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Seksjon 1

1 OPPGAVE

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PROJECT TITLE:

DYNAMIC MODELLING OF A HEX WITH PHASE CHANGE

By

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Abstract

This project is written as part of the Process System Engineering Specialization at the Department of Chemical Engineering at the Norwegian University of Science and Technology.

The objective of the project is to develop a dynamic heat exchanger model which can handle both single and multiphase flows as well as phase changes. The application of the model is found in on optimal operation of LNG refrigeration cycles.

The challenge with modelling a phase change heat exchanger is that the location of the phase change is not known beforehand. In order to determine if a stream changes its phase, the heat exchanger is modelled as a series of cells (lumps) in which a flash calculation is performed to determine the composition of the vapor and liquid phases. The thermodynamics properties are modelled using Soave-Redlich-Kwong cubic equation of state which is incorporate in the model. First the model equations are formulated and an analysis of the model is made. Further, the model performance is tested for different phase transitions.

Acknowledgment

I would like to thank my co-supervisor Adriana Reyes-Lúa for her time, continuous support, encouragement and feedback throughout this project. I would also want to thank my supervisor Sigurd Skogestad for his interest in this project and useful discussions.

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Chapter 1

Introduction

The main objective of this project is to develop a robust dynamic heat exchanger model which can handle multicomponent streams subject to phase changes. The immediate application of such a model is found in optimal operation of refrigeration cycles where several heat exchangers of this type are used to assure maximum heat transfer efficiency of the process.

The challenge with developing such a model arises form the fact that it is not known *a priori* where the location of the transition between vapor and liquid phases occurs [Watson et al., 2016]. A few methods to overcome this challenge are presented in the open literature, based either on heat integration analysis either on solving a DAEs system, also known as Thermodynamic Differential Algebraic Equation (TDAE) method.

Kamath et al. [2012] apply the pinch analysis on a multistream heat exchanger where each stream subject to phase change is divided into there different sections corresponding to superheated, 2 phase and subheated fluids. The phase transition is identified calculating the bubble and dew point of each respective section by a series of flash calculations. However this framework requires solving a nonlinear problem subject to complementarity constraints where Boolean variables are needed in order to determine the phase change which significantly increase the size of system of equations to be solved. Watson and Barton [2017] also describes the use of the pinch approach and separation of the stream into different substreams. The difference is that the method relies on solving nonsmooth equations for vapor-liquid equilibrium and also for defining the inlet and outlet temperatures, method which reduces the number of equations to be solved compared with the previous approach. A down side of the method described in Watson and Barton [2017] is that it does not include non-ideal thermodynamics. Another disadvantage of both approaches is that they do no include model dynamics, the models being formulated at steady state.

The second method, TDAE, is discussed by Wilhelmsen et al. [2013]. The authors suggest modifying the system of DAE accordingly to the possible conditions of the stream, thus using a series of logical propositions. The phase boundary is traced by using an event detection function handled the DAE solver which is based on a series of flash calculation in addition to dew and bubble points. However, the thermodynamic properties of this method are obtained from look-up tables which while it may be a good approach to reduce the computational time is not the best in terms of model convergence [Reyes-Lúa et al., 2016].

In contrast, the framework of this work implies modelling the heat exchanger as a series of lumps or cells having a fixed volume and solving a flash calculation in each of them to determine the location of the phase change. The finite control volume method is not new and it is reported in the work of Mathisen [1994] for single phase where ideal thermodynamics model is used and also in the work of Rasmussen and Shenoy [2012] for two phases where thermodynamic look-up tables are used although it does not account for phase change localization. The difference of this work is that it incorporate the SRK equation of state to model non-ideal thermodynamical properties. Thus, this model formulation involves solving simultaneously the DAE system formed of the SRK equations and flashes for all cells.

A dynamic model offers more information compared with a steady-state one, information which could be use if it desired to design a control system for example [Moe et al., 1995]. For this reasons, a dynamic model of the HEX is chosen in this project.

A few process data need in the project are taken from the small LNG refrigeration unit on board of gas carriers presented by Nekså et al. [2010] where all HEX have only two streams.

Chapter 2

Theory

2.1 Heat Exchanger

Normally, the heat exchangers that are used in a refrigeration cycle are plate and fin heat exchangers, which is also the case for the process that is used as a base of this work [Nekså et al., 2010]. However, for modelling purposes, the heat exchanger is modelled in this work as a counter current heat exchanger using the finite volume control method. A counter-current is chosen since it has a higher efficiency compared with a co-current one. The heat exchanger has only two streams, cold fluid and hot fluid. A simple illustration of the HEX is presented in 2.1. A detailed representation is presented in section 3.3.

2.2 Thermodynamic Model

The thermodynamic properties required for the HEX model (enthalpy, compressibility factor, fugacity) are calculated using the Soave-Redlich-Kwong cubic equations of state [Soave, 1972] while the correction presented in Péneloux et al. [1982] is applied for the molar volume calculation. The SRK EoS is chosen to represent the thermodynamics of this model considering that it can be applied to VLE calculations for mixtures of nonpolar substances, which is normally the case in a LNG refrigeration cycle [Soave, 1972].

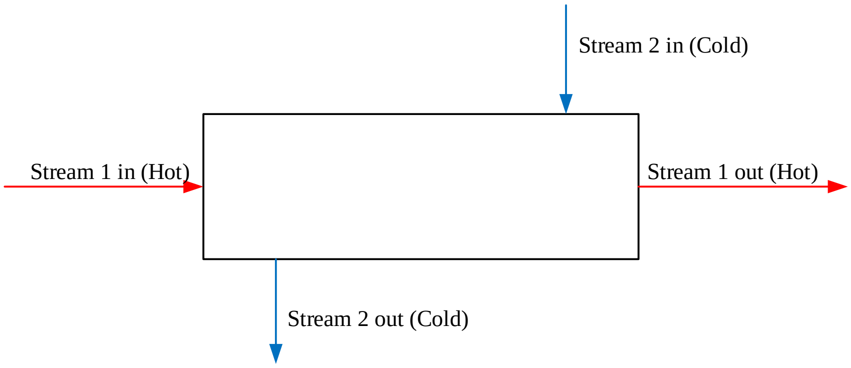

Figure 2.1: Counter-current heat exchanger

2.2.1 SRK EoS

First, the SRK equations for one component are presented to provide an overview of the EoS. Second, mixture rules are introduced to account for the multicomponent system which is used in this work.

The SRK EoS for a single component is given by equation 2.1. In equation 2.1a, the compressibility factor Z account for the non-ideal behavior of a component. A small value of Z correspond to liquid phase while a large value is attributed to vapor phase. The fugacity of the component is also calculated as a function of Z by applying equation 2.1h.

$$Z^3 - Z^2 + Z(A - B - B^2) - A \cdot B = 0 \tag{2.1a}$$

$$A = 0.42747 \cdot \alpha(T) \cdot \frac{P_r}{T_r^2} \tag{2.1b}$$

$$B = 0.08664 \cdot \frac{P_r}{T_r} \tag{2.1c}$$

$$P_r = \frac{P}{P_c} \tag{2.1d}$$

$$T_r = \frac{T}{T_c} \tag{2.1e}$$

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 \tag{2.1f}$$

$$m = 0.48 + 1.574 \cdot \omega - 0.176 \cdot \omega^2 \tag{2.1g}$$

$$\ln \frac{\phi}{P} = Z - 1 - \ln(Z - B) - \frac{A}{B} \ln(\frac{Z + B}{Z}) \tag{2.1h}$$

In order to extend the single components SRK formulation to multicomponent, mixing rules have to be applied. In this work, Van der Waals mixing rules are used [Reid et al., 1987]. In addition, to account for the non-ideal behavior of the mixture, binary interaction parameters $k_{i,j}$ are used (even though the number of components could be greater than two in each of the streams). The mixing rules calculate first a geometric average of each parameter followed by a weighting based on molar composition to obtain the average mixture parameters, as it can be seen in equations 2.2a, 2.2b and 2.2c. The fugacity of each components is then calculated with equation 2.2d, where a correction term is used to account for non-ideality. The component fugacity is needed because it is further used in the VLE modelling.

$$A_{i,j} = \sqrt{A_i \cdot A_j} \tag{2.2a}$$

$$B = \sum_{i}^{NC} x_i \cdot B_i \tag{2.2b}$$

$$A = \sum_{i}^{NC} \sum_{j}^{NC} x_i \cdot x_j \cdot A_{i,j} \cdot (1 - k_{i,j}) \tag{2.2c}$$

$$\ln \phi_i = (Z-1)\frac{B_i}{B} - \ln(Z-B) - \frac{A}{B}\ln\left(\frac{Z+B}{Z}\right)\left(2\delta_i \frac{A_i^{0.5}}{A} - \frac{B_i}{B}\right) \tag{2.2d}$$

$$\delta_i = \sum_{j}^{NC} x_j \cdot A_j^{0.5} \cdot (1 - k_{i,j}) \tag{2.2e}$$

2.2.2 Molar Volume Calculation

The molar volume is also needed in the model as it is further discussed in 3.5. This is calculated as a function of compressibility, temperature and pressure using equation 2.3.

$$V_m = \frac{ZRT}{P} \tag{2.3}$$

However, while equation 2.3 is well used for the vapor phase, the results for liquid phase do not have a high accuracy and a correction is need. The correction used in this work is the one recommend by Péneloux et al. [1982]. The correction is given by equation 2.4.

$$V_m = \frac{ZRT}{P} - c \tag{2.4a}$$

$$c = 0.40768 \cdot \left(0.29441 - Z_{RA}\right)\frac{RT_c}{Pc} \tag{2.4b}$$

The Z_{RA} factor in equation 2.4b is the Rackett compressibility factor from Spencer and Danner [1972] which is an unique constant for each compound and it can be estimated using equation 2.5 as a function of the acentric factor.

$$Z_{RA} = 0.29056 - 0.0877 \cdot \omega \tag{2.5}$$

2.2.3 Enthalpy Calculation

Enthalpy calculation plays a crucial role in modelling a process with heat transfer at its core. In this project non-ideal enthalpy based on the SRK EoS is calculated for each component. The real enthalpy is calculated by subtracting a departure factor is subtracted from the ideal enthalpy using equation 2.6 Reid et al. [1987]. Next, the calculation method for one component i is presented.

$$H_i = H_{ideal,i} - H_{SRK,i} \tag{2.6}$$

The ideal enthalpy is given by its definition, equation 2.7.

$$H_{ideal,i} = \int_{T_{ref}}^{T} C_{P,i}(T)dT \tag{2.7}$$

The integral term from equation 2.7 is calculated considering the specific capacity C_p as a polynomial function of temperature, T given by equation 2.8.

$$C_{P,i} = A_i + B_i T + CT^2 + D_i T^3 + E_i T^4 \tag{2.8}$$

Thus, equation 2.9 is derived from equations 2.7 and 2.8 by using well-known integration rules.

$$H_{ideal,i} = A_i(T - T_{ref}) + \frac{1}{2}B_i(T^2 - T_{ref}^2) + \frac{1}{3}C(T^3 - T_{ref}^3) + \frac{1}{4}D_i(T^4 - T_{ref}^4)T^3 + \frac{1}{5}E_i(T^5 - T_{ref}^5) \tag{2.9}$$

It should be noted that in solving the problem, T_{ref} was set equal to 298 K.

The departure factor for enthalpy is calculated from equation 2.10 Reid et al. [1987], where the parameters A and B come from the SRK EoS formulation, 2.2.

$$H = \frac{1}{BRT} \cdot \left(\frac{AR^2T^2}{P^2} - T\frac{\partial A}{\partial T} \right) \ln \left(\frac{Z}{Z+B} + RT(Z-1) \right) \tag{2.10}$$

It can be observed that a derivative factor in a form of $\frac{\partial A}{\partial T}$ appears in equation 2.10. This factor can be derived considering the mixing rules 2.2 after which equation 2.11 is obtained.

$$\frac{dA}{dT} = -\frac{R}{2}\left(\frac{0.42747}{T}\right)^{0.5}\sum_{i}^{NC}\sum_{j}^{NC} x_i \cdot x_j \cdot \left(m_i\sqrt{\left|A_i \cdot \frac{T_{c,j}}{P}\frac{T^2}{P_{c,j}\cdot R^2}\right|} + m_j\sqrt{\left|A_j\frac{T_{c,i}}{P}\frac{T^2}{P_{c,i}\cdot R^2}\right|}\right) \tag{2.11}$$

The mixture enthalpy is calculated using molar weighting, equation similar with 2.2b, where B is substituted with H after which equation 2.12 is derrived.

$$H = \sum_{i}^{NC} x_i \cdot H_i \tag{2.12}$$

2.3 VLE Calculation

As mentioned in chapter 1, a flash calculation is performed in each of the cells that the HEX is divided in. Vapor-liquid equilibrium stands at the core of flash calculations and thus it is further discussed. VLE implies that at given temperature and pressure, the chemical potential of the vapor and liquid phases in a system are equal, which further expand to the compositions of each phase are implicitly given. There are different ways of expressing in a mathematical formulation the equilibrium between a vapor and liquid phase from which the composition of each phase can be determined [Skogestad, 2008]. All of them imply using the equilibrium constant K of teh two phases.

