Please cite as:

Martinez-Hernandez, Elias; Sadhukhan, Jhuma; Campbell, Grant M. *Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis*. Applied Energy 2013; 104:517-526.

Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis

Elias Martinez-Hernandez[a], Jhuma Sadhukhan[b]* and Grant M. Campbell[c]

[a]Centre for Process Integration, School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, M13 9PL, UK

[b]Centre for Environmental Strategy, University of Surrey, Guildford, GU2 7XH, UK

[c]Satake Centre for Grain Process Engineering, School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, M13 9PL, UK

Abstract

A biorefinery involving internal stream reuse and recycling (including products and co-products) should result in better biomass resource utilisation, leading to a system with increased efficiency, flexibility, profitability and sustainability. To benefit from those advantages, process integration methodologies need to be applied to understand, analyse and design highly integrated biorefineries. A bioethanol integration approach based on mass pinch analysis is presented in this work for the analysis and design of product exchange networks formed in biorefinery pathways featuring a set of processing units (sources and demands) producing or utilising bioethanol. The method is useful to identify system debottleneck opportunities and alternatives for bioethanol network integration that improve utilisation efficiency in biorefineries with added value co-products. This is demonstrated by a case study using a biorefinery producing bioethanol from wheat with arabinoxylan (AX) co-production using bioethanol for AX precipitation. The final integrated bioethanol network design allowed the reduction of bioethanol product utilisation by 94%, avoiding significant revenue losses.

Keywords: biorefinery, bioethanol, pinch analysis, arabinoxylan

* Corresponding author. E-mail: jhumasadhukhan@gmail.com, Tel.: +44 1483 68 6642, Fax: +44 1483 68 6671.

1. Introduction

Starch crops (e.g. corn, wheat), sugar crops (sugar cane and sugar beet) and lignocellulosic material (agricultural residues, wood, grass, etc.) are the main biomass feedstocks employed for bioethanol production [1–4]. Even in the case of processes using biomass feedstocks, such as algae [5, 6] and black liquor [7] to produce other biofuels such as biodiesel or methanol, some valuable components in these feedstocks represent a significant fraction that ends up in low value by-products. In the case of starch crops, the by-product is the Distillers Dried Grains with Solubles (DDGS). As supply of bioethanol increases, more DDGS is produced resulting in a lower market value. Extraction of valuable biomass feedstock fractions in added value products along with process integration is then necessary to enhance the economics of biorefinery systems producing bioethanol [8–10]. In addition to its intended application as a product to be used as transportation fuel, ethanol could also become an important intermediate feedstock or utility that could be used within a biorefinery. For example, ethanol can be used as a solvent for fractionation or extraction of added value products from biomass [8]. This offers potential for effective integration of various processing pathways to achieve efficient use of bioethanol within a biorefinery, especially where there are various source streams containing bioethanol at different concentrations and various demands requiring bioethanol.

Methodologies for biorefinery process design have emerged to address the particular nature of biomass processing and the complexity of the task of biorefinery integration at different levels. Feedstocks, processing technologies and products are the three levels of complexity concerning the integration of biorefineries [11]. There are methodologies based on process integration and assessment tools to improve internal material and energy recovery within a site and reduce external resource requirements. In the case of bioethanol production, heat pinch analysis, water pinch analysis and life cycle assessment have been applied to several configurations including value added production pathways and combined heat and power generation [11–23]. In addition, there are methodologies that combine process synthesis and optimisation through mathematical programming allowing screening of alternatives and creation of innovative biorefinery configurations [24–27]. Pham and El-Halwagi have proposed a “forward-backward” approach for biorefinery process synthesis and optimisation when a feedstock and a target product are specified using matching and interception procedures [25]. The method was applied for bio-alcohols production from lignocellulosic feedstocks and provided a configuration with optimised pathways between feedstock and end products along with possible open pathways for by-product production. However, the pre-treatment of biomass is not included as a conversion step and the biorefinery integration at the product level (i.e. potential utilisation of the various products within the biorefinery processes) is not considered. The interactions resulting from product integration could potentially reduce import of raw materials.

Whilst optimisation frameworks are worthwhile when well established technologies and real plant data are available, their solutions can be computationally demanding as more advanced and complex process technologies will emerge. Methods giving knowledge about the behaviour of integrated biorefinery processing networks, by intervention of the process engineers throughout the design task, can be of great value at the current stage of the learning curve of the field of biorefineries. The knowledge acquired then can be introduced within the mathematical formulations for better representation of a process and improved optimisation results. Furthermore, the potential for mass integration of biorefinery products within the processes has not been explored in the mentioned methodologies. In this sense, conceptual developments using the pinch analysis approach based on source–demand models of process integration can prove to be valuable as in the case of energy sector planning [28,29].

As discussed above, although the traditional process integration tools have been successfully applied for reduction of energy and environmental impact and to maximize profits, new tools are required to enable integrated processing of starch and lignocellulosic feedstocks for bioethanol production, in which ethanol can be used as utility for biomass fractionation or pretreatment as well as chemical reactant. A systematic “bioethanol pinch” methodology for the design and analysis of bioethanol exchange networks is proposed in this paper, adapted from hydrogen pinch analysis [30]. The methodology is a particular case of mass pinch analysis for synthesis of mass exchange networks [31]. According to the extended definition recently introduced by Ponce-Ortega et al. [32], it is an example of process intensification which includes any activity that reduces the use of material utilities and/or feedstock. The case study elaborated in the current paper is arabinoxylan (AX) extraction integrated with bioethanol production, in which ethanol streams of different purities are required for arabinoxylan precipitation and for feedstock washing [8,33,34]. The proposed methodology has been used to minimise the bioethanol requirement within the biorefinery.

In **Fig. 1**, opportunities for bioethanol integration between sources and demands (streams numbered 1 to 12) within a biorefinery producing bioethanol and arabinoxlylans from wheat have been identified. The route to extract arabinoxylans (AX) using bioethanol to precipitate the extracted AX presented in this figure has recently been explored [8,33,34]. In this process ethanol is used for bran purification (at 70% purity) and for AX precipitation and washing (at 96% purity). In a more complex design, the Organosolv process could be used to fractionate lignocellulosic materials for the production of bioethanol and other added value products. The Organosolv process similarly uses ethanol within the process at 50-60% purity to separate lignocellulosic feedstock into cellulose, hemicellulose and lignin [35]. The cellulose and hemicellulose fractions are sent to hydrolysis to produce more bioethanol whilst the lignin fraction is refined for further valorisation (in composites, wood-adhesives, fuel additives, etc.) or as fuel. Some furfural is also produced which can be sold as a solvent. A third common process pathway of bioethanol is its conversion into ethylene and subsequent polymerization into polyethylene [36].

A preliminary set of demands and sources for the targeted product interacting in the form of a *product exchange network* (PEN) can be constructed and analysed following the approach from pinch analysis [37], water pinch analysis [38–40], hydrogen pinch analysis [30,41], CO_2 emissions targeting [28] and mass pinch analysis [24,31]. The sub-network generated would contain all the integration alternatives between product sources and product demands also in relation to co-products from a biorefinery. The sources and demands would produce intermediate streams containing the targeted product at different purities. The PEN can be expanded to include all intermediate unit operations and streams with more detailed process data and constraints. New routes for biomass processing can be synthesised with emphasis on efficient use of feedstocks, waste minimisation and polygeneration flexibility. Even more, alternative or complementary feedstocks can be also identified. If the PEN operates at or near the minimum supply and within the constraints set by the requirements of the product demands (both in quality and quantity), then the system is expected to operate in the most efficient manner. However, without a targeting method for the minimum bioethanol supply, it is difficult to know how well the network is performing. A systematic approach for targeting for minimum fresh marketable product requirement in a PEN within a biorefinery is presented in this paper, taking the particular case of bioethanol. **Fig. 1** illustrates a complex biorefinery with integrated AX extraction in which ethanol features as a process stream of varying purity as well as a product of the biorefinery.

