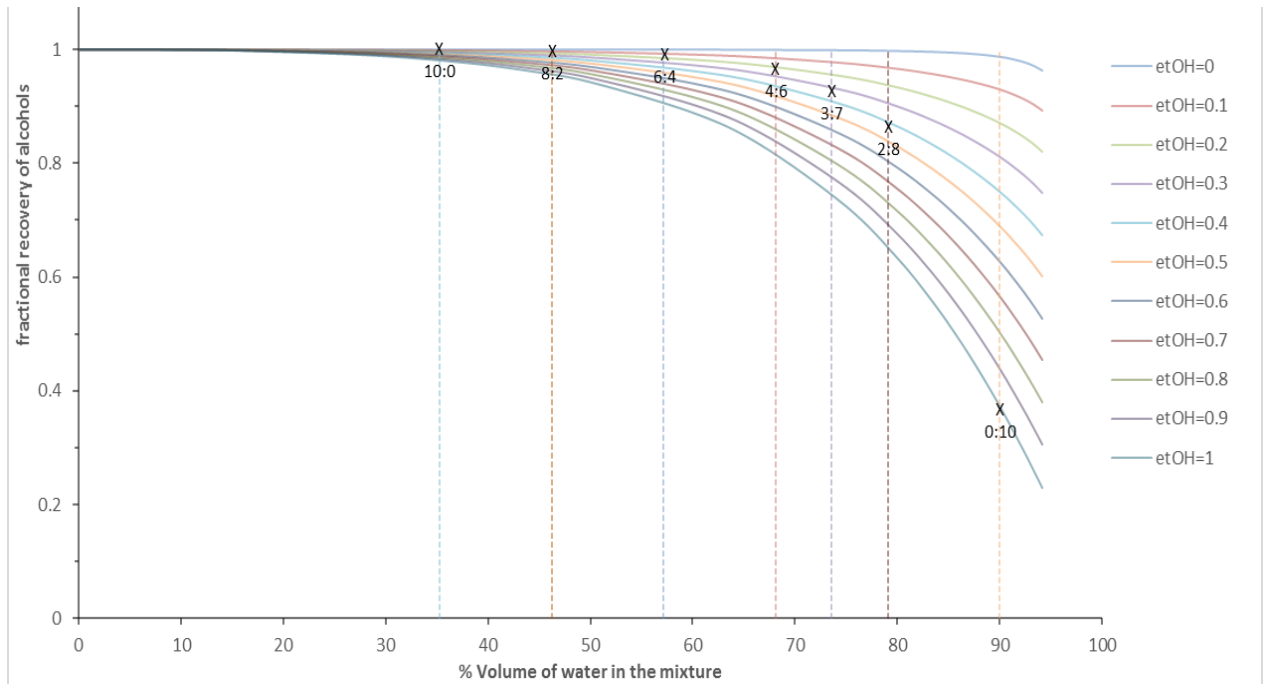


Figure 9. The effect of mixing a butanol rich stream (point 10:0) and an ethanol poor stream (point 0:10) on the fractional recovery of both alcohols in the fuel phase.

It is also apparent that near-complete recovery is achievable if the butanol-rich stream predominates, at a proportion of 8:2. The resulting process therefore achieves butanol recovery with 17.2% less separation energy than conventional processes while also achieving ethanol recovery with no separation energy whatsoever. To recover 1l of butanol along with 0.04l of ethanol would require 17.0MJ of energy but here, the only energy expenditure is that of the initial separation of butanol and hence, the total energy savings are now 19%.

