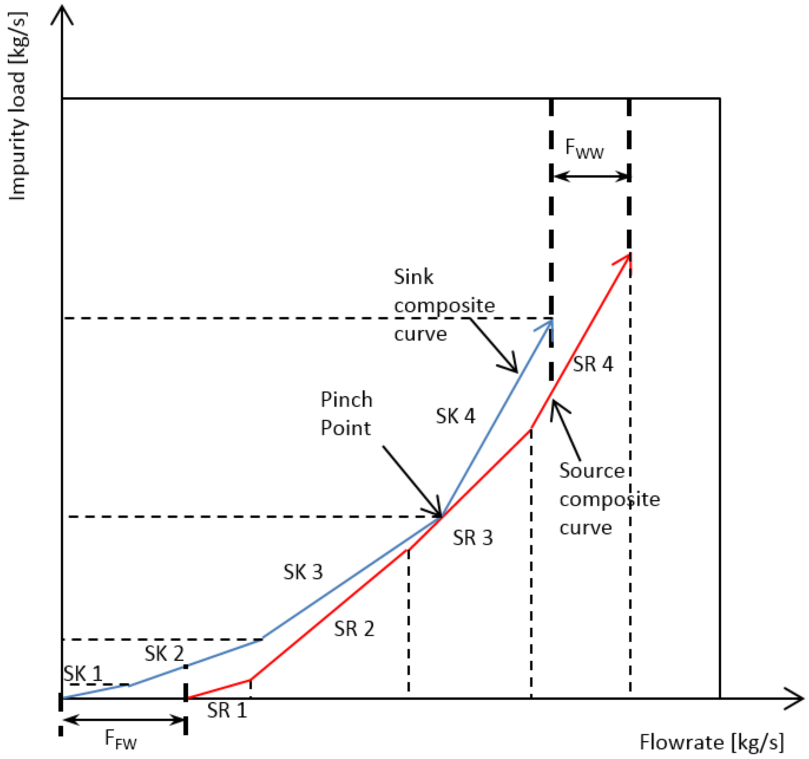


Water Pinch Analysis of a Lignocellulosic Ethanol Production Process

Development of an Excel application for multiple contaminants

Master's Thesis within the Innovative and Sustainable Chemical Engineering programme

ALEXANDRA ROLÉN

Department of Energy and Environment
Division of Industrial Energy Systems and Technologies
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2015

MASTER'S THESIS

Water Pinch Analysis of a Lignocellulosic Ethanol Production Process

Development of an Excel application for multiple contaminants

Master's Thesis within the Innovative and Sustainable Chemical Engineering programme

ALEXANDRA ROLÉN

SUPERVISORS:
Rickard Fornell
Elin Svensson

EXAMINER:
Simon Harvey

Department of Energy and Environment
Division of Industrial Energy Systems and Technologies
CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2015

Water Pinch Analysis of a Lignocellulosic Ethanol Production Process
Development of an Excel application for multiple contaminants
Master's Thesis within the Innovative and Sustainable Chemical Engineering programme
ALEXANDRA ROLÉN

Department of Energy and Environment
Division of Industrial Energy Systems and Technologies
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: + 46 (0)31-772 1000

Cover:
A Material Recovery Pinch Diagram, used to find the fresh water need in a process within Water Pinch Analysis.

Chalmers Reproservice
Göteborg, Sweden 2015

Water Pinch Analysis of a Lignocellulosic Ethanol Production Process
Development of an Excel application for multiple contaminants
Master's Thesis in the Innovative and Sustainable Chemical Engineering programme
ALEXANDRA ROLÉN
Department of Energy and Environment
Division of Industrial Energy Systems and Technologies
Chalmers University of Technology

SUMMARY

The renewable fuels industry is faced with significant challenges related to increasing concerns about global warming and environmental impact. Bio-ethanol is a renewable fuel produced in large quantities, and its productions needs to be improved continuously, in particularly with respect to fresh water usage and waste-water effluent. This thesis uses a methodology for establishing targets and identifying design configurations for reduced fresh water usage and waste water effluent for a lignocellulosic bio-ethanol production plant. One of the major challenges for this type of analysis is the ability to take multiple contaminants into account. The objective of this thesis was to develop an analysis tool that is able to handle up to three types of contaminants.

The work resulted in an application for Microsoft Excel that calculates targets for the minimum fresh water usage and waste water effluent release of a given process and proposes a water network configuration that is able to achieve these targets. The tool is based on methodologies proposed by Zhang et al. (2013). A simpler analysis and design tool with the capacity to handle a single contaminant only based on Foo (2013) was also developed for comparison purposes.

Trying to perform a water pinch analysis revealed problems related to setting reasonable constraints for the maximum level of contaminant concentrations that the process units in the ethanol production process can tolerate. The results presented should only be considered as preliminary suggestions for opportunities to improve this type of process. For the lignocellulosic bio-ethanol process investigated, the single contaminant analysis tool indicates that the fresh water usage could be decreased by up to 23%. However, when three different types of contaminant are considered in the analysis, the potential fresh water savings are reduced to 13%, which underlines the importance of considered multiple contaminants in the analysis. The potential savings presented for single contaminants are on the same order of magnitude as numbers found in the literature.

Key words: Water Pinch Analysis, WPA, Water Minimization, Multiple Contaminants, Lignocellulosic Ethanol Production, Biomass Ethanol

Vattenpinchanalys av en lignocellulosabaserad etanolproduktionsanläggning
Utveckling av en Excelapplikation för multipla kontaminenter.
Examensarbete inom mastersprogrammet Innovativ och Hållbar Kemiteknik
ALEXANDRA ROLÉN
Institutionen för Energi och Miljö
Avdelningen för Industriella energisystem och -tekniker
Chalmers tekniska högskola

SAMMANFATTNING

Industrin för förnyelsebara bränslen står inför en betydande utmaning vad gäller ökad oro för global uppvärmning och miljöpåverkan. Bioetanol är ett förnybart bränsle som produceras i stora mängder och dess produktion måste ständigt förbättras, särskilt vad gäller färskvattenanvändning och avloppsvattenhantering. Detta projekt använder en metodik för att bestämma målsättning och identifiera en nätverkskonfiguration för minskad färskvattenanvändning och avloppsvattensmängd för en lignocellulosabaserad bioetanol produktionsprocess. En av de största utmaningarna för den här typen av analys är möjligheten att ta hänsyn till multipla kontaminenter. Målet med detta projekt var att utveckla ett analysverktyg som kan hantera upp till tre typer av kontaminenter.

Arbetet resulterade i en applikation i Microsoft Excel som beräknar målsättningen för minsta möjliga färskvattensåtgång och avfallsvattenutsläpp från en given process och föreslår en vattennätverkskonfiguration som kan uppnå dessa målsättningar. Verktyget är baserat på metodiker föreslagna av Zhang et al. (2013). Ett enklare analys- och designverktyg med kapaciteten att hantera endast en kontaminent baserat på Foo (2013) utvecklades också för att kunna göra jämförelser.

Genom att försöka utföra en vattenpinchanalys upptäcktes problem med att sätta lämpliga gränsvärden för hur höga koncentrationer processenheterna i etanolproduktionsanläggningen kunde tåla. Resultaten skall endast ses som preliminära förslag på möjligheter att förbättra denna typ av process. För den undersökta lignocellulosabaserade bioetanolanläggningen, indikerar verktyget för en kontaminent att färskvattenanvändningen kan minskas med upp till 23%. Dock indikerar verktyget för tre kontaminenter att den potentiella färskvattenbesparingen sjunker till 13% vilket understryker betydelsen av att ta hänsyn till flera kontaminenter i analysen. De potentiella besparingarna för en kontaminent är nära samma storleksordning som värden från litteraturen.

Nyckelord: Vattenpinchanalys, WPA, Vattenminimering, Multipla kontaminenter, Lignocellulosa, Etanolproduktion, Bioetanol

Contents

Preface

In order to perform this master's thesis I have been supported by many people, but I would like to thank some of them extensively, especially my two supervisors. Doctor Rickard Fornell has always been there to answer my many questions and guide me when I have been doubtful in which direction to keep going. Doctor Elin Svensson was of great support during the first months of my work by helping me understand methodologies, programming and much more. Of course I would also like to give many thanks to my examiner Professor Simon Harvey who has been a great support to the progress of my project and encouraging me both during "fika"-talk and during meetings.

I would like to thank SP for the opportunity to perform my master's thesis for their company and Industrial BioTechnology at Chalmers for providing me with better knowledge about the case study process.

Last but not least, thanks to all the wonderful people at IEST at Chalmers who have been so caring and fun to be working around. I am so glad I was located at your department!

Göteborg June 2015

Alexandra Rolén

Notations

Letters

c	Concentration
F	Flowrate
m	Load

Subscripts

A	Contaminant A
B	Contaminant B
C	Contaminant C
f	Fresh feed
FW	Fresh Water
i	Sink i
j	Source j
k	Concentration level k
SR	Source
SK	Sink
WW	Waste Water

Abbreviations

BDP	Biorefinery Demo Plant
HMF	Hydroxyl Methyl Furfural
MRPD	Material Resource Pinch Diagram
NN	Nearest Neighbour
NNA	Nearest Neighbour Algorithm
PT	Pre-Treatment
SSCF	Simultaneous Saccharification and CoFermentation
SSF	Simultaneous Saccharification and Fermentation
TDS	Total Dissolved Solids
TS	Total Solids
TSS	Total Suspended Solids
VBA	Visual Basic for Applications
WMH	Water Minimization Hierarchy
WPA	Water Pinch Analysis
WWTP	Waste Water Treatment Plant

List of figures

List of tables

1 Introduction

Water is a commonly used resource in industrial processes, where it serves for many and often unavoidable purposes (Wan Alwi & Manan 2013). The deficit of water in many parts of the world has prevented water intensive industries from being successful in these places. In other parts of the world where the supply of water is not a problem, there is a struggle with other problems due to the large use of water. The cost of both freshwater and waste water treatment has increased due to environmental restrictions (Feng & Deng 2013). This, together with the scarcity of water, is the reason why methods to improve water use efficiency have been developed (Feng & Deng 2013).

The Water Management Hierarchy (WMH), see Figure 1.1, can be used to minimize the water consumption in a process. The hierarchy shows that the first step in reducing the industrial water consumption should be to eliminate it and avoid using it at all. For example, if water is being used as a cooling media, another media e.g. air could be used instead. However, it is seldom possible to have a process without any water present, so the next step should be to reduce the water use by e.g. choosing certain equipment for the process. This could for example be choosing an ion-exchange separation device instead of a water intensive extraction tower. When the water is taken directly into in another process unit without doing any regeneration or cleaning first, this is called direct reuse. Direct reuse of the water should be considered next, if reduction is not an option, or only possible to a certain extent. There are different reasons why this could be unfeasible; one could be contaminants in the water flow that are not allowed to enter the next unit without being regenerated or cleaned first, which is the next step in the hierarchy. Finally, if no other option to minimize the water use can be implemented, or if the wastewater needs to be diluted, then using fresh water is the only alternative. (Wan Alwi & Manan 2013) The minimization of water use by working according to the WMH is a good starting point, but it can easily be imagined that it will be a complex problem for any larger process. This is the reason why a systematic approach to minimize the water use is needed.

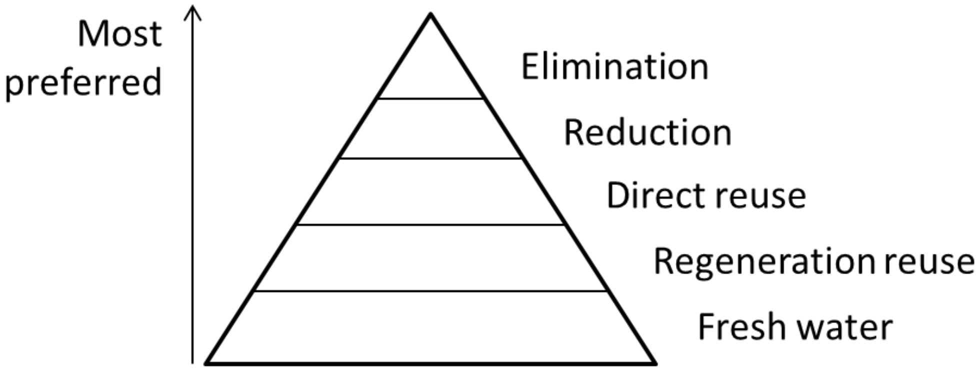


Figure 1.1 The Water Management Hierarchy explains how the minimizations of water use should be performed in order to be as sustainable as possible. The most preferred option is at the top and the least preferred at the bottom. (Wan Alwi & Manan 2013)

The problem with the diminishing finite energy resources and the greenhouse effect are getting even more attention in today's society (Ricardo Soccol et al. 2011). Combustion of fossil fuels such as petrol and diesel emit large amounts of CO_2 and 25% of the global emissions originates from the transportation industry where 75% of this is due to road transports (Palmqvist 2014). In order to decrease these emissions, increased use of renewable fuels is often presented as an important measure. Bioethanol is a suitable renewable alternative to petroleum based fuels due to its high octane number (measure of petrol quality) and high heat of vaporization (Ricardo Soccol et al. 2011).

When combustion of pure ethanol takes place in the engine, the only products are carbon dioxide (CO_2), water and heat.

$$3\ C_2H_5OH + 10\ O_2\ \rightarrow 6\ CO_2 + 8\ H_2O + heat$$

However, this carbon dioxide can be assumed not to contribute to the greenhouse effect if the ethanol is made from renewable sources. This is because renewable material, such as lignocellulose, captures CO_2 when it grows and this amount is equal to the CO_2 released from combustion of the ethanol. As a result, vehicles running on bioethanol emit less net CO_2 than conventional vehicles. (U.S. Department of Energy 2014) Such fuels are often referred to as carbon neutral. According to the American Heritage Dictionary the definition of carbon neutral is "Of or relating to a process or activity in which the total amount of carbon in carbon-containing gases released into the environment is offset by the amount of carbon in such gases removed from the environment." (American Heritage Dictionary 2014) A schematic of the circular lifecycle of biofuels, e.g. bioethanol, can be seen in Figure 1.2 and compared with the flow of fossil based fuels in Figure 1.3, where the latter results in much higher net greenhouse gas emissions. This is because there is no end consumer of CO_2.

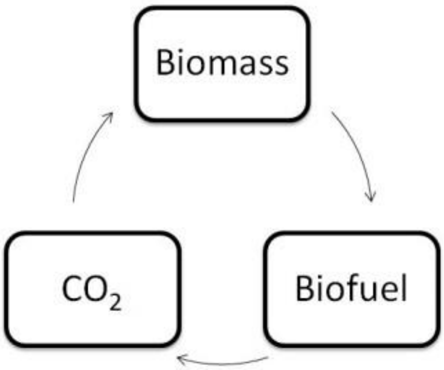


Figure 1.2 A schematic of how carbon dioxide emitted from biofuel can be seen in a circular lifetime. The released CO_2 is absorbed by other sources for biofuel production.

Figure 1.3 A schematic of how carbon dioxide is emitted from fossil based fuels. There is no consumer of CO_2 which then contributes to the greenhouse effect.

Bioethanol is currently the almost common biofuels and it has replaced about 3% of the fossil based fuels in the world (Palmqvist 2014). The annual global production of bioethanol in 2006 was 13.5 billion gallons (51.1 billion litres) and that was more than 94% of the global biofuel production (Balat et al. 2008). The European production of bioethanol for fuel purposes was estimated to be 4.6 billion litres for 2012 and expected to increase to 8.5 billion litres during 2014. This bioethanol was produced in the approximately 70 existing refineries and mainly from sugar beet, wheat and corn, but also from barley and rye. (USDA Foreign Agricultural Service 2013) Two main advantages of lignocellulose as raw material for bioethanol production are that it is the most abundant renewable resource on earth and that it is often available in material that otherwise would be classified as waste e.g. forestry residuals, agricultural harvest residues and the organic fraction from municipal solid waste. Lignocellulosic based ethanol production is often referred to as a second generation biofuel. (Ricardo Soccol et al. 2011)

There are only a few plants producing ethanol from second generation biomass and only four of them are in commercial scale, but several are being planned and funded (European Biofuels Technology Platform 2014a). The difficulties with scaling up a demo or pilot plant to full-scale for ethanol production from lignocellulosic biomass are many. First, the cost for producing this type of bioethanol must be further reduced (Hahn-Hägerdal et al. 2006). The raw material price of the lignocellulosic biomass is much lower than for starch crops, but the costs for turning lignocellulose into sugar are more costly than for starch material (Galbe & Zacchi 2002). This is the reason why starch based ethanol fuels have been commercialized, but not the plants producing ethanol from lignocellulose to the same extent. It has been estimated that the ethanol production cost could be reduced by 20% for Swedish conditions by integrating the bioethanol plant with a combined heat and power plant (Hahn-Hägerdal et al. 2006). Other difficulties include how to optimize the fermentation technology, enzyme engineering and metabolic engineering (Hahn-Hägerdal et al. 2006). One of the commercial sized bioethanol plant working with second generation biomass (and currently the largest one (European Biofuels Technology Platform 2014b)) is situated close to the city of Crescentino, Italy (Novoenzymes 2013).

One of the issues with the production of bioethanol is its high consumption of water which in many places of the world is a limited resource and therefore makes the process unfeasible. A corn-based ethanol production plant requires about 5.6 litres of water per kilo of corn grain in the fermentation and distillation processes only. After the fermentation, 13 litres of water must be removed and taken care of for each litre of ethanol. (Pimentel & Patzek 2005)

Analyses of water consumption for biomass-based ethanol processes can be found in the scientific literature. A study by Alkasrawi et al. from 2002 aimed at decreasing the use of both energy and fresh water for a Simultaneous Saccharification and Fermentation (SSF) process by recirculation of process streams. Depending on where in the process the recirculation was performed, reductions of 40% to 60% in fresh water use were possible with cost reductions of 12% and 17%, respectively, for the two design cases. The main drawback with recirculation in fermentation processes is the presence of substances that inhibit the fermentation and hydrolysis. If the recirculation is performed before the distillation, a reduction of 0-39% in fresh water usage leads to a decrease of ethanol yield of 88-85%. For a 49% reduction of water the yield of ethanol dropped down to 40% and for reductions of 59% or higher the ethanol yield in the SSF process was 0%. However, if the recirculation was performed after distillation, the ethanol yield was only marginally affected. A fresh water reduction of both 49% and 59% resulted in an ethanol yield of 88%, and a reduction of water usage to 68% resulted in a yield of 80%. (Alkasrawi et al. 2002)

In 2010, Ahmetović et al. investigated the possibilities of simultaneously increasing energy- and fresh water efficiency for a first generation corn-based ethanol process. They found that the consumption of fresh water could be reduced significantly compared to normal levels in current processes. Usage of water as low as 1.54 litre of water per litre of ethanol were shown to be possible to achieve, compared to reported values from processes of 3-15 litre water per litre of ethanol. (Ahmetović et al. 2010)

A continuation of this study evaluated the water consumption in second generation biomass ethanol processes. The results from the hydrolysis process showed that water usage of 2 litres of water per litre of ethanol could be achieved. This can be compared with reported water consumption values of 6-9.8 litres of water per litre of ethanol (switchgrass) and 1.94-2 litre of water per litres of ethanol (hybrid poplar). For thermal based ethanol producing processes, where ethanol is produced by synthesis or fermentation of syngas generated from gasification of the raw material, the fresh water used can be as low as 0.4-1.7 litres of water per litre of ethanol when maximization of heat recovery has been performed. (Martín et al. 2011)

1.1 Aim

The aim of this project was to examine if and how water pinch analysis can be applied to an ethanol production process fed with lignocellulosic biomass in order to minimize its water use. An analysis method was identified and programmed in Visual Basic as an application to Microsoft Excel to make it user-friendly for process water analysis. This tool was thereafter applied in a case study by identifying sinks and sources in a water network for a conceptual ethanol production process. The aim for the tool was the ability to handle both single and multiple contaminants separately in order to evaluate differences between the different methodologies. The methodologies used to build the application in Excel and how the program works are described in Chapter 3. Data was extracted from a computer model of the process which was based on data from tests made at the SP Biorefinery Demo Plant, literature references and laboratory work. Different number of contaminants and methodologies and different options of recirculation were examined in order to shown and discuss differences in the results. A small sensitivity analysis was also made where the influence of an intermediate regeneration unit was examined with respect to one group of contaminants.

1.2 Limitations

This project did not take into consideration how different substances affect each other. The variation in efficiency in the chemical and biological processes due to varying concentrations was not included in the project. Implementation of Water Pinch Analysis (WPA) and the analysis tool was only performed for one predefined process concept, the multi-feed process described in Section 3.1. Techno-economic analyses of the results was not included in the project. The number of streams requiring and supplying water in the process was limited to ten streams of each.

2 Theory

According to the Water Minimization Hierarchy (WMH), the first step in reducing the water usage is to eliminate water usage where possible, for example by replacing water cooling with air cooling instead. However, air cooling requires large fans and results in a higher electricity consumption than water cooling. Another way to eliminate water could be to perform the water intensive process operations in cooperation with another process. In this project, these types of changes were not examined further. The next step in the hierarchy is to reduce the water use. This can be done by running the process at a higher dry content. However, in an ethanol production process, this is associated with other negative effects. At higher dry content, the concentration of the inhibitors gets higher and slows the process down. Therefore this was not examined further in this project and the focus was put on direct water reuse that is the third step in the WMH. To evaluate the possibilities for this, the systematic methodology Water Pinch Analysis (WPA) was used to identify a target for the minimum fresh water needed in the process, as described in Section 2.1. WPA was used in terms of two different methodologies, described in Section 2.2 and 2.3 respectively. The fourth alternative in the WMH, regeneration was also examined to some extent. The reason why the regeneration alternative was not examined completely was that the associated methodology differs too much from the direct reuse methodology in order to finish the project on time. The last alternative, i.e. to use fresh water was only used when there was no other alternative.

It should be mentioned that the WMH might not be the best choice seen from an energy, environmental or economic perspective. The goal of the WMH is simply to minimize the water use and does not take other aspects into account. As mentioned above, higher electricity usage and higher dry content might not be better for the plant's economic or environmental performance than the reference case is. Therefore, the water minimization hierarchy should not be the only way to improve a process.