2. Methodology

2.1. Constraints for bioethanol pinch analysis

The bioethanol pinch analysis tool is intended to establish the minimum flow rate of bioethanol that can be used as a target for an integrated biorefinery design. In principle, this target can be decided assuming that any source can supply any demand. However, the minimum fresh bioethanol supply required by a system is driven by the constraints imposed by the processes involved and material conservation principles. Those constraints include the pressure, temperature, amount and nature of impurities, flow rate, purity, etc. Furthermore, the constraints may specifically include: minimum flow rate and/or purity of supply to a demand (e.g. 70% bioethanol for bran purification), limiting bioethanol content for process unit operations (e.g. a bioethanol concentration of 65% required for AX precipitation), limiting impurity content, etc. The nature of the feedstock and the composition of the intermediate streams as well as the purpose of the product are also important. Since the chemical species involved in various bioethanol pathways may not be the same, the bioethanol-containing streams in **Fig. 1** are not all necessarily exchangeable. For example, the AX pathway involves components like protein, sugars and glucans, and the final product must meet certain composition specification in order to be used as food additive or other potential application. Thus, an ethanol recovery unit in the AX process might be required. The purity and flow rate constraints imposed by the bioethanol demand streams are captured by formulating a material balance on the total streams and a material balance on bioethanol. This formulation constitutes the main underlying principle for the bioethanol integration technique presented here.

From conservation principles, the total amount of ethanol available from the sources must be in excess or equal to the total amount of ethanol required by the demands as a first necessary condition for the network to be feasible. The condition for material balance of the whole bioethanol network can be expressed in Equation 1.

$$\sum_{i=1}^{n_S} F_{S,i} = \sum_{j=1}^{n_D} F_{D,j} + \sum_{k=1}^{n_W} F_{W,k} \qquad (1)$$

where $F_{S,i}$ is the flow rate available from source i; $F_{D,j}$ is the flow rate required by demand j; $F_{W,k}$ is the flow rate of waste stream k sent to treatment (e.g. ethanol recovery or wastewater treatment); and n_S, n_D and n_W are the numbers of sources, demands and waste streams, respectively, in the network.

2.2. Bioethanol composite curves

After the selection of appropriate bioethanol sources and demands, the source and demand streams are combined into the source composite curve (SCC) and the demand composite curve (DCC), respectively, on purity against flow rate plots, following the construction of composite curves for mass exchanger network designs

[30,31,38–41]. The composite curve represents the total amount of mass flow rate to be removed in each purity interval. **Fig. 2a** shows a generic diagram with the SCC and DCC comprising three source streams and three demand streams. To construct the SCC, the source streams are plotted in the order of decreasing purity and cumulative flow rates forming a cascade of horizontal steps. Each step in the SCC indicates the total flow rate of bioethanol streams available at the corresponding purity level. The DCC is constructed following the same procedure. Each step in the DCC indicates the total flow rate of bioethanol streams required at the corresponding purity level. According to the bioethanol conservation principle, a SCC shorter than the DCC would indicate that the material balance on the total stream is violated for at least one of the demand streams. If the area covered by the SCC is larger than that of the DCC, then there is excess bioethanol in the system. When the excess bioethanol comes from a source stream that is not exchangeable or has low ethanol content, some amount of bioethanol would be lost into wastewater treatment (WWT).

The areas enclosed between the SCC and DCC represent the bioethanol pockets in the system, indicated in **Fig. 2a**. If the SCC is above the DCC for a given range of bioethanol purity, then the sources provide more bioethanol than is required by the demands at that particular purity range. Here, a bioethanol excess or surplus (+) appears. This surplus can be made available to compensate for a deficit in bioethanol supply at a lower purity. If the SCC is below the DCC, the bioethanol from the sources is not enough to cover the demands producing a deficit (–) of bioethanol. This means that the demands require bioethanol at purity higher than the purity of the corresponding sources. This deficit can be compensated only by the surplus bioethanol of a higher purity which can be mixed with the lower purity sources to raise the bioethanol content until the purity constraint of the demand is met. The balance of bioethanol pockets (surplus and deficits) at the various purity levels is the key for systems integration and debottlenecking.

2.3. Bioethanol surplus diagram

In addition to the amount required, bioethanol must also be supplied at appropriate purities required by the demand streams. Thus, the bioethanol excess/deficit must be identified at various purity levels from the composite curves. The bioethanol excess or deficit can be determined for each flow interval of the combined SCC and DCC. The diagram in **Fig 2a** is divided into six flow intervals (I to VI). The number of intervals in the system is equal to the total number of flow rate segments. The area between the SCC and DCC in a particular interval *i* represents the material balance and it is equal to the bioethanol flow rate b_i, as shown in Equation 2:

$$b_i = (x_{Si} - x_{Di}) \times (F_{Ui} - F_{Li}) \quad (2)$$

where x_{Si} and x_{Di} are the purities of the source and demand in the interval, respectively; F_{Ui} and F_{Li} are the upper and lower bounds of the flow interval, respectively. The net cumulative surplus (or deficit) bioethanol at each given flow rate, when plotted in purity vs. flow rate, forms the *bioethanol surplus diagram*. The bioethanol surplus diagram generated from the bioethanol composite curves in **Fig. 2a** is presented in **Fig. 2b**, showing the pocket areas represented as horizontal segments. In this representation, the maximum value between x_S and x_D is taken for the *y*-axis, in order to set a common scale.

The *bioethanol surplus diagram* displays the net flow rate characteristics of a network versus the purity of bioethanol. The significance of the surplus diagram is that it indicates if the flow rates of bioethanol utilities can be reduced, lowering the fresh bioethanol requirement, within given constraints. If the surplus is negative at any flow interval between F_{Ui} and F_{Li} (i.e. surplus curve crosses *y*-axis), then the system is not receiving the required amount of ethanol at the adequate purity. In that case, at least one of the constraints on bioethanol flow rate imposed by the demands cannot be satisfied by the sources, rendering the system unfeasible. This situation would lead to using additional amounts of fresh ethanol or higher-purity ethanol. Therefore, the second necessary condition for system feasibility is that the material balance on ethanol in the overall system (i.e. the cumulative ethanol flow rate) must always be positive. This means that if the entire bioethanol surplus curve lies at or above zero bioethanol flow rate, then the second condition for a feasible system is achieved. If both the first (Equation 1) and second necessary conditions are met, then the bioethanol integration problem has at least one feasible solution.

One of the possible solutions is when the bioethanol network is constrained on bioethanol supply. In this case the bioethanol requirements are just met so that any reduction in the supply creates a negative surplus making the network unfeasible. A bioethanol network featuring such a constraint would present at least one place in the bioethanol surplus diagram where the bioethanol surplus is equal to zero. At this point, a pinch can be appreciated where the bioethanol surplus curve touches, but does not cross, the *y*-axis. This "bioethanol pinch" sets the minimum bioethanol consumption in the network.

2.4. Bioethanol pinch and targeting

The bioethanol pinch corresponds to the point at which the bioethanol network has neither excess nor deficit. As in other process integration techniques, identification of the pinch point helps establishing the minimum bioethanol utility targets, corresponding to the maximum bioethanol reuse in view of an integrated and efficient biorefinery flowsheet design. If a network has excess ethanol sources even after maximum reuse indicated by the bioethanol pinch point, opportunities for system improvement or debottlenecking can be further explored by adding bioethanol production or purification units or by fresh ethanol imports.

Fig. 2c illustrates how the flow rate of the first source is varied until a pinch occurs in the bioethanol surplus diagram (**Fig. 2d**). The purity of the bioethanol source at the pinch corresponds to the bioethanol pinch purity (x_P). The bioethanol pinch appears in the surplus diagram by a discontinuity segment at surplus equal to zero between x_P and the corresponding x_D. In the pinched diagram (**Fig. 2d**), the surplus curve is shifted towards the *y*-axis showing a reduction in the bioethanol utility requirement. Similar to the hydrogen pinch, the bioethanol pinch divides the overall bioethanol network into a subsystem with net zero ethanol surplus (region above the pinch) and a subsystem with net positive ethanol surplus (region below the pinch). Above the pinch, there is a portion of the flow rate from the source stream at the pinch purity indicated as F_{PR} (**Fig 2c**). This flow rate corresponds to the amount that must be reused by the demand streams above the pinch to meet the bioethanol supply target. In intervals where a net flow rate surplus exists, the net flow rate can be cascaded to lower purity intervals. Once the demand for bioethanol at lower purity intervals is entirely satisfied, any other excess bioethanol available can be sold to the market. In intervals where a net deficit of bioethanol flow rate exists, the excess bioethanol from higher purity intervals must be used first. Only after exhausting flow rate surpluses from higher purity intervals, external bioethanol utilities can be applied. Other implications from the bioethanol pinch for the integration of a bioethanol exchange network are discussed below.