For ideal mixtures, equation 2.13 is commonly used. In this case K is independent of composition and it is expressed as a function of temperature and pressure. It can be computed from Henry's law for diluted mixture

$$K_i = \frac{y_i}{x_i} \tag{2.13}$$

For non-ideal mixture two approaches are common. The first one is presented in 2.14 where two different equations of state are respectively used to computed the liquid fugacity as a function of the activity coefficient on one side and the vapor fugacity on the other side. This method is used at moderate pressures.

$$\phi_i^V y_i = \phi_i^L(\gamma_i) x_i \tag{2.14}$$

The second method for non-ideal mixtures is given by equation 2.15a, where a single equation of state is used to determine both the vapor and liquid fugacity as a function of composition, temperature and pressure. This final approach is uesd in this project where the fugacities are determined from the SRK ROS according to equation 2.2d.

$$\phi_i^V y_i = \phi_i^L y_i \tag{2.15a}$$

$$K_i = \frac{\phi_i^V}{\phi_i^L} \tag{2.15b}$$

The implementation of the VLE in the HEX model is presented in HEX model equations from section 3.5.

Chapter 3

HEX Model Formulation

This chapter presents the key features of the HEX model: scope, assumptions, states, equations and graphical representation.

3.1 HEX Scope

As mentioned in chapter 1 the HEX is modelled with the purpose of representing a real process, a LNG refrigeration cycle which is not easy to model due to not knowing *a priori* where the phase change happens. The possible conditions for the inlet and outlet of each stream are given in table 3.1. Table 3.1 should be read adjoining to the PH diagram from figure 3.1. The PH diagram illustrated how the phase transitions from vapor to liquid when the enthalpy or pressure changes. In figure 3.1 the blue points, *A* and *B*, represent streams in vapor phase, the purple points, *C* and *D*, represent streams in liquid-vapor phase and the red points, *E* and *F*, represent streams in liquid phase. The possible transitions from points A to F are not illustrated on the figure to avoid Figure 3.1 is a mere qualitative representation of the PH diagram and any other transition from one point to another not represented is of course possible.

Having the possible transitions in in mind, it is desired to have a single robust model which is able to simulate all HEXs in the process regardless if a phase transitions could happen or not. The initial HEX model is developed with the purpose of simulating the simplest of the heat exchangers (without phase change, transition A→ B in table 3.1) to see if it is a good representation and to use it a building block for the other heat exchangers (with phase change).

Table 3.1: Possible phase transitions

Transition	Inlet	Outlet
A → B	V	V
A → C		L-V
A → E		L
C → B	L-V	V
C → D		L-V
C → E		L
E → B	L	V
E → C		L-V
E → F		L

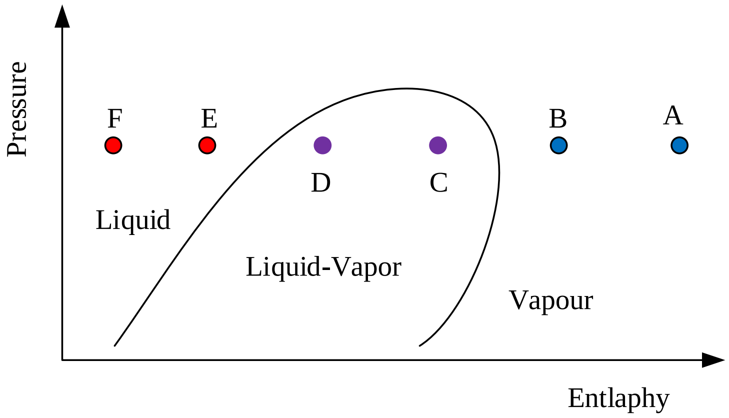

Figure 3.1: PH diagram

3.2 Assumptions

Assumptions have the role of simplifying the model in order to make it easier to solve the equations while at the same time it remains a good approximation of the real process. A few assumptions have already been stated in previous chapters. However they will also be mentioned in the following for a better overview.

Assumptions & other considerations:

- the model is dynamic with the purpose of capturing all (or as many as possible) process characteristics.

- as a starting point only the one stream which could change phase is modelled as a series of lumps while for the second stream the inlet and outlet temperatures are given and the temperature profile along the HEX is considered linear since this stream does not change phase.
- the volume of each lump is constant.
- in each cell a flash calculation is performed in order to determine if there is or not a phase change and also the composition of each phase.
- perfect mixing in each cell. This implies that the outlet flow of each cell has the same conditions as the cell inside (e.g. temperature, composition etc). In addition, linear mixing rules could be used to calculate different mixing properties (e.g. density, enthalpy etc.) of the system consisting of both vapor and liquid phases.
- the vapor and liquid phases have the same velocities which implies no slip or slip ratio equal to one.
- the wall capacitance is neglected.
- constant specific heat for the cooling agent.
- initially, constant pressure is assumed. This assumption actually brings a few issues which are discussed in 4.
- initially, due to the facts that the cooling agent has constant capacity, its temperature profile is linear and each cell has constant volume (and as a result constant area), it is considered that the heat transferred from the hot fluid to the cooling agent is equal for the same cell. This approximation is a bit ruff and may not be a good representation of reality and thus it is further discussed in section 4.

Based on the results of simulating for the simplest HEX of the process, modifications of this assumptions should be made. The first and most important assumption that must be changed is that also the hot fluid is modelled as a series of lumps with finite constant volume. As a consequence other assumptions should be reconsidered, mainly the ones involving constant properties of the cooling agent.

3.3 Model Illustration

The lumped HEX model is illustrated in figure 3.2 and 3.3. Figure 3.2 represents the case when only one of the streams is considered to potential change phase while figure 3.3 represents the case where both streams could change phase. The temperature profile along the HEX length is also showed in the figures. Since the temperature is constant in each cell, the resulting temperature profile is a step profile. In figure 3.3 the temperature profile corresponding to a countercurrent flow is showed. Both illustrations are constructed on the base of the assumptions stated and also the representative figure 2.1 of the HEX.

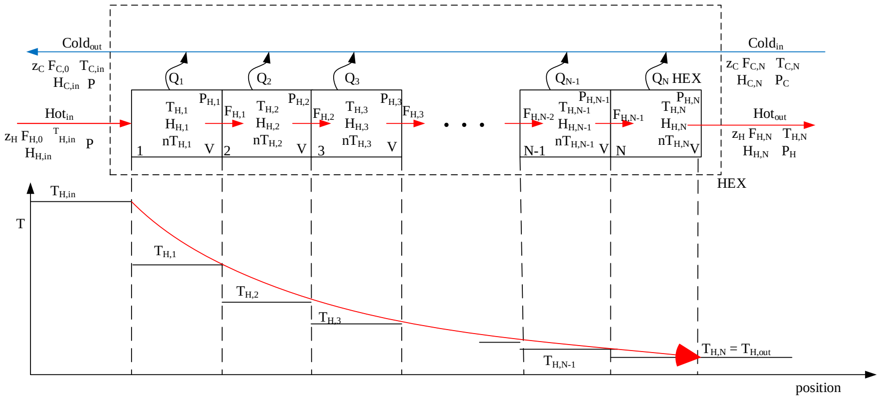

Figure 3.2: HEX lumped model for one of the two stream

3.4 States

The states and their corresponding number for each cell of the HEX are given in table 3.2. Each cell has one total holdup, one internal energy, temperature in both phases, one liquid volume, one vapor compressibility, one liquid compressibility and same pressure in each phase while the component holdup, liquid and vapor compositions are given for the number of component fro which the component mass balance is written, $NC-1$. The total number of states for the lumped HEX is obtained by multiplying the number of states per cell with the number of cells, N. The units of the state are given for consistency and are subject of change in the case of numerical problems with the chosen solver.

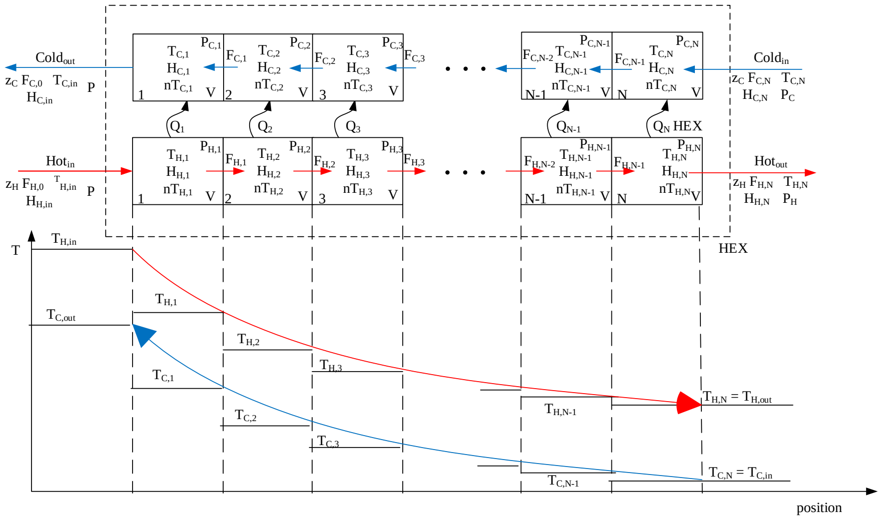

Figure 3.3: HEX lumped model

Remark: * The pressure was not initially considered as state and was added afterwards. The reasons are discussed in chapter 4.

3.5 Model Equations

This section presents the mass and energy balances formulated as dynamic equations for the heat exchanger model along with other algebraic equations. Having both differential and algebraic equations, the model falls into the category of DAEs (differential algebraic equations). The equations are written for component *i* and cell *j*. The model is adapted from the distillation column model presented by Reyes-Lúa et al. [2016] since the core of both models is a series of flash calculations. For a better understanding of the actual properties that are being calculated and how they related to the lumped HEX model, a representative cell is shown in figure 3.4. As mentioned section 3.2 only the fluid that could potentially change phase is modelled as a series of lumps initially. Thus the equations bellow should be understood as written only for this particular stream. This situation would correspond to case

The overall mass balance is given equation 3.1. The accumulation of mass (given by the total holdup) inside a cell is given by the difference between the in- and outflows of each cell

Table 3.2: HEX Model States

State	Symbol	Units	Number
Total holdup	nT	kmol	N
Component holdup	n	kmol	N · (NC-1)
Internal energy	U	$\frac{kJ}{kmol}$	N
Temperature	T	K	N
Liquid composition	x	$\frac{kmol}{kmol}$	N · (NC-1)
Vapor composition	y	$\frac{kmol}{kmol}$	N · (NC-1)
Liquid volume	VL	m^3	N
Vapor compressibility	ZG	–	N
Liquid compressibility	ZL	–	N
Pressure	P*	kPa	N

respectively. It is should be noted that the outlet of cell *j* is the inlet of cell *j+1*.

$$\frac{dnT_j}{dt} = F_{j-1} - F_j \tag{3.1}$$

Due to the fact that the streams are multicomponet, the component mass balances must also be specified in order to not have an undetermined system of equations. The number of mass (or equivalently mole) balances should be equal to the number of components with one of those equations being the overall mass balance, equation 3.1. Hence, the component mass balances are written and solved for *NC-1* components and are given by equation 3.2. The accumulation of each component in a cell is given by the difference of the component in- and outflows respectively. The component inflow is give by the total inflow times the component compositions. It should be noted that each cell has only one mass inflow and one mass outflow, and the cell is considered perfectly mixed with no slip. Thus the overall composition *z* along the heat exchanger is constant, the only changes being the composition of the vapor or liquid phases, *y* and *x* respectively.

$$\frac{dn_{i,j}}{dt} = F_{j-1} \cdot z_i - F_j \cdot z_i \tag{3.2}$$

The energy balance is written in the same way as the mass balance, namely the accumulations of

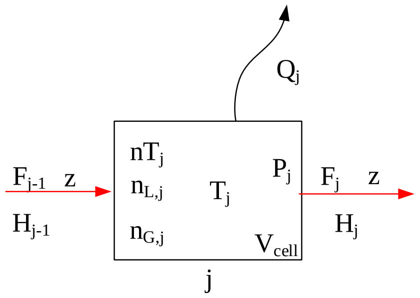

Figure 3.4: Representative cell of the HEX

internal energy is given by its in and outflow, the difference this time being that heat is removed for the cell by heat transfer to the other stream. The enthalpy of a flow is calculated using a linear mixing rules (since perfect mixing is assumed) between the liquid and vapor holdup fraction and their respective enthalpies. The phase enthalpy calculation is done accordingly to section 2.2.3. With this considerations, the energy balance is given by equation 3.3.