2.1 Water Pinch Analysis

Water Pinch Analysis is an insight-based technique that aims to identify targets for maximum water efficiency which can be done in different ways. One way is to find the solution by visual analysis of the curves produced from process data to find the optimal integration of the different parts in the process. Another way is to implement the method in a computer algorithm to identify the targets. WPA was initiated in the mid 1990's and has been developed a lot since then. Mathematical optimization is an alternative to this technique and finds the optimum by calculations and iterations. (Foo 2009) WPA has analogies to energy pinch analysis, where processes are integrated in order to save heat energy and is based on a study of a water network in a process including water as sources (excess) and sinks (demands) (El-Halwagi et al. 2003). Energy is the quantity variable in energy pinch analysis and mass flowrate is the quantity variable in WPA. The quality variable in energy pinch analysis is temperature and the corresponding quality variable in WPA is concentration of contaminants.

In 1996, Dhole et al. used this way of thinking to create a graphical method to identify the pinch (bottleneck) of the system by creating a supply composite and a demand composite and then see where they met in a concentration versus mass flow diagram (El-Halwagi et al. 2003). This pinch could only be eliminated by mixing the source streams and the idea had a great impact on the water use minimization (El-Halwagi et al. 2003). However, Dhole et al. did not provide any systematic method for the process of stream mixing and this graphical tool therefore became the subject of future research (El-Halwagi et al. 2003). Polley and Polley (2000, cited in El-Halwagi et al. 2003) formulated sequential mixing rules, Sorin and Bedard (1999, cited in El-Halwagi et al. 2003) came up with an algebraic method and Hallale (2002, cited in El-Halwagi et al. 2003) tried to solve for systems with more than one global pinch based on the work of Alves (1999, cited in El-Halwagi et al. 2003) (El-Halwagi et al. 2003). Based on the previous research, El-Halwagi (2003) proposed a rigorous graphical targeting method to conserve resources through material recycle or reuse networks, a material recovery pinch diagram. This model is generally known as the fixed flowrate problem and is one of the two main approaches adopted for water network synthesis problems. This category of WPA focuses on the flowrate with the use of the sink and source perspective as described above. From the mid 1990's until 2000, fixed load problems were the main focus of water minimization. Instead this category has its main focus on removing a certain load from a rich stream and the flowrate is considered constant over a process unit, i.e. the inlet flowrate is equal to the outlet flowrate in e.g. an adsorption tower. In his review article from 2009, Foo investigated which approach generated the most published articles and the most common approach during the 90's was fixed loads problems. This later shifted towards fixed flowrate during the early 2000's and is the most common one in articles today. (Foo 2009)

There are a lot of different ways to work with this technique, which, according to Foo makes the WPA tool for water minimization broad, dynamic and useful for different applications (Foo 2009). Processes that have been investigated through application of WPA include corn processing, paper mills, oil refining, citrus processing and a plant for beet sugar. Flow reductions of up to 70% have been reported. (Wan Alwi & Manan 2013) It has also been shown that the use of process water decreases when an energy pinch analysis is performed (Ahmetović et al. 2010).

WPA can be used for both new processes that are to be designed and for retrofit of existing processes. Even if the processes for which WPA is applied varies greatly, the method of WPA for retrofit can be divided into five key steps listed below and described in detail in Section 2.1.1 to 2.1.4. (Wan Alwi & Manan 2013)

(i) Analysis of water network. The water flows in the existing network are identified. Decision of which contaminant(s) to be included should be made.
(ii) Data extraction of flowrates and concentration(s). The water sinks and sources available for reuse and recycling are identified and extraction of the limiting water flowrate and the limiting concentration data is performed.
(iii) Targeting of the minimum fresh water supply.
(iv) Water network design/retrofit. Designing of the new network to try to achieve the minimum use of water identified in (iii).
(v) Economic evaluation. Calculation of the cost of the new network. Will it be more or less profitable than the existing one?

Over the last years, research has been carried out to find a methodology based on WPA that can handle more than one contaminant. This has resulted in several works proposed by different research teams. The work by Zhao et al. was made for hydrogen minimization with more than one contaminant, but is said to be applicable for water minimization with multiple contaminants as well (Zhao et al. 2007). The biggest drawback with this methodology is that it only provides a tool for targeting, but how to design the network to obtain this target is not addressed. Recently, there has been more work focusing on multiple contaminant systems since this is a more realistic situation in a process. One example of such work is the methodology proposed by Zhang et al. who presented a way to both target and design a water network in a process with multiple contaminants (Zhang et al. 2013). They use the methodology as a graphical solution to minimize hydrogen consumption, but it can also be presented as material balances that should be fulfilled and applied for water use problems. This methodology is described in detail in Section 2.3. WPA has been proved useful in representing both quality and quantity of the system, resulting in true targets for the minimization and effective use of the process water (Wan Alwi & Manan 2013).

2.1.1 Analysis of water network

First the process chosen for analysis must be studied in order to identify the possibilities for recirculation. Streams containing water that goes to waste discharge are the sources that could be used as water supply for a water demanding process unit. The process units that receive a stream with water are the sinks in the process. Possible sinks are also flows of e.g. chemicals, raw material etc. that need to be diluted before entering a process unit. At this point, it is necessary to decide what contaminant or contaminants should be considered in the analysis. The choices could be either to look at one single contaminant or a group of contaminants added together, a pseudo-contaminant. An example of a pseudo-contaminant could be e.g. salts, Chemical Oxygen Demand (COD) or Total Solids (TS). Then the choice could be to look at multiple contaminants, multiple pseudo-contaminants or a mix of these two. Which alternative that is chosen, should be based on the effect of the contaminant in the process. The more a contaminant or group of contaminants affect the process, the more important is it to include it in the study.

2.1.2 Data extraction

When the process has been studied and the sources and sinks are identified, data must be extracted in order to perform the targeting and network design later on. For the sources, the data needed are the flowrate of the streams and the concentration of the chosen contaminant(s) in the streams. For the sinks, the flowrate of the water demand is the data needed together with the constraints of concentrations in the process unit. The constraints are set with respect to what kind of unit operation that is performed and to what other contaminants that are present and could be inhibited by a too high concentration of the chosen contaminant. For both the sinks and sources, the needed data are concentrations and flowrates, but for the sources it is the present value of these two and for the sinks, it is the need of water and constraints of concentrations that are used.

2.1.3 Targeting

The first step is to rank the sources and sinks separately in ascending order of the contaminant concentration. Then calculate the maximum accepted load for the sinks by multiplying the flowrate with the concentration level. The load should be calculated for the sources as well, but here it is the real concentration level in the stream that is multiplied with the flowrate of the source. Starting with the highest ranked (highest quality and lowest concentration) sink from origin, the sink streams should be plotted with the flowrate on the x-axis and the load on the y-axis beginning. The second sink should start at the end of the line of the previous sink. (El-Halwagi et al. 2003) In this way the sinks together will construct a sink composite curve as can be seen in Figure 2.1.

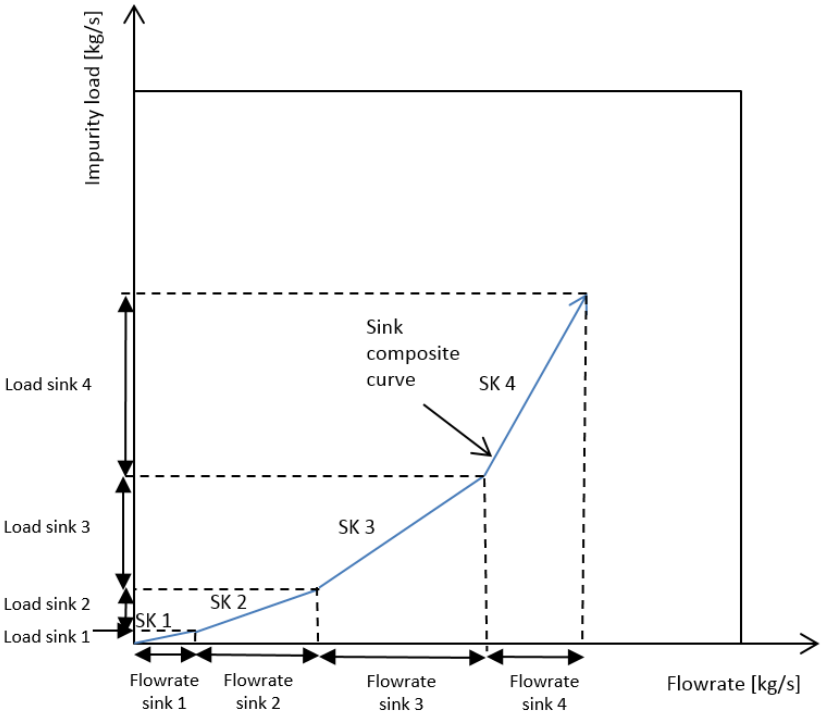


Figure 2.1 The continuous line is the sink composite curve and SK stands for sink. The flowrates and loads of the sinks are pointed out.

The same curve is constructed for the sources and can be seen in Figure 2.2. Then those two curves are plotted in the same diagram. In order for the sources to provide the sinks with water their load must be lower or equal to the load of the sinks. Therefore, the source line is slid until the line is under or touching the sink line. When this is done, the pinch point is activated where the two lines touch as shown in Figure 2.3. This means that the match between the sources forming the pinch point with the sink is an exact match. Elsewhere, the mixing of the sources results in loads lower than the sink requires. The overlap created when the source curve has been slid represent how much of the sources that can be recycled to the sinks. The gap under the sink composite curve seen on the x-axis shows how much clean fresh resource that is needed to fill up the demand of the sink. The gap over the source composite curve projected onto the x-axis shows how large the waste flowrate will be. These features of this so called Material Recovery Pinch Diagram (MRPD) are shown in Figure 2.3. (El-Halwagi et al. 2003)

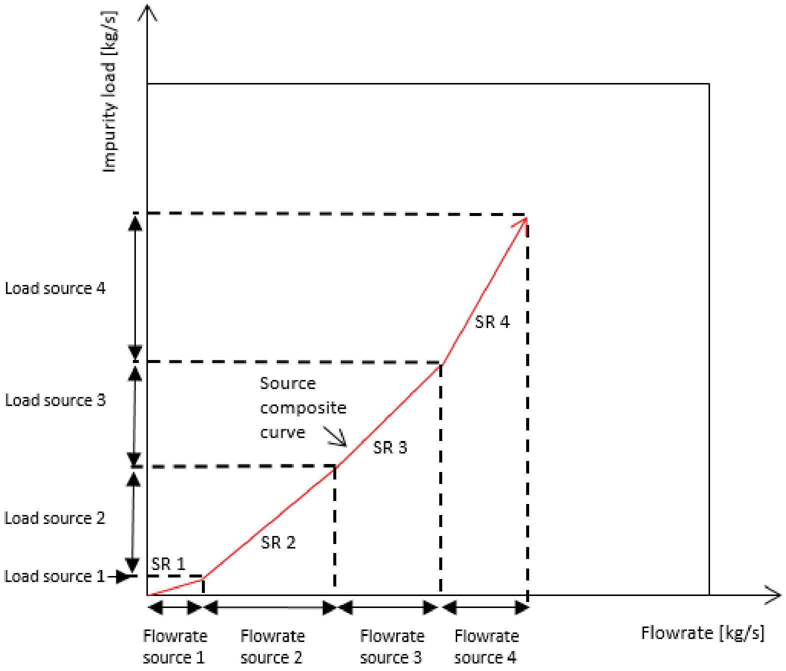


Figure 2.2 The continuous line is the source composite curve and SR stands for source. The flowrates and loads of the sources are pointed out.

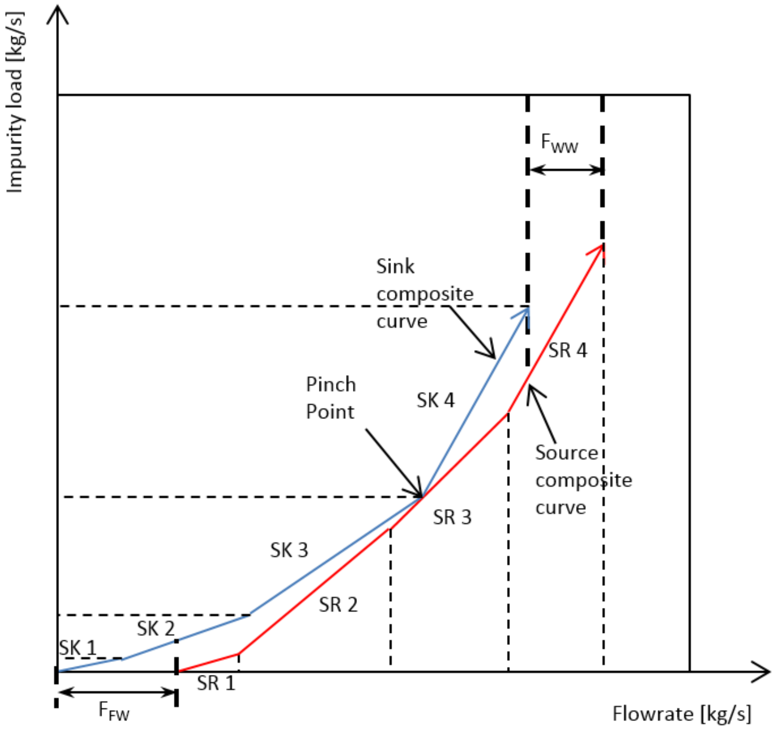


Figure 2.3 An example of what the graphical representation of a WPA can look like. SK stands for water sink, SR for water source, F_{WW} *marks the flow of waste water and* F_{FW} *marks the flow of fresh water. The sink composite curve is placed above the source composite curve. The pinch point is found where the two composite curves meet. The units on the axis are just examples.*

2.1.4 Network design

From the MRPD shown in Figure 2.3, the design of the water network needed in order to reach the fresh water usage and waste water effluent found in the targeting, can be extracted. Since the sources must always have at least the same flowrate as needed in the sink and lower load of the contaminant of interest, the targets are fulfilled when the source composite curve is below the sink composite curve. The sources used to fulfil a sink is therefore the sources that are overlapped by a sink. In Figure 2.4, sink 1 and sink 2 from Figure 2.3 is enlarged. Sink 1 has no source under the line and the flowrate demand will have to be fulfilled by fresh water. The fresh water need to sink 1 is the same as the horizontal projection of sink 1 on the x-axis. Also sink 2 will need fresh water, but only to a limit. As can be seen in Figure 2.4, sink 2 is overlapping both fresh water, source 1 and source 2. This means that in order to fulfil sink 2, water flowrates from three different water sources must be mixed. The flowrate of each of them can be seen by the projection of sink 2 over the sources to the x-axis.

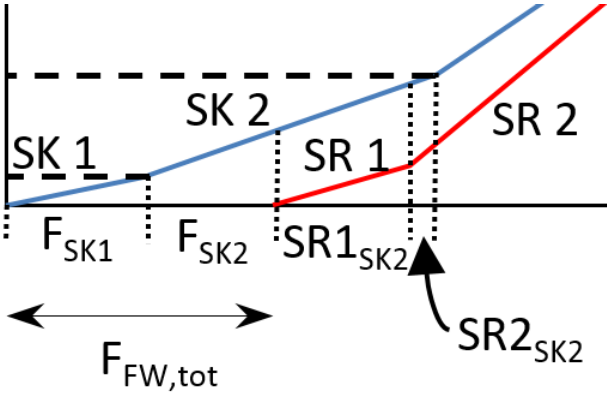


Figure 2.4 Enlarged MRPD of sink 1 and sink 2. $SR1_{SK2}$ means the flowrate of source 1 used to fulfill sink 2 etc.

Sink 3 and sink 4 are enlarged in Figure 2.5 and it can be seen that sink 3 will be fulfilled by source 2 and source 3, while the water demand of sink 4 will be fulfilled by source 3 and source 4. The remaining flowrate of source 4 is waste water effluent.

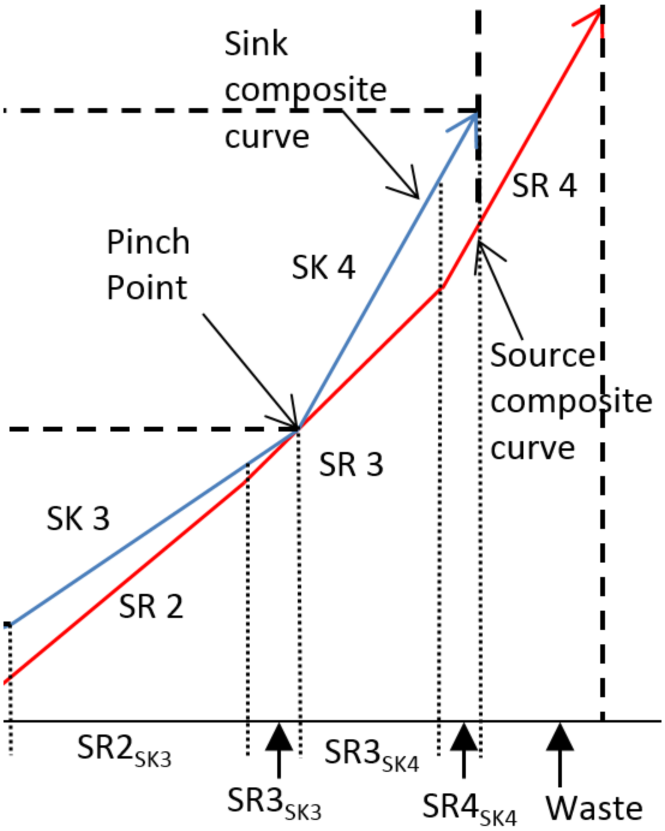


Figure 2.5 Enlarged MRPD of sink 3 and sink 4. $SR2_{SK3}$ *means the flowrate of source 2 used to fulfil sink 3 etc.*

The results of the network design can be seen in Figure 2.6 and Table 2.1.

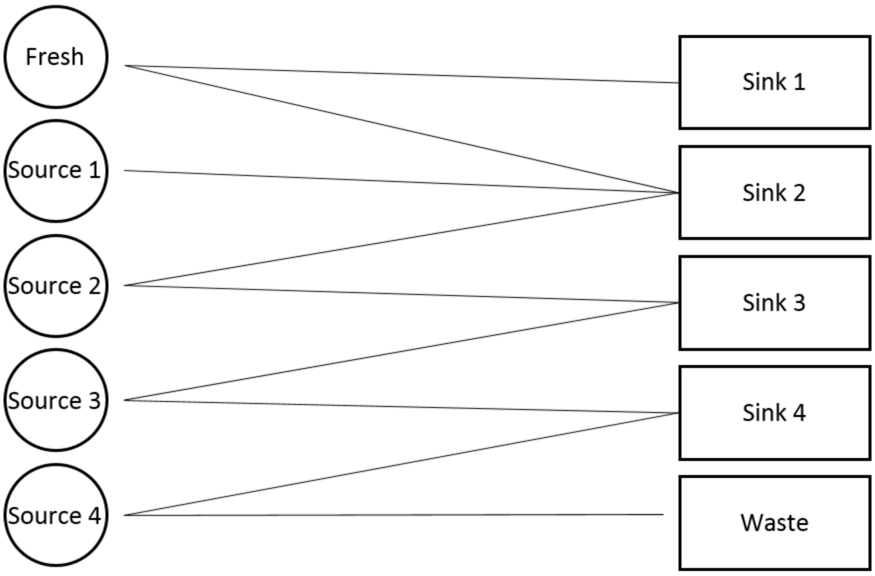


Figure 2.6 The network design achieved from the targeting of minimum fresh water consumption.

Table 2.1 The flowrates in the network designed from fresh water minimization targeting.

	Sink 1	**Sink 2**	**Sink 3**	**Sink 4**	**Waste**
Fresh	F_{SK1}	F_{SK2}	0	0	0
Source 1	0	$SR1_{SK2}$	0	0	0
Source 2	0	$SR2_{SK2}$	$SR2_{SK3}$	0	0
Source 3	0	0	$SR3_{SK3}$	$SR3_{SK4}$	0
Source 4	0	0	0	$SR4_{SK4}$	Waste

The economic evaluation of the designed network was not included in this project and is therefore not described in this report.

2.2 Illustration of a single contaminant methodology

WPA is a powerful tool to find the minimum water use in a process when only one contaminant is of interest in the water network (Foo 2013). It is usually divided into two main parts, targeting and network design. To start with, the input data of sources and sinks are ranked separately in ascending order with respect to their concentration of the contaminant. This is shown in Table 2.2.

Table 2.2 Input data ranked in ascending order of the contaminant concentration for sources and sinks respectively.

Sinks	**Process**	**Flowrate [kg/s]**	**Conc. [%]**	**Sources**	**Process**	**Flowrate [kg/s]**	**Conc. [%]**
1	A	1.2	0	1	C	0.8	0
2	B	5.8	10	2	D	5	14
				3	E	5.9	25
				4	F	1.4	34

The sink composite curve of the example is shown in Figure 2.7 and the source composite curve is shown in Figure 2.8.

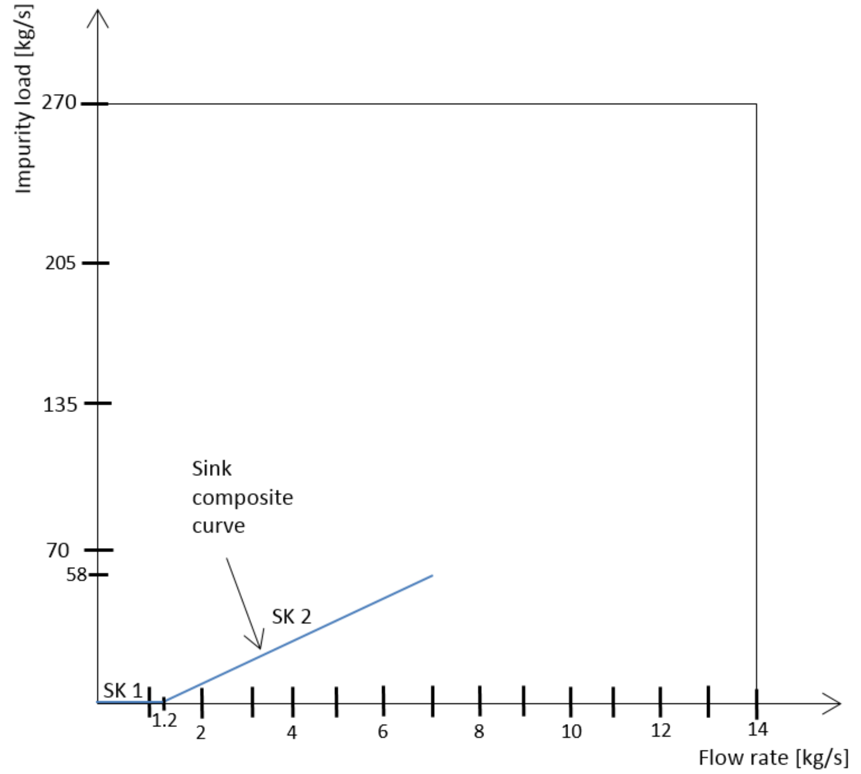


Figure 2.7 Sink composite curve for the single contaminant example.