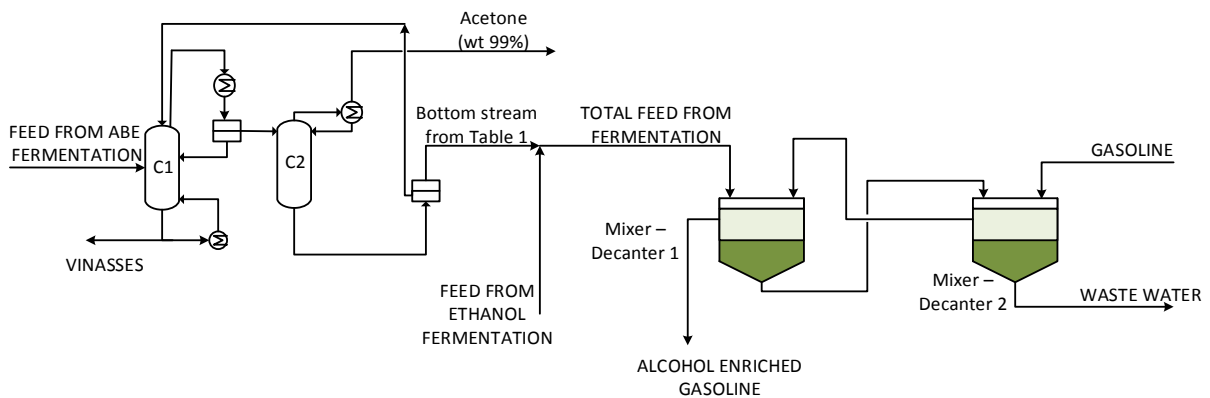


Figure 10: Mixing and subsequent preblending of ABE stream of water, ethanol and butanol and a stream from ethanol fermentation products.

Figure 10 is by no means a refined or optimized process. Instead, it simply takes streams that are present in existing processes and identifies opportunities to utilize them in gasoline pre-blending processes. The distillation columns that are included were designed and optimized for the goal of achieving pure products and not intended for gasoline pre-blending. That it has been possible to achieve energy savings by doing this is indicative firstly of the potential value of combining ethanol- and butanol-producing processes with gasoline pre-blending and, secondly, of the usefulness of these graphs to the process of synthesizing and evaluating such processes.

Conclusions

The graphs displayed in this paper offer a comprehensive summary of gasoline pre-blending processes utilizing both ethanol and butanol, offering a tool for predicting the performance of any process of this type. This approach enables a designer to compare processes from within a radically enlarged optimization space when compared to conventional processes.

It has been demonstrated that even dilute butanol mixtures offer excellent recovery, particularly at high blending ratios, where starting compositions as low as 10% butanol offer almost complete recovery. This suggests that with the benefits offered by gasoline pre-blending, butanol may prove to be more economical than ethanol in a direct comparison. However, it has also been found that the presence of butanol drastically improves the recovery of ethanol in a gasoline pre-blending process. Hence, incorporating both alcohols offers certain synergies taking advantage of the easier production of ethanol coupled with the easier recovery of butanol.

A strong case can therefore be made in favour of both gasoline pre-blending and alcohol co-production. This is a broad class of processes offering many possibilities for process design and significant improvements in energy efficiency. It is not possible at this preliminary stage of analysis to claim that a specific process is optimal; the relative costs and values of feedstocks and products

will dictate context-specific solutions. This paper has therefore aimed at offering a tool to enable rapid design in any context despite the complexities posed by the expanded optimization space. A case studies have been presented, firstly to illustrate the design methodology that has been developed and to present promising flowsheets that offer improvements on existing process.

It has been found that the final two distillation columns in a conventional ABE process can be replaced with a two-stage gasoline pre-blending step, achieving almost complete recovery of alcohols without the separation energy involved in those distillation steps. The resulting process results in a fuel mixture containing both ethanol and butanol with drastically reduced separation energy compared to processes purifying either component.

It has also been shown that the presence of butanol results in drastically improved recovery of ethanol, suggesting that even if ethanol remains economically preferable, and some amount of butanol production could still offer economic advantages.