$$\frac{du_j}{dt} = F_{j-1} \cdot \left(H_{L,(j-1)} \cdot \frac{n_{L,(j-1)}}{nT_{j-1}} + H_{G,(j-1)} \cdot \frac{n_{G,(j-1)}}{nT_{j-1}} \right) - F_j \cdot \left(H_{L,j} \cdot \frac{n_{L,j}}{nT_j} + H_{G,j} \cdot \frac{n_{G,j}}{nT_j} \right) - Q_j \tag{3.3}$$

Both liquid and vapor holdups can be written as a function of the cell volume, the molar volume calculated from section 2.2.2 and the liquid volume (state, see table 3.2) according to equation 3.4. The volume of each cell is equal to the total volume of the HEX divided by the number of cell since all cells are considered to have the same volume.

$$V_{cell} = \frac{V_{HEX}}{N} \tag{3.4a}$$

$$V_{G,j} = V_{cell} - V_{L,j} \tag{3.4b}$$

$$n_{L,j} = \frac{V_{L,j}}{V_{m_{L,j}}} \tag{3.4c}$$

$$n_{G,j} = \frac{V_{G,j}}{V_{m_{G,j}}} \tag{3.4d}$$

One can also define another variable, the vapor fraction ν, as the report of the vapor phase to the total holdup with the purpose to write in a more convenient and easy to follow equation 3.3. The vapor fraction ϵ is here defined (equation 3.5) since it is useful also in calculating mixture properties.

$$\epsilon_j = \frac{n_{G,j}}{nT_j} \tag{3.5a}$$

$$1-\epsilon_j = \frac{n_{L,j}}{nT_j} \tag{3.5b}$$

The energy balance can be reformulated intro equation 3.6.

$$\frac{du_j}{dt} = F_{j-1}\cdot\left(H_{L,(j-1)}\cdot(1-\epsilon_{j-1}) + H_{G,(j-1)}\cdot\epsilon_{j-1}\right) - F_j\cdot\left(H_{L,j}\cdot(1-\epsilon_j) + H_{G,j}\cdot\epsilon_j\right) - Q_{cell,}j \tag{3.6}$$

The only term from the energy balance that has not been explained so far is the last one, accounting for the heat transferred to the cooling agent. Based on the assumptions stated in section 3.2, for the stream that does not exchange phase and constant heat Q for each cell, the calculation of Q are given by equation 3.7 considering the mass flow, specific mass heat and the difference in temperature between in inlet and outlet. This approximation is further discussed in section 3.6.

$$\Delta T_c = T_{c,in} - T_{c,out} \tag{3.7a}$$

$$Q = q_c \cdot c_{p_c} \cdot \Delta T_c \tag{3.7b}$$

$$Q_{cell} = \frac{Q}{N} \tag{3.7c}$$

The internal energy of each cell needed in the energy balance is calculated from the thermodynamic definition of enthalpy, equation 3.8. By applying equation 3.8 to the HEX cell the algebraic equation 3.9 is derived.

$$H = U + PV \tag{3.8}$$

$$u_j + P_j \cdot V_{cell} - H_{L,j}\cdot n_{L,j} - H_{G,j}\cdot n_{G,j} = 0 \tag{3.9}$$

The component holdup is also included among the algebraic equations and it is given by equation 3.10 derived form considering that the component holdup is a linear combination of the phase holdup and phase composition. The equations are implemented for *NC-1* components.

$$n_{i,j} - x_{i,j}\cdot n_{L,j} - y_{i,j}\cdot n_{G,j} = 0 \tag{3.10}$$

The vapor-liquid equilibrium needed in the flash calculation of the cell is given by the algebraic equation 3.11. The equilibrium constant is calculated from fugacities as explained in section 2.3. The equations are implemented for *NC-1* components.

$$y_{i,j} - K_{i,j} \cdot x_{i,j} = 0 \tag{3.11}$$

The algebraic equation for the total holdup is given by equation 3.12. The total holdup is the sum of the vapor holdup and liquid holdup.

$$nT_j - n_{L,j} - n_{G,J} = 0 \tag{3.12}$$

The algebraic equation for the gas compressibility is given in equation 3.13, according to equation 2.1a of the SRK EOS .

$$Z_{G,j}^3 + Z_{G,j}^2 + Z_{G,j} \cdot (A_{G,j} - B_{G,j} - B_{G,j}^2) - A_{G,j} \cdot B_{G,j} = 0 \tag{3.13}$$

The algebraic equation for the liquid compressibility is given in equation 3.14, according to equation 2.1a of the SRK EOS .

$$Z_{L,j}^3 + Z_{G,j}^2 + Z_{L,j} \cdot (A_{L,j} - B_{L,j} - B_{L,j}^2) - A_{L,j} \cdot B_{L,j} = 0 \tag{3.14}$$

By including the gas and liquid compressibility as states and as part of the DAE set implies that the SRK EOS is incorporated in the model and the cubic equation of state is not solved for Z outside the model. The alternative would be to separate the SRK EOS from the set of DAEs and solve explicitly for the compressibility factor. However solving for Z outside the DAE solvers would require that convergence is reached for solving the cubic equation of state at each step that the SRK function is called. It should be noted that only equations 3.1, 3.2, 3.3, 3.8, 3.10, 3.11, 3.12, 3.13 and 3.14 are part of the DAE system that it is passed to the solver. The total numbers of equations in the DAE system for each cell is $3 \cdot (NC-1) + 6$, where $2 + (NC-1)$ are dynamic (overall mass, energy and $(NC-1) \cdot$ component) and $2 \cdot (NC-1) + 4$ are algebraic (the rest).

3.6 Model Inputs

For simplicity and generality, let the stream names of the HEX be stream 1 and stream 2. In connection with the representation of a counter-current HEX from figure 2.1, stream 1 is the hot stream and stream 2 is the cold stream. The primary output of the model is the temperature profile of stream 1 along the HEX. The second output is the phase composition of either stream 1 or both streams. A few parameters are specified as inputs since the model of this work is not developed with the purpose of design but operation of a given process. The general HEX model inputs are presented bellow. Particular values are give when simulation cases are presented in the next sections.

- given inlet flow for stream 1
- given inlet temperatures for stream 1
- given streams composition
- given inlet pressure
- given pressure drop
- given volume of the HEX
- given inlet, outlet temperature, flow and composition for stream 2
- given number of cells.

Specifying the inlet, outlet temperature, flow and composition for stream 2 is equivalent to specifying the heat flow removed (or by case received). Another option would be to have the heat transfer area from design and calculate the heat exchanger using equation 3.15a. However the heat transfer area is not given in this case. In addition, this approach would require the approximation of the heat transfer coefficient which is not straightforward for streams with phase change. Moreover, the derivation of equation 3.15a assumes steady-state, no phase change and constant specific heat which is not the case in this work. One could also think of a better approximation would consists of writing equation 3.15a for each cell in part and hence not having one equation for the whole HEX. In this project, the exchanged heat is specified either by having the conditions of stream 2, as it was mentioned in section 3.5, equation 3.7, either by giving an arbitrary value and test the outcome.

$$Q = UA\Delta T \tag{3.15a}$$

$$\Delta T = \frac{(T_{1,in} - T_{2,out}) - (T_{1,out} - T_{2,in})}{\ln \frac{T_{1,in} - T_{2,out}}{T_{1,out} - T_{2,in}}} \tag{3.15b}$$

3.7 Method For Solving The Model

Considering that the set of equations has both differential and algebraic equations, a DAEs solver is required to solve all equations simultaneously. For this purpose, the function *ode15s* from Matlab® is chosen in this project to also cover the stiffness of the system of equations. The function solves equations written accordingly to equation 3.16. The mass matrix M is a sparse matrix used to specify which equations are differential and which are algebraic. The diagonal of the mass matrix has 1 for differential equations and 0 for the algebraic ones. An important aspect to mention regarding all ODE solver in Matlab® is that they require consistent initial conditions and do not solve systems with an order and differential index higher than one. The former imply that all equations must have maximum first order derivatives and that the number of derivatives needed to rewrite a DAE system as an ODE system is not greater than 1 [Matlab, 2016].

$$M\frac{dy}{dt} = f(t,y) \tag{3.16}$$

Chapter 4

Model Analysis

The first simulations in Matlab® brought up a few challenges with the HEX model. In order to have a better understanding of the issues and find methods to overcome them, a step further is taken and a model analysis is made.

4.1 Differential Index

The index order of the DAE system is a recurrent challenge throughout the project and thus is hereby discussed. As indicated in section 3.1 the model is first tested for the situation with no phase change which corresponds to transitions A → B from figure 3.1. In addition the pressure drop is neglected. The reason for assuming constant pressure is due to the different time scale separation. Mechanical dynamics (pressure) are faster compared with thermal dynamics (temperature), which are of interest in this work [Rasmussen, 2012].

However, while trying to solve the DAEs for the HEX model with the above considerations, Matlab® indicates that the index is greater than 1. As mentioned in section 3.7 Matlab® is only able to handle DAEs with index 0 or 1. Moe et al. [1995] defines the index of as measure of the challenges related to having consistent initial conditions and integrating the set of DAEs. As the index of a dynamic model increases, the problem is more difficult to initialize and solve. Mathematically, the index of a DAE set, also knows as differential index is related to the definition of matrix index which is the *least non-negative integer* ν *such that rank(*A^{ν}*) = rank(*$A^{\nu+1}$) [Moe et al., 1995]. Translated to a linear set of DAEs, the index represent the number of times that the algebraic equations $F(z,t) = 0$ have to be differentiated in respect to t to obtain a set of ODE.

The idea behind it is that for some cases, the algebraic and differential equations are not independent of each other and the algebraic equations can be seen as constraints or specification that the differential variables have to fulfill. This is also the reason that DAEs systems are more difficult to initialize compared to ordinary differential equations.

In most cases a dynamic model with a higher index can be reformulated as a system of index one by manipulating symbolically the algebraic variables. The possibilities are either substituting some differential variables with algebraic variables either introducing new equations of the algebraic variables [Moe et al., 1995].

Moe et al. [1995] also discuss that it is common to have a index greater then 1 for a DAE set formulated for gas phases systems where the pressure is specified and represent a constraint on the energy and mass, which is the case for the HEX model with constant pressure. A method of reducing the index of such systems is to remove the specification on the pressure and let it vary. As a consequence the model was revised and it was decided to introduce the pressure as a state.

4.1.1 Revising The Model I

By introducing a new state, a new equation has to be also introduced and attributed to solving for the new state, pressure. Two different equations are taken into consideration:

1. The first option is to to write the momentum equation to account for the change in pressure, as it is written is equation 4.1 [Jakobsen, 2014]. However, this would require design data (which is not available in this work) to compute the friction forces σ In addition, it is desired to have a robust model which can be used regardless of the geometrical characteristics of the HEX. For this reasons, the momentum equation is not chosen for implementation in the model.
$$\frac{\partial}{\partial t}(\rho v) + \nabla \cdot (\rho v v) = -\nabla P - \nabla \cdot \sigma + \rho g \tag{4.1}$$
2. The second option is to use the VLE of the last component (equation 4.2) to solve for the pressure. Although the pressure is not explicitly given in equation 4.2, it is implicitly given in the equilibrium constant K. The equation also represent an indirect way of making sure that the total composition is each phase is equal to 1 since the composition of the last component is calculated by subtracting the compositions of all other components from 1.
$$(1 - \sum_{i=1}^{NC-1} y_{i,j}) - K_{n,j} \cdot (1 - \sum_{i=1}^{NC-1} x_{i,j} = 0 \tag{4.2}$$

For the mentioned reasons, the second option is chosen to be added to the model equation from section 3.5

Another aspect worth mentioning is that for some simulations carried in this work in Matlab ® (where the pressure was considered as a state), the index is sensitive to the initial conditions given which would indicate a numerical problem. Considering that it would be more appropriate to investigate this aspect in parallel with specific simulations and results, the discussion is let for section 5.4.1.

4.1.2 Model Stiffness

By introducing the pressure as a state, the model becomes stiff. A physical description of stiffness is that the model includes both slow and fast phenomena, thus having different time scale. The slow dynamics correspond to the temperature in this work while the fast correspond to the pressure. The stiffness of a system can be quantitatively measured by computing the eigen values of the system. As the eigen values approach infinity, so does the stiffness [Moe et al., 1995]. The computation of the eigen values is not straightforward for the presented model and hence the stiffness of the model formulated in section 3.5 is appreciated only by the physical description of stiffness.

4.2 Incidence Matrix

By adding a new state and a new equation the number of states per cell increases from 9 to 10 while the number of equations per cell increases in the same manner. It naturally follows that each state can be attributed to one equation. This can be observed by constructing the incidence matrix. The incidence matrix provides a clear overview of the connections between equations and unknown variables. The incidence matrix (table 4.1) has the model equations written in the first column while the variables are written in the first row. It should be noticed that some variables are part of the states indicated in table 3.2 while the other variables are a function of a state. The particular state is indicate in parenthesis for the dependent variables.