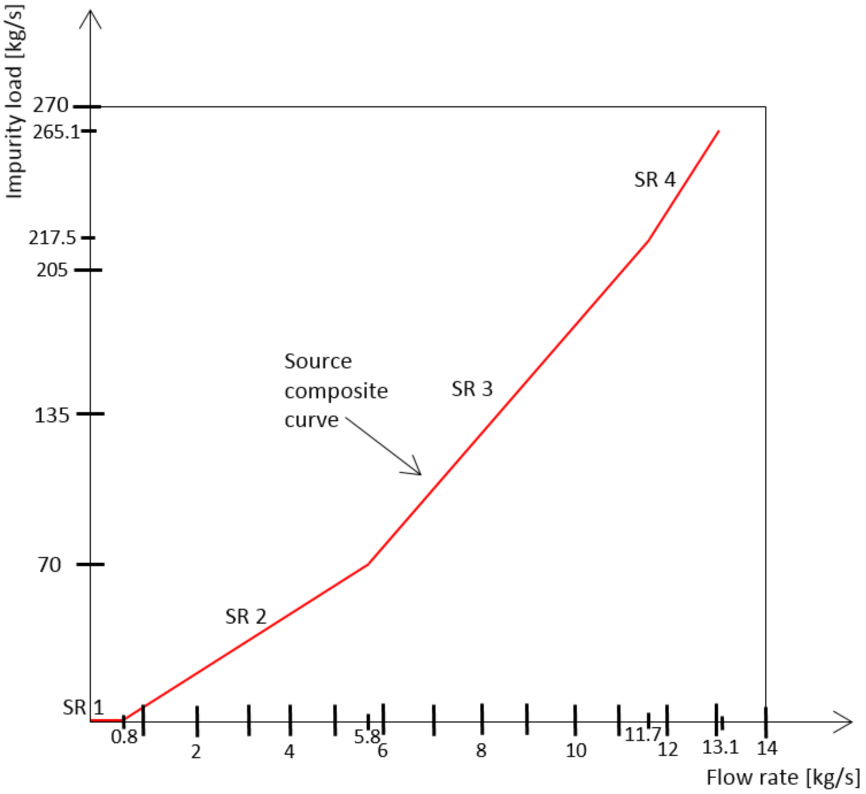


Figure 2.8 Source composite curve for the single contaminant example

When constructing the MRPD it first looks like in Figure 2.9 with a deficiency of water due to the total higher flowrate of the sinks. However, after sliding the source composite curve, the final MRPD shown in Figure 2.10 can be achieved. From this diagram, it can be seen that the fresh water need is 2.06 kg/s and the waste water effluent is 8.16 kg/s.

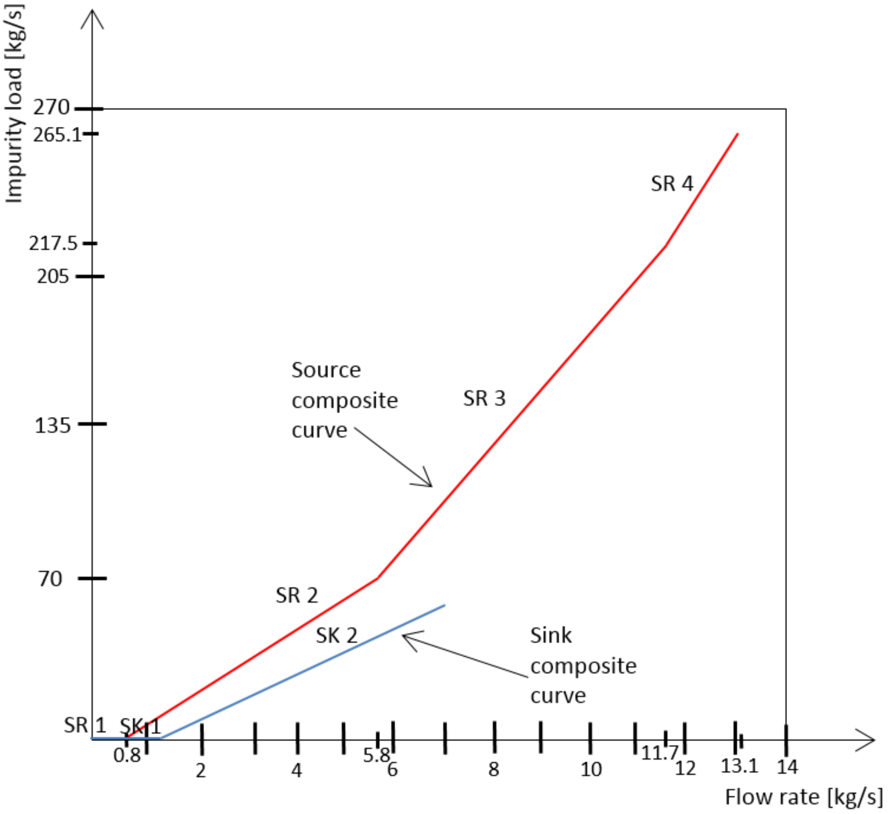


Figure 2.9 MRPD for the single contaminant example before sliding the source composite curve. There is a deficiency of water, since the sinks have a total higher flowrate than the sources and the sources are of lower quality than the sinks.

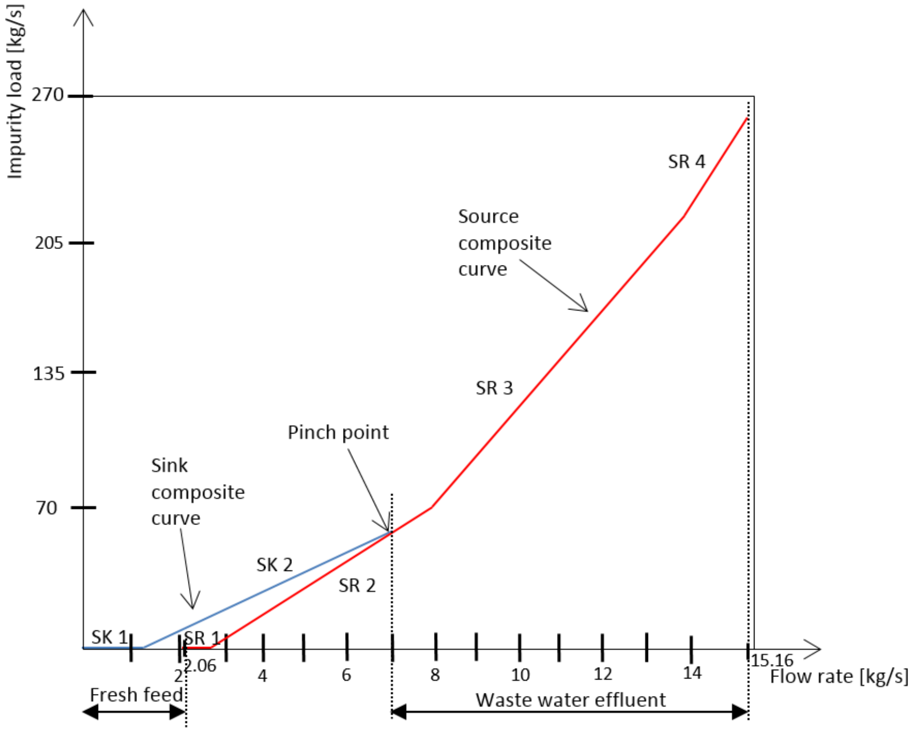


Figure 2.10 MRPD for the single contaminant example after sliding the source composite curve. The fresh water need is 2.06 kg/s and the waste water effluent is 8.16 kg/s.

A cascade table is the computational equivalent to the sliding of curves described in the previous section. A sample table of the cascade table for the single contaminant methodology is shown in Table 2.3. Initially, it is assumed that no fresh water flowrate is supplied to the process. When sliding the source composite curve, this is the same thing as inserting the source and sink composite curve in the same diagram, both starting from the origin (no fresh flow). In the cascade calculation procedure, then the value in the previous column i.e. flowrate needed, is subtracted from the starting guess flowrate. After cascading down the flowrates, the minimum fresh flowrate and the minimum waste-water effluent can be read from the table as described below. The calculations are performed in the columns counted from left to right and are described and illustrated below.

The concentration levels, C_k, of both sources and sinks are written in the first column in ascending order. The last concentration is a dummy concentration used to be able to calculate a difference to the last real concentration. The differences between concentration levels, ΔC_k are then calculated in the second column.

The flowrates of the sources and the sinks at the concentration levels are shown in the next two columns and then the difference between them is calculated in the fifth column.

The cumulative difference flowrate is calculated and cascaded down in column number six by, starting from 0, add the difference, positive or negative, to the previous value. Starting from 0 means that one first assumes that no fresh flow is needed.

The delta load, Δm_k, is achieved by multiplying the concentration with the cascaded flowrate difference, and typed in the seventh column. These loads are then used to calculate the cumulative load in the next column. If the cumulative load value is negative, the calculations continue. Otherwise the value at the bottom in the column with the cumulative difference of flowrates is the waste flowrate from the process. The assumption that no fresh flow was needed is also true in that case.

If there is a negative cumulative load the interval fresh resource, $F_{FW,k}$, is calculated for each value of cumulative load by taking the delta load and divide it by the difference between the current concentration level and the cleanest concentration level at the top.

The new guess of fresh flowrate in the next column is the highest negative value of the interval fresh resource. This is the largest deficit of water in the process and the minimum need of fresh water. This new guess is the minimum need of fresh flowrate and the generated waste-water effluent can be seen in the last row of this column.

A new load is calculated in the next column by multiplying the new cascaded flowrate with the concentration difference from before. At last the cumulative load is calculated again, now there should not be a negative value in this column. The pinch concentration is the concentration at which the value in the last column is 0.

A special case of the methodology is when either the fresh flow or the waste flow becomes zero. This is called a threshold problem. (Foo 2013) The cascade table of the example is shown in Table 2.3.

Table 2.3 The cascade table for the single contaminant methodology example. The content in the table columns are described above.

C_k	ΔC_k	$\sum_i F_{SKi}$	$\sum_i F_{SRi}$	$\sum_i F_{SRi}$ - $\sum_i F_{SKi}$	$F_{C,k}$	Δm_k	**Cum.** Δm_k	$F_{FW,k}$	$F_{C,k}$	Δm_k	**Cum.** Δm_k
					0				2.06		
0		1.2	0.8	-0.4							
	10				-0.4	-4			1.66	16.57	
10		5.8		-5.8			-4	-0.400			16.57
	4				-6.2	-24.8			-4.14	-16.57	
14			5	5			-28.8	-2.057			0.00
	11				-1.2	-13.2			0.86	9.43	
25			5.9	5.9			-42	-1.680			9.43
	9				4.7	42.3			6.76	60.81	
34			1.4	1.4			0.3	0.009			70.24
	999,97				6.1	6099,80			8.16	8156,87	
1000,00							6099,80	6.100			8156,93

To minimize the fresh water need, the recirculation of available sources should be maximized (Foo 2013). The possibility of reusing available water effluent streams as feed for water demands in the process, depends on the concentration of the contaminant in the water streams and constraints in the process unit. To be able to use a water effluent stream to fulfil a demand in the process, the concentration must not be higher than the constraint of the current process part and the flowrate must be at least the same. To make the most efficient and systematic use of the water streams an algorithm is used to motivate the recirculation choices.

One way to do this is to use the Nearest Neighbour Algorithm (NNA). This algorithm uses the concentration of the sinks and of the sources and takes the differences of them into account when designing the network. By using the sources that are closest in concentration to a sink to fulfil its water demand, the need of fresh water will be as low as possible. This will be true when the pinch point in the MRPD is activated. By mixing sources of both higher and lower concentration than the sink concentration, it is possible to make use of the higher concentration sources that otherwise would be useless. It is important that the higher concentration of the source is as close as possible to the sink concentration constraint, in order to not use more of the cleaner sources or fresh water than necessary. This is why the nearest neighbours to the sink concentration should be used first. In fact, this is what is described in Figure 2.4 - Figure 2.6 in Section 2.1.4. The nearest neighbour of sink 2 are pointed out in Table 2.4.

Table 2.4 The nearest lower and nearest higher neighbours to the second sinks. The blue circle (at the top) marks the lower concentration neighbour and the red circle (at the bottom) the higher concentration neighbour.

Sinks	**Process**	**Flowrate [kg/s]**	**Conc. [%]**	**Sources**	**Process**	**Flowrate [kg/s]**	**Conc. [%]**
1	A	1.2	0	1	C	0.8	0
2	B	5.8	10	2	D	5	14
				3	E	5.9	25
				4	F	1.4	34

If there is one, the first choice of source to the current sink is a source of the same concentration level as the maximum concentration level that the sink can tolerate. If this is not possible, or only possible to a limit, then the algorithm makes use of the nearest neighbours, and mix them to achieve the correct concentration. When one neighbour source is empty and there still is flow needed to the sink, the source next above or below the used neighbour source is utilized next. In order to find the flowrate of the different sources to be mixed, material balances seen in Equation (1) and (2) are used.

$$F_{f,i}c_f + F_{j,i}c_j = F_{SK,i}c_i \tag{1}$$

$$F_{f,i} + F_{j,i} = F_{SKi} \tag{2}$$

Where $F_{f,i}$ is the flowrate of the fresh feed i.e. the lower concentration neighbour to sink i, $F_{j,i}$ is the flowrate of the higher concentration neighbour to sink i, c_f and c_j are the concentrations of the contaminant in the fresh feed and the higher concentration neighbour respectively, $F_{SK,i}$ is the flowrate of the current sink and c_i is the concentration of contaminant i in the sink. In Table 2.5 the resulting network from the WPA can be seen.

Table 2.5 Results from the WPA of the single contaminant example. The flowrates are in [kg/s].

	SK 1	**SK 2**	**Waste**
Fresh feed	0.4	1.66	0
SR 1	0.8	0	0
SR 2	0	4.14	0.86
SR 3	0	0	5.9
SR 4	0	0	1.4

2.3 Illustration of a multiple contaminants methodology

Handling multiple contaminants in water minimization is more complicated than handling a single contaminant. The main reason is that when fulfilling the sink demand with respect to one contaminant, it might be interfering with the order of the other contaminants. The first issue is when constructing the ranked order among the sinks and sources. The ranking should be in ascending order of contaminant concentration, but most likely the order will not be the same for the different contaminants. Research has been performed in this area and in 2007, Zhao et al. presented a way to target the minimum fresh utility use for hydrogen (Zhao et al. 2007). They use a so called surplus diagram and iterative calculations to find how much water that is available and how much that is needed. By constructing one surplus diagram for each contaminant, they got around the ranking problem and were able to target the minimum water use for each contaminant. If the stream order of the sink and sources is the same, the final target is then the minimum of all of them. One could think that a possible way to find the minimum water needed for a process simply would be to do the targeting for one contaminant at a time and then pick the worst case scenario. This will unfortunately not result in the true minimum use of water due to two reasons. First, the different contaminants are transferred simultaneously from the source to the sink and the constraints of all contaminants might not be fulfilled just because one of them is fulfilled. The other reason is that in order to achieve the minimum target, the dirtiest source must be used first. This is not possible if the ranking order of the sources and sinks does not take the other contaminants into account. (Zhao et al. 2007) The proposed method by Zhao et al. does not provide guidelines for designing the water network. Prior to 2013, the methodologies that simultaneously targets and designs the water network were unable to handle systems with multiple contaminants.

However, in 2013, Zhang et al. presented a methodology developed to simultaneously target and design a resource conservation network in a process with multiple contaminants. This methodology is formulated with respect to hydrogen networks, but can be used for water as well. The main advantage compared to other methodologies is that they use ranking rules that can give a reasonable order among the sinks and sources with respect to all contaminants. Based on this ranking, the methodology then maximizes the direct reuse by targeting and designing the network. The ranking rules used makes the target as close as possible to the optimum and compared to other articles the results are close or similar to them. As already mentioned, the work by Zhang et al. also includes a methodology for generating a network design which makes it a superior methodology. (Zhang et al. 2013) This is the methodology used in this thesis to handle the multiple contaminants case. Since the methodology is limited to three contaminants, it might be cumbersome to decide which ones that should be included in the analysis if there are more than three contaminants present in the process. To get as good results as possible, the most inhibiting contaminants should be chosen since they will affect the process the most if there are no constraints for them. Using a group of contaminants that affect the process in similar way and add their concentrations might also be an option to choose three variables. This latter suggestion is implemented in this thesis.

The ranking of the sources and sinks are made separately and is also using NNA as in the book by Foo for a single contaminant. The first step in the ranking procedure is to rank the sinks and sources according to the total contaminant load i.e. all the concentrations of the different contaminants added together. Then consecutive steps follow as described below.

Start by ranking the sinks and sources (including the fresh resource) separately in ascending order according to total contaminant concentration. It can be seen in Table 2.6 that the complexity of the problem increases when adding two more contaminants to take into account.

Table 2.6 Input data table for multiple contaminant problem. The number of sources and sinks can be up to ten of each.

Sinks	**Process**	**Flowrate [kg/s]**	**Contaminant A [%]**	**Contaminant B [%]**	**Contaminant C [%]**	**Total [%]**
1	A	1.2	0	5	2	7
2	B	5.8	10	0	20	30
Sources	**Process**	**Flowrate [kg/s]**	**Contaminant A**	**Contaminant B**	**Contaminant C**	**Total** [%]
1	C	0.8	0	1.3	0	3.3
2	D	5	14	2	5.2	21.2
3	E	5.9	25	12	3	40
4	F	1.4	34	0	1.2	35.2

Then place the sinks with the fresh resource as one neighbour (with respect to any contaminant) prior to the other sinks. Among the sinks with highest quality sources as neighbours, the ones with the same nearest neighbours should be ranked behind the ones with differing neighbours. The sinks apart from the fresh resource as neighbour are now at the bottom of the ranked list and should also be ranked according to whether they have the same nearest neighbour as any other sink. The ones with differing neighbours should be placed above the ones that have the same neighbours.

To rank the sources, place the fresh resource at the top of the sources since it is of the highest quality. Then place the source that is the nearest neighbour to the highest quality sink after the fresh resource. The source that is the nearest neighbour of the last sink should be ranked last among the sources. If two or more sources are neighbours to the same sinks, their initial order of total concentration can be kept as it is as long as they are ranked to their neighbouring sink number. (Zhang et al. 2013) These ranking rules result in a ranking order that is not constructed with respect to only one contaminant and is therefore a better alternative than the ranking procedure in Zhao et al. (Zhang et al. 2013).

The methodology by Zhang et al. is often described as a graphical method, but can also be described as material balances that have to be fulfilled. The triangle rule for multiple source - one sink match is a graphical way of presenting a fulfilled material balance. It is presented in a diagram with the contaminant load on the y-axis and the mass flowrate on the x-axis. Lines are drawn according to the flowrate and the concentration of the sink and of the sources. If the lines form a closed triangle, then the mass balance is fulfilled. The triangle rule is shown in Figure 2.11.

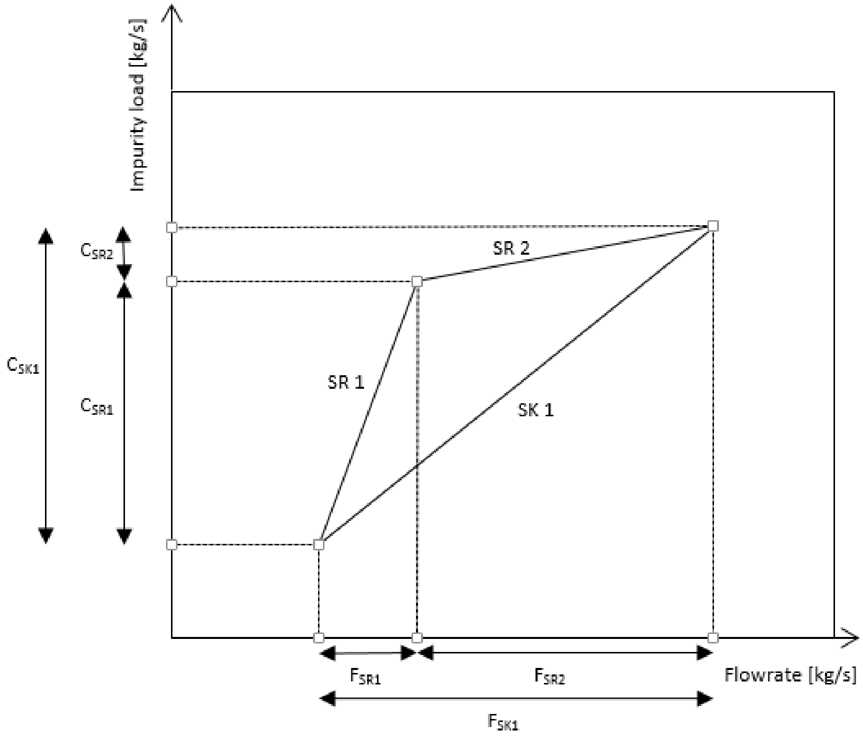


Figure 2.11 The triangle rule. When the triangle is closed, the mass balances are fulfilled.

This way of seeing the fulfilling of the mass balances is described by Zhang et al. as sliding of the sink and source curves simultaneously to make the lines in the diagram touch each other. When there are multiple contaminants in the sinks and sources, they will have to be represented separately since the concentrations of the contaminants will differ. The sliding of the curves must be made simultaneously so that e.g. not just the flowrate of source 2 with respect to contaminant A is used to a sink, while the same source is unused with respect to contaminant B. The sliding of curves easily gets uncontrollable and complicated the more sources and sinks that are present. An example of how sliding of the sink and source curves can look like is shown in Figure 2.12. It is easy to understand that this way of solving for multiple contaminants gets complicated when the number of sources and sinks increase.

