



NTNU – Trondheim
Norwegian University of
Science and Technology

Feasibility study and modelling of multistage amine reclaimer

Sigrun Dyvik Berstad

Chemical Engineering and Biotechnology

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Supervisor: Hallvard Fjøsne Svendsen, IKP

Co-supervisor: Stig Brustad, Kanfa Ingenium Process

Norwegian University of Science and Technology
Department of Chemical Engineering

Declaration

I hereby declare that the following work has been performed independently and in accordance with the regulations for the studies of Master of Architecture and Technology at the Norwegian University of Science and Technology (NTNU).

Trondheim, June 20, 2013



Sigrun Dyvik Berstad

Preface

This master thesis was carried out at the Department of Chemical Engineering at the Norwegian University of Science and Technology (NTNU) in collaboration with Kanfa Ingenium Process (KIP) the spring of 2013.

I would like to thank Hallvard F. Svendsen for taking on this project even though it was not one of his own, and Stig Brustad and KIP for consultation and for giving me this project. I would also like to thank Tore Haug-Warberg who has given me good advice.

I also have to send my gratitude to my parents and sister who have kept up with my nagging this past semester, and Atle Antonsen and Johan Golden with their radio show 'Misjonen' which has kept me sane through countless hours of programming.

Abstract

One of the largest expenses in CO₂ capture is the transport and disposal of waste from the amine reclaimer, and top up of fresh amine [KIP]. The main reason for this is because the waste stream contains quite large amounts of fresh amine, and the sheer volume of waste. If amount of MEA in waste could be reduced, both the volume of waste would be reduced, which lowers the transport and disposal cost, and the amount of amine for top up would be reduced. In other words, the total operational cost of the system could be considerably lowered.

This study investigated the possibility of reducing the amine (MEA) in the waste stream by looking at a two stage reclaiming process. A model based on the work done by Linn Christine Loe Haaversen was developed to include several new features, including a second stage. This model was the basis of cost optimization.

The cost optimization took several factors into account. The cost of waste transportation and handling, top up amine cost, cost of compressing low pressure lean amine to the pressure of main system and heat input to reclaimer vessels all were included the objective function subject to minimization. The unconstrained variables in this optimization were heat entered into both stages, and pressure in second stage.

From the results of the optimization, a second low pressure stage is beneficiary from an operating cost perspective. A cost minimum was detected where 63.9 % of the MEA fed into the system was returned to the main carbon capturing plant, 36.5 % in first stage, and 27.4 % in second stage. At optimum, the pressure of the second stage was 65.1 kPa.

The optimization is only for steady state. Start-up and shut-down is not included. This can be looked at for future work. There are uncertainties linked to properties of compounds, and the model output have not been compared to actual values from a carbon capturing plant. This is due to low availability of information. This study is only looking on operation cost, so there should also be a investment cost analysis before concluding that a second stage is profitable or not.

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Nomenclature

Latin and Greek Letters

A, B, C	constants [-]
A	Linear constraint matrix [-]
C	Concentration [kmol/m ³]
C	Cost related constants [-]
$C_{p,i}$	Heat capacity [kJ/kmol,K]
E	Energy [kJ]
\dot{E}	Energy rate [kJ/h]
H	Enthalpy [kJ/kg]
M	Total mass [kg]
\dot{M}	Total mass rate [kg/h]
M_w	Molar weight [kg/kmol]
P	Pressure [kPa]
\dot{Q}	Heat rate [kJ/h]
\dot{Q}'	Adjusted heat rate [kJ/h]
R, R'	Some inactive part of a compound in reaction
R	Reaction rate [kmol/m ³ h]
T	Temperature [°C], [K]
U	Internal energy [kJ/kg]
V	Volume [m ³]
\tilde{V}	Specific molar volume [m ³ /kmol]
\dot{V}	Volume rate [m ³ /h]
X_i	Scaled vector element of variable i [-]
b	Solution vector for constraints [-]
c	Non-linear constraint function [-]
g	Gravitational acceleration [m/h ²]
h	Levitation [m]
k	Coefficient of reaction [m ³ /kmol,h]
m	Mass [kg]
\dot{m}	Mass rate [kg/h]
n	Mole [kmol]
\dot{n}	Mole rate [kmol/h]
t	Time [h]
v	stoichiometric coefficient
x	Weight fraction [-]
y	Vapour mass fraction [-]

ΔH_{vap}	Enthalpy of evaporation [kJ/kmol]
ΔH_{rx}	Heat of reaction [kJ/kmol]
α	Pressure ration [-]
β	Evaporation function [m ³ ,kmol/kJ,h]
ρ	Density [kg/m ³]

Sub- and superscripts

1	First of two reclaimer steps
2	Second of two reclaimer steps
A	MEA
B	water
C	HEF
D	NaOH
E	HSS
F	HEPO
G	CO ₂
corr	Correlation
depo	Waste handling
el	Electricity
eq	Equality
gen	Generated
i	Some parameter defined when used
in	Inlet
j	$j \in [A, B, C, D, E, F, G]$
k	Integer, time step in iteration
liq	Liquid
loss	Loss of energy
lost	Lost energy
makeup	Makeup amine
out	Outlet
sat	Saturated
tank	Transportation of liquid
Rec	Reclaimer
requ	Recuired
vap	Vapour
waste	Waste

Abbreviations

CCS	Carbon Capture and Storage
CSTR	Continuously Stirred Tank Reactor
KIP	Kanfa Ingenium Process
lb	Lower bound
ODE	Ordinary Differential Equation
QP	Quadratic Programming
SQP	Sequential Quadratic Programming
SSS	Semi-Steady State
TCM	Technical Center Mongstad
ub	Upper bound

Chemical abbreviations

BHEOX	N,N'-bis(2-hydroxyethyl) oxalamide
CO ₂	Carbon dioxide
H ₂ O	Water
HEA	N-(2-hydroxyethyl) acetamide
HEEDA	N-(2-aminoethyl)-N'-(2-hydroxyethyl) imidazolidinone
HEF	N-(2-hydroxyethyl) formamide
HEHEAA	N-(2-hydroxyethyl)-2-(2-hydroxyethylamino) acetamide
HEI	N-(2-hydroxyethyl) imidazole
HEIA	N-(2-hydroxyethyl) imidazolidinone
HEPO	4-(2-hydroxyethyl) piperazin-2-one
HHEA	2-hydroxy-N-(2-hydroxyethyl) acetamide
HSAS	Heat Stable Amine Salts
HSS	Heat Stable Salts
MEA	Monoethanolamine
NaF	Sodium formate
NaOH	Sodium hydroxide
NO ₂	Natrium dioxide
O ₂	Oxygen (dioxide)
OZD	2-oxazolidinone
SO ₂	Sulfur dioxide

1 Introduction

The temperature of the planet is increasing, and there is now a consensus in the scientific society that this is man made climate change due to emission of greenhouse gasses [Cook et al.]. In fact it is predicted that even though emissions stops completely, there are long term consequences for the environment spanning into the next millennium [Solomon et al., 2008]. The list of possible scenarios is long [Intergovernmental Panel on Climate change, 2007]. Arctic ice is retreating as temperature increase. As the ocean is heated, thermal expansion along with released water from ice leads to rising sea levels. Increasing heavy rainfall and flooding can be expected in certain areas, while others are already experiencing drought. Loss of glaciers and snowpack changes the predictability of water supplies, which effects agriculture among other. An earlier spring peak can cause more extreme ice- and snow melting, which can lead to flooding in glacier- and snow-fed rivers. The acidity of sea water can rise as the concentration of CO₂ rises, which has consequences for the many ecosystems in it. In other words, the worst case scenario of man made climate changes are severe.



Figure 1: *Scenes that may well be more frequent with climate change. From left: Flooding of the river Sjoa in Gudbrandsdalen Norway spring of 2013, glacier ice melting, and dead cattle caused by drought in Kenya 2009.*

During the past ten years [Suganthi and Samuel], energy demand in the world has increased exponentially, and at present 80 % of the global energy consumption is delivered from fossil fuels like coal, oil and natural gas. According to Rochelle et al [2009], 50 % of the 300000 MW power capacity of USA, and more than 30 % of the CO₂ emissions came from coal-fired power plants alone.

In a world with increasing demand of energy, it is not feasible to cut such a huge source of energy. It is in other words a great need for technology that can reduce the emissions from fossil fuels.

An important step in this process is capture and storage of carbon dioxide [Smith et al., 2007]. As a exporter of these resources and technology related to production, Norway is in a good position, and is in some aspect obligated, to take responsibility for some of

this development. The TCM CO₂ capturing plant on Mongstad, opened in May 2012 [Mongstad, 2013] is an example of Norwegian will to invest in projects concerning carbon capturing.

One of the largest expenses in CO₂ capture is the transport and disposal of waste from the amine reclaimer, and top up of fresh amine [KIP]. The main reason for this is because the waste stream contains quite large amounts of fresh amine, and the sheer volume of waste. If amount of amine in waste could be reduced, both the volume of waste would be reduced, which lowers the transport and disposal cost, and the amount of amine for top up would be reduced. In other words, the total operational cost of the system could be considerably lowered.

This study is looking at a reclaimer system where MEA is the CO₂-absorbing amine.

2 Capture of carbon dioxide by amine absorption

CO₂ capture by amine absorption has been used for decades, in e.g. coal gasification and manufacturing of hydrogen [Veawab et al., 1999]. This fact makes it a good alternative for post-combustion CO₂ capture, as it is a well known technology. In addition, it is easy to retrofit into already existing plants. There are however several disadvantages [Yu et al., 2012]:

- Low CO₂ loading capacity of amine
- High equipment corrosion rate
- Degradation by SO₂, NO₂, O₂ (oxidative degradation) and heat, which demands replacement of the degraded amine
- High energy consumption
- Large equipment

Despite these draw backs, amine absorption is still currently the most used technology considering post-combustion CO₂ capture. Rochelle et al [2009] suggested a goal for energy consumption per tonne CO₂ captured and compressed, to be 0.72 GJ (theoretical value: 0.40 GJ), while the US DOE CO₂ capture goal was set to 90 % CO₂ capture efficiency and less than 35 % increase in overall cost of the power plant [Yu et al., 2012]. This means that the efficiency and cost (energy consumption and amine loss) has to be reduced for this to be a feasible process in commercial power plants. At present, the goal of 90 % capture efficiency is feasible, but the energy consumption is 3.6 GJ/tonn CO₂ captured (using MEA as solvent) [Knudsen et al., 2009].

2.1 The plant

Figure 2 shows a simple outline of a post-combustion CO₂ capturing plant [KIP] [Romeo et al., 2007] [Dave et al.]. As can be seen, flue gas from a combustion power plant is fed into the absorber where the gas is contacted with liquid amine (1). The liquid then leaving the absorber, is amine loaded with CO₂. Before this stream reaches the regenerator, it is preheated by the the lean amine leaving the regenerator (2). It then enters the regenerator (3) where a reboiler (4) heats the loaded amine which causes the amine to release the CO₂. Common practise for MEA is less than 122 °C in this reboiler [Romeo et al., 2007]. The released CO₂ leaves the regenerator in vapour phase. The lean amine then is lead back to the heat exchanger (2), and then cooled further before entering the absorber. This is the main cycle of the amine.

Due to degradation, the amine stream will after some time be contaminated, which effects

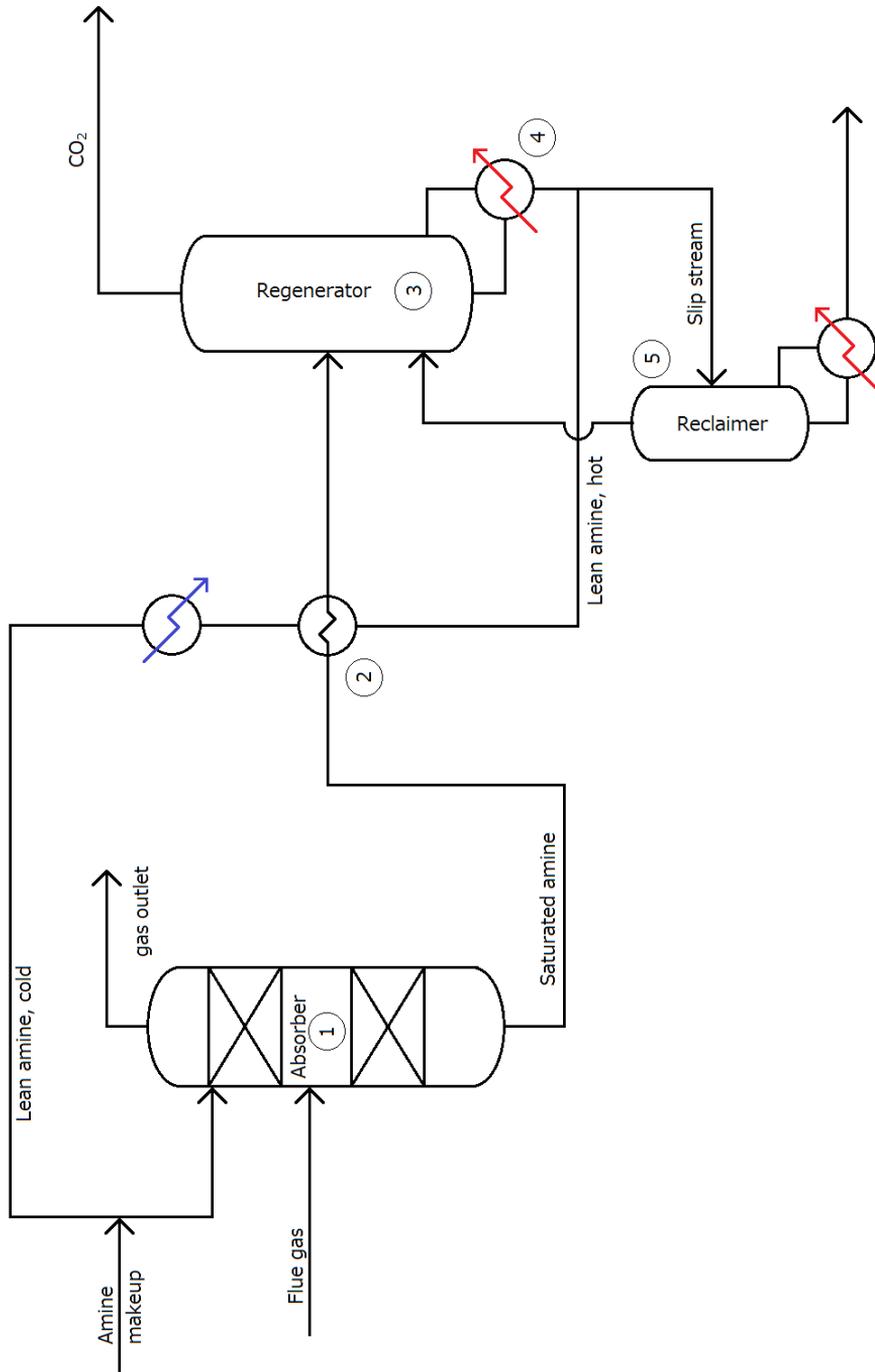


Figure 2: Illustration of typical post-combustion CO_2 capture plant. Amine absorb CO_2 in absorber, heat is added in the regenerator where the CO_2 is desorbed from amine.

the ability to absorb CO_2 [Du et al.], and also lead to further corrosion of equipment [Du-Part et al., 1993]. To remove this, a reclaimer (5) is used. A part of the lean amine

stream (slip stream) is lead to an additional vessel where fresh amine is flashed of, and returned into the regenerator. Before entering the reclaimer, there can also be a vessel for flashing of ammonia and CO₂. The bottom product is a slurry consisting of different degradation products, water and amine. The reclaimer is heated by steam, and kept at a temperature of 150 °C [KIP]. The lean amine from the reclaimer is re-entered into the regenerator where the energy put into evaporation of amine is re-used in the desorption process. In other words, the reclaiming process is not a large consumer of energy as it acts at part of the heating in the regenerator.

3 Degradation

3.1 Degradation products

Much of the research on CO₂ capture by amine absorption is concerning degradation of amine under the conditions of a post combustion capturing plant. Lepaumier et al. [2011] did a study where thermal and oxidative degradation of MEA was viewed separately. The result was then compared with the analysis of amine in a pilot plant in Esbjerg. The main degradation products found in the three different analyses are shown in Table 1.

The conclusion drawn from the results in Esbjerg [Lepaumier et al., 2011] was that oxidative degradation is dominating. This result is supported by Moser et al. [2011].

Several of the components identified in Esbjerg are products of a condensation between some carboxylic acid and MEA [da Silva et al., 2012]. In the pilot plant [Moser et al., 2011] in Niederaussem Germany, acetate was found to be the main anion of carboxylic acid, followed by formate. There was also found traces of oxalate. Concentrations found after 5000 hours of operation are shown in Table 2.

Carboxylic acids can react with MEA to several of the degradation products listed in Table 1. The link between the carboxylic acids and degradation products are shown in the following equation and list.



- $R = H$: Formic acid, product is HEF.
- $R = CH_3$: Acetic acid, product is HEA.
- $R = CH_2OH$: Oxalic acid, product is HHEA.
- $R = (CO)(NH)(CH_2)_2OH$: HHEA, product is BHEOX.

Notice that oxalic acid has two acid-groups, and is therefore able to react with amine in two stages. Initial reaction produces HHEA. If condensation occur on the second acid group, BHEOX is produced.

An identified mechanism of degradation is carbamate polymerization [Knudsen et al., 2009]. Here, OZD is an intermediate product [Lepaumier et al., 2011], and polymerization progress by ring opening and closing. Products resulting from this is HEEDA, HEIA and AEHEIA, which are mainly products of thermal degradation, and thus neglected in

Table 1: Overview of degradation products of MEA identified by [Lepaumier et al., 2011]. The study included experiments to look at thermal and oxidative degradation separately, and results from analysis in the pilot plant in Esbjerg.