The process of constructing the matrix is as follows: a 0 is placed if the variable does not appear in the equation; a black X is written if the variables appear in the equations while a blue X is written if that particular equations is attributed to solving a variable (or state). Considering that more than one variable could be function of the same state, it is normal to have two blue X on the same row. Each equation is however attributed to solving for one state from table 3.2. For the rows that have two unknown variables marked with X, the equations is attributed to solving for the state that is indicated in the parenthesis, next to the variables. For the rows that have one unknown variable (equal to a state) marked with X, the respective equations from the first column are attributed.

Table 4.1: Incidence Matrix

	Variables												
Equation	F	nT	n	$H_L(T)$	$H_G(T)$	U	x	y	$n_L(V_L)$	$n_G(V_L)$	Z_G	Z_L	P
Overall mass balance 3.1	X	X	0	0	0	0	0	0	0	0	0	0	0
Component mass balance 3.2	X	0	X	0	0	0	0	0	0	0	0	0	0
Energy balance 3.3	0	X	0	X	X	X	0	0	X	X	0	0	0
Internal energy 3.9	0	0	0	X	X	X	0	0	X	X	0	0	X
Component holdup 3.10	0	X	0	0	0	0	X	X	X	X	0	0	0
VLE 3.11	0	0	0	0	0	0	X	X	0	0	0	0	X
Total holdup 3.12	0	X	0	0	0	0	0	0	X	X	0	0	0
Vapor compressibility 3.13	0	0	0	0	0	0	0	0	0	0	X	0	0
Liquid compressibility 3.14	0	0	0	0	0	0	0	0	0	0	0	X	0
Pressure 4.2	0	0	0	0	0	0	X	X	0	0	0	0	X

4.2.1 Revising The Model II

The important information that is derived from the incidence matrix is that there is no equation attributed to solving for the algebraic variable flow F, nor is the flow is a function of a state. In order to initialize and run the simulations without syntax errors, the outflow of each cell was given equal to the HEX inlet flow. However, having the outlet flow equal to the inlet implies that the accumulation of mass is 0 in each cell and overall mass balance (equation 3.1) and component mass balance (equation 3.2 are no longer a dynamic but a steady-state equation and valuable information (such as variation of holdup) could potentially be lost.

To circumvent this issues, the flow should be written as function of one (or potentially two) of the states. The first option that comes to mind is to express the outlet flow of each cell as a function of the pressure drop of the same cell, by using a resistance equation derived from turbulent equation, which is in fact similar to the valve equation. The equation is presented by Lee et al. [2016] and is given in equation 4.3b. The notations are given in reference to figure 3.4. The pressure drop of a cell is calculate as the difference between the outlet and inlet pressures, equation 4.3c. The constant k' is calculate as a function of the total HEX pressure drop ΔP_{HEX}, average molar volume along the HEX $V_{m,HEX}$ and the inlet flow F_0. The average molar density along the HEX is calculated as the average between the inlet and outlet molar volumes with, equation 4.3e, where the respective inlet and outlet molar volumes are given by equations 4.3f and 4.3g. Thus equation 4.3 is written.

$$F_j = \sqrt{k' \cdot \Delta P} \tag{4.3a}$$

$$\Delta P = P_{j-1} - P_j \tag{4.3b}$$

$$k' = F_0 \sqrt{\frac{\Delta P_{HEX}}{V_{m,HEX}}} \tag{4.3c}$$

$$V_{m,HEX} = \frac{V_{m,in}}{V_{m,out}} \tag{4.3d}$$

$$V_{m,in} = (1 - \epsilon_{in}) \cdot V_{m,L_{in}} + \epsilon_{in} \cdot V_{m,G_{in}} \tag{4.3e}$$

$$V_{m,out} = (1 - \epsilon_{out}) \cdot V_{m,L_{out}} + \epsilon_{out} \cdot V_{m,G_{out}} \tag{4.3f}$$

$$\tag{4.3g}$$

This possibility of expressing the flow as a function of pressure was indeed tried during simulations in Matlab®. However, solving for the DAEs failed to be initialized (the initial conditions were not consistent) with this method resulting in an error, even if the tolerance and maximum step were set as small as 10^{-5}. The probable cause is that averaging for properties only based on the inlet and outlet conditions is a bad assumption for a HEX with phase change. It should be mentioned that the initial condition for composition and compressibility factors were taken from Aspen Hysys®, while for the other variables a linear profile was given as initial conditions.

As a consequence, a new option of expressing the outlet flow as a function of one or several states has to be found. It should be remembered that the basic assumption of the HEX model is doing a flash calculation in each cell. In a flash tank, controller are used to manipulate the outlet flows to control the pressure and level in the tank. With this justification, it is chosen to use imaginary P-controllers (P in this case is from proportional and should not be confused with pressure P) with infinite large gain to control the inventories in each cell (pressure and level) with the outlet flows. Although adding P-controllers for each cell may seem physical unnatural, it has the effect of stabilizing the integrating process that is level variation in the cell [Skogestad, 2007].It follows that N cell would have an N^{th} integrating order. This method is proven to be successful in solving for the DAEs system. The further implications of the application in the HEX model are discussed in parallel with the results in section 5.4.1 for a better overview.

Chapter 5

Simulation

This chapter presents different simulations that were carried out having in mind the scope of the HEX model described in section 3.1. The SRK Matlab ® scripts used throughout the simulations in this chapter are a modified version (to account for the particular components in this project) of the SRK scripts available on Sigurd's Skogestad webpage [Skogestad et al., 2013].

5.1 Stream Conditions

Section 3.2 states that only the stream that could potentially change phase is modelled as series of lumps. The general given conditions for that stream used in the simulations are presented here. The name of the stream is mixed refrigerant, a terminology well used in refrigeration cycles. The mixed refrigerant molar composition is given in table 5.1 while other properties such as specific heat capacity, acentric factor and critical pressures and temperatures properties are given in the appendix B.3.

Table 5.1: Mixed refrigerant molar composition

Component	Molar fraction
Nitrogen	0.06
Methane	0.4
Ethane	0.4
Propane	0.14

The inlet mixed refrigerant flow and pressures are taken from the process presented in Nekså et al. [2010]. The MR flow reported in Nekså et al. [2010] is $4073\frac{kg}{h}$ which with the composition from table 5.1 becomes $F_0 = 0.0445\ \frac{kmol}{s}$ while the pressure is 18 bar. The volume of the HEX is taken as 0.2 m^3 as a start and could be subject to change. If pressure drop along the HEX is considered, the maximum values is 5 mbar. Particular conditions are specified for each simulation if it needed.

5.2 Initial Conditions

Due to the unavailability of real process data, another approach for guessing good initial conditions has to be found since the solver used. *ode15s* requires consistent initial conditions for the DAEs set. The process of obtaining the initial conditions is shortly summarized as follows. The mixture proprieties are calculated by the general rule of mixing by molar weight, as it was already discuss when the vapor fraction was used to rewrite the energy balance 3.6. Equation 5.1 is written for a general mixing property calculation θ.

$$\theta_{mixture} = (1-\epsilon)\cdot\theta_L + \epsilon\cdot\theta_G \tag{5.1}$$

- the cell volume is considered given and it is constant throughout the simulation
- the pressure drop is considered to have a linear profile
- the initial conditions that are not dependent of the cell volume (such as compositions, vapor fraction, temperature or compressibility factor) are taken from Aspen Hysys ®
- the total holdup (cell volume dependent) is considered to have a linear profile between the first and last cell holdup which is calculated as the report of cell volume and mixture molar volume
- the component holdup is calculated as the product of the total holdup and the component concentration from table 5.1
- the internal energy (cell volume dependent) for each cell are calculated using the mixture enthalpy, pressure and cell volume as it is mentioned in equation 3.8
- the liquid volume (cell volume dependent) is calculated as the product between the liquid fraction of each cell (calculated as 1 - vapor fraction, ϵ) and the cell volume.

It can be observed that the initialization procedure is cumbersome and is is not that precise. In addition, it could represent a bottleneck in solving the problem.

5.3 One Phase Simulation

This simulation has the purpose to model the HEX without phase change, the inlet and outlet flow being in vapor phase. Hence it corresponds to transition A → B from figure 3.1. It should be mentioned that this simulation was carried out as a consequence of the challenge of differential index greater than 1 mentioned in section 4.1 but before finding a way to overcome it. Therefor, the original idea behind conducting this simulations is to identify the probable cause of the index issue. The model equations are simplified to exclude the equations and terms accounting for liquid phase or vapor-liquid equilibrium and are summarized in equations 5.2, 5.3, 5.5 and 5.6. They are given in respect to the representative HEX cell from figure 3.4.

Overall mass balance

$$\frac{dnT_j}{dt} = F_{j-1} - F_j \tag{5.2}$$

Component mass balance

$$\frac{dn_{i,j}}{dt} = F_{j-1} \cdot z_i - F_j \cdot z_i \tag{5.3}$$

Energy balance

$$\frac{du_j}{dt} = F_{j-1} \cdot H_{G,(j-1)} - F_j \cdot H_{G,j} - Q_j \tag{5.4}$$

Internal energy

$$u_j + P \cdot V_{cell} - H_{G,j} \cdot n_{G,j} = 0 \tag{5.5}$$

Vapor compressibility

$$Z^3_{G,j} + Z^2_{G,j} + Z_{G,j} \cdot (A_{G,j} - B_{G,j} - B^2_{G,j}) - A_{G,j} \cdot B_{G,j} = 0 \tag{5.6}$$

A few remarks are required about the conditions of this simulation. First, the pressure is considered to be constant in each cell. Second, the flow is not considered an unknown algebraic variable and it is given equal to the nominal value (inlet flow). The reasonable explanation about why this one phase model does not have an index greater than 1 is that the equilibrium

Table 5.2: One phase simulation conditions

Cold fluid	Sea water (SW)
Hot fluid	Mixed refrigerant (MR)
$T_{MR,in}$	67 $°C$
$T_{SW,in}$	5 $°C$
$T_{SW,out}$	15 $°C$
$c_{p_{SW}}$	4.118 $\frac{kJ}{kg \cdot K}$
q_{SW}	2.2 $\frac{kg}{s}$

is removed and with it the number of constraints for the variables is decreased. Third, since the one phase case does not involve a vapor-liquid mixture, it follows that the mixture properties calculation for initial conditions do not apply and single phase properties are used.

The conditions for the simulation are presented in table 5.2. The purpose is to model the precooler presented in work of Nekså et al. [2010] where mixed refrigerant is cooled from 67 $°C$ to 33 $°C$ with sea water. The conditions for the cooling agent are not presented in the work of Nekså et al. [2010] and reasonable engineering values are assumed.

Even though this simulation may seem outside the scope of developing a robust model for all possible phase transitions, it is also the source of valuable information regarding the assumptions made in formulating the model in section 3.2. In the next two subsections, it is presented how the one phase HEX model behaves when parameters such as cells number or cell volume are changed.

5.3.1 Cell Number Sensitivity

The change in the temperature profile when the number of cells is changed is investigated and the results for 10, 20 and 60 cells are respectively showed in figure 5.1. The volume of the HEX is 0.2 m^3. The temperature changes steps wise since the it is considered constant in each cell and thus a temperature discretization is made. As expected, as the discretization is finer made, the profiles approaches a linear trend and it becomes more smooth.

It can be observed that the outlet temperature does not change for the chosen number of cells and has the values of 32 $°C$. What is the most interesting to observe is what happens in the

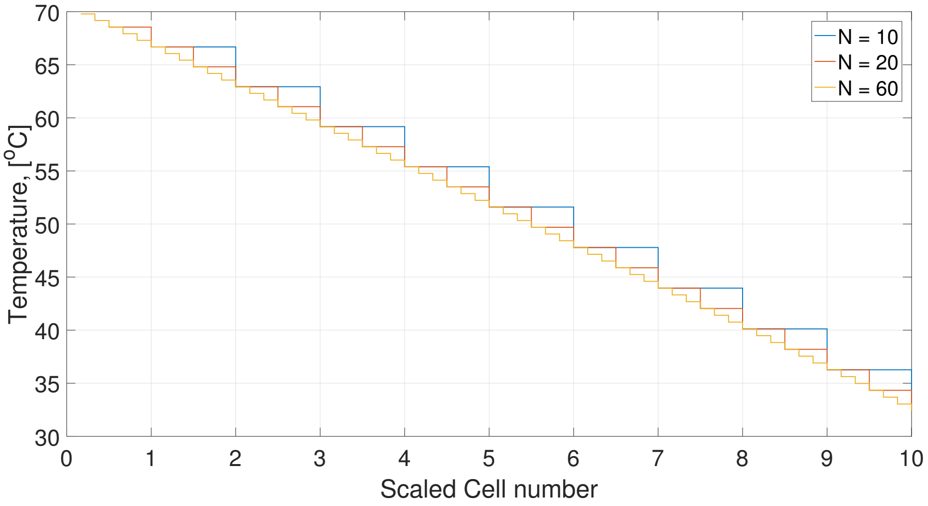

Figure 5.1: Temperature profile as a function of cells number

first cell of all three cases. The $T_{MR,in}$ is 67 $°C$ and since it is cooled down, the temperature in the first cell should be smaller than the inlet temperature. While the temperature is smaller for the cases of 10 and 20 cells, it is not for the case with 60 cells. A reasonable explanation is that the dynamic behavior is dependent of the volume of each cell which decreases as the number of cells increases while the total volume is maintained constant (see equation 3.4b). It is assumed that the exchanged heat is constant for each cell and it is given as input. This could signify that in the case of 60 cells, the heat is not enough to properly balance the internal energy of the cell which is volume dependent and an increase in the MR temperature is seen in the first cells. Another possible explanation is that it is a numerical problem related to scaling as part of the initial conditions are dependent of the cell volume and their values would become smaller as the cell volume decreases.