As mentioned before, the network is divided into a region above and below the pinch as shown in the pinched surplus diagram (continuous line in **Fig. 2d**). Since the subsystem above the pinch is balanced, reusing a bioethanol stream from below the pinch implies the transference of the same amount from a source above the pinch (at higher purity) across the pinch to preserve the material balance. This produces a reduction in ethanol surplus above the pinch, and additional utility must be supplied as a penalty to keep the system balanced. Finally, the requirement of fresh ethanol would exceed the minimum target identified by the bioethanol pinch method. Thus, the bioethanol streams must never be directly exchanged across the pinch. As with pinch analysis in other contexts, this is the first fundamental principle for the design of a bioethanol exchange network at minimum supply.

A second bioethanol integration principle is deduced for the purifier placement from the implications of the pinch point. A purifier placed below the pinch purity would make purer ethanol in a region of surplus that will end up as waste stream since it can not be exchanged to supply a demand above the pinch. Thus, a purifier should always be placed across the pinch purity in order to exchange ethanol from a region of surplus to a region of limited supply. This can lead to a further minimization of the fresh bioethanol utility. The application of the bioethanol pinch targeting method to minimise the fresh bioethanol utility supply and the use of the integration principles for the design of a bioethanol exchange network are demonstrated in the following section using a case study. The general strategy for network analysis, design and integration is depicted in **Fig. 3**.

2.5. Case study

For an effective demonstration of the bioethanol integration method, the processing pathways co-producing AX in **Fig. 1** were analysed. The initial PEN showing the bioethanol demands and sources is depicted in **Fig. 4**. The bases are: a biorefinery processing capacity of 340000 t/y of wheat from which 13600 t/y of bran is separated to produce 2460 t/y of 70% purity AX [8].

2.5.1. Demands and sources

The main source is the fresh bioethanol produced at 99.6% purity, which is diluted to supply 96% ethanol to the precipitation unit (PPU-1) and washing unit 2 (WSU-2). The AX precipitation requires enough ethanol for a final concentration of about 65%. The waste streams rich in bioethanol resulting from PPU-1, WSU-2 and centrifugation (CFG-2) are recycled and supplemented with a fresh bioethanol top-up stream. Those streams are mixed to supply the 70% ethanol required by the treatment unit 1 (TMU-1) and sieving and washing unit 1 (SWU-1). The stream resulting from SWU-1 contains the ethanol extractable components from the bran which are not desirable for the AX product. Therefore, this stream can not be directly exchanged in the system. The sieving and washing unit 2 (SWU-2) produces a waste stream with high flow rate but poor ethanol content. Streams from SWU-1 and SWU-2 can be sent to the recovery section or wastewater treatment (WWT). The vapour stream from the rotary dryer (RDY-2) is lost as waste but, if it is condensed, an exchangeable bioethanol rich stream could be generated. Source and demand streams in the order of decreasing purity are presented in **Table 1** for the data extracted from the example bioethanol network in **Fig. 4**.

2.5.2. Finding the bioethanol pinch and target

The SCC (initial) and DCC generated for the data in **Table 1** are presented in **Fig. 5a**. Two pockets of high amounts of ethanol in excess and one small pocket of ethanol in deficit can be observed. This indicates that the system may not be using the bioethanol available in an efficient manner. To determine how well the system is performing in terms of efficient reuse of bioethanol, the bioethanol targeting approach discussed in section 2.4 is applied. In order to find the bioethanol supply target, the surplus curve must firstly be pinched by varying the flow rate of bioethanol supplied to the network. Not all the sources can accept the flow rate to be changed or reduced since these flow rates may be required for the normal operation of the processes. The bioethanol sources that are flexible with respect to flow rate are thus the utility imports to the network from external suppliers or other processes within the biorefinery. In case of AX co-production the interest is to reduce the amount of fresh bioethanol product to be used, thus the flow rate of this utility can be varied. This corresponds to the bioethanol stream with the highest purity which would also have the highest cost. The targeting procedure thus can be applied to reduce the bioethanol utility supply with the highest flow rate and/or with the highest cost or purity.

The fresh bioethanol supply (at 99.6% purity) was reduced (**Fig. 5a**) until a bioethanol pinch occurred at a purity of 91.52% (**Fig. 5b**) for a flow rate of 12512 t/y. This corresponds to the target for the minimum ethanol import for a feasible exchange network. The length of the displacement of the first step in the SCC indicates the amount of fresh bioethanol product (at 99.6% purity) that can be saved. Thus, the amount of ethanol utility import can be reduced by 28650 t/y from the initial 41162 t/y (**Table 1**). This means almost 70% less bioethanol product would be spent in AX co-production. Since the integrated design needs to be economically viable, the bioethanol network integration options need to achieve an increase in profitability. The analysis may require several iterations and a spreadsheet tool would avoid the tedious calculation and graphical construction. Thus, the bioethanol pinch method has been adapted to a user friendly software tool using Excel-VBA that can be made available upon request.

2.5.3. Bioethanol network design and integration

Fig. 5b reveals that the ethanol supplied to the initial bioethanol network is not being used efficiently. The arrows showing the displacement between the original and the pinched diagram indicate that there are substantial amounts of ethanol that can be saved for other purposes. This sets the scope for improvement of the network design following the bioethanol integration strategy in **Fig. 3**. The pinch point indicates that all units producing and requiring ethanol at purity equal or higher than x_P must be exchanged above the pinch. Then, simultaneous mass balances must be solved to determine the flow rates exchanged between them.

Figure 6 shows the resulting bioethanol exchange network above the pinch. Notice that some of the bioethanol from WSU-2 is sent below the pinch, but not across the pinch since the stream is at the pinch purity x_P =91.52%. Thus, the first criterion for bioethanol exchange network design is satisfied. This in turn also shows that the initial network was violating this criterion by using great amounts of fresh bioethanol (at 99.6%) from above the pinch to supply a demand (at 70%) below the pinch, crossing x_P. Notice how the recycle flow rate F_{PR} (**Fig. 5a)** from WSU-2 is used efficiently. Although **Fig. 5a** indicates that the remaining stream from WSU-2 at 91.52% can be mixed with the stream from SWU-1 at 68.22% to supply ethanol for TMU-1 and SWU-1 at 70%, due to the impurity content (ethanol extractable components) of the stream from SWU-1, this option can not be considered. In this case, other debottlenecking options must be explored to improve the network design and performance. One of the options is to import a utility with higher purity in order to increase the exchangeable surplus. However, in the example network the ethanol is supplied at the highest possible purity, which corresponds to the pure bioethanol product. Another option is to purify a stream in order to make more ethanol available to the system at a higher purity. The integration of a purification unit is thus evaluated in this case study by using the bioethanol pinch analysis method.

Although the bioethanol pinch does not indicate which stream to purify, the technique is useful to determine whether the integration of a purification unit to the system has a potential for additional savings. The first stream of interest is the waste from SWU-1. This stream has a high flow rate (55633 t/y) at medium level purity of 68.22% (**Table 1**), but the stream contains impurities not desirable in the downstream processing. Since most of the impurities are solids, they can be easily separated. Although the ethanol content is appropriate for the rectifier column from the purification section of the biorefinery, adding a stream with high solids content (more than 20%) could not be desirable for the operation of the column since at this stage almost all the solids from fermentation have been removed. Furthermore, the installation of an additional unit would provide operational flexibility for ethanol purification. Assuming 98% ethanol recovery, the new purification unit produces 38745 t/y at 96% purity and 16888 t/y of a solids-containing stream with an ethanol content of 4.49%. The bottom stream of the purifier is not exchangeable because it contains the impurities removed. Thus, this source stream is excluded from further analysis. The purity profiles and the surplus diagram, after the introduction of a purifier in the network and before finding the pinch, are depicted in **Fig. 5c and Fig**. **5d**, respectively. The new step in the SCC represents the new stream source in the system.