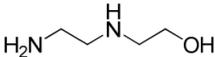
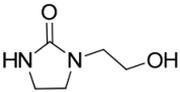
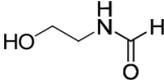
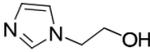
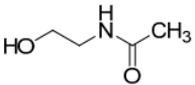
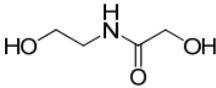
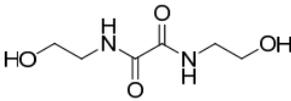
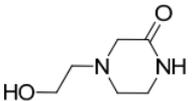
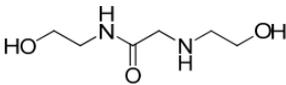
Compound name	Abbreviation	Structure	Comment
2-oxazolidinone	OZD		Thermal and oxidative
N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidinone	HEEDA		Thermal
N-(2-hydroxyethyl)imidazolidinone	HEIA		Thermal
N-(2-hydroxyethyl)formamide	HEF		Oxidative
N-(2-hydroxyethyl)imidazole	HEI		Oxidative
N-(2-hydroxyethyl)acetamide	HEA		Oxidative
2-hydroxy-N-(2-hydroxyethyl)acetamide	HHEA		Oxidative
N,N'-bis(2-hydroxyethyl)oxalamide	BHEOX		Oxidative
4-(2-hydroxyethyl)piperazin-2-one	HEPO		Oxidative Major product, pilot plant
N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide	HEHEAA		Oxidative Major product, pilot plant

Table 2: Concentration [Moser et al., 2011] of carboxylic acid anions in pilot plant in Niederaussem, Germany. The solvent used was MEA, and values shown in table are after 5000 hours operation.

Compound	Weight percent
Acetate	1.8
formate	0.2
oxalate	> 0.1

model. The mechanism will not be elaborated here as it is not of consequence in this study.

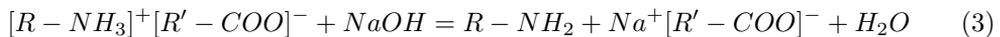
3.2 Releasing bounded MEA form degradation products

Another class of components that can occur when carboxylic acids are present in amine, is Heat-Stable Amine Salts (HSAS). This is a product of a reaction of an amine and a carboxylic acid. The reaction is shown in equation 2.

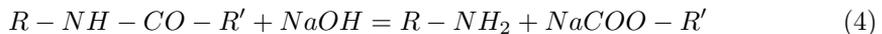


In this equation, R and R' denotes some inactive part of the compounds. In the case of MEA and formic acid, R denotes ethanol, and R' , a hydrogen ion.

This compound can be neutralized by adding some base into the equation, for instance NaOH. This is shown in equation 3. The result is releasing of the bounded amine, and that the caboxylic acid is turned into a Heat Stable Salt (HSS).



In a similar manor, HEF, HEA and other components of MEA-acid condensation can react to MEA and HSS. This is shown in equation 4.



R is here the ethanol-group of the MEA, and R' are the same chains as listed in the latter section. This is why, into the reclaimer, the feed is added NaOH-solution. As mentioned, this results in an increase in the MEA available for reclaiming, along with increase in the HSS concentration of the waste.

3.3 Rate of degradation and effects of contaminations

The two pilot plants [Moser et al., 2011] [Lepaumier et al., 2011] in Esbjerg and Niederaussem gives different results when considering amount of degradation products. MEA loss in Esbjerg was found to be 1.4 - 2.4 $\frac{kgMEA}{tonnCO_2}$, while the pilot plant in Niederaussem had MEA loss at only 0.3 $\frac{kgMEA}{tonnCO_2}$.

The concentration of HSS seems to increase linear over time, and seems to be in correlation to the amount of iron-ions in the solution [Knudsen et al., 2009]. Production of carboxylic acid seems to be catalysed by metallic ions introduced by corrosion of equipment which releases them into the amine solution [Rooney et al., 1996/1997] [Moser et al., 2011]. In other words, the HSS-concentration is dependant on the production rate of carboxylic acid, which is catalysed by iron in the solution.

Other ions found in the Niederaussem-study were chlorine (Cl), nickel (Ni) and sulphur (S). There was not found any correlation between the concentration of Ni and S and the degradation of MEA [Moser et al., 2011]. Surprisingly, there seems to be a correlation between Cl and degradation. According to Moser Moser et al. [2011], this is probably not because of an effect of Cl on MEA, but rather that it is a marker of change in the operating boundary conditions of the process that also effects the MEA degradation rate.

The exact concentration of degradation products in an actual plant is hard to predict as most studies available have focused on qualitative analysis more than quantitative, or is focusing on some specific class of degradation product. Therefore, the concentration used when modelling are educated guesses done in cooperation with Stig Brustad [KIP], and on the basis of information in literature.

4 The reclaiming process viewed

A sketch of the reclaiming system that is viewed in this study is shown in Figure 3. It also outlines the part of the amine capturing plant that the MATLAB-model concerns. The optimization also includes the compression of the low pressure MEA/water vapour.

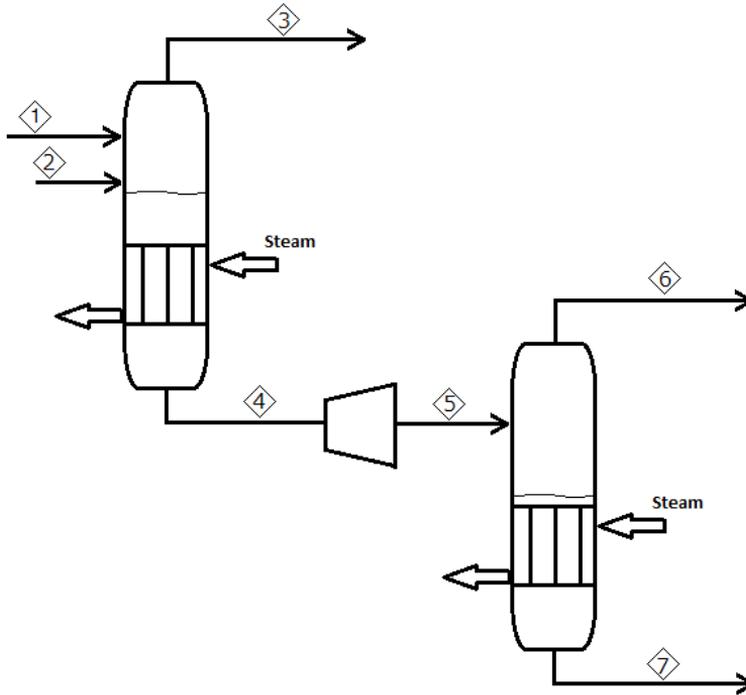


Figure 3: *Two stage reclaiming process subject to optimization. The liquid outlet of the first stage enters into second vessel, which holds lower pressure. The liquid flow out of second stage is considered waste. The vapour flows are returned back into main carbon dioxide capturing plant.*

In the above figure, stream 1 is the slip stream entering reclaimer. 2 symbolises the NaOH-solution for releasing bounded MEA. The streams leaving the first reclaimer, 3 and 4, are MEA and water vapour and partially concentrated degradation products in liquid phase, respectively. Stream 3 is returned to regenerator, while 4 is lowered in pressure (stream 5), and led into the second stage reclaimer vessel. Low pressure MEA and water vapour leaves the vessel (stream 6), and low pressure concentrated degradation product leaves second reclaimer stage in liquid phase (stream 7).

It is assumed that there has been an ammonia and CO₂ flasher preceding the reclaimer. Only the major degradation products are considered.

This study is only concerning the operational costs of the system. The economics of construction and procuring of equipment is not viewed.

The reclaimer runs in semi-batches, meaning that it is started when degradation products have accumulated in the main stream and is running until it has reached an acceptably low level. The timespan of the process is decided by the capacity of the reclaimer system, and how much solution that needs to be processed. It has been decided in consultation with KIP that this should be 2500 kg/h and 88 000 kg, respectively. This means that roughly 35 hours of operation is sufficient:

$$t_{end} = \frac{88000kg}{2500kg/h} = 35.5h \quad (5)$$

After 35 hours, the inlet flow is cut, and the reclaimer is drained while heat still is fed into the system thus evaporating MEA and water also in the end phase of the run.

The assumed composition of the inlet flow is mainly guesses done in cooperation with KIP and from literature [Moser et al., 2011] [Lepaumier et al., 2011], and are listed in Table 3 along with some other fixed variables in the model. Other constants are given in Appendix B.

Table 3: *Constant values used when simulating two step reclaimer process.*

Variable	Value
Mass fraction, MEA	0.485
Mass fraction, water	0.454
Mass fraction, HEF	0.013
Mass fraction, NaOH	0.01
Mass fraction, HSS	0.001
Mass fraction, HEPO	0.002
Mass fraction, CO ₂	0.035
Bulk volume, 1st stage [m ³]	9
Bulk volume, 2nd stage [m ³]	4

The bulk volume of liquid at steady state is only guesses. For increased stability of optimization model, these are kept constant.

5 Modelling the Reclaimer process

The model used for the two stage reclaiming is based on a model developed in the master thesis of Linn Christine Loe Haaversen [Haaversen, 2010]. This model was rewritten and expanded to also include an outlet flow after some given time, while temperature and accumulated mass is kept constant. It is also manipulated so that the output is more suitable for optimization.

5.1 Mass balance

The general mass balance for the reclaimer is described by the principle in - out + generated = accumulated.

$$\frac{dm_j}{dt} = \dot{m}_{in,j} - \dot{m}_{out,j} + \dot{m}_{gen,j} \quad (6)$$

Here, \dot{m} represents mass rate, [kg/h]. $\dot{m}_{out,j}$ includes both vapour and liquid phase outlet. The subscript j represents any component $j \in \{A, B, C, D, E, F, G\}$. The mass rate can be denoted to $\dot{m}_j = M_{w,j}\dot{n}_j$, where $M_{w,j}$ is molar weight of component j and \dot{n}_j is the molar flow rate. The term considering the reaction can be denoted to $\dot{m}_{gen,j} = \pm M_{w,j}RV_{Rec}$, where R is the reaction rate and V_{Rec} is the volume of liquid in the reclaimer vessel viewed. The sign depends on if it is a reactant or a product.

5.1.1 Dynamic model

In semi-steady state mode, a CSTR (Continuously stirred tank reactor) model is used. Please note that semi-steady state here means that total mass is constant, while mass of each component can change. The mass balances will then be given as following:

MEA (A)

MEA and is fed into the reclaimers, is a product in the reaction and is evaporated. The mass balance shown in equation 7 therefore contains inlet, outlet, evaporation and reaction terms.

$$\frac{dm_A}{dt} = \dot{m}_{A,in} - \dot{m}_{A,vap} - \dot{m}_{A,out} + \dot{m}_{A,gen} = \dot{m}_{A,in} - \dot{m}_{A,vap} - \dot{m}_{A,out} + M_{w,A}RV_{Rec} \quad (7)$$

Water (B)

Water is fed into the reclaimers, and is evaporated. The mass balance equation shown in 8 is in other words only containing convective terms.

$$\frac{dm_B}{dt} = \dot{m}_{B,in} - \dot{m}_{B,vap} - \dot{m}_{B,out} \quad (8)$$

HEF (C) and NaOH (D)

The HEF is the product of reaction between formate, a product of degradation of amine that and lean MEA. HEF and NaOH are both fed into the reclaimer, and are reactants in the process. HEF and NaOH are not volatile, and will therefore not evaporate. The formation of HEF is further elaborated in Chapter 3.

$$\frac{dm_i}{dt} = \dot{m}_{i,in} - \dot{m}_{i,out} + \dot{m}_{i,gen} = \dot{m}_{i,in} - \dot{m}_{i,out} - M_{w,i}RV_{Rec} \quad i \in [C, D] \quad (9)$$

HEPO (F) and CO₂ (G)

Both HEPO, a compound originating from oxidative degradation of MEA [Moser et al., 2011] [Lepaumier et al., 2011], and CO₂ are inert compounds in this process. The difference between them is that CO₂ is very volatile and in gas phase at ambient pressure and temperature, while HEPO is not. Therefore, the HEPO stay in liquid phase, while CO₂ will leave the reclaimer in vapour stream. For CO₂, the mass balance equation will be of no consequence for the accumulated mass in reclaimer, as shown in equation 10.

$$\frac{dm_G}{dt} = \dot{m}_{G,in} - \dot{m}_{G,vap} = 0 \quad (10)$$

The amount of HEPO accumulating in the reclaimer is described by equation 11.

$$\frac{dm_F}{dt} = \dot{m}_{F,in} - \dot{m}_{F,out} \quad (11)$$

HSS (E)

The formation of Sodium-formate is also a degradation product, and the product of reaction in the reclaimer. As is elaborated in Chapter 3, this is a product of the reaction between HEF and NaOH. Therefore, the accumulation of Sodium-formate is dependent

on concentration in slip stream, and the reaction rate as shown in equation 12. Please note that HSS is a collective term for all heat stable salts, including salts of several carboxylic acids and different metallic ions. These HSSs entering the system are treated as inert, only adding the amount produced in the HEF-NaOH reaction.

$$\frac{dm_E}{dt} = \dot{m}_{E,in} - \dot{m}_{E,out} + \dot{m}_{E,gen} = \dot{m}_{E,in} - \dot{m}_{E,out} + M_{w,NaF}RV_{Rec} \quad (12)$$

5.1.2 Start-up and shut down

During start-up of the reclaiming process, the system is running in batch mode until the bulk liquid has reached desired total mass. During this period, outlet is closed ($\dot{m}_{j,out} = 0$).

When the required volume has been led into the system, inlet flow is closed. After this, outlet, vaporization and reaction is cause of change in mass and composition. In other words, $\dot{m}_{j,in} = 0$.

5.2 Releasing bounded MEA

The reaction converting HEF and NaOH to HSS and MEA is assumed to be a second order reaction, described by equation 13.

$$R = kC_C C_D \quad (13)$$

Here, R is the reaction rate [$kmol/m^3, h$], k is the reaction coefficient [$m^3/kmol, h$], assumed constant. C_C and C_D are concentration of HEF and NaOH respectively. The converting term can be seen in equation 7.

5.3 Energy balance

The energy balance is given by a heat transfer term, a term for energy entering with inlet stream, energy consumed in evaporation, heat of reaction and PV-work. The derivation of the energy balance given in equation 14 is given in Appendix A.

$$\frac{dT_{Rec}}{dt} = \frac{\dot{Q} - \sum_{j=1}^n \dot{n}_{j,in} C p_j [T_{Rec} - T_{in}] - \sum_{j=1}^n \dot{n}_{j,out} \Delta H_{j,vap}(T_{Rec}) + \Delta H_{rx}(RV_{Rec}) - P \frac{dV_{rec}}{dt}}{\sum_{j=1}^n n_j C p_j} \quad (14)$$

5.4 Gas-liquid equilibrium

The derivation of equations for evaporation of water and MEA is shown in Appendix A. These equations are based on the assumptions of equilibrium between vapour and liquid phases, the Antoine's equation, and Raolt's law. It is assumed that CO₂ is so volatile that it does not influence the equilibrium. Equations 15 and 16 are used to calculate the rate of vapour flow rate for MEA and water respectively.

$$\dot{n}_{A,vap} = \beta_A M_{w,A} (P_{sat,A} - P_A) \quad (15)$$

$$\dot{n}_{B,vap} = \beta_B M_{w,B} (P_{sat,B} - P_B) \quad (16)$$

In these equations, $P_{sat,j}$ is the saturated pressure of component j , and P_j is the actual partial pressure of component j in the reclaimer. β_j is an evaporation function.

5.5 Making the model suitable for optimization

When working with optimization, it can be crucial that the vector consists of variables of close to equal size for the algorithm to succeed. Therefore, the variables in the vector of optimization are scaled. For compound mass equations, the mass fractions are returned instead of the mass. The mass fractions are calculated from equation 17. Combined with equation 18, the change in mass fraction can be calculated by equation 19.

$$x_i = \frac{m_i}{M} \quad (17)$$

$$M^{k+1} = M^k + \frac{dM}{dt} \quad (18)$$

$$\frac{dx_i}{dt} = x_i^{k+1} - x_i^k = \frac{m_i^{k+1}}{M^{k+1}} - x_i^k = \frac{m_i^k + \frac{dm_i}{dt}}{M^k + \frac{dM}{dt}} - x_i^k = \frac{x_i^k * M_i^k + \frac{dm_i}{dt}}{M^k + \frac{dM}{dt}} - x_i^k \quad (19)$$

The k and $k+1$ in the latter equations marks variable at time k , $k+1$ is the same variable after one step in time.

Other variables are scaled by dividing them with some feasible value for the variable in question. Equation 20 shows an example of this, here with temperature. $\frac{dX_{Ti}}{dt}$ is here the time differential of scaled temperature for reclaimer i . This variable has upper/lower bounds of [0,1]. Other scaling factors are shown in Table 4.

$$\frac{dX_{Ti}}{dt} = \frac{dT_i}{428K} \quad (20)$$

The scaling of parameters shown in Table 4 is done in both the ODE-solver models and

Table 4: *Scaling parameters for the variables in output vector of simulation and optimization of a two stage MEA reclaimer system.*

Variable scaled	Symbol	Scaling factor
First stage		
Volume [m^3]	X_{V1}	10
Temperature [K]	X_{T1}	428
Total mass [kg]	X_{M1}	10000
Total mass, vapour flow [kg/h]	$X_{\dot{M}_{vap,1}}$	1000
Total mass, liquid flow [kg/h]	$X_{\dot{M}_{liq,1}}$	1500
Heat input [kJ/h]	$X_{\dot{Q}1}$	10^6
Second stage (low pressure)		
Volume [m^3]	X_{V2}	5
Temperature [K]	X_{T2}	428
Total mass [kg]	X_{M2}	5000
Total mass, vapour flow [kg/h]	$X_{\dot{M}_{vap,2}}$	650
Total mass, liquid flow [kg/h]	$X_{\dot{M}_{liq,2}}$	1000
Heat input [kJ/h]	$X_{\dot{Q}2}$	10^6
Pressure [kPa]	X_{P2}	100

the optimisation constraint model. However, as can be seen in Appendix C, these two models differs in some other aspects. To simulate the filling and emptying of the reclaimer to desired amount of bulk liquid, a control structure is imposed on the system. This is done simply by adding some if-loops, defining the liquid outlet to equal zero under start up, and inlet stream as zero under emptying. This is not necessary in the optimization as it looks only at steady state.