5.3.2 Cell Volume Sensitivity

After the cells number analysis, another parameter with dynamic effect that is investigated is the cell volume. Figure 5.2 illustrates how the outlet temperature of the mixed refrigerant changes as the total HEX volume increases. The number of cells is 10 for all cases and the sea water flow is from table 5.2. As expected, and as seen in the previous sensitivity analysis of the cells number, a change in volume has an effect on the change in the outlet temperature. This can be explained with the same reasoning as in the previous case, based that the internal energy is a function of volume. This analysis proofs that the total volume has to obtained form real design data if a thoroughly simulations is required.

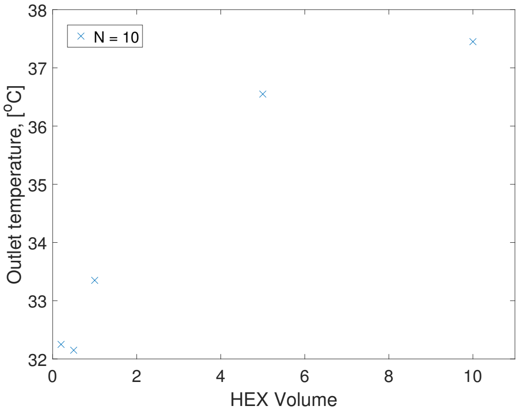

Figure 5.2: Outlet temperature as a function of HEX volume

5.3.3 Model Validation

A model validation is desired for the one phase simulation. A steady state simulation was performed is Aspen Hysys® with the parameters from table 5.2 and the outlet temperature obtained is 29 $°C$, compared with the 32 $°C$ obtained by simulation the model in Matlab®. The results does not match very well. However, a fair comparison is difficult to be made considering the two sensitivity analysis from above which showed effect of the volume.

The two sensitivity analysis from above also demonstrate that keeping constant exchanged heat throughout the HEX length is not an accurate assumption and it should be reconsidered. A possible solution is to keep count of the thermal kinetics and use the approach presented in section 3.6. However, for the moment being, the constant exchanged heat assumption is not changed and it is continued to be used in the next simulations.

5.4 Two Phase simulation

The simulations in this section correspond to a transition from one liquid-vapor state to another liquid-vapor state. With respect to figure 3.1, the transition is C → D. The model equations are the ones formulated in section 3.5, along with the VLE for the last component, equation 4.2 to account for the change in pressure (added as a state in section 4.1.1). In addition P-controller with large gain are used for the reasons mentioned in section 4.2.1.

5.4.1 Flash Calculation

First a flash calculation is performed for one tank with heat source which in this project has the significance of a representative cell (given volume and energy). The base of the model is a dynamic flash using SRK EOS [Skogestad et al., 2013] whose equations have been changed to match the one of the HEX model.For illustration purposes, the flowsheet of the process is illustrated in figure 5.3. A flash tank separates one outlet into two outlet stream (gas and liquid). However, such model with outlets has no significance for a lumped HEX model, where each cell has a single inlet and outlet. Hence, in this work, it is considered that as the inlet streams enters the cell it flushes (due to the heat source), then the composition of the phases changes in accordance to vapor-liquid equilibrium and then the gas and liquid stream are mixed back. The pressure in the cell is controlled by manipulating the gas outlet while the liquid inventory is controlled by the liquid flow. Both gas and liquid outlet do not have a physical meaning based on the perfect mixing assumption mentioned in section 3.2.

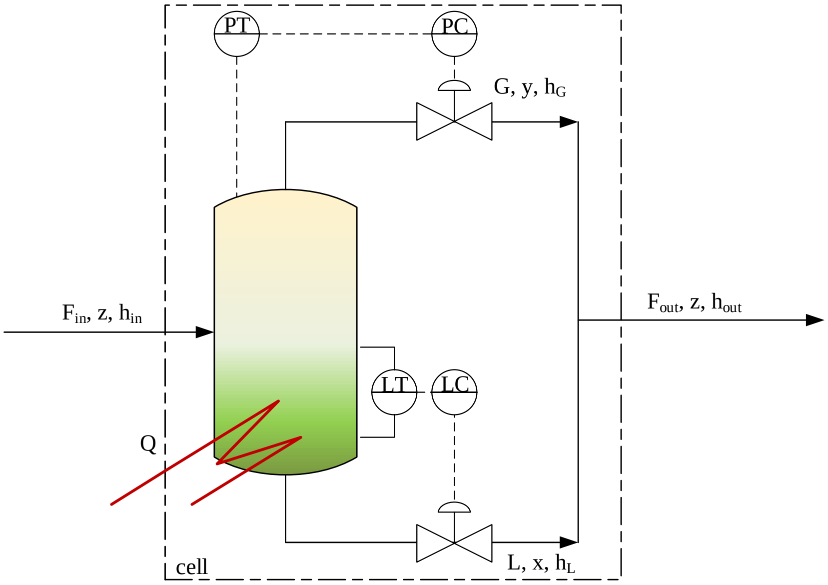

Figure 5.3: Flash tank with heat source

From figure 5.3 it follows that the outlet flow is given by equation 5.7 (sum of gas and liquid flows). The rest of the equations are the same as in the HEX model and the states correspond with the ones from table 3.2.

$$F_{out} = G + L \tag{5.7}$$

In the first simulation of the single cell flash, the compressibility factor Z was not included as a state since the original scripts used did not have the compressibility factor explicitly given in the model and it was calculating externally using the root function in Matlab®. A few observation have to be made. When running the simulation it was discovered that while using all 15 decimals for the initial conditions for the the composition supplied by Aspen Hysys® there was and error message that in index of DAE is greater than 1. It was then tried to use only 4 decimals in the initial conditions and do a flash calculation at -15 $°C$ with no heat removed the DAE system was solved. However, when it was tried to do a flash calculation -65 $°C$ with no heat removed the DAE system could not be initialized even if the tolerance and maximum step were decreased to 10^{-5} or the cell volume was changed. It is important to mention that the differential index is calculated *before* the verification of the consistency of the initial conditions in the function *daeic12* called by the solver *ode15s*. This observations indicate the index error message could have as a source a numerical problem related with the inconsistent initialization of the DAE set.

In order to make the one flash calculation representative for this project, the initial script was changed to compressibility factor as a state. With this modification, the DAE system could be initialized for a flash calculation at -65 $°C$, where the simulation without having Z as a state failed. It it thus another argument in favour of incorporating the equations for compressibility inside the model and not solved for them outside.

Only the numerical results where Z is included as a state are presented in this report. Different mixed refrigerant inlet temperatures are tested along with energy values for the heat source. The results are presented in table 5.3.

It should be mentioned that the units for the states and variables have been changed for energy terms to MJ, pressure to MPa and mass flowrate to $\frac{kmol}{min}$, the rest remaining the same. Another important mentions is that the volume of the cell was changed from 0.2 m^3 as in is stated in the section 5.1 to 0.66 m^3 for the simulations started with a mixed refrigerant temperature of $T_{MR,in} = -15°C$ while 1 m^3 was used as a volume for the simulations starting at $-65°C$ due to solver stability issues. Since the real process desired to be simulated is a cooling process, heat is removed from the cell.

The source of the differences in temperature when no heat was supplied can be caused by

Table 5.3: Flash results

$Q\ \frac{MJ}{min}$	0	10	23	0	10
$T_{MR,in}\ ^\circ C$	-15	-15	-15	-65	-65
$T_{MR,out}\ ^\circ C$	-15.4	-32.8	-62.3	-67	-94.5
Hysys® $T_{MR,out}\ ^\circ C$		-31.8	-61		-95.7
x_{N_2}	0.0038	0.0052	0.0097	0.011	0.0296
x_{CH_4}	0.00171	0.1048	0.2038	0.225	0.3663
$x_{C_2H_6}$	0.4337	0.514	0.5628	0.5516	0.4445
$x_{C_3H_8}$	0.5454	0.349	0.2237	0.2124	0.1576
y_{N_2}	0.064	0.0847	0.139	0.1505	0.3014
y_{CH_4}	0.4258	0.5329	0.7085	0.723	0.6674
$y_{C_2H_6}$	0.3974	0.3365	0.144	0.1202	0.0302
$y_{C_3H_8}$	0.1124	0.0459	0.0085	0.0063	0.001

the fact the inlet enthalpy was given as a number with 1 or 0 decimals and since its units are in MJ, a not very precise values for the inlet enthalpy could lead to large variations in temperature or it can be attributed to a numerical problem. The results are also compared with results from Hysys® stream analysis and it can be observed that the difference are of maximum 1 $^\circ C$.

5.4.2 HEX Simulation

The next step after simulating a flash with heat source for cell is to simulate the HEX with a transition C → D from figure 3.1, from a liquid-vapor phase to a liquid-vapor phase. The total volume of the HEX is given as 10 m^3 to avoid numerical problems with a too small cell volume as the cell number increases. The heat is specified as 23 $\frac{MJ}{min}$, corresponding approximately to a change in temperature from -15 $^\circ C$ to -65 $^\circ C$ as observed in the case of a single flash calculation, in table 5.3. The behaviour of the model is investigated for two different cells numbers: 10 cells and 60 cells. The steady-state temperature profile along the cells is presented in parallel in figure 5.4. In terms of axes choices, the best option would to plot the temperature profile along the length of the HEX. However, the length is not available from design data and the analysis is made on a scaled cell number is chosen instead. As expected, as the number of cells increases, a more precise temperature profile is observed. The temperature profile for a higher number

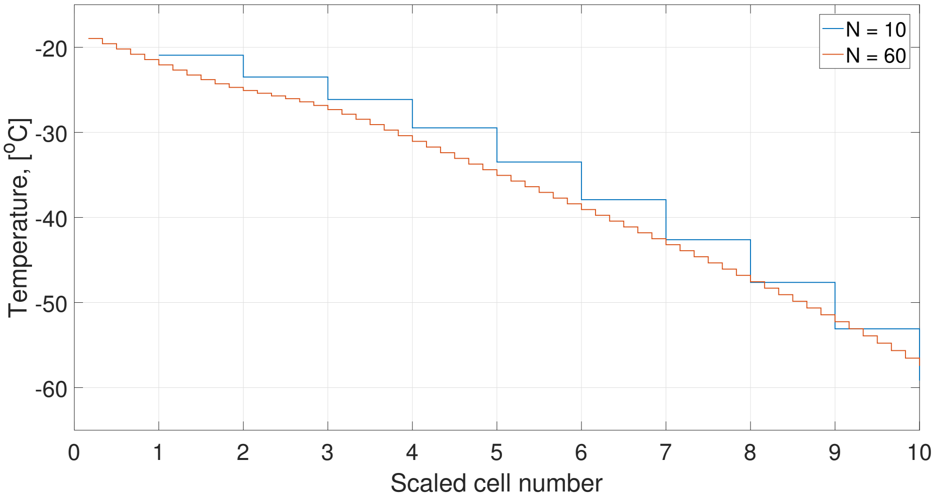

Figure 5.4: Temperature profile for 2 phase HEX

of cells is smoother and is slightly non linear, where as the profile for 10 cells is approximately constantly decreasing.

5.5 Phase Boundary Transition

The most challenging transition from a two phase flow to a one phase flow (or the oposite transition) is left to be discussed last. It corresponds to a transition D → E from figure 3.1, crossing thus the boundary from a liquid-vapor phase to a liquid phase which makes the behaviour discontinuous. Again, a flash calculation is first performed followed by the HEX simulation.

5.5.1 Flash Calculation

The simulation is done in the same manner as in section 5.4.1, the only difference being that the specified heat should be enough for a transition to the liquid phase. The volume of the flash tank is taken as 1 m^3 The values for the heat are taken from Hysys® stream analysis. A comparison between the temperatures obtain by simulation in Matlab® and Hysys® is given in table 5.4. This time the difference are more significant compared to the results from the previous flash calculation in section 5.4.1.