Fig. 5c shows how the SCC moves towards the right between the purity of the purified stream and the pinch purity interval, indicating that an ethanol surplus has been introduced to this region. However, for other purity intervals, the SCC moves towards the left since part of the initial surpluses has been moved to a higher purity by the new ethanol purification unit. The area reduction between the SCC and DCC in the region below the pinch is equal to the area increase above the pinch. The above observations indicate that the conditions for network feasibility stated in Section 3 are not violated. The effect of the changes made to the network is illustrated in **Fig. 5d**. There is a change from a system constraint on ethanol supply above the pinch to a system with ethanol surplus indicated by the large arrow in the second step (the new source at ethanol fraction of 0.96) of the diagram. The surplus generated above the pinch can be exchanged with the ethanol demands to decrease the need for fresh bioethanol product, resulting in a lower target. The new minimum bioethanol makeup flow rate is found by following the targeting procedure described above. **Fig. 5e** and **Fig. 5f** depict the pinched bioethanol networks with and without the purification unit, respectively.

The reduction in the total bioethanol makeup flow rate and the consequent reduction in the flow rate of the waste stream are clearly indicated by the arrows in **Fig. 5e**. The great reduction in the ethanol waste is obvious in the pinched surplus diagram in **Fig. 5f**, indicating the system is now utilising the available ethanol more efficiently. A remarkable effect of the purification unit is that the pinch is lowered to an ethanol content of x_P=0.0249. This opens the opportunity to use source streams at ethanol content from as high as 0.9960 to as low as 0.0249 to supply a demand at any purity in between, which was not allowed in the initial pinched system according to the first bioethanol integration criterion. The source streams from PPU-1 (892 t/y at 64.00% purity), CFG-2 (1437 t/y at 15.09% purity), WSU-2 (21670 t/y at 91.52% purity) and

RDY-2 (2049 t/y at 50.95% purity) can be exchanged without impurity concerns since they come from the last steps of the AX purification. However, it must be acknowledged that in principle, impurities in certain ethanol-containing streams could constrain their use. In this particular example of bioethanol and arabinoxylan co-production, the processes are not particularly sensitive such that the nature of the impurities is unlikely to impose significant constraints of this sort (although this may need to be verified experimentally for certain operations). The “impurities” (principally bran and protein) are similar in the various process streams and are relatively innocuous, and the intention is that all of them should end up ultimately in the DDGS.

3. Results and discussion

The final network design along with the flow rates and purities of the exchanged and waste streams are depicted in **Fig. 7**. These values represent the mass balance on ethanol also indicating that the fresh ethanol utility imported to the system is equal to the amount of ethanol going to wastewater treatment. Since the introduction of the purifier modifies the network significantly, the final design is different to that in **Fig. 6**. Note that the streams imported and from the sources, PPU-1, CFG-2, WSU-2, RDY-2 and SWU-2 at purity levels between 0.0249 and 0.9960 are combined to supply the demands TMU-1 and SWU-1 at the intermediate purity level of 70%. The source stream from SWU-2 is a poor ethanol stream and it is mainly used for dilution of other source streams with higher purity, thus saving fresh water. Recycling part of that stream containing AX would increase recovery in the bran purification steps (TMU-1, SWU-1). The bioethanol makeup required for the co-production of AX is now 2459 t/y. Thus, the integration of the purification unit can save 10053 t/y of bioethanol product additional to the savings from the first pinched system to make a total saving of 38703 t/y. This means that the fresh bioethanol makeup required can be reduced by up to 94% from the 41162 t/y in the initial network (**Fig. 4**).

Table 2 summarises the economic effects of the modifications to the initial network from the bioethanol integration using pinch targeting method. The revenue losses from bioethanol product utilisation are estimated assuming a bioethanol price of 590 £/t [8]. The distillation columns were simulated in Aspen Plus for preliminary sizing and their bare module capital cost was estimated by typical correlations available in the literature [42]. The capital cost was annualised using the same capital charge of 28% as in [8]. After the pinch targeting method is applied to the initial network, the biorefinery could avoid revenue losses of 16.9 M£/y without any change in the capital cost. However, purification of streams has been recommended from the pinch analysis as discussed before.

The system including the integration of a new purifier column (**Fig. 7**) was compared to the alternative system where the waste streams from SWU-1 and SWU-2 are sent back to the recovery and purification sections of the main bioethanol production process (**Fig. 1**). **Table 2** shows that the total avoided losses in biorefinery revenues after bioethanol pinch analysis is 22.83 M£/y for the system with a new purifier column. The impact of installing a purification unit additional to the rectifier column in the main production process is a 15% increase in capital costs. This is less than the 24% cost increase for the installation of distillation columns designed for the increased capacity due to the processing of the waste streams from SWU-1 and SWU-2. In this alternative, the mass balance indicates that the fresh bioethanol surplus is reduced to 2282 t/y. Although the reduction is higher and therefore more revenue losses are avoided, the capital cost is also higher leading to a minimal difference in increased profitability between the two purification alternatives shown in Table 2. The impact on the capital costs is favourable for the installation of a new purification unit which also offers more process flexibility.

Another advantage of the final integrated network design in **Fig. 7** is that the condensation of the stream from RDY-2 makes some heat available that can be used to preheat the AX stream to be dried to save drying heat duty. Therefore, the bioethanol pinch method illustrated here is not only helpful to devise integration strategies for increasing the ethanol use efficiency but can further be complemented with water and heat integration approaches for the production of a biorefinery design that is more efficient with respect to usage of bioethanol, water and heat.

4. Conclusions

A bioethanol pinch analysis method has been presented here as an effective tool for the design of bioethanol-based biorefineries utilising feedstock more efficiently through integrated bioethanol exchange networks. The tool allows targeting for minimum fresh bioethanol consumption, thus preventing product and revenue losses. It also proved useful for evaluation of debottlenecking or improvement options. Integration principles and strategies helped to achieve an efficient, highly integrated bioethanol network. Combination of analytical-graphical and cost-benefit analysis can facilitate the whole bioethanol based biorefinery process synthesis and retrofit designs. The bioethanol pinch analysis approach could be adopted by other comparable product-based biorefineries.

Acknowledgements

The authors are grateful for the financial support from the National Council of Science and Technology (CONACYT) of Mexico to undertake this work.

References

[1] Cardona CA, Sanchez OJ. Fuel ethanol production: process design trends and integration opportunities. Bioresource Technol 2007;98(12):2415–57.

[2] Ekman A, Wallberg O, Joelsson E, Börjesson P. Possibilities for sustainable biorefineries based on agricultural residues – A case study of potential straw-based ethanol production in Sweden. Appl Energy 2012; In Press.

[3] Starfelt F, Daianova L, Yan J, Thorin E, Dotzauer E. The impact of lignocellulosic ethanol yields in polygeneration with district heating – A case study. Appl Energy 2012;92:791–99.

[4] Yan J, Lin T. Biofuels in Asia. Appl Energy 2009;86(1):S1-S10.

[5] Daroch M , Geng S, Wang G. Recent advances in liquid biofuel production from algal feedstocks. Appl Energy 2012; In Press.

[6] Chisti Y, Yan J. Energy from algae: Current status and future trends: Algal biofuels – A status report. Appl Energy 2011;88(10):3277–79.

[7] Naqvi M, Yan J, Dahlquist E. Bio-refinery system in a pulp mill for methanol production with comparison of pressurized black liquor gasification and dry gasification using direct causticization. Appl Energy 2012;90(1):24–31.

[8] Sadhukhan J, Mustafa MA, Misailidis N, Mateos-Salvador F, Du C, Campbell GM. Value analysis tool for feasibility studies of biorefineries integrated with value added production. Chem Eng Sci 2008;63:503–19.