A problem encountered when a small volume is in the reclaimer vessel at start up- and shut down-phase of the simulation, was the system's sensitivity to heat flow. It quite easily moved into a infeasible region in where it was not possible to continue the simulation. To avoid this, there is put a simple control structure on the heat flow while reclaimer is filling up to fit the amount of liquid. If volume of step $i \in [1, 2]$ (V_i) is less than e certain required volume $V_{requ,i}$, the heat flow is calculated by equation 21. For filling and emptying of first stage, $V_{requ,1}$ was set to be $7 m^3$. For filling of second stage, $V_{requ,2} = 4$. Emptying of second stage is an exception. Temperature tended to rise very high. Therefore, it was decided that if total volume was less than $4 m^3$, the $V_{requ,2}$ in equation 21 should be $7 m^3$. Again, this is not necessary for optimization.

$$\dot{Q}'_i = \frac{\dot{Q}_i}{V_{requ,i}} V_i \quad (21)$$

For emptying of reclaimer vessels, the outlet stream is adjusted. In semi-steady state mode this is controlled by the amount entering the vessel to keep total mass constant. When inlet stream is closed, the outlet stream needs to be defined from some other variable. This is done by looking at the ratio between total mass and mass rate of outlet stream at semi-steady state. These ratios are calculated in equation 22 for the first stage, and 23 for second stage. These were used to scale the outlets as shown in 24 and 25.

$$\frac{\dot{M}_{out,SSS,1}}{M_{SSS,1}} = 0.097s^{-1} \quad (22)$$

$$\frac{\dot{M}_{out,SSS,2}}{M_{SSS,2}} = 0.14s^{-1} \quad (23)$$

$$\dot{M}_{out,1} = M_1 * 0.097s^{-1} \quad (24)$$

$$\dot{M}_{out,2} = M_2 * 0.14s^{-1} \quad (25)$$

This is only done in 'deriveods2', the ODE-solver model for optimal solution with termination.

6 Optimization

6.1 Optimization problems

In an optimization, the object is to find an optimal point X^* that minimizes some object function $f(X)$ [Nicedal and Wright, 2006]. A general optimization problem is shown in equations 26 through 31.

$$\min_X f(X) \quad \text{subject to} \quad (26)$$

$$A_{eq}X = b_{eq} \quad (27)$$

$$A * X \leq b \quad (28)$$

$$c_{eq}(X) = 0 \quad (29)$$

$$c(X) \leq 0 \quad (30)$$

$$lb \leq X \leq ub \quad (31)$$

There are several classes of constraints represented in the latter equations:

- Equality constraints (27 and 29) demands that for X to be a feasible point, the equations defined in $c_{eq}(X)$ or in matrix A_{eq} must give zero, or a predefined solution vector b respectively.
- Inequality constraints (28 and 30) demands that X is so that $A * X$ and $c(X)$ are less than the right hand side of the equation.
- The constraints shown in equation 31 are those of a bounded problem. This imposes some borders in which the X cannot cross. For instance, mass fractions can never be more than 1 or less than 0. Therefore, mass fraction is bounded by $0 \leq x_i \leq 1$.

These can again be divided into linear and non-linear constraints. Equations 27 and 28 are equality constraints, demanding a linear combination of X being equal to, or equal or smaller than some solution vector b_{eq}/b (e.g. mass fraction should always sum to 1). Non-linear constraints (29 and 30) are, as the name says, a demand of e.g. the product of variables or the ratio between variables are kept constant or has a roof.

When finding optimum operation conditions for some process is the object of the optimization, model equations are formulated as constraints. In the program written and shown in Appendix C, the model equations are written as non-linear equality constraints,

demanding that the derivatives are equal to 0, thus finding a steady state point.

The function subject to minimization, the objective function, and its properties are crucial when deciding how to solve the optimization problem. The term 'convex' describes a function that has one global minimum in the feasible region [Nicedal and Wright, 2006]. Therefore, if one minimum is found, this is also the global minimum, and therefore the optimal solution. For non-convex problems several minima can occur. Most algorithm will stop at this point and return this as an optimal solution. Therefore, for non-convex problem, several starting points should be tried out to see if other minima can be detected.

Considering the optimizing problem in question, this seems not to be a convex function. There could be several local minima. This will further be elaborated in Chapter 7.

6.2 Solving reclaimer problem

The MATLAB-program used to solve the the optimization problem of the reclaimer, is 'fmincon'. This is a built-in MATLAB function that has the ability to take in linear equality and inequality constraints, non-linear equality and inequality constraints, and lower and upper bound constraints. There are several options for algorithm, like trust region reflective (default), interior point algorithm and SQP (sequential quadratic programming). The last is the one used to solve the reclaimer problem.

The SQP is a class of methods for solving large-scale optimization problem where the non-linearity of the constraints is significant [Nicedal and Wright, 2006]. In short, SQP methods simplifies the optimization problem by, for each iteration, solving a quadratic programming sub-problem with linearised constraints. The solution of the QP problem (quadratic programming problem) gives the search direction. Then a so called merit function ensures that the next step does not violate constraints, and that the main problem converges.

6.2.1 The MATLAB program

The actual MATLAB code can be found in Appendix C. The structure of the program is shown in figure 4. The order of the program is listed below.

- 'main' sends initial values and simulation time scale to 'odsmain'.
- 'odsmain' starts up ods15s that solves differential problem given in 'deriveods'. 'deriveods' calls 'fraccont', which ensures that the model operates with feasible weight fractions ($\sum_j x_j = 1$).

- 'odsmain' returns a close-to steady state vector to 'main', which is sent to 'fmincon' and used as an initial point in the optimization.
- Constraints of optimization are defined in 'nonlCon', where it is demanded that the output of 'derivev1', i.e. the derivatives of the model, are close to zero, and thus are at steady state. Here is also demands linked to keeping bulk at a specific volume.
- 'fmincon' also calls 'objfunc', the objective function subject to minimization.
- When 'fmincon' finds a minimum which is returned to 'main', where it is sent again to 'odsmain'. A new dynamic simulation is done with the new inputs, now on a shorter time scale. This time, 'ods15s' calls 'deriveods2', which also terminates the process by cutting inlet to first stage after a given time.

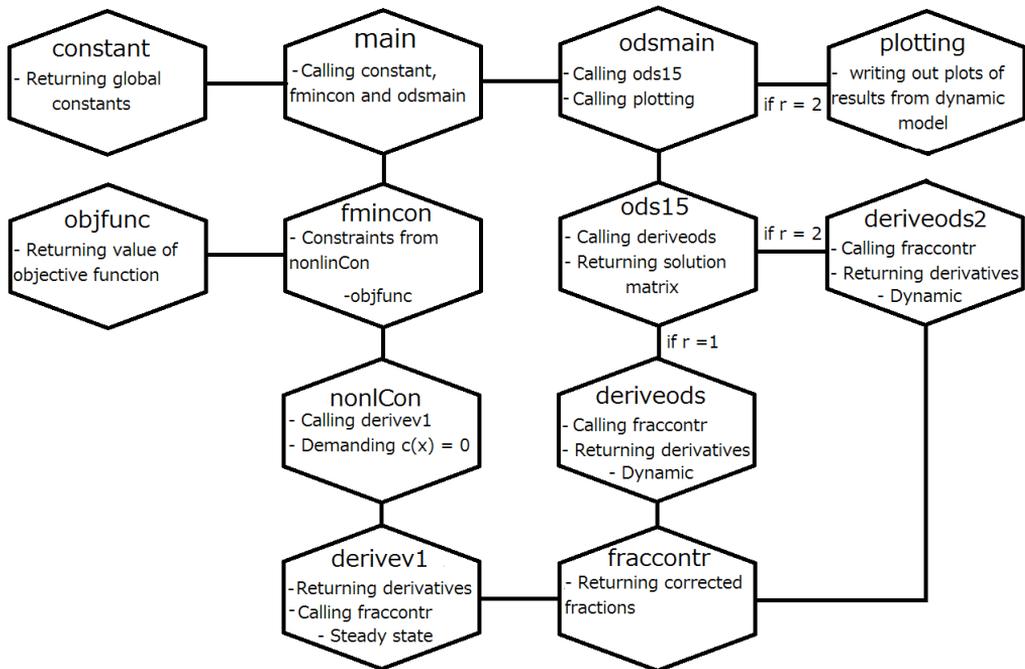


Figure 4: Structure of MATLAB program made to solve steady state optimization and dynamic simulation of a MEA reclaiming system.

6.2.2 Objective function

The parameters used in the objective function are accounted for in Appendix D. The values subjected to optimization that also appears in objective function are as follows:

- Energy lost with waste stream (\dot{Q}_{lost})
- Pressure of second stage (P_2)
- Vapour from second stage ($\dot{M}_{vap,2}$)
- Makeup amine, estimated as waste excluding water (\dot{M}_{makeup})
- Amount of waste (\dot{V}_{waste})

Costants taken into the objective function are shown in Table 5.

Table 5: *Cost parameters used in optimization of a two stage reclaiming process.*

Parameter	Symbol	Value
Electricity cost $\left[\frac{NOK}{kJ/h}\right]$	C_{el}	$1.00 * 10^{-4}$
Makeup amine $[NOK/kg]$	C_{makeup}	11.1
Transport cost $[NOK/m^3]$	C_{tank}	170
Destruction $[NOK/kg]$	C_{depo}	1.5
Correlation factor* $\left[\frac{kJ^2 * kPa}{kg^2}\right]$	C_{corr}	1.78

*The correlation factor is a constant for the covariance of compression work, and mass and pressure. This way, energy consumption can be written as a function of mass and pressure $\dot{W}(P_2, \dot{M}_{waste})$. The derivation of this is shown in Appendix D.

The objective function subject to minimization then becomes as shown in equation 32.

$$cost[NOK/h] = C_{el} * \dot{Q}_{lost} + C_{tank} * \dot{V}_{waste} + C_{makeup} * \dot{M}_{makeup} + C_{el} * \sqrt{\frac{C_{corr}}{P_2}} * \dot{M}_{vap,2} \quad (32)$$

Please notice that even though the evaporators are heated by steam, electricity cost is used here too. This is a simplification.

In the MATLAB optimization, the objective function is scaled to match values of variables of optimization X by a factor of 10^{-4} .

It should be noticed that there is not done an optimization considering total mass and volume. The mass of the bulk liquid of the evaporators are set and volume is calculated from this to simplify the optimization. This was done because fmincon struggled to find a

feasible point. By fixing these variables, two degrees of freedom were removed. The total mass therefore works as a controlled variable [Nicedal and Wright, 2006]. As a demand set by the ODE-solution (see script in Appendix C), this also makes a connection between the ODE-solutions and the solution of the optimization.

For comparison, there can also be done a run where some constraints are added. There is demanded that vapour flow in second stage is close to zero, the pressure is the same in both reclaimer vessels and that heat feed to second stage is zero. The result of this is that the second stage is ignored. This is done to look at a one stage system, giving a value of the objective function for a single stage system.

7 Results

There were detected two minima when different initial conditions were tried out. It seems to be one minimum where the low pressure evaporator is dominating, while the other stage is passive. It was however located an apparent global minimum where both evaporators are active, and where objective function is at its lowest of the minima found ($1.49 * 10^4 NOK/h$ and $0.735 * 10^4 NOK/h$ respectively). This assumed global minimum vector is shown in Table 6, the other can be seen in Appendix E. The third column is output of 'deriveods' at optimal operating conditions, not 'deriveods2'. The ODE-solver optimal output with 'deriveods2'-model is shown in figures 5 through 11. The optimization run where second stage is ignored gave an objective function value of $1.38 * 10^4 NOK/h$. The plots of this run for the first stage is included in figure 12.

Notice that the output of the program varies in different runs even though initial values are the same. The pressure of the second stage is the variable changing most from run to run, along with the value of objective function.

The model is very sensitive to change, and many iterations are needed to satisfy the constraints. Therefore, the demand for constraints to be satisfied are set to quite loose (10^{-5}), and instead of bounds between 0 and 1, the upper bound is set to 1.1 to help `fmincon` to find a minimum. This causes the temperature to rise higher than actual operating temperature in the first reclaimer. Still, it doesn't reach the maximum set by the optimization. This is probably why it does not work when the constraint is tightened: The constraint turns active, and the algorithm cannot handle this. It was not identified why. For the study done in this paper it is not of great consequence, but for future work, this can be looked into.

Table 6: *Output of the three different solvers used in MATLAB-script. The input to optimization is a solution given by an ODE-solver. This is a steady state solution, run for 5000 hours. The second column is an optimization finding an optimum for heat input in both stages, and pressure in second stage. The third is a ODE-solver output for optimal values after a run of 5000 hours.*

Variable	Input to optimization	Output of optimization	Optimal solution (at steady state)
First stage bulk			
MEA [wt%*100]	0.6286	0.5988	0.5988
H ₂ O [wt%*100]	0.3175	0.3649	0.3649
HEF [wt%*100]	0.0076	0.0083	0.0083
NaOH [wt%*100]	0.0153	0.0112	0.0112
NaF [wt%*100]	0.0254	0.0132	0.0132
HEPO [wt%*100]	0.0057	0.0036	0.0036
Volume [m ³]	9.018	9.018	9.018
Temperature [°C]	434.2	427.5	427.5
CO ₂ [wt%*100]	0	0	0
Total mass [kg]	9000	9000	9000
First stage vapour outlet			
MEA [wt%*100]	0.4183	0.3531	0.3531
H ₂ O [wt%*100]	0.5278	0.5674	0.5674
CO ₂ [wt%*100]	0.0539	0.0796	0.0796
Total mass [kg]	1623.1	1099.9	1099.9
First stage liquid outlet			
MEA [wt%*100]	0.6286	0.5988	0.5988
H ₂ O [wt%*100]	0.3175	0.3649	0.3649
HEF [wt%*100]	0.0076	0.0083	0.0083
NaOH [wt%*100]	0.0153	0.0112	0.0112
NaF [wt%*100]	0.0254	0.0132	0.0132
HEPO [wt%*100]	0.0057	0.0036	0.0036
Total mass [kg]	876.9	1400.1	1400.1
Second stage, bulk			
MEA [wt%*100]	0.5869	0.7093	0.7093
H ₂ O [wt%*100]	0.1208	0.2251	0.2251
HEF [wt%*100]	0.0009	0.0048	0.0048
NaOH [wt%*100]	0.0715	0.0174	0.0174
NaF [wt%*100]	0.1858	0.0362	0.0362
HEPO [wt%*100]	0.0341	0.0073	0.0073
Volume[m ³]	4.008	4.008	4.008
Temperature [°C]	424.9	408.0	408.0
Total mass [kg]	4000	4000	4000

Table continued

Variable	Input to optimization	Output of optimization	Optimal solution (at steady state)
Second stage vapour outlet			
MEA [wt%*100]	0.6431	0.5010	0.5010
H ₂ O [wt%*100]	0.3569	0.4990	0.4990
CO ₂ [wt%*100]	0	0	0
Total mass [kg]	730.4	715.0	715.0
second stage liquid outlet			
MEA [wt%*100]	0.5869	0.7093	0.7093
H ₂ O [wt%*100]	0.1208	0.2251	0.2251
HEF [wt%*100]	0.0009	0.0048	0.0048
NaOH [wt%*100]	0.0715	0.0174	0.0174
NaF [wt%*100]	0.1858	0.0362	0.0362
HEPO [wt%*100]	0.0341	0.0073	0.0073
Total mass [kg]	146.4	685.1	685.1
Heat input 1st stage [kJ/h*10 ⁶]	0.3000	0.2140	0.2140
Heat input 2nd stage [kJ/h*10 ⁶]	0.1000	0.1083	0.1083
Pressure, 2nd stage [kPa*100]	0.7000	0.6511	0.6511

The amount of MEA entering the reclaiming is 1212.5 kg/h. The amount of MEA processed throughout the operational time of 35 hours of feeding, is roughly 42.4 metric tons. As mentioned in Chapter 4, the evaporation does not stop at 35 hours, but are simulated for 50 hours. The total of MEA reclaimed during this time is 27133 kg: 15506 kg in first stage, and 11627 kg in second. This means that 63.9 % of the MEA is returned into the main stream of the CO₂ capturing plant, 36.6 % from first stage and 27.4 % from second. 36.1 %, roughly 15.2 metric tons, are lost. This is removed with the rest of the waste. The total amounts of MEA in streams were calculated by summing up the amount in stream $i \in [vap, liq]$ in all time steps k . The amount of MEA in each time step was calculated by equation 33.

$$m_{tot,i}^k = (t^k - t^{k-1}) * \dot{m}_{MEA}^k \quad (33)$$

As can be seen from figures 5, 6 and 7, the batch mode of first stage last for almost 5 hours. Then this reaches semi-steady state mode, and outlet is opened. This marks the start up of second stage, which is in batch mode for approximately 2.5 hours. The

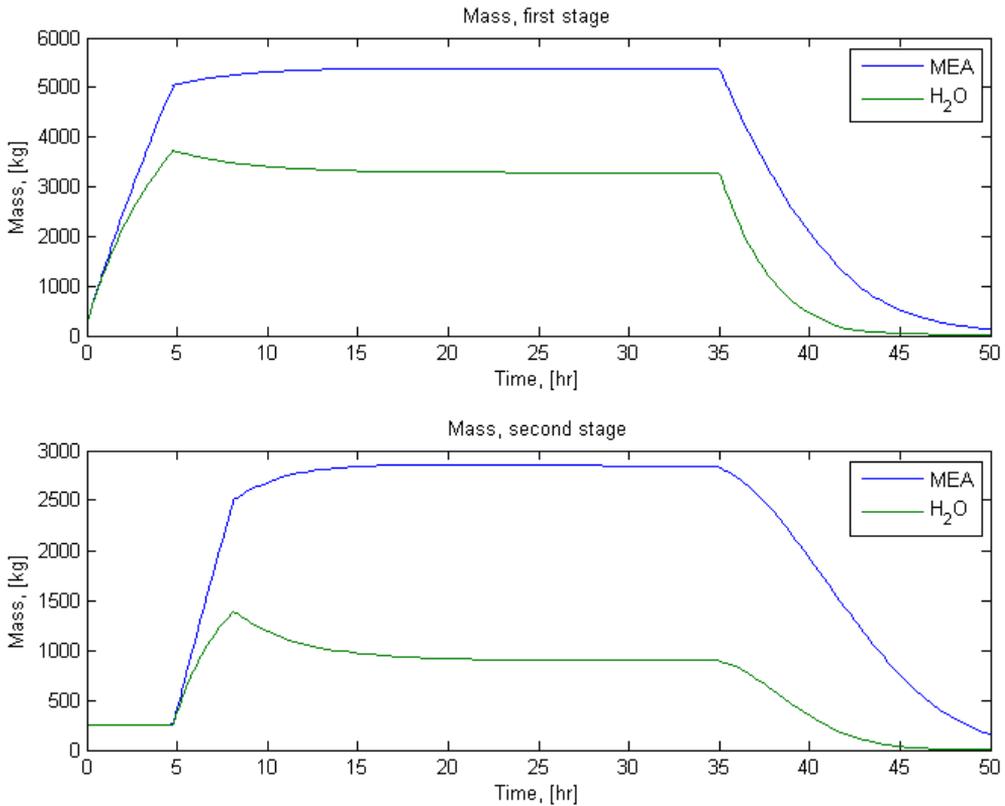


Figure 5: *Mass of MEA and water in two step MEA reclaiming, operated at cost optimized process conditions.*

termination starts for both stages at 35 hours after opening of inlet to first stage. When looking at component plot in figures 5 and 6, the first stage seems to reach a close-to steady state at 32 hours. The second stage is changing all through the operating time, never reaching an steady state.

