Reactant Separation from a Pharmaceutical Waste Stream

Lærke Jo Ernlund Nielsen, c971547

Department of Chemical Engineering Technical University of Denmark

July 4^{th} 2003

Reactant Separation from a Pharmaceutical Waste Stream

Pre Master Dissertation

Supervisors at DTU : Jens Abildskov and Sten Bay Jørgensen

External supervisors : Christian Kliim and Joan Degn Roll Syntese A/S

Written by : Lærke Jo Ernlund Nielsen, c971547

CAPEC Department of Chemical Engineering Technical University of Denmark

July 4^{th} 2003

Abstract

The requests for a separation of the waste stream from the 5–Amino–salicylic–acid production was that the annual expense of 1.002 million Danish kroner for transportation to and 7.95 million Danish kroner for disposal at Kommunekemi a/s was reduced, and that the 90(w/w)% of the aniline in the waste stream was purified for recycling, to reduce the annual aniline expense of 6.98 million Danish kroner. For this problem two separation schemes have been determined.

For both the schemes, a separation of the two liquid phases the waste stream formes is made resulting in two phases. A water phase containing 3.39(w/w)% aniline and an aniline phase containing 21.3(w/w)% water.

The first scheme suggests that both the two phases are distilled. When distilling the water phase, the distillate will be pure water, while the bottom product will be an aniline–water azeotrope. The distillate can be disposed of directly to a waste water treatment plant, while the aniline–azeotrope can be recycled back to the unseparated waste stream. This separation requires energy corresponding to an annual expense of 800000 Danish kroner.

The distillation of the aniline phase is not as energy requiring, and is therefore a preferable separation method. But if aniline is only recovered from the aniline phase, the requirement of a 90(w/w)% is not respected. Taking both the recovered aniline and the energy required for the water phase distillation into account, but not looking at equipment expenses, the annual expense is reduced to 3.49million Danish kroner.

The second scheme suggests that the water phase is extracted with toluene, which is cheap and easy to get a hold of. By making the water phase basic, only six extraction stages can reduce the aniline concentration to the required 2(w/w)ppm, with a toluene volume of 7.8m³ corresponding to 6780kg in each stage. The solvent loss can be kept at 5(w/w)%, which gives a low annual expense for solvent. The basic water can be used to neutralize an other waste stream at Syntese A/S. The concentration of toluene will be above the environmental required, but activated carbon can reduce the concentration in the water to the allowed concentration, so the water can be sent directly to a waste water treatment plant after the adsorption.

The solvent saturated with aniline will leave the extraction as extract, and the toluene is separated from the aniline by distillation. Because toluene is more volatile than aniline, this is not an extremely energy requiring separation. The toluene is recycled to the extraction again, while the aniline bottom product is added to the aniline phase. This phase is sent to distillation recovering 90(w/w)% of the aniline, and the purities are sent to disposal at Kommunekemi.

The extraction scheme will give an annual expense of 3.1 million Danish kroner, including expenses for solvent, energy required for distillation and purchase and disposal of activated carbon.

If equipment is bought for both the extraction and the distillation with a pay back time of two years, and with a 10% interest rate, the annual expense will be 4.9 million Danish kroner the first two years, an annual reduction of 11 million Danish kroner.

Preface

This pre master dissertation is submitted as a partial fulfillment of the requirements for the chemical masters degree at Technical University of Denmark. The work has been carried out at Department of Chemical Engineering from February 2003 to June 2003 under the supervision of Jens Abildskov and Professor Sten Bay Jørgensen.

I would like to thank both Jens Abildskov and Sten Bay Jørgensen for extremely good assistance. And also Christian Kliim and Joan Degn Roll for taking the time in their busy schedules to explain whatever whenever.

A special thank you to Hanne H. Munksgaard from Syntese A/S for the HPLC results. Also Thanks to Loic d'Anterroches for always being willing to help with computer problems.

Resumé på dansk

Syntese A/S ønsker at få identificeret en separations process som kan rense en spildevandsstrøm for aniline og samtidig muliggøre det at genanvende anilinen, for at reducere den årlige udgift på transport, 1.002 millioner kroner, og bortskaffelse af en spilde vands strøm, 7.95 millioner kroner. Den årlige udgift på aniline er 6,98 millioner kroner.

For at vandet kan sendes direkte til et rensningsanlæg skal anilin indholdet reduceres til et maksimum på 2(w/w)ppm, mens hvis anilinen skal recirkuleres til produkt syntesen igen, skal den have en renhed på 99.5(w)w%. Syntese A/S ønsker at genanvende mindst 90(w/w)% af anilinen.

Spildevandsstrømmen består af 6-7(w/w)% aniline og 93-94(w/w)% vand, og skiller derfor i to faser, så for at simplificere separationen separeres de to til en vand og en aniline fase.

Til yderligere separation med og henblik på at genanvende anilinen er foreslået to separations mulighed.

Den første separations mulighed er at destillere de to faser. Destilleres vand fasen, vil destillatet være rent vand, som kan sendes direkte til et rensningsanlæg, mens bund produktet vil bestå af en anilin-vand azeotrope, som kan recirkuleres til den useparerede spild strøm. Destillation af vand fasen er energi krævende da en stor del vand skal fordampes. Destilleres aniline fasen vil bundproduktet give rent anilin som bund produkt, men ikke de ønskede 9090(w/w)%. En destillation af anilin fasen er ikke så energi krævende som vand fasen og er derfor en økonomisk udmærket mulighed. Hvis de to faser destilleres vil de årlige udgifter reduceres til 3.49 millioner kroner, hvilket er en væsentlig ændring i forhold til den nuværende udgift.

Den anden separations mulighed er at ekstrahere vand fasen med toluen. Med en seks trins ekstraktion efterfulgt af en destillation, hvor toluenen og anilinen bliver separeret, er det muligt at regenerere en stor del af anilinen fra vand fasen, mens vand fasens aniline indhold bliver reduceret til de 2(w/w)ppm. Når toluen bruges som solvent, er det dog nødvendigt at reducere toluen koncentrationen i vandet ved at sende det igennem aktivt kul, hvilket giver en ekstra omkostning. Ledes bundproduktet fra destillationen af toluen og anilin sammen med aniline fasen, og destilleres blandingen er det muligt at recirkulere en stor del anilin, hvilket resultere i en årlige udgift på kun 3.1 millioner kroner.

Problem formulation

In the company Syntese A/S the active pharmaceutical ingredient 5–Amino–Salicylic– Acid is produced. This results in a waste stream (up to $5000m^3$ per year) containing 93–94(w/w)% water and 6–7(w/w)% aniline, which is sent to Kommunekemi a/s for disposal. This gives an annual expense of 1.002 million Danish kroner for transportation from Syntese A/S to Kommunekemi a/s, and 7.95 million Danish kroner for the disposal.

In this report the possibility of reducing the aniline concentration in the waste stream will be investigated. If an adequate reduction of aniline (i.e. to 2(w/w)ppm or less) is possible, then the water can be sent directly to a waste water treatment plant. Furthermore, if the aniline is purified to more than 99.5(w/w)%, it could be recycled to take part in the synthesis again. Syntese A/S has requested that at least 90(w/w)% of the aniline is recycled, to reduce the present aniline annual expense of 6.98 million Danish kroner.

In the report different separation processes will be discussed and evaluated regarding the separation of aniline from water. The process flow sheet will first of all be chosen from the physical properties and equilibrium behaviour of the binary system, but also based on economical considerations.

A design of the optimal separation process from the polluted waste stream to the clean water going to a waste water treatment plant will be drafted, along with estimation of the equipment size and expenses.

Contents

1	Intr	roduction	1
2	Pro	perties of the Waste Stream	3
	2.1	Properties of Pure Aniline and Pure Water	3
		2.1.1 Temperature Independent Properties	4
		2.1.2 Temperature Dependent Properties	4
	2.2	Equilibrium Behaviour of Aniline–Water Systems	5
		2.2.1 Liquid–liquid Properties	6
		2.2.2 Vapor–Liquid Properties	7
3	\mathbf{Sep}	aration Processes for Liquid–Liquid Binary Mixtures	9
	3.1	The Composition of the Waste Stream	9
	3.2	Separation Processes	10
		3.2.1 Distillation	10
		3.2.2 Stripping	11
		3.2.3 Adsorption	11
		3.2.4 Emulsion Liquid Membranes	12
		3.2.5 Liquid–liquid Extraction	12
	3.3	Discussion of Separation Processes	12
	3.4	Summary	20
4	Cho	posing a Solvent	22
	4.1	Presentation of ProCAMD	22
	4.2	Environmental Demands	23
	4.3	Properties Entered ProCAMD	25
	4.4	Results from ProCAMD	27
5	Inv	estigating the Properties of the Solvents	30
	5.1	Physical Properties of the Solvent	30
		5.1.1 Temperature Independent Properties	30
		5.1.2 Temperature Dependent Properties	31
	5.2	Equilibrium Behaviour Between Aniline and Solvents	33
		5.2.1 n–Heptane \ldots	34
		5.2.2 Toluene and Xylene	36

6	Testing the Solvents	41
	6.1 Experimental Procedure	. 41
	6.2 Experimental Results	. 42
	6.3 pH Influence	. 45
	6.4 Influence of Stirring Time	. 46
	6.5 Stirring Time and pH Raised	. 48
	6.6 Discussion of Results	. 49
7	Economic Evaluation	53
	7.1 Two Distillations	. 53
	7.2 Extraction and Two Distillation	. 53
	7.3 Comparison of the Two Separation Schemes	. 58
	7.4 Equipment Sizing and Expense	. 59
	7.5 Capital Investment	. 60
8	Conclusion	61
\mathbf{A}	Economical Calculations	65
	A.1 Present Annual Expenses	. 65
	A.2 Reduction in Expenses	. 66
в	Impurities in the Waste Stream	67
\mathbf{C}	Physical Properties of the Waste Stream	68
	C.1 Vapor Pressure	. 69
	C.2 Antoine Vapor Pressure	. 70
	C.3 Density	. 71
	C.4 Solubility	. 72
D	Physical Properties of the Solvents	73
	D.1 Vapor Pressure	. 74
	D.2 Antoine Vapor Pressure	. 75

List of Figures

1.1	Reaction scheme for the synthesis of 5-Amino-Salicylic-Acid $\ .\ .\ .\ .$	1
2.1	VLE diagrams for the binary aniline/water system at 1atm. The left diagram is experimentally determined, and the right is estimated using the VLE UNIFAC model.	8
$3.1 \\ 3.2$	Distillation separation scheme	14 20
$5.1 \\ 5.2$	Ternary diagram for toluene, water, and aniline with binodal curve at 25° C Ternary diagram for n-heptane with binodal curves at 25° C. The top diagram is estimated using LLE UNIFAC, the lower left is estimated using VI E UNIFAC and the lower right using Modified UNIFAC Lyngby	32 35
$5.3 \\ 5.4$	Experimental determined VLE diagram for aniline and n-heptane at 1 atm Ternary diagram for toluene with binodal curves at 25°C. The top diagram is estimated using LLE UNIFAC, the lower left is estimated using VLE	36
5.5	UNIFAC and the lower right using Modified UNIFAC Lyngby Ternary diagram for xylene with binodal curves at 25°C. The top diagram is estimated using LLE UNIFAC, the lower left is estimated using VLE	37
$5.6 \\ 5.7$	Experimental VLE diagram for aniline and p-xylene at 1 atm	38 39 40
$ \begin{array}{r} 6.1 \\ 6.2 \\ 6.3 \\ 6.4 \end{array} $	Aniline concentration in the raffinate after the 6 extraction stages Aniline concentration in the raffinate when pH of the water is raised to 13 Aniline concentration in the raffinate at different stirring times Aniline concentration in the raffinate at different stirring times and pH=13. Toluene and base(1) is stirred for 15 minutes, while toluene and base(2) is stirred for 60 minutes	44 46 48 50
C.1 C.2 C.3 C.4	Vapor Pressure of aniline and water at different temperatures Antoine Vapor Pressure of aniline and water at different temperatures Density of aniline and water at different temperatures Solubility of aniline in water and water in aniline at different temperatures	69 70 71 72

D.1	Vapor Pressure of the three solvents at different temperatures	74
D.2	Antoine Vapor Pressure of the three solvents at different temperatures	75
D.3	Density of the three solvents at different temperatures	76

List of Tables

$2.1 \\ 2.2 \\ 2.3$	Physical properties for aniline and water $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$ Solubility of aniline in water and water in aniline $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$ Model Parameters and γ_i^{∞} for different models $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	$4 \\ 6 \\ 7$
3.1	Physical influence on the separation processes	13
$4.1 \\ 4.2 \\ 4.3$	Values for the different properties entered in ProCAMD	27 28 28
$5.1 \\ 5.2 \\ 5.3$	Physical properties of the four solvents $\ldots \ldots \ldots$	31 33 34
$6.1 \\ 6.2 \\ 6.3 \\ 6.4$	Aniline concentration in the water and organic phases after extraction Aniline concentrations in raffinate when the pH of the water is increased to 13	43 47 49 51
$7.1 \\ 7.2$	Expenses corresponding to number of extraction stages and toluene amount Test of constraint	$\frac{55}{56}$
C.1 C.2 C.3 C.4	Vapor Pressure of aniline and water at different temperatures Antoine Vapor Pressure of aniline and water at different temperatures Density of aniline and water at different temperatures Solubility of aniline in water and water in aniline at different temperatures	69 70 71 72
D.1 D.2 D.3	Vapor Pressure of the three solvents at different temperatures Antoine Vapor Pressure of the three solvents at different temperatures	74 75 76

Chapter 1 Introduction

The active pharmaceutical ingredient 5–Amino–Salicylic–Acid, 5–ASA, is used against Crone's decease and Colitis Uleritis in the intestines.

5–ASA is produced in a diazotization reaction yielding a diazonium salt, $Ph - N^+ \equiv N$, which is very reactive. The salt is formed in a reaction between aniline and sodium– nitrite in the presence of an inorganic acid, and added to a solution containing salicylic acid, yielding the intermediate 5-phenylazosalicylic acid. Reduction of this component gives 5–ASA and aniline. Figure 1.1 shows the reaction scheme.



Figure 1.1: Reaction scheme for the synthesis of 5-Amino-Salicylic-Acid

Aniline is removed from the reaction mixture by flash distillation, giving a waste stream containing 6-7(w/w)% aniline. Since aniline is not a desired component in the environment, the waste stream containing aniline is sent to Kommunekemi a/s for disposal. Syntese A/S produces up to 5000 m³ fluid waste per year, and therefore this is an expensive solution, Syntese A/S annually spends 8.952 million Danish kroner on transportation and disposal of the waste stream, and are therefore interested in alternatives.

One solution could be to reduce the aniline concentration sufficiently for direct disposal to a waste water treatment plant. Furthermore, the removed aniline could be purified for recycled to take part in the reaction again. The annual expense for aniline is 6.98 million Danish kroner.

For feasibility the aniline concentration in the water must be reduced to less than 2(w/w)ppm, while the purity of aniline must exceed 99.5(w/w)%. Furthermore at least 90(w/w)% of the aniline should be recycled.

If it is possible to make a separation which respect the requirements, the annual expenses can be reduced from 15.9 million Danish kroner to 850000 Danish kroner, only taking recovered aniline, transportation and disposal into account.