[9] Demirbas A. Competitive liquid biofuels from biomass. Appl Energy 2011;88:17–28.

[10] Demirbas MF. Biorefineries for biofuel upgrading: A critical review. Appl Energy 2009;86:S151–S161.

[11] Alvarado-Morales M, Terra J, Gernaey KV, Woodley JM, Gani R. Biorefining: Computer aided tools for sustainable design and analysis of bioethanol production Chem Eng Res Des 2009;87(9):1171–83.

[12] Furlan FF, Costa CBB, Fonseca GDC, Soares RDP, Secchi AR, Cruz AJGD, et al. Assessing the production of first and second generation bioethanol from sugarcane through the integration of global optimization and process detailed modelling. Comput Chem Eng 2012;43:1–9.

[13] Fujimoto S, Yanagida T, Nakaiwa M, Tatsumi H, Minowa T. Pinch analysis for bioethanol production process from lignocellulosic biomass. Appl Therm Eng 2011;31(16):3332–36.

[14] Modarresi A, Kravanja P, Friedl A. Pinch and exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw. Appl Therm Eng 2012;43:20–8.

[15] Kravanja P, Modarresi A, Friedl A. Heat integration of biochemical ethanol production from straw – A case study. Appl Energy 2012; In press.

[16] Dias MOS, Modesto M, Ensinas AV, Nebra SA, Filho RM, Rossell CEV. Improving bioethanol production from sugarcane: Evaluation of distillation, thermal integration and cogeneration systems. Energy 2011;36(6):3691–703.

[17] Franceschin G, Sudiro M, Ingram T, Smirnova I. Brunner G, Bertucco A. Conversion of rye straw into fuel and xylitol: A technical and economical assessment based on experimental data. Chem Eng Res Des 2011;89(6):631–40.

[18] Zheng Y, Yu C, Cheng, YS, Lee C, Simmons CW, Dooley TM, et al. Integrating sugar beet pulp storage, hydrolysis and fermentation for fuel ethanol production. Appl Energy 2012;93:168–75.

[19] Cherubini F, Ulgiati S. Crop residues as raw materials for biorefinery systems – A LCA case study. Appl Energy 2010;87(1):47–57.

[20] Srirangan K, Akawi L, Moo-Young M, Chou CP. Towards sustainable production of clean energy carriers from biomass resources. Appl Energy 2012;100:172–186.

[21] Ilic DD, Dotzauer E, Trygg. District heating and ethanol production through polygeneration in Stockholm. Appl Energy 2012;91(1):214–221.

[22] Heyne S, Harvey S. Assessment of the energy and economic performance of second generation biofuel production processes using energy market scenarios. Appl Energy 2012; In Press.

[23] Daianova L, Dotzauer E, Thorin E, Yan J. Evaluation of a regional bioenergy system with local production of biofuel for transportation, integrated with a CHP plant. Appl Energy 2012;92:739–49.

[24] Ng DKS. Automated targeting for the synthesis of an integrated biorefinery. Chem Eng J 2010;162:67–74.

[25] Pham V, El-Halwagi M. Process synthesis and optimization of biorefinery configurations. AIChE J 2012;58(4):1212–21.

[26] Martín M, Grossmann IE. BIOpt: A library of models for optimization of biofuel production processes. Comput Aided Chem Eng 2012;30:17–20.

[27] Ponce-Ortega JM, Pham V, El-Halwagi MM, El-Baz AA. A disjunctive programming formulation for the optimal design of biorefinery configurations. Ind Eng Chem Res 2012;51(8):3381–400.

[28] Tan RR, Foo DCY. Pinch analysis approach to carbon-constrained energy sector planning. Energy 2007;32:1422–29.

[29] Tan R.R. A general source-sink model with inoperability constraints for robust energy sector planning. Appl Energy 2011;88:3759–64.

[30] Alves JJ, Towler GP. Analysis of refinery hydrogen distribution systems. Ind Eng Chem Res 2002;41:5759–69.

[31] El-Halwagi MM, Manousiouthakis V. Synthesis of mass exchange networks. AIChE J 1989;35:1233–44.

[32] Ponce-Ortega JM, Al-Thubaiti MM, El-Halwagi MM. Process intensification: New understanding and systematic approach. Chem Eng Process 2012;53:63–75.

[33] Du C, Campbell GM, Misailidis N, Mateos-Salvador F, Sadhukhan J, Mustafa M, Weightman RM. Evaluating the feasibility of commercial arabinoxylan production in the context of a wheat biorefinery principally producing ethanol. Part 1. Experimental studies of arabinoxylan extraction from wheat bran. Chem Eng Res Des 2009;87:1232–38.

[34] Misailidis N, Campbell GM, Du C, Sadhukhan J, Mustafa M, Mateos-Salvador F, Weightman RM. Evaluating the feasibility of commercial arabinoxylan production in the context of a wheat biorefinery principally producing ethanol. Part 2. Process simulation and economic analysis. Chem Eng Res Des 2009;87:1239–50.

[35] Van der Linden R, Huijgen WJJ, den Uil H. Conceptual Process Design of an Organosolv-based Wheat Straw Biorefinery for Co-Production of Bioethanol, Furfural and Lignin, 7th International Conference on Renewable Resources & Biorefineries, June 8–10. Bruges, Belgium, 2011.

[36] Huang H. Microbial ethanol, its polymer polyethylene, and applications. Microbiol Monogr 2010;14:389−404.

[37] Linnhoff B. Pinch Analysis –A state of the art overview. Trans IchemE 1993;71(A):503.

[38] Wang YP, Smith R. Wastewater minimisation. Chem Eng Sci 1994;49:981–1006.

[39] Majozi T, Brouckaert CJB, Buckley CAB. A graphical technique for wastewater minimisation in batch processes. J Environ Manage 2006;78(4):317–29.

[40] Tan RR, Foo DCY, Aviso KB, Ng DKS. The use of graphical pinch analysis for visualizing water footprint constraints in biofuel production. Appl Energy 2009;86:605–9.

[41] Nelson AM, Liu YA. Hydrogen pinch analysis made easy. Chem Eng 2008;115(6):56−61.

[42] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. Analysis, Synthesis and Design of Chemical Processes. 3rd ed. New York: Prentice Hall; 2009.

Table 1 Bioethanol demand and source data extracted from the example bioethanol network

ID	Process Unit	Stream in Fig. 1	Flow rate (t/y)	Ethanol mass fraction	Cumulative flow (t/y)
Demands					
D1	PPU-1	8	11888	0.9600	11888
D2	WSU-2	9	10679	0.9600	22567
D3	TMU-1	1	38695	0.7000	61262
D4	SWU-1	2	18380	0.7000	79642
Sources					
S1	Fresh bioethanol		41162	0.9960	41162
S2	WSU-2	7	21670	0.9152	62832
S3	SWU-1	3	55633	0.6822	118465
S4	PPU-1	5	892	0.6400	119357
S6	RDY-2	10	2049	0.5095	121406
S7	CFG-2	6	1437	0.1509	122843
S8	SWU-2	4	80304	0.0249	203147

Table 2 Summary of the impact of the various modifications from bioethanol network integration on fresh bioethanol product utilisation and economic indicators.

System	Fresh bioethanol (t/y)	Revenue losses (M£/y)	Avoided revenue losses (M£/y)	Column size (m^3)	Bare module capital cost (M£)	Net additional capital cost (M£)	Annualised additional capital cost (M£/y)	Net profit increase (M£/y)
Initial network	41162	24.29	Base system	244	2.49	Base cost	Base	Base
Pinched (initial) network	12512	7.38	16.90	244	2.49	0	0	16.90
With centralised purification column designed for increased capacity	2282	1.35	22.94	293	3.08	0.59	0.17	22.77
With additional purification unit in AX process	2459	1.45	22.83	244 (initial) 27 (additional)	2.49 0.381	0.381	0.11	22.72

Figure captions

Fig. 1 Bioethanol pathways in a biorefinery using starch and lignocellulosic feedstock. The various bioethanol rich streams are indicated by the dashed lines. SW: Sieving and washing, UF: ultrafiltration, AX: arabinoxylan, DDGS: Distillers Dried Grains with Solubles.