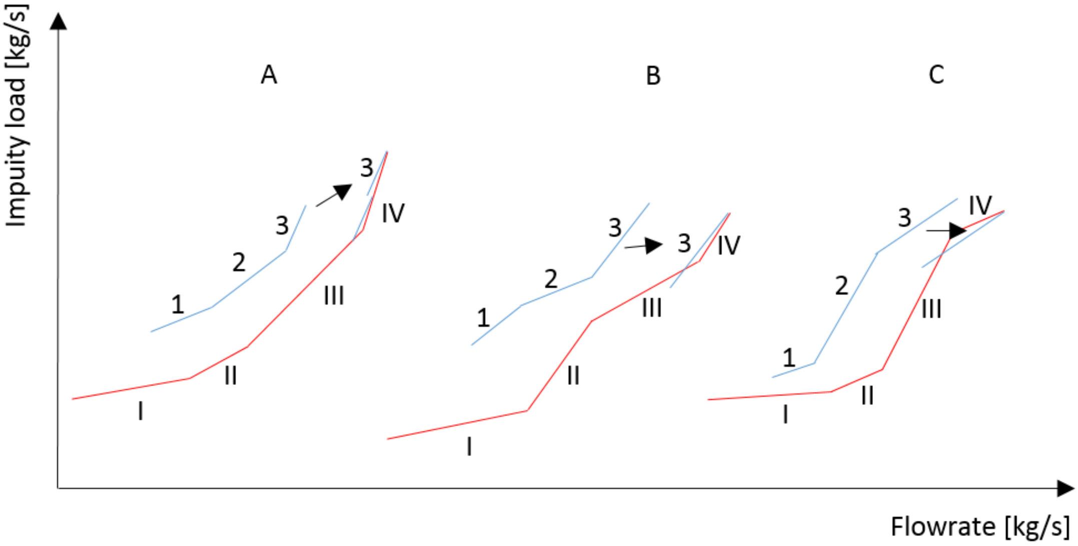


Figure 2.12 A graphical representation of the sliding of sink and source curves for multiple contaminants. A, B, and C are the different contaminants. The Arabic numbers are the sinks and the roman numbers are the sources.

Because of this complicated graphical solution, this methodology can be converted into inequalities and equalities instead. In this way it is possible to run an optimization solver based on these equalities and inequalities in Excel and solve for the target of the process. The equations that should be fulfilled are described below in Equations (3)-(9) (Zhang et al. 2013)

The total flowrates of the sources to be mixed should equal the need of the sink.

$$F_{SR1} + F_{SR2} + F_{SR3} = F_{SK} \tag{3}$$

The used flowrate of the first source must be equal to or lower than what is available in that source.

$$F_{SR1} \leq F_{SR1,max} \tag{4}$$

The used flowrate of the second source must be equal to or lower than what is available in that source.

$$F_{SR2} \leq F_{SR2,max} \tag{5}$$

The used flowrate of the third source must be equal to or lower than what is available in that source.

$$F_{SR3} \leq F_{SR3,max} \tag{6}$$

The flowrate times the concentration of contaminant A for all sources added together must be equal to or lower than the flowrate times the concentration of contaminant A for the sink.

$$F_{SR1}\, c_{SR1,A} + F_{SR2}\, c_{SR2,A} + F_{SR3}\, c_{SR3,A} = F_{SK}\, c_A \tag{7}$$

The flowrate times the concentration of contaminant B for all sources added together must be equal to or lower than the flowrate times the concentration of contaminant B for the sink.

$$F_{SR1}\, c_{SR1,B} + F_{SR2}\, c_{SR2,B} + F_{SR3}\, c_{SR3,B} = F_{SK}\, c_B \tag{8}$$

The flowrate times the concentration of contaminant C for all sources added together must be equal to or lower than the flowrate times the concentration of contaminant C for the sink.

$$F_{SR1}\, c_{SR1,C} + F_{SR2}\, c_{SR2,C} + F_{SR3}\, c_{SR3,C} = F_{SK}\, c_C \tag{9}$$

Where F is the flowrate, c is the concentration, SR represent sources, SK represent the sink, A, B & C are the different contaminants and $1, 2$ & 3 are the number of the nearest neighbour mixed to the sink. When the flowrates of the different nearest neighbours have been optimized for the first sink, the used flowrates of the sources are deleted from the original source flowrates. The new value is the new maximum flowrate of the nearest neighbour sources to the next sink. (Zhang et al. 2013)

In the methodology it is assumed that only three contaminants are taken into account and that it is not convenient to mix more than three sources to fill the demand of the sink. More assumptions made are presented in Section 3.2.1.

3 Methodology

The aim of this thesis work was to implement WPA in an Excel application and to test the application for a case study using two different methodologies, calculate the fresh water flowrates needed for each of them and then compare the results. The thesis work began with a literature study where the previous research on industrial water minimization was investigated. Candidate potential methodologies for analysing the water usage in an ethanol production process were identified and the most promising method was implemented as an application in Excel. The project was completed by performing a case study on a defined conceptual lignocellulosic ethanol production process, described in detail in this chapter.

3.1 Case study: Ethanol production process

In the case study a lignocellulosic ethanol production process has been analysed by using the methodology described in the previous chapter.

In Sweden the main lignocellulosic feedstocks (i.e. feedstock that mainly consist of the polysaccharides cellulose and hemicellulose, and the organic polymer lignin) for ethanol are wood and agricultural residues such as straw. To be able to turn the sugars in the raw material into ethanol, the raw material must first be pre-treated with for example steam and chemicals in order to make the polysaccharides accessible for further treatment. After pre-treatment the polysaccharides are split up into monosaccharides (sugars) by aid of enzymes in a process called saccharification. The sugars are then fermented into ethanol by for example yeast. The most frequently used yeast for ethanol production is *Saccharomyces cerevisiae*, which is the same as ordinary baker's yeast (Galbe & Zacchi 2002). When using *Saccharomyces cerevisiae*, ethanol is fermented as shown in the overall balance below (Müller 2008):

$$glucose \rightarrow 2CO_2 + 2\ ethanol$$

By glycolysis the yeast ferments glucose into pyruvate. The pyruvate is then decarboxylated into acetaldehyde and carbon dioxide. Acetaldehyde is reduced to ethanol by $NADH_2$, generated from a reaction with dehydrogenase (an enzyme increasing the removal of hydrogen) and the metabolic pathway intermediate product glyceraldehyde 3-phosphate. The key enzyme of this fermentation by yeast is pyruvate decarboxylase, which catalyses the reaction. (Müller 2008) A schematic of the fermentation process can be seen in Figure 3.1.

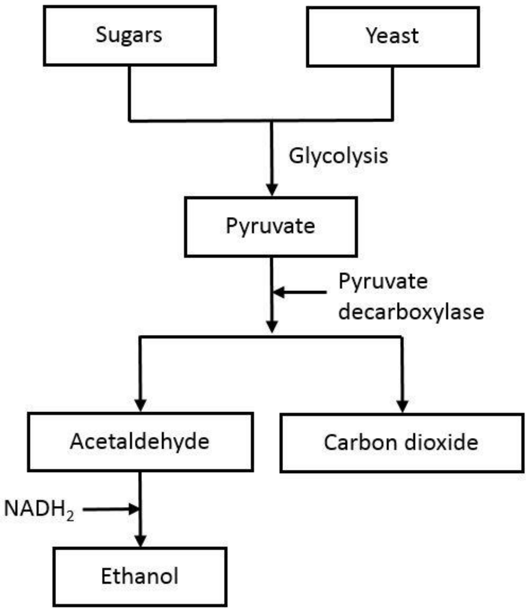


Figure 3.1 A schematic of the fermentation process of sugars from lignocellulosic biomass to ethanol.

After the fermentation the ethanol is at a low concentration, and needs to be concentrated in order to achieve a final product. The stream containing ethanol is normally sent to distillation columns for this purpose. The slurry leaving the bottom of the distillation columns contains a lot of organic material and most of the lignin. There are several ways of utilizing this slurry, but a common approach is to separate solid and liquid fractions and use the solid fraction as fuel in the boiler to cover for steam and electricity demand in the process. Waste water streams containing a lot of organic compounds are sent to a Waste Water Treatment Plant, where biogas could be produced by anaerobic digestion. The exact process set-up in the case study is described in Section 3.1.1.

The specific ethanol process investigated in this case study is based on the multifeed concept of Simultaneous Saccharification and CoFermentation (SSCF) and can be seen in Figure 3.2. The data used in the case study comes from a computer model of the ethanol process, which in turn is based on experimental data at Chalmers IBT, data gathered from running the pre-treatment, saccharification and fermentation processes at the SP Biorefinery Demo Plant in Örnsköldsvik, and from information gathered from other studies found in the scientific literature. The modelling was not a part of this thesis but was the source of data extraction in this case study.

3.1.1 Process description

A block flow diagram of the process in this case study is shown in Figure 3.2 and data for the case study can be seen in Table 3.1.

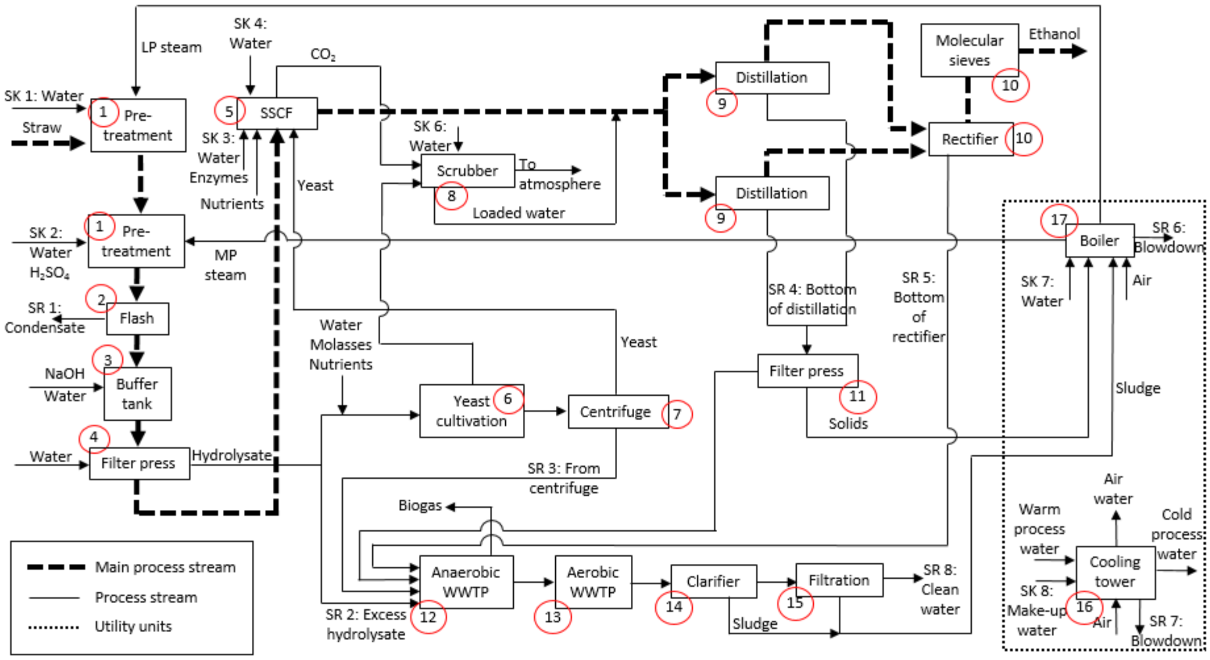


Figure 3.2 A simplified sketch of the process analyses in the case study. The thick, dotted lines are the process streams from straw to ethanol. SR stands for source and SK for sink. The data of the sources and sinks can be found in Table 3.2 and Table 3.3 respectively.

Table 3.1 A summarising table of the inputs and outputs of the main process units. The numbers refer to the numbers in Figure 3.2.

Process unit number	Process unit name	Main Inputs	Main Outputs
1	Pre-treatment	Water, straw, H_2SO_4	Sugars, lignin, water
2	Flash	Sugars, lignin, cellulose, water	Flash steam condensate, slurry
3	Buffer tank	Slurry, NaOH	Slurry
4	Filter press	Slurry	Hydrolysate, solids
5	SSCF	Solids, enzymes, water, nutrients, yeast	CO_2, ethanol/water, residues
6	Yeast cultivation	Hydrolysate, water, molasses, nutrients	Dilute yeast mixture
7	Centrifuge	Dilute yeast mixture	Concentrated yeast mixture, water/residues
8	Scrubber	Water, CO_2, impurities	Loaded water, cleaned CO_2
9	Distillation	Ethanol/water mixture	Ethanol/water (top), water with residues (bottom)
10	Rectifier + molecular sieves	Ethanol/water	99% Ethanol
11	Filter press	Water with residues	Solids, waste water
12	Anaerobic WWTP	Waste water	Waste water, biogas
13	Aerobic WWTP	Waste water	Waste water
14	Clarifier	Waste water	Waste water, solids/sludge
15	Filtration	Waste water	Clean water, sludge
16	Cooling tower	Air, warm process water, make-up water	Air, cool process water, blowdown
17	Boiler	Water, air, sludge, solids	Flue gases, steam, blowdown

The raw material in the case study process was wheat straw (36.1% w/w Cellulose, 24.2% w/w Hemicellulose, 26.5% w/w Lignin), 200 000 tons dry straw/year or 104 MW calculated from the flowrate and heat value (Biomass Energy Center 2011). The straw has a dry content of 87.5% when it enters the process but is hydrated with fresh water in order to have a Total Solids (TS) content of 24% after the pre-treatment. The pre-treatment is performed in two reactors and is heated by direct injection of medium and low pressure steam (7.45 kg/s). Sulphuric acid is used as catalyst in the pre-treatment reactor, and concentrated (95%) H_2SO_4 diluted with water to a 5% solution is added to the second reactor (at 0.2% w/w loading). In the pre-treatment 90% of the hemicellulose and 10% of the cellulose is converted to monomeric sugars, and 5% of the hemicellulose and 0.3% of the cellulose is converted to furan aldehydes (Hydroxyl Methyl Furfural (HMF) and furfural, respectively). 5% of the lignin is dissolved in the liquid.

After the pre-treatment the process stream is concentrated in a flash and sent to a filter press, passing through a buffer tank where the pH is increased by addition of NaOH. It is assumed that the NaOH solution is bought as 25% solution. In the filter press, the solid and liquid fractions of the process stream are separated. The liquid fraction, the hydrolysate, contains most of the monomeric sugars, furanaldehydes and dissolved lignin from the pre-treatment, and has a TS of around 10%. This stream is partially (around 15% of the total stream) mixed with molasses (a sugar solution) and used for cultivation of yeast. In the yeast cultivation reactors sugars from the molasses and the hydrolysate is used by yeast to grow new cells, at a yield of around 50% w/w. The product stream from yeast cultivation contains about 5% yeast and over 90% water, and is sent to a centrifuge where the yeast cells are separated and sent to the SSCF-reactor. The liquid stream from the centrifuge is sent to the anaerobic digestion. The hydrolysate that is not sent to the yeast cultivation (i.e. 85% of the total stream) is directed to the anaerobic digestion reactor for production of biogas.

The solid stream from the filter press is sent to the bioreactor. In this bioreactor enzymes are first added in order to initiate saccharification of the remaining cellulose and hemicellulose to monomeric sugars (85% conversion of the polysaccharides to sugars). In the reactor yeast is also added in order to ferment sugars to ethanol. 95% of the glucose (hexoses) and 85% of the xylose (pentoses) is converted to ethanol and CO_2. Side reactions are also included in this step, where small amounts of lactic acid, glycerol and succinic acid are assumed to be produced. CO_2 is formed as a by-product both in the yeast cultivation and in the SSCF-bioreactor, and is vented to a scrubber unit, where ethanol is re-absorbed by a water flow before a fairly pure CO_2-stream is vented to the atmosphere. The loaded scrubber water is mixed with the ethanol-rich slurry leaving the SSCF-bioreactor.

The outlet ethanol stream from the fermentation, at 5% ethanol concentration, is sent to the distillation plant to increase the purity of the ethanol. The distillation plant is designed with two parallel beer columns, and then one rectifier column in series. The three columns are heat integrated with the highest pressure in the rectifier (3 bar), and the other two columns working at atmospheric and below atmospheric pressure. After the rectifier the near-azeotropic ethanol-water stream is sent to a set of molecular sieves for purification up to over 99% with an energy value of 10.4 MW calculated from the flowrate and the heat value (The Engineering ToolBox 2015). The bottom streams from the beer columns contain a lot of organic material, and are sent to a liquid/solid separation. The solid part, containing most of the lignin, is sent to a boiler for steam and electricity production, and the liquid fraction is sent to the anaerobic digestion. The bottom stream from the rectification column is mainly water, and is sent to the anaerobic digestion.

The total flow to the Waste Water Treatment Plant (WWTP) originating from water effluents in the entire process is almost 41 kg/s. The water treatment consists of two steps, one anaerobic digestion reactor and then an aerobic bio-oxidation step. In the anaerobic digestion, 90% of the COD (Chemical Oxygen Demand) in the waste stream entering the plant is turned into biogas (53% CO_2, 20% CH_4, and 22% H_2O), and the remaining organic material and water leaves the plant and is sent to the aerobic part of the WWTP. In the aerobic well-stirred bio oxidation reactor, 96% of the remaining COD is removed, and the purified water stream is taken to a clarifier in order to remove solids (sludge). Finally the water is assumed to pass through a filtration unit and is then sent to the recipient. The sludge from the WWTP is assumed to be sent to the boiler.

The hot utility in the process is steam produced in the boiler. The boiler is fed with by-products and effluents from the ethanol production (mainly lignin). Approximately 14.2 kg/s of steam at 450°C and 60 bars can be produced in the boiler. 5% (0.7 kg/s) of the steam is assumed to be blowdown, in order to not build up the concentration of contaminants in the system. The remaining 95% of the steam is passing through a turbine, generating electricity, medium (12 bar) and low (4.5 bar) pressure steam for the process. A condensing tail is included in order to maximise the production of electricity. The boiler feed water makeup consists of losses due to the blowdown of steam, and due to the direct injection of steam in the pre-treatment reactors.

The cooling in the process is achieved by using cooing water. However, this water must be regenerated and cooled again somewhere. Therefore, a cooling tower is used where air is blowing through the water and cooling it by evaporation. A blowdown of 3% of the circulating water flowrate is needed in order to not accumulate any contaminants in the cooling water circuit. (Fornell 2015)

In order to validate the results and make them comparable to results from the literature, a small sensitivity analysis was made. This was done by adding a fictional unit that removes approximately 90% of the TDS/TS going into the boiler and to the cooling tower, reverse osmosis can be considered for this purpose. This cleaning unit will result in that more sources can be utilized in the boiler and cooling tower after passing through the reverse osmosis units. (Martín et al. 2011)

3.1.2 Choice of streams

In order to minimize the fresh water consumption, the water should be as clean as possible when recirculating in order to be able to use it in most of the process units. In order to investigate recirculation both before and after the WWTP, the streams used in the analysis differ a bit. This analysis considers the whole plant, not just the parts existing at the BDP. This includes the WWTP, boiler and cooling tower for example. Flowrates and concentration levels were extracted from the process model which is based on results from analysis of experiments performed at the BDP, laboratory work and scientific literature. In order to minimize the size of the water treatment unit, the streams should preferably be recycled before the WWTP. The size of the WWTP is of interest, especially if the ethanol production plant is to be integrated with an existing plant and have to be adjusted to fit the existing WWTP.

The streams of water leaving the process, either to the WWTP or as a loss, are the ones available for regeneration. After studying the production process plant model, seven streams were found to be available for recirculation before the WWTP. When analysing the recirculation possibilities after the WWTP, this number was three. The sources available for recirculation after the WWTP are the boiler and cooling tower make-up water and the stream out from the WWTP. The stream out from the WWTP replaces all others streams except the make-up streams.

The units that should be the sinks in the analysis are the ones that require fresh water in any way. This can for example be as dilution for chemicals and biomaterial entering the process or as make-up water for the boiler at the plant. In total eight units needing water was found in the process model. For the analysis of only one contaminant, the same sources and sinks was used with the same flowrates. The water streams used and the process areas receiving water are shown in Figure 3.3.