The aniline concentration in the waste water must be reduced to 2(w/w) ppm to uphold the environmental requirements set by the Danish Environmental Protection Agency for the aniline content in waste water sent to waste water treatment plants. The aniline must be purified to 99.5(w/w)%, because if it is recycled to take part in the production synthesis, it must be pure to ensure a pure product. Syntese A/S has requested that 90(w/w)% of the aniline is recycled.

If it is not possible to purify the aniline to the wanted limit, the impure aniline could be sold to another company and used for a different purpose.

In this report different methods of separating aniline from water are investigated. Taking environmental and economic aspects into account, a solution to the problem is determined, and a design is proposed.

The first chapters will present the physical properties of water and aniline, and on the basis of these properties alternative separation schemes are suggested.

From earlier investigations (17), extraction has been determined to be a good separation choice for the separation of aniline from water. Therefore suitable solvents will be identified using ProCAMD, Computer Aided Molecular Design, in ICAS, Intergraded Computer Aided System.

In the following chapters, the physical properties of the economically and environmentally interesting solvents are presented, along with laboratory results from the extractions using the same solvents.

In the last part an economic analysis is performed, and based on the conclusions made in the first chapters a final design of the optimal separation process from the polluted waste stream to the clean water going to a waste water treatment plant is made, and the equipment size and expenses are estimated.

Chapter 2 Properties of the Waste Stream

The waste stream is a two phase binary mixture containing 6-7(w/w)% aniline and 93-94(w/w)% water. There are also some other components/impurities in the mixture, but they are only present in a very low concentration, <1000(w/w)ppm, and will therefore be neglected. In appendix B a list of the impurities can be seen.

In this chapter the physical properties of pure aniline and pure water, and the equilibrium behaviour of an aniline–water binary mixture will be investigated. Since the waste stream is not sent directly to further separation after the separation from the 5–ASA product but put in a storage tank outdoors, the temperature of the mixture will vary from summer to winter. Knowing the temperature dependence of the relevant properties may therefore be necessary.

2.1 Properties of Pure Aniline and Pure Water

Aniline is a highly polar, aromatic amine, which has a low water–solubility. As amines, aniline forms hydrogen bonds, which results in a high boiling point compared to alkanes with similar molecular weight. General for amines is the lone electron pair on the nitrogen, which makes amines both basic and nucleophilic.

Aniline is highly toxic for both humans and for the environment. It is also considered carcinogenic. From the web page of The Danish Environmental Protection Agency, the Effect List (19) gives aniline the following R-sentences:

- R20/21/22 Harmful if inhaled, in contact with skin and if swallowed
- R40 possible risk of irreversible effects
- R48/23/24/25 toxic if inhaled, in contact with skin, if swallowed. Danger of serious damage to health by prolonged exposure
- R50 very toxic to aquatic organisms

2.1.1 Temperature Independent Properties

From the database dippr.mdb in ICAS some important physical properties of the two pure components have been found and can be seen in table 2.1.

	Aniline	Water
Chemical Formula	C_6H_7N	H_2O
$(\boldsymbol{M}_{\boldsymbol{w}}) \; (\mathrm{g/mol})$	93.128	18.015
Tb (K)	457.15	373.15
T _m (K)	267.13	273.15
Antoine A	7.43481	8.02927
Antoine B(°C)	1813.917	1713.681
Antoine C(°C)	213.709	232.633
Vapor pressure A	66.287	73.649
Vapor pressure $\mathbf{B}(\mathbf{K})$	-8207.1	-7258.2
Vapor pressure C	-6.0132	-7.3037
Vapor pressure D	$2.84 \cdot 10^{-18}$	$4.17 \cdot 10^{-6}$
Vapor pressure E	6	2
Density $A(kmol)$	1.0405	5.459
Density $B(m^3)$	0.2807	0.30542
Density C(K)	699.0	647.13
Density D	0.29236	0.081

Table 2.1: Physical properties for aniline and water

The Antoine, vapor pressure and density constants are used in the next section to find the vapor pressures and densities at different temperatures.

A comparison of the normal boiling and melting points of the two components shows that aniline melts at the lowest temperature and boils at the highest.

2.1.2 Temperature Dependent Properties

Physical properties such as the density, ρ , and the vapor pressure, p^{sat} , are also relevant properties, but they depend on the temperature.

In appendices C.1, C.2 and C.3 tables and figures of the density and the vapor pressures determined in two ways can be seen for different temperatures for each of the two components.

The vapor pressure in appendix C.1 is found using an equation from ICAS.

$$p^{sat}(Pa) = exp\left(A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T^E\right)$$
(2.1)

Here A, B, C, D, and E are constants shown as vapor pressure constants in table 2.1. The temperature is entered in Kelvin.

The vapor pressure in appendix C.2 is found using the Antoine equation, Smith et al. (13).

$$p^{sat}(mmHg) = 10^{\left(A - \frac{B}{T+C}\right)} \tag{2.2}$$

where A, B, and C are the Antoine constants shown in table 2.1. The temperature is entered in degrees Celsius.

The liquid density is found using an equation from ICAS.

$$\rho_{liq}\left(\frac{kmol}{m^3}\right) = \frac{A}{B^{\left(1 + \left(1 - \frac{T}{C}\right)^D\right)}}$$
(2.3)

again the constants A, B, C, and D are given in table 2.1. The temperature is entered in Kelvin.

Because the vapor pressure is estimated, it is found using the two different equations, which can be compared to ensure the estimate is reasonable. This is the case with the estimation here. If it was possible, the same would have been done for the liquid density. The vapor pressure figures show that both the vapor pressure of aniline and water increase with increasing temperature. They also show that the vapor pressure of water is more sensitive to a temperature change than aniline, since water shows a greater increase with increasing temperature than aniline, corresponding to the higher normal boiling point of water.

The density figure shows aniline has a larger density than water at low temperatures, while the reverse is the case for temperatures above 65°C. The figure also shows that the density of aniline is more temperature sensitive than the density of water.

2.2 Equilibrium Behaviour of Aniline–Water Systems

To design a separation process, the equilibrium behaviour of the water–aniline mixture must be known. For extraction, liquid–liquid equilibrium is of interest, whereas for distillation the vapor–liquid equilibrium is to be known.

In the beginning of the chapter aniline is presented as a polar component, with the option to form hydrogen bonds. This is a strong indication that ideal liquid solution assumptions are invalid, and regular solution theory will not be applicable. Therefore deviations from ideal behaviour must be into account, which is done with the activity coefficient, γ_i .

If distillation is to be performed, it is important to investigate if the binary system forms an azeotrope. An azeotrope occurs for a boiling mixture when the different component's vapor mol/weight fractions are the same as the liquid mol/weight fractions, $y_1 = x_1$ and $y_2 = x_2$, giving the relative volatility a value of 1 (the relative volatility is defined in the next chapter). In this case separation can not be done by boiling or condensation, because there is no change in the liquid composition as it evaporates. Therefore the temperature and composition of an azeotrope should be found, so the possible distillation separation can be determined.

2.2.1 Liquid–liquid Properties

If liquid–liquid extraction is to be performed, the liquid–liquid equilibrium behaviour must be known.

An important liquid–liquid temperature dependent property is the solubility. From Sørensen et al. (14) mol percents representing aniline dissolved in water and water dissolved in aniline are shown in table 2.2.

Temperature (°C)	Mol percent aniline	Mol percent water
20.0	0.674	21.3
25.0	0.679 21.8	
	Weight percent aniline	Weight percent water
20.0	Weight percent aniline 3.39	Weight percent water 4.98

Table 2.2: Solubility of aniline in water and water in aniline

The solubility of aniline dissolved in water from table 2.2 show that water is more soluble in aniline than aniline is in water. The low solubility of aniline in water corresponds with the pK_b-value of 9.37 (7), which also shows that aniline is a weak base.

In appendix C.4 the solubility of aniline in water and water in aniline are shown for temperatures up to 140° C, at greater temperatures the water will be present as vapor, and the solubility difficult to measure. The appendix shows that the solubility increases with increasing temperature. The appendix also shows a figure of the temperature as a function of the aniline mol percents. This Tx-figure shows the phase split of the aniline–water system.

Since aniline is very little soluble in water and present in more than the 0.67(mol/mol)% or 3.39(w/w)% at 20°C, which is soluble in water, the waste stream will consist of two liquid phases. It is assumed that equilibrium is reached between aniline and water in these two phases, and the mol/weight percent of the components in the two phases are as listed in table 2.2. The phases will be referred to as the water phase, for the top phase mainly containing water, and as the aniline phase, the bottom phase mainly containing aniline.

2.2.2 Vapor–Liquid Properties

If distillation separation is to be used to separate the mixture, the vapor-liquid behaviour must be known, and because the aniline-water system does not behave ideally, the activity coefficients are of interest. From Gmehling et al (2) the Margules, van Laar, Wilson, NRTL and UNIQUAC model parameters are listed in table 2.3.

· ·				
	A_{12}	A_{21}	γ_1^∞	γ_2^∞
Margules	1.0041	3.1217	2.73	22.68
Van Laar	1.2006	8.3006	3.32	4026.37
Wilson	1608.4375	2513.9461	3.11	229.00
NRTL	6945.2299	-2651.2199	3.68	104.01
UNIQUAC	1439.0048	-379.5945	3.49	554.62

Table 2.3: Model Parameters and γ_i^{∞} for different models

In table 2.3 index 1 represents water and index 2 aniline.

All the methods show that $\gamma_1^{\infty} < \gamma_2^{\infty}$, which is consistent with table 2.2, which shows that aniline is less soluble in water than water is in aniline. The large γ_2^{∞} found by the Van Laar model is not a typing error, and therefore a strong confirmation of the low solubility of aniline in water.

Investigations of a VLE-diagram show that an azeotrope exists for the aniline-water binary system. Horyna et al (16) have found the azeotrope to be at a water weight fraction of $x_1 = 0.808$ (water mol fraction of 0.956) and a temperature of 98.6°C, at a pressure of 742mmHg. A VLE-diagram estimated using the VLE UNIFAC model at 760mmHg in SMSWIN is shown in figure 2.1 to the right. It is similar to the proportional diagram from Gmehling et al (2), the diagram to the left. Both diagrams show an azeotrope at the weight fraction $x_1 \approx 0.96$, corresponding to the one determined by Horyna et al, indicating that the VLE UNIFAC model is a good approximating for the vapor-liquid behaviour of a aniline-water binary system.



Figure 2.1: VLE diagrams for the binary aniline/water system at 1atm. The left diagram is experimentally determined, and the right is estimated using the VLE UNIFAC model.

Chapter 3

Separation Processes for Liquid–Liquid Binary Mixtures

Before the different separation process are presented, the weight and composition of the two fases in the waste stream is found, because this also will have an influence on which separation process to chose. The calculation are done on the basis of the experimental determined solubilities, (2) and (14), and found in the previous chapter.

3.1 The Composition of the Waste Stream

At Syntese A/S two productions are run at the same time. The smaller one gives a waste stream with a volumen of 2.5m^3 and the bigger a waste stream of 5m^3 . In the following calculations the two streams will be seen as one stream with a volumen of 7.5m^3 , because the waste streams are led to the same tank before the water is purified.

At 20°C the waste stream has a density of

$$\rho_{waste~water} = 1020.16 kg/m^3 \cdot 0.07 + 996.29 kg/m^3 \cdot 0.93 = 997.96 kg/m^3$$

so the weight of the produced waste stream will be

$$997.96kg/m^3 \cdot 7.5m^3 = 7485kg$$

Of these 7485 kg 93% will be water, that is

$$7485kg \cdot 0.93 = 6961kg = 386.4kmole$$

while 524kg = 5.6kmole will be aniline.

In the following calculations it is assumed that the water phase has a 0.67(mol/mol)% aniline content, while the aniline phase has a 21.3(mol/mol)% water content, both at

 20° C, see table 2.2.

A mole balance gives the mole content in the two phases:

$0.0067 \cdot n_{total \ in}$	$water + 0.787 \cdot n_{total in aniline}$	=	5.6kmole aniline
$0.9933 \cdot n_{total \ in}$	$water + 0.213 \cdot n_{total in aniline}$	=	$386.4 kmol\ water$

Solving these two equations with two unknowns gives

n_{total} in water	=	388.2 kmole
$n_{total \ in \ aniline}$	=	3.8 kmole
$n_{aniline\ in\ water\ phase}$	=	2.6 kmole
$n_{water\ in\ water\ phase}$	=	385.6 kmole
$n_{aniline\ in\ aniline\ phase}$	=	3.0 kmole
$n_{water\ in\ aniline\ phase}$	=	0.8 kmole

This means the water phase will have a weight of

 $93.128 kg/kmol \cdot 2.6 kmole + 18.015 kg/kmol \cdot 385.6 kmol = 7188.7 kg$

and using the mass fractions, the density is determined

 $\rho_{water\ phase} = 0.03 \cdot 1020.16 kg/m^3 + 0.97 \cdot 996.29 kg/m^3 = 997.0 kg/m^3$

The water phase has a volumen of 7.2m^3 and the aniline phase a volumen of 0.3m^3 and a weight of 305.8kg.

3.2 Separation Processes

In the following different separation processes regarding separation of liquid–liquid mixtures will be presented. From the aniline–water system's physical properties and equilibrium behaviour, a process will be determined. The feed, product and recovery specifications also play an important part, and therefore these will also have an influence on which process to choose.

3.2.1 Distillation

Distillation is one of the most commonly used separation methods when separating chemical liquid mixtures, though it is an energy requiring technique. Distillation is used for separating both binary and multi–component mixtures. It is, however, only a possible separation method when the species in the feed to be separated vary in volatility/ boiling point.

The principle of distillation is to have a vapor and a liquid phase, which can be separated as a vapor top and a liquid bottom product.

The more volatile component will be the primary component in the distillate, whereas the bottom product mainly will contain the less volatile component. When the distillate is taken out in the top of the distillation column, it can be condensed and in some cases lead back to the column as liquid. This type of process is called rectification or distillation with reflux.

The vapor phase is made either by increasing the temperature of the mixture to a temperature where the more volatile component will evaporate, or by reducing the pressure of the mixture, so the component with the lowest vapor pressure evaporates.

The separation can take place in one or several stages, and with and without reflux. A single stage separator with no reflux is known as Flash distillation. The separation can also be performed both as a batch and a continuous process.

3.2.2 Stripping

Stripping, also called desorption, is a separation method where the multi-component liquid and a gas are made to contact, to move a component from the liquid to the gas phase. During a stripping process, the temperature may be increased, the pressure reduced, or both. Stripping is often used to remove small amounts, ppm, of gas or organic solvent from water.

3.2.3 Adsorption

Liquid adsorption is performed by bringing a liquid in contact with a solid. This is done by sending the liquid through a micro porous solid, making certain components in the liquid attach to the solid surface. The solid, on which the adsorption takes place, must be insoluble in the liquid for the separation to take place.

The adsorption takes place both on the outside of the solid surface and, because the solid is porous, inside the pores. It can also take place on specific sites in the particles. The solid particles are usually held in a fixed-bed, where the liquid is passed through continuously until the solid is saturated. With the solid saturated, the desired separation can no longer be archived, and a new fixed-bed of solids is used.