Fig. 2 (a) Source composite curve (SCC) and demand composite curve (DCC) showing how the areas in the pockets are related to the horizontal segments in the corresponding (b) bioethanol surplus diagram. The bioethanol surplus is calculated for each of the flow rate intervals (I to VI). (c) The reduction in utility flow rate displaces the SCC towards the left producing a (d) shift in the surplus diagram until pinched with the y-axis.

Fig. 3 General strategy for bioethanol integration

Fig. 4 Bioethanol network in the production process of arabinoxylan (70% purity) from wheat bran. The balance in the first diamond knot is water required for bioethanol dilution from 99.6% purity to 96% purity. WWT: wastewater treatment. Flow rates in t/y.

Fig. 5 Evolution of the bioethanol composite curves and surplus diagram throughout the bioethanol integration process. (a) The initial and pinched bioethanol composite curves and the corresponding (b) bioethanol surplus diagrams for the example network. (c) The composite curves and (d) bioethanol surplus diagrams before and after integrating a purification unit to the system. (e) The pinched ethanol composite curves and (f) surplus diagram with and without purifier.

Fig. 6 The bioethanol exchange network design above the pinch for the target fresh bioethanol makeup. Flow rates in ton/yr.

Fig. 7 The bioethanol exchange network design after integrating a purification unit. Flow rates in t/y.

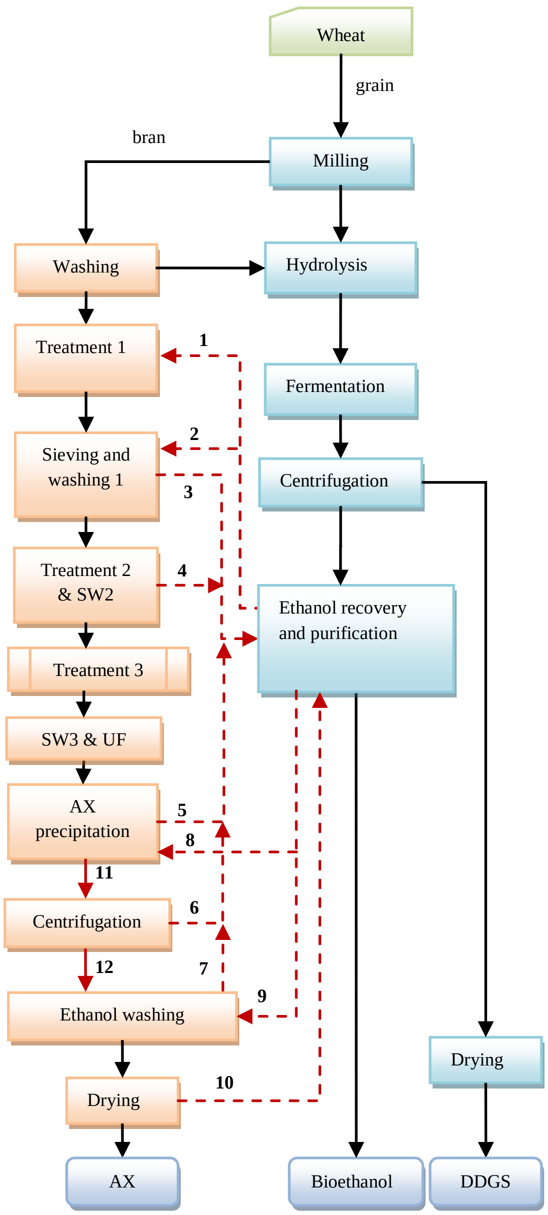
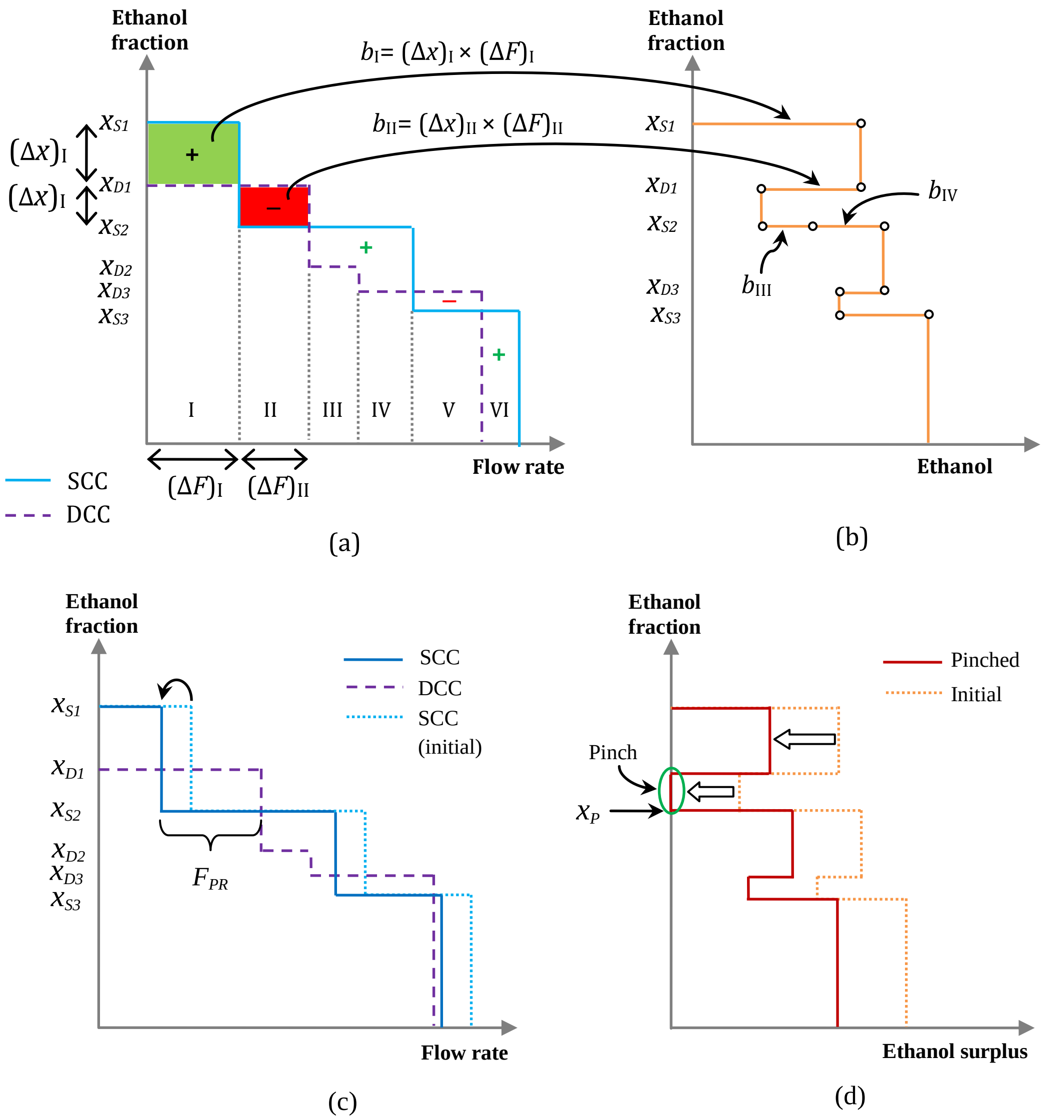

Wheat
grain
bran
Milling
Washing
Hydrolysis
Treatment 1
1
Fermentation
Sieving and washing 1
2
3
Centrifugation
Treatment 2 & SW2
4
Ethanol recovery and purification
Treatment 3
SW3 & UF
AX precipitation
5
8
11
Centrifugation
6
12
7
Ethanol washing
9
Drying
Drying
10
AX
Bioethanol
DDGS