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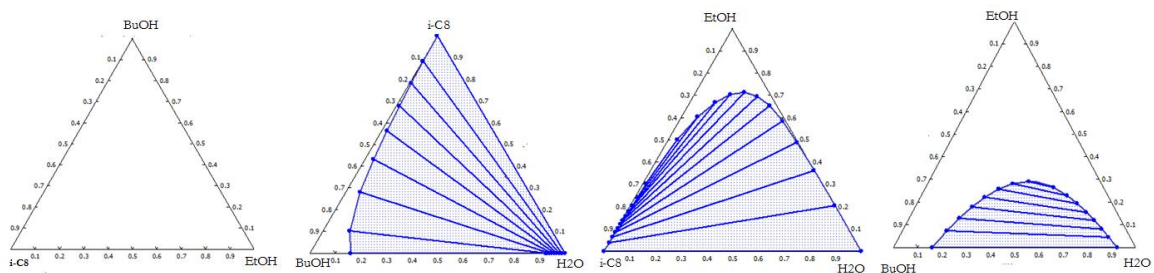


Figure 1. Four sides of the LLE tetrahedron obtained with ASPEN through UNIQUAC at 25°C and 1 atm. 1-BuOH = 1-butanol, EtOH = Ethanol, H₂O=water and i-C8 = isooctane

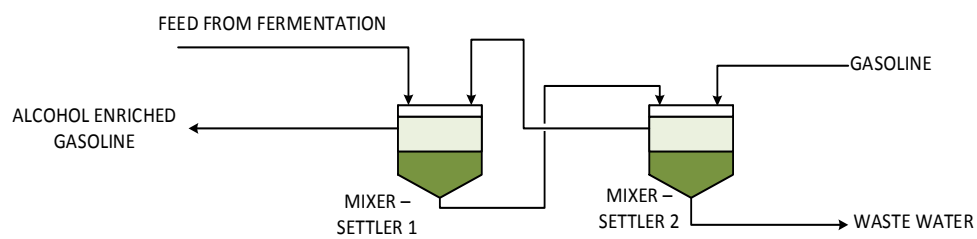


Figure 2. Sketch of the flowsheet used in this study.

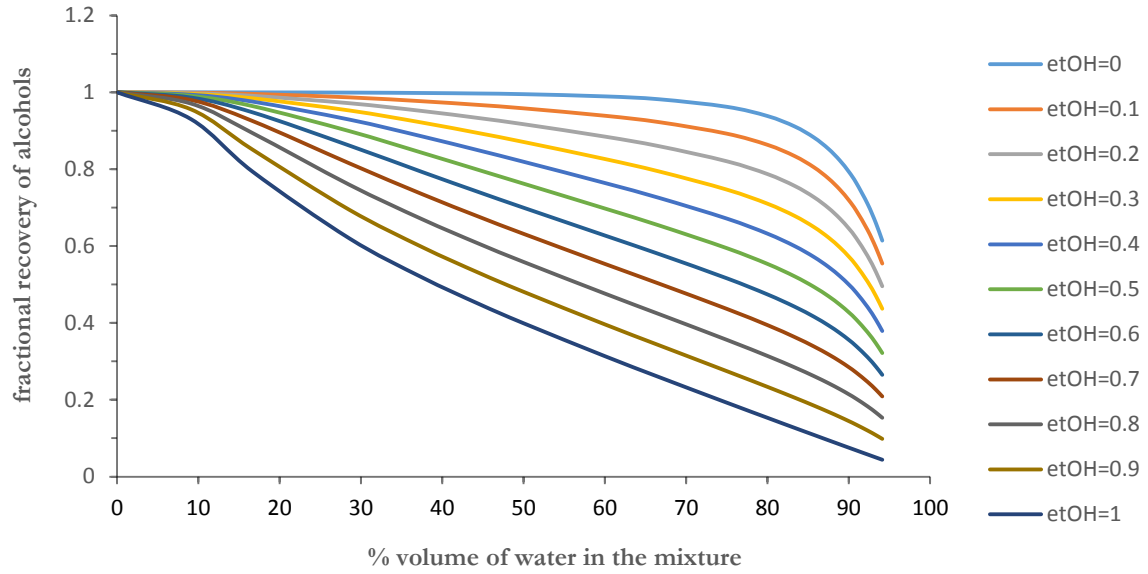


Figure 3. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a feed mixture of butanol, ethanol and water using gasoline at a blending ratio of 1:9. The legend is such that the volume fraction of alcohols is unity, mathematically $etOH + buOH = 1$, therefore if, for example, $etOH=0.3$ then $buOH=0.7$.