Table 5.4: Comparison between Matlab® and Hysys® Flash results

$Q \frac{MJ}{min}$	16	20	25
$T_{MR,in}$ °C	-65	-65	-65
$T_{MR,out}$ °C	-107.4	-114	-120.3
Hysys® $T_{MR,out}$ °C	-120	-143	-172.8

Eventhough the results from table 5.4, are not promising, it is also desired to analyses if the model is able to detect liquid phase if enough heat is removed. For this purpose, three different values for the removed heat have been tested and the results are presented in table 5.5. Indeed, if enough heat is removed, the composition of the liquid phase approached the composition of the inlet from table 5.1. It is expected that the vapor composition will never reach 0 for all components if VLE is assumed since this would imply that the corresponding liquid composition is also 0 according to the VLE equation 3.11 which is physical unfeasible. This results demonstrate that the model is able to handle a transition from a two phase region to a one phase region.

Table 5.5: Flash calculation for boundary transition

$Q \frac{MJ}{min}$	100	200	500
$T_{MR,in}$ °C	-65	-65	-65
$T_{MR,out}$ °C	-150	-176	228
x_{N_2}	0.07505	0.0649	0.06
x_{CH_4}	0.39597	0.3982	0.4
$x_{C_2H_6}$	0.3918	0.39765	0.4
$x_{C_3H_8}$	0.1371	0.1392	0.14
y_{N_2}	0.7966	0.8972	0.9995
y_{CH_4}	0.203	0.1026	0.0005
$y_{C_2H_6}$	0.0004	2.3634e-5	≈ 0
$y_{C_3H_8}$	1.5658e-06	≈ 0	≈0

5.5.2 HEX Simulation

An investigation on how the HEX model behaves on a transition from liquid-vapor to liquid phase is also made. The volume of the total HEX is taken as 10 m^3. The heat is specified as 500 MJ/min. The cells number is 10. The steady-state temperature profile is illustrated in figure 5.5. The temperature profile does in fact present a plateau which correspond to condensation.

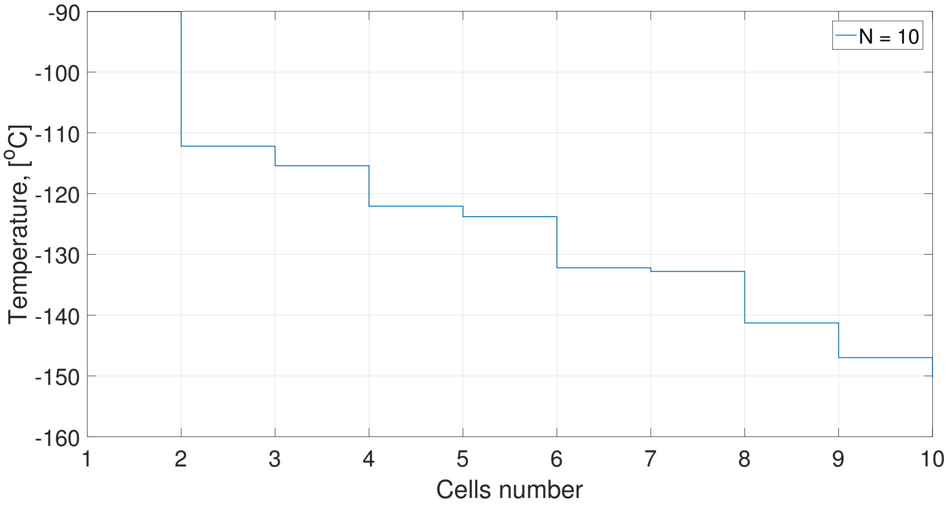

Figure 5.5: Temperature profile for HEX simulation from LV phase to L phase

It was also tried to simulated for a number of 60 cells to obtain a more precise results but the solver failed to initialized.

All the scripts are given in appendix C.2 for one phase simulation, **??** for one flash calculation and **??** for HEX simulation.

Chapter 6

Discussion and Future Recommendations

Throughout the previous section different issues have been mentioned regarding the solvability of the model. When the pressure was considered constant, the formulated model has an index greater than 1, a system which is not solvable in Matlab®. By including the pressure as a state and let it vary, the model could be solved. However, there have a few occasions when the initial conditions (provided by Hysys®) stream analysis) supplied to the *ode15* solver were not consistent. A way of avoiding having numerical problems as a recurrent issued is naturally desired. An option would be to reconsider the model equations and formulate it in terms of extensive variables instead of intensive variables as it is presented in this work. A second option could represent to change the solver and an alternative is CasADi. The advantage of using CasADi is that variables are evaluated symbolically (with a higher speed than Matlab does). In this way, the index problem can be reevaluated and an index reducing algorithm which handles symbolic variables could be used. Further, since the model is intended for optimal operation, CasADi could provide a more valuable analysis.

The simulations that were carried out in this work correspond only to cooling process. The other possible transitions from table 3.1 should also be investigates as future work.

Based on the simulation, the assumptions from section 3.2 involving the exchanged heat should be reconsidered. A lumped model should be implemented as well for the second stream and the thermal dynamics of both streams have to be coupled. However, as the model is implemented for one stream, implementation for two streams should be easily done.

The model performed well for the the case of multiphase flow in liquid-vapor region. However, the results for a boundary transition from one phase to another are significantly different from the ones obtained by stream analysis in Hysys ®. This implies that the boundary transition has to be more carefully handled. A possibility to handle the boundary transition is found in the work of Watson and Barton [2017] which uses nonsmooth functions.

The model should be also tested with real process data, if available.

Chapter 7

Conclusion

This project presents dynamic HEX model developed with the purpose of handling any transition from vapor, liquid-vapor and liquid region. The model is implemented in Matlab® and SRK EoS is incorporated in the model to model the non-ideal thermal properties.

The heat exchanger is modelled as a series of lumps and in each lump a flash calculation is performed to determine the composition of the phases. For the moment, only the stream that could change phase is modelled as a series of cell.

A few challenges appeared during the model development the initial simulations. A model analysis was made and as a result pressure was introduced as a state, along with the VLE for the last component to solve for it.

Simulations were carried out for a vapor stream that does not change phase, a multiphase stream that undergoes a temperature changed but remains inside the liquid-vapour region and a two phase stream that transitions the boundary from the liquid-vapor region to the liquid region. The model is able to handle all the mentioned regions. However, while the results look promising for the first two simulations, for the last of them (phase boundary transition) the outlet temperature does not match veryy well when compared with a commercial process simulator Hysys®).

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Appendix A

Notations

Acronyms

DAE Differential Algebraic Equations

EoS Equation of State

FCV Finite Control Volume

HEX Heat exchanger

LC Level Controller

LT Level Transmitter

LNG Liquid Natural Gas

MHEX Multistream Heat Exchnager

MR Mixed Refrigerant

NC Number of Components

ODE Ordinary Diferential Equations

PH Pressure Entlahpy

PC Pressure Controller

PT Pressure Transmitter

SRK Soave Redlich Kwong

SW Sea Water

TDAE Thermodynamic Differential Algebraic Equation

VLE Vapor-Liquid Equilibrium

List of Symbols

A SRK parameter

B SRK parameter

c Correction factor for liquid molar volume

C_P Specific heat

F Molar flow

g Gravity acceleration

h enthalpy

H specific enthalpy

K VLE constant

k interaction parameter

M Mass matrix

m SRK parameter (slope)

N cells number

n holdup

nT Total holdup

P Pressure

Q Exchanged heat

q mass flow

R Universal gas constant

T Temperature

u Internal energy

U Specific internal energy

UA Heat transfer coefficient times transfer area

V Volume

v velocity

$\mathbf{V}_m$ Molar volume

$\mathbf{V}_L$ Liquid volume

x Vapour molar composition

y Liquid molar composition

z Molar composition

Z Compressibility factor

$\mathbf{Z}_{RA}$ Rackett compressibility factor

A, B, C, D, E polynomial coefficients for specific heat

Subscripts

0 inlet/initial

c critical in respect to SRK Eos

c cold in respect to HEX model

cell applies for one cell

G Gas

HEX Applies along the heat exchanger

i component number

in inlet

j cell number

L Liquid

out outlet

r reduced

Greek Letters

α SRK correction parameter

δ fugacity correction parameter

Δ difference

ϵ vapour fraction

γ activity coefficient

ν differential index

ϕ fugacity

ρ density

θ general property

σ tension force

ω acentric factor

Appendix B

Thermodynamical constants

B.1 Coefficients for specific heat

Table B.1: Polinomial coeffiecients for calculation of $\frac{C_p}{R}$

Coefficient	A	$B \cdot 10^3$	$C \cdot 10^5$	$D \cdot 10^8$	$E \cdot 10^1 1$
Nitrogen	3.539	-0.261	0.007	0.157	-0.099
Methane	4.568	-8.975	3.361	-3.407	1.091
Ethane	4.178	-4.427	5.660	-6.651	2.487
Propane	3.837	5.131	6.011	-7.893	3.079

Prausnitz J. M. [2001]

B.2 Interaction Parameters

From Aspen Hysys

Table B.2: Interaction Parameters

Component	Nitrogen	Methane	Ethane	Propane
Nitrogen	0	3.11990007758e-2	3.18990014493e-2	8.86000022292137e-002
Methane	3.119900077581e-2	0	2.24137306213379e-3	6.82878494262e-3
Ethane	3.189900144934e-2	2.24137306213e-3	0	1.25795602798e-3
Propane	8.860000222921e-2	6.82878494265e-3	1.25795602798e-3	0

B.3 Critical Pressure, Temperature and Acentric Factor

From Prausnitz J. M. [2001]

Table B.3: Critical Pressure, Temperature and Acentric Factor

Component	P_c MPa	T_c K	ω
Nitrogen	3.398	126.2	0.037
Methane	4.599	190.56	0.011
Ethane	4.872	305.32	0.099
Propane	4.4248	369.83	0.0152

compDataPc = [33.98 45.99 48.72 42.48]*0.1; compData.Tc = [126.20 190.56 305.32 369.83]; compData.w = [0.037 0.011 0.099 0.152];

Appendix C

Matlab Scripts

C.1 SRK Script

```
function [phi,H,Vm,A,B]= srkHEXV3(Z,x,T,P)
% In: compositon x (vector), Temperature T [K], pressure p [MPa]
% OUT: Compressibility Z, Fugacity coeff.(vector) phi [-], enthalpy H [MJ/kmol]
% Molar Volume V [m3/kmol]

% Authors: Andreas Linhart and Sigurd Skogestad. NTNU. 2008
% Modifications (Cristina Zotica): changed components; added 5th term of Cp
% in calculating H, changed P in MPa and H in MJ/kmol,
% added interaction parameters from Hysys
% removed 'phase' as input and added a a

%Components N2 C1 C2 C3 C4
NC=4;  % Number of components (1)Nitrogen - (2)Methane - (3)Ethane - (4)Propane

%Component data from: Reid RC, Prausnitz JM, Poling BE.
%The properties of gases \& liquids (5th edition). New York: McGraw-Hill, Inc., 2001.

compData.Pc = [33.98  45.99  48.72  42.48 ]*0.1;     % [MPa]
compData.Tc = [126.20 190.56 305.32 369.83];         % [K]
compData.w  = [0.037  0.011  0.099  0.152 ];         % acentric factor [-]

R = 8.314/1000; % MJ/kmol/K
```

```
% Ideal has heat capacity (See Hid below):
compData.Cp(:, 1) = [3.539 -0.261e-3 0.007e-5   0.157e-8 -2.099e-11]' * R;    % Nitrogen
compData.Cp(:, 2) = [4.568 -8.975e-3 3.631e-5  -3.407e-8  1.091e-11]' * R;    % Methane
compData.Cp(:, 3) = [4.178 -4.427e-3 5.660e-5  -6.651e-8  2.487e-11]' * R;    % Ethane
compData.Cp(:, 4) = [3.847  5.131e-3 6.011e-5  -7.893e-8  3.079e-11]' * R;    % Propane

compData.Tref = 298.15;     % [K], for Ideal gas heat capacity


% SRK binary interaction parameters from Aspen Hysys V9
kinteraction(:,1)=[0 3.11990007758141e-2 3.18990014493465e-002  8.86000022292137e-2];
%Nitrogen
kinteraction(:,2)=[3.11990007758141e-2  0   2.24137306213379e-3 6.82878494262695e-3];
%Methane
kinteraction(:,3)=[3.18990014493465e-2  2.24137306213379e-3 0   1.25795602798462e-3];
%Ethane
kinteraction(:,4)=[8.86000022292137e-2  6.82878494262695e-3 1.25795602798462e-3 0];
%Propane


%% Initialize

Pc = compData.Pc;
Tc = compData.Tc;
w = compData.w;
ZRA = 0.29056-0.08775*w;
Cp = compData.Cp;
Tref = compData.Tref;

% Calculations for given T, P  and composition (x)
Tre = T./Tc;
Pre = P./Pc;
m = 0.480+1.574.*w-0.176.*w.^2;
a = (1+m.*(1-Tre.^0.5)).^2;
Ap = 0.42747.*a.*Pre./Tre.^2;
Bp = 0.08664.*Pre./Tre;

% Start calculations

% Binary a's:
%Mixing rules
Ab = zeros(NC,NC);
```

```
for i = 1:NC
    for j = 1:NC
        Ab(i,j) = (Ap(i)*Ap(j))^0.5;
    end
end

% Mixture a and b
A = 0;

    for i = 1:NC
        for j = 1:NC
            A = A+x(i)*x(j)*Ab(i,j)*(1-kinteraction(i,j));
        end
    end


B = 0;
for i = 1:NC
    B=B+x(i)*Bp(i);
end

%phi
corrphi=zeros(1,NC);
for i = 1:NC
    for j =1:NC
        corrphi(i) = corrphi(i) + x(j) * Ap(j)^0.5 * (1-kinteraction(i,j));
    end
end

phi = exp((Z-1).*Bp/B-log(Z-B)-A/B*log((Z+B)/Z).*((corrphi.*2.*Ap.^0.5./A)-Bp./B));

%end

% Enthalpy
dadT = 0;
for i = 1:NC
    for j = 1:NC
        dadT = dadT -R / 2 * sqrt(abs(0.42748 / T)) * x(i) * x(j) * (m(j) *...
        sqrt(abs(Ap(i)*(Tc(j)/P*(T^2)/(Pc(j))*(R^2)))) + m(i) *...
        sqrt(abs(Ap(j) * (Tc(i)/P*(T^2)/(Pc(i))*(R^2))))) ;
    end
end
```

```
H = (1/ (B*R*T/P)) * ( A*R^2*T^2/P - T*dadT) * log(Z / (Z + B)) + R * T * (Z - 1) ;


for i = 1:NC
    H = H+(x(i)* (Cp(1,i) * (T - Tref) + 1/2 * Cp(2,i) * (T^2 - Tref^2) +...
    1/3 * Cp(3,i) * (T^3 - Tref^3) + 1/4 * Cp(4,i) * (T^4 - Tref^4) +...
    1/5 * Cp(5,i) * (T^5 - Tref^5)));
end


% Molar volume

if Z<0.2 % Correct liquid SRK-volume using Peneleoux correction
     c=0;
     for i=1:NC
     c=c+x(i) * (0.40768 * (0.29441 - ZRA(i)) * (R * Tc(i)) / (Pc(i))) ;
     end
  Vm = ((Z * R * T / P)- c);
else
    Vm = Z * R * T / P;
end
```