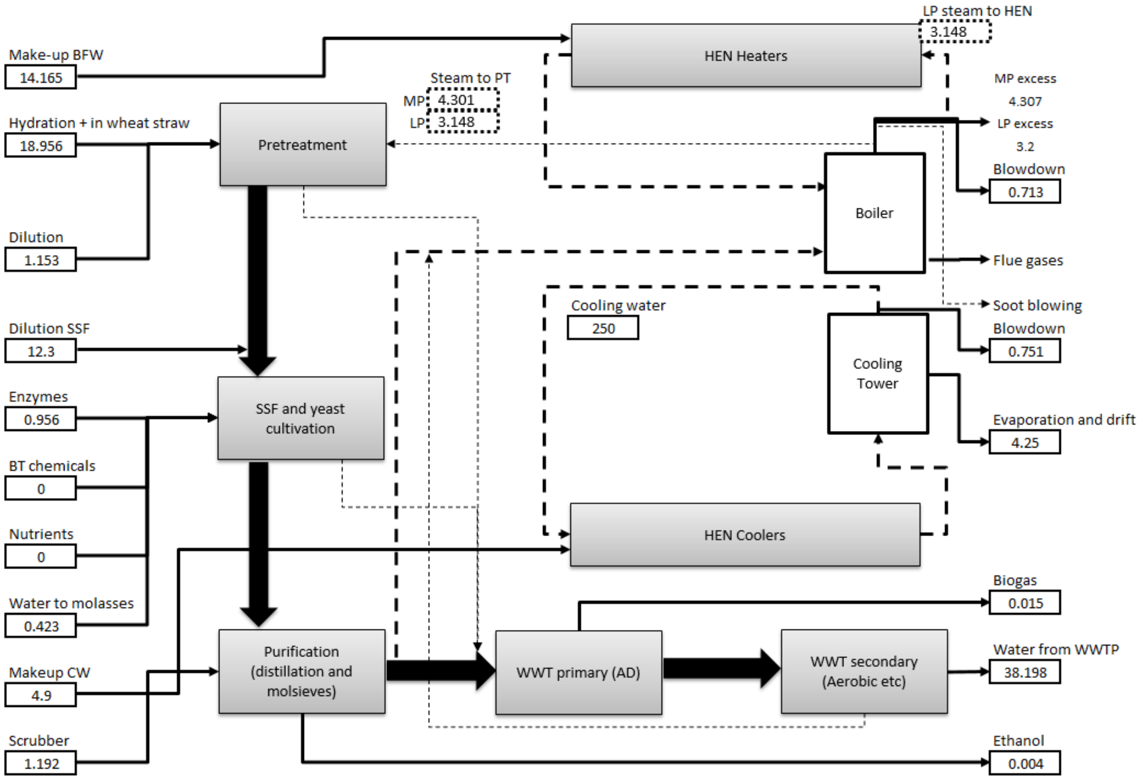


Figure 3.3 A schematic of the water balance in the process in the reference case. The name of the box specifies with what the water is added. All values are in kg/s and it is assumed that all excess water is taken to the WWTP. (Fornell 2015)

3.1.3 Setting constraints and extraction of data

Concentration limits of the contaminants in the units are hard to set and several assumptions had to be made in order to do so. One assumption is that the different contaminants do not inhibit or react with each other. This might lead to an over- or under-estimation of the water needed, but which of them is not known. Another assumption is that the choice of contaminants is representative for the process. The process contains a lot of components which can either enhance or inhibit the functionality. It is therefore important to know the concentrations of them in different parts of the process. However, as discussed previously, there are currently no methods that can handle a large number of contaminants when trying to establish a target for minimum water consumption. The methodology used in this thesis is limited to three contaminants and in discussion with researchers at Industrial Biotechnology, Chalmers, it was decided to focus on three contaminants or groups of contaminants. The contaminants chosen were the groups Total Dissolved Solids (TDS), organic acids and furan aldehydes for the multiple case study and TDS for the single contaminant case. Furfural was chosen to approximate the furan aldehydes since it is produced more than HMF (Franzén 2015) and because it inhibits the production of ethanol (Palmqvist & Hahn-Hagerdal 2000). Organic acids do not inhibit all parts of the process and streams, not even at relatively high concentrations. First it was decided to look at the ions Na^+ that influences the boiler and cooling system (Martín et al. 2011) in the process by formation of salts. However, since the model did lack of that data in some streams, this was changed to TDS or in some streams to TS (Total Suspended Solids TSS+TSS). The values of TDS/TS concentration are rough estimations since many process streams were missing data for this concentration. However, the validation and testing of the methodologies and the Excel application can still be performed for the process case study. (Franzén 2015)

Data used to find the minimum fresh flowrate target was extracted from a worksheet generated by the model in SuperPro Designer©. The input data to the modelling program was taken from tests performed at the BDP, from laboratory work performed at Industrial BioTechnology at Chalmers, but also from scientific literature. However, some further calculations of the data had to be done in order to perform the analysis.

The flowrates in the worksheet were given in kg/s which is a suitable unit also for the analysis in the Excel application. The concentrations of the constraints for the sinks however, were given in g/l and had to be converted to percentage of the total flowrate which is the working unit in the program. This was done by first assuming that the concentration of the contaminants were low so that the density of water could be used for the calculations. The flowrate of water was then multiplied with the concentration of the contaminant. The product was then divided by the density of water to give the weight of contaminant per second in the stream. This value was then divided by the total flowrate and multiplied by 100 to give the percentage of contaminant in the water. The calculations are presented in Equations (10)-(12).

$$\frac{\left[\frac{kg\ water}{s}\right]\cdot\left[\frac{kg\ contaminant}{m^3\ water}\right]}{\left[\frac{kg\ water}{m^3\ water}\right]}=\left[\frac{kg\ contaminant}{s}\right] \tag{10}$$

$$\frac{\left[\frac{kg\ contaminant}{s}\right]}{\left[\frac{total\ kg}{s}\right]}=\left[\frac{kg\ contaminant}{total\ kg}\right] \tag{11}$$

$$\left[\frac{kg\ contaminant}{total\ kg}\right]\cdot 100=\%\ contaminant \tag{12}$$

For the sources, the flowrates of the contaminants were given in kg/s in the worksheet together with the water flowrate. In order to achieve the percentage of contaminant for the sources, the flowrate of component had to be divided by the total water flowrate and then multiplied by 100 to get the percentage.

However, for TDS, the value was not reported for any streams except for the cooling tower blowdown, boiler blowdown and the stream from the WWTP. These values were given in mg/l and had to be re-calculated to g/l and then to % contaminant according to Equation

(10)-(12) in order to be used in the application. For the other streams, the concentration of TDS was approximated as TS and were calculated from the total flowrate and the flowrate of water according to Equation (13) and (14). This hade to be done since no data of TDS could be achieved for the process streams that do not leave the process.

$$TS = total\ flowrate - water\ flowrate \tag{13}$$

$$\frac{TDS\ flowrate}{total\ flowrate} \cdot 100 = \%\ contaminant \tag{14}$$

The need of make-up water for the boiler and cooling tower could not be found in the worksheet and had to be calculated. For the boiler, this was done by adding up all losses and usage (for other purposes than heat exchangers) of steam produced in the process. This includes the direct steam preheating of the pre-treatment reactors with low and medium pressure steam and the blowdown. The blowdown is performed in order to avoid accumulation of salts, organics and other components in the otherwise closed boiler system. The losses in the cooling tower correspond to the water lost through the air outflow and through blowdown. The cooling air for the cooling water circuit entrains water droplets when it leaves the cooling tower. The blowdown has the same function in the cooling circuit as in the boiler circuit. The concentration limits of TDS, acids and furfural in the make-up water for the boiling and cooling water system were taken from literature (Chavez-Rodriguez et al. 2013).

The streams available for recirculation before and after the WWTP, their positions, flowrates and concentrations can be seen in Table 3.2. The sink units together with their flowrates, concentration constraints and position are listed in Table 3.3.

When the sensitivity analysis was made, the reverse osmosis was assumed to remove approximately 90% of the TDS/TS going into it. Since the cleaning step was not modelled, the removal of TDS/TS can be realized in the Excel application as setting the constraints of these contaminants higher than in the reference case and make sure that more options of recirculation becomes possible. In the literature, it is often assumed that the process studied has both a water treatment unit and smaller units to clean the streams going into the boiler and cooling tower (Martín et al. 2011). The sensitivity analysis with new constraints on TDS is therefore only performed on the case with recirculation after the WWTP in order to be comparable to the results found in the literature. The constraints of TDS in both the boiler and the cooling tower were increased to 0.1% in order to be able to utilize the stream out from the WWTP. The sensitivity analysis constraints of TDS/TS concentration in the boiler and cooling tower is shown in Table 3.4.

Table 3.2 Streams available for recirculation before the WWTP are the first seven ones. After the WWTP it is only blowdowns from the boiler and the cooling tower and stream number 8 that are used. The sum of this case is written in italics. Values marked with an asterisk are values of TDS, the rest in that column are TS.

Source nr	**Position**	**Flowrate [kg/s]**	**Conc. acids [%]**	**Conc. furfural [%]**	**Conc. TDS/TS [%]**
SR 1	Condensate from flash	4.68	0.30	0.78	1.16
SR 2	Excess of hydrolysate	13.17	0.50	0.01	10.22
SR 3	From centrifuge	2.33	0.46	0.08	2.75
SR 4	Bottom of distillation towers	17.46	0.03	0.04	1.72
SR 5	Bottom of rectifier	1.14	3.54	0.00	4.30
SR 6	Boiler Blowdown	0.71	0.00	0.00	0.00*
SR 7	Cooler blowdown	0.75	0.00	0.00	0.22*
(SR 8	From WWTP	38.20	0.00	0.00	0.01*)
SUM		40.24/ *(39.66)*			

Table 3.3 Process units that are sinks in the water analysis in the case study and their constraints of concentrations. Values marked with an asterisk are values of TDS, the rest in that column are TS.

Sink nr	Position	Flowrate [kg/s]	Conc. acids [%]	Conc. furfural [%]	Conc. TDS/TS [%]
SK 1	Hydration	17.96	0.05	0.02	0.02
SK 2	Dilution in pre-treatment	1.15	0.05	0.02	0.02
SK 3	Water to enzymes	0.96	0.50	0.10	1.40*
SK 4	Dilution to SSF	12.30	0.50	0.10	1.40*
SK 5	Water to molasses	0.42	0.50	0.10	1.40*
SK 6	Water to scrubber	1.96	$5 \cdot 10^{-4}$	0.00	0.05
SK 7	Make-up boiler water	8.16	$0.25 \cdot 10^{-4}$	$0.25 \cdot 10^{-4}$	0.02
SK 8	Make-up cooling water	4.9	$1 \cdot 10^{-4}$	$10 \cdot 10^{-4}$	0.05
SUM		47.81			

Table 3.4 The updated concentration constraints of TDS/TS for the boiler and cooling tower, used in the sensitivity analysis.

Sink nr	Position	Flowrate [kg/s]	Conc. acids [%]	Conc. furfural [%]	Conc. TDS/TS [%]
SK 7	Make-up boiler water	8.16	$0.25 \cdot 10^{-4}$	$0.25 \cdot 10^{-4}$	0.1
SK 8	Make-up cooling water	4.9	$1 \cdot 10^{-4}$	$10 \cdot 10^{-4}$	0.1

3.1.4 Targeting and network design

To analyse the results of the methodology for multiple contaminants, the WPA targeting was performed for two different set-ups of the process for methodologies for a single and multiple contaminants. By executing WPA for different set-ups, the validity and accuracy of the methodologies could be assessed. By comparing the design and flowrates suggested by the application to the values from the modelled process with the same design, important knowledge about the methodologies could be obtained. The different set-ups were chosen with care to be as well-reasoned as possible and to contribute to better understanding of the process and the methodologies.

In order to minimize the fresh water consumption, it is desirable to reuse as much of the excess water as possible in the process. This means that the recirculation and direct reuse of the sources in the process should be maximized. (Foo 2013) If it is possible to reuse the water streams before any regeneration of the water is done, then both fresh water consumption, water effluent plant size and piping could be decreased. The two latter ones are effects of the water reuse since the sources are used in the process, and will not have to be taken to the WWTP to the same extent. This might be of interest when e.g. integrating the bioethanol production plant with an existing process plant. One of the set-ups is therefore water reuse performed prior to the WWTP. This was done for both the multiple contaminant methodology with three contaminants taken into account and with the single contaminant methodology.

The other set-up is when no stream is used before the waste water treatment plant and all effluents, except boiler and cooling blowdowns, are taken to regeneration. The outlet stream from the WWTP can then be used as a source for the sinks in the process. A set-up like this will result in a larger WWTP than for the previous case since almost all excess water in the process will have to be treated there. However, it might also be the set-up with the lowest fresh water need since the outlet from WWT is rather clean and can be utilized in many process units. That might be of interest in areas with a restricted water supply. This set-up was performed for the multiple methodology with three contaminants and with the single contaminant methodology. The different set-ups are summarized in Table 3.5. The results of the recirculation before the WWTP are presented in Chapter 4 and the results of the recirculation after the WWTP are presented in Appendix A.

Table 3.5 The different analysed combinations of set-ups.

	Single contaminant	**Multiple contaminant**	**Recirculation before WWTP**	**Recirculation after WWTP**
1	x		x	
2	x			x
3		x	x	
4		x		x

3.2 Implementation in Excel application

The application developed during this thesis was made in order to automate the procedure of targeting and designing the water network in a process. It is written in Visual Basic for Applications (VBA) as an application to Microsoft Excel. Excel is a commonly used software among companies and the resulting application can therefore be used by a lot of people. The choice of Excel as software was also made due to its user friendly interface. By typing instructions in the cells and having the methodology code hidden behind buttons, it is easy for users who are not familiar with VBA to use the application. The WPA tool program is manoeuvred from Excel worksheets by typing in process data and clicking buttons. The application is written as modules that are run from different buttons and together with the information in the Excel sheets, the code executes the methodologies described in Section 2.2 and 2.3. A simple schematic of the working procedure in the application is shown in Figure 3.4.

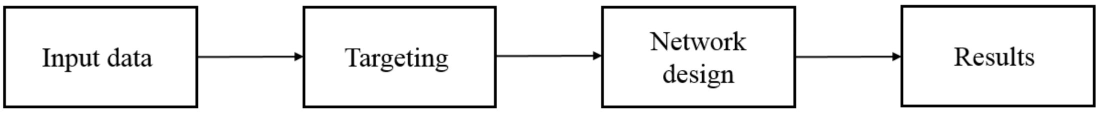


Figure 3.4 A simple schematic of how the Excel application is working.

The application is divided into two parts according to the different methodologies for single and multiple contaminants. First the user is instructed to go to the Information Sheet in order to set up the computer for using this application. There the user then specifies if it is a single or multiple contaminant problem that is to be analysed. The single contaminant button leads to a sheet where input data i.e. flowrates and concentrations, for the process are inserted before pressing the next button. This changes sheet again and creates the cascade table for this process. Depending on the results in the calculations, the table can be smaller or larger to find the minimum fresh feed target. The next button is coupled to code that goes through all sinks and sources in order to match them to reach the target by finding the higher and lower Nearest Neighbour (NN) to the current sink. The NNA is coded in the module connected to the button and a lot of different scenarios are possible in order to succeed in finding the optimal network.

If one at the information sheet chooses the multiple contaminants button the first new sheet shown is an input data sheet where up to three concentrations can be typed in together with the flowrates of the sinks and sources. By clicking the left button, the ranking of the sinks and sources are performed and the Multiple Resource Pinch Diagram (MRPD) is constructed from calculations in the code and exported to cells below the visible interface. Here also the NN's are found and stored as parameters in the code. The right button on this sheet takes the user to next sheet where the optimization is performed based on data exported from the input data sheet.

The optimization is done by using the solver in Excel and minimizing the goal cell selected in the code. The goal cell is chosen so it is the cleanest NN used to the current sink. The method chosen in the solver is LP Simplex which is suitable for linear mathematical problems. Equations (3)-(9) are typed into the solver in the code and the equations are based on the NN's. This means that the solver is updated with new goal cells to minimize for each sink to be filled. To start with, the optimization tries to minimize the NN of highest quality by changing the flowrates of all NN's. If this fails, the fresh feed is added as an extra source and the optimization solver can now be run. The solver starts with the sink with the highest concentration tolerance since this is the easiest to fill with recirculated source streams. The results of the optimization are exported to the next sheet when clicking on the network button. There the connections between all sinks and sources are shown in a network matrix.

The structure of the application is shown graphically in Figure 3.5. In Appendix B screenshots of the sheets in the Excel application are shown.

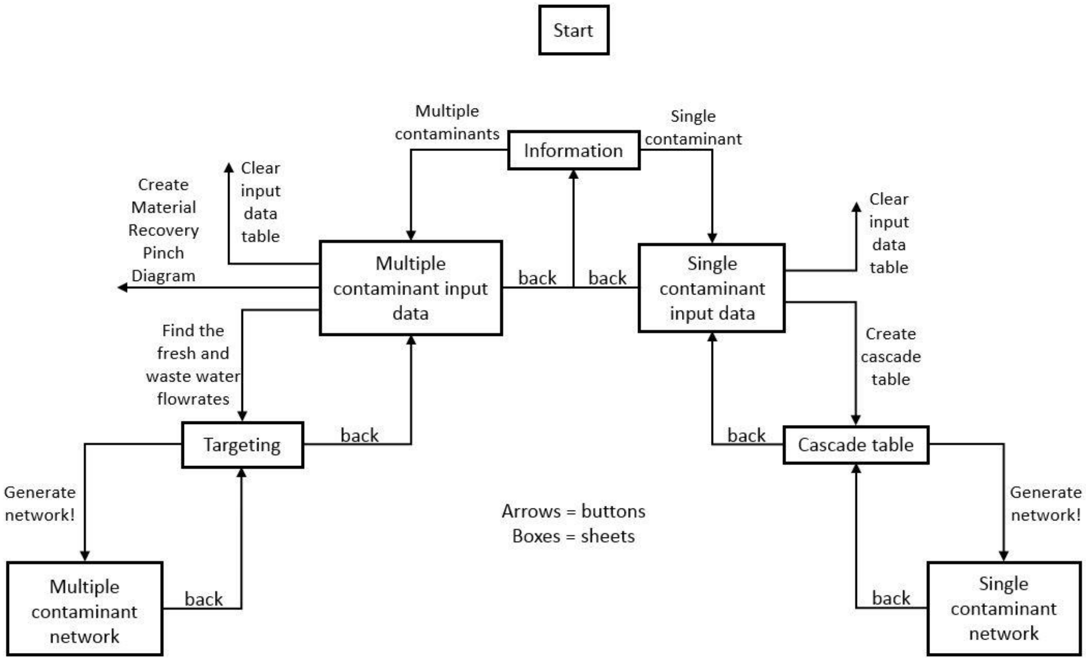


Figure 3.5 A Schematic of how the Excel application is constructed. The boxes indicate the worksheets and the arrows are the clickable buttons.

3.2.1 Assumptions

Both in the advanced and in the simple methodology for one contaminant, assumptions must be made in order to be able to write an application that is not too complicated. One assumption for the simple case that was made was that only one fresh water source is used and that it is clean, i.e. the concentration of the contaminant is zero. The process is only examined for its possibilities for direct recycle and reuse and for a major regeneration case with a waste water treatment plant. If the streams were allowed to be purified first, the results would be different. It was also assumed that the network that was object for the water minimization consisted of at most ten sources and ten sinks. This was mostly due to the complexity of a large network and its possibilities for recycling. In order to be successful with WPA, the network should not be too large and by looking at examples in the literature for WPA, it was decided that ten streams and ten process units should be enough to represent a process of accepted size.

For the more advanced methodology taking multiple contaminants into account, a lot more assumptions had to be made in order to perform a resource minimization. The first thing that had to be regulated was the number of different contaminants in the system that should be considered to make it manageable. Based on the number in Zhang et al. the number was chosen to be three. In this case, as well as for the single contaminant case, the maximum number of sinks and sources in the system was set to be ten of each. Zhang et al. describes that it is unfeasible to mix more than three sources in order to fulfil the need of the sink and this was used in the water minimization program (Zhang et al. 2013). This can be understood since all sources used for a sink must be mixed to correct concentration, which requires both accurate measuring of the flows and piping which are both costly and bulky in the process. Therefore the maximum number of mixed sources was set to three, excluding the fresh water feed. Since the fresh feed always needs to be connected to the process equipment due to unexpected stops in the process, this requires no additional piping than it should have done from the start.

Both the single contaminant and the multiple contaminant cases only consider direct reuse or recycling. No intermediate regeneration of the water is considered besides when the Waste Water Treatment Plant (WWTP) is taken into account and the reuse is done after that.

It should be recalled that WPA is, as described in Section 2.1, not a perfect methodology since it is not as precise as mathematical optimization. However, it is easier to understand and receives results that are close to the minimum ones. (Foo 2009)

4 Results

The reference case of the process does not include water recirculation and it is assumed that all excess water streams are sent to the WWTP to be cleaned and then released to the drain. The sum of the flowrates of the streams recognized as sources in Section 3.1.2 presented in Table 3.2 is therefore the total waste water flowrate from the process. This results in a waste water flowrate of 40.24 kg/s. The fresh water need in the process without any recirculation is the sum of all flowrates of the sinks seen in Table 4.1, i.e. 47.81 kg/s. With this use of water, the production of ethanol out from the process is 1.36 kg/s according to the modelling performed, which means that the process requires 35.15 kg water/kg ethanol produced in the reference case.

The water network design in the reference case is shown schematically in Figure 4.1 and the sinks are listed in Table 4.1. It should be mentioned that Figure 4.1 is the same as Figure 3.2 and that Table 4.1 is the same as Table 3.3.

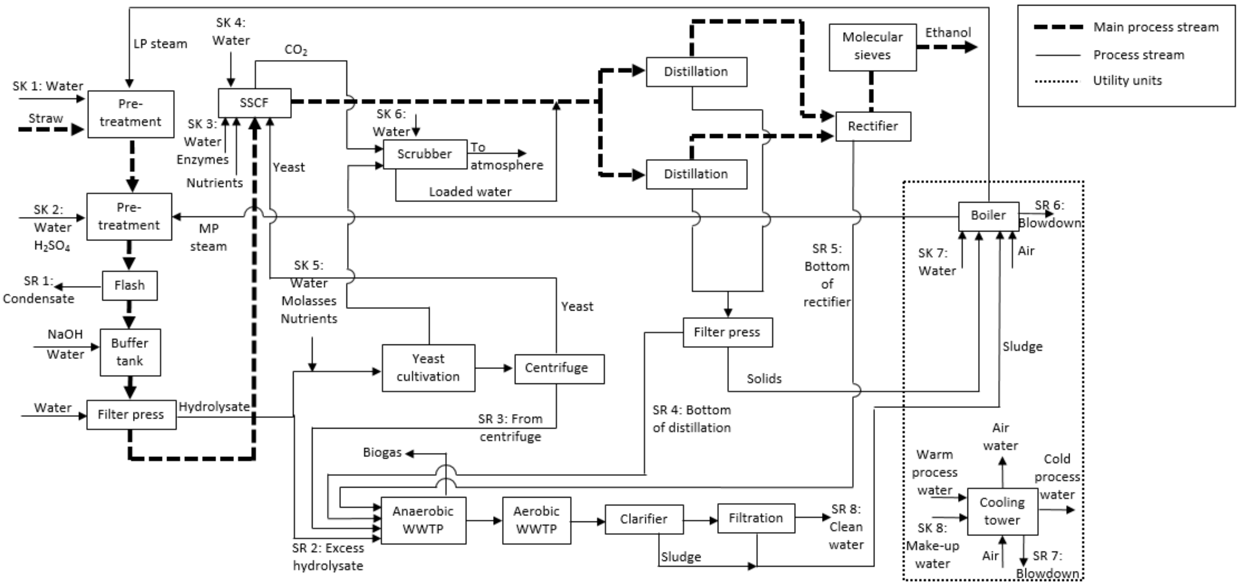


Figure 4.1 The water network design in the reference case. The fresh water flowrate to the units are listed in Table 4.1.

Table 4.1 The water need in the reference case. All water used is fresh feed.