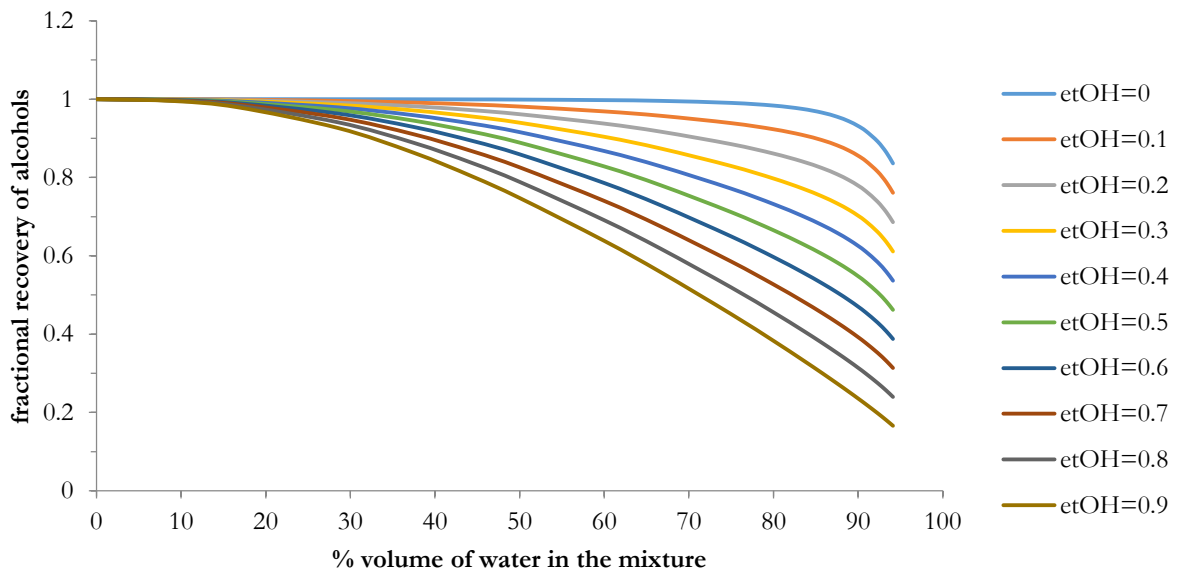


Figure 4. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a mixture of ethanol, butanol and water using gasoline at a blending ratio of 1:19. Refer to Figure 3 for description of legend.