Separation using adsorption occurs because of molecular differences. A molecules weight, shape or polarity are properties that have influence on how strongly molecules are held on the surface, but the size also has an effect. If a molecule is too large to enter the particle pores, the particle will act as a filter, and thereby separating the larger molecules from the smaller ones.

3.2.4 Emulsion Liquid Membranes

The principle of emulsion liquid membrane separation is to get the unwanted components to diffuse from one phase to another, thereby reducing the component concentration in e.g. a waste stream.

An emulsion liquid membrane process consists of three phases. The external phase where the solute/pollutate diffuses to the membrane. The membrane phase which separated the internal and external phase, and through which the solute permeates from the external phase to the internal phase. The internal phase in which the solute is converted by reaction so it does not diffuse back to the external phase.

3.2.5 Liquid–liquid Extraction

Separation by liquid–liquid extraction is a reasonable alternative when distillation is not an effective solution. Extraction is used for separating mixtures with close boiling temperatures, or ones that can not withstand the temperature of distillation, even under vacuum.

In liquid–liquid extraction a solvent is added to the mixture that is to be separated. The solvent must be brought to equilibrium with the mixture, so the component in the mixture, which is to be removed, is ensured transferred to the solvent.

Extraction can be done as both a batch and a continuous operation. For both operations the principle is the same; a liquid feed is mixed with a solvent, after which the mixture is made to settle, and the separation can take place.

When the mixture has settled two phases are present, the extract and the raffinate. The extract is the phase containing the added solvent and the extracted solute, and the raffinate is the phase from which the solute has been removed.

The extract settles either at the top or the bottom of the mixture depending on which of the two phases are lighter.

For a batch operation both the mixing and the settling can take place in one tank, whereas continuous operation usually has mixing in one tank and settling in an other.

3.3 Discussion of Separation Processes

In the light of the properties in chapter 2, the above mentioned separation processes will be discussed regarding the separation of aniline from water. Table 3.1 shows which properties influence the different separation processes, and from these properties an optimal separation will be determined.

Distillation	Adsorption	Stripping	Membrane	Liq-liq
			separation	Extraction
Boiling	Polarity	Solute	Concentration	Miscibility
point		concentration	difference	
Vapor	Molecule	Volatility	Permeability	Phase
pressure	weight	of components	of solute	split
Vapor-liquid	Solid–liquid	Gas-liquid		Liquid–liquid
equilibrium	equilibrium	equilibrium		equilibrium

Table 3.1: Physical influence on the separation processes

From Lorenz et al. (5) and Cussler et al. (1) it is an accepted heuristic that the simplest separation is to be performed first. In the present problem the simplest separation is to separate the aniline phase from the water phase, since the waste stream consists of two phases. The separation of the two phases in the distillate results in a water phase containing a small amount of aniline, 3.39(w/w)%, and an aniline phase containing a water amount of 4.98(w/w)%.

The greater part of the water will be in the water phase, since the solubilities are not larger than they are. In the following discussion the separation of aniline from water will refer to the purification of the water phase, unless anything else is stated.

Distillation is, as mentioned, a widely used process, and could also be a solution for purifying the water phase.

According to Seader er al. (12) a relative volatility value of 10000 will give an almost perfect separation in a single stage, while a relative volatility value of 1.10 will need hundreds of stages to give a complete separation, so from this point of view, distillation is not an optimal solution (the relative volatilities are determined below). It is also known that an azeotrope can have an influence on the distillation, in the sense that the desired compositions of the distillate and bottom product can be impossible to reach unless the pressure is changed, to reject the azeotrope. Despite the fact that an aniline–water system forms an azeotrope, distillation is still a possible separation process.

A distillation process could be to distill the water phase, so the distillate consisted of pure water, while the bottom product would be the aniline–water azeotrope, due to the normal boiling points of the components.

If the aniline phase is distilled, the distillate could consist of the water–aniline azeotrope, while the bottom product could consist of pure aniline.

The azeotrope mixture could be sent back to the two phase waste stream, and the whole separation scheme could start over again.



A flow sheet of the separation can be seen in figure 3.1.

Figure 3.1: Distillation separation scheme

An estimated number of the distillation stages needed to perform the distillations in figure 3.1 can be found using the Margules equations from Smith et al. (13) and short cut formulas, equations (3.5), (3.5), and (3.6), from Lorenz et al. (5).

The Margules equations represent a commonly used empirical model of solution behaviour and are defined as

$$\ln \gamma_1 = x_2^2 \left[A_{12} + 2 \left(A_{21} - A_{12} \right) x_1 \right]$$
(3.1)

and

$$\ln \gamma_2 = x_1^2 \left[A_{21} + 2 \left(A_{12} - A_{21} \right) x_2 \right]$$
(3.2)

From the values of A_{12} and A_{21} given in table 2.3, the activity coefficients can be determined, and in relation to the vapor pressures, the relative volatility can be determined as done by King (4)

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 \cdot P_1^{sat}}{\gamma_2 \cdot P_2^{sat}}$$
(3.3)

Because the fraction of vapor at the standard temperature is low compared to the fractions of liquid, it is of no interest to find the relative volatility at these temperatures. However if distillation is to be performed, the mixture will be heated to get a significant vapor fraction. Water and aniline both have high normal boiling points, and therefore the mixture will require a large amount of energy for distillation to be performed. Since water has the lower boiling point and the higher vapor pressure, see table 2.1 and appendices C.1 and C.2, this will be the more volatile component of water and aniline, and will therefore be component 1 in equation (3.3). This also means that the distillation will evaporate a large fraction of the large amount of water in the water phase for the separation to take place. This requires a great amount of energy, and therefore seems to be an expensive solution.

Looking at a temperature of 100.56° C, the bubble point of the system determined by the mole fractions and the normal boiling points, the vapor pressures found with the Antoine equation (2.2) and the activity coefficients give a relative volatility value for the water phase of

$$\begin{aligned} \alpha_{12} &= \frac{\exp(x_2^2(A_{12} + 2(A_{21} - A_{12})x_1)) \cdot P_1^{sat}}{\exp(x_1^2(A_{21} + 2(A_{12} - A_{21})x_2)) \cdot P_2^{sat}} \\ &= \frac{\exp(0.0067^2(1.0041 + 2(3.1217 - 1.0041) \cdot 0.9933)) \cdot 767.6mmHg}{\exp(0.9933^2(3.1217 + 2(1.0041 - 3.1217) \cdot 0.0067)) \cdot 45.9mmHg} \\ &= 0.79 \end{aligned}$$

and for the aniline phase 98.6°C, which is where the azeotrope will be present

$$\begin{aligned} \alpha_{12} &= \frac{\exp(x_2^2(A_{12} + 2(A_{12} - A_{21})x_1)) \cdot P_1^{sat}}{\exp(x_1^2(A_{21} + 2(A_{12} - A_{21})x_2)) \cdot P_2^{sat}} \\ &= \frac{\exp(0.787^2(1.0041 + 2(3.1217 - 1.0041) \cdot 0.213)) \cdot 717.2mmHg}{\exp(0.213^2(3.1217 + 2(1.0041 - 3.1217) \cdot 0.787)) \cdot 42.3mmHg} \\ &= 56.0 \end{aligned}$$

For the water phase, the more volatile component is water, when comparing water and the aniline–water azeotrope, and therefore this will be the distillate. The azeotrope will be the bottom product. When the water is to be purified, the distillate must consist of approximately 100% water (maximum 2(w/w)ppm aniline), while the azeotrope has a water weight fraction of 0.808 (16), and a mass balance therefore gives

For aniline :
$$7188.7kg \cdot 0.0339 = 0.192 \cdot b + 0.000002 \cdot d$$

For water : $7188.7kg \cdot 0.9661 = 0.808 \cdot b + 0.999998 \cdot d$

Solving these two equations gives b=1269.2kg and d=5919.5kg. Using the short cut formulas from Lorenz et al. (5), the number of stages can be estimated. First the top and bottom recoveries are defined

$$\beta_{lk} = \xi_{lk} \tag{3.4}$$

$$\beta_{bk} = 1 - \xi_{hk} \tag{3.5}$$

the light component is the same as the more volatile component, so equations (3.5) and (3.5) become

and

$$\begin{array}{rcl} \beta_{lk} &=& \xi_{lk} &=& 0.852 \\ \beta_{hk} &=& 1 - \xi_{hk} &=& 0.999957 \end{array}$$

The number of stages is estimated using equation

$$N_i = \frac{12.3}{(\alpha_{lk/hk} - 1)^{2/3} \cdot (1 - \beta_i)^{1/6}}$$
(3.6)

For the distillate and the bottom product, the number of stages is determined

The actual number of stages can be found using equation (3.8)

$$N_T = 0.8 \cdot max_i(N_i) + 0.2 \cdot min_i(N_i)$$

$$= 0.8 \cdot 186 + 0.2 \cdot 48$$

$$= 149 stages$$
(3.7)

The large number of stages is a strong indication that distillation is not an economically favorable solution for separation of the water phase.

The energy needed to heat water from 20° C to 100° C is found using the change in heat capacity, while the heat needed to vaporize the water at 100° C is found using ICAS. An expression for the heat capacity of liquid water is found in Smith et al. (13)p.658.

$$\frac{C_p}{R} = 8.712 + 1.25 \cdot 10^{-3} \cdot T(K) - 0.18 \cdot 10^{-6} \cdot T(K)^2$$
(3.8)

Using this expression and the energy needed to vaporize the water, the total energy needed is found

$$\Delta H = \Delta_{vap} H(373.15^{\circ}C) + R \cdot \int_{293.15K}^{373.15K} \frac{C_p}{R} dT$$

= 4.0799 \cdot 10^4 J/mol + 728.7K \cdot 8.31451 J/(mol \cdot K))
= 46857.8J/mol

The amount of water exiting as distillate from the first distillation is 5919.5kg/production (because of the low aniline concentration, the distillate is seen as pure water), so the amount of energy needed is

 $\frac{46.9 \cdot 10^{6} J/kmol \cdot 5919.5 kg/production}{18.015 kg/kmol} = 15 \cdot 10^{9} J/production = 4280.7 kWh$

From the web page of NESA(21), the marketing price for electricity is found to be 28øre/kWh.

This gives an indication of the price one distillation of the water phase will cost

 $4280.7kWh/production \cdot 0.28dkr/kWh = 1198.6dkr/production = 799469dkr/year$

If the aniline phase is to be separated, a mass balance will give

For water :
$$305.8kg \cdot 0.05 = 0.808 \cdot d + 0.005 \cdot b$$

For aniline : $305.8kg \cdot 0.95 = 0.192 \cdot d + 0.995 \cdot b$

Solving these two equations gives d = 17.1kg and b = 288.7kg. The number of stages needed for the separation is found to be 2 stages. This number is found as above for the water phase.

When two distillations are used, the total aniline recovery is

$$\frac{288.7 \cdot 0.995}{93.128 kg/kmol \cdot (3kmol + 2.6kmol)} \cdot 100\% = 55.1(w/w)\%$$

and this does not respect the request of a 90(w/w)% aniline recovery made by Syntese A/S.

The energy needed to evaporate the aniline–water azeotrope is found in the same way as above. The energy needed to heat aniline–water azeotrope composition from 20°C to 98.6°C is found using the change in heat capacity, while the heat needed to vaporize the aniline–water azeotrope at 98.6°C is found using ICAS. An expression for the heat capacity of liquid aniline is found in Smith et al.(13)p.658.

$$\frac{C_p}{R} = 15.819 + 29.03 \cdot 10^{-3} \cdot T(K) - 15.8 \cdot 10^{-6} \cdot T(K)^2$$
(3.9)

Using this expression and the energy needed to vaporize the aniline–water azeotrope, the total energy needed is found

$$\begin{split} \Delta H &= 0.956 \cdot \Delta_{vap}^{water} H(371.75^{\circ}C) + 0.044 \cdot \Delta_{vap}^{aniline} H(371.75^{\circ}C) \\ &+ R \cdot 0.986 \cdot \int_{293.15K}^{371.75K} \frac{C_p(water)}{R} dT \\ &+ R \cdot 0.044 \cdot \int_{293.15K}^{371.75K} \frac{C_p(aniline)}{R} dT \\ &= 91700 + 6550.6 \\ &= 98250.6J/mol \end{split}$$

The amount of azeotrope exiting as distillate from the second distillation is kg/production, so the amount of energy needed is

 $\frac{98.3 \cdot 10^{6} J/kmol \cdot 17.1 kg/production}{0.808 \cdot 18.015 kg/kmol + 0.192 \cdot 93.128 kg/kmol} = 8.6 \cdot 10^{6} J/production = 2.4 kWh/production$

Giving an annual expense of

$$2.4kWh/production \cdot 0.28dkr/kWh = 0.7dkr/production = 448.2dkr/year$$

a reasonable cost.

Stripping could be an option when using the right gas to absorb aniline and not water. Aniline would be recovered from the gas using condensation, and therefore one of the requirements to the gas is that it is non condensable to ensure only aniline is condensed, giving pure aniline.

The pure aniline is recycled to take part in the 5–ASA product reaction again, and to make the purification less energy requiring, the amount of gas should be kept at a minimum. This however means that the stripping column will have to be considerably higher than if a larger amount of gas is used. The aniline amount in the waste stream is in percent and not in ppm, which means that the column already will need a large number of stages to ensure the aniline concentration is reduced to the wanted 2(w/w)ppm, using a moderate amount of gas.

Besides a purer separated aniline, the recovery of the aniline after the stripping separation, will require less energy in the condensation ,if a minimum amount of gas is used. If stripping is to be used as the separation method, an energy and economic analysis should be made to determine the optimal gas flow to give the smallest energy amount needed for both the stripping column and the condensation, but because of the aniline amount in the waste stream, stripping will not be the economically optimal separation process.

Adsorption is another possible separation process for separating aniline from the waste stream, when the right adsorbent is identified. The adsorbent will adsorb the aniline, which can be recovered again by passing a solvent through the solid bed. The aniline must favor to be in the solvent more than in the solid, so a majority of the aniline goes out in the solvent stream, and can this way be recovered. The solvent should be chosen, so a separation from aniline is easy and requires a minimum of energy. Because both aniline and water are polar components, this property can have an influence on the adsorbent choice, since it is not desirable that the adsorbent is saturated with water instead of aniline.

Because the aniline content in the waste stream is in percent and not ppm, a significant amount of adsorbent is needed to reduce the aniline concentration to the required, and because the amount of solid is large, a corresponding large volume of solvent must be used to recover the aniline from the solid again. If i.e. distillation is used for the separation of the solvent and aniline, a larger number of stages is needed when the solvent volume is increased, resulting in an increase in energy required for the separation.

The disposal of the deactivated adsorbent is an expense which must also be taken into account along with loss of solvent.

Membrane separation is known to be a usable separation method for reducing the aniline concentration in water to a minimum.

However membrane separation requires driving force which is made as a difference in the solute concentration, here the aniline concentration, between the external and internal phases. The aniline concentration in the internal phase is reduced to zero (or a minimum) by converting aniline to another component. Because the aniline is to be recycled, the other component must be capable of converting back to aniline. It is feasible to get aniline with a purity of 99.5%, otherwise a purification must be made in another way.

Liquid–liquid extraction is an option because water and aniline are immiscible, and a solvent therefore should be easy to determine.