Sink nr	Position	Flowrate [kg/s]	Conc. acids [%]	Conc. furfural [%]	Conc. TDS/TS [%]
SK 1	Hydration	17.96	0.05	0.02	0.02
SK 2	Dilution in pre-treatment	1.15	0.05	0.02	0.02
SK 3	Water to enzymes	0.96	0.50	0.10	1.40*
SK 4	Dilution to SSF	12.30	0.50	0.10	1.40*
SK 5	Water to molasses	0.42	0.50	0.10	1.40*
SK 6	Water to scrubber	1.96	$5\cdot10^{-4}$	0.00	0.05
SK 7	Make-up boiler water	8.16	$0.25\cdot10^{-4}$	$0.25\cdot10^{-4}$	0.02
SK 8	Make-up cooling water	4.90	$1\cdot10^{-4}$	$10\cdot10^{-4}$	0.05
SUM		47.81			

4.1 Single contaminant

With only one contaminant, the methodology by Foo was used to target the minimum water usage and design the network. This was done by analysing recirculation both before and after the WWTP. The results of the recirculation before the WWTP are presented in detail below, but for detailed results of the recirculation after the WWTP the reader is referred to Appendix A.

The methodology by Foo was programmed in the application, but can be performed by hand as well. As mentioned previously, the contaminant of interest was TDS or TDS approximated by TS. After ranking and construction of the cascade table the fresh feed need was found out to be 39.20 kg/s and the waste water flowrate was 25.61 kg/s. However, when inspecting the network matrix generated in the network sheet, this was found to be incorrect. The proposed design was working but did not agree with optimal design. After performing the material balances calculations by hand, the fresh feed was found to be much higher than before. It also had to be taking into account that the boiler blowdown cannot be recirculated into the boiler and the cooling tower blowdown cannot be recirculated into the cooling tower. The final results of the fresh water flowrate was 36.79 kg/s and a waste flowrate of 29.17 kg/s. This means a decrease in fresh water needed of 11.0 kg/s or 23.0% compared to the reference case. In order to achieve this decrease of water resource, the network shown in Table 4.2 should be implemented. PT in the table stands for Pre-Treatment. The proposed network is shown in Figure 4.2.

Table 4.2 The minimum water consuming network for recirculation before the WWTP with one contaminant. All flowrates are in kg/s.

	Hydration	**Make-up boiler**	**Make-up cooling**	**Dil. PT**	**Dil. SSF**	**Scrubber**	**Enzymes**	**Molasses**
Fresh	17.65	7.41	4.64	1.13	4.00	1.96		
Cooler blow-down		0.75						
Boiler blow-down								
From centrifuge								
Cond. from flash	0.31		0.21	0.020	3.04	0.08	0.55	0.24
Excess of hydrolysate								
Bottom rectifier								
Bottom distillation					5.26		0.41	0.18

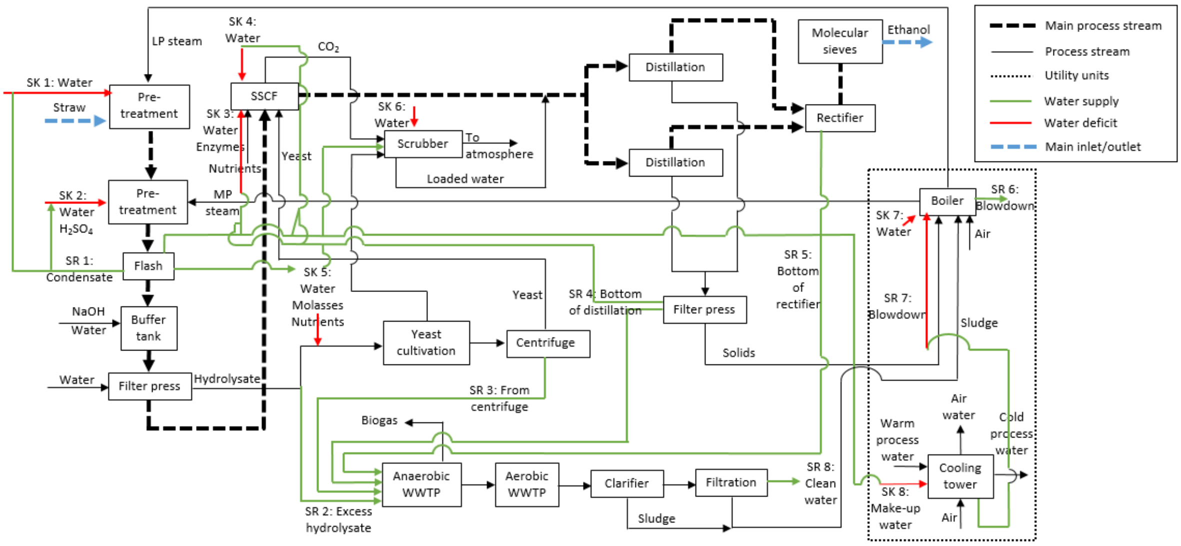


Figure 4.2 The final water network after applying the changes proposed by the methodology in the Excel application for a single contaminant. The green lines are the new water supplies and the red arrows are the water demand.

If it is assumed, as in the reference case, that all excess water in the process is taken to the WWTP before it is recirculated, the results are different from the ones for recirculation before the WWTP. In this case there are only three sources in total that can be recirculated. The final results showed that the fresh water need was found to be 25.13 kg/s and the waste water flowrate was 16.97 kg/s. This is a larger decrease than for the case with recirculation before the WWTP. In this set-up, the reduction of fresh water became 22.68 kg/s or 47.44% compared to no recirculation. The results are presented in detail in Appendix A.

4.2 Multiple contaminants

The water system with multiple contaminants case was analysed with the methodology proposed by Zhang et al. The more contaminants and process properties taken into account, the more accurate the targeting of the flowrates can be done. The results of recirculation before and after the WWTP are described below, but for details about the recirculation after the WWTP are presented in Appendix A.

If the same network as for the single contaminant was used while taking three contaminants into account, the concentration constraints of the process units would have been violated. By multiplying the concentration of the contaminants with the flowrates proposed by the single contaminant network for each unit and then divide by the sink flowrate according to Equation (15) and (16), it could be found if the constraints of the units were violated or fulfilled. Violations were found in five units and are marked with bold text and red squares in Figure 4.3 and in Table 4.3.

$$F_{SR1}c_{SR1} + F_{SR1}c_{SR2} + F_{SR1}c_{SR3} = F_{SK1}c_{SK1} \qquad (15)$$

$$\frac{F_{SK1}c_{SK1}}{F_{SK1}} = c_{SK1} \tag{16}$$

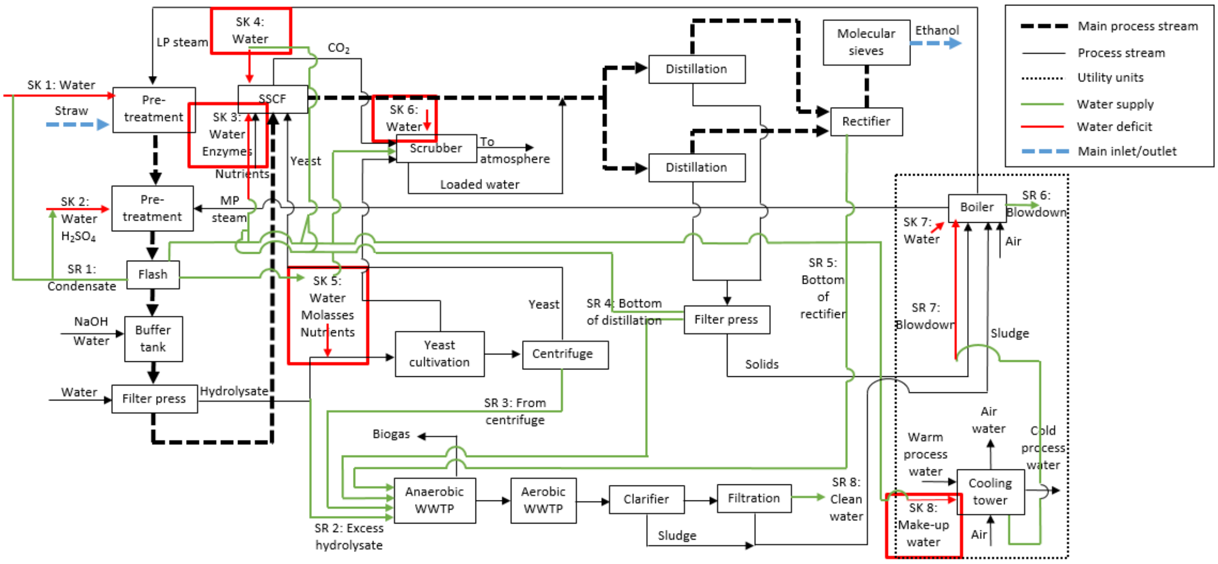


Figure 4.3 The violations in concentration constraints when the single contaminants network is used while taking three contaminants into account. The violations of the sink concentration constraints are marked with bold text and a red square.

The violations occurred due to a too high concentration of furfural in SK 3 (water to enzymes) and SK 5 (water to molasses) and due to both the furfural and acid concentration in SK 4 (Dilution SSF), SK 6 (Water to scrubber) and SK 8 (Make-up cooling water). Because of these violations, a methodology taking multiple contaminants into account is needed.

Table 4.3 The calculated concentrations of the contaminants in the streams entering the sinks. The value in brackets is the maximum tolerable in that sink. Red cells are violating that value.

	Hydration	**Makeup boiler**	**Makeup cooler**	**Dilution SSCF**	**Dilution PT**	**Scrubber**	**Enzymes**	**Molasses**
Acids [%] (max %)	0.005 (0.05)	0 (0.000025)	0.013 (0.0001)	0.011 (0.5)	0.005 (0.05)	0.013 (0.0005)	0.181 (0.5)	0.181 (0.5)
Furfural [%] (max %)	0.013 (0.02)	0 (0.000025)	0.034 (0.001)	0.210 (0.1)	0.013 (0.02)	0.034 (0)	0.464 (0.1)	0.464 (0.1)
TDS/TS [%] (max %)	0.020 (0.02)	0.017 (0.02)	0.05 (0.05)	1.022 (1.4)	0.02 (0.02)	0.050 (0.05)	1.4 (1.4)	1.4 (1.4)

When taking three components into account the accuracy of the calculations is increased since more limitations will give a result closer to what would be possible in reality. When the recirculation is done before the WWTP the optimization in the Excel application calculated the minimum possible fresh water need for the process to be 41.53 kg/s and the waste stream to be 33.95 kg/s. This is a decrease of 6.28 kg/s or 13.14% for the fresh water needed. The network generated by the application can be seen in Table 4.4 and Figure 4.4.

Table 4.4 The minimum water consuming network for recirculation before the WWTP with three contaminants. All flowrates are in kg/s.

	Hydration	**Make-up boiler**	**Make-up cooling**	**Dil. PT**	**Dil. SSF**	**Scrubber**	**Enzymes**	**Molasses**
Fresh	17.96	8.16	4.9	1.04	7.93	1.96	0.15	0.07
Cooler blow-down				0.11				
Boiler blow-down								
From centrifuge					0.71			
Cond. from flash					2.33			
Excess of hydrolysate					1.33		0.09	0.04
Bottom rectifier								
Bottom distillation							0.72	0.32

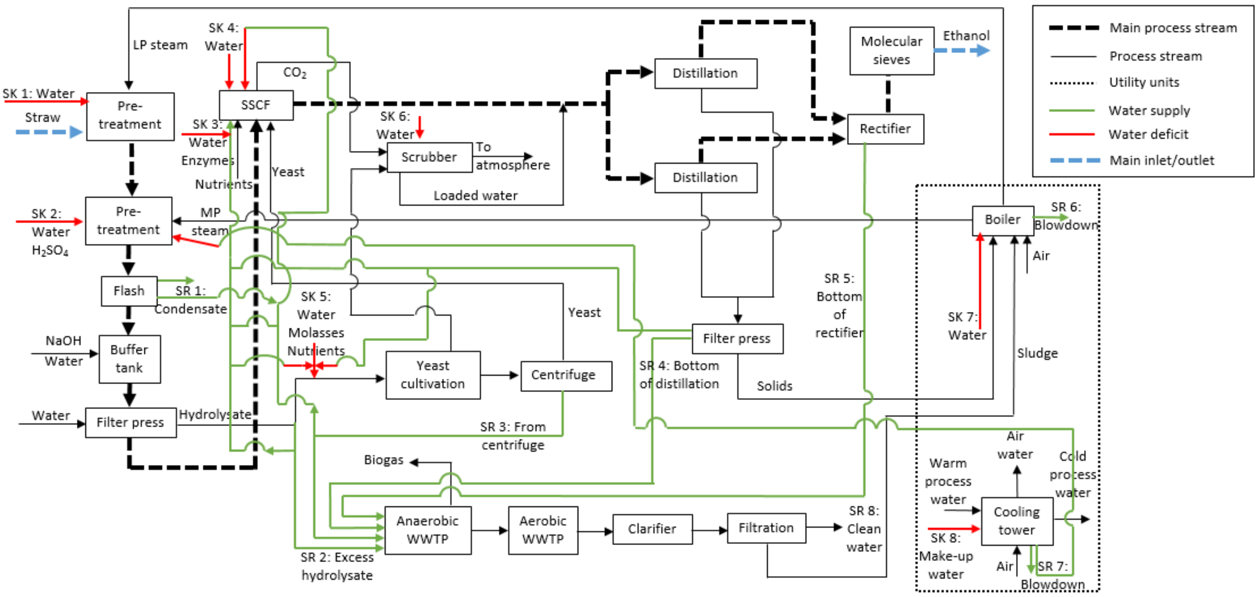


Figure 4.4 The final water network after applying the changes proposed by the methodology in the Excel application for multiple contaminants. The green lines are the new water supplies and the red arrows are the water demand.

After the WWTP most of the contaminants are removed and the stream out from the reactors can be utilized a lot in the process units. The fresh water need for the process with the network design shown in Table A.2 in Appendix A became 43.96 kg/s and the waste water produced is 35.80 kg/s. This is a decrease of 8.0% or 3.85 kg/s for the fresh water streams compared to the reference case. It should be a larger decrease after the WWTP so it might be suspected that something is wrong with this analysis.

The final results of all different set-ups are showed in Table 4.5. It can be seen from the tables above that the fresh water needed is smaller for both of the cases performed with single contaminant methodology than for the multiple contaminant methodology. One can also see that the decrease for the cases calculated with the single contaminant methodology is much larger than for the other case. This is a good reason to believe that the accuracy of WPA with only one contaminant is not so high. However, it is a bit confusing how the fresh water need can be higher for the case with recirculation after the WWTP. However, only three of the sinks have a concentration constraint that allows the stream out from the WWTP to be used, which leads to a high fresh water demand.

The use of fresh water per ethanol produced is decreased to 30.5 kg water per kg ethanol produced for the case of recirculation before the WWTP with multiple contaminants. This case also results in a waste water flowrate of 25 kg water per kg ethanol produced that must be taken care of.

Table 4.5 The final results of the water minimisation of the ethanol production process. The decrease in percent of fresh water is compared to the reference case.

	Reference case	**Recirculation before, single**	**Recirculation after, single**	**Recirculation before, multiple**	**Recirculation after, multiple**
Fresh water need [kg/s]	47.81	36.79	25.13	41.53	43.96
Waste water [kg/s]	40.24	29.17	16.97	33.95	35.80
Decrease fresh [%]	-	23.05	47.44	13.14	8.05
Decrease fresh [kg/s]	-	11.02	22.68	6.28	3.85

When assuming that a regeneration unit is added before the boiler and the cooling tower by increasing the concentration constraints of TDS in these units, the results were different. Since the whole stream from the WWTP could be utilized in the boiler and the cooling tower, the fresh water need and the waste water effluent decreased. The analysis was only performed for the cases with recirculation after the WWTP in order to be comparable to the literature. For the single contaminant case the new fresh water need was 15.38 kg/s and the waste water effluent 7.22 kg/s. This represent decreases of 67.83% and 82.06% respectively compared to the reference case with a fresh water need of 47.81 kg/s and a waste water effluent of 40.24 kg/s. For the multiple case, the fresh water needed decreased to 32.17 kg/s and the waste water effluent to 24.01 kg/s which is a decrease of 32.71% and 40.33% respectively compared to the reference case. When using a cleaning equipment like reverse osmosis, the water usage per ethanol produced is 11.31 kg in the single contaminant case and 23.65 kg water per kg ethanol produced for the multiple contaminant case. This is much lower than the 30.5 kg of water needed per kg ethanol produced with no regeneration in the multiple contaminant case.

Table 4.6 The results of the sensitivity analysis. The reference constraints for the boiler was 0.05% and 0.02% for the cooling tower. The decrease calculated from the reference case with no recirculation.

	Recirculation after WWTP, single	**Recirculation after WWTP, multiple**
Fresh water need, standard constraints [kg/s]	25.13	43.96
Fresh water need, constraints = 0.1% [kg/s]	15.38	32.17
Decrease of fresh water needed from standard constraints [kg/s]	9.75	11.79
Decrease of fresh water needed from reference case [%]	67.83	32.71
Waste water effluent, reference case constraints [kg/s]	16.97	35.80
Waste water effluent, constraints = 0.1% [kg/s]	7.22	24.01
Decrease of waste water effluent from standard constraints [kg/s]	9.75	11.79
Decrease of waste water effluent from reference case [%]	82.06	40.33

5 Discussion

From the results of the optimization of the water network in Chapter 4, it can be seen that the higher fresh flowrate for the multiple cases comes from the lack of recirculation. Consider for example the condensate for the flash stream in the cases with recirculation before the WWTP. It is used for all but one sinks for the single case, but only for one for the multiple case. On the other hand, the excess of hydrolysate is used for three sinks in the multiple case, but not for any sink for the single case. This illustrates the effect of the pinch or bottleneck in the system. The bottleneck is the concentration that inhibits any more possibilities to recirculate streams. This can be seen from the results of the multiple methodology after the WWTP. One idea is that since the stream out from the WWTP is so clean, it should not be any big problems with utilizing it in the process. However, the concentration that is the highest in that stream is for TDS/TS and that is unfortunately the same contaminant with only three sinks with lower constraints than that. This makes it hard to utilize the stream from the WWTP. When increasing the concentration constraints of TDS in the boiler and cooling tower, this resembles a cleaner input into these units. By increasing the constraint to a higher concentration than the stream from the WWTP has, this stream can now be utilized in the boiler and cooling tower. This decreases the fresh water need with up to 38 kg/s instead of 25 kg/s in the single contaminant case.

When performing WPA it is of interest to question the proposed design. If it is only recirculating a small flow or if the processes that should be connected are located too far away geographically at the plant to make the match unfeasible, the design should be revised. The same is true if the optimized design mixes more than three sources except the fresh feed. Theoretically it is possible, but in reality the control of more than three sources to fill up the need of a sink could be cumbersome. Unexpected stops in the process can lead to stops of the sources to the sink which will obstruct the filling of the sink demand even more. The solution to this is to have an input of fresh resource to all water requiring process units to start when needed.

When trying to target and design large networks the methodology of WPA can be hard to use, especially if it is performed graphically it will be hard to handle too many lines in one diagram. Then the use of mathematical modelling will be both easier and more accurate to use, due to its algebraic structure. This is true also for smaller process systems, but the main disadvantage of mathematical programming is still that it lack the possibility to see and easier understand what is happening. This can be a problem when process knowledge must be taken into account in order to create a feasible water network.

It is seen from the results that the fresh water need varies a lot when taking one or three contaminants into account. This is due to the number of constraints limiting the process. For only one constraint in the system, it might look like there are a lot of possible matches among the sinks and sources. When taking more contaminants into account, it was seen that the matches were not the same and the fresh water need increased. If the process water network would be analysed with even more substances in it, the fresh water need would probably increase even further. This is a situation where mathematical programming also would be of interest. It would then be possible to analyse the network, without any assumptions on how the substances do or do not interact, how many contaminants there are and how many sources and sinks that can be present in the analysis.

The assumptions made in this project can either over estimate or under estimate the need of fresh water usage. The assumption that only three sources should be mixed to fulfil the demand of a sink is one assumption that over estimates the fresh water usage. If more sources would have been mixed, the constraint might have been fulfilled without taking the fresh water as the final source and fill up the remaining need to the sink. If intermediate regeneration would have been performed, more recirculation possibilities would exist. This can be verified by comparing the results from the single contaminant case with recirculation before and after the WWTP. With recirculation before the WWTP the fresh water need was 36.79 kg/s compared to recirculation after the WWTP of 25.13 kg/s. When performing reverse osmosis before the boiler and the cooling tower, the fresh water flowrate needed becomes 15.38 kg/s. However, even if the fresh water need can be decreased with regeneration of the water before recirculation, this must be compared to the feasibility and the process changes associated to that option.

The methodology of WPA does not always find the minimum water need, but it is as close as possible to it (Zhang et al. 2013). The result of 30.5 kg water per kg ethanol produced is much higher than reported values from other studies in literature. Usage of water as low as 1.54 kg of water per kg of ethanol was possible to achieve in another study performed (Ahmetović et al. 2010) which is far from values obtained using the Excel application developed in this project. This is far from the results in the project even with the extra regeneration unit in the sensitivity analysis. In that analysis the need of fresh water was 23.65 kg water per kg ethanol produced for multiple contaminants taken into account and 11.31 kg water per kg ethanol produced for a single contaminant, which are closer to the literature value than without the extra regeneration. However, Ahmetović et al. decreased the water need from the eairlier reported values of 3-15 kg water per kg of ethanol produced. In this range, the result from the sensitivity analysis in this project is within the limits.

A study by Alkasrawi et al. from 2002 found that depending on where in the process the recirculation was performed, reductions of 40% to 60% in fresh water use were possible (Alkasrawi et al. 2002). This is not close to the 6-22% decrease in this work, but when comparing the results achieved in the sensitivity analysis to the results from Alkasrawi et al. (2002), the fresh water decrease of 68% and 33% for single and multiple contaminants case respectively are the same or better than in the literature. This proves that the influence of the assumptions made, are of big importance for the results and conclusions. The reason for this large deviation can be that Ahmetović et al. performed their study with only one contaminant, and not a pseudo-contaminant, taken into account. Another reason might be that they used mathematical programming in order to find the minimum possible values. When comparing the results to a methodology handelling multiple contaminats, decreases of fresh water usage of 50% have been reported in the literature (Zhang et al. 2013) which are quite close to the 47% decrease in the single contaminant methodology case afte the WWTP in this project. Differences in water usage decreases depending on the process considered is to be expected, but also suggests that the accuracy of this methodology is not always perfect.

In the case of multiple contaminants with recirculation before the WWTP, the amount of waste water produced is 25 kg per kg ethanol produced in total and 15.29 kg water per kg ethanol after the fermentation. In the literature this latter value, for a corn based ethanol production process, is found to be approximately 13 kg water per kg ethanol (Pimentel & Patzek 2005) which is quite close to the one achieved in this study.