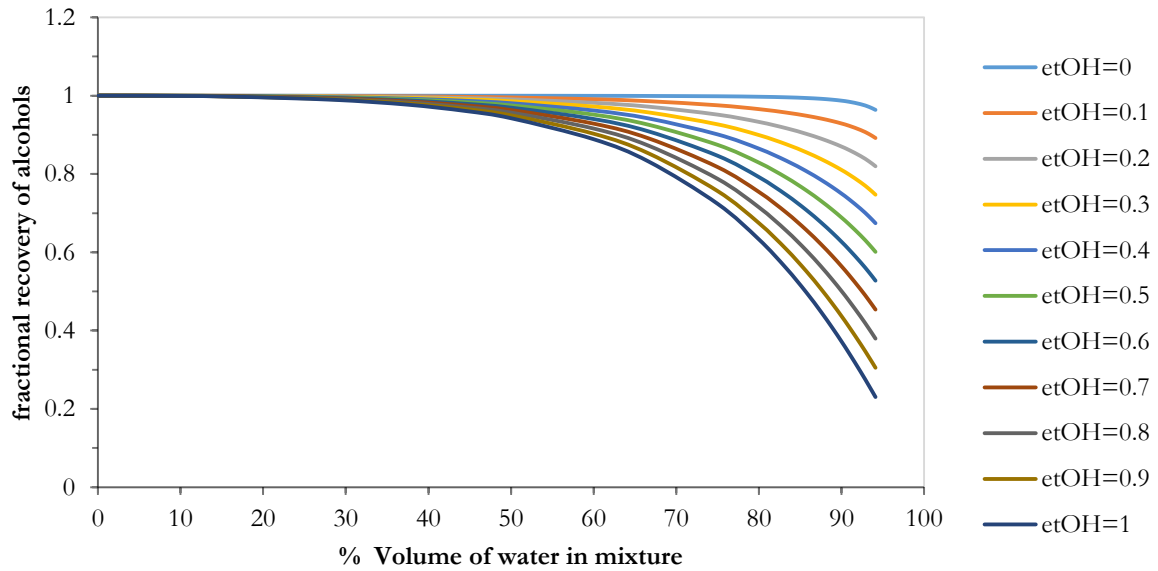


Figure 5. Results of simulation runs in ASPEN PLUS of a two stage preblending process of a mixture of ethanol, butanol and water using gasoline at a blending ratio of 1:49. Refer to Figure 3 for description of legend.

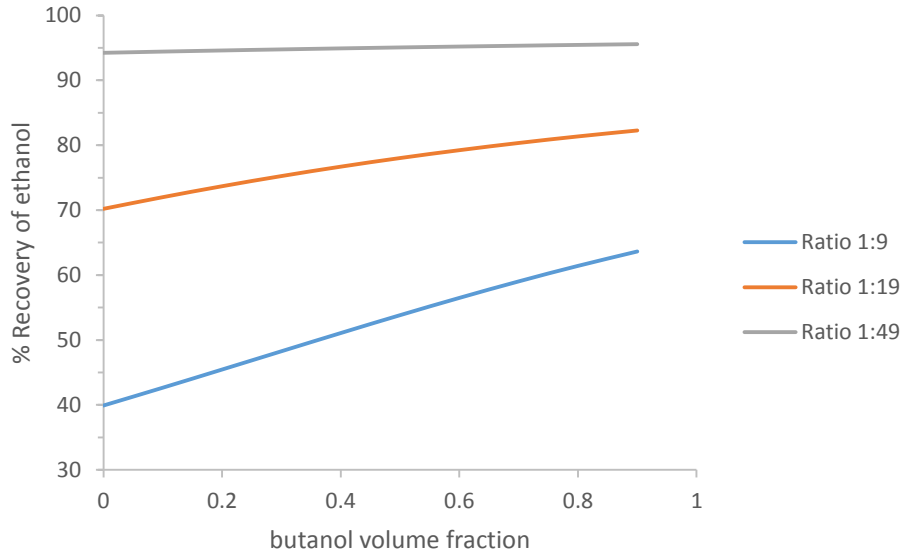


Figure 6. The trend of recovery of ethanol as a function of butanol volume fraction for a stream comprising of 50% water by volume. Refer to Figure 3 for description of butanol volume fraction.

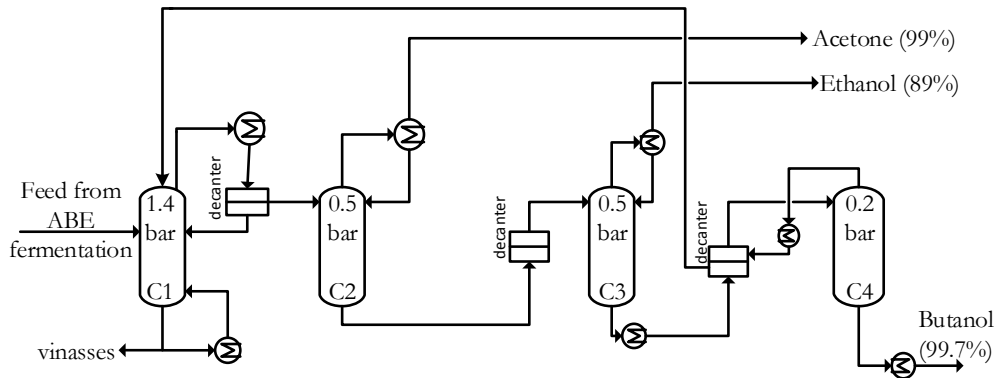


Figure 7. Process flow diagram for producing pure butanol and pure ethanol from ABE fermentation using four distillation columns. All the concentrations depicted here are in wt%.¹⁹