In Figure 6, there is a rising amount of HSS in the first stage at the start of the shut down phase, and the amount of HSS is declining slower than for other components in the second stage. This is probably because of the reaction still present after the inlet is closed. As the concentration of MEA and water is descending, the concentrations of reactants are rising, which also rises the reaction rate (see equation 13 in Chapter 5.2). Therefore, the reactants are decreasing faster, and HSS is increasing.

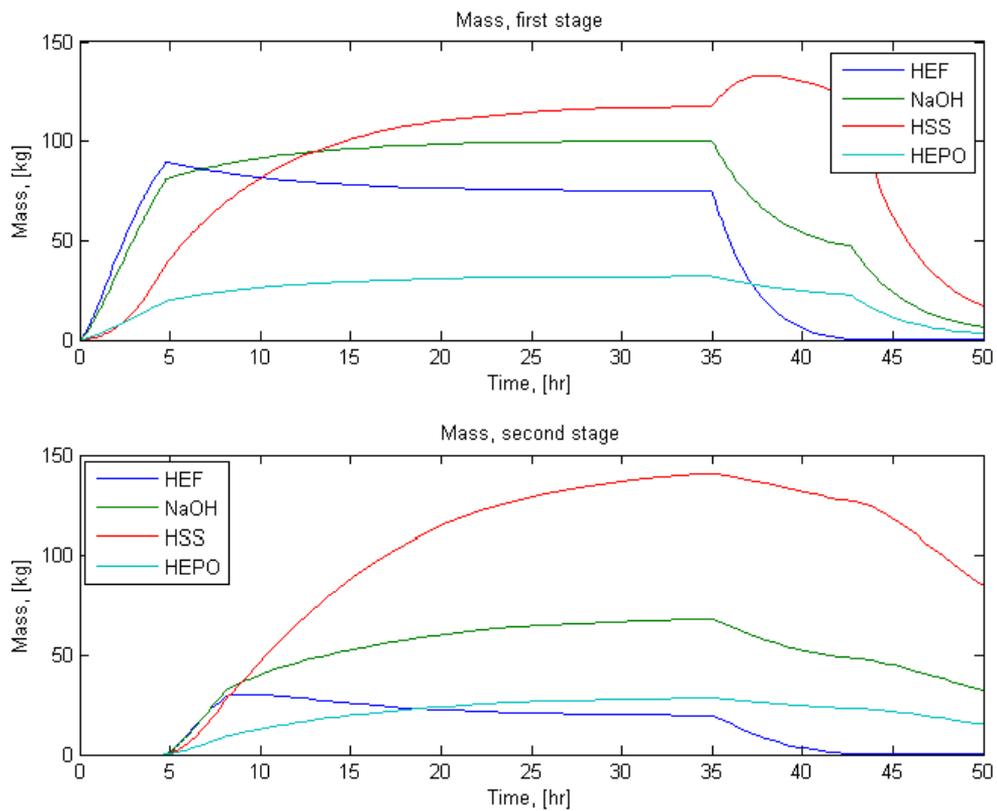


Figure 6: *Mass of degradation products in two step MEA reclaiming, operated at cost optimized process conditions.*

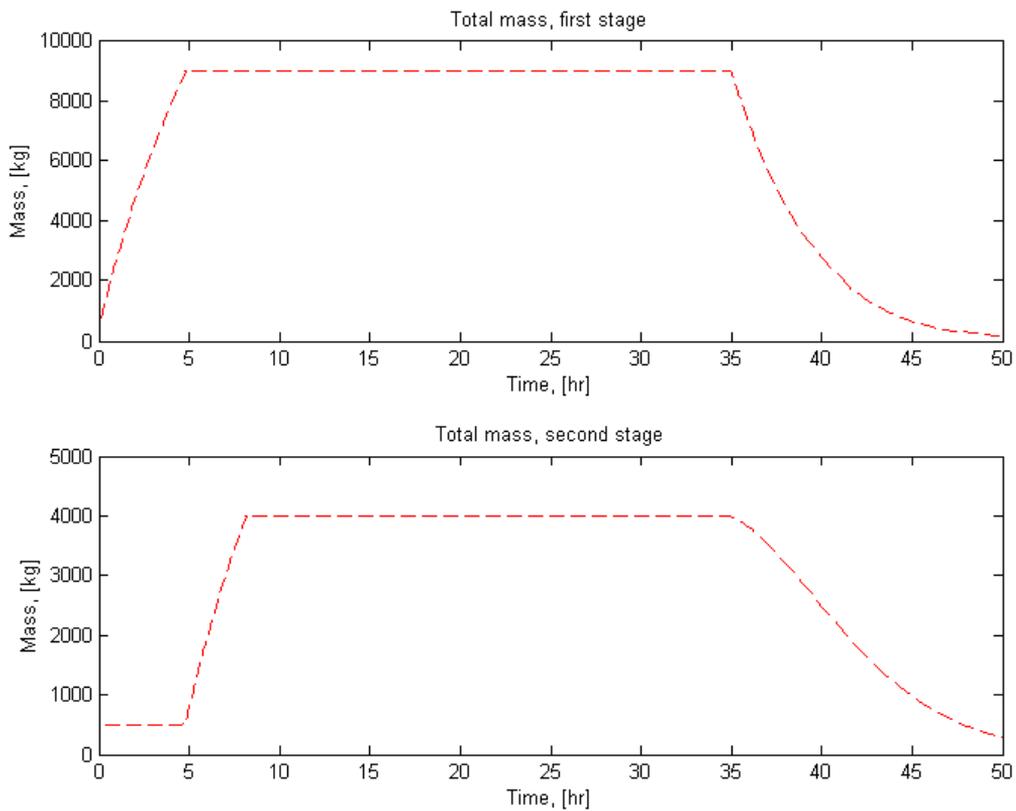


Figure 7: Total mass in tanks in two step MEA reclaiming, operated at cost optimized process conditions.

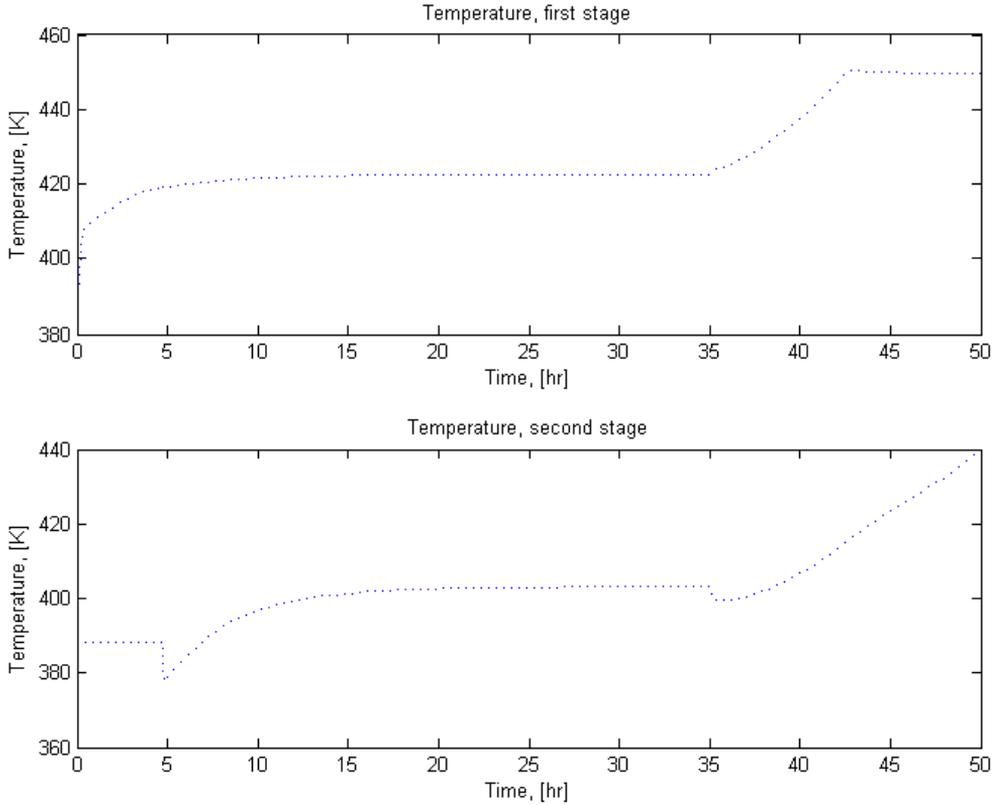


Figure 8: *Temperature in two step MEA reclaiming, operated at cost optimized process conditions.*

Figure 8 shows the development of temperature throughout the running time of the reclaiming. As can be seen, the temperature is rising while the vessels are filling up, then stabilizing gradually in the semi-steady state period. Under termination, the temperature is rising dramatically, specially in the second stage. This is probably because of the high concentration of degradation products, no cold inlet that needs heating, and increased reaction rate.

The plots in Figure 9 reflects the fact that water is more volatile than MEA. Much of the water is evaporated in first stage, and second stage vapour stabilizes at equal amount of MEA and water in vapour stream. The vaporization of MEA is at its highest in the first stage right after termination has been initiated. This is probably because the temperature is rising while the composition and amount has not been effected too greatly right after inlet closing. In second stage, however, the vapour stream is effected immediately. This is probably because this is a smaller volume, and a change in inlet composition has a greater effect.

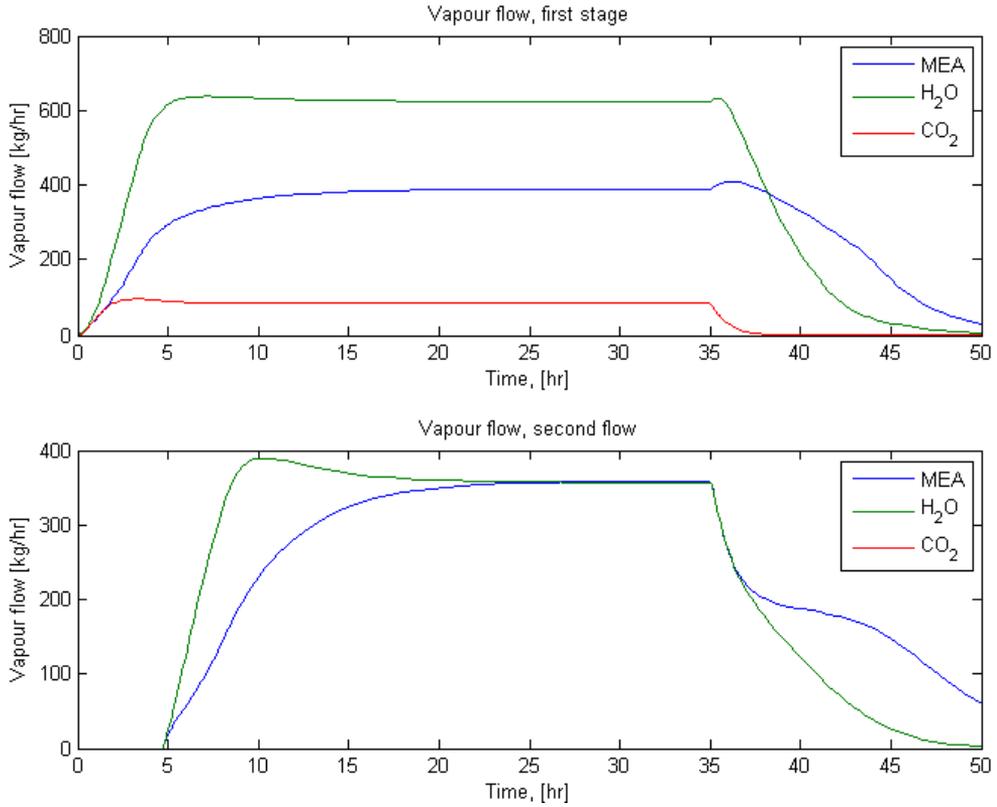


Figure 9: *Vapour flow in two step MEA reclaiming, operated at cost optimized process conditions.*

As expected, the liquid outlet follows the total mass of the reclaiming vessels, see figure 10. It only deviates in total amount (the ratio between components is the same), and when the batch mode is running.

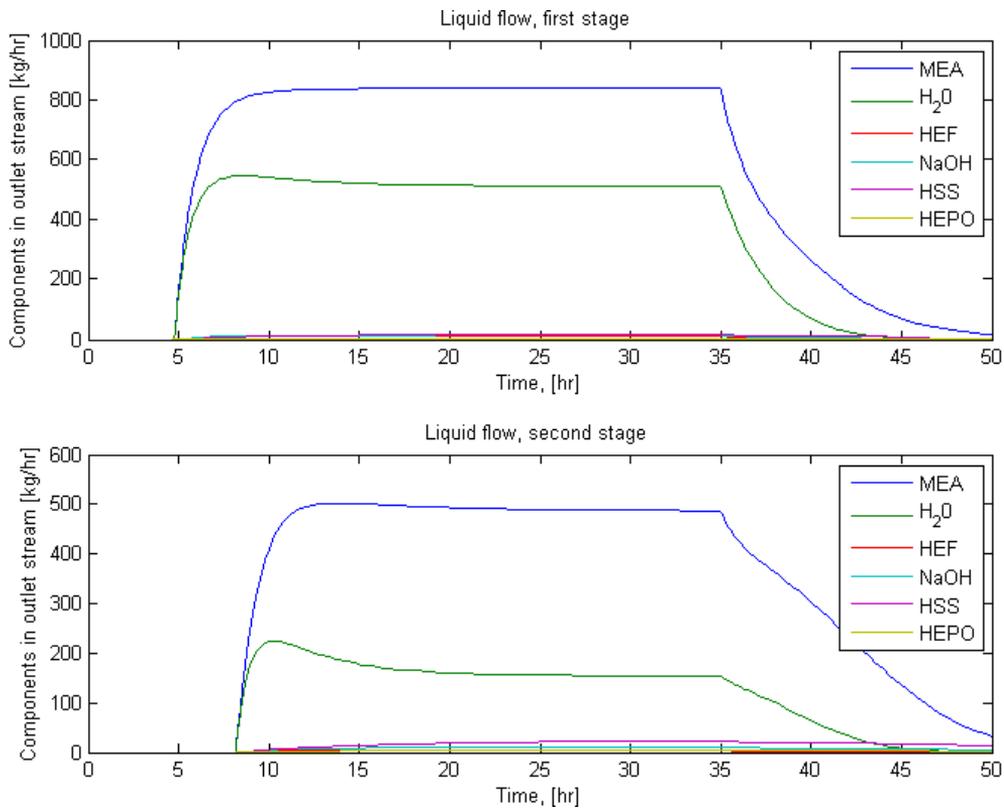


Figure 10: *Liquid flow in two step MEA reclaiming, operated at cost optimized process conditions.*

The minimum found is one where heat flow into first stage is approximately twice the amount that enters the second stage, see Figure 11. This is probably linked to the total mass of the bulk liquid: the first stage has more than twice the volume than the second.

The heat of the second stage starts up before the inlet is opened, i.e. while first stage still is in batch mode. This is because the heat input is defined from volume. To avoid problems, a small volume is assumed present also before start up for both reclaiming vessels. Therefore, heat flow will not be zero though the vessel is inactive. Due to rising temperatures, the heat lost is decreasing slower than the heat input of the vessels in termination phase.

When comparing the output of the first stage with and without an active second stage, the outputs are close to identical. The main difference is the amount of heat lost shown in Figure 12 e, which increases considerably when second is ignored.

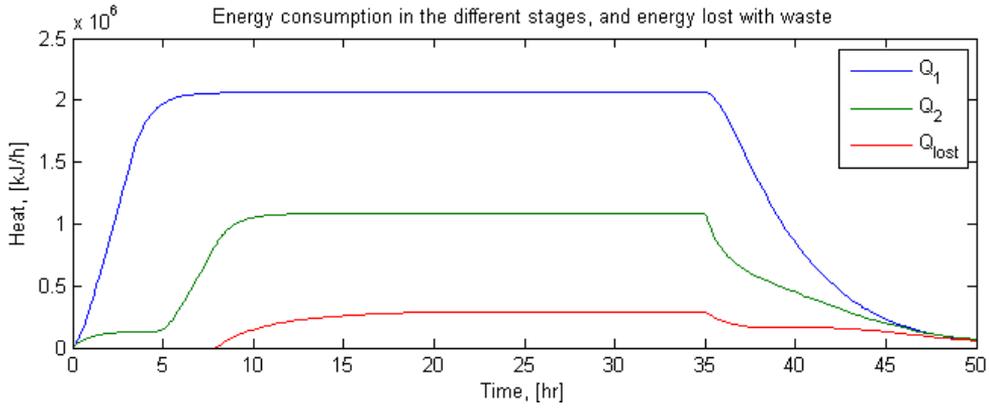


Figure 11: *Energy consumption in two step MEA reclaiming, operated at cost optimized process conditions.*

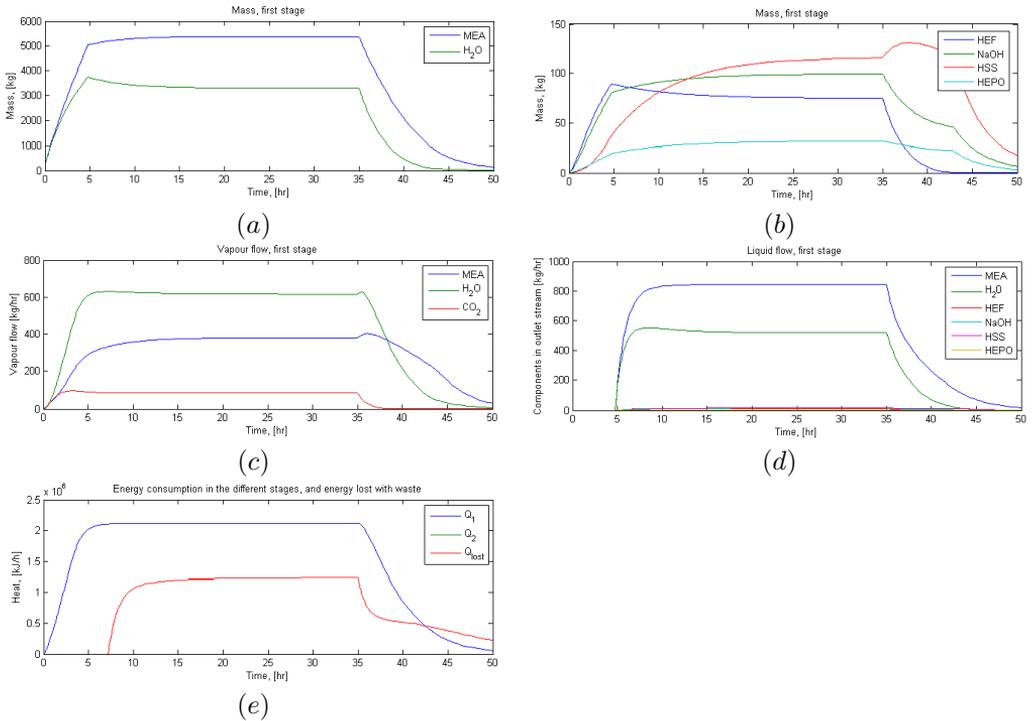


Figure 12: *Output from optimization when low pressure stage is kept inactive. (a): mass of water and MEA in first stage. (b): Degradation products in first stage. (c): Vapour flow out of first stage. (d): Liquid flow out of first stage. (e): Heat input and lost heat in waste.*

8 Discussion

Based on the optimization results, it is evident that a second, low pressure stage is profitable in steady state operation. The temperature in the first stage is close to maximum (428 K). In other words, this stage is working at almost maximum capacity. Also, as shown in section 7, the is at optimal operation independent of the second stage. This means that without the second stage, only 36.5 % of the MEA in the slipstream is returned to the main plant.