Extraction can be done at standard temperature, so the boiling points and vapor pressures play no role in this process, and with a solvent which forms a phase split from water's, the separation should be straightforward.

With a sufficient number of stages, extraction alone should be enough to reduce the aniline concentration in the water phase to the required 2 ppm or less.

Extraction will produce two streams, the raffinate containing water and a reduced concentration of aniline, and the extract containing the solvent with aniline. The solvent should be chosen, so separation of aniline from the solvent is possible with e.g. distillation.

A separation scheme using extraction could be to have the number of extraction stages that ensure the sufficient reduction of aniline in the water phase from the waste stream. The raffinate would then be pure water with only traces of aniline and solvent, while the extract would contain solvent and aniline, which could be distilled to pure solvent as the distillate and aniline as the bottom product. The aniline could then be added to the aniline phase from the waste stream and this could be distilled to give impurities as the distillate and purified aniline as the bottom product.

A flow sheet of the separation can be seen in figure 3.2.



Figure 3.2: Extraction separation scheme

The only problem with an extraction separation, is to determine a solvent. The solvent should be chosen to have a low boiling point so the energy needed for the distillation separating the solvent from the aniline is minimized, but also to have low solubility in water, so the waste stream is not polluted with the solvent after the reduction of aniline.

3.4 Summary

When a series of separations are to be performed, the simplest should be made first. The waste stream consists of two phases and therefore the simplest separation is to separated these two, giving an aniline–saturated water phase and a water–saturated aniline phase. The water phase must be purified so it can be sent directly to a waste water treatment plant, while 90(w/w)% of the aniline is to be recovered for recycling.

For the purification of the water from the water phase, distillation is a usable method.

It is, however, quite energy requiring and therefore not satisfactory, also because the aniline in the water phase was not recovered. Distilling the aniline phase seems to give a reasonable result, but the 90(w/w)% aniline recovery is not upheld when only this separation purifies aniline.

For equipment and economical reasons stripping, adsorption and membrane will not be treated further as separation options, even though they could be used.

Liquid–liquid extraction is an obvious solution for the purification of both water and aniline, because the two components are immiscible. Extracting the water phase will purify the water, while, with the right solvent, the aniline recovery from the water phase should be straight forward. If the distillation of the bottom product from the separation of the solvent and aniline, and the aniline phase can give the required 90(w/w)% purified aniline, this seems to be the optimal solution. However an economic comparison between the extraction and the distillation scheme should be made before any conclusions are made. This is what is done in the following chapters.

Chapter 4 Choosing a Solvent

In the previous chapter liquid-liquid extraction was determined as one solution for the separation of aniline from the water phase of the waste stream. In this chapter a number of solvents for this extraction separation will be found using ProCAMD in ICAS, and on the basis of the Danish Environmental Law regarding organic compounds in waste stream, some possible solvents will be chosen. When finding a solvent also the fact that the extract must be separated from aniline again, maybe by distillation, is taken into account.

4.1 Presentation of ProCAMD

ProCAMD, Computer Aided Molecular Design, is a package able to identify components with specific properties. The user determines a number of physical and chemical properties the wanted component must respect, and the program is then able to estimate molecular structures that correspond to these properties by investigating fragments in different components. Because the properties related to the fragments, and thereby also the molecules, are estimated, they should be regarded critically. The data and models used as basis for the molecule designs are important for the result, and should therefore be investigated, if unexplainable result are given.

As mentioned, the physical and chemical properties the wanted component must uphold are entered in the program. The properties are divided into six constraints.

- General Problem Control
- Non–Temperature Dependent Properties
- Temperature Dependent Properties
- Mixture Properties
- Azeotrope/Miscibilty Calculations

• Biodegradation Calculations

In *Generel Problem Control* the type of component which to determine is selected. If the program is to generate acyclic, cyclic, or aromatic and if they have to be alcohols, ketones and so on is selected in this part.

In Non–Temperature Dependent Properties the temperature independent properties the solvent must have, such as the molecular weight, boiling point, melting point, and $\log P_{(Octanol/water)}$, are selected. They are selected to have either a minimum, a maximum, both, or a goal value, whatever the user determines.

In the *Temperature Dependent Properties* the temperature dependent properties are defined. These are among others the density and the vapor pressure. Again a minimum, a maximum or a goal value is determined.

In *Mixture Properties* the thermodynamic model is selected along with the conditions, temperature and pressure, under which the calculations are to be made. Here the key components and their amounts in e.g. the mixture to be separated by extraction are presented. Also the solute is selected.

Finally the constraints such as solvent loss and the separation factor are determined.

Whether or not different components should be miscible with the solvent, and if an azeotrope should or should not exist is determined in *Azeotrope/Miscibility Calculations*.

Biodegradation Calculations is used to determine the biodegradation requirements the solvent must respect.

From the entered constraints, the program searches in the ICAS database for components that fulfil the properties, but it also designs molecules that match the target properties. The molecules are design by different fragments(building blocks) with corresponding properties.

4.2 Environmental Demands

To ensure the solvents ProCAMD find respect the restrictions made by The Danish Environmental Protection Agency, the requirements are investigated and shortly presented.

The environmental aspect is based on a guidance made by The Danish Environmental Protection Agency from 2002, *Vejledning fra Miljøstyrelsen* p.27–30 (8).

The Danish Environmental Protection Agency has divided the organic compounds found in waste streams into three groups concerning the harmful effect a chemical can have on humans, the chemical's capacity to make biodegradation, and any effect the chemical may have on the organisms living in water. The three groups are listed as list A, list B, and list C.

List A Chemicals, who's properties make them unwanted in the waste water treatment plants, because they consists of chemicals that are capable of causing incurable sickness to humans. They are not easily degradable and they are very toxic for aquatic organisms.

These chemicals should be replaced or reduced to a minimum.

Chemicals with human damaging R–sentences 39, 40, 45, 46, 48, 60, 61, 62, 62 and 64.

List B Chemicals should only be present in small concentrations in the waste streams to uphold the environmental demands. The chemicals in this group are therefore ones that are not easily degradable and are somewhat toxic for aquatic organisms. Selected chemicals have limiting values.

The chemical should also be regulated according to the easiest accessible technique, e.g. extraction to reduce an aniline concentration.

List C Chemicals which do not, despite their properties, have a limiting value, and do not give reason to have one, are in this group. Chemicals which do not come under list A nor B will be on list C.

The list C components must be easy to decompose using an OECD scanning test, a standard method when determining EC, LC and LD. The compounds must also have a low EC_{50} -value(less than 100mg/l), and must not be potentially bioaccumulated $(\log P_{(Octanol/water)} > 3)$. EC₅₀, Effect Concentration, is the concentration that under known conditions and in a given time will give a definite effect to 50% of the test organisms. The $\log P_{octanol/water}$ value is a measure for the solubility of a component in water compared to the solubility in octanol to determine whether the molecule is bioaccumulable or not.

In appendices 1 and 2 in *Vejledningen fra Miljøstyrelsen* (8) tables with some common organic compounds are shown.

Appendix 1 shows a list of some compounds risk towards humans, volatility, and biodegradability. It shows whether or not $EC_{50} < 1$ and <100 and bioaccumulated is respected, and the amounts allowed in water along with the limiting values.

Appendix 2 shows some physical properties of the compounds. Appendix 2 contains measures for the Henry constant, logP(Octane/water), the molecular weight, the water solubility and the vapor pressure.

The Henry constant is used to calculate the concentration of the volatility of a component, to determine whether or not the component gives reason for explosion precautions.
4.3 Properties Entered ProCAMD

The water phase is to be extracted at constant atmospheric pressure but at different temperatures dependent on the time of year. Therefore the temperature will be approximated to be standard temperature, 298K.

In 2000 Harper (3) used ProCAMD to find a solvent to replace toluene as a solvent in a liquid–liquid extraction for removing phenol from water. Because this problem is similar to the present, the property requirements are determined according to those Harper made.

The temperature and non-temperature dependent properties are determined on the basis of the fact that the water phase is first to be extracted and the extract distilled. Therefore the following requirements are made for the solvent when the extraction is taken into account

- Boiling point must be higher than the operating temperature
- Melting point must be lower than the operating temperature
- Liquid density must be lower than water's density. The ratio of the densities at the operating temperature must be at least 1.05
- The existence of a liquid–liquid split in water

and for the distillation performed to separate the aniline from the solvent

- Difference in boiling point. The ratio of the boiling points of aniline and the solvent must be higher than 1.02
- Difference in vapor pressure at operating temperature. The ratio of the vapor pressures of aniline and the solvent must be higher than 1.5
- Absence of azeotrope between aniline and the solvent

These requests led to the following corresponding values entered as in *Non–Temperature* and *Temperature Dependent Properties*

- the boiling point is set to be maximum 430K
- the vapor pressure set to minimum 0.0006bar
- $\bullet\,$ the melting point is set to a maximum of 273.15K
- liquid density $< 1 \text{ g/cm}^3$ put to maximum of 0.9g/cm^3
- two liquid phases must form when mixed with the water phase containing aniline
- Solvent must not form azeotrope with aniline

The boiling point is set to a maximum of $430 \text{K} \left(\frac{183+273.15}{1.06}\right)$, because aniline has a relatively high boiling point, which will result in an energy requiring distillation if the aniline is the more volatile compared to the solvent. The solvent is this way chosen to be the more volatile. When the solvent is to be vaporized of the aniline, the vapor pressure of the solvent must be higher than the vapor pressure of aniline. This is ensured by setting the vapor pressure of the solvent to have a minimum value of the vapor pressure of aniline at 293.15K.

To ensure a phase split between the water and the solvent, the density of the solvent must be lower than the density of water. This is ensured by setting the density maximum to 0.9g/cm³.

The melting point must be higher than the operating temperatures, to ensure the solvent phase is liquid.

When distillation is to be performed, azeotropes can cause problems, so to prevent these problems, it is requested that the solvent and aniline do not form an azeotrope.

The vapor pressure and the liquid density of water and aniline are found using equations (2.2) and (2.3) presented in chapter 2.

Furthermore the solvent must posses the economic properties

- Solvent loss must be as low as possible
- Separation factor must be as high as possible

The solvent loss is defined as $\frac{1}{\gamma_{solvent\ in\ water}^{\infty}}$, a high γ^{∞} value indicates low solubility corresponding to this definition. The separation factor is defined as $\frac{x_{aniline\ in\ solvent}\cdot x_{water\ in\ water}}{x_{aniline\ in\ water}\cdot x_{water\ in\ solvent}}$ similar to equation (3.3).

And the environmental constraints

- Open cup flash temperature should be above the operating temperature
- Compound should not react with air or other compounds in the mixture
- The component should be on the list C, $\log P > 3$

The flash temperature is the highest temperature a liquid can have, before the vapor just above it does not ignite, and should therefore be above operating the temperature. The $\log P_{octanol/water}$ should, according to the list C, be larger than 3.

The additional constraints are specified in respectively *Temperature Dependent Proper*ties and *Mixture Properties*

- The solvent loss is set to a maximum of 0.001
- The separation factor is set to a value of minimum 1000

- Open cup flash point set to minimum 250K
- logP(octanol/water) set to 1

Even though the logP should be higher than 3 it is only set to 1, and the open cup flash point should be above it is set to 250K, to get a larger selection of compounds. This is done, because it turns out that there are no hits for aromatic compounds if the logP value is set to minimum 3, and only a small number of hits for non aromatic components, when the flash point is too high.

Finally some desired properties are

- Solvent must for a homogeneous system at all compositions with aniline
- Low enthalpy of vaporization

In *General Problem Control* alcohols, ketones, aldehydes, acids, esters and amines are chosen as wanted solvent types. This is, as mentioned, done for both acyclic and aromatic compounds.

In *Mixture Properties* the thermodynamic model, Original UNIFAC LLE, because this is the only LLE model present in the program. Here also the feed streams mole fractions and the constrains are entered.

In *Azeotrope/Miscibility Calculations* azeotrope for the solvent and aniline, and miscibility for the solvent and water, are dismissed.

To sum up table 4.1 shows what properties have been entered in the program

$\max.430$
max. 293
$\min 250$
min. 1
max. 0.9
min. 0.0006
0.001
1000

Table 4.1: Values for the different j	properties entered	in	ProCAMD
---------------------------------------	--------------------	----	---------

4.4 Results from ProCAMD

ProCAMD finds 405 acyclic and 8 aromatic molecules having the desired properties. For each of the found molecules the properties, which the user has made requirements about, are listed below the molecular structure. In table 4.2 the 8 aromates and the 12 acyclic molecules with the most solvent interesting properties are listed. The 12 acyclic molecules are found by listing the properties according to the highest logP–value, the highest flash point, the highest separation factor and the lowest solvent loss. The 12 molecules are the ones which are represented the most times.

Aromatic molecules
Styrene
Ethyl benzene
Cumene
The three xylenes
Toluene
Benzene
Acyclic molecules
n-methyloctane
n–octane
n-hexane
n-heptane
2,3,4-trimethylpentane
2,2,3,3-tetramethylbutane
2,3–and 2,4–dimethylpentane
n-methylheptane
Isobutyl isobutyrate
n-butyl propionate
Diisopropylether

Table 4.2: Interesting solvents found by ProCAMD

The list is reduced by finding the ones which are well known, easy to get a hold of, cheap, have high separation factors, low solvent losses, and high logP–values and by judgement of Syntese A/S. The selected ones can be seen in table 4.3

	$\log P$	Separation	Solvent	Flash	Price
	(octanol/water)	factor	loss	cup point	
				(K)	(dkr/kg)
n–Hexane	3.22	$4.8 \cdot 10^{7}$	$5.4 \cdot 10^{-5}$	253.5	4.89
n–Heptane	3.72	$4.7 \cdot 10^7$	$1.6 \cdot 10^{-5}$	270.9	4
n–Octane	4.23	$4.6 \cdot 10^{7}$	$4.5 \cdot 10^{-5}$	286.5	7.5
Toluene	2.72	1833	$8.3 \cdot 10^{-5}$	309.8	5
Xylenes	3.19	1917	$1.8 \cdot 10^{-5}$	322.7	5

Table 4.3: Interesting solvents found by ProCAMD

The prices for n-heptane, toluene and xylene are given as estimated prices by Jørgen Erhardsen, Helm Scandinavia, who delivers chemicals to Syntese A/S. Xylene is sold as a mixture of orto-, meta-, and para-xylene, because it is expensive to separative the three isomers. Para-xylene is the main isomer in the mixture. The prices for n-hexane and n-octane are found on the internet.

When checking the A–, B–, and C–lists it turns out that n–hexane is A–listed, and is therefore rejected as a candidate. Toluene and p–xylene are both c–listed, while n– heptane and n–octane are not listed at all, n–octane is however rejected because of it's price compared to n–heptane.

To see if they are unwanted by the Danish Environmental Protection Agency, the List of undesirable substances 2000(22) and Effektlisten 2000(19), the effect list, from the web page mst.dk is investigated.

The Effect list (19) is a list of components that are thought to have a health and environmental effect, while the List of Undesirable Substances (22) is a list of components from the Effect list that are known to be used in larger amounts than 100tons/year. n-heptane is on the Effect list with the R-warning/safety sentences:

- **R11** highly flammable
- **R38** irritating to skin
- $\mathbf{R50/53}$ very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
- R65 Harmful : may cause lung damage if swallowed

These R-sentences are not the ones which A list a chemical, so the Henry constants for the n-heptane is found. It has a value of $0.9 \text{atm} \cdot \text{m}^3/\text{mol}$, which is too high compared to the explosion limit that allows a Henry constant with value $10^3 \text{atm} \cdot \text{m}^3/\text{mol}$.