It should be kept in mind when discussing the results and findings that the constraints for the process units are rough, the concentration of contaminants in the sources are received from a model or estimated.

Decreases of fresh water used were found in this project work, but the results should be seen more as guidelines of possible recirculation possibilities than definite water savings. The importance of making good assumptions have been shown and should be taken into account when evaluating results from WPA of a process.

6 Conclusion

In this project the possibilities to minimize fresh water usage in a case study of a lignocellulosic ethanol production process was evaluated. This was achieved using two different methodologies based on the insight-based methodology water pinch analysis, one for a single contaminant and one for multiple contaminants. The methodologies were programmed in Visual Basic for Applications as an add-in to Microsoft Excel in order to automatize the process of finding the minimum possible water usage for the process. The application is divided into two main parts, one related to targeting and the other to network design. The methodology was then used in a case study in which two different set-ups with recirculation of water streams before and after the waste water treatment plant were examined for both the single and the multiple contaminant methodology.

The results from the case study showed that a decrease of fresh water usage is possible. For the cases where only one contaminant was taken into account the decrease was larger than for the multiple contaminant cases. For the single contaminant methodology the decrease before and after the WWTP were approximately 23% and 47%, respectively, compared to the reference case with no recirculation. These numbers for the multiple contaminant cases were 13% and 8%, respectively.

One reason why larger decreases were achieved for the single contaminant methodology is due to the lower accuracy compared to several contaminants taken into account. The result of possible fresh water decreases for single and multiple contaminants are on the same order of magnitude as results reported in the literature when the process set-ups are similar. However, when the results of three contaminants are analysed and no regeneration is performed, they differ from literature results regardless of whether the literature results compared are generated using a methodology for one or multiple contaminants. To handle three or more contaminants in an accurate and good way, mathematical programming would probably be a better option.

This project has also revealed that the choice of assumptions, number of contaminants and concentration constraints all have a large impact on the results of a water pinch analysis and should be chosen with care. The process chosen to perform the study on should preferably not be too complicated or large in order to succeed with WPA, even though the theoretical limits of the tool are generous.

7 Future work

This thesis work has investigated water pinch analysis and its possibilities to be applied on a lignocellulosic ethanol production process. However it has also revealed a lot that can be further analysed and investigated in the future.

First, the code that executes the methodologies can be further developed by someone with proper software programming skills in order to both make it more accurate and to speed up the calculation processes.

A possible expansion of the application is possible by allowing more than ten sources and sinks and more than three contaminants. However, it should first be supported by literature that such an expansion of number of contaminants is possible.

Another potential development of the program is to use more than one fresh feed and to allow contamination of them. This changes the calculation procedure somewhat and might result in other conclusions.

The WPA can also be performed again with different process set-ups, assumptions, constraints and with properly calculated flowrates.

The way of tackling the resource minimization in this thesis have been recirculation and direct reuse except for in the sensitivity analysis. This could be expanded by evaluating results from all parts of the WMH e.g. regeneration between process units. Another way to expand the possibilities with WPA would be to allow shifting the flowrates after achieving a network proposal in order to get a less complicated network than the minimum possible one. This is described further by Foo (2013).

The final remark is however, as discussed in the previous chapter, that it might not be feasible to perform WPA on a bio-technological process due to its complicated function and therefore the difficulties with setting reasonable constraints.

References

Ahmetović, E., Martín, M. & Grossmann, I.E., 2010. Optimization of energy and water consumption in corn-based ethanol plants. *Industrial & Engineering Chemistry Research*, 49(17), pp.7972–7982.

Alkasrawi, M., Galbe, M. & Zacchi, G., 2002. Recirculation of process streams in fuel ethanol production from softwood based on simultaneous saccharification and fermentation. *Applied biochemistry and biotechnology*, 98-100, pp.849–861.

American Heritage Dictionary, 2014. American Heritage Dictionary of the English Language. Available at: https://www.ahdictionary.com/word/search.html?q=carbon+neutral [Accessed February 5, 2015].

Balat, M., Balat, H. & Öz, C., 2008. Progress in bioethanol processing. *Progress in Energy and Combustion Science*, 34, pp.551–573.

Biomass Energy Center, 2011. Straw. Available at: http://www.biomassenergycentre.org.uk/portal/page?_pageid=75,17972&_dad=portal&_schema=PORTAL [Accessed June 9, 2015].

Chavez-Rodriguez, M.F. et al., 2013. Water reuse and recycling according to stream qualities in sugar-ethanol plants. *Energy for Sustainable Development*, 17(5), pp.546–554. Available at: http://dx.doi.org/10.1016/j.esd.2013.08.003.

El-Halwagi, M.M., Gabriel, F. & Harell, D., 2003. Rigorous Graphical Targeting for Resource Conservation via Material Recycle/Reuse Networks. *Industrial & Engineering Chemistry Research*, 42(19), pp.4319–4328.

European Biofuels Technology Platform, 2014a. Cellulosic Ethanol.

European Biofuels Technology Platform, 2014b. Cellulosic Ethanol. Available at: http://www.biofuelstp.eu/cellulosic-ethanol.html [Accessed January 27, 2015].

Feng, X. & Deng, C., 2013. Synthesis of Water Networks with Water Loss and Gain via an Extended Pinch Analysis Technique. In J. J. Klemeš, ed. *Handbook of Process Integration (PI) Minimisation of Energy and Water Use, Waste and Emissions*. Woodhead Publishing, pp. 401–421.

Foo, D.C.Y., 2013. *Process Integration for Resource Conservation* 1 st.,

Foo, D.C.Y., 2009. State-of-the-Art Review of Pinch Analysis Techniques for Water Network Synthesis. *Industrial & Engineering Chemistry Research*, 48(11), pp.5125–5159.

Fornell, R., 2015. *Personal Communication*, Franzén, C.-J., 2015. *Personal Communication*,

Galbe, M. & Zacchi, G., 2002. A review of the production of ethanol from softwood. *Applied Microbiology and Biotechnology*, 59(6), pp.618–628.

Hahn-Hägerdal, B. et al., 2006. Bio-ethanol - the fuel of tomorrow from the residues of today. *Trends in Biotechnology*, 24(12), pp.549–556.

Martín, M., Ahmetović, E. & Grossmann, I.E., 2011. Optimization of water consumption in second generation bioethanol plants. *Industrial and Engineering Chemistry Research*, 50, pp.3705–3721.

Müller, V., 2008. Bacterial fermentation. *eLS*.

Novoenzymes, 2013. World's first advanced biofuels facility opens. Available at: http://www.novozymes.com/en/news/news-archive/Pages/World%E2%80%99s-first-advanced-biofuels-facility-opens.aspx [Accessed January 23, 2015].

Palmqvist, B., 2014. *Processing Lignocellulosic Biomass into Ethanol Implications of High Solid Loadings*. Lund University.

Palmqvist, E. & Hahn-Hagerdal, B., 2000. Fermentation of lignocellulosic hydrolyzates. II: inhibitors and mechanisms of inhibition. *Bioresource technology*, 74, pp.25–33.

Pimentel, D. & Patzek, T.W., 2005. Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower. *Natural Resources Research*, 14(1), pp.65–76.

Ricardo Soccol, C. et al., 2011. Lignocellulosic bioethanol: Current status and future perspectives. In A. Pandey et al., eds. *Biofuels*. Elsevier Inc., pp. 101–122.

The Engineering ToolBox, 2015. Fuels- Higher Calorific Values. Available at: http://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html [Accessed June 9, 2015].

U.S. Department of Energy, 2014. Ethanol Vehicle Emissions. Available at: http://www.afdc.energy.gov/vehicles/flexible_fuel_emissions.html [Accessed February 5, 2015].

USDA Foreign Agricultural Service, 2013. *EU Biofuels Annual 2013*, Available at: http://gain.fas.usda.gov/Recent GAIN Publications/Biofuels Annual_The Hague_EU-27_8-13-2013.pdf [Accessed February 5, 2015].

Wan Alwi, S.R. & Manan, Z.A., 2013. Water Pinch Analysis for Water Management and Minimisation: An Introduction. In J. J. Klemeš, ed. *Handbook of Process Integration (PI) Minimisation of Energy and Water Use, Waste and Emissions*. Woodhead Publishing, pp. 353–382.

Zhang, Q., Feng, X. & Chu, K.H., 2013. Evolutionary graphical approach for simultaneous targeting and design of resource conservation networks with multiple contaminants. *Industrial and Engineering Chemistry Research*, 52(3), pp.1309–1321.

Zhao, Z., Liu, G. & Feng, X., 2007. The Integration of the Hydrogen Distribution System with Multiple Impurities. *Chemical Engineering Research and Design*, 85(9), pp.1295–1304.

Appendix A

Detailed results of recirculation after the WWTP

Single contaminant methodology

The final results showed that the fresh water need was found to be 25.13 kg/s and the waste water flowrate was 16.97 kg/s. This is a larger decrease than for the case with recirculation before the WWTP. In this set-up, the reduction of fresh water became 22.68 kg/s or 47.44% compared to no recirculation. In order to achieve this decrease of water resource, the network shown in should be implemented. PT in the table stands for Pre-Treatment. The water network design can be seen in Table A.1.

Table A.1 The minimum water consuming network for recirculation after the WWTP with one contaminant. All flowrates are in kg/s.

	Hydration	**Make-up boiler**	**Make-up cooling**	**Dil. PT**	**Dil. SSF**	**Scrubber**	**Enzymes**	**Molasses**
Fresh	14.24	6.47	2.36	0.91		0.94	0.21	
From WWTP	3.73	1.69	2.54	0.24	12.30	1.02		0.42
Cooler blow-down							0.75	
Boiler blow-down								

Multiple contaminant methodology

The fresh water need for the process with recirculation after the WWTP, shown in Table A.2 was found to be 43.96 kg/s and the waste water effluent was 35.8 kg/s. This is a decrease of 8.05% or 3.85 kg/s for the fresh water streams compared to the reference case.

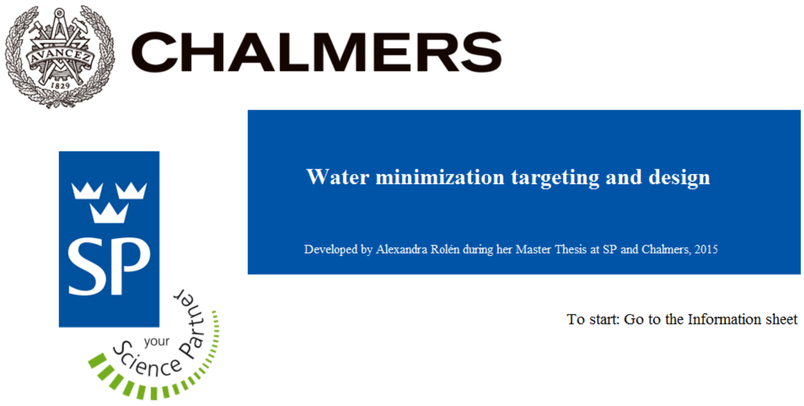
Table A.2 The minimum water consuming network for recirculation after the WWTP with three contaminants. All flowrates are in kg/s.

	Hydration	**Make-up boiler**	**Make-up cooling**	**Dilution PT**	**Dilution SSF**	**Scrubber**	**Enzymes**	**Molasses**
Fresh	17.96	8.16	4.90	1.15	10.84	0.94		
Cooler blow-down					0.75			
Boiler blow-down					0.71			
From WWTP						1.02	0.96	0.42

Appendix B

Excel application screenshots

Start:

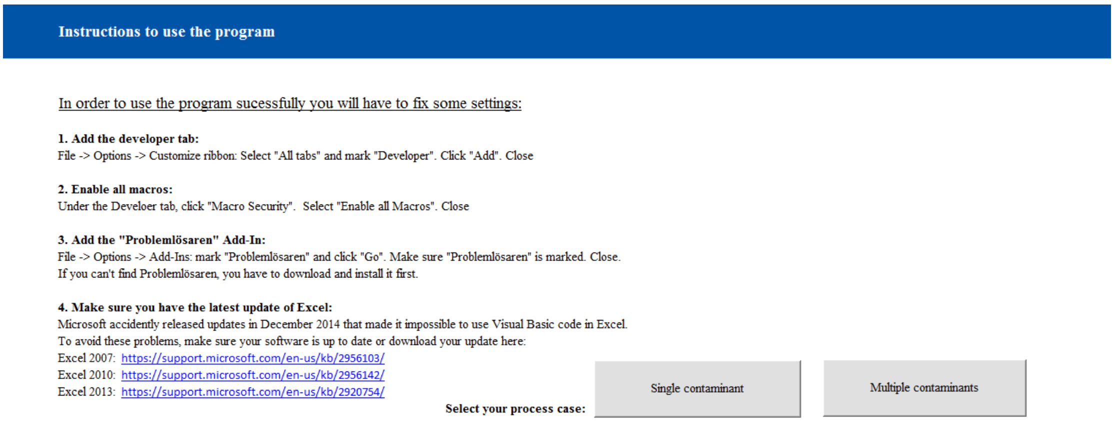


Water minimization targeting and design

Developed by Alexandra Rolén during her Master Thesis at SP and Chalmers, 2015

To start: Go to the Information sheet

Information:



Instructions to use the program

In order to use the program sucessfully you will have to fix some settings:

1. Add the developer tab:
File -> Options -> Customize ribbon: Select "All tabs" and mark "Developer". Click "Add". Close

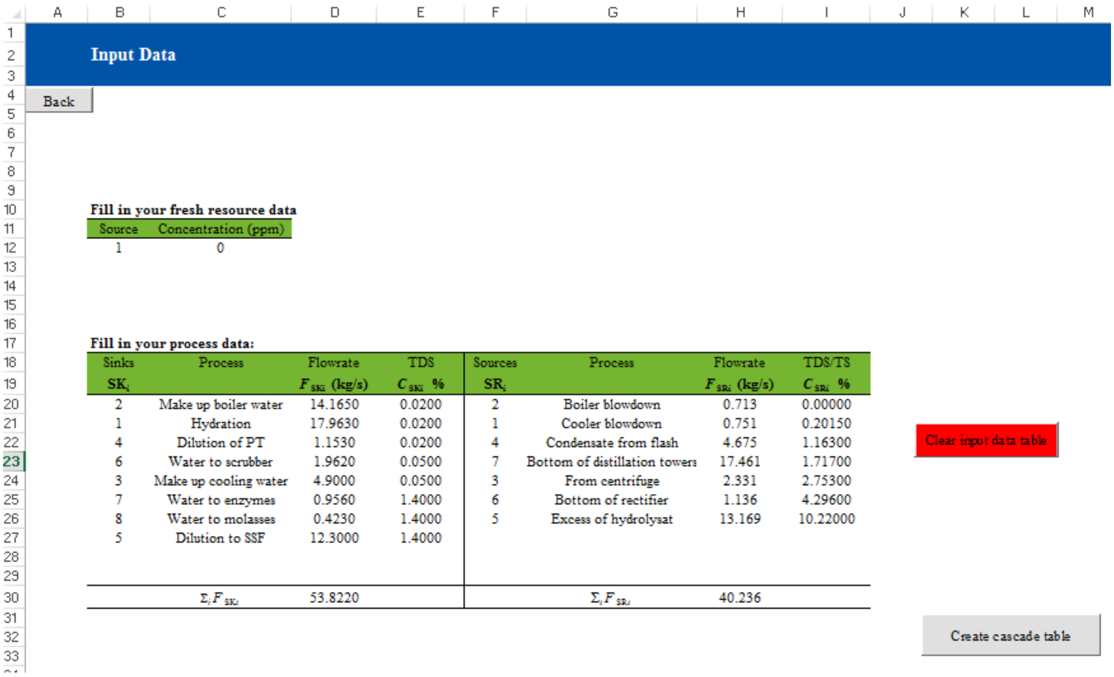
2. Enable all macros:
Under the Develoer tab, click "Macro Security". Select "Enable all Macros". Close

3. Add the "Problemlösaren" Add-In:
File -> Options -> Add-Ins: mark "Problemlösaren" and click "Go". Make sure "Problemlösaren" is marked. Close.
If you can't find Problemlösaren, you have to download and install it first.

4. Make sure you have the latest update of Excel:
Microsoft accidently released updates in December 2014 that made it impossible to use Visual Basic code in Excel.
To avoid these problems, make sure your software is up to date or download your update here:
Excel 2007: https://support.microsoft.com/en-us/kb/2956103/
Excel 2010: https://support.microsoft.com/en-us/kb/2956142/
Excel 2013: https://support.microsoft.com/en-us/kb/2920754/

Select your process case:

Input data:



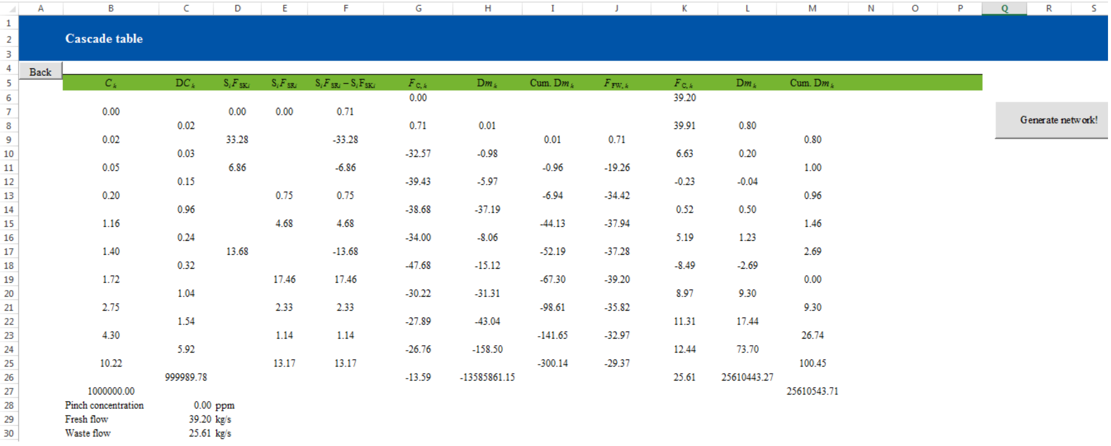
Fill in your fresh resource data

Source	Concentration (ppm)
1	0

Fill in your process data:

Sinks SK_i	Process	Flowrate F_{SKi} (kg/s)	TDS C_{SKi} %	Sources SR_i	Process	Flowrate F_{SRi} (kg/s)	TDS/TS C_{SRi} %
2	Make up boiler water	14.1650	0.0200	2	Boiler blowdown	0.713	0.00000
1	Hydration	17.9630	0.0200	1	Cooler blowdown	0.751	0.20150
4	Dilution of PT	1.1530	0.0200	4	Condensate from flash	4.675	1.16300
6	Water to scrubber	1.9620	0.0500	7	Bottom of distillation towers	17.461	1.71700
3	Make up cooling water	4.9000	0.0500	3	From centrifuge	2.331	2.75300
7	Water to enzymes	0.9560	1.4000	6	Bottom of rectifier	1.136	4.29600
8	Water to molasses	0.4230	1.4000	5	Excess of hydrolysat	13.169	10.22000
5	Dilution to SSF	12.3000	1.4000				
	$\Sigma_i F_{SKi}$	53.8220			$\Sigma_i F_{SRi}$	40.236	

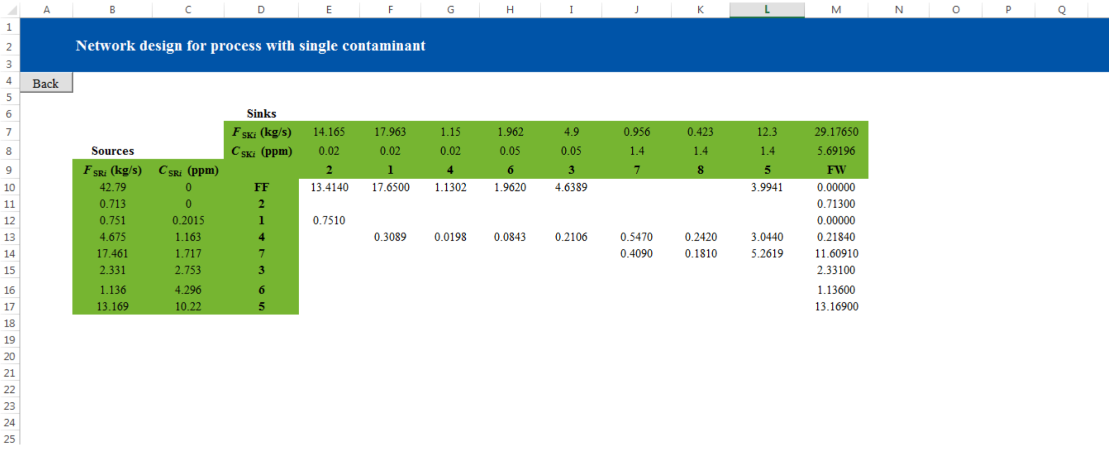
Cascade table:



C_k	DC_k	$S_i F_{SKi}$	$S_i F_{SRi}$	$S_i F_{SRi} - S_i F_{SKi}$	$F_{C,k}$	Dm_k	Cum. Dm_k	$F_{FW,k}$	$F_{C,k}$	Dm_k	Cum. Dm_k
					0.00				39.20		
0.00		0.00	0.00	0.71							
	0.02				0.71	0.01			39.91	0.80	
0.02		33.28		-33.28			0.01	0.71			0.80
	0.03				-32.57	-0.98			6.63	0.20	
0.05		6.86		-6.86			-0.96	-19.26			1.00
	0.15				-39.43	-5.97			-0.23	-0.04	
0.20			0.75	0.75			-6.94	-34.42			0.96
	0.96				-38.68	-37.19			0.52	0.50	
1.16			4.68	4.68			-44.13	-37.94			1.46
	0.24				-34.00	-8.06			5.19	1.23	
1.40		13.68		-13.68			-52.19	-37.28			2.69
	0.32				-47.68	-15.12			-8.49	-2.69	
1.72			17.46	17.46			-67.30	-39.20			0.00
	1.04				-30.22	-31.31			8.97	9.30	
2.75			2.33	2.33			-98.61	-35.82			9.30
	1.54				-27.89	-43.04			11.31	17.44	
4.30			1.14	1.14			-141.65	-32.97			26.74
	5.92				-26.76	-158.50			12.44	73.70	
10.22			13.17	13.17			-300.14	-29.37			100.45
	999989.78				-13.59	-13585861.15			25.61	25610443.27	
1000000.00											25610543.71