As discussed in Chapter 7, the model outputs are logical compared to what is expected for the model equations.

As mentioned the output of the program varies in different runs. The pressure of the second stage is the variable changing most from run to run, along with the value of objective function. It seems to be stopping and returning answers around a minimum. This is probably due to the loose demands of accuracy set in options for the optimization: the point reached is "close enough" to satisfy the defined tolerances for the optimization, though not at the minimum. Approaches from different sides of the minimum will then return different values. For future work, it could be an idea looking into ways of doing this more robust.

'fmincon' and 'ods15s' have different approaches to solving the model: ods15s works from a dynamic approach, starting at $t = 0$ when the slip stream is opened. From this it is changing with time reaching steady state, only dealing with realistic solutions for the system. The optimization is not working relative to time, and iterations can move freely outside conditions realistic for the system, and change them to fit the demands set by the model. As the tolerance for the constraints of optimization are quite loose, the error could have been considerable. But it is apparent that the two different approaches are reaching the same steady state point. As shown in Table 6, there is no difference in atleast the four first significant figures between the solution found by 'fmincon' and the steady state solution of 'ods15s' with optimal input.

It should be mentioned that the models for evaporation, reaction and many of the parameters used are based on assumptions. There is a big lack of knowledge considering non-ideal behaviour and properties of compounds in this process. The mechanisms of degradation and reaction is not yet fully understood, and information is kept secret for commercial reasons. The model for evaporation is simple, and model outputs are not compared to actual values. Therefore, it is difficult to say how accurate this is. For future work, a better model should be included. This, however, is the case for both reclaiming stages. Therefore this does not necessarily mean that the advantage of a second stage changes

though the liquid-vapour equilibrium might.

There is not included in the model any equations of degradation. Though residence time is relatively short compared to the residence time of the entire plant, the temperature is higher. Therefore it is possible that some degradation will take place in the reclaimer. It is also assumed constant composition in inlet. Over time, the degradation products will be removed from the main stream, and the concentration will consequently be reduced. This is not taken into account in the model as the optimization is looking at steady state.

The profitability of a second stage is not only depending on the operating cost. A second low pressure stage will increase the building cost and cost of investment. There will be need for one more heat exchanger to exploit the heat in the low pressure vapour stream, and a pump to increase the pressure so the mentioned stream can re-enter into the main stream. There is also some extra piping, equipment for lowering pressure in liquid stream between first and second stage, and a second vessel that can withstand vacuum. If a second stage is profitable considering this is not investigated.

9 Conclusion

From the perspective of operational costs, the optimization shows that the two stage reclaiming process is a feasible project for further investigation. At optimum operation conditions, 63.9 % of the MEA lead into the reclaimer is returned to the main CO₂ capturing plant, 36.5 % in first stage and 27.4 % in second stage. The amount of MEA reclaimed is in other words almost doubled, only costing a small amount of power for compressing the low pressure vapour stream up to the pressure of the rest of the system (after condensation). If the model is close to correct, it is reasonable to recommend looking into the building costs, and do a new feasibility study on the basis of this.

The model used in this study have however not been tested against values from an actual reclaimer. It is therefore difficult to actually say something definite from the results found. There are several insecurities concerning actual inlet composition, degradation products properties of degradation products, degradation rate, reaction rate and vapour/liquid equilibrium. For some of these insecurities are equal for both reclaimer, and therefore is not necessarily of too grave.

The program seems to have a good enough structure, though some work is needed to find initial points that returns global minimum. It seems that the objective function is sensitive to change in the pressure of second stage close to minimum. Due to the need for quite high error tolerance in the optimization, this leads to somewhat different solution vectors for each run.

9.1 Recommendation for future work

For future work, the following items can be investigated.

- Gather more information about properties of degradation products
- Include a better model of evaporation
- Test model against actual plant outputs
- Do a complete economic analysis of the entire reclaimer system
- Looking into ways of making the optimization more robust, especially considering second stage pressure and objective function relation.

A Derivation of model equations

A.1 Mass balances

In general, the mass balance equations derives from the general balance equation a-1. Mass balance for a species i can be written as shown in equation a-2.

$$Accumulation = In - Out + Generated \quad (a-1)$$

$$\frac{dm_i}{dt} = \dot{m}_{i,in} - \dot{m}_{i,out} + \dot{m}_{i,gen} = M_{w,i}\dot{n}_{i,in} - M_{w,i}\dot{n}_{i,out} + M_{w,i} * R * V_{Rec} \quad (a-2)$$

The outlet can again be separated into liquid and vapour flow $\dot{m}_{i,out} = \dot{m}_{i,vap} + \dot{m}_{i,liq}$. For total mass, the change per time can be written as a sum of change in all species.

$$\frac{dM}{dt} = \sum_i \frac{dm_i}{dt} \quad i \in [A, B, C, D, E, F, G] \quad (a-3)$$

In iterations, mass is directly calculated from $m_{new} = m_{old} + \frac{dm}{dt}$. This is further used to calculate volume (V). The problem is simplified with the assumption of constant density (ρ) (see equation a-4). The differential volume can then be calculated by the change in mass (equation a-5).

$$V = \frac{M}{\rho} \quad (a-4)$$

$$\frac{dV}{dt} = \frac{\frac{dM}{dt}}{\rho} \quad (a-5)$$

It should be noted that this is done for the two stages of the semi multi-effect reclaimer separately. It is viewed as two different control volumes, where liquid outlet of first stage is fed into the next stage: $\dot{m}_{liq,1} = \dot{m}_{in,2}$.

A.2 Energy balance

A typical energy balance equation is shown (a-6) where heat rate into system (\dot{Q}), work done by system on surroundings (\dot{W}) and energy entering and leaving system with mass flow, is included.

$$\frac{dE_{Rec}}{dt} = \dot{Q} - \dot{W} + \sum_i \dot{n}_{i,in} E_{i,in} - \sum_i \dot{n}_{i,out} E_{i,out} \quad (a-6)$$

The work term can be divided into several different classes of work, e.g. shear work, shaft work and flow work. Only the last is included in the model, and is shown in equation a-7. P is in this equation the total pressure of the system. \tilde{V}_i is the specific molar volume of

component i .

$$\dot{W} = - \sum_i \dot{n}_{i,in} P \tilde{V}_{i,in} + \sum_i \dot{n}_{i,out} P \tilde{V}_{i,out} \quad (\text{a-7})$$

Energy of mass flows can consist of internal, potential and other types of energy:

$$E_i = U_i + gh_i + [...] \quad (\text{a-8})$$

All these except internal energy are neglected, and energy of mass flow is assumed equal to internal energy.

$$E_i = U_i \quad (\text{a-9})$$

By combining equations a-6, a-7 and a-9, the following equation is derived.

$$\frac{dE_{Rec}}{dt} = \dot{Q} + \sum_i \dot{n}_{i,in} [U_{i,in} + P \tilde{V}_{i,in}] - \sum_i \dot{n}_{i,out} [U_{i,out} + P \tilde{V}_{i,out}] \quad (\text{a-10})$$

From Legendre transform of internal energy $U(S, V, n)$ with on volume, an expression for enthalpy can be found.

$$H_i = U_i + P \tilde{V}_i \quad (\text{a-11})$$

By substitution equation a-11 into a-10, an energy equation based on enthalpy is formed.

$$\frac{dE_{Rec}}{dt} = \dot{Q} + \sum_i \dot{n}_{i,in} H_{i,in} - \sum_i \dot{n}_{i,out} H_{i,out} \quad (\text{a-12})$$

The energy in outlet can be separated into liquid and vapour outlet. The liquid outlet is assumed to have the same composition, pressure and temperature as the reclaimer. Therefore, the molar enthalpy is the same in reclaimer and in outlet stream.

$$\sum_i \dot{n}_{i,out} H_{i,out} = \sum_i [\dot{n}_{i,out}^{vap} H_{i,vap} + \dot{n}_{i,out}^{liq} H_{i,out}^{liq}] = \sum_i [\dot{n}_{i,out}^{vap} H_{i,out}^{vap} + \dot{n}_{i,out}^{liq} H_{i,Rec}] \quad (\text{a-13})$$

Looking at left hand side of the equation, a new expression can be derived by looking on the energy of the bulk liquid of the reclaimer.

$$E_{Rec} = \sum_i \dot{n}_i E_{i,Rec} = \sum_i \dot{n}_i (H_{i,Rec} - P \tilde{V}_i) \quad (\text{a-14})$$

assuming ideal mixture of components, i.e. $\sum_i \tilde{V}_i = V_{Rec}$. Differentiating equation a-14 gives an expression for the change in energy of the reclaimer, shown in equation a-15. Here, pressure is assumed constant.

$$\frac{dE_{Rec}}{dt} = \sum_i n_{i,Rec} \frac{dH_{i,Rec}}{dt} + \sum_i H_{i,Rec} \frac{dn_i}{dt} - P \frac{dV_{Rec}}{dt} \quad (\text{a-15})$$

Enthalpy of a component can be written as following:

$$H_i = H^\circ(T_R) + \int_{T_R}^T C_{p,i} dT \quad (\text{a-16})$$

Here, T_R is some reference temperature. Assuming constant heat capacity and differentiating this with respect on time, this becomes:

$$\frac{dH_i}{dt} = C_{p,i} \frac{dT}{dt} \quad (\text{a-17})$$

The second term of equation a-15 is given by the mass balance equation a-1.

$$\frac{dn_i}{dt} = \dot{n}_{i,in} - \dot{n}_{i,out}^{vap} - \dot{n}_{i,out}^{liq} - v_i RV_{Rec} \quad (\text{a-18})$$

In equation a-18, v_i is the stoichiometric coefficient of species i . Inserted these into equation a-15, this becomes:

$$\frac{dE_{Rec}}{dt} = \sum_i n_i C_{p,i} \frac{dT}{dt} + \sum_i H_{i,Rec} (\dot{n}_{i,in} - \dot{n}_{i,out}^{vap} - \dot{n}_{i,out}^{liq}) - \sum_i H_{i,Rec} v_i RV_{Rec} - P \frac{dV_{Rec}}{dt} \quad (\text{a-19})$$

Then two expressions for $\frac{dE_{Rec}}{dt}$ is found, and equations can be put together.

$$\begin{aligned} & \dot{Q} + \sum_i \dot{n}_{i,in} H_{i,in} - \sum_i [\dot{n}_{i,out}^{vap} H_{i,vap} + \dot{n}_{i,out}^{liq} H_{i,Rec}] \\ &= \sum_i n_i C_{p,i} \frac{dT}{dt} + \sum_i H_{i,Rec} (\dot{n}_{i,in} - \dot{n}_{i,out}^{vap} - \dot{n}_{i,out}^{liq}) - \sum_i H_{i,Rec} v_i RV_{Rec} - P \frac{dV_{Rec}}{dt} \end{aligned} \quad (\text{a-20})$$

Rearranging the latter equation gives equation a-22. The reaction term is abbreviated by introducing heat of reaction:

$$\sum_i v_i H_{i,Rec} = \Delta H_{rx} \quad (\text{a-21})$$

$$\dot{Q} + \sum_i \dot{n}_{i,in} (H_{i,in} - H_{i,Rec}) - \sum_i \dot{n}_{i,out}^{vap} (H_{i,vap} - H_{i,Rec}) + \Delta H_{rx} RV_{Rec} + P \frac{dV_{Rec}}{dt} \quad (\text{a-22})$$

Please notice that in equation a-20, there were two terms of $\dot{n}_{i,out}^{liq} H_{i,Rec}$ with different signs. Therefore these cancels each other, and this term disappears.

Enthalpy

The enthalpy terms of equation a-22 (excluding reaction of heat) needs to be further investigated.

There are three terms to consider when looking at enthalpy in the reclaimer. There

is energy leaving with the vapour, with the liquid outlet, and energy entering and is used for heating the inlet stream. As mentioned above, the energy leaving with liquid outlet is cancelled out, and therefore the two others are the only concerns.

Following MEA or water from entering the reclaimer until it is evaporated, it needs to be heated from inlet temperature to boiling point, and an amount of heat to evaporate. This can be written as shown in equation a-23.

$$dH_{i,vap} = \int_{T_{in}}^{T_b} C_{p,i} d\tau + \Delta H_{i,vap}(T_b) \quad (\text{a-23})$$

Enthalpy entering the system with inlet flow:

$$H_{i,in}(T_{in}) = H_i^\circ(T_{ref}) + \int_{T_{ref}}^{T_{in}} C_{p,i} d\tau \quad (\text{a-24})$$

Molar enthalpy in reclaimer can also be written as the enthalpy of the inlet flow + the difference between molar enthalpy in reclaimer and the inflow:

$$H_{i,Rec} = H_{i,in}(T_{in}) + \int_{T_{in}}^{T_{Rec}} C_{p,i} d\tau \quad (\text{a-25})$$

By combining equations a-23, a-24 and a-25, the energy leaving vapour can be written:

$$H_{i,vap} = H_{i,in} + dH_{i,vap} = H_{i,Rec}(T_{Rec}) + \Delta H_{i,vap}(T_b) \quad (\text{a-26})$$

Back to equation a-22, the terms of change in energy due to mass transfer can be written as follows:

$$\begin{aligned} \sum_i \dot{n}_{i,in} (H_{i,in} - H_{i,Rec}) &= - \sum_i \dot{n}_{i,in} ([H_{i,in}(T_{in}) + \int_{T_{in}}^{T_{Rec}} C_{p,i} d\tau] - H_{i,in}) \\ &= - \sum_i \dot{n}_{i,in} \int_{T_{in}}^{T_{Rec}} C_{p,i} d\tau \end{aligned} \quad (\text{a-27})$$

$$\sum_i \dot{n}_{i,out}^{vap} (H_{i,vap} - H_{i,Rec}) = \sum_i \dot{n}_{i,out}^{vap} ([H_{i,Rec}(T_{Rec}) + \Delta H_{i,vap}(T_b)] - H_{i,Rec}) = \Delta H_{i,vap} \quad (\text{a-28})$$

Assuming constant heat capacity, and solving equation a-22 with respect on $\frac{dT}{dt}$, it is possible to calculate the time differential of temperature by equation a-29.

$$\frac{dT}{dt} = \frac{\dot{Q} - \sum_i \dot{n}_{i,in} C_{p,i} (T_{Rec} - T_{in}) - \sum_i \dot{n}_{i,out}^{vap} \Delta H_{i,vap} + \Delta H_{rx} RV_{Rec} + P \frac{dV_{Rec}}{dt}}{\sum_i n_i C_{p,i}} \quad (\text{a-29})$$

A.3 Vapour-liquid equilibrium

To calculate the pure vapour pressures of MEA and water, Antoine's equation is used, see equation a-30.

$$\log(P_i) = A - \frac{B}{T + C} \quad (\text{a-30})$$

In this equation, P_i is the vapour pressure of component i , T is the temperature of the system (in this case, T_{Rec}), and A , B and C are the Antoine constants. These constants for MEA and water are presented in Table a-1. It is assumed that the liquid in the

Table a-1: *Constants of Antoine's equation for MEA and water*

Species	A	B	C
MEA	7.96681	1668.210	228.00
Water	8.02401	1921.6	203.3

reclaimer is an ideal solution. This is probably not feasible, but it is difficult to find any information on the mixture. The saturated vapour pressure is calculated by Raoult's law:

$$P_{sat,i} = x_i P_j \quad (\text{a-31})$$

In this equation, x_i is the fraction of the species i in the bulk liquid. In the case of reclaiming, MEA and water are assumed that the only species volatile enough for vaporizing in the reclaimer (excluding CO_2 which already is in vapour phase).