The selected solvents are therefore reduced to toluene and o,m,p–xylenes, which also have a reasonable price.

In the next chapter the physical properties for the solvents will be investigated more closely.

Chapter 5

Investigating the Properties of the Solvents

The previous chapter presented a number of solvents that were found using ProCAMD in ICAS. The environmental requirements and the chemical prices, regarding each solvent, were investigated, and the solvents not of environmental and economical interest were rejected, resulting in two solvents; Toluene and Xylene. Xylene is cheapest to buy as a mixture of orto-, meta- and para-xylene isomers, with p-xylene as the main isomer in the mixture, and therefore the properties of xylene will be referred to as the properties of para-xylene.

Despite the environmental investigation result, n-heptane will also be tested in the laboratory, and therefore the physical properties of this component is also shown.

This chapter will investigate these three solvents, with respect to their physical properties and their binary behaviour with respectively aniline and water.

5.1 Physical Properties of the Solvent

As in chapter 2 the properties are presented as the temperature dependent and temperature independent.

5.1.1 Temperature Independent Properties

In table 5.1 the temperature independent physical properties of the three interesting solvents are listed. All the values have been found in the database in ICAS. These properties will be used when determining the amount of solvent to be used in one extraction stage, the number of distillation stages needed to separate the aniline from the solvent and so on.

	Toluene	p–Xylene	n–Heptane
Chemical Formula	C_7H_8	$C_8 H_{10}$	$C_7 H_{16}$
$(\boldsymbol{M_w}) \; (\mathrm{g/mol})$	92.141	106.167	100.204
Antoine A	7.1441	7.105	7.096
Antoine B(°C)	1528.363	1535.466	1381.677
Antoine C(°C)	223.262	219.964	228.794
Vapor pressure A	80.877	85.475	87.829
Vapor pressure $\mathbf{B}(\mathbf{K})$	-6902.4	-7595.8	-6996.4
Vapor pressure C	-8.7761	-9.378	-9.8802
Vapor pressure D	$5.8034 \cdot 10^{-6}$	$5.6875 \cdot 10^{-6}$	$7.2099 \cdot 10^{-6}$
Vapor pressure E	2	2	2
Density $A(kmole)$	0.8488	0.6816	0.61259
Density $B(m^3)$	0.26655	0.25963	0.26211
Density C(K)	591.8	616.23	540.2
Density D	0.2878	0.2768	0.28141
Т <i>b</i> (К)	383.78	411.51	371.38
$T_{\boldsymbol{m}}(K)$	178.18	286.41	182.57

Table 5.1: Physical properties of the four solvents

5.1.2 Temperature Dependent Properties

The temperature dependent properties can be seen in appendices D.1, D.2 and D.3. Here both tables and figures of the Antoine vapor pressure in Bar, the vapor pressure in Pa and the densities of the solvents can be seen.

The figure of the two different estimated vapor pressures show similar curves as expected, since the main difference, despite the different equation used to estimate the pressure, is the unit. From the two vapor pressure figures it can be seen that n-Heptane has the highest vapor pressure at calculated temperatures, while p-xylene has the lowest of the three. This shows that n-heptane is preferable regarding the distillation separation of aniline from the solvent. The figure of the densities show that n-heptane has the lowest density at all the calculated temperatures, whereas toluene and p-xylene have similar high densities, compared to n-heptane which indicates that n-heptane will give an easier separation from water.

When determining the number of extraction stages needed to reduce a solute concentration in i.e. a waste stream, a ternary diagram is used. The ternary diagram for aniline, water and toluene, estimated using the LLE UNIFAC model at a temperature of 25° C, is shown in figure 5.1. The ternary diagrams are made using the program SMSWIN. The figure shows that aniline and water are partially miscible, they form two phases when the aniline ratio is below 0.8, which is in good agreement with the measured value found in chapter 2, which show that 21.8(mol/mol)% water is soluble in aniline at a



Figure 5.1: Ternary diagram for toluene, water, and aniline with binodal curve at 25°C

temperature of 25°C. The figure also shows that toluene and aniline seem to be completely miscible, and water and toluene seem to be completely immiscible. The phase split is seen by the curved line. Above the curve is one phase, while two phases are present under the curve. Because water and toluene are almost completely immiscible, the mixture will form two phases instantly after the solvent has been added.

The straight lines are called tie lines, and are used to determine the composition of respectively the extract and the raffinate, according to the amount of solvent added to the mixture to be separated.

The number of extraction stages needed to reduce the aniline concentration in the water phase can be found by e.g. using the McCabe–Thiele method. This is done by plotting the mol/mass fraction of the solute in the extract against the mol/mass fraction of the solute in the raffinate. The values are found in the ternary diagrams using the ends of the tie lines.

From the present ternary diagram it seems as if only one extraction stage is needed to purify the water completely, since the tie lines all go toward 100(mol/mol)% water. This is not necessarily the case, since it is not possible to see if the tie lines actually go towards very small mol fractions of aniline. The precise coordinates are to be known to make the extraction stage determination by the McCabe–Thiele method, and unfortunately it is not possible to get the exact coordinates for aniline mol/mass fractions as low as needed here.

In the present problem the aniline–water mixture consists of 0.67(mol/mol)% aniline

and the rest water, which means the mixture composition is down in the left corner of the diagram.

One of the requirements for the solvent is that the amount of solvent in the water after the extraction must be less than a given amount, so the solubility of the solvents in water is also an important property. The solvent amount in the water phase is determined by Syntese A/S, and is set to uphold the environmental requirements. The solubilities are found in Sørensen et al (14), and are listed in table 5.2

Temperature (°C)	Toluene	p-Xylene	n–Heptane	
	(mol/mol)ppm	(mol/mol)ppm	(mol/mol)ppm	
0	142	24.7	0.61	
10	128		0.56	
20	113	28.4	0.53	
25	106	29.5	0.50	
	(w/w)ppm	(w/w)ppm	(w/w)ppm	
0	726	126	3.13	
10	654		2.85	
20	578	145	2.69	
25	542	151	2.56	
Maximum	290	285	680	

Table 5.2: The solubilities of the three solvents in water

The solvent which is least soluble in water is n-heptane. It upholds the request of it's maximum concentration, while toluene is much too soluble in water, giving too high concentrations. There is not given a maximum value for the p-xylene concentration in water, so one is estimated from the maximum COD-value of 900mg Oxygen/l. From the program SuperPro Design, the COD-value for o-xylene is found to be 3.165g Oxygen/g, giving a maximum content in water of $\frac{900mgOxygen/l}{3.165mgOxygen/mg} = 285 \text{mg/l}.$

5.2 Equilibrium Behaviour Between Aniline and Solvents

When running ProCAMD, no constraint against aniline and the solvent forming two phases was made. Therefore it is investigated if this is the case for any of the three solvents. It turns out that aniline and n-heptane form a two phase system, while both the other solvents are completely miscible with aniline. Therefore the equilibrium behaviour will be presented in two sections, one for n-heptane and one for toluene and p-xylene. The estimated ternary diagrams for n-heptane, aniline and water, using SMSWIN for three different thermodynamic models; LLE UNIFAC, VLE UNIFAC and Modified UNI-FAC Lyngby, see figure 5.2, do however not show that aniline and n-heptane form two phases, properly because groups in n-heptane do not tend to form two phases with aniline, and therefore the models do not take this into account.

It could also be because the models are based on experimental data. Table 5.3 shows the γ^{∞} -values between the solvents and aniline.

	$\gamma_{solvent}^{\infty}$	$\gamma_{aniline}^{\infty}$
Toluene	1.61	1.65
p-Xylene	2.19	2.27
n-Heptane	9.67	10.13
Water	3.49	555

Table 5.3: γ^{∞} for aniline and the three solvents

The γ^{∞} -values for n-heptane are not significantly larger than the γ^{∞} -values of the two other solvents, compared to the γ^{∞} -value for aniline in water, which indicates a very low solubility. Therefore there is no indications from the γ^{∞} -values that aniline and water form two phases.

The high γ^{∞} -value for aniline in water could also be the reason, the tie lines all go towards 100(mol/mol)% water in just one step.

5.2.1 n–Heptane

As mentioned aniline and n-heptane form two phases when mixed. At 25° C only 7.58(mol/mol)% aniline is soluble in n-heptane, (14).

The phase split is not shown on neither diagram in figure 5.2. They all also shows that water and n-heptane are almost completely immiscible, which corresponds to the low solubility of n-heptane in water.

The ternary diagram shows that only a very small amount of n-heptane is needed to remove, what tends to be, all the aniline from the water, resulting in a completely pure water phase in just one stage. Comparisons with the simulations made by Eden et al (17), who used 10 stages and the VLE UNIFAC model to get the aniline concentration reduced to 2(w/w)ppm with n-heptane as the solvent, this is not what is expected, and therefore the ternary diagram is estimated again using two different thermodynamic models, VLE UNIFAC and Modified UNIFAC Lyngby. They also tend to show that only one stage is need to purify the water completely.

The LLE UNIFAC ternary diagram, however, shows that 20(mol/mol)% water is soluble in aniline when the LLE model is used, which is in good agreement with the theory. The VLE UNIFAC and modified UNIFAC Lyngby do not show this, therefore the LLE diagram is the most reliable. The binodal curve does not go all the way out to the binary aniline–water system in the Modified UNIFAC Lyngby diagram because of numeric problems. An estimation is made by solving a number of equations, and these have no more numeric solutions, the estimation stops.



Figure 5.2: Ternary diagram for n-heptane with binodal curves at 25°C. The top diagram is estimated using LLE UNIFAC, the lower left is estimated using VLE UNIFAC and the lower right using Modified UNIFAC Lyngby

One of the requirements when choosing a solvent, was that no azeotrope was formed between the solvent and aniline, but because the solvents are found as a result of estimations, it is investigated if an azeotrope does exist anyway. Experimental data from (2) in figure 5.3, show that this is not the case, and therefore there is no need to worry about azeotropes.



Figure 5.3: Experimental determined VLE diagram for aniline and n-heptane at 1 atm

5.2.2 Toluene and Xylene

The ternary diagrams, estimated using the LLE UNIFAC model in SMSWIN, of toluene and p-xylene are shown in figures 5.4 and 5.5. As with n-heptane is seems that only one stage, using a small amount of solvent is needed, which is not expected, and therefore the ternary diagrams are also estimated using the VLE UNIFAC and modified UNIFAC Lyngby. However these also show that only one stage is needed.



Figure 5.4: Ternary diagram for toluene with binodal curves at 25°C. The top diagram is estimated using LLE UNIFAC, the lower left is estimated using VLE UNIFAC and the lower right using Modified UNIFAC Lyngby





Figure 5.5: Ternary diagram for xylene with binodal curves at 25°C. The top diagram is estimated using LLE UNIFAC, the lower left is estimated using VLE UNIFAC and the lower right using Modified UNIFAC Lyngby

As for n-heptane the LLE UNIFAC model diagrams shows, as the only one of the three, show that about 20(mol/mol)% water is soluble in aniline, while the VLE UNIFAC and the Modified UNIFAC lyngby models give uncompleted binodal curves.

To ensure no azeotrope is formed between neither toluene and aniline nor p-xylene and aniline, experimentally VLE diagrams are investigated for the two solvents. The VLE diagram for toluene from (2) can be seen in figure 5.6



Figure 5.6: Experimental VLE diagram for aniline and toluene at 1 atm

while figure 5.7 shows the experimental VLE diagram for p-xylene Neither of the two diagrams show the presents of an azeotrope, so the separation of the solvent from aniline should be straight forward.



Figure 5.7: Experimental VLE diagram for aniline and p-xylene at 1 atm

Chapter 6

Testing the Solvents

In chapter 5 the three solvents, which are candidates for the extraction separation of aniline from water, are investigated on literature and model basis.

In the present chapter the results of laboratory experiments made using the three solvents will be presented. The solvents are tested by experiments to ensure they are capable of reducing the aniline concentration in the water phase, since they have been chosen only on the basis of estimations.

6.1 Experimental Procedure

Liquid-liquid extraction is a process which transfers a component from one liquid phase to another liquid phase. In this case the aniline in the water phase is transferred from the water to the solvent. Liquid-liquid extraction can be done as a mixer-settler operation, which is what has been use when testing the solvents in the laboratorium.

In a mixer–settler unit, a solvent is lead to the binary solution which is to be separated. The solution and the solvent are mixed till equilibrium is ensured. The mixture is then lead away from the mixing area, and left to settle and split into two liquid phases. The heavier one will be in the bottom and the light one at the top.

The experiments were carried out by adding 50ml of the aniline–water solution to 50 ml of the solvent, and leaving the mixture to stir for 15 minutes using a magnetic stirrer. In later experiments the stirring time was changed to 60 minutes.

The mixture was then poured into a separation funnel, where it was given time to settle. This was when a clear phase split was seen. The water phase was the heavier one and was taken out as the raffinate, while the organic phase was the extract containing the aniline and the solvent.

The raffinate was poured into a beaker, and about 2ml was taken for a HPLC analysis. The extract was poured into another beaker, from where 2ml was taken for HPLC anal-

ysis.

To the raffinate, a new clean amount of solvent was added, and the mixture was again mixed and settled as described above.

For each solvent six extraction stages were carried out. This number was chosen, because the ternary diagrams suggested that only one stage was needed, while Eden et al (17)used ten simulated stages when using n-heptane as a solvent, and therefore a number in between was selected. For all the three solvents, the same volumen water phase distillate and solvent was used (50ml).

6.2 Experimental Results

To ensure the solvents and the aniline are miscible, 50ml of each solvent was mixed with 50ml of aniline. It turned out that only toluene and p-xylene were completely miscible with aniline, formed one phase, while n-heptane formed two liquid phases when aniline was added. This is what was found in the previous chapter.

The solvents were then tested on the water phase of the distillate containing 0.67 (mol/mol)% aniline.

The water phase had a trace of yellow coloring, most likely partly from the aniline and partly from impurities. After having been left at 20°C for 20 days, the color had changed to being slightly pink.

For each of the three solvents a six stage extraction, using 50ml aniline–water and 50ml solvent, was performed. The HPLC analysis results of the first experiments, where the three solvents each were used, can be seen in table 6.1.