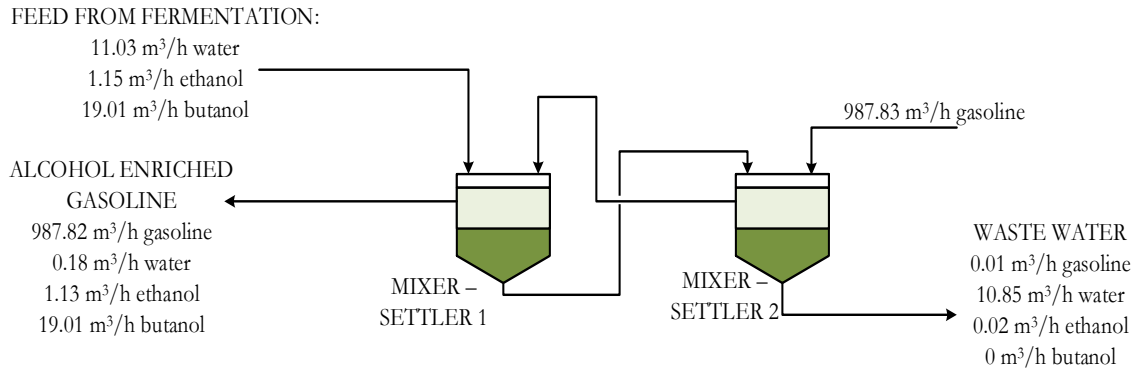


Figure 8. Results of an ASPEN simulation of a two-stage gasoline blending process of the bottom stream from the acetone recovery column (C2 in Figure 7) with gasoline for with a blending ratio of 1:49.