C.2 One Phase Simulation

C.2.1 Model

```
function F1=HEXV6(t,w)

%Model of HEX for one phase and different for loops for ist cell and the
%rest

% INPUT: Time t and state vector w
% OUTPUT: Right hand side of DAE set: M dw/dt = f(w)


N=60;  % Cells numbers
NC = 4; % Number of components (1)Nitrogen - (2)Methane - (3)Ethane - (4)Propane

% Given feed: flow F, composition z, pressure and enthalpy
```

```
z = [0.06 0.4 0.4];    % Specified composition [kmol1/kmol]
P = 18*0.101325;       % Pressure, Pa
Z0 = 0.9994;           % from Hysys
T0 = 67+273;           % MR inlet temperature, K
[~, hf] = srkHEXV3(Z0,[z,1-sum(z)],T0,P);          % Specific enthalpy [kJ/kmol]
F0 =0.0445;             % Specified feed rate [kmol/s]
F = ones(N,1)*F0;
h0 = hf;


SW.q = 2.2 ;           % seawater mass flow, kg/s
SW.cp = 4.118;         % seawater cp, kJ/kg/K
SW.dT = 10;            %seawater temperature difference, K, from 5 drgC to 15 drgC
SW.Q = SW.q*SW.cp*SW.dT/N*1e-3; %heat per each cell, kJ/s, kW

%volume of one cell, considering a total volume of 0.2 m3.
Vcell =10/N;            %total volume of each cell, [m3]

%===========================================================================
% II. Extract present value of states
 %w=w';
  nT = w(1:N);                             %total holdup in        [kmol]
  n(1:(NC-1)*N) = w(N+1:N+N*(NC-1));       % component 1 holdup in tank [kmol1]
  U = w(N+(NC-1)*N+1:2*N+(NC-1)*N);        % total internal energy   [kJ]
  T = w(2*N+(NC-1)*N+1:3*N+N*(NC-1));      % temperature   [K]
  Zg = w(3*N+N*(NC-1)+1:4*N+N*(NC-1));     % gas compressibility



%===========================================================================
% Fugacity, enthalpy and volumes from SRK

y=zeros(1,(NC-1)*N); %conidering no phase change and the vapor composition
%will be the same as the inlet composition
for i=1:NC-1:(NC-1)*N
    y(i)=z(1);
    y(i+1)=z(2);
    y(i+2)=z(3);
end

for j=1:N
```

```
   [phig_temp,hg_temp,Vgm_temp,Ag_temp,Bg_temp]=srkHEXV3(Zg(j),...
   [y(j*(NC-1)-2) y(j*(NC-1)-1) y(j*(NC-1)) 1-(y(j*(NC-1)-2)+...
   y(j*(NC-1)-1)+y(j*(NC-1)))], T(j), P);      % vapor


    phig(j,1)=phig_temp(1);
    phig(j,2)=phig_temp(2);
    phig(j,3)=phig_temp(3);
    phig(j,4)=phig_temp(4);

    hg(j)=hg_temp;
    Vgm(j)=Vgm_temp;
    Ag(j)=Ag_temp;
    Bg(j)=Bg_temp;

end

% ==========================================================================

 % Gas houldup
nG = Vcell./ Vgm(j); % gas holdup                            [kmol]


% ==========================================================================
% IIIb. Evaluate right hand side of DAE-set: M dy/dt = f(y)
% f1 =dn/dt  Dynamic (1): Overall mass balance
% f2 =dn1/dt Dynamic (NC-1): Component 1 mass balance
% f3 =dU/dt  Dynamic (1): Energy balance
% f4 = 0     Algebraic (1): Internal energy U (can find T from this)
% f5 = 0     Algebraic (1): Compressibility Zg gas phase
% f9 = 0     Algebraic (1): Compressibility Zl liquid phase

% ==========================================================================


for j=1


    f1(j) = F0-F(j);
    f2((NC-1)*j-2:(NC-1)*j) = F0*z - F(j)*z;
    f3(j) = F0*h0 - F(j)*hg(j)-SW.Q;
    f4(j) = U(j) + P*Vcell - hg(j).*nG(j);
```

```
    f5(j) = Zg(j)^3-Zg(j)^2+Zg(j)*(Ag(j)-Bg(j)-Bg(j)^2)-Ag(j)*Bg(j);


end



for j=2:N

    f1(j) = F(j-1)-F(j);
    f2((NC-1)*j-2:(NC-1)*j) = F(j-1).*z - F(j).*z;
    f3(j) = F(j-1)*hg(j-1) - F(j)*hg(j)-SW.Q;
    f4(j) = U(j) + P*Vcell - hg(j)*nG(j);
    f5(j) = Zg(j)^3-Zg(j)^2+Zg(j)*(Ag(j)-Bg(j)-Bg(j)^2)-Ag(j)*Bg(j);


end

F1  = [f1'; f2';f3'; f4'; f5'; ];
```

C.2.2 Main Script

```
clear
clc
close all

% the initial condition are given based on a hysys simulation of the HEX
% a linear variation of properties along the cell has been used


N=10; %Number of cells
NC=4;  %Number of components
P = 18*0.101325; %pressure, kPa

%ODE solver options*********************************************************

nrDyn = NC-1+2; %number of dynamic equations per cell
nrAlg = 2; %number of algebraic eq per cell


%initial conditions
```

```
z0 = [0.06 0.4 0.4]; %inlet composition

%initial conditions for MR temperature
Tin = 67+273; %MR inlet temperature, K
Tout = 33+273; %MR outlet temperature, K
T00 = linspace(Tin, Tout, N+1); %considering a linear variation from 67 degC to 33 degC
T0 = T00(2:end);

%initial conditions for total holdup
V = 10; %volume, m3
Vcell = V/N; %VOlume of one cell, m3
Zin = 0.994;
Zout = 0.992;
[~,Hin,Vm_in,~,~ ] = srkHEXV3(Zin,[z0, 1-sum(z0)],T0(1),P);
[~,Hout,Vm_out,~,~ ] = srkHEXV3(Zout,[z0, 1-sum(z0)],Tout,P);

nT0 = linspace(Vcell/Vm_in, Vcell/Vm_out, N); %total holdup, assuming linear change
% in density, kmol

%Initial condition for internal energy
U0 = linspace(Hin,Hout,N).*nT0-P*Vcell; %[kmol]

y0=zeros(1,(NC-1)*N); %conidering no phase change and the vapor composition
% will be the same as the inlet composition
for i=1:NC-1:(NC-1)*N
    y0(i)=z0(1);
    y0(i+1)=z0(2);
    y0(i+2)=z0(3);
end

n0 = zeros(1,(NC-1)*N);
for j=1:N
    n0((NC-1)*j-2:(NC-1)*j) = nT0(j).*z0;
end

Zg0 = ones(1,N)*0.99;        % gas compressibility considering no phase change

w0 = [nT0,n0,U0,T0,Zg0]; % vector of initial condition

I_N = eye(N);
Dyn = eye(nrDyn);
Alg = zeros(nrAlg);
Mass = blkdiag(Dyn, Alg);
```

```
MassExt = kron(I_N,Mass);

d1 = ones(1,nrDyn*N);
d2 = zeros(1,nrAlg*N);
Mass1 = diag([d1,d2]);
options = odeset('mass',Mass1);

%ODE solver
[t,w]=ode15s(@HEXV6,[0 10],w0,options);       % integrate

nT = w(:,[1:N]);
n = w(:, [N+1:(NC-1)*N]);
U = w(:, [N+(NC-1)*N+1:2*N+(NC-1)*N]);
T = w(:, [2*N+(NC-1)*N+1:3*N+N*(NC-1)]);
Zg = w(:,[3*N+N*(NC-1)+1:4*N+N*(NC-1)]);

figure
plot(t,T)

figure
stairs(T(end,:))
xlabel('Cell #')
ylabel('Temperature, [K]')
xlim([1 N])
legend('2.2 kg/s SW')

figure
plot(T(end,:)-273)
xlabel('Cell #')
ylabel('Temperature [^oC]')
legend('2.2 kg/s SW')
xlim([1 N])
```

C.3 Flash Calculation

C.3.1 Moldel

```
function F=topflash3compV2(t,w) %F=f(t,w)

% This is file flashsrk.m (DYNAMIC FLASH with given energy and volume)
```

```
% INPUT: Time t and state vector w
% OUTPUT: Right hand side of DAE set: M dw/dt = f(w)
% Modified (CZ) to have Z as states

liquid=1;vapor=2;

% Given feed data: flow F, composition z1 and enthalpy
NC=4;                                           % Number of components
F=0.0445*60;                                    % Specified feed rate [kmol/min]
z = [0.06 0.4 0.4];                             % Specified composition [mol1/mol]
hf = -13;                                       % Specified enthalpy  [MJ/kmol = KJ/mol]

% Other data
Vtot = 1;                                     % m3    (total tank volume)

% II. Extract present value of states
nT=w(1);                                      % total holdup in tank (both phases)
[kmol]
n(1:NC-1)=w(2:NC);                            % component 1 holdup in tank (both phases) [mo
U=w(NC+1);                                    % total internal energy (both phases)
[MJ]
T=w(NC+2);                                    % temperature (same in both phases)
[K]
x(1:NC-1)=w(NC+3:2*NC+1);                     % liquid composition
y(1:NC-1)=w(2*NC+2:3*NC);                     % vapor composition
p =w(3*NC+1);                                 % pressure [MPa]
VL=w(3*NC+2);                                 % liquid volume [m3]
Zg =w(3*NC+3);
Zl=w(3*NC+4);

%composition and  holdup of last component

x(NC)=1-sum(x(1:NC-1));
y(NC)=1-sum(y(1:NC-1));
n(NC)=nT-sum(n(1:NC-1));


% Fugacity, enthalpy and volumes from SRK
[phil, hl,Vlm, Al,Bl] = srkHEXV3(Zl, x, T, p);
[phig, hg, Vgm, Ag, Bg] = srkHEXV3(Zg,y,T,p);

K = phil./phig;
```

```
% Phase distribution
VG = Vtot - VL;                    % gas volume
[m3]
nL = VL / Vlm;                     % liquid holdup                        [kmol]
nG = VG / Vgm;                     % gas holdup                           [kmol]

% Vapor and liquid flow
kp=100000;            % pressure controller gain
kl=10000;             % level controller gain
ps=1.8;               % setpoint p
G0=1.055e3;           % "bias"
G=kp*(p-ps)+G0;       %[kmol/min]
VLs = Vtot/2;         % Setpoint level (volume): keep 50% liquid in tank      [m3]
L0=1.725e3;           % "bias"
L = kl*(VL-VLs) + L0; % Level controller with proportional gain kl            [kmol/min]

F2 = G+L; %outlet flow
v = nG/nT; % vapor fraction
Q = 25; % given heat MJ/min
%============================================================================

% Model: Evaluate right hand side of DAE-set: M dy/dt = f(y)
f1 = F - F2;
% =dn/dt  Dynamic (1): Overall mass balance
f2(1:NC-1) = F*z(1:NC-1) - F2*z(1:NC-1);
% =dn1/dt Dynamic (NC-1): Component 1 mass balance
f3 = (F*hf - v*F2*hg - F2*(1-v)*hl-Q);
% =dU/dt  Dynamic (1): Energy balance
f4 = (U + p.*Vtot - hl.*nL - hg.*nG);
% = 0     Algebraic (1): Internal energy U (can find T from this)
f5(1:NC-1) = n(1:NC-1) - x(1:NC-1).*nL - y(1:NC-1).*nG;
% = 0     Algebraic (NC-1): Component holdup n1   (can find x1 from this)
f6(1:NC-1) = y(1:NC-1) - K(1:NC-1).*x(1:NC-1);
% = 0     Algebraic (NC-1): VLE for comp. 1 (can find y1 from this)
f7 = y(NC) - K(NC)*x(NC);
% = 0     Algebraic (1): VLE for last component (can find p from this)
f8= nT-nG-nL;
% = 0     Algebraic (1): Total holdup -(can fin VL)
f9 = Zg^3-Zg^2+Zg*(Ag-Bg-Bg^2)-Ag*Bg;
%
f10= Zl^3-Zl^2+Zl*(Al-Bl-Bl^2)-Al*Bl;

F  = [f1; f2'; f3; f4; f5'; f6'; f7'; f8';f9';f10'];
```