Extraction	Phase	Solvent	Aniline
stage			Concentration
			(w/w)(ppm)
1	Raffinate	Toluene	4070.6
1	Extract	Toluene	33894
2	Raffinate	Toluene	589.6
2	Extract	Toluene	3324.9
3	Raffinate	Toluene	199.4
3	Extract	Toluene	348.4
4	Raffinate	Toluene	124.3
4	Extract	Toluene	63.2
5	Raffinate	Toluene	87.6
5	Extract	Toluene	29.5
6	Raffinate	Toluene	54.8
6	Extract	Toluene	18.0
1	Raffinate	o,m,p–Xylene	5383.7
1	Extract	o,m,p–Xylene	33059.2
2	Raffinate	o,m,p–Xylene	944.6
2	Extract	o,m,p–Xylene	4464,66
3	Raffinate	o,m,p–Xylene	294,4638
3	Extract	o,m,p–Xylene	589,174
4	Raffinate	o,m,p–Xylene	184,4916
4	Extract	o,m,p–Xylene	90,137
5	Raffinate	o,m,p–Xylene	126,9904
5	Extract	o,m,p–Xylene	30,8389
6	Raffinate	o,m,p–Xylene	112.9
6	Extract	o,m,p–Xylene	16.9
1	Raffinate	n–Heptane	15108.6
1	Extract	n–Heptane	17626.2
2	Raffinate	n–Heptane	7842.9
2	Extract	n–Heptane	7018.3
3	Raffinate	n–Heptane	5866.5
3	Extract	n–Heptane	4538.5
4	Raffinate	n–Heptane	1782.5
4	Extract	n–Heptane	2360.8
5	Raffinate	n–Heptane	918.0
5	Extract	n–Heptane	784.9
6	Raffinate	n–Heptane	764.8
6	Extract	n–Heptane	585.8

Table 6.1: Aniline concentration in the water and organic phases after extraction

The aniline concentration in the water phase before any separation was performed was 33785(w/w) ppm, corresponding to the expected mass fraction of 0.0339(33900(w/w) ppm).

The aniline concentration was measured in both the water and the solvent phase, respectively the raffinate and the extract, just after the extraction.

Figure 6.1 shows the reduction in aniline concentration in the water phase after the six extraction stages.



Figure 6.1: Aniline concentration in the raffinate after the 6 extraction stages

The figure shows the aniline concentration is not reduced sufficiently after six extractions. This could be because equilibrium had not occurred between the two phases, or because six stages is not enough to reduce the aniline concentration to the wanted 2(w/w)ppm. The figure also shows that toluene followed by o,m,p-xylene give the best result regarding the reduction of aniline concentration compared to n-heptane, indicating that these two are the optimal solvents. It seems that both xylene and n-heptane tend to have reached a limit, where no more aniline can be removed. This is however not necessarily the case, but more extraction stages need to be performed before anything can be concluded for sure.

After the six extractions, the water phase was not completely clear, suggesting that the impurities were not removed with the solvent. In appendix B the majority of the impurities are seen to be amines. Since these are similar to aniline it is expected that they

will go in the solvent phase. The ester, on the other hand, is present with the largest concentration of the impurity. This is a component that does not necessarily go in the solvent, so this could therefore be the component, causing the slight color.

6.3 pH Influence

In chapter 5 the pK_b value for the aniline/water equilibrium is stated as 9.37, which means the $K_b = 10^{-9.37} = 4.3 \cdot 10^{-10}$. The water phase is measured, using pH measuring sticks, to have a pH of 7, which means that the OH⁻ concentration in the mixture is

$$pH = -\log [H^+] = 7$$

$$\downarrow \qquad [H^+] = 10^{-7}$$

$$\downarrow \qquad [OH^-] = 10^{-7}$$

because

$$K_W = \left[H^+\right] \cdot \left[OH^-\right] = 10^{-14}$$

The equilibrium constant is determined as corresponding to

$$H_2O + Ph - NH_2 \rightleftharpoons OH^- + Ph - NH_3^+$$
$$K_b = \frac{[OH^-] \left[Ph - NH_3^+\right]}{[Ph - NH_2]} \tag{6.1}$$

In the reaction and the equation the aromatic ring is presented as Ph, phenyl.

Insertion of the OH^- concentration and the K_b in equation (6.1) gives

$$\begin{array}{rcl}
4.3 \cdot 10^{-10} &=& \frac{10^{-7} \left[Ph - NH_3^+ \right]}{\left[PH - NH_2 \right]} \\ & \downarrow \\ & \underbrace{\left[Ph - NH_3^+ \right]}_{\left[Ph - NH_2 \right]} &=& 4.3 \cdot 10^{-3} \end{array}$$

Because aniline is very little soluble in water, the equilibrium is shifted to the left. This is seen by the fact that the Ph-NH₃⁺ concentration is smaller than the PH-NH₂ concentration. To see if it has an effect on the separation if the pH was raised, and the equilibrium shifted even more to the left, NaOH was added to the water phase, to give a pH of approximately 13. This means the ratio between Ph-NH₃⁺ and Ph-NH₂ was changed to $4.3 \cdot 10^{-9}$. The result of this change can be seen in figure 6.2. Toluene was used as the solvent because this was the solvent which gave the lowest aniline concentration after six extraction stages in the first experiments.



Figure 6.2: Aniline concentration in the raffinate when pH of the water is raised to 13

In only six stages the aniline concentration was reduced to 2.76(w/w) ppm, which is very close to the maximum allowed aniline concentration. The corresponding values can be seen in table 6.2, along with the aniline concentration in the extract phase after the different extractions.

From the result in the figure, it seems as if raising the pH value is a solution, if the number of extraction stages is to be reduced. However it must be taken into account that if base is added to the water phase, the pH must be reduced again, before the water can be led to a waste water treatment plant.

This problem could however be solved by using the basic water to neutralize another waste stream produced at Syntese A/S, which has a pH–value that is too low.

6.4 Influence of Stirring Time

Because the models tended to show that only one stage was necessary and this was not the case, the influence of the stirring time is investigated. Thermodynamic model can not calculate the time before equilibrium has been reached, and therefore the only way

 Table 6.2: Aniline concentrations in raffinate when the pH of the water is increased to

 13

Extraction	Phase	Aniline
stage		concentration
		(w/w)ppm
0	Raffinate	33785
0	Extract	0
1	Raffinate	2324.8
1	Extract	35021
2	Raffinate	189.1
2	Extract	2538.3
3	Raffinate	17.5
3	Extract	196.8
4	Raffinate	4.6
4	Extract	17.1
5	Raffinate	2.9
5	Extract	1.7
6	Raffinate	2.8
6	Extract	0.6

to find the optimal stirring time is by trying.

This was done by stirring the solvent with the water phase for first 5 minuts, then pouring the mixture into a separation funnel and letting it settle. A sample was taken from both phases for HPLC analysis, and the same water and solvent was again poured into a beaker and stirred again for 5 minutes. This was continued till a stirring time of 70 minutes was reached.

The result of the stirring time investigation can be seen in figure 6.3. Again toluene was used as the solvent, because this gave the best results in the first experiments. The corresponding values can be seen in table 6.3.

Figure 6.3 shows that the aniline concentration seems to stabilize after 15 minuts, but then after 40 minuts, it decreases again and stabilizes again after 50 minuts. The reduction in aniline after just one stage, when the stirring time is 50 minutes, is 4 times as large as the reduction after 15 minuts.

The reason it seems as if there are two stabilizing stages, could be because of the low aniline concentrations. It should be taken into account that there very likely is some standard error on all the measured aniline concentrations, because they only are present in ppm.

From table 6.3 the aniline concentration in the extract phase can be seen. The table



Figure 6.3: Aniline concentration in the raffinate at different stirring times

shows that the aniline concentration in a strange way also decreases, which makes no sense, since the aniline taken from the water phase will go the the solvent phase, resulting in an increase in aniline concentration in the extract phase, and this is not the case.

This only shows that the measured aniline concentrations should be seen as an indication of the actual concentrations, since the concentrations are so small that they are difficult to determine exactly.

6.5 Stirring Time and pH Raised

From the experiment results from above, it is found that raising the stirring time and the pH in the water could have a significant effect on the aniline reduction in the water phase. To investigate if the number of stages could be reduced if the pH and the stirring time were raised, toluene and n-heptane were tested again. Toluene and p-xylene gave similar results in the first experiment, and therefore this solvent was not tested again. In this experiment 50ml water phase was added NaOH to raise the pH to 13, and the stirring time was raised to 60 minutes. The result of the two experiments can be seen

Stirring	Phase	Aniline
time		concentration
(min)		(w/w)ppm
5	Raffinate	4245
5	Extract	34447
10	Raffinate	1925
10	Extract	31281
15	Raffinate	1941
15	Extract	32061
35	Raffinate	1952
35	Extract	32674
50	Raffinate	1161
50	Extract	6449
70	Raffinate	1161
70	Extract	6454

Table 6.3: Aniline concentrations in raffinate after different stirring times

in figure 6.4. The corresponding concentrations can be seen in table 6.4

Figure 6.4 shows that even when the pH is raised to 13, n-heptane can not reduce the aniline concentration in the water to the required 2(w/w)ppm. After six extraction the aniline concentration is 1227(w/w)ppm, while six extractions using toluene reduce the concentration to 2.39(w/w)ppm. The 2.39(w/w)ppm could be, due to standard deviation, below 2(w/w)ppm, and is therefore accepted as a significant reduction.

A comparison of the two extractions with different stirring times, show that there seems to be no influence of the stirring time.

6.6 Discussion of Results

With six extraction stages and a stirring time of 15 minuts, the three solvents were not able to reduce the aniline concentration in the water phase to the wanted 2(w/w)ppm. In six stages toluene reduced the aniline concentration to 54.8(w/w)ppm, while p-xylene reduced the concentration to 112.9(w/w)ppm and n-heptane to 764.8/w/w)ppm. From these results the best of the three solvents seem to be toluene, and therefore this was used for the following experiments.

One reason for the high aniline concentrations could be the fact that equilibrium is not reached. If this is the case, the stirring time should be increased, and therefore this was investigated in one of the next experiment.

Another reason could be because aniline forms $Ph-NH_3^+$ in water. To prevent this the pH was raised in one of the next experiments.

Other reasons could be a low number of extractions stages or a small amount of solvent



Figure 6.4: Aniline concentration in the raffinate at different stirring times and pH=13. Toluene and base(1) is stirred for 15 minutes, while toluene and base(2) is stirred for 60 minutes.

used. An increase in stages or solvent amount will reduce the aniline concentration further. With the right number of stages the aniline concentration would reach the wanted 2(w/w)ppm with a smaller amount of solvent, while an increase of solvent would decrease the stages needed.

When the stirring time influence was investigated using toluene as the solvent, it turned out that the aniline concentration after just one stage could be reduced from 4070.6(w/w)ppm to 1161(w/w)ppm when the stirring time was increased from 15 to 50 minuts. This shows that one reason for the high aniline concentrations in the water after six extractions, could be lack of equilibrium. From the stirring time investigation it seems as if equilibrium was not reached after just 15 minuts of stirring, but that the stirring time should be increased to at least 50 minuts.

When the pH value was increased, the aniline concentration after six extraction stages came very close to the wanted maximum of 2(w/w)ppm, when toluene was used as a solvent. This shows that forcing the equilibrium reaction to the left, has an influence on the separation.

Again the stirring time could play an important role in the separation, since lack of

Extraction	Phase	Solvent	Aniline
\mathbf{stage}			Concentration
			(w/w)(ppm)
1	Raffinate	Toluene	3529.4
1	Extract	Toluene	35187.7
2	Raffinate	Toluene	427.1
2	Extract	Toluene	3777.1
3	Raffinate	Toluene	52.2
3	Extract	Toluene	435.9
4	Raffinate	Toluene	8.0
4	Extract	Toluene	44.9
5	Raffinate	Toluene	3.1
5	Extract	Toluene	5.1
6	Raffinate	Toluene	2.4
6	Extract	Toluene	1.0
1	Raffinate	n–Heptane	22315.1
1	Extract	n–Heptane	21361.4
2	Raffinate	n–Heptane	11668.4
2	Extract	n–Heptane	11000.3
3	Raffinate	n–Heptane	7118.3
3	Extract	n–Heptane	6170.1
4	Raffinate	n–Heptane	2083.9
4	Extract	n–Heptane	3216.7
5	Raffinate	n–Heptane	1571.3
5	Extract	n–Heptane	1464.9
6	Raffinate	n–Heptane	1227.2
6	Extract	n–Heptane	763.5

Table 6.4: Aniline concentration in the water and organic phases after extraction

equilibrium means that more stages are needed to get the wanted reduction. But raising the pH value seems to be a solution to get the wanted reduction of aniline in the water phase.

However it must be taken into account that the water phase must be made neutral again before being sent to a waste water treatment plant.

To get an idea of how much influence the stirring time and pH have on the reduction of aniline in water, an increase both was tested using toluene and n-heptane. The pH was raised to 13, and the stirring time to 60 minutes.

Comparing the aniline concentration in the water phase for a stirring time of 15 minutes to one of 60 minutes show no big difference, suggesting that when the pH is 13, equilibrium is reached faster than for lower pH.

n-Heptane was tested on the raised pH water phase because of it's low solubility in water. If n-heptane could be used as the solvent, there is no further separation of the water phase needed before the water is sent to a waste water treatment plant, whereas if toluene is used, the solvent concentration will need to be reduced before the water can be disposed. When the extraction stages and solvent amount is taken into account, n-heptane is rejected as a solvent.

p-Xylene could be a possible candidate, but because there is only one experiment with this solvent, no conclusions can be made for it. From the first experiment it also seems as if toluene is able to reduce the aniline in less stages, using less solvent, and since they cost the same toluene is preferred.

To sum up, the required reduction of the aniline concentration to 2(w/w)ppm in the waste stream can be reached when the pH in the water is raised to 13 and when the solvent used is toluene. The stirring time seems to play only a small part in the reduction, when the pH is changed.

If toluene is used as the solvent, the solvent concentration in the aniline reduced waste stream must also be reduced before the water can be sent to a waste water treatment plant. In the next chapter, an economical evaluation is made, taking the problem of the solvent concentration in the water into account.

Chapter 7 Economic Evaluation

In appendix A the detailed calculation present annual expenses are presented.

The annual expenses is at the present time 15.9 million danish kroner. This includes transportation of the waste stream to Kommunekemi A/S, disposal of the waste stream at Kommunekemi A/S, and the annual purchase of aniline to the production.

7.1 Two Distillations

One suggestion for a separation scheme was that two distillations were made, one for the water phase and one for the aniline phase. However when this separation method is used, the aniline recovery can not uphold the requirement of 90(w/w)%, but only recover 55(w/w)%. This will, not taking equipment into account, give an approximate annual expense of

Distillation of water phase :	799469 dkr
Distillation of aniline phase :	448 dkr
Recovered aniline :	3.14million dkr
Total	3.94 million dkr

7.2 Extraction and Two Distillation

Extraction followed by a distillation separation aniline from a solvent, and another distillation purifying aniline was the other separation method which was of interest. The solvent which gave the best results, regarding aniline reduction in the water phase, was toluene, and therefore the economical evaluation will only include this solvent.

In the experiments only one amount of toluene was tested, but from the aniline concentration in the extract, the economically optimal amount of toluene can be determined. This is done by formulating an objective function with a constraint that takes the toluene concentration in the extract into account. The objective function is formulated as the expense Syntese A/S will have the first year the purchase is made, including a start payment for extraction equipment, the optimal toluene amount for a specific number of extraction stages, the annual toluene expense once the process runs, and the interest rate on the extraction equipment. There are many other expenses, such as pumping, stirring, electricity and so on, which also should be taking into the objection function, but to make it as simple as possible, to start with, these are over looked. Because a small amount of toluene also will result in an easy/cheaper distillation of toluene from aniline, the distillation expenses is not taking into the objection function.