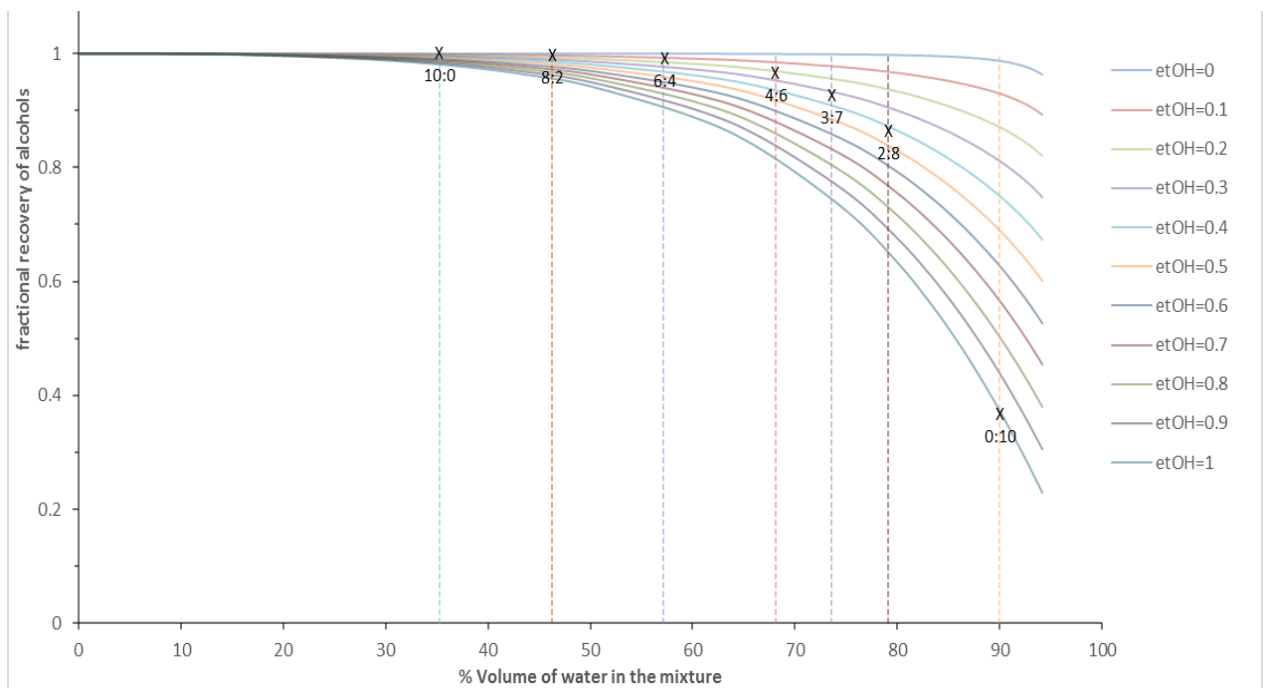


Figure 9. The effect of mixing a butanol rich stream (point 10:0) and an ethanol poor stream (point 0:10) on the fractional recovery of both alcohols in the fuel phase.

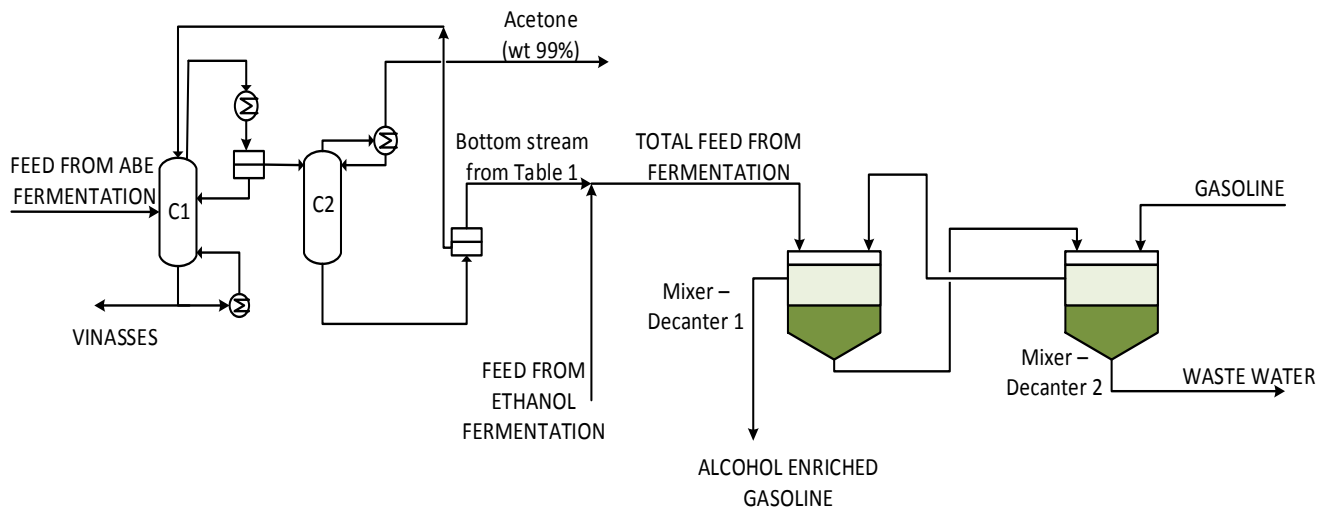


Figure 10: Mixing and subsequent preblending of ABE stream of water, ethanol and butanol and a stream from ethanol fermentation products.

Table 1. Bottom stream from the acetone recovery column (C2 in Figure 7) from ABE fermentation according to Van Der Merwe.²⁰ The trace compounds have been ignored for the calculation of the last column.

Species	Bottom stream of column C2 (kg/h)	Bottom stream (vol%)
H ₂ O	10967.54	35.3
Butanol	15350.43	61,0
Ethanol	915.53	3.7
Acetone	5.69	-
Butyric Acid	1.77	-
Acetic Acid	3.81	-
CO ₂	0.00	-
H ₂	0.00	-