The amount of MEA and water is calculated from the ratio between the saturation pressures.

$$\alpha = \frac{P_{MEA}}{P_{H_2O}} \quad (\text{a-32})$$

The fraction of the vapour can be calculated from the pressure as following:

$$y_{MEA} = \frac{P_{MEA}}{P_{tot}} \quad (\text{a-33})$$

Rearranging the latter equation, an expression for weight fraction of water as an expression of weight fraction of MEA.

$$y_{H_2O} = \alpha * y_{MEA} \quad (\text{a-34})$$

The mass fractions sums up to one.

$$y_{H_2O} + y_{MEA} = 1 \quad (\text{a-35})$$

Inserting equation a-34 into a-35, equation a-36 can be derived.

$$\alpha * y_{MEA} + y_{MEA} = 1 \quad (\text{a-36})$$

Solving this with respect on y_{MEA} , the composition of the gas phase can be calculated.

$$1 = y_{MEA}(1 + \alpha) \quad (\text{a-37})$$

$$y_{MEA} = \frac{1}{1 + \alpha} \quad (\text{a-38})$$

Combining equations a-33 and a-38 and the fact that $P_{tot} = \sum_j P_j$ gives the actual pressure of each species.

$$P_{MEA} = P_{tot} \frac{1}{1 + \alpha} \quad (\text{a-39})$$

$$P_{H_2O} = P_{tot} - P_{MEA} \quad (\text{a-40})$$

The difference between the saturation pressure and actual pressure of the components is the driving force of evaporation. Therefore, the amount of MEA and water can be calculated from this, times a scaling constant β .

$$\dot{n}_{MEA} = \beta_{MEA} * (P_{sat,MEA} - P_{MEA}) * M_{w,MEA} \quad (\text{a-41})$$

$$\dot{n}_{H_2O} = \beta_{H_2O} * (P_{sat,H_2O} - P_{H_2O}) * M_{w,H_2O} \quad (\text{a-42})$$

B Parameters and properties used in model

Table a-2: *Parameters used in modelling and optimization of a two stage MEA reclaimer process.*

Variable	Unit	Value
Heat capacity		
MEA	kJ/kmol,K	155.8
Water	kJ/kmol,K	75
HEF	kJ/kmol,K	100*
NaOH	kJ/kmol,K	90
HSS	kJ/kmol,K	83*
HEPO	kJ/kmol,K	100*
CO ₂	kJ/kmol,K	0**
Molar mass		
MEA	kg/kmol	61.8
Water	kg/kmol	18
HEF	kg/kmol	89.08
NaOH	kg/kmol	40
HSS	kg/kmol	68*
HEPO	kg/kmol	144.17
CO ₂	kg/kmol	44
Heat of evaporation (ΔH_{vap})		
MEA	kJ/kmol	50438
Water	kJ/kmol	44000
Boiling points		
MEA	°C	170.5
Water	°C	100
Evaporation flux function (β)		
MEA	-	1*
Water	-	1*
Other		
Heat of reaction	kJ/kmol	-10000
Reaction rate	m ³ /kmol,h	1*
Pressure, first stage	kPa	190

*Values not available, educated guesses based on similar values.

** Excluded from calculation of heating, heat capacity not necessary.

C Matlab code

main: Main script

```
1  %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
2  %
3  %           Main script for steady state optimization of           %
4  %                   amine absorption model                       %
5  %                   Master thesis if Sigrun Dyvik Berstad       %
6  %                   Institute of chemical process technology, NTNU %
7  %                   Trondheim, spring 2013                     %
8  %
9  %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
10 clear all
11 clc
12 clear functions
13 constant
14 close all
15 global ssM x0
16 q_init = [0.3 0.1 0.8 0 5000];
17 x0 = odsmain(q_init,1)
18 lb = zeros(1,length(x0));
19 ub = ones(1,length(x0)).*1.1;
20 ssM = [x0(10) x0(30)];
21 %ub(8) = 30/31;
22 ub(21) = 2500/1500;
23 ub(41) = 2500/1000;
24 options = optimset('TolFun',0.006,'TolCon',10e-5,'Display','on',...
25 'UseParallel','always','Algorithm','sqp','Diagnostics',...
26 'on','MaxFunEval',200000,'TolX',10e-15,'MaxIter',10000);
27 %[Aeq,beq] = lincon(x0);
28 [x,fval,exitflag,hessian]=fmincon(@(x)objfunc(x),x0,[],[],[],[],lb,ub,@(x)nonlCon(x),options)
29 fval
30 exitflag
31 M = odsmain([x(42:44) 0 50],2);
32 [M(1:45); x; x0]
```

constant: Constants called by main, global parameters

```
1 function [] = constant()
2 global p str
3 p.slips = 2500;%kg/hr
4 %      MEA  water HEF   NaOH HSS   HEPO   CO2
5 %wp = [0.5 0.5 0 0 0 0 0]';
6 wp = [0.485 0.454 0.013 0.01 0.001 0.002 0.035]';
7 %      A    B  C    D  E  I    J
8 p.CP = [155.8 74 100 90 83 100 0.]';
9 %      A    B  C      D  E  I      J
10 p.MW = [61.08 18 89.08 40 68 144.17 44]';
11 %      A    B
12 p.Hvap = [50438 44000]';
13 p.Hrx = 10000;
14 p.k = 1;
15 p.Ptot = 190;
16 p.Tin = 273.15 + 119;
17 %p.Q = 100000;
18 p.Qloss = 18000;
19 str.Minn = p.slips.*wp;
20 p.rho = 998;
21 %p.P2
```

odsmain: Main script for ordinary differential solver

```
1 function x0 = odsmain(q,r)
2 global p
3 M0 = zeros(1,45);
4 %initial concentrations and conditions
5 M0(10) = 500/10000; %Initial: 500 kg mix in first stage. Deviding with
6 %10000 so that all x-es are in the same scale.
7 M0(1:2) = 0.5; %Weight fraction, MEA and water
8 M0(7) = M0(10)*10000/p.rho/10; %Volume – calculate from mass and density.
9 %Devide by 10 to get into scale, max = 1.
10 M0(8) = 393/(155+273); %Initial temperature, scaled so max = 1
11 M0(11:12) = 0.5; %Initial wt fraction, vapour stage 1
12 M0(14) = 0; %Initial vapour flow from stage 1
13 M0(15:16) = 0.5; %Wt frac, liquid stage 1
14 M0(21) = 0; %Initial liquid flow, stage 1
15 M0(30) = 500/5000; %Initial: 200 kg mix in second stage. Derived with 5000.
16 M0(22:23) = 0.5; %Weight fraction MEA and water, stage 2
17 M0(28) = M0(30)*5000/p.rho/5; %Volume stage 2 – scaled to max = 1
18 M0(29) = 393/(155+273); %Initial temperature stage 2, scaled to max = 1
19 M0(31:32) = 0.5; %Wt frac, vapour stage 2
20 M0(34) = 0; %Initial vapour flow from stage 2
21 M0(35:36) = 0.5; %Wt frac, liquid stage 2
22 M0(41) = 0; %Initial liquid flow, stage 2
23 M0(42) = q(1); %Energy consumption, 10^6 kJ stage 1
24 M0(43) = q(2); %Energy consumption, 10^6 kJ stage 2
25 M0(44) = q(3); %Pressure, stage 2. 10^2kPa
26 t = [q(4) q(5)];
27
28 options = odeset('RelTol',1e-4,'AbsTol',1e-4);
29 if r == 1
30 [t,X] = ode15s(@deriveods,t,M0,options);
31 %X(:,46) = X(:,42).*10^6;
32 %X(:,47) = X(:,43).*10^6;
33 n=1;
34 n = plotting2(t,X,n);
35 elseif r == 2
36 M0(46) = 0;
37 M0(47) = 0;
38 [t,X] = ode15s(@deriveods2,t,M0,options);
39 else
40 disp('invalid choise input')
41 end
42 x0 = X(end,:);
43 %disp(X(:,7))
44 %disp(X(:,45))
45 if r == 2
46 n = 1;
47 n = plotting(t,X,n);
```

```
48 else
49 end
50 end
```

deriveods: Script returning derivatives of vector

```
1 function massder = deriveods(t,M) ...
    %Comments for transformation to steady state
2 global p str %outlet
3 %Ensuring that volume feasible relative to mass
4 Mtot1 = M(10)*10000;
5 Mtot2 = M(30)*5000;
6
7 %Ensuring all weight fractions are feasible
8 x1 = fraccontr(M(1:6));
9 %v1 = fraccontr(M(11:13));
10 %l1 = fraccontr(M(15:20));
11 x2 = fraccontr(M(22:27));
12 %v2 = fraccontr(M(31:33));
13 %l2 = fraccontr(M(35:40));
14 V1 = Mtot1/p.rho;
15 V2 = Mtot2/p.rho;
16 mass1 = x1.*Mtot1;
17 mass2 = x2.*Mtot2;
18 T1 = M(8)*(155+273);
19 T2 = M(29)*(155+273);
20 P2 = M(44)*100;
21 if V1<7
22     Q1 = M(42)*10e6/7*V1;
23 else
24     Q1 = M(42)*10e6;
25 end
26 if V2<4
27     Q2 = M(43)*10e6/4*V2;
28 else
29     Q2 = M(43)*10e6;
30 end
31 C = mass1./p.MW(1:6)./V1; %Concentration of components [kmol/m^3]
32 C2 = mass2./p.MW(1:6)./V2; %Concentration of components [kmol/m^3]
33 %M(10) = sum(mass1) + M(9); %Total mass
34 %M(22) = sum(mass2);
35 %Min2 = M(15:20);
36 %Partial pressure, pure of A and B
37 %1st stage
38 Pp(1) = (10^(8.024 - (1921.6/(T1 - 273.15 + 203.3))))/760*1.0135*100;
39 Pp(2) = (10^(7.966 - (1668.21/(T1 - 273.15 + 228))))/760*1.0135*100;
40 %2nd stage
41 Pp(3) = (10^(8.024 - (1921.6/(T2 - 273.15 + 203.3))))/760*1.0135*100;
42 Pp(4) = (10^(7.966 - (1668.21/(T2 - 273.15 + 228))))/760*1.0135*100;
43
44 %wt. fraction in liquid
45 x = x1(1:2); %1st stage
46 x(3:4) = x2(1:2); %2nd stage
```

```

47 PS = x.*Pp'; %Equillibrium/saturated pressures (Raoult's law)
48 %Pressure ration
49 ryayb = (Pp(1)*x(1))/(Pp(2)*x(2)); %1st stage
50 ryayb2 = (Pp(3)*x(3))/(Pp(4)*x(4)); %2nd stage
51 %Pressure, B
52 P(2,1) = p.Ptot*(1/(1+ryayb)); %1st stage
53 P(4) = P2*(1/(1+ryayb2)); %2nd stage
54 %Pressure, A
55 P(1) = p.Ptot -P(2); %1st stage
56 P(3) = P2 -P(4); %2nd stage
57 %Reaction rate: C + D = A + B + E [kmol/m^3,hr]
58 R = p.k*C(3)*C(4); %1st stage
59 R(2) = p.k*C2(3)*C2(4); %2nd stage
60 %Heating, inlet flow [kJ/hr]
61 Q = str.Minn./p.MW.*p.CP*(T1-p.Tin); %Heating, inlet
62 Qtot = sum(Q); %--||--
63 beta = [1 1]'; %suggestion [kmol/kPa,hr]
64 alpha = p.MW(1:2).*beta;
65 n = [alpha; alpha].*(PS - P); %kg/h ...
    Gas outlet - amine and water
66 %ensuring positive flow of vapour
67
68 if min(n) < 0
69     if n(1) < 0
70         n(1) = 0;
71     end
72     if n(2) < 0
73         n(2) = 0;
74     end
75     if n(3) < 0
76         n(3) = 0;
77     end
78     if n(4) < 0
79         n(4) = 0;
80     end
81 end
82 MtotVap1 = sum([n(1:2); str.Minn(7)]);
83 MtotVap2 = sum(n(3:4));
84 Hvap = [p.Hvap; p.Hvap].*(n./[p.MW(1:2); p.MW(1:2)]); ...
    %Heat to evaporate [kJ/hr]
85 Qrx = p.Hrx*R(1)*V1; %Heat of reaction [kJ/hr]
86 Qrx2 = p.Hrx*R(2)*V2;
87 dM = V1*p.MW*R(1); %Conversion by reaction [kmol/hr]
88 dM2 = V2*p.MW*R(2);
89
90 %calculating liquid outlet nessecary to maintain mass concervation
91 Mtotout1 = sum(str.Minn) - sum(MtotVap1);
92 if Mtot1>=9000
93     Minn2 = Mtotout1.*x1;
94 else

```

```

95     Minn2(1:6,1) = 0;
96 end
97 %Calculating change in components, 1st stage
98 Mder = str.Minn(1:2) - n(1:2) + [dM(1); 0] - Minn2(1:2);    %Accumulation = ...
    inn - out + produced
99 Mder(3:4) = str.Minn(3:4) -dM(3:4) -Minn2(3:4);
100 Mder(5) = str.Minn(5) + dM(5) -Minn2(5);
101 Mder(6) = str.Minn(6) -Minn2(6);
102 Mder(9) = 0;
103 Mder(10) = sum(Mder);                                     %Total mass balance
104 Mder(7) = Mder(10)*V1/Mtot1;                             %Change in volume
105 Qb = Q1 - p.Qloss - Qtot - sum(Hvap(1:2)) + Qrx +p.Ptot*Mder(7);%Energy balance
106 QT = mass1(1:6) ./p.MW(1:6) .*p.CP(1:6);               %Energy balance, components
107 Mder(8) = Qb./sum(QT);                                   %Change in temperature
108 %Mder(14) = 0;
109 %second stage
110 %calculating liquid outlet nessecary to maintain mass concervation
111 Qtot2 = sum(Minn2 ./p.MW(1:6) .*p.CP(1:6) *(T2-T1));    %2nd ...
    stage
112 waste = sum(Minn2) - MtotVap2;
113 if Mtot2 >= 4000
114     Mout2 = waste.*x2;    %calculating mass of components leaving 1st
115 else                                %stage, entering 2nd
116     Mout2(1:6,1) = 0;
117 end    %Calculating change in ...
    components, 1st stage
118 Mder(22:23) = Minn2(1:2) - n(3:4) + [dM2(1);0] -Mout2(1:2);    %Accumulation ...
    = inn - out + produced
119 Mder(24:25) = Minn2(3:4) - dM2(3:4) -Mout2(3:4);
120 Mder(26) = Minn2(5) + dM2(5) -Mout2(5);
121 Mder(27) = Minn2(6) - Mout2(6);
122
123 Mder(30) = sum(Mder(22:27));                                %Total mass ...
    balance
124 Mder(28) = Mder(30)*V2/Mtot2;                             %Change in volume
125 Qb2 = Q2 - Qtot2 - sum(Hvap(3:4)) + Qrx2 +P2*Mder(28);%Energy balance
126 %remember: removed Qloss from latter line
127 QT2 = mass2 ./p.MW(1:6) .*p.CP(1:6);                   %Energy balance, components
128 Mder(29) = Qb2./sum(QT2);                                %Change in temperature
129 %Mder(34) = sum(n(3:4))/650 - M(34);
130 %Mder(41) = sum(waste)/ - M(41);
131
132 %-----Scaled diff-----
133 %First stage
134 %comp. in reclaimers
135 Mdersc = zeros(45);
136 Mdersc = (x1*Mtot1 + Mder(1:6))/(Mtot1 + Mder(10)) - M(1:6);
137 Mdersc(9) = - M(9); %keeping = 0
138 %Vaporation
139 if MtotVap1 <= 0

```

```

140     Mdersc(11:13) = 0;
141 else
142     Mdersc(11:13) = [n(1:2); str.Minn(7)]./MtotVap1 - M(11:13);
143 end
144 Mdersc(14) = MtotVap1/1000 - M(14);
145 %Liquid outlet
146 if sum(Minn2)>0
147     Mdersc(15:20) = Minn2./sum(Minn2)- M(15:20);
148     Mdersc(21) = sum(Minn2)/1500 - M(21);
149 else
150     Mdersc(15:21) = 0;
151 end
152 %Temperature
153 Mdersc(8) = Mder(8)/(155+273);
154 %Volume
155 Mdersc(7) = V1/10 - M(7);
156 %Total mass in reclaimers
157 Mdersc(10) = Mder(10)/10000;
158
159
160 %second stage
161 if Mtot1 >= 9000
162 Mdersc(22:27) = (x2*Mtot2 + Mder(22:27))/(Mtot2 + Mder(30)) - M(22:27);
163 %vaporation
164 if MtotVap2 <= 0
165     Mdersc(31:33) = 0;
166 else
167     Mdersc(31:33) = [n(3:4); 0]/MtotVap2 - M(31:33);
168 end
169 Mdersc(34) = MtotVap2/650 - M(34);
170 %liquid outlet
171 if sum(Mout2) > 0
172     Mdersc(35:40) = Mout2./sum(Mout2) - M(35:40);
173     Mdersc(41) = sum(Mout2)/1000 - M(41);
174 else
175     Mdersc(35:41) = 0;
176 end
177 %Temperatures
178 Mdersc(29) = Mder(29)/(155+273);
179 %Volumes: Only correcting for deviation between calculated and
180 Mdersc(28) = V2/5 - M(28);
181 %Total mass in reclaimers
182 Mdersc(30) = Mder(30)/5000;
183 %Energy lost in waste i.e. not led back into main process simple
184 %calculation.
185 Mdersc(45) = (Mout2./p.MW(1:6))*p.CP(1:6)*(T2-p.Tin).*10e-7 - M(45);
186 else
187     Mdersc(22:45) = 0;
188 end
189 massder = Mdersc;