Before the objective function is presented, some assumptions are made. The first one is that the interest rate is 10% per year and that Syntese A/S during the first year pays 50% of the extraction equipment. It is also assumed that 95(w/w)% of the toluene is recycled. This gives an objective function formulated as

$$F_{obj} = cost = n \cdot L(m^3) \cdot 869.2kg/m^3 \cdot 5dkr/kg + 0.05 \cdot 667L(m^3) \cdot 869.2kg/m^3 \cdot 5dkr/kg + 0.1 \cdot n \cdot equipment price + 0.5 \cdot n \cdot equipment price$$
(7.1)

In equation (7.1) n is the number of extraction stages and L is the toluene amount needed. The equipment price is given by a Swedish company, MEAB Metallextraktion AB (20) who specialize in extraction equipment. The price taken, is for a continuous five tank system of 3l active volume each plus an extra tank when the annual expense for n=6 is determined, both prices include stirring equipment(mixer motor and stirrer) and a settler tank with an active volumen of $15m^3$. The material of the equipment is either polypropylene or polyvinyl chloride, both of which should be fine to used with water, aniline and toluene. The price for this system is 355500 + 9200 = 364700 Swedish kroner. 3l is too small a volume if the whole of the waste stream is to be present in one tank along with solvent, so the price is used to give a rough estimate of the price for a $20m^3$ 6 tank system. The estimated price is 3 million Danish kroner, that is 500000 Danish kroner per tank. This is a very high price, only used to give an idea of what an extraction could cost.

The constraint corresponding to the objective function is as formulated equation 6.2–13, p.170 in Cussler et al. (1).

$$f = \frac{\sum_{i=1}^{n} (L/n) \cdot x_i}{H \cdot y_{10}}$$
(7.2)

The constraint is an expression for the amount of aniline extracted. L is the amount of solvent used, n is the number of stages used, H is the amount of water phase to $extract(7.2m^3)$, x_i is the mole fraction of aniline in the solvent after each extraction stage, and y_{10} is the mole fraction of aniline in the water phase before the separation. The amount of aniline to be extracted corresponds to an aniline reduction in the water phase

to 2(w/w) ppm. When the starting concentration in the water phase is 3.3875(w/w)%, this gives an amount to extract of

$$\frac{0.033785 - 2^{-6}}{0.033785} = 0.999941$$

giving a constraint function as

$$f = \frac{\sum_{i=1}^{n} (L/n) \cdot x_i}{7.2m^3 \cdot 0.0067} = 0.999941$$

The solver used to solve the problem is *Modelling Testbed*, MoT, in ICAS. Because this program can not solve sums, as present in the constraint, the number of stages is changed manually. In table 7.1 the optimized value for L and the resulting first year expense is shown for one to six stages. From the values of L, the optimal amount of solvent is chosen. The x_i values entered are the mol fractions aniline in the extract phase after the experiment made with a stirring time of 60 minutes and a pH in the water of 13, see table 6.4 which shows the mass fractions, the y_{10} is the mol fraction aniline in the water phase before separation, 0.0067.

Table 7.1: Expenses corresponding to number of extraction stages and toluene amount

Number	Toluene	Expense
of stages	volumen	first year
	(m^{3})	(dkr)
6	7.76	3126137
5	6.46	2577046
4	5.17	2039206
3	3.88	1512832
2	2.60	999392
1	1.39	508123

The objective function gives that the lowest expense is when one stage is used with $1.3m^3$ toluene. This is not what was expected, and therefore it is tested if this really fulfils the constrain

$$\frac{1.4m^3 \cdot 0.0346}{7.2 \cdot 0.0067} = 0.996973$$

this does not satisfy the constrain, even though it was stated. Because this optimization did not satisfy the constraint, it is tested if this is the case for the other optimizations by entering the optimized toluene amounts in the expression for the constraint. The result can be seen in table 7.2

From table 7.2 it is seen that only six stages, using an amount of 7.8m³ toluene, gives the required reduction of the aniline concentration in the water phase, therefore this number of stages and amount of toluene is used in the following calculations. This solute volume

	Table 7.2: Test of constraint			
Number	Toluene	Constraint		
of stages	volumen	value		
	(m^3)			
6	7.76	0.999941		
5	6.46	0.999603		
4	5.17	0.999946		
3	3.87	0.997557		
2	2.49	0.996216		
1	1.40	0.996973		

$\mathbf{I} (\mathbf{u} \mathbf{J} \mathbf{v}) = \mathbf{I} \cdot \mathbf{\omega} \cdot \mathbf{I} \cdot \mathbf{v} \cdot $	Table	7.2:	Test	of	constraint
---	-------	------	------	----	------------

and number of stages is also chosen, because it is known from the experiment results, that this stage number should be enough to reduce the aniline concentration sufficiently. The increase in toluene volumen found by the optimization should compensate for the 0.4(w/w)ppm over the wanted 2(w/w)ppm found in the last experiment.

It is found from experiments (2), that the toluene concentration in the extracted water is higher than allowed, and therefore it must be reduced. This can be done with activated carbon/coal. One kg coal can approximately clean 1m³ water reducing the toluene content of 500(w/w) ppm to the allowed 250(w/w) ppm. This means that each year approximately 4802m³ water must be cleaned, corresponding to 4802kg coal. An estimated price for the coal is 22dkr/kg giving an yearly expanse of 105644 Danish kroner. Disposal of the deactivated coal will be 4.38dkr/kg, giving an annual expense of 21032dkr at Kommunekemi a/s. The coal is identified as H waste. The price for transportation of solids is not known, and is therefore not included in the calculation. The amount of coal to used and the price is given by Flemming Zwicky, who delivers activated carbon to Syntese A/S.

Because 500(w/w) ppm toluene will go in the water phase, the solvent loss to the water is 2.6kg/year or 0.004kg/production. This means that the solvent amount sent to distillation is

$$7.8m^3 \cdot 869.2kg/m^3 - 0.004kg = 679.756kg$$

Because the solvent loss in the water phase is so low compared to the total amount of solvent, the loss to the water is not taken into account.

When the aniline extracted is 99.9941(mol/mol)% of 2.6kmol(found in chapter 3, the mol fraction in the $7.8 \text{m}m^3$ toluene will be

$$\frac{0.999941 \cdot 2.6 kmol}{\frac{7.8m^3 \cdot 869.2 kg/m^3}{92.141 kg/kmol} + 0.999941 \cdot 2.6} = 0.034$$

The relative volatility is determined at the normal boiling point of toluene, 110.6° C, so

the number of stages needed for the distillation separating toluene from aniline can be found. Equations (3.1), (3.2) and (3.3) are used, along with the Margules constants from (2).

$$\alpha_{12} = \frac{\exp(0.034^2(0.4723 + 2(0.5017 - 0.4723) \cdot 0.963)) \cdot 743.6mmHg}{\exp(0.963^2(0.5017 + 2(0.4723 - 0.5017) \cdot 0.037)) \cdot 69.4mmHg} = 6.7$$

Because toluene is the more volatile of aniline and toluene, this will be the main component in the distillate, and because 95(w/w)% is to be recycled, at least this amount should come out in the distillate, while the aniline amount in the distillate should be kept at a minimum, so 90(w/w)% can be recirculated. 95(w/w)% toluene recycled is

$$0.95 \cdot 7.8m^3 \cdot 869.2kq/m^3 = 6440.8kq = 69.9kmol$$

and the amount of aniline in the distillate should be kept at a minimum, so the recycled toluene can be saturated with aniline from the waste stream again. For these reasons the distillate composition is chosen to be 99.9(w/w)% toluene and the rest aniline. This gives the distillate weight

$$0.999 \cdot d = 6440.8kg \Rightarrow d = 6446.4kg$$

and therefore an aniline amount in the distillate of

$$6446.4kg - 6440.8kg = 5.6kg = 0.06kmol$$

while the toluene in the bottom product is

$$0.05 \cdot 7.8m^3 \cdot 869.2kg/m^3 = 339.0kg = 3.68kmol$$

and the aniline amount in the bottom product will therefore be

$$2.6 kmol \cdot 93.128 kg/kmol \cdot 0.999941 - 0.001 \cdot 6440.8 kg = 177.7 kg = 1.9 kmol$$

The short cut formulas, (3.5) and (3.5), along with equation (3.6) gives a stage number of 7.

The energy needed to heat toluene and aniline from 20° C to 110° C is found using the change in heat capacity, while the heat needed to vaporize the toluene and aniline at 110° C is found using ICAS. An expression for the heat capacity of liquid toluene is found in Smith et al. (13)p.658. The corresponding expression can be seen as equation (3.9)

$$\frac{C_p}{R} = 15.133 + 6.79 \cdot 10^{-3} \cdot T(K) + 16.35 \cdot 10^{-6} \cdot T(K)^2$$
(7.3)

ICAS gives respectively $\Delta H_{vap} = 3.35351 \cdot 10^7 \text{J/kmol}$ for toluene and $5.0006 \cdot 10^7 \text{J/kmol}$ for aniline. The energy required to vaporize the wanted distillate composition is therefore

 $520.9J/kg \cdot 6440.8kg/production = 3355012.7J/production = 0.93kWh/production$

giving an annual energy expense of

 $0.93kWh \cdot 667 \cdot 0.28dkr/kWh = 173.7dkr.$

When an aniline recovery of 90(w/w)% is taken into account, the annual expense will be

Extraction of water phase :	2.26 million dkr
Distillation of solvent Phase phase :	160 dkr
Distillation of aniline from solvent and aniline phase : 2000 dkr	
Coal expense :	$126676~\mathrm{dkr}$
Aniline :	698000 dkr
Total	3.1 million dkr

The 2000 dkr is a guess of what the energy required for the separation of pure aniline from impurities will be, since the exact composition of the stream has not been determined. For this scheme disposal of the impurities should also be taken into account, when the second distillation is defined.

7.3 Comparison of the Two Separation Schemes

Comparing the annual energy expense of the distillation of the water phase, 799469dkr, with the annual energy expense for the distillation separating toluene from aniline and the annual expense of toluene which is

 $160dkr + 0.1 \cdot 7.8m^3 \cdot 667 \cdot 869.2kg/m^3 \cdot 5dkr/kg = 2.26million Danish kroner$

shows that the distillation should be chosen, but when the aniline recovery is taken into account the two distillation will cost 3.94 million Danish kroner, while the extraction followed by two distillation annually will cost 3.1 million Danish kroner, which is an a significant reduction.

It has thus been determined that the most economic separation is an extraction of the water phase using six stages of $7.8m^3$ toluene, followed by a distillation where toluene is separated from aniline and recycled to the extraction. The bottom product from the distillation, mainly containing aniline, is mixed with the aniline phase, and the mixture is separated by distillation.

7.4 Equipment Sizing and Expense

The optimal separation is an extraction using six stages, represented by six mixer–and a settler–tank. Their exact price is not known, but it is assumed to be 3 million for the whole system, including stirring mixer and motor, and settler tank. Pumping expanses are not taken into account here.

The distillation column to be used for separating toluene from aniline is found to have 7 stages, when the feed has a temperature of 110° C, and the pressure is kept constant. From Lorenz et al. (5) the height of the column can be found to be the sum of the tray stack(N-1), the extra feed space(1.5m), the disengagement space(3.0m) and the skirt height(1.5). The heights in parentheses are taken from (5)p.123. For a tray stack with 24in.(0.6m) spacing the height becomes

$$(7-1) \cdot 0.6m + 1.5m + 3m + 1.5m = 9.6m = 31.5ft$$

To simplify the calculation, it is assumed that the distillation is performed continuously and without reflux. The diameter is then found at the top and the bottom of the column, to find the larger one. The larger one is found because this is the one to be used when the price of the column is calculated.

The liquid density corresponds to the density of the liquid phase, which consists of 339kg toluene and 178kg aniline per production. The liquid density is found as

$$0.656 \cdot 791.8kg/m^3 + 0.344 \cdot 953.9kg/m^3 = 847.6kg/m^3$$

And the vapor using the ideal gas law, which can be done because the pressure is assumed constant at 1 atm. Because the aniline concentration is so low in the vapor phase compared to the toluene concentration, the molecule weight is set to toluene's

$$\rho_g = \frac{p \cdot M}{R \cdot T} = \frac{101325 Pa \cdot 92.141 g/mol}{8.31451 j/(K \cdot mol) \cdot 383K} = 2931 g/m^3 = 2.9 kg/m^3$$

The mass flow rates are found above as the rate of respectively the flow of the distillate as the vapor flow, V = 6446.4kg/production, and the bottom product as the liquid flow, L = 516kg/production. If it is assumed that one distillation takes one hour, the mass flow rates will be 6446.4kg/h = 1.80kg/s and 516kg/h = 0.14kg/s. The liquid surface tension is chosen to be as on p.123 (5), $\sigma = 0.07$ N/m. The dimensionless flow parameter gives

$$F_{lv} = (L/V)(\rho_q/\rho_L)^{0.5} = (1.8kg/s/0.14kg/s)(2.9kg/m^3/847.6kg/m^3)^{0.5} = 0.75$$

For a 24in tray spacing figure 4.4 in Lorenz et al.(5) gives a capacity parameter of 0.13 ft/s. Solving for the flooding velocity gives

$$U_{nf} = C_{sb}(\sigma/20)^{0.2} \cdot [\rho_l/\rho_g - 1]^{0.5} = 0.13 \cdot 0.7^{0.2} \cdot (847.6/2.9 - 1)^{0.5} = 2.1 ft/s = 0.67 m/s$$

If there is 80% flooding the flooding velocity is 0.538m/s.

The diameter in the top of the column can now be found as, the trays are assumed to be bubble cup trays, so $\varepsilon = 0.6$

$$V = \rho_g U \varepsilon \pi D^2 / 4 \Rightarrow D = \sqrt{\frac{1.8kg/s \cdot 4}{2.9kg/m^3 \cdot 0.538m/s \cdot 0.6 \cdot \pi}} = 2.4m = 7.5ft$$

and the diameter in the bottom is found in a similar way to be

$$L = \rho_l U \varepsilon \pi D^2 / 4 \Rightarrow D = \sqrt{\frac{0.14 kg/s \cdot 4}{847.6 kg/m^3 \cdot 0.538m/s \cdot 0.6 \cdot \pi}} = 0.006m$$

The larger of the two diameters is used to estimate the cost of a distillation column to ne used in the separation of toluene from aniline. The Guthrie equation and base cost values from table 4.11, p.134(5) is used to estimate the cost

$$C = C_0 (L/L_0)^{\alpha} (D/D_0)^{\beta}$$

$$= 690 \$ (31.5 ft/4)^{0.78} (2.4/3)^{0.98}$$

$$= 2773.1 \$ \cdot 3.18 \cdot 6.5 dkr/\$$$

$$= 57318 dkr$$
(7.4)

So the distillation column should have a height of 9.6m, a top diameter should be 2.4m and the bottom should be 0.006m, very narrow. A column like this will cost approximately 57318 Danish kroner.

7.5 Capital Investment

Syntese A/S want to the pay back time for the equipment to be 2 years. The cost for the equipment is 3.06 million Danish kroner. If the interest rate is 10%, and if two payments are made, one each year, the size of these payments must be

payment size =
$$3.06 milliondkr \frac{0.1}{1 - (1 + 0.1)^{-2}} = 1.76 million dkr$$
 (7.5)

This means that the first two years the annual expenses will be 3.1 million dkr + 1.76 million dkr = 4.9million Danish kroner. This is a reduction of 15.9million dkr - 4,9million dkr = 11 million Danish kroner the first two years, and 15.9million dkr - 3.1million dkr = 12.8 million Danish Kroner on the long bases.
Chapter 8 Conclusion

By flash distillation a waste stream containing 6-7(w/w)% and 93-94(w/w)% water is separated from a product, 5-amino-salicylic-acid, 5-ASA.