Pinch concentration	0.00	ppm
Fresh flow	39.20	kg/s
Waste flow	25.61	kg/s

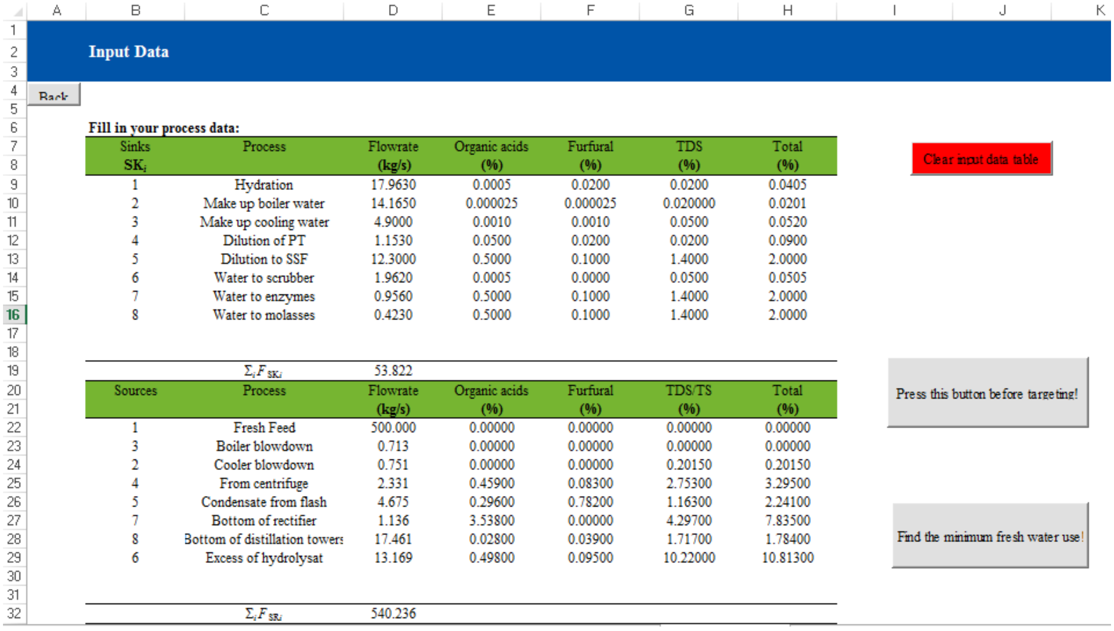
Network design:



Network design for process with single contaminant

		Sinks									
		F_{SKi} (kg/s)	14.165	17.963	1.15	1.962	4.9	0.956	0.423	12.3	29.17650
Sources		**C_{SKi} (ppm)**	0.02	0.02	0.02	0.05	0.05	1.4	1.4	1.4	5.69196
F_{SRi} (kg/s)	**C_{SRi} (ppm)**		**2**	**1**	**4**	**6**	**3**	**7**	**8**	**5**	**FW**
42.79	0	**FF**	13.4140	17.6500	1.1302	1.9620	4.6389			3.9941	0.00000
0.713	0	**2**									0.71300
0.751	0.2015	**1**	0.7510								0.00000
4.675	1.163	**4**		0.3089	0.0198	0.0843	0.2106	0.5470	0.2420	3.0440	0.21840
17.461	1.717	**7**						0.4090	0.1810	5.2619	11.60910
2.331	2.753	**3**									2.33100
1.136	4.296	**6**									1.13600
13.169	10.22	**5**									13.16900

Input data multiple contaminant:



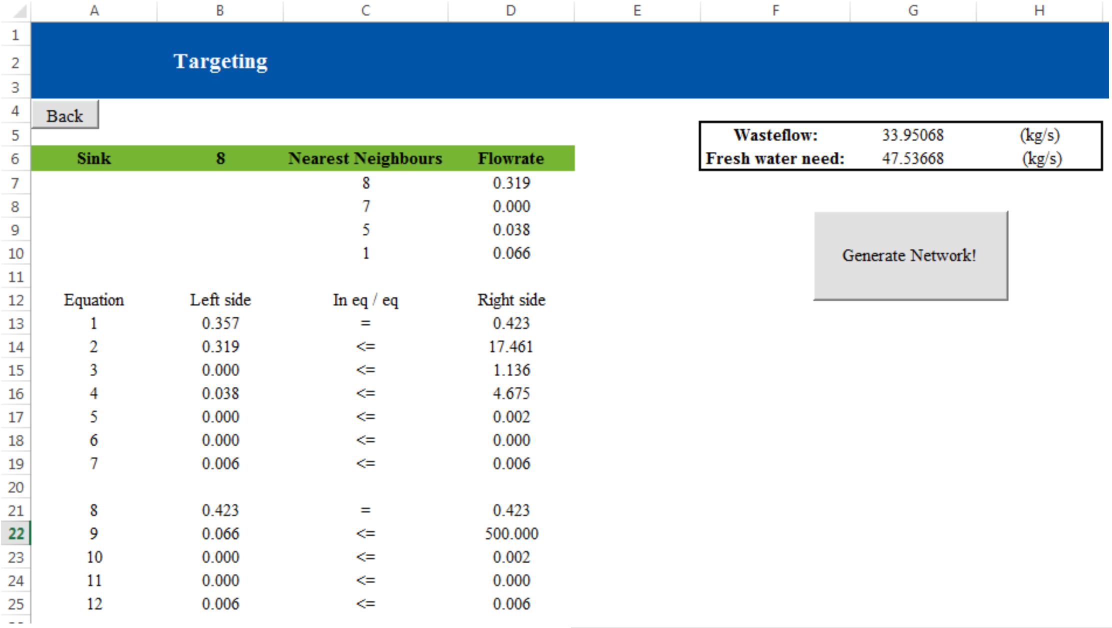
Input Data

Fill in your process data:

Sinks **SK_i**	Process	Flowrate **(kg/s)**	Organic acids **(%)**	Furfural **(%)**	TDS **(%)**	Total **(%)**
1	Hydration	17.9630	0.0005	0.0200	0.0200	0.0405
2	Make up boiler water	14.1650	0.000025	0.000025	0.020000	0.0201
3	Make up cooling water	4.9000	0.0010	0.0010	0.0500	0.0520
4	Dilution of PT	1.1530	0.0500	0.0200	0.0200	0.0900
5	Dilution to SSF	12.3000	0.5000	0.1000	1.4000	2.0000
6	Water to scrubber	1.9620	0.0005	0.0000	0.0500	0.0505
7	Water to enzymes	0.9560	0.5000	0.1000	1.4000	2.0000
8	Water to molasses	0.4230	0.5000	0.1000	1.4000	2.0000
	$\Sigma_i F_{SKi}$	53.822				

Sources	Process	Flowrate **(kg/s)**	Organic acids **(%)**	Furfural **(%)**	TDS/TS **(%)**	Total **(%)**
1	Fresh Feed	500.000	0.00000	0.00000	0.00000	0.00000
3	Boiler blowdown	0.713	0.00000	0.00000	0.00000	0.00000
2	Cooler blowdown	0.751	0.00000	0.00000	0.20150	0.20150
4	From centrifuge	2.331	0.45900	0.08300	2.75300	3.29500
5	Condensate from flash	4.675	0.29600	0.78200	1.16300	2.24100
7	Bottom of rectifier	1.136	3.53800	0.00000	4.29700	7.83500
8	Bottom of distillation towers	17.461	0.02800	0.03900	1.71700	1.78400
6	Excess of hydrolysat	13.169	0.49800	0.09500	10.22000	10.81300
	$\Sigma_i F_{SRi}$	540.236				

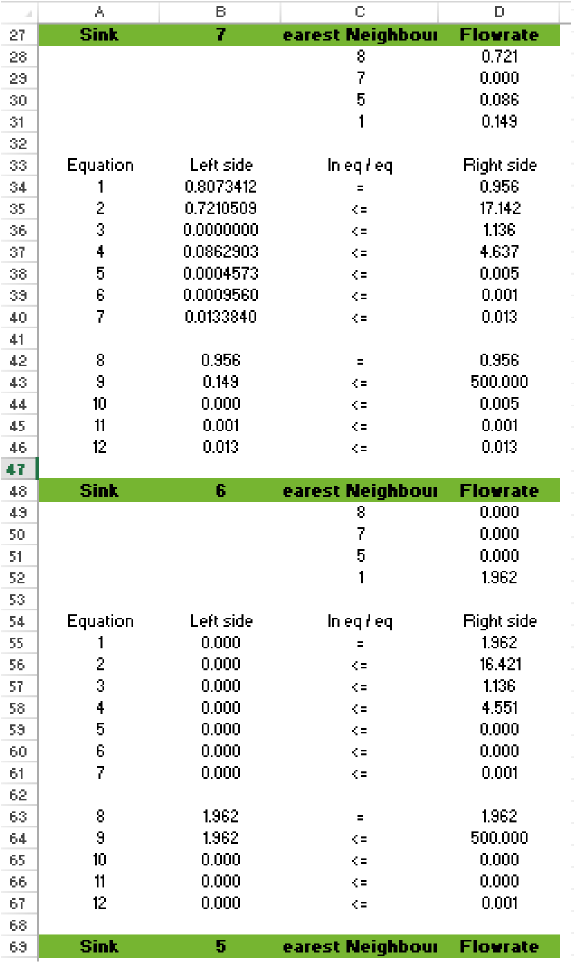
Targeting:



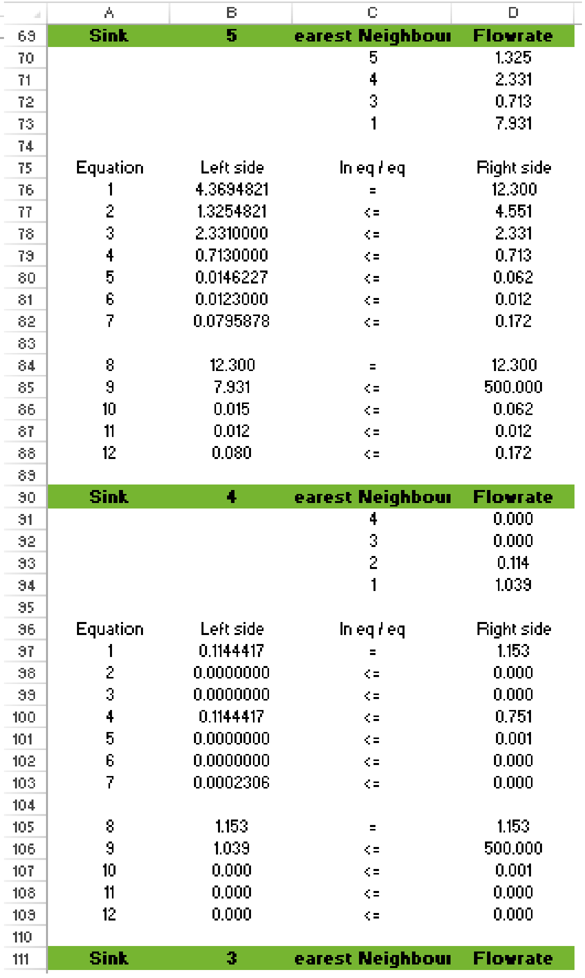
Targeting

	Wasteflow:	33.95068	(kg/s)
	Fresh water need:	47.53668	(kg/s)

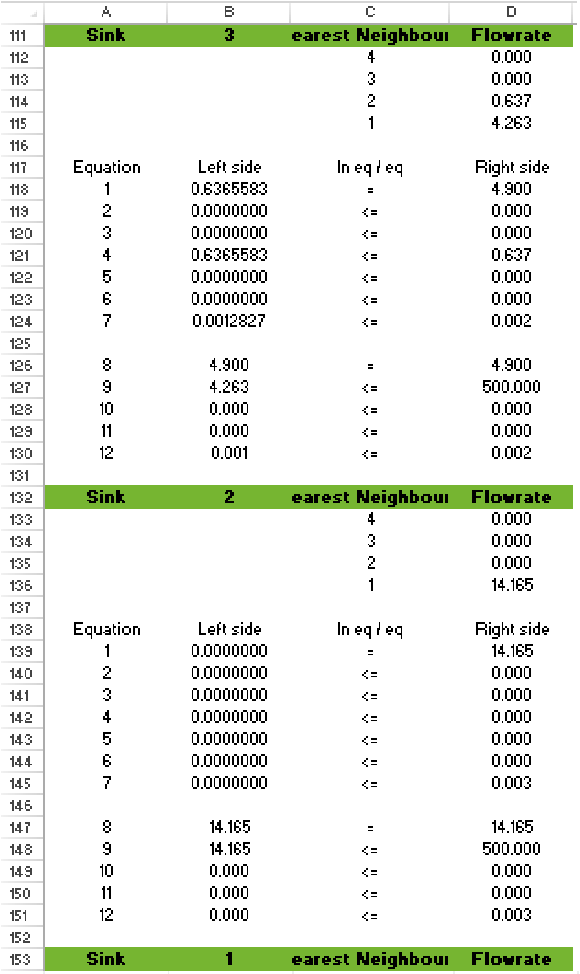
	A	B	C	D
6	**Sink**	**8**	**Nearest Neighbours**	**Flowrate**
7			8	0.319
8			7	0.000
9			5	0.038
10			1	0.066
11				
12	Equation	Left side	In eq / eq	Right side
13	1	0.357	=	0.423
14	2	0.319	<=	17.461
15	3	0.000	<=	1.136
16	4	0.038	<=	4.675
17	5	0.000	<=	0.002
18	6	0.000	<=	0.000
19	7	0.006	<=	0.006
20				
21	8	0.423	=	0.423
22	9	0.066	<=	500.000
23	10	0.000	<=	0.002
24	11	0.000	<=	0.000
25	12	0.006	<=	0.006



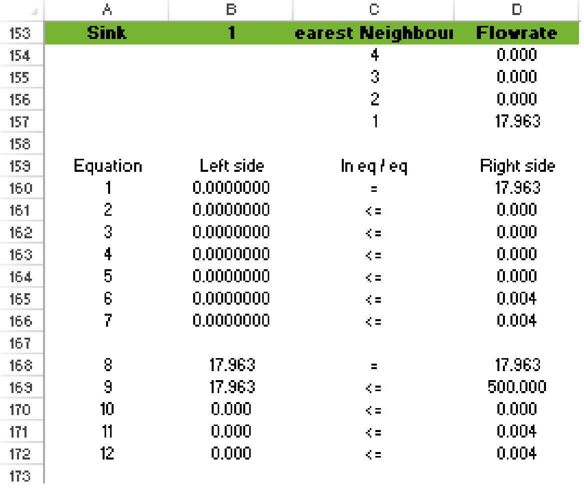
	A	B	C	D
27	**Sink**	**7**	**earest Neighbour**	**Flowrate**
28			8	0.721
29			7	0.000
30			5	0.086
31			1	0.149
32				
33	Equation	Left side	In eq / eq	Right side
34	1	0.8073412	=	0.956
35	2	0.7210509	<=	17.142
36	3	0.0000000	<=	1.136
37	4	0.0862903	<=	4.637
38	5	0.0004573	<=	0.005
39	6	0.0009560	<=	0.001
40	7	0.0133840	<=	0.013
41				
42	8	0.956	=	0.956
43	9	0.149	<=	500.000
44	10	0.000	<=	0.005
45	11	0.001	<=	0.001
46	12	0.013	<=	0.013
47				
48	**Sink**	**6**	**earest Neighbour**	**Flowrate**
49			8	0.000
50			7	0.000
51			5	0.000
52			1	1.962
53				
54	Equation	Left side	In eq / eq	Right side
55	1	0.000	=	1.962
56	2	0.000	<=	16.421
57	3	0.000	<=	1.136
58	4	0.000	<=	4.551
59	5	0.000	<=	0.000
60	6	0.000	<=	0.000
61	7	0.000	<=	0.001
62				
63	8	1.962	=	1.962
64	9	1.962	<=	500.000
65	10	0.000	<=	0.000
66	11	0.000	<=	0.000
67	12	0.000	<=	0.001
68				
69	**Sink**	**5**	**earest Neighbour**	**Flowrate**



	A	B	C	D
69	**Sink**	**5**	**earest Neighbour**	**Flowrate**
70			5	1.325
71			4	2.331
72			3	0.713
73			1	7.931
74				
75	Equation	Left side	In eq / eq	Right side
76	1	4.3694821	=	12.300
77	2	1.3254821	<=	4.551
78	3	2.3310000	<=	2.331
79	4	0.7130000	<=	0.713
80	5	0.0146227	<=	0.062
81	6	0.0123000	<=	0.012
82	7	0.0795878	<=	0.172
83				
84	8	12.300	=	12.300
85	9	7.931	<=	500.000
86	10	0.015	<=	0.062
87	11	0.012	<=	0.012
88	12	0.080	<=	0.172
89				
90	**Sink**	**4**	**earest Neighbour**	**Flowrate**
91			4	0.000
92			3	0.000
93			2	0.114
94			1	1.039
95				
96	Equation	Left side	In eq / eq	Right side
97	1	0.1144417	=	1.153
98	2	0.0000000	<=	0.000
99	3	0.0000000	<=	0.000
100	4	0.1144417	<=	0.751
101	5	0.0000000	<=	0.001
102	6	0.0000000	<=	0.000
103	7	0.0002306	<=	0.000
104				
105	8	1.153	=	1.153
106	9	1.039	<=	500.000
107	10	0.000	<=	0.001
108	11	0.000	<=	0.000
109	12	0.000	<=	0.000
110				
111	**Sink**	**3**	**earest Neighbour**	**Flowrate**

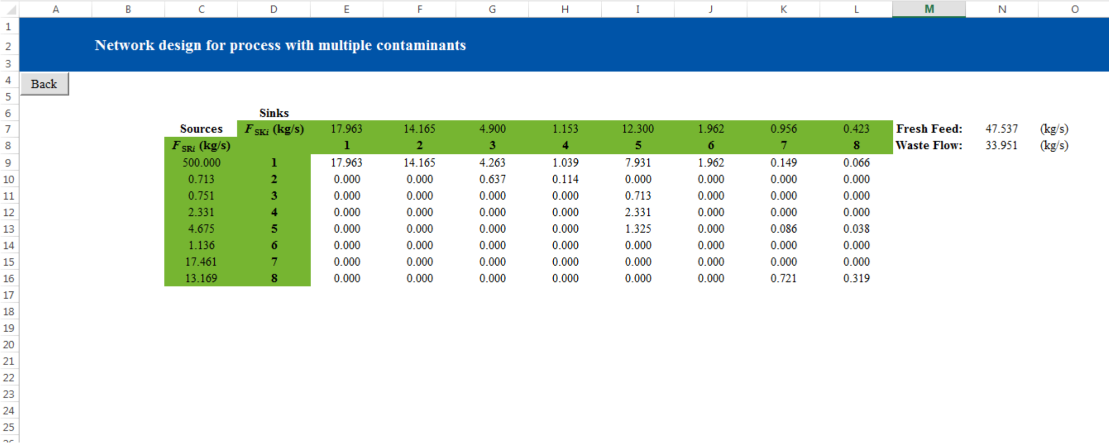


	A	B	C	D
111	**Sink**	**3**	**earest Neighbou**	**Flowrate**
112			4	0.000
113			3	0.000
114			2	0.637
115			1	4.263
116				
117	Equation	Left side	In eq / eq	Right side
118	1	0.6365583	=	4.900
119	2	0.0000000	<=	0.000
120	3	0.0000000	<=	0.000
121	4	0.6365583	<=	0.637
122	5	0.0000000	<=	0.000
123	6	0.0000000	<=	0.000
124	7	0.0012827	<=	0.002
125				
126	8	4.900	=	4.900
127	9	4.263	<=	500.000
128	10	0.000	<=	0.000
129	11	0.000	<=	0.000
130	12	0.001	<=	0.002
131				
132	**Sink**	**2**	**earest Neighbou**	**Flowrate**
133			4	0.000
134			3	0.000
135			2	0.000
136			1	14.165
137				
138	Equation	Left side	In eq / eq	Right side
139	1	0.0000000	=	14.165
140	2	0.0000000	<=	0.000
141	3	0.0000000	<=	0.000
142	4	0.0000000	<=	0.000
143	5	0.0000000	<=	0.000
144	6	0.0000000	<=	0.000
145	7	0.0000000	<=	0.003
146				
147	8	14.165	=	14.165
148	9	14.165	<=	500.000
149	10	0.000	<=	0.000
150	11	0.000	<=	0.000
151	12	0.000	<=	0.003
152				
153	**Sink**	**1**	**earest Neighbou**	**Flowrate**



	A	B	C	D
153	**Sink**	**1**	**earest Neighbou**	**Flowrate**
154			4	0.000
155			3	0.000
156			2	0.000
157			1	17.963
158				
159	Equation	Left side	In eq / eq	Right side
160	1	0.0000000	=	17.963
161	2	0.0000000	<=	0.000
162	3	0.0000000	<=	0.000
163	4	0.0000000	<=	0.000
164	5	0.0000000	<=	0.000
165	6	0.0000000	<=	0.004
166	7	0.0000000	<=	0.004
167				
168	8	17.963	=	17.963
169	9	17.963	<=	500.000
170	10	0.000	<=	0.000
171	11	0.000	<=	0.004
172	12	0.000	<=	0.004
173				

Network design multiple contaminant:



Network design for process with multiple contaminants

Sources	Sinks F_{SKi} (kg/s)	17.963	14.165	4.900	1.153	12.300	1.962	0.956	0.423
F_{SRi} (kg/s)		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
500.000	**1**	17.963	14.165	4.263	1.039	7.931	1.962	0.149	0.066
0.713	**2**	0.000	0.000	0.637	0.114	0.000	0.000	0.000	0.000
0.751	**3**	0.000	0.000	0.000	0.000	0.713	0.000	0.000	0.000
2.331	**4**	0.000	0.000	0.000	0.000	2.331	0.000	0.000	0.000
4.675	**5**	0.000	0.000	0.000	0.000	1.325	0.000	0.086	0.038
1.136	**6**	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
17.461	**7**	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
13.169	**8**	0.000	0.000	0.000	0.000	0.000	0.000	0.721	0.319

Fresh Feed: 47.537 (kg/s)
Waste Flow: 33.951 (kg/s)