Fig. 1



Ethanol fraction
$b_{I} = (\Delta x)_{I} \times (\Delta F)_{I}$
$b_{II} = (\Delta x)_{II} \times (\Delta F)_{II}$
$(\Delta x)_I$
$(\Delta x)_I$
x_{S1}
x_{D1}
x_{S2}
x_{D2}
x_{D3}
x_{S3}
I
II
III
IV
V
VI
$(\Delta F)_I$
$(\Delta F)_{II}$
Flow rate
SCC
DCC
(a)
Ethanol fraction
b_{IV}
b_{III}
Ethanol
(b)
Ethanol fraction
SCC
DCC
SCC (initial)
F_{PR}
Flow rate
(c)
Ethanol fraction
Pinched
Initial
Pinch
x_P
Ethanol surplus
(d)

Fig. 2

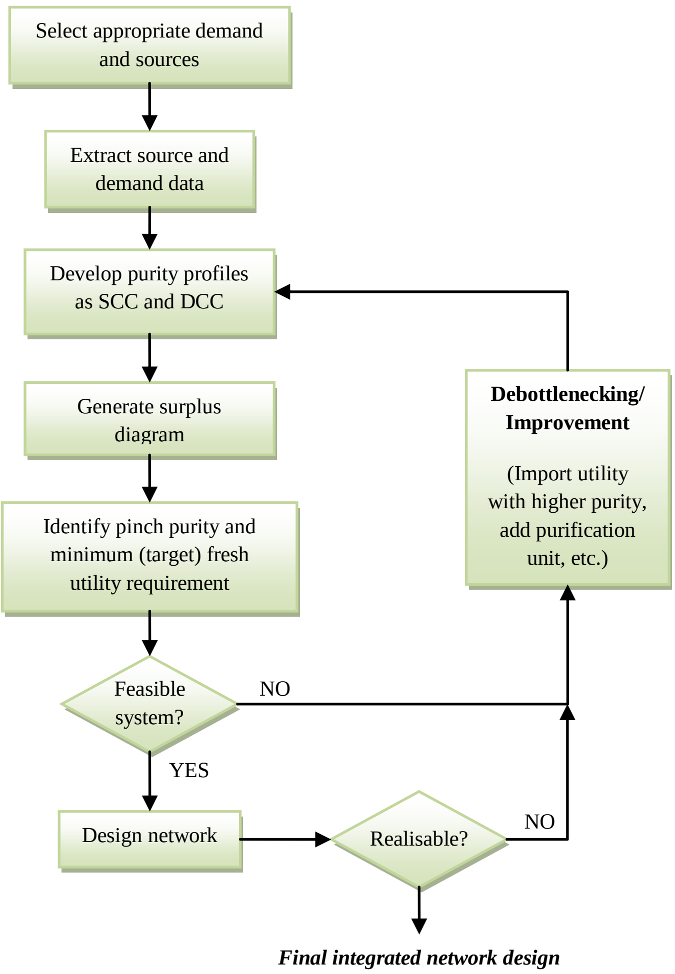

Select appropriate demand and sources
Extract source and demand data
Develop purity profiles as SCC and DCC
Generate surplus diagram
Identify pinch purity and minimum (target) fresh utility requirement
Feasible system?
NO
YES
Design network
Realisable?
NO
Debottlenecking/ Improvement
(Import utility with higher purity, add purification unit, etc.)
Final integrated network design

Fig. 3

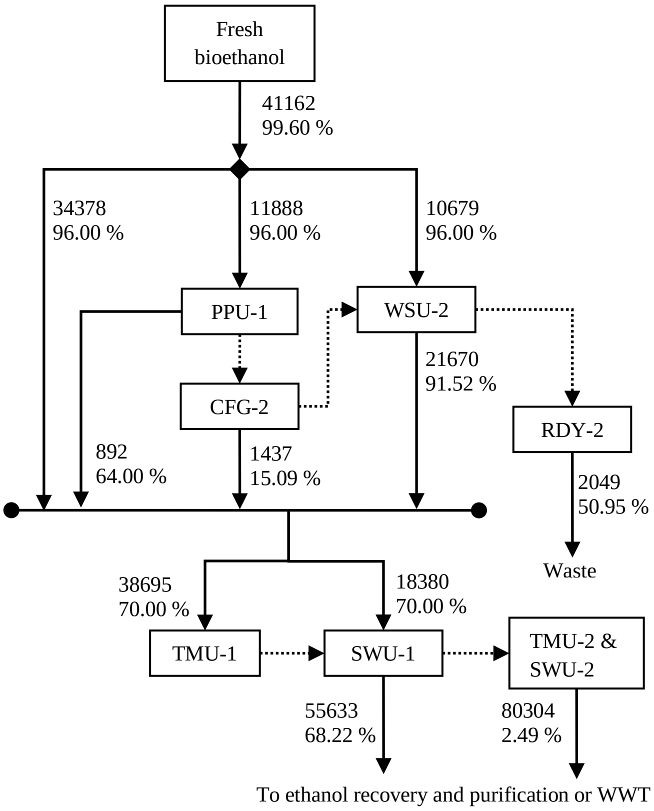
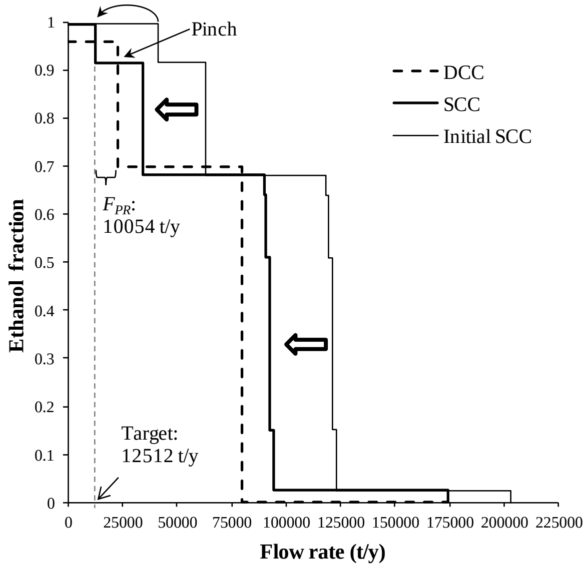
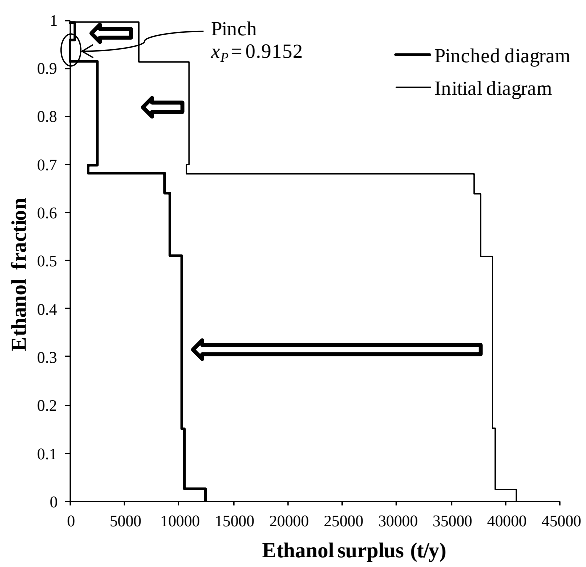

Fresh bioethanol
41162
99.60 %
34378
96.00 %
11888
96.00 %
10679
96.00 %
PPU-1
WSU-2
CFG-2
21670
91.52 %
RDY-2
892
64.00 %
1437
15.09 %
2049
50.95 %
Waste
38695
70.00 %
18380
70.00 %
TMU-1
SWU-1
TMU-2 & SWU-2
55633
68.22 %
80304
2.49 %
To ethanol recovery and purification or WWT

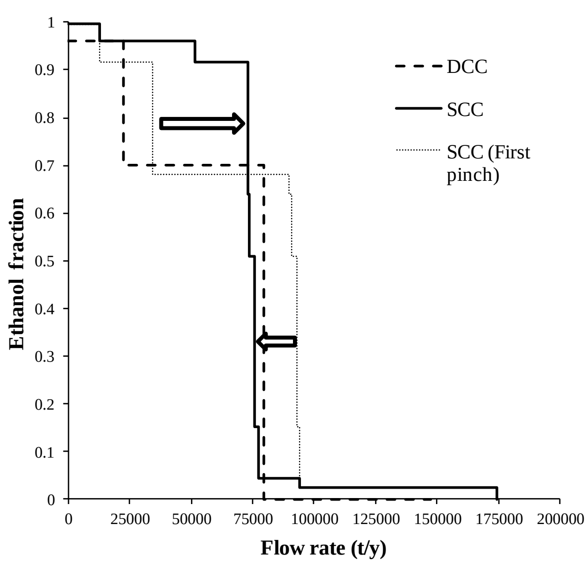
Fig. 4


Pinch
DCC
SCC
Initial SCC
F_{PR}:
10054 t/y
Target:
12512 t/y
Ethanol fraction
Flow rate (t/y)

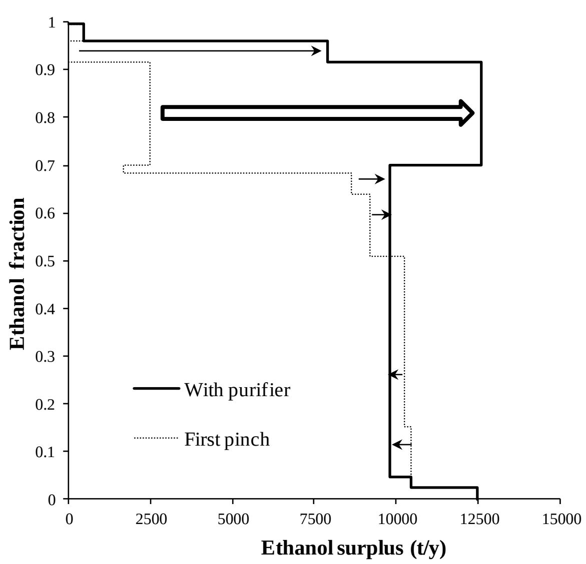
(a)


Pinch
x_P = 0.9152
Pinched diagram
Initial diagram
Ethanol fraction
Ethanol surplus (t/y)

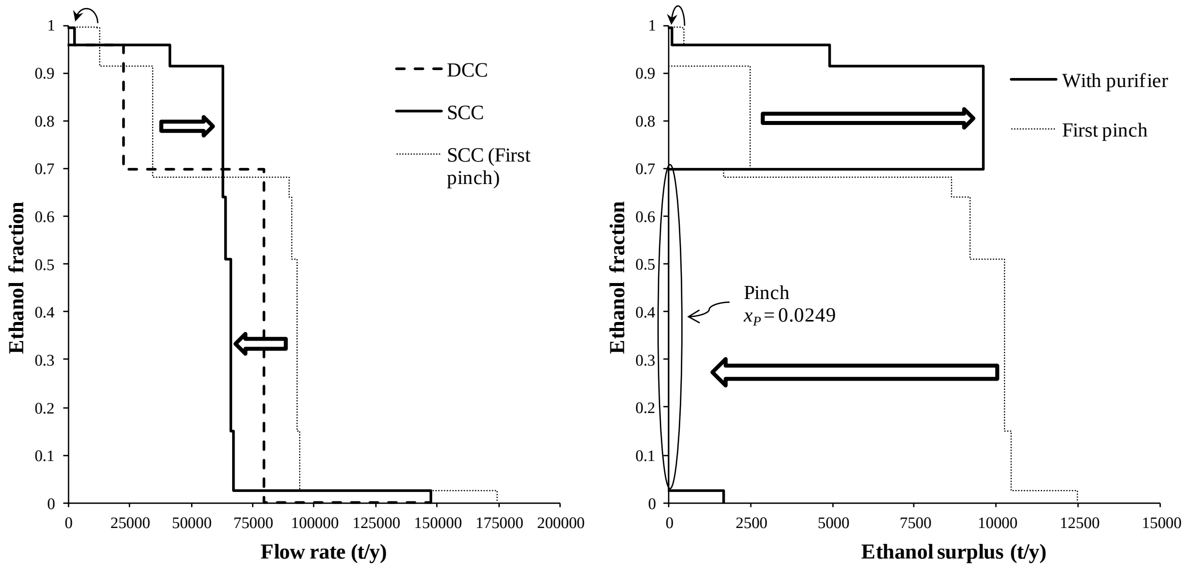
(b)


DCC
SCC
SCC (First pinch)
Ethanol fraction
Flow rate (t/y)

(c)


With purifier
First pinch
Ethanol fraction
Ethanol surplus (t/y)

(d)


Ethanol fraction
Flow rate (t/y)
DCC
SCC
SCC (First pinch)
Ethanol surplus (t/y)
With purifier
First pinch
Pinch
$x_P = 0.0249$

(e) (f)

Fig 5

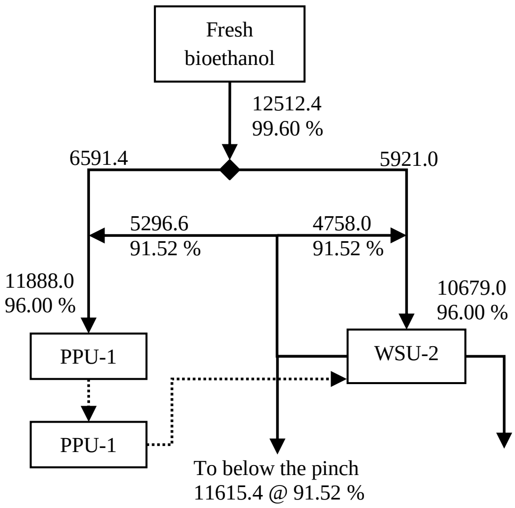

Fresh bioethanol
12512.4
99.60 %
6591.4
5921.0
5296.6
91.52 %
4758.0
91.52 %
11888.0
96.00 %
10679.0
96.00 %
PPU-1
WSU-2
PPU-1
To below the pinch
11615.4 @ 91.52 %

Fig. 6

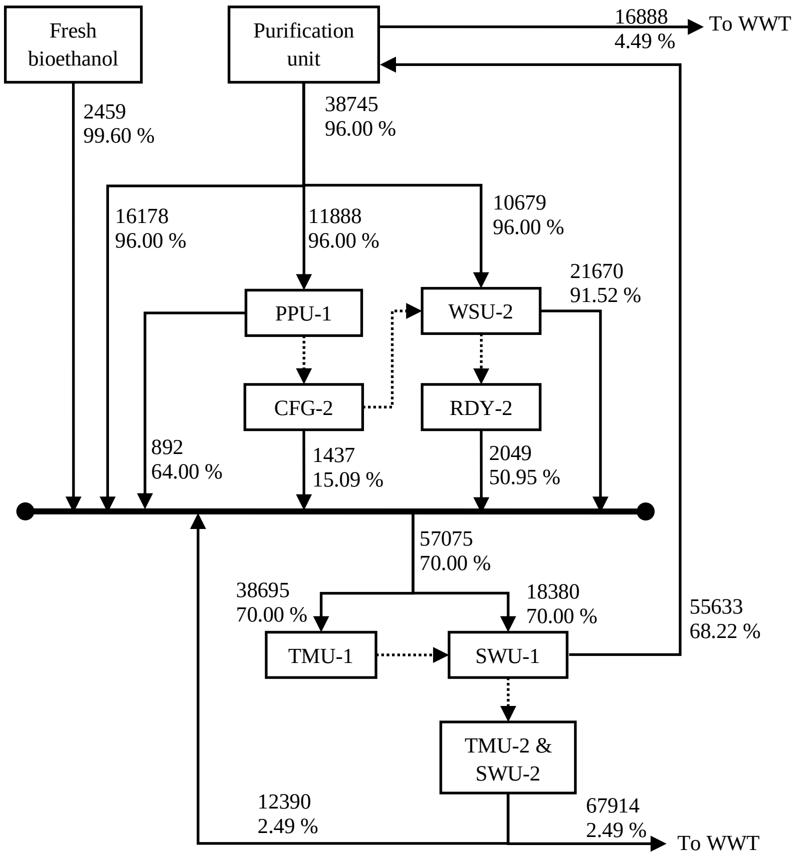


Fig. 7 The bioethanol exchange network design after integrating a purification unit. Flow rates in t/y.