```

190 end

fraccontr: Script ensuring weight fractions sums to 1

```
1 function frac = fraccontr(x)
2
3 for i = 1:length(x)
4     if x(i)<0
5         x(i) = 0;
6     else
7         end
8 end
9
10 frac = x./sum(x);
```

derivev1: Script returning derivatives of vector as constraints in optimization

```
1 function massder = derivev1(t,M) ...
    %Comments for transformation to steady state
2 global p str %outlet
3
4 %Ensuring that volume feasible relative to mass
5 Mtot1 = M(10)*10000;
6 Mtot2 = M(30)*5000;
7 %Ensuring all weight fractions are feasible
8 x1 = fraccontr(M(1:6));
9 %v1 = fraccontr(M(11:13));
10 %l1 = fraccontr(M(15:20));
11 x2 = fraccontr(M(22:27));
12 %v2 = fraccontr(M(31:33));
13 %l2 = fraccontr(M(35:40));
14 V1 = Mtot1/p.rho;
15 V2 = Mtot2/p.rho;
16 mass1 = x1.*Mtot1;
17 mass2 = x2.*Mtot2;
18 T1 = M(8)*(155+273);
19 T2 = M(29)*(155+273);
20 P2 = M(44)*100;
21 Q1 = M(42)*10e6;
22 Q2 = M(43)*10e6;
23 C = mass1./p.MW(1:6)./V1; %Concentration of components [kmol/m^3]
24 C2 = mass2./p.MW(1:6)./V2; %Concentration of components [kmol/m^3]
25 %M(10) = sum(mass1) + M(9); %Total mass
26 %M(22) = sum(mass2);
27 %Min2 = M(15:20);
28 %Partial pressure, pure of A and B
29 %1st stage
30 Pp(1) = (10^(8.024 - (1921.6/(T1 - 273.15 + 203.3))))/760*1.0135*100;
31 Pp(2) = (10^(7.966 - (1668.21/(T1 - 273.15 + 228))))/760*1.0135*100;
32 %2nd stage
33 Pp(3) = (10^(8.024 - (1921.6/(T2 - 273.15 + 203.3))))/760*1.0135*100;
34 Pp(4) = (10^(7.966 - (1668.21/(T2 - 273.15 + 228))))/760*1.0135*100;
35
36 %wt. fraction in liquid
37 x = x1(1:2); %1st stage
38 x(3:4) = x2(1:2); %2nd stage
39 PS = x.*Pp'; %Equilibrium/saturated pressures (Raoult's law)
40 %Pressure ration
41 ryayb = (Pp(1)*x(1))/(Pp(2)*x(2)); %1st stage
42 ryayb2 = (Pp(3)*x(3))/(Pp(4)*x(4)); %2nd stage
43 %Pressure, B
44 P(2,1) = p.Ptot*(1/(1+ryayb)); %1st stage
45 P(4) = P2*(1/(1+ryayb2)); %2nd stage
46 %Pressure, A
```

```

47 P(1) = p.Ptot -P(2); %1st stage
48 P(3) = P2 -P(4); %2nd stage
49 %Reaction rate: C + D = A + B + E [kmol/m^3,hr]
50 R = p.k*C(3)*C(4); %1st stage
51 R(2) = p.k*C2(3)*C2(4); %2nd stage
52 %Heating, inlet flow [kJ/hr]
53 Q = str.Minn./p.MW.*p.CP*(T1-p.Tin); %Heating, inlet
54 Qtot = sum(Q); %---||---
55 beta = [1 1]'; %suggestion [kmol/kPa,hr]
56 alpha = p.MW(1:2).*beta;
57 n = [alpha; alpha].*(PS - P); %kg/h ...
    Gas outlet - amine and water
58 %ensuring positive flow of vapour
59
60 if min(n) < 0
61     if n(1) < 0
62         n(1) = 0;
63     end
64     if n(2) <0
65         n(2) = 0;
66     end
67     if n(3) <0
68         n(3) = 0;
69     end
70     if n(4) <0
71         n(4) = 0;
72     end
73 end
74 MtotVap1 = sum([n(1:2); str.Minn(7)]);
75 MtotVap2 = sum(n(3:4));
76 H vap = [p.Hvap; p.Hvap].*(n./[p.MW(1:2); p.MW(1:2)]); ...
    %Heat to evaporate [kJ/hr]
77 Qrx = p.Hrx*R(1)*V1; %Heat of reaction [kJ/hr]
78 Qrx2 = p.Hrx*R(2)*V2;
79 dM = V1*p.MW*R(1); %Conversion by reaction [kmol/hr]
80 dM2 = V2*p.MW*R(2);
81
82 %calculating liquid outlet nessecary to maintain mass concervation
83 Mtotout1 = sum(str.Minn) - sum(MtotVap1);
84 Minn2 = Mtotout1.*x1; %calculating mass of components leaving 1st
85 %stage, entering 2nd
86 %Calculating change in components, 1st stage
87 Mder = str.Minn(1:2) - n(1:2) + [dM(1); 0] - Minn2(1:2); %Accumulation = ...
    inn - out + produced
88 Mder(3:4) = str.Minn(3:4) -dM(3:4) -Minn2(3:4);
89 Mder(5) = str.Minn(5) + dM(5) -Minn2(5);
90 Mder(6) = str.Minn(6) -Minn2(6);
91 Mder(9) = 0;
92 Mder(10) = sum(Mder); %Total mass balance
93 Mder(7) = Mder(10)*V1/Mtot1; %Change in volume

```

```

94 Qb = Q1 - p.Qloss - Qtot - sum(Hvap(1:2)) + Qrx + p.Ptot*Mder(7);%Energy balance
95 QT = mass1(1:6)./p.MW(1:6).*p.CP(1:6);           %Energy balance, components
96 Mder(8) = Qb./sum(QT);                             %Change in temperature
97 %Mder(14) = 0;
98 %second stage
99 %calculating liquid outlet nessecary to maintain mass concervation
100 Qtot2 = sum(Minn2./p.MW(1:6).*p.CP(1:6)*(T2-T1)); %2nd ...
    stage
101 waste = sum(Minn2) - MtotVap2;
102 Mout2 = waste.*x2;           %calculating mass of components leaving 1st
103                                 %stage, entering 2nd
104 %Calculating change in components, 1st stage
105 Mder(22:23) = Minn2(1:2) - n(3:4) + [dM2(1);0] -Mout2(1:2); %Accumulation ...
    = inn - out + produced
106 Mder(24:25) = Minn2(3:4) - dM2(3:4) -Mout2(3:4);
107 Mder(26) = Minn2(5) + dM2(5) -Mout2(5);
108 Mder(27) = Minn2(6) - Mout2(6);
109
110 Mder(30) = sum(Mder(22:27)); %Total mass ...
    balance
111 Mder(28) = Mder(30)*V2/Mtot2; %Change in volume
112 Qb2 = Q2 - Qtot2 - sum(Hvap(3:4)) + Qrx2 +P2*Mder(28);%Energy balance
113 %remember: removed Qloss from latter line
114 QT2 = mass2./p.MW(1:6).*p.CP(1:6); %Energy balance, components
115 Mder(29) = Qb2/sum(QT2); %Change in temperature
116
117 %-----Scaled diff-----
118 %comp. in reclaimers
119 Mdersc = zeros(45,1);
120 Mdersc(1:6) = (x1*Mtot1 + Mder(1:6))/(Mtot1 + Mder(10)) - M(1:6);
121 Mdersc(22:27) = (x2*Mtot2 + Mder(22:27))/(Mtot2 + Mder(30)) - M(22:27);
122 Mdersc(9) = - M(9);
123 %vaporation
124 if MtotVap1 <= 0
125     Mdersc(11:13) = 0;
126 else
127     Mdersc(11:13) = [n(1:2); str.Minn(7)]./MtotVap1 - M(11:13);
128 end
129 if MtotVap2 <= 0
130     Mdersc(31:33) = 0;
131 else
132     Mdersc(31:33) = [n(3:4); 0]/MtotVap2 - M(31:33);
133 end
134 Mdersc(14) = MtotVap1/1000 - M(14);
135 Mdersc(34) = MtotVap2/650 - M(34);
136 %liquid outlet
137 Mdersc(15:20) = Minn2./sum(Minn2)- M(15:20);
138 Mdersc(35:40) = Mout2./sum(Mout2) - M(35:40);
139 Mdersc(21) = sum(Minn2)/1500 - M(21);
140 Mdersc(41) = sum(Mout2)/1000 - M(41);

```

```

141 %Temperatures
142 Mdersc(8) = Mder(8)/(155+273);
143 Mdersc(29) = Mder(29)/(155+273);
144 %Volumes: Only correcting for deviation between calculated and
145 %Mdersc(7) = V1/10 - M(7);
146 %Mdersc(28) = V2/5 - M(28);
147 %Total mass in reclaimers
148 Mdersc(10) = Mder(10)/10000;
149 Mdersc(30) = Mder(30)/5000;
150 %Energy lost in waste i.e. not led back into main process simple
151 %calculation.
152 Mdersc(45) = (Mout2./p.MW(1:6))*p.CP(1:6).*(T2-p.Tin).*10e-7 - M(45);
153
154 %massder = [Mdersc(1:10) Mdersc(22:30) Mdersc(36) Mdersc(41:45)];
155 massder = Mdersc;%[Mdersc(1:10); zeros(10,1); Mdersc(21); Mdersc(22:30); ...
    zeros(5,1); Mdersc(36); zeros(4,1); Mdersc(41:45)];
156 end

```

nonlCon: Non-linear constraints demanding steady state and mass conservation

```
1 function [c,ceq] = nonlCon(x)
2 global ssM p
3 c = 0;
4 ceq = [derivev1(1,x'); (ssM(1) - x(10)); (ssM(2) - x(30)); ...
        (ssM(1)*10000/p.rho - 10*x(7)); (ssM(2)*5000/p.rho - 5*x(28))];
5 end
```

objfunc: Objective function in optimization

```
1 function cost = objfunc(x)
2 global p
3 q = x(45)*10e7;
4 waste = x(41)*1000;
5 Amineloss = waste - (x(36)*waste);
6 Lowpres = x(34)*650;
7
8 %Prices
9 qpr = 0.0001; %NOK pr kJ
10 makeup = 11.1;
11 wastehand = 1.5;
12
13 cost = (qpr*q + 2554/15*waste/p.rho + waste*wastehand + Amineloss*makeup + ...
         qpr*sqrt(1.78/x(44)*100)*Lowpres)/10000;
14 end
```

deriveods2: Script returning derivatives of vector with termination

```
1 function massder = deriveods2(t,M)                                     ...
    %Comments for transformation to steady state
2 global p str %outlet
3 %Ensuring that volume feasible relative to mass
4 Mtot1 = M(10)*10000;
5 Mtot2 = M(30)*5000;
6 if Mtot1<0
7     Mtot1 = 0;
8 end
9 if Mtot2 <0
10    Mtot2 = 0;
11 end
12 %Ensuring all weight fractions are feasible
13 x1 = fraccontr(M(1:6));
14 %v1 = fraccontr(M(11:13));
15 %l1 = fraccontr(M(15:20));
16 x2 = fraccontr(M(22:27));
17 %v2 = fraccontr(M(31:33));
18 %l2 = fraccontr(M(35:40));
19 V1 = Mtot1/p.rho;
20 V2 = Mtot2/p.rho;
21 mass1 = x1.*Mtot1;
22 mass2 = x2.*Mtot2;
23 T1 = M(8)*(155+273);
24 T2 = M(29)*(155+273);
25 P2 = M(44)*100;
26 if V1<7
27     Q1 = M(42)*10e6/7*V1;
28 else
29     Q1 = M(42)*10e6;
30 end
31 if V2<4
32     Q2 = M(43)*10e6/4*V2;
33 else
34     Q2 = M(43)*10e6;
35 end
36 if t>35
37     if V1<9
38         Q1 = M(42)*10e6/9*V1;
39     else
40         Q1 = M(42)*10e6;
41     end
42     if V2<4
43         Q2 = M(43)*10e6/4*V2;
44     else
45         Q2 = M(43)*10e6;
46     end
```

```

47 end
48 C = mass1./p.MW(1:6)./V1;           %Concentration of components [kmol/m^3]
49 C2 = mass2./p.MW(1:6)./V2;         %Concentration of components [kmol/m^3]
50 %M(10) = sum(mass1) + M(9);         %Total mass
51 %M(22) = sum(mass2);
52 %Min2 = M(15:20);
53 %Partial pressure, pure of A and B
54 %1st stage
55 Pp(1) = (10^(8.024 - (1921.6/(T1 - 273.15 + 203.3))))/760*1.0135*100;
56 Pp(2) = (10^(7.966 - (1668.21/(T1 - 273.15 + 228))))/760*1.0135*100;
57 %2nd stage
58 Pp(3) = (10^(8.024 - (1921.6/(T2 - 273.15 + 203.3))))/760*1.0135*100;
59 Pp(4) = (10^(7.966 - (1668.21/(T2 - 273.15 + 228))))/760*1.0135*100;
60
61 %wt. fraction in liquid
62 x = x1(1:2);                       %1st stage
63 x(3:4) = x2(1:2);                  %2nd stage
64 PS = x.*Pp';                       %Equilibrium/saturated pressures (Raoult's law)
65
66 %Pressure ration
67 ryayb = (Pp(1)*x(1))/(Pp(2)*x(2)); %1st stage
68 ryayb2 = (Pp(3)*x(3))/(Pp(4)*x(4)); %2nd stage
69 %Pressure, B
70 P(2,1) = p.Ptot*(1/(1+ryayb));     %1st stage
71 P(4) = P2*(1/(1+ryayb2));          %2nd stage
72 %Pressure, A
73 P(1) = p.Ptot -P(2);               %1st stage
74 P(3) = P2 -P(4);                   %2nd stage
75 %Reaction rate: C + D = A + B + E [kmol/m^3,hr]
76 R = p.k*C(3)*C(4);                 %1st stage
77 R(2) = p.k*C2(3)*C2(4);            %2nd stage
78 %Heating, inlet flow [kJ/hr]
79 Q = str.Minn./p.MW.*p.CP*(T1-p.Tin); %Heating, inlet
80 Qtot = sum(Q);                      %---||---
81 if t>35
82     Qtot = 0;
83 end
84 beta = [1 1]';
85 alpha = p.MW(1:2).*beta;
86 n = [alpha; alpha].*(PS - P);        %kg/h ...
87 %ensuring positive flow of vapour
88
89 if min(n) < 0
90     if n(1) < 0
91         n(1) = 0;
92     end
93     if n(2) < 0
94         n(2) = 0;
95     end

```

```

96     if n(3) <0
97         n(3) = 0;
98     end
99     if n(4) <0
100        n(4) = 0;
101    end
102 end
103 MtotVap1 = sum([n(1:2); str.Minn(7)]);
104 if t>35
105     MtotVap1 = sum([n(1:2); 0]);
106 end
107 MtotVap2 = sum(n(3:4));
108 Hvap = [p.Hvap; p.Hvap].*(n./[p.MW(1:2); p.MW(1:2)]);           ...
        %Heat to evaporate [kJ/hr]
109 Qrx = p.Hrx*R(1)*V1;                                           %Heat of reaction [kJ/hr]
110 Qrx2 = p.Hrx*R(2)*V2;
111 dM = V1*p.MW*R(1);                                             %Conversion by reaction [kmol/hr]
112 dM2 = V2*p.MW*R(2);
113
114 %calculating liquid outlet nessecary to maintain mass concervation
115 Mtotout1 = sum(str.Minn) - sum(MtotVap1);
116 if Mtot1>=9000 && t <= 35
117     Minn2 = Mtotout1.*x1;
118 else
119     Minn2(1:6,1) = 0;
120 end
121 if t>35
122     Mtotout1 = 0.097*Mtot1;
123     Minn2 = Mtotout1.*x1;
124 end
125 %Calculating change in components, 1st stage
126 Mder = str.Minn(1:2) - n(1:2) + [dM(1); 0] - Minn2(1:2);      %Accumulation = ...
        inn - out + produced
127 Mder(3:4) = str.Minn(3:4) -dM(3:4) -Minn2(3:4);
128 Mder(5) = str.Minn(5) + dM(5) -Minn2(5);
129 Mder(6) = str.Minn(6) -Minn2(6);
130 Mder(9) = 0;
131 Mder(10) = sum(Mder);                                           %Total mass balance
132 Mder(7) = Mder(10)*V1/Mtot1;                                    %Change in volume
133 Qb = Q1 - p.Qloss - Qtot - sum(Hvap(1:2)) + Qrx +p.Ptot*Mder(7);%Energy balance
134 QT = mass1(1:6) ./p.MW(1:6) .*p.CP(1:6);                      %Energy balance, components
135 Mder(8) = Qb./sum(QT);                                          %Change in temperature
136 if t>35
137     Mder = - n(1:2) + [dM(1); 0] - Minn2(1:2);                %Accumulation = inn - out ...
        + produced
138     Mder(3:4) = -dM(3:4) -Minn2(3:4);
139     Mder(5) = + dM(5) -Minn2(5);
140     Mder(6) = -Minn2(6);
141     Mder(9) = 0;
142     Mder(10) = sum(Mder);                                       %Total mass balance

```

```

143     Mder(7) = Mder(10)*V1/Mtot1;                                %Change in volume
144     Qb = Q1 - p.Qloss - Qtot - sum(Hvap(1:2)) + Qrx +p.Ptot*Mder(7);%Energy ...
        balance
145     QT = mass1(1:6)./p.MW(1:6).*p.CP(1:6);                    %Energy balance, ...
        components
146     Mder(8) = Qb./sum(QT);                                    %Change in temperature
147 end
148 %Mder(14) = 0;
149 %second stage
150 %calculating liquid outlet nessecary to maintain mass concervation
151 Qtot2 = sum(Minn2./p.MW(1:6).*p.CP(1:6)*(T2-T1));            %2nd ...
        stage
152 waste = sum(Minn2) - MtotVap2;
153 if Mtot2 >= 4000
154     Mout2 = waste.*x2;          %calculating mass of components leaving 1st
155 else                            %stage, entering 2nd
156     Mout2(1:6,1) = 0;
157 end                                %Calculating change in ...
        components, 1st stage
158 if t > 35
159     waste = Mtot2*0.14;
160     Mout2 = waste*x2;
161 end
162 Mder(22:23) = Minn2(1:2) - n(3:4) + [dM2(1);0] -Mout2(1:2);    %Accumulation ...
        = inn - out + produced
163 Mder(24:25) = Minn2(3:4) - dM2(3:4) -Mout2(3:4);
164 Mder(26) = Minn2(5) + dM2(5) -Mout2(5);
165 Mder(27) = Minn2(6) - Mout2(6);
166 Mder(30) = sum(Mder(22:27));                                %Total mass ...
        balance
167
168 Mder(28) = Mder(30)*V2/Mtot2;                                %Change in volume
169 Qb2 = Q2 - Qtot2 - sum(Hvap(3:4)) + Qrx2 +P2*Mder(28);%Energy balance
170 %remember: removed Qloss from latter line
171 QT2 = mass2./p.MW(1:6).*p.CP(1:6);                        %Energy balance, components
172 Mder(29) = Qb2/sum(QT2);                                    %Change in temperature
173 %Mder(34) = sum(n(3:4))/650 - M(34);
174 %Mder(41) = sum(waste)/ - M(41);
175
176 %-----Scaled diff-----
177 %First stage
178 %comp. in reclaimers
179 Mdersc = zeros(45,1);
180 if min(x1*Mtot1 + Mder(1:6)) <0
181     Mdersc(1:6) = 0;
182 else
183     Mdersc = (x1*Mtot1 + Mder(1:6))/(Mtot1 + Mder(10)) - M(1:6);
184 end
185 Mdersc(9) = - M(9); %keeping = 0
186 %Vaporation