Aniline is highly toxic, and direct disposal of the stream to a waste water treatment plant is therefore not an option for Syntese A/S to dispose of the waste stream. The stream is instead sent to Kommunekemi a/s for disposal, giving an annual expense of 1.002 million Danish krone for transportation to Kommunekemi a/s from Syntese A/S, and an expense of 7.95 million Danish kroner for the disposal. Also Syntese A/S annually spends 6.98 million Danish krone on aniline for their synthesis. The total annual expense for disposal of the waste stream and the purchase of aniline is 15.9 million Danish kroner.

To reduce this expense, it has been investigated if a separation process of the waste stream could result in pure water which could be sent directly to a waste water treatment plant, and also give a purified aniline that could be recirculated to take part in the synthesis of 5–ASA again, and thereby reduce the annual expenses.

An investigation of the physical properties resulted in two suggestions for the desired separation. The aniline content in the waste stream is above the amount soluble in water, so the waste stream forms two phases, a water phase saturated with aniline, and an aniline phase saturated with water.

Two separation schemes were suggested for the purification of water and aniline. In both of them, the two phases were separated to start with.

After the phase separation the water phase could be sent to a distillation column, where the water could be evaporated from the aniline–water azeotrope. This separation is very energy requiring because of the large amount of water that has to be evaporated, the aniline–water azeotrope is recycled to the waste stream, to take place in the distillation with the next waste stream. The aniline phase is also distillated, evaporating the aniline–water azeotrope and recovering the purified aniline as the bottom product. This separation scheme will reduce the annual expenses, but it is energy requiring and the recovery of aniline is not as sufficient, since it is only the aniline in the aniline phase that is recovered.

After the phase separation, the water could be extracted with a usable solvent. A number of solvent were identified as candidates, but by a further investigation only three; toluene, o,m,p-xylene and h-heptane, were finally chosen. From Laboratory experiments n-heptane and o,m,p-xylene were rejected resulting in toluene as the optimal solvent.

With toluene as the solvent, a six stage continuous extraction could be made giving an extract phase of aniline saturated toluene, and a purified water phase. The aniline saturated toluene could be distilled and the toluene recycled while the aniline could be recovered as bottom product. The aniline phase should then be added to the bottom product containing aniline, and this mixture should be distilled to purify the aniline. Because both the aniline from the water phase and the aniline phase is recovered, the annual expense for aniline could be reduced sufficiently.

The problem with this separation scheme is that to get the required aniline reduction, the water phase must be made basic before the extraction is performed, and also the solubility of toluene in water is greater than the toluene concentration allowed in waste water. Syntese A/S has an other waste stream which is acid, so the basic water could be used to neutralize this stream. The toluene concentration in the water phase could be reduced with activated carbon, which then would have to disposal at Kommunekemi a/s.

An economic comparison of the two separation schemes show that the extraction will give the greater annual reduction in expenses, despite the use of a solvent and the need of disposal of activated carbon. This is due to the energy requiring separation of the water phase. When a pay back time of the equipment is two years, there will be a significant annual reduction already the first year, even though both the equipment and the operating expenses are taken into account.

Bibliography

Literature

- Cussler, E.L. and G.D. Moggridge, *Chemical Product Design*, Cambridge University Press, New York, 2001
- [2] Gmehling, J., U. Onken, and J. R. Rarey Nies, Vapor-Liquid Equilibrium Data Collection, Aqueous Systems, (Supplement 2), Schön & Wetzel GmbH, Frankfurt/Main, Germany, 1988
- [3] Harper, Peter M., A Multi-Phase, Multi-Level Framework for Computer Aided Molecular Design, Ph.D Thesis, Tekst og Tryk A/S, Vedbæk, Denmark, 2000
- [4] King, C. J, Separation Processes, McGraw–Hill, New York, 1980
- [5] Lorenz, T. Biegler, Ignacio E. Grossmann and Arthur W. Westerberg, Systematic Methods of Chemical Process Design, Prentice Hall, New Jersey, 1999
- [6] McCabe, Warren L., Julian C. Smith, and Peter Harroit, Unit Operations of Chemical Engineering, McGraw-Hill, New York, 1993
- [7] McMurry, John, Fundamentals of Organic Chemistry, 4th edition, Brooks/Cole Publishing Company, California, 1998
- [8] Miljøstyrelsen, Tilslutning af industrispildevand til offentlig spildevandsanlæg, Vejledning Nr.11, Miljøministeriet, 2002
- [9] Perry, R.H, D.W. Green, and J.O. Maloney, Perry's Chemical Engineers Handbook, 7thedition, McGraw–Hill, New York, 1997
- [10] Ricci, Larry and the Staff of Chemical Engineering, Separation Techniques 1: Liquid-Liquid Systems, McGraw-Hill, New York, 1980
- Schweitzer, Philip A., Handbook of Separation Techniques for Chemical Engineers, McGraw-Hill, New York, 1997
- [12] Seader, J.D and Ernest J. Henley, Separation Process Principles, John Wiley and Sons, Inc., New York, 1998

- [13] Smith, J.M., H.C. Van Ness, and M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, New York, 2001
- [14] Sørensen J.M. and W. Arlt, Liquid-liquid equilibrium data collection, vol.1 Binary systems, Frankfurt/Main, 1979

Articles

- [15] Devulapalli, Ramanamurthy, Francis Jones, Separation of aniline from aqueous solutions using emulsion liquid membranes, Journal of Hazardous Material, Department of Chemical Engineering, Louisiana Tech University, Ruston, USA, 1999
- [16] Horyna and Coll, Azeotropes, Chechoslovacian Chemical Community 24, 3253, CA, 54 10436, Chechoslovacia, 1959

Reports

[17] Eden, Mario Richard, Peter Mathias Harper, Rafique Gani and Sten Bay Jørgensen, Design af separationsanlæg for Syntese A/S, Kemiteknik, Danmarks Tekniske Universitet, Lyngby, Denmark

Databases

[18] People at CAPEC, DIPPR in ICAS

Web pages

- [19] The Danish Environmental Protection Agency, Effectlisten 2000, link : $\frac{\text{http://www.mst.dk} \rightarrow \text{Udgivelser} \rightarrow \text{Publikationsdatabase} \rightarrow \text{Navn i titel} = \text{Effektlisten} \rightarrow \text{Effektlisten} 2000$
- [20] MEAB Metallextraktion AB, link: http://www.meab-mx.se/en/pl/ms-price.htm
- [21] NESA, link : http://www.nesa.dk/privat/prv_el_prisen/prv_prisliste_elprisen.htm
- [22] The Danish Environmental Protection Agency, List of undesirable substances 2000, link : <u>http://www.mst.dk</u> → Udgivelser → Publikationsdatabase → Navn i titel = uønskede stoffer → Listen over uønskede stoffer 2000

Appendix A

Economical Calculations

A.1 Present Annual Expenses

The total waste stream volumen produced in one year is $5000m^3$. The density of this stream is 997.96kg/m^3 , see appendix ??, giving a annual production of

 $5000m^3 \cdot 997.96kg/m^3 = 4989800kg \approx 5000tons$

This is brought to Kommunekemi A/S in Nyborg by the transport company Leif M Jensen A/S.

A truck can/is allowed to carry 30tons/trip. The annual number of trips must then be

$$\frac{5000 tons}{30 tons/trip} = 167 trips$$

From Syntese A/S to Kommunekemi a/s the transportation price is 6000dkr, including the bridge fair and cleaning at Kommunekemi a/s. Therefore the annual cost for transportation is

$$167 trips \cdot 6000 dkr/trip = 1002000 dkr = 1.002 \cdot 10^{6}$$

The waste stream is categorized by Kommunekemi as being in the H waste group. The price for this waste group is 1.59 dkr/kg, so the annual expense for disposal of the waste stream is

$$4989800kg \cdot 1.59dkr/kg = 7950000dkr = 7.96 \cdot 10^{6}$$

The annual amount of aniline sent to disposal is $0.07 \cdot 5000$ tons = 349tons. The price of aniline is 20 dkr/kg, meaning that Syntese A/S annual spends $349000 \cdot 20$ dkr/kg = 6980000 dkr ≈ 7 million danish kroner on aniline.

This results in annual expenses of 15.9 million danish kroner, on aniline and disposal of the waste stream.

A.2 Reduction in Expenses

If the aniline is separated from the waste stream, so 90(w/w)% can be recycled, the annual aniline expanse can be reduced to

 $0.1 \cdot 6980000 dkr = 698000 dkr$

Because the waste stream is purified enough to be sent directly to a waste water treatment plant, there is no expense for transportation and disposal. However to sent the water to a waste water treatment plant costs $17.5 dkr/m^3$, resulting in an annual expanse of

$$0.93 \cdot 5000m^3 \cdot 17.5dkr/m^3 = 81375dkr$$

There will also be a small transportation and disposal expense, because not all the aniline is recycled, and some water will also be in the aniline phase. Therefore there will be an annual aniline amount to be sent for disposal

 $0.1 \cdot 0.07 \cdot 5000m^3 \cdot 997.96kg/m^3 = 34928.6kg$

the transport expense for this aniline amount is

 $\frac{35 tons/year}{30 tons/trip} \cdot 6000 dkr/trip = 12000 dkr/year$

and the disposal expense is

 $34928.6kg/year \cdot 1.59dkr/kg = 55536.5dkr/year$

This gives a total annual expense of 846912 Danish kroner.

Appendix B Impurities in the Waste Stream

The waste water stream consists of two phases, a water phase with dissolved aniline and an aniline phase with dissolved water.

These two phases have been sent to the company Eurofins Danmark A/S, to determine the exact contents of the waste steam. The result can be seen in table B

	Water phase	Aniline phase
	(mg/l)	(mg/l)
(1,1-Biphenyl)-2-amine	6,81	408,87
(1,1-Biphenyl)-3-amine	1,02	$16,\!55$
Biphenyl	0,01	8,24
Diphenylamine	1,48	$519{,}59$
Hexanedonic acid, bis(2-ethylhexyl)ester	8,05	1,16
Diphenyl-benzenamine	0,05	10,79

Appendix C Physical Properties of the Waste Stream

In this appendix the physical properties of water and aniline dependant of temperature are shown in both tables and figures.

C.1 Vapor Pressure

Temperature (°C)	Aniline(Pa)	Water(Pa)
0.0	12.3	610.0
10.0	28.6	1227.4
20.0	62.4	2339.3
30.0	128.5	4247.9
40.0	251.0	7386.3
50.0	467.8	12351.8
60.0	835.3	19940.3
70.0	1434.6	31181
80.0	2378.0	47368
90.0	3816.4	70091
100.0	5946.2	101261

Table C.1: Vapor Pressure of aniline and water at different temperatures



Figure C.1: Vapor Pressure of aniline and water at different temperatures

C.2 Antoine Vapor Pressure

Temperature (°C)	Aniline (bar)	Water(bar)
0.0	0.0001	0.0061
10.0	0.0003	0.0122
20.0	0.0006	0.0232
30.0	0.0013	0.0420
40.0	0.0025	0.0729
50.0	0.0047	0.1217
60.0	0.0084	0.1961
70.0	0.0145	0.3061
80.0	0.0239	0.4645
90.0	0.0381	0.6869
100.0	0.0591	0.9922

Table C.2: Antoine Vapor Pressure of aniline and water at different temperatures



Figure C.2: Antoine Vapor Pressure of aniline and water at different temperatures

C.3 Density

$Temperature(^{\circ}C)$	$Aniline(kg/m^3)$	$Water(kg/m^3)$
0.0	1036.1	1001.3
10.0	1028.3	998.8
20.0	1020.4	996.3
30.0	1012.4	993.7
40.0	1004.3	991.0
50.0	996.1	988.3
60.0	987.8	985.5
70.0	979.5	982.6
80.0	971.1	979.8
90.0	962.5	977.0
100.0	953.9	974.2

Table C.3: Density of aniline and water at different temperatures



Figure C.3: Density of aniline and water at different temperatures

C.4 Solubility

From Liquid–liquid equilibrium data collection, vol.1 Binary systems (14) recommended values for the solubility of aniline in water is listed in the table bellow at different temperatures.

Temperature (°C)	Aniline in water(mole %)	Water in aniline(mole %)
20.0	0.674	21.3
25.0	0.679	21.8
40.0	0.721	23.7
60.0	0.847	26.5
80.0	1.11	30.6
100.0	1.52	36.0
120.0	2.11	42.2
140.0	3.02	51.1

Table C.4: Solubility of aniline in water and water in aniline at different temperatures



Figure C.4: Solubility of aniline in water and water in aniline at different temperatures

Appendix D

Physical Properties of the Solvents

In the present appendix the temperature dependant physical properties, vapor pressure and density, for the four solvents are shown as both figures and in tables.

D.1 Vapor Pressure

Temperature (°C)	Toluene (Pa)	\mathbf{p} -Xylene(Pa)	n–Heptane (Pa)
0.0	903.5	171.9	1517.8
10.0	1661.4	345.7	2736.7
20.0	2909.8	657.1	4703.3
30.0	4879.4	1187.6	7745.5
40.0	7870.0	2052.1	12279.0
50.0	12258.3	3405.9	18813.4
60.0	18503.7	5451.1	27956.6
70.0	27151.8	8443.5	40415.3
80.0	38835.7	12696.7	56993.7
90.0	54275.3	18586.8	78589.8
100.0	74274.5	26554.2	106191

Table D.1: Vapor Pressure of the three solvents at different temperatures



Figure D.1: Vapor Pressure of the three solvents at different temperatures

D.2 Antoine Vapor Pressure

Temperature (°C)	Toluene (Bar)	p-Xylene(Bar)	n–Heptane (Bar)
0.0	0.009	0.002	0.015
10.0	0.016	0.003	0.027
20.0	0.028	0.007	0.046
30.0	0.047	0.012	0.075
40.0	0.076	0.020	0.119
50.0	0.118	0.034	0.182
60.0	0.178	0.054	0.270
70.0	0.261	0.083	0.390
80.0	0.373	0.124	0.551
90.0	0.521	0.182	0.761
100.0	0.715	0.260	1.030

Table D.2: Antoine Vapor Pressure of the three solvents at different temperatures



Figure D.2: Antoine Vapor Pressure of the three solvents at different temperatures

D.3 Density

Temperature (°C)	$Toluene(kg/m^3)$	\mathbf{p} -Xylene (kg/m^3)	$n-Heptane(kg/m^3)$
0.0	887.1	896.4	702.3
10.0	878.2	888.5	694.1
20.0	869.2	880.4	685.8
30.0	860.0	872.2	677.3
40.0	850.7	864.0	668.7
50.0	841.3	855.7	659.9
60.0	831.7	847.2	651.0
70.0	822.0	838.6	641.8
80.0	812.1	829.8	632.5
90.0	802.1	821.0	622.9
100.0	791.8	811.9	613.1

Table D.3: Density of the three solvents at different temperatures



Figure D.3: Density of the three solvents at different temperatures