C.4 HEX Model

C.4.1 Model equations

```
function F1=HEXV16(t,w)

%Model of HEX

% INPUT: Time t and state vector w
% OUTPUT: Right hand side of DAE set: M dw/dt = f(w)
% this scripts also has pressure as a state
% 10 eq in DAE and 10 states
% pressure, MPa, energy kJ
% used to testing L-V to L-V


N = 60;  % Cells numbers
NC = 4; % Number of components (1)Nitrogen - (2)Methane - (3)Ethane - (4)Propane


% I. Given feed: flow F, composition z, pressure and enthalpy
F0 = 0.0445*60;
% Feed rate [kmol/s]
z = [0.06 0.4 0.4];
% Specified composition [kmol1/kmol]
P0 = 18*0.101325;
% Pressure, MPa
T0 = -15+273;
% MR inlet temperature, K
x0 = [3.17767964108482e-003 6.88654919614773e-002 0.424283041276263];
% liquid composition for MR at -15 degC from Hysys
y0 = [6.33288720745304e-002 0.419399144733269 0.398577405190801];
% vapor composition from MR at -15 deg C from Hysys
ZG0 = 0.86;
% from Hysys
ZL0 = 6.182e-2;
% from Hysys
[~, hfG] = srkHEXV3(ZG0,[x0,1-sum(x0)],T0,P0);
% Specific enthalpy for vapor[kJ/kmol]
[~, hfL] = srkHEXV3(ZL0,[y0,1-sum(y0)],T0,P0);
% Specific enthalpy for liquid[kJ/kmol]
```

```
v0 = 0.944658252981209;
% inlet vapor phase from Hysys
hf = v0*hfG + (1-v0)*hfL;
% Specific feed enthalpy [kJ/mol]
h0 = hf;
% Given heat

Q = 200/N; % [MJ/min]

% volume of one cell, considering a total volume of 10 m3.
Vcell =10/N;                                                % volume of each cell, [m3]

%===========================================================================
% II. States
 %w=w';
  nT = w(1:N)';
  % total holdup in  (both phases)       [kmol]
  n(1:(NC-1)*N)  = w(N+1:N+N*(NC-1))';
  % component 1 holdup in tank (both phases) [kmol1]
  U = w(N+(NC-1)*N+1:2*N+(NC-1)*N);
  % total internal energy (both phases)      [MJ]
  T = w(2*N+(NC-1)*N+1:3*N+N*(NC-1))';
  % temperature (same in both phases)        [K]
  x(1:(NC-1)*N)  = w(3*N+N*(NC-1)+1:3*N+2*N*(NC-1))';      % liquid composition
  y(1:(NC-1)*N)  = w(3*N+2*N*(NC-1)+1:3*N+3*N*(NC-1))';    % vapor composition
  VL = w(3*N+3*N*(NC-1)+1:4*N+3*N*(NC-1))';                % vapor fraction [-]
  Zg  = w(4*N+3*N*(NC-1)+1:5*N+3*N*(NC-1))';               % compress  gas [-]
  Zl  = w(5*N+3*N*(NC-1)+1:6*N+3*N*(NC-1))';               % compress liquid [-]
  P  = w(6*N+3*N*(NC-1)+1:7*N+3*N*(NC-1))';                % pressure, [MPa]

%===========================================================================
% Fugacity, enthalpy and volumes from SRK

for j=1:N

    [phil_temp,hl_temp,Vlm_temp,Al_temp,Bl_temp]=srkHEXV3(Zl(j),...
    [x(j*(NC-1)-2) x(j*(NC-1)-1)  x(j*(NC-1)) 1-(x(j*(NC-1)-2)+...
    x(j*(NC-1)-1)+x(j*(NC-1)))], T(j),P(j));    % liquid
    [phig_temp,hg_temp,Vgm_temp,Ag_temp,Bg_temp]=srkHEXV3(Zg(j), ...
    [y(j*(NC-1)-2) y(j*(NC-1)-1) y(j*(NC-1)) 1-(y(j*(NC-1)-2)+...
    y(j*(NC-1)-1)+y(j*(NC-1)))], T(j), P(j));      % vapor
```

```
    phil(j,1)=phil_temp(1);
    phil(j,2)=phil_temp(2);
    phil(j,3)=phil_temp(3);
    phil(j,4)=phil_temp(4);


    hl(j)=hl_temp;
    Vlm(j)=Vlm_temp;
    Al(j)=Al_temp;
    Bl(j)=Bl_temp;

    phig(j,1)=phig_temp(1);
    phig(j,2)=phig_temp(2);
    phig(j,3)=phig_temp(3);
    phig(j,4)=phig_temp(4);

    hg(j)=hg_temp;
    Vgm(j)=Vgm_temp;
    Ag(j)=Ag_temp;
    Bg(j)=Bg_temp;

end

K = phil./phig;  % VLE constant


% ===========================================================================
% Phase distribution
VG = Vcell-VL;    % gas volume [m3]
nL = VL./Vlm;     % liquid holdup                          [kmol]
nG = VG./Vgm;     % gas holdup                             [kmol]
v = nG./nT;       % vapor fraction


% Vapor and liquid flows

kp=100000;            % pressure controller gain
kl=10000;             % level controller gain
ps=1.8;               % setpoint p
G0=1.055e3;           % "bias"

VLs = Vcell/2;         % Setpoint level (volume): keep 50% liquid in tank
```

```
[m3]
L0=1.725e3;             % "bias"
for j=1:N
    G(j)=kp*(P(j)-ps)+G0;        %[kmol/min]
    L(j) = kl*(VL(j)-VLs) + L0; % Level controller with proportional gain kl
[kmol/min]
end

F2 = G+L; % outlet flow

% ==========================================================================
% III. Evaluate right hand side of DAE-set: M dy/dt = f(y)
% f1 =dn/dt  Dynamic (1): Overall mass balance
% f2 =dn1/dt Dynamic (NC-1): Component 1 mass balance
% f3 =dU/dt  Dynamic (1): Energy balance
% f4 = 0     Algebraic (1): Internal energy U (can find T from this)
% f5 = 0     Algebraic (NC-1): Component holdup n (can find x from this)
% f6 = 0     Algebraic (NC-1): VLE for comp NC-1 (can find y from this)
% f7 = 0     Algebraic (1): holdup to find vapor fraction
% f8 = 0     Algebraic (1): Compressibility Zg gas phase
% f9 = 0     Algebraic (1): Compressibility Zl liquid phase
% f10 = 0    Algebraic (1): composition for last componnet to calculate pressure

% ==========================================================================


K4=K(:,NC)';  %K for last compontent

% Model equations

for j=1 %first cell

    K1=K(j,:);
    y4 = 1-(y(j*(NC-1)-2) + y(j*(NC-1)-1)+ y(j*(NC-1)));
    % vapor composition of last component
    x4 = 1-(x(j*(NC-1)-2)+ x(j*(NC-1)-1)+x(j*(NC-1)));
    % liquid composition of last component

    f1(j) = F0-F2(j);
    f2((NC-1)*j-2:(NC-1)*j) = F0*z - F2(j)*z;
    f3(j) = F0*h0 - F2(j)*v(j)*hg(j) - F2(j)*(1-v(j))*hl(j) - Q;
    f4(j) = U(j) + P(j)*Vcell - hl(j).*nL(j) - hg(j).*nG(j);
    f5((NC-1)*j-2:(NC-1)*j) = n((NC-1)*j-2:(NC-1)*j) - x((NC-1)*j-2:(NC-1)*j).*nL(j)...
```

```
    - y((NC-1)*j-2:(NC-1)*j).*nG(j);
    f6((NC-1)*j-2:(NC-1)*j) = y((NC-1)*j-2:(NC-1)*j) - K1(1:(NC-1))...
    *x((NC-1)*j-2:(NC-1)*j);
    f7(j) = nT(j)-nG(j)-nL(j);
    f8(j) = Zg(j)^3-Zg(j)^2+Zg(j)*(Ag(j)-Bg(j)-Bg(j)^2)-Ag(j)*Bg(j);
    f9(j) = Zl(j)^3-Zl(j)^2+Zl(j)*(Al(j)-Bl(j)-Bl(j)^2)-Al(j)*Bl(j);
    f10(j)= y4-K4(j)*x4;



end

for j=2:N % equations from second cell to the last one

    K1=K(j,:);

    y4 = 1-(y(j*(NC-1)-2) + y(j*(NC-1)-1)+ y(j*(NC-1))); % vapor composition of last compon
    x4 = 1-(x(j*(NC-1)-2)+ x(j*(NC-1)-1)+x(j*(NC-1))); % liquid composition of last compone

    f1(j) = F2(j-1)-F2(j);
    f2((NC-1)*j-2:(NC-1)*j) = F2(j-1).*z - F2(j).*z;
    f3(j) = F2(j-1)*(1-v(j-1))*hl(j-1) + F2(j-1)*v(j-1)*hg(j-1) -...
    F2(j)*(1-v(j))*hl(j) - F2(j)*v(j)*hg(j) - Q;
    f4(j) = (U(j) + P(j)*Vcell- hl(j)*nL(j) - hg(j)*nG(j));
    f5((NC-1)*j-2:(NC-1)*j) = n((NC-1)*j-2:(NC-1)*j) - x((NC-1)*j-2:(NC-1)*j)...
    *nL(j) - y((NC-1)*j-2:(NC-1)*j).*nG(j);
    f6((NC-1)*j-2:(NC-1)*j) = y((NC-1)*j-2:(NC-1)*j) - K1(1:(NC-1))...
    *x((NC-1)*j-2:(NC-1)*j);
    f7(j)= nT(j)-nG(j)-nL(j);
    f8(j) = Zg(j)^3-Zg(j)^2+Zg(j)*(Ag(j)-Bg(j)-Bg(j)^2)-Ag(j)*Bg(j);
    f9(j) = Zl(j)^3-Zl(j)^2+Zl(j)*(Al(j)-Bl(j)-Bl(j)^2)-Al(j)*Bl(j);
    f10(j) = y4-K4(j)*x4;

end

F1  = [f1'; f2'; f3'; f4'; f5'; f6'; f7'; f8'; f9'; f10';];
```

C.4.2 Main

```
clear
close all
```

```
clc

% the initial condition are given based flash calculation in hysys
% a linear variation of properties along the cell has been used
% pressure in MPa and energy in MJ
% added P controllers for volume and pressure

% load flash results
load FlashResults60

Data = FlashResults';

N = 60;  % Number of cells
NC = 4;  % Number of components
Pin = 18*0.101325; % pressure, MPa
Pout = (18-5*1e-3)*0.101325; % presuure, MPa assuming 5 mbar pressure drop

% initial conditions
z0 = [0.06 0.4 0.4];                 %inlet composition

x = Data(NC+1:2*NC-1,2:end);
% liquid composition from Hysys Flash, 3 X 10