Conceptual design of integrated production of arabinoxylan products using bioethanol pinch analysis

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Abstract

This paper presents the application of mass pinch analysis for integration of bioethanol streams in biorefineries. A new case study is presented, comprising a wheat-based bioethanol production process retrofitted to produce arabinoxylan oligosaccharides (AXOS) precipitated using ethanol at different concentrations, in addition to the co-production of arabinoxylan (AX), giving more ethanolic streams and greater scope for integration. The application of mass pinch analysis reduced the amount of fresh, high purity bioethanol by up to 95% compared to a non-integrated system. The work illustrates how major advances in biorefineries could be achieved by retrofitting existing biorefineries using well-established process integration techniques for integrated value-added production. The work also highlights the potential to co-produce a range of AX and AXOS fractions, made feasible through the judicious integration of the ethanolic

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streams, and offering the potential for a new class of food ingredients arising from the opportunity afforded from integration with bioethanol production.

Keywords: mass pinch analysis, bioethanol, biorefinery, process integration, arabinoxylan, arabinoxylan oligosaccharides, graded ethanolic precipitation

Nomenclature

Sets

I	sources
J	demands
SAP	subset of I denoting sources above the pinch
SBP	subset of I denoting sources below the pinch
p	purifier unit

Parameters

F_i^{target}	Target for minimum flow rate of fresh source i = fresh bioethanol input
F_j^D	Total stream flow rate required by demand j
F_i^S	Total stream flow rate available from source i
x_i, x_j	Ethanol purity in mass fraction in source i or demand j
R	Ethanol recovery in purifier
x_d	Specified ethanol purity of the distillate from the purifier

Variables

F_{ij}	Flow rate of a stream from source i to demand j

41 F_p^S Flow rate of the purified source stream from the purifier

42

1. Introduction

Biorefineries are processing systems that integrate chemical (e.g. hydrolysis, esterification), thermochemical (e.g. gasification, pyrolysis), mechanical (e.g. comminution, filtration) and biochemical (e.g. fermentation) processes to convert biomass into multiple products such as power, biofuels, food ingredients or bio-chemicals (Sadhukhan et al., 2014; Ruiz et al., 2017). However oil refineries, from which biorefineries take their inspiration and with which biorefineries compete, are clearly several steps ahead concerning the sophistication of their technology and of their use of process integration for enhanced efficiency Lynd et al. (2009). Oil refineries have been operating since the early 1900s and have had more than a century to perfect their technology. Moreover, oil refineries produce a very large range of co-products which enhance their economies and add considerable complexity. This complexity is crucial because it gives scope to create a highly integrated and optimised plant and thus become more flexible and profitable. While there are a lot of oil refineries, there are still few large biorefineries featuring a sufficient range of co-products and sufficiently complex operations to allow the efficiencies of extensive process integration to be exploited.

As in oil refineries, process integration is playing a key role in biorefineries and will become more prominent as they develop as multi-feedstock and multiproduct systems in order to become more competitive (Martinez-Hernandez et al., 2014). After the usefulness of energy pinch analysis had been demonstrated in oil refineries and other industries (Linnhoff, 1993), several mass pinch developments followed for water, hydrogen and carbon emissions, as reviewed in Klemes et al. (2013) and Foo et al. (2012). A unified targeting algorithm for diverse integration problems has also significantly contributed to the field of process integration (Shenoy, 2011). Other

integration methods have been developed for biorefineries (Ng, 2010; Phan and El-Halwagi, 2012; Ponce-Ortega, 2012; Ng et al., 2013; Tang et al., 2013). The latest developments in process integration for biorefineries can be found in Ng et al. (2016). While mathematical methods allow screening of alternatives and creation of grass-root biorefinery designs, approaches that provide insight into the interactions between processes and co-products that could assist in retrofitting existing biorefineries are also needed at the initial stage of biorefinery development.

Bioethanol production is driving much of the development of biorefineries globally and heat integration opportunities are already being exploited (Kravanja et al., 2013; Cardona et al., 2007). The major co-product of bioethanol production from cereals is the distillers dried grain with solubles (DDGS), a low value product mainly sold as animal feed. Lately, studies have focused on the production of arabinoxylans (AX), a component of the wheat bran, as an additional higher value co-product that could have potential in both food and non-food industries (Du et al., 2009; Rosa-Sibakov et al., 2015; Aguedo et al., 2015; Jacquemin et al., 2015). As AX extraction requires a large amount of ethanol to precipitate the AX and perform the several washing steps, the co-production of AX within a biorefinery producing bioethanol appears to be a particularly interesting match, allowing new opportunities for integration as well as offering a high value co-product (Sadhukhan et al., 2008; Misailidis et al., 2009). Targeting AX as a co-product has the advantage that the raw material, bran, is already present in commercially operating bioethanol plants; this is advantageous compared with, for example, possible lignocellulosic raw materials that are not already accessible within existing commercial bioprocesses. The same reasoning would apply to AX from

sugarcane bagasse, which is already within processing plants converting sugar to ethanol and could similarly be targeted as a source for AX-based co-products.