```

```

187 if MtotVap1 <= 0
188     Mdersc(11:13) = 0;
189 else
190     Mdersc(11:13) = [n(1:2); str.Minn(7)]./MtotVap1 - M(11:13);
191 end
192 if t>35
193     Mdersc(11:13) = [n(1:2); 0]./MtotVap1 - M(11:13);
194 end
195 Mdersc(14) = MtotVap1/1000 - M(14);
196 %Liquid outlet
197 if sum(Minn2)>0
198     Mdersc(15:20) = Minn2./sum(Minn2)- M(15:20);
199     Mdersc(21) = sum(Minn2)/1500 - M(21);
200 else
201     Mdersc(15:21) = 0;
202 end
203 %Temperature
204 Mdersc(8) = Mder(8)/(155+273);
205 %Volume
206 Mdersc(7) = V1/10 - M(7);
207 %Total mass in reclaimers
208 Mdersc(10) = Mder(10)/10000;
209
210
211 %second stage
212 if Mtot1 >= 9000 && t<=35
213     if min(x2*Mtot2 + Mder(22:27))<0
214         Mdersc(22:27) = 0;
215     else
216         Mdersc(22:27) = (x2*Mtot2 + Mder(22:27))/(Mtot2 + Mder(30)) - M(22:27);
217     end
218     %vaporation
219     if MtotVap2 <= 0
220         Mdersc(31:33) = 0;
221     else
222         Mdersc(31:33) = [n(3:4); 0]/MtotVap2 - M(31:33);
223     end
224     Mdersc(34) = MtotVap2/650 - M(34);
225     %liquid outlet
226     if sum(Mout2) > 0
227         Mdersc(35:40) = Mout2./sum(Mout2) - M(35:40);
228         Mdersc(41) = sum(Mout2)/1000 - M(41);
229     else
230         Mdersc(35:41) = 0;
231     end
232     %Temperatures
233     Mdersc(29) = Mder(29)/(155+273);
234     %Volumes: Only correcting for deviation between calculated and
235     Mdersc(28) = V2/5 - M(28);
236     %Total mass in reclaimers

```

```

237     Mdersc(30) = Mder(30)/5000;
238     %Energy lost in waste i.e. not led back into main process simple
239     %calculation.
240     Mdersc(45) = (Mout2./p.MW(1:6))*p.CP(1:6)*(T2-p.Tin).*10e-7 - M(45);
241     else
242         Mdersc(22:45) = 0;
243     end
244     if t>35
245         Mdersc(22:27) = (x2*Mtot2 + Mder(22:27))/(Mtot2 + Mder(30)) - M(22:27);
246         %vaporation
247         if MtotVap2 <= 0
248             Mdersc(31:33) = 0;
249         else
250             Mdersc(31:33) = [n(3:4); 0]/MtotVap2 - M(31:33);
251         end
252         Mdersc(34) = MtotVap2/650 - M(34);
253         %liquid outlet
254         if sum(Mout2) > 0
255             Mdersc(35:40) = Mout2./sum(Mout2) - M(35:40);
256             Mdersc(41) = sum(Mout2)/1000 - M(41);
257         else
258             Mdersc(35:41) = 0;
259         end
260         %Temperatures
261         Mdersc(29) = Mder(29)/(155+273);
262         %Volumes: Only correcting for deviation between calculated and
263         Mdersc(28) = V2/5 - M(28);
264         %Total mass in reclaimers
265         Mdersc(30) = Mder(30)/5000;
266         %Energy lost in waste i.e. not led back into main process simple
267         %calculation.
268         Mdersc(45) = (Mout2./p.MW(1:6))*p.CP(1:6)*(T2-p.Tin).*10e-7 - M(45);
269     end
270     Mdersc(46) = Q1 - M(46);
271     Mdersc(47) = Q2 - M(47);
272     if (M(46)+Mdersc(46)) <= 0
273         Mdersc(46) = -M(46);
274     elseif (M(47) +Mdersc(47)) <= 0
275         Mdersc(46) = -M(47);
276     end
277     massder = Mdersc;
278     end

```

plotting Script for plotting result - with termination

```
1 function n = plotting(t,X,n)
2 figure(n)
3 subplot(2,1,1)
4 x11 = X(:,1:2).*[X(:,10).*10000 X(:,10).*10000];
5 plot(t,x11)
6 title('Mass, first stage')
7 xlabel('Time, [hr]')
8 ylabel('Mass, [kg]')
9 legend('MEA', 'H_2O')
10 subplot(2,1,2)
11 x11 = X(:,22:23).*[X(:,30).*5000 X(:,30).*5000];
12 plot(t,x11)
13 title('Mass, second stage')
14 xlabel('Time, [hr]')
15 ylabel('Mass, [kg]')
16 legend('MEA', 'H_2O')
17 n = n+1;
18 figure(n)
19 subplot(2,1,1)
20 x11 = X(:,3:6).*[X(:,10).*10000 X(:,10).*10000 X(:,10).*10000 X(:,10).*10000];
21 plot(t,x11)
22 title('Mass, first stage')
23 ylabel('Mass, [kg]')
24 xlabel('Time, [hr]')
25 legend('HEF', 'NaOH', 'HSS', 'HEPO')
26 subplot(2,1,2)
27 x11 = (X(:,24:27)).*[X(:,30).*5000 X(:,30).*5000 X(:,30).*5000 X(:,30).*5000];
28 plot(t,x11)
29 title('Mass, second stage')
30 ylabel('Mass, [kg]')
31 xlabel('Time, [hr]')
32 legend('HEF', 'NaOH', 'HSS', 'HEPO')
33 n = n+1;
34 figure(n)
35 subplot(2,1,1)
36 plot(t, (X(:,7)).*10)
37 title('Volume, first stage')
38 ylabel('Volume, [m^3]')
39 xlabel('Time, [hr]')
40 %legend('Volume')
41 subplot(2,1,2)
42 plot(t, (X(:,28)).*5)
43 title('Volume, second stage')
44 ylabel('Volume, [m^3]')
45 xlabel('Time, [hr]')
46 %legend('Volume')
47 n = n+1;
```

```

48 figure(n)
49 subplot(2,1,1)
50 plot(t, (X(:,8) .* (150+273)), 'b:')
51 title('Temperature, first stage')
52 xlabel('Time, [hr]')
53 ylabel('Temperature, [K]')
54 %legend('Temperature')
55 subplot(2,1,2)
56 plot(t, (X(:,29) .* (150+273)), 'b:')
57 title('Temperature, second stage')
58 xlabel('Time, [hr]')
59 ylabel('Temperature, [K]')
60 %legend('Temperature')
61 n = n+1;
62 figure(n)
63 subplot(2,1,1)
64 plot(t, (X(:,10) .*10000), 'r—')
65 title('Total mass, first stage')
66 xlabel('Time, [hr]')
67 ylabel('Mass, [kg]')
68 %legend('Total mass')
69 subplot(2,1,2)
70 plot(t, (X(:,30) .*5000), 'r—')
71 title('Total mass, second stage')
72 xlabel('Time, [hr]')
73 ylabel('Mass, [kg]')
74 %legend('Total mass')
75 n = n+1;
76 figure(n)
77 subplot(2,1,1)
78 plot(t, (X(:,1:6)))
79 title('Weight fractions, first stage')
80 xlabel('Time, [hr]')
81 ylabel('Weight fraction')
82 legend('MEA', 'H_2O', 'HEF', 'NaOH', 'HSS', 'HEPO')
83 subplot(2,1,2)
84 plot(t, (X(:,22:27)))
85 title('Weight fractions, second stage')
86 xlabel('Time, [hr]')
87 ylabel('Weight fraction')
88 legend('MEA', 'H_2O', 'HEF', 'NaOH', 'HSS', 'HEPO')
89 n = n+1;
90 figure(n)
91 subplot(2,1,1)
92 x11 = X(:,11:13) .*[X(:,14) .*1000 X(:,14) .*1000 X(:,14) .*1000];
93 plot(t,x11)
94 title('Vapour flow, first stage')
95 xlabel('Time, [hr]')
96 ylabel('Vapour flow [kg/hr]')
97 legend('MEA', 'H_2O', 'CO_2')

```

```

98 subplot(2,1,2)
99 xvap2 = X(:,31:33).*[X(:,34).*650 X(:,34).*650 X(:,34).*650];
100 plot(t,xvap2)
101 %hold on
102 %plot(t,(X(:,32).*X(34).*650))
103 %hold off
104 xlabel('Time, [hr]')
105 ylabel('Vapour flow [kg/hr]')
106 legend('MEA','H_2O','CO_2')
107 title('Vapour flow, second flow')
108 n = n+1;
109 figure(n)
110 subplot(2,1,1)
111 x11 = X(:,15:20).*[X(:,21).*1500 X(:,21).*1500 X(:,21).*1500 X(:,21).*1500 ...
    X(:,21).*1500 X(:,21).*1500];
112 plot(t, x11)
113 legend('MEA','H_2O','HEF','NaOH','HSS','HEPO')
114 xlabel('Time, [hr]')
115 ylabel('Components in outlet stream [kg/hr]')
116 title('Liquid flow, first stage ')
117 subplot(2,1,2)
118 x11 = X(:,35:40).*[X(:,41).*1000 X(:,41).*1000 X(:,41).*1000 X(:,41).*1000 ...
    X(:,41).*1000 X(:,41).*1000];
119 plot(t, x11)
120 legend('MEA','H_2O','HEF','NaOH','HSS','HEPO')
121 xlabel('Time, [hr]')
122 ylabel('Components in outlet stream [kg/hr]')
123 title('Liquid flow, second stage ')
124 n = n+1;
125 figure(n)
126 x11 = [X(:,46:47) X(:,45).*10e6];
127 plot(t,x11)
128 legend('Q_1','Q_2','Q_l_o_s_t')
129 xlabel('Time, [hr]')
130 ylabel('Heat, [kJ/h]')
131 title('Energy consumption in the different stages, and energy lost with waste')

```

D Basis of cost function

Cost of electricity

Basis of electric cost calculation is based on Statistics Norway's (Statistisk sentralbyrå) average of non-energy intensive industry for 2012 [StatisticsNorway]. This was found to be 0.361 NOK/kWh. Calculation to $\frac{NOK}{kWh}$ is shown in equation a-43.

$$elcost\left[\frac{NOK}{kJ/h}\right] = 0.361\frac{NOK}{kWh} * 1h * \frac{1}{3600\frac{s}{h}} = 0.000100\frac{NOK}{kJ/h} \quad (a-43)$$

Cost of makeup amine

It is thought that the low pressure MEA returned into main amine stream after heat exchanging with some stream, e.g. preheating of makeup MEA of as part of the heating of CO₂-leded MEA, condensing it to liquid, then pumped up to the pressure of the rest of the system.

The market price of MEA was according to ICISpricing [2012] of 1450-1500 *euro/tonne*. The value of euro in NOK is 7.53 *NOK/euro* (at 24th of may 2013 [NorgesBank]). The price of MEA was averaged, and the calculation to find *NOK/kg* is shown in equation a-44.

$$MEAcost[NOK/kg] = \frac{7.53NOK/euro * 1475euro/tonne}{1000kg/tonne} = 11,1NOK/kg \quad (a-44)$$

Cost of energy used to compress low pressure reclaimed MEA

The cost of electricity needed for compressing the MEA that is reclaimed at second stage is based on Honeywell UniSim, using the Amine fluid package. A picture of the simulation is shown in Figure a-1. The conditions kept constant in these simulations are given in Table a-3, and the resulting energy consumption of the pump with different pressures and total mass is shown in Table a-4.

Table a-3: *Parameters kept constant under simulation of compression of reclaimed MEA-solution. Weight fractions are based on output form MATLAB optimization of reclaimers system. Pressure is from [KIP], and temperature is assumed.*

<i>Parameter</i>	<i>Value</i>
Weight fraction, MEA	0.4135
Weight fraction, water	0.5865
Temperature [°C]	70
Pressure downstream pump [kPa]	190

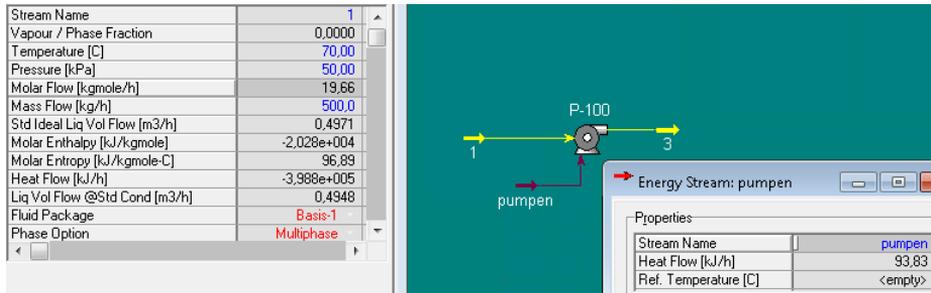


Figure a-1: *UniSim simulation used to calculate cost of compression of lowpressure reclaimed MEA*

Table a-4: *UniSim output of energy consumption of the pump compressing condensed MEA solution. All numbers in main table is given in kJ/h.*

Total mass [kg/h]	1000	750	500
Pressure [kPa]			
50	187.7	140.7	93.83
60	174.3	130.7	87.13
70	160.9	120.6	80.43
80	147.5	110.6	73.73

It was found that energy consumption in the pump is linearly dependent of the total mass passing through. By trying and failing, there were found that energy consumption could be approximated by equation a-45. \dot{W} , \dot{M} and p denotes work, reclaimed MEA liquid flow and pressure respectively.

$$\left(\frac{\dot{W}}{\dot{M}}\right)^2 * p \approx 1.78 \quad (\text{a-45})$$

The actual solutions are given in Table a-5. The average of this is what is put into the cost function, and shown in equation a-45.

Table a-5: *Actual calculation solutions of the latter equation and table. This is the basis for calculation of energy used to compress MEA-solution reclaimed in low pressure stage.*

Total mass [kg/h]	1000	750	500
Pressure [kPa]			
50	1.76	1.76	1.76
60	1.82	1.82	1.82
70	1.81	1.81	1.81
80	1.74	1.74	1.74

Amount of energy lost in waste stream

As the reclaimed amine re-enters the system, only some of the energy entered into the reclaimer is lost. Therefore, only the energy used in heating of the waste leaving the second stage of the reclaimer system. This is calculated by equation a-46.

$$Q_{lost}[kJ/h] = \sum_i \frac{m_i}{M_{i,w}} * C_{p,i} * (T_{out} - T_{inn}) \quad (\text{a-46})$$

In this equation, Q_{lost} abbreviate the lost heat, m_i is the mass of a component i , $M_{i,w}$ and $C_{p,i}$, the molar mass and heat capacity of this component respectively, T_{inn} the temperature of the slip stream entering the system, and T_{out} is the temperature of the waste leaving the system.

Cost of transportation and waste handling

All the prices used are from [Gravco Vann- og Avløpssenter]. Parameters gathered are shown in Table a-6. There was no price available for handling of amine waste, so the price used is for disposal of oil contaminated sludge.

Table a-6: *Parameters used in calculation of cost of transport and disposal of waste from the reclaimer system.*

Parameter	Symbol	Value
Volume, tank truck [m^3]	V_{tank}	15
Hire of truck [NOK]	C_{rent}	2554
Waste disposal [NOK/tonn]	C_{depo}	1502

The cost is calculated from equation a-47. V_{waste} and M_{waste} are the volume and mass of waste respectively.

$$Wastecost[NOK] = \dot{V}_{waste} * \frac{C_{rent}}{V_{tank}} + C_{depo} * \dot{M}_{waste} \quad (\text{a-47})$$

E Alternative minima detected

Table a-7: *Output of the three different solvers used in MATLAB-script where the low pressure stage is the dominating one. The input to optimization is a solution given by an ODE-solver. This is a steady state solution, run for 2000 hours. The second column is an optimization finding an optimum for heat input in both stages, and pressure in second stage. The third is a ODE-solver output for optimal values.*

Variable	Input to optimization	Output of optimization	Optimal solution
First stage bulk			
MEA [wt%*100]	0.5065	0.5065	0.5065
H ₂ O [wt%*100]	0.4705	0.4705	0.4705
HEF [wt%*100]	0.0078	0.0078	0.0078
NaOH [wt%*100]	0.0078	0.0078	0.0078
NaF [wt%*100]	0.0054	0.0054	0.0054
HEPO [wt%*100]	0.0021	0.0021	0.0021
Volume[m ³]	9.018	9.018	9.018
Temperature [°C]	390.1	407.3	407.3
CO ₂ [wt%*100]	0	0	0
Total mass [kg]	9000	9000	0.9000
First stage vapour outlet			
MEA [wt%*100]	0	0	0
H ₂ O [wt%*100]	0	0	0
CO ₂ [wt%*100]	1	1	1
Total mass [kg]	87.5	87.5	87.5
First stage liquid outlet			
MEA [wt%*100]	0.5065	0.5065	0.5065
H ₂ O [wt%*100]	0.4705	0.4705	0.4705
HEF [wt%*100]	0.0078	0.0078	0.0078
NaOH [wt%*100]	0.0078	0.0078	0.0078
NaF [wt%*100]	0.0054	0.0054	0.0054
HEPO [wt%*100]	0.0021	0.0021	0.0021
Total mass [kg]	2412.5	2412.5	2412.5
Second stage, bulk			
MEA [wt%*100]	0.5111	0.5898	0.5898
H ₂ O [wt%*100]	0.4668	0.3801	0.3801
HEF [wt%*100]	0.0061	0.0072	0.0072
NaOH [wt%*100]	0.0071	0.0093	0.0093
NaF [wt%*100]	0.0068	0.0106	0.0106
HEPO [wt%*100]	0.0021	0.0029	0.0029
Volume[m ³]	4.008	4.008	4.008
Temperature [°C]	382.8	400.6	400.6
Total mass [kg]	4000	4000	4000

Variable	Input to optimization	Output of optimization	Optimal solution
Second stage vapour outlet			
MEA [wt%*100]	0.2115	0.3151	0.3151
H ₂ O [wt%*100]	0.7885	0.6849	0.6849
CO ₂ [wt%*100]	0	0	0
Total mass [kg]	27.26	715.0	715.0
second stage liquid outlet			
MEA [wt%*100]	0.5111	0.5898	0.5898
H ₂ O [wt%*100]	0.4668	0.3801	0.3801
HEF [wt%*100]	0.0061	0.0072	0.0072
NaOH [wt%*100]	0.0071	0.0093	0.0093
NaF [wt%*100]	0.0068	0.0106	0.0106
HEPO [wt%*100]	0.0021	0.0029	0.0029
Total mass [kg*1000]	2385.2	1697.5	1697.5
Heat input 1st stage [kJ/h*10 ⁶]	0	0.0135	0.0135
Heat input 2nd stage [kJ/h*10 ⁶]	0	0.1330	0.1330
Pressure, 2nd stage [kPa*100]	70.00	76.96	76.96

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