Hemicelluloses are the second most abundant plant materials after celluloses, and are closely associated with celluloses and lignin to form structural components of many plants (Peng et al., 2009; Broekaert et al., 2011). Arabinoxylans are the major hemicelluloses of cereal grains, sometimes called pentosans as they are comprised of five-carbon sugars xylose and arabinose, the former making up the linear backbone, with arabinose singly or doubly substituted as side units. They are the major polymers of cell walls in wheat grains, comprising around 2.2% of wheat flour and up to 38-55% of the outer tissues of the wheat grain and 20% of the aleurone layer (Saulnier et al., 2007). The physico-chemical characteristics and functional properties of AX, such as water solubility, viscosity, gelling and hydration, depend *inter alia* on their molecular weight, chain conformation and A/X ratio. In general the A/X ratio in the outer layers is higher (around 1) than in the endosperm (around 0.5), while AX in the aleurone layer has a lower A/X ratio of 0.3-0.4, reflecting their different physiological purposes in the seed, and affecting their technological performance in cereal-based products and their physiological performance as dietary fibre (Saulnier at al., 2007).

Thus the properties of potential AX co-products of a biorefinery depend on the part of the wheat grain from which they originate. In the context of a biorefinery, it is the bran material (comprising the outer layers plus aleurone) that is of most relevance as a potential source of AX (Aguedo et al., 2015). As noted above, in current bioethanol plants, the bran material forms part of the DDGS animal feed co-product. However, AX is dietary fibre. In terms of human nutrition, increasing consumption of dietary fibre is a desirable goal for improving the health of the population and reducing the

114 "diseases of Western civilisation" (Fisher and Berry, 1980) such as heart disease, Type
115 2 diabetes and colon cancer. However, for animal feed nutrition, consumption of fibre
116 is undesirable as it is nutritionally inert and reduces rates of growth. The opportunity to
117 extract AX in a biorefinery in order to remove it from the animal feed chain, where it is
118 not needed, and divert it into the human food chain, where it is needed, represents a
119 synergistic win-win situation.

120 Arabinoxylans therefore represent an important opportunity for wheat biorefineries to
121 introduce new product streams of commercial interest that would benefit human
122 nutrition (as well as being functional ingredients for both food and non-food products)
123 while also enhancing animal feed by reducing its fibre content. AX-based products
124 have potential for use in a wide range of food and non-food applications including film
125 forming, thickeners, emulsifiers, stabilisers and binders in the food, pharmaceutical and
126 cosmetic industries (Aguedo et al., 2015; Jacquemin et al., 2015).

127 However, as Jacquemin et al. (2015) note, "the problems [of] alcohol recycling (costs
128 and security) hinder the industrial development of xylan production." Addressing the
129 cost issue of ethanol usage for AX production is key to successfully bringing new AX-
130 based products to market and is the focus of the current paper (however the security
131 issue is outside the scope of this paper).

132 Martinez-Hernandez et al. (2013) applied mass pinch analysis for integration of
133 bioethanol streams in biorefineries producing ethanol and also utilising ethanol as a
134 working fluid within the process to extract AX. This highlighted that within a
135 biorefinery there may be product streams that are also potentially working fluids (e.g.
136 solvents and precipitants as in the case of ethanol, chemical raw materials and fuels for
137 utility generation) and how the resulting complexity can be used to generate integrated

biorefinery designs. This work was followed by an algebraic method for designing the bioethanol network (Shenoy and Shenoy, 2014). This demonstrates the advances in process integration strategies that could be achieved by retrofitting existing infrastructures in sugar and cereal biorefineries, with a view to transferring these strategies to lignocellulosic biorefineries once these become commercially available. Meanwhile, AX co-products offer attractive new revenue streams for current bioethanol plants. They also represent an opportunity for synergistic benefits for the food industry and for non-food applications arising from the recent emergence of biorefineries, in offering functional ingredients and materials not currently commercially available, but which could be commercially viable in the context of an integrated biorefinery.

In the context of the general interest in creating commercial sources of arabinoxylan products with a range of functional properties for food and non-food uses, there is a specific interest around arabinoxylan-oligosaccharides (AXOS). AXOS, along with XOS (xylo-oligosaccharides), exert prebiotic effects in in the colon of humans and animals through selective stimulation of beneficial intestinal microbiota (Swennen et al., 2006; Grootaert et al., 2007; Broekaert et al., 2011). AXOS can be co-extracted with AX or can be produced by hydrolysis of AX via hydrothermal and/or enzymatic treatments (Aguedo et al., 2015). Oligosaccharides are generally considered to have degrees of polymerisation (DP) in the range 3-10, although Aguedo et al. (2015) considered the AXOS fraction to comprise the DP range 2-20. As noted above, AX is recovered through precipitation in ethanol, typically at 65% concentration (Hollmann and Lindhauer, 2005). The smaller AXOS molecules precipitate at higher ethanol concentrations (Swennen et al., 2006; Bian et al., 2010), which is more costly, hence making efficient ethanol use through integration even more pressing. Swennen et al.

(2006), for example, used graded ethanolic precipitation to produce AX and AXOS fractions for ethanol concentrations increasing from 20 to 90% v/v in 10% increments. At 40-50% ethanol concentration, the average DP of the precipitated fractions was 59, decreasing to 30, 16, 10 and 4 for 50-60%, 60-70%, 70-80% and 80-90% ethanol, respectively. Therefore a biorefinery producing a range of AX and AXOS products would entail a range of ethanol streams of varying concentration, extending the scope for integration and its importance for economic operation.

With this context, the present work further demonstrates the usefulness of mass pinch analysis and combines the targeting and insights obtained with a linear programming approach for designing a bioethanol network arising from co-production of a range of AX and AXOS products through fractional ethanolic precipitation. A new case study is developed in order to demonstrate the key role of process integration approaches in the design of integrated biorefineries for retrofitting purposes. The case study involves the co-production of bioethanol, DDGS and AX with the addition of AXOS precipitated at higher ethanol concentrations, increasing the number and variety of ethanolic streams and hence the complexity and scope for process integration.

2. Materials and methods

2.1.Process integration using mass pinch analysis

The scope to treat ethanol not just as a product of a biorefinery but as a process fluid, with varying requirements for ethanol purity, allowed a new application of mass pinch analysis for integration of bioethanol in a scenario in which AX was co-produced in a wheat biorefinery, with ethanol used to precipitate the AX and to wash various feedstock streams (Martinez-Hernandez et al., 2013). This is an example of how a process integration methodology can be useful for the unique situation of biorefineries

and the opportunities they present. The current work extends the scope by adding ethanolic streams required to allow precipitation of AXOS fractions as additional high value co-products, using higher ethanol concentration streams.

The methodology can be summarised as follows (Martinez-Hernandez et al., 2013):

1. The source and demand streams are combined in decreasing order of their purities into the source composite curve (SCC) and the demand composite curve (DCC). Then, the SCC and the DCC are plotted as functions of the cumulative flow rate of the streams. The areas between the SCC and the DCC represent the bioethanol surpluses (if the SCC is above the DCC) and deficits (if the DCC is above the SCC) in the system.
2. The surpluses or deficits are plotted as functions of the flow rate to give the surplus diagram which helps to find the amount of bioethanol that can be reduced.
3. The flow rate of the highest purity ethanol supply is reduced until there is one place in the bioethanol surplus diagram where the bioethanol surplus is equal to zero. When the bioethanol surplus touches the *y*-axis, then a pinch has been established which sets the minimum bioethanol consumption in the network.
4. As in other pinch analysis techniques, the pinch point provides a starting point for design and divides the network into below and above the pinch, such that each section can be designed separately.
5. Further reduction can be achieved by integrating a purifier to treat a stream below the pinch to produce a stream of purity higher than the purity at the pinch point (the pinch purity). A new target can be established for minimum fresh

bioethanol flow rate by following the steps 1-4, which will result in a new design.

The methodology also provides the following guidelines for design:

- Do not directly exchange bioethanol streams across the pinch.
- 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, i.e. purify a stream below the pinch to a purity above the pinch.

Despite the usefulness of the methodology, the authors did not provide a method for designing the bioethanol network itself; an algorithmic method to complement the graphically-based approach to assist the design of bioethanol networks was presented by Shenoy and Shenoy (2014). Alternatively, once the targets are known, a more direct design using a mathematical approach can be used. A method combining the graphical pinch analysis with simple linear programming (LP) is used in the present work for designing a bioethanol network.

2.2. Designing bioethanol networks

The problem of designing a bioethanol network can be stated as follows:

Given a set of bioethanol sources and demands, find the flow rates for the optimal design that achieves the target for the minimum fresh bioethanol input while observing the constraints given by the mass pinch analysis and process constraints.

Figure 1 shows a generic superstructure showing all the possible connections of the processes to be integrated in a bioethanol network. Based on this, the task is to find the connectivity indicated by the flow rates (F_{ij}) of each possible connection between

sources (*i*=1 to *I)* and demands *(j*=1 to *J)*, so as to minimise an objective function. In this case, the target for minimum fresh bioethanol (F_i^{target}) is known from the graphical pinch analysis. The design that is able to achieve this target can be found by formulating and solving a linear programming (LP) problem as follows. This approach has been proved useful for designing water (Hallale, 2002) and hydrogen networks (Hallale and Liu, 2001) and is applied here for designing the bioethanol network.

Although there are various sources of ethanol, it is the fresh high purity bioethanol stream that needs to be minimised. Therefore, the objective function can be formulated for the flow rate of a fresh input (*i*= fresh high purity stream) as:

Minimise

$$\sum_{j \in J} F_{ij} - F_i^{target} \quad , \quad i = fresh\ input \qquad \text{Equation 1}$$

F_{ij} is the flowrate of bioethanol source *i* to demand *j*. In the objective function only the flows from *i*=fresh input to the demands *j* is required.

Subject to:

Supply of total stream demand (F_j^D)

$$\sum_{i \in I} F_{ij} = F_j^D \quad , \quad \forall\, j \in J \qquad \text{Equation 2}$$

Supply of total bioethanol demand at required purity (x_j) from a mix of sources at their corresponding purities (x_i)

$$\sum_{i \in I} F_{ij} x_i = F_j^D x_j \quad , \qquad \forall\, j \in J \qquad \text{Equation 3}$$

Total stream flow rate availability of the sources (F_i^S)

$$\sum_{j \in J} F_{ij} \leq F_i^S \quad , \qquad \forall\, i \in I \qquad \text{Equation 4}$$

Note that required purities by the demands are obtained by mixing streams of higher and lower purities and this is where cross-pinch transfer could arise. However, this is avoided by specifying the target for minimum fresh bioethanol at the pinch point. This is enough to meet the first guideline of the mass pinch analysis, because any mixing of streams across the pinch would automatically lead to a fresh bioethanol flow rate higher than the target; therefore such a match would not be selected in the solution.

When a purifier is introduced into the network, additional constraints are needed as shown in Equations 5 and 6:

Avoid purifying streams above the pinch (SAP)

$$\sum_{i \in SAP} F_{ip} = 0 \ , \qquad p = purifier \qquad \text{Equation 5}$$

Mass balance around the purifier given a recovery (R) and purity desired (x_d) using only streams below the pinch (SBP):

$$R \sum_{i \in SBP} F_{ip} x_i = F_p^S x_d \ , \qquad p = purifier \qquad \text{Equation 6}$$

The purified stream is then included in the set of sources I to design the network. The difference then makes the flow rate (F_{pw}) that goes from the purifier to wastewater treatment (WWT) as shown in Equation 7.

$$F_{pj} = \sum_{i=\in SBP} F_{ip} - F_p^S \ , \qquad p = purifier; j = WWT \qquad \text{Equation 7}$$

Additional process constraints to restrict undesirable connections due to process or economic reasons can also be included depending on the case study. The simple models are solved using the Solver facility in Microsoft Excel® using the Simplex LP option. Note that it is not the intention of this paper to present a complex modelling exercise, rather to illustrate how insight-based tools for process integration can support the development of more advanced biorefinery designs. The methodology is illustrated in the case study presented in the following section.

3. Results and Discussion – Case study on retrofitting bioethanol biorefinery with AX and AXOS co-production

The case study develops process integration in a wheat-based biorefinery where a conventional bioethanol production process is retrofitted to produce arabinoxylan (AX) and arabinoxylan oligosaccharides (AXOS) as co-products, in addition to bioethanol and DDGS. The extraction of AX based on Hollmann and Lindhauer's process (Hollmann and Lindhauer, 2005) has previously shown potential to improve the economics of bioethanol production while introducing a new class of ingredients to the food industry (Sadhukhan et al., 2008; Misailidis et al., 2009). Other studies have shown that AXOS is also a promising prebiotic product that can be recovered by precipitation of the low molecular weight materials present in the permeate after extraction of AX, using graded ethanolic precipitation (Swennen et al., 2006). The approach is also relevant to AX and AXOS production from other sources; for example,

283 Peng et al. (2009) applied graded ethanolic precipitation to recover hemicelulose
284 fractions from sugarcane bagasse, while Bian et al. (2010) similarly fractionated
285 hemicelluloses from *Caragana korshinskii* (a grassland and desert shrub species from
286 the northwest of China and Mongolia).

287 As the precipitation of smaller molecules requires higher ethanol purity and the
288 precipitation of the low concentrated permeate would require an enormous amount of
289 ethanol, co-production of AXOS had not been considered for retrofitting and integration
290 in previous works. Its inclusion in the current work adds new high purity ethanol flows
291 to the system and allows a more extensive case study. From a commercial perspective,
292 economic production of arabinoxylan-based products is likely to be achieved not by
293 targeting a single product of a specific molecular weight range, but by producing a
294 range of AX products of varying molecular weights, including lower molecular weight
295 AXOS fractions, and with different functionalities and markets. Production of a range
296 of AX and AXOS fractions could be achieved by fractional ethanolic precipitation,
297 entailing use of ethanol at different concentrations, hence making the optimisation via
298 mass pinch analysis critical to the successful operation of the process.

299 Figure 2 shows the biorefinery process analysed in this case study. In order to extend the
300 process studied in Martinez-Hernandez et al. (2013), the additional process units
301 considered in the present work are briefly described as follows. After using 65% ethanol
302 to precipitate AX, the liquid left over is mixed with a 99.6% ethanol stream to bring
303 everything to a concentration of 90% in order to precipitate the AX(OS) that was not
304 precipitated during the 65% ethanol precipitation. This will increase AX recovery and
305 add new streams to consider for the mass pinch analysis. Also in this scenario, after the
306 first ultrafiltration (UF) using a membrane with a molecular weight cut-off of 10 kDa, a

second ultrafiltration is performed. The permeate of this first ultrafiltration is passed through a second UF using a membrane with a molecular weight cut-off of 3 kDa. The retentate of the second UF is then precipitated using 90% ethanol. This scenario offers the precipitation of the smaller molecules which leads to a biorefinery producing two different co-products, as well as adding more ethanol streams to the process and hence complexity to the biorefinery and scope for integration. The mass pinch analysis method was applied followed by the LP-based design presented in section 2.

3.1.Bioethanol network without purifier

The sources and demands are identified in Figure 2 for the initial bioethanol network without an additional ethanol purifier. Data extracted is presented in Table 1.

Using data in Table 1, the bioethanol composite curves and surplus diagram were generated and are shown in Figure 3. Figure 3a shows that the fresh bioethanol supply can be reduced until a pinch occurs in Figure 3b at a purity of 89.78% for a flowrate of 37,230 t/y. This provides the target for the minimum fresh ethanol use for a feasible exchange network, reducing by 69,499 t/y the initial 106,729 t/y of 99.6% bioethanol provided by the main process. This means a 65% reduction of fresh bioethanol use, compared with an unintegrated system.

Based on the results from the graphical analysis, the solution of the LP problem using Equations 1 to 4 gives the bioethanol network design shown in Figure 4. Note that no constraint was added to restrict the combination of streams containing impurities that might not be desirable in a certain process unit or product. Also, note that any excess of bioethanol sources is assumed to go to a wastewater treatment process as these will generally be the ones with the lowest purity (sending them back to the ethanol

distillation columns would require additional distillation capacity). Table 2 summarises the flow rates of the resulting network design, from the sources to the demand processes as well as to treatment. There is a total of 118,723 t/y of streams sent to treatment, which indicates that there are still significant amounts of ethanol that could be saved in the bioethanol network. An option is to add a purification unit to upgrade some of the lower purity streams to make more ethanol available at a higher purity and so to further reduce the amount of fresh bioethanol supply. This option is explored in the next section.

3.2. Bioethanol network with purifier

This scenario explores the introduction of a new purifier unit, in addition to the one in the main bioethanol production process. The recycling of diluted ethanol streams to the main production would require additional distillation capacity which may not be available; a separate purifier just to deal with the streams in the AX section provides more process flexibility, allowing control over ensuring purification occurs across the pinch. The purified stream and the bottom streams from the purifier are added to the network. A constraint is added to the LP formulation to avoid exchanging the bottom stream, which may contain undesired purities, and is used together with constraints in Equation 5 and 6. The mass balance constraint in Equation 6 assumes an ethanol recovery of 98% with a purity of 96%. Although the pinch point does not tell us which streams to purify, the decision is left to the LP problem with the restriction of purifying only those streams below the pinch purity and omitting the stream with the lowest purity for technical and economic feasibility reasons.

352 The starting point is the bioethanol network design from the case without purifier which
353 requires now only 32,230 t/y of fresh bioethanol input. In this case the target was set to
354 zero so that the LP problem provides the final bioethanol network design while
355 minimising the total fresh bioethanol input. However, the value of the graphical pinch
356 analysis was already demonstrated in the previous section and provided the basis for the
357 design of the bioethanol network without purifier.

358 Figure 5 shows the bioethanol network design after the integration of the new purifier
359 unit. Note that the three possible sources to purify (streams from WSU-2, RDY-2 and
360 SWU-1) are sent to the purifier in order to minimise the fresh bioethanol input. The new
361 bioethanol availability in the system now allows decreasing the pinch purity and further
362 exchange between sources and demands. The purifier itself now supplies completely the
363 three precipitation units and partially the washing and sieving unit WSU-2. The bottoms
364 stream from the purifier is sent to wastewater treatment. Table 3 summarises the flow
365 rates of the resulting network design. Note how the fresh bioethanol use is further
366 reduced to 5678 t/y. This translates into 85% reduction with respect to the network
367 without purifier, and an overall 95% reduction from the initial 106,729 t/y. The amount
368 of streams going to treatment is also reduced by about 27% with respect to the design
369 without the purifier. This means there are strong incentives to further investigate the
370 possibilities for retrofitting a wheat-based biorefinery with additional processes
371 integrated in the bioethanol network.

372 A thorough techno-economic analysis is worth investigating once all the individual
373 processes are well understood, optimised and scaled up from the current lab scale. The
374 introduction of the purifier was economically favourable for the co-production of AX,
375 as the capital cost was more than offset by the reduction in bioethanol losses, and gave

greater process flexibility (Martinez-Hernandez et al., 2013). Comparing the results from the previous study with the results after further retrofitting with AXOS co-production, fresh bioethanol use was reduced by similar percentages but more bioethanol is required in the retrofitted biorefinery because of the additional demands to precipitate the AXOS at very high ethanol concentrations, concentrations that would be infeasibly high from an economic perspective without process integration.

In summary, the current paper builds on the case study published previously by demonstrating the effectiveness of mass pinch analysis when the biorefinery is retrofitting for additional and more demanding co-production processes. Furthermore, this work applies a hybrid methodology that allows both targeting the minimum fresh bioethanol use and designing the integrated bioethanol network, as done previously for mass integration of water and hydrogen networks. The work provides practical guidance for how to make AXOS production commercially feasible in the context of producing a range of AX fractions of different functionality and for different markets.

4. Conclusions

Biorefineries need to exploit extensive integration to maximise efficiencies in energy and materials usage and be able to compete in this respect with oil refineries. As demonstrated in the current paper, mass pinch analysis can be effectively used in bioethanol-producing biorefineries retrofitted with additional processes for added value co-production of arabinoxylan and arabinoxylan oligosaccharide fractions. Mass pinch analysis allowed targeting the minimum amount of fresh, high purity bioethanol use, thus reducing losses of both bioethanol and revenue. This strengthens the technical and

economic bases by which a wheat-based biorefinery might be retrofitted to produce a range of arabinoxylan-based products.

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Figure captions

Figure 1 Generic superstructure for a bioethanol exchange network

Figure 2 Biorefinery process for the production of bioethanol, DDGS, arabinoxylan (AX) and arabinoxylan oligosaccharides (AXOS) showing the streams (dashed lines) to be integrated in a bioethanol network

Figure 3 Evolution of the bioethanol composite curves and surplus diagram. (a) Initial and pinched composite curves and the corresponding (b) bioethanol surplus diagram

Figure 4 Bioethanol network design without purifier

Figure 5 Bioethanol network design with purifier

509 **Tables**

510 **Table 1** Bioethanol demand and source data for initial bioethanol network

Process unit	Stream in Fig. 2	Flow rate (t/y)	Ethanol mass fraction	Cumulative flow (t/y)
Sources		F_i^S	x_i	
Fresh bioethanol		**106,729**	0.9960	70,000
WSU-3	12	2,142	0.9345	72,142
RDY-3	14	203	0.9345	72,345
WSU-4	18	8,558	0.9258	80,903
RDY-4	20	809	0.9258	81,712
PPU-2	9	16,065	0.9160	97,777
CFG-3	11	142	0.9137	97,919
CFG-4	17	568	0.8978	98,487
PPU-3	15	22,150	0.8978	120,637
WSU-2	6	19,285	0.8409	139,922
RDY-2	8	1,823	0.8409	141,746
SWU-1	3	55,633	0.6822	197,379
SWU-2	4	80,304	0.0249	277,683
Demands		F_j^D	x_j	
PPU-1	5	11,888	0.9600	11,888
PPU-2	10	16,389	0.9600	28,277
PPU-3	16	26,063	0.9600	54,340
WSU-2	7	9,503	0.9600	63,843
WSU-3	13	1,055	0.9600	64,898
WSU-4	19	4,216	0.9600	69,115
TMU-1	1	38,695	0.7000	107,809
SWU-1	2	18,380	0.7000	126,189

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513 **Table 2** Flow rates from sources (rows) to demands (columns) in the bioethanol

514 network design without purifier.

From/To	PPU-1	PPU-2	PPU-3	WSU-2	WSU-3	WSU-4	TMU-1	SWU-1	To treatment	Sum
Fresh bioethanol	5501	8461	14335	5914	580	2440	0	0	0	**37230**
WSU-3	2142	0	0	0	0	0	0	0	0	2142
RDY-3	203	0	0	0	0	0	0	0	0	203
WSU-4	4042	4516	0	0	0	0	0	0	0	8558
RDY-4	0	0	0	0	0	809	0	0	0	809
PPU-2	0	3412	11728	446	475	0	0	4	0	16065
CFG-3	0	0	0	142	0	0	0	0	0	142
CFG-4	0	0	0	0	0	0	0	568	0	568
PPU-3	0	0	0	3002	0	967	10195	7986	0	22150
WSU-2	0	0	0	0	0	0	19285	0	0	19285
RDY-2	0	0	0	0	0	0	1823	0	0	1823
SWU-1	0	0	0	0	0	0	0	7512	48,121	7512
SWU-2	0	0	0	0	0	0	7392	2310	70,602	9702
Sum	11888	16389	26063	9503	1055	4216	38695	18380	118,723	

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Table 3 Flow rates from source (rows) to demands (columns) in the bioethanol network design with purifier.

From/To	PPU-1	PPU-2	PPU-3	WSU-2	WSU-3	WSU-4	TMU-1	SWU-1	Purifier	To treatment	Sum
Fresh bioethanol	0	0	0	3110	514	2054	0	0	0		**5678**
WSU-3	0	0	0	2142	0	0	0	0	0	0	2142
RDY-3	0	0	0	203	0	0	0	0	0	0	203
WSU-4	0	0	0	1525	541	2162	0	4330	0	0	8558
RDY-4	0	0	0	0	0	0	809	0	0	0	809
PPU-2	0	0	0	0	0	0	6518	9547	0	0	16065
CFG-3	0	0	0	0	0	0	142	0	0	0	142
CFG-4	0	0	0	0	0	0	144	0	0	424	143.5
PPU-3	0	0	0	0	0	0	22150	0	0	0	22150
WSU-2	0	0	0	0	0	0	0	0	19285	0	19285
RDY-2	0	0	0	0	0	0	0	0	1823	0	1823
SWU-1	0	0	0	0	0	0	0	0	55633	0	55633
SWU-2	0	0	0	0	0	0	8933	4503	0	66,868	13436
DISTILLATE	11888	16389	26063	2523	0	0	0	0	0	0	56863
BOTTOMS										19,878	19,878
Sum	11888	16389	26063	9503	1055	4216	38695	18380	76741	87,171	

Figures

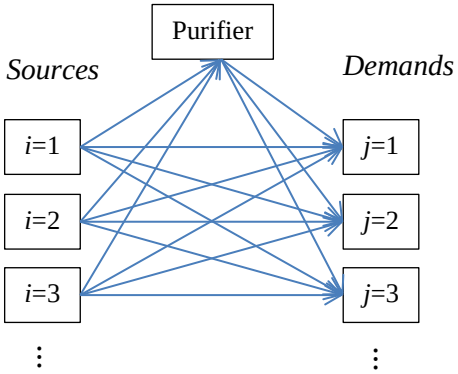

Figure 1

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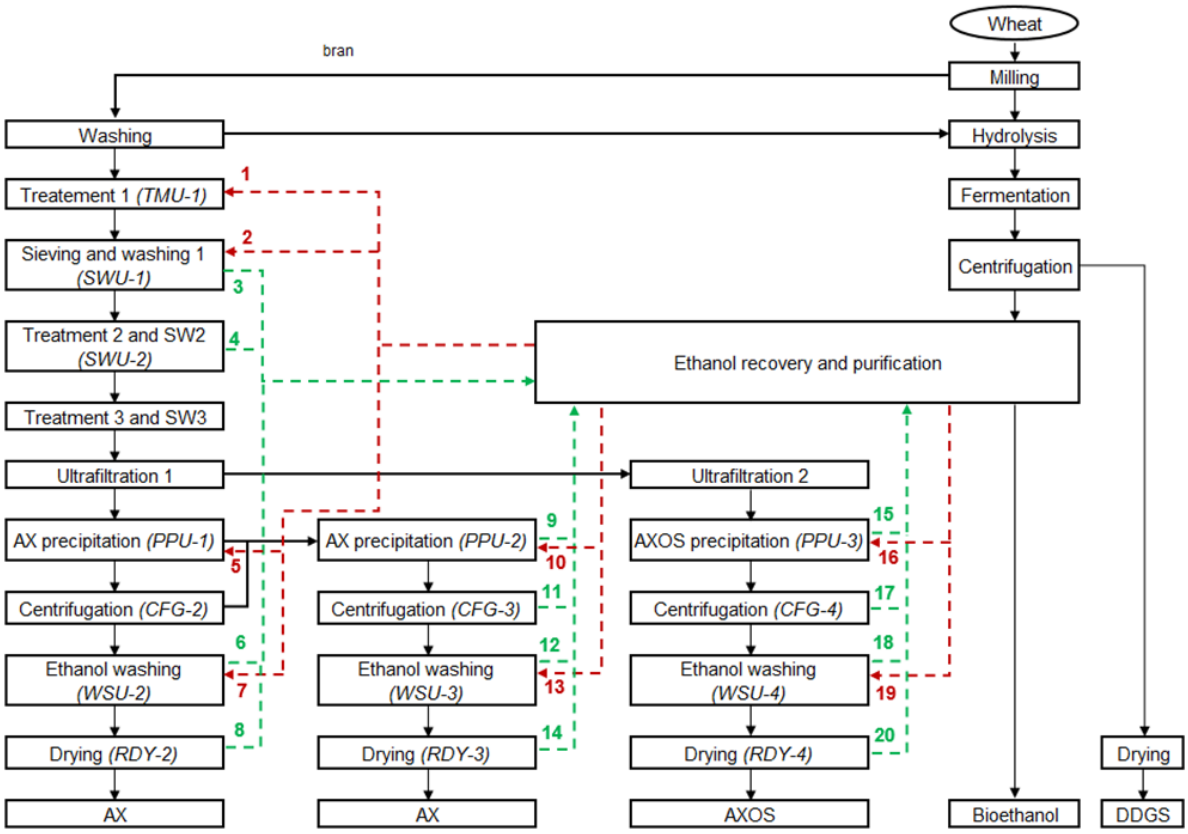

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538 **Figure 2**

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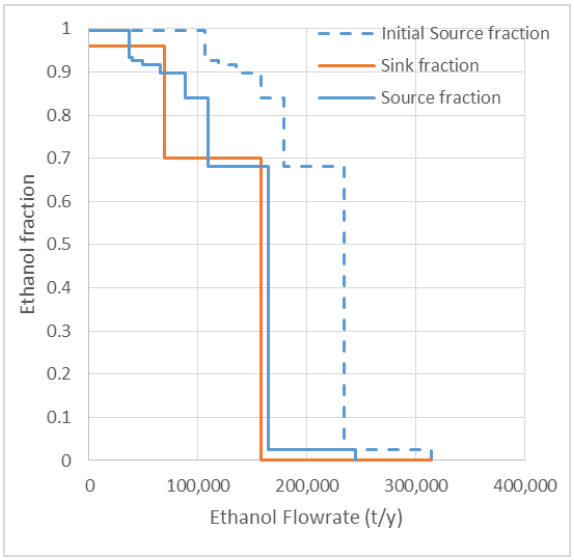
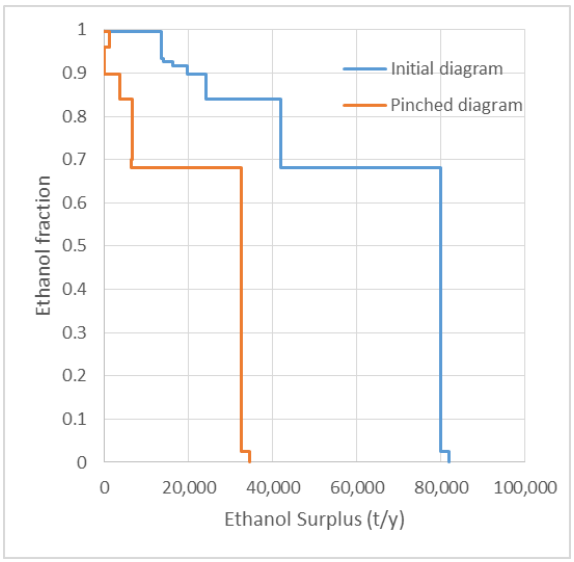

Initial Source fraction
Sink fraction
Source fraction
Ethanol fraction
Ethanol Flowrate (t/y)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
100,000
200,000
300,000
400,000

(a)


Initial diagram
Pinched diagram
Ethanol fraction
Ethanol Surplus (t/y)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
20,000
40,000
60,000
80,000
100,000

(b)

Figure 3

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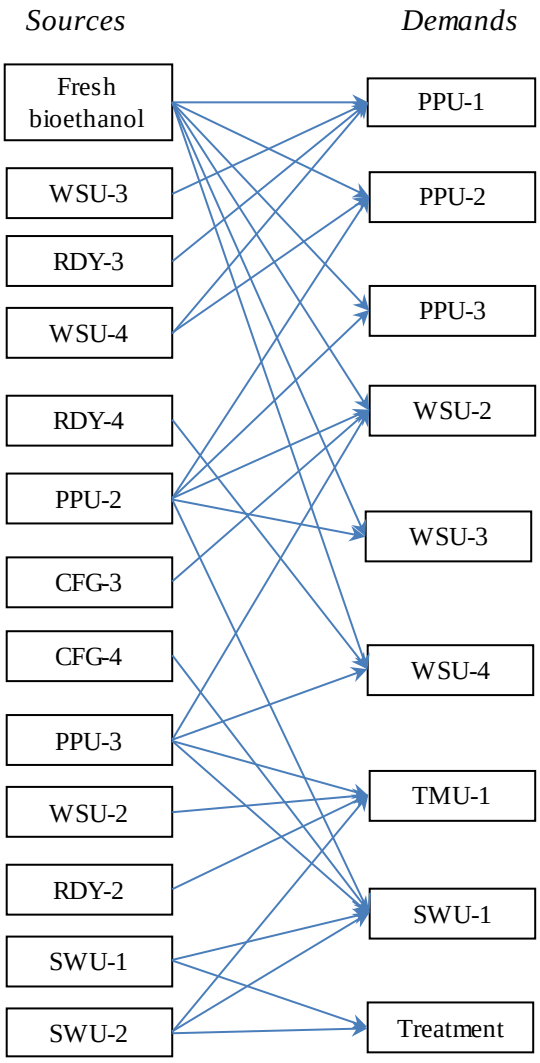

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548 **Figure 4**

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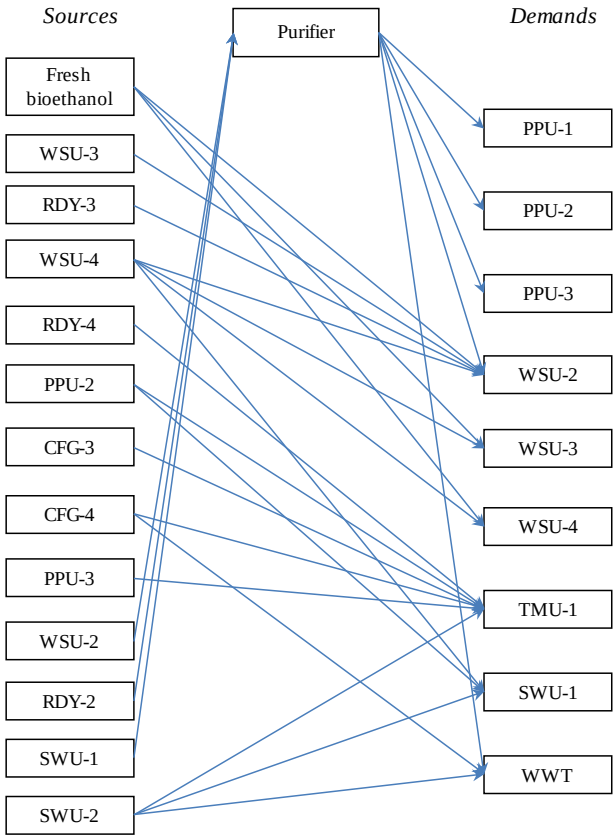

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552 **Figure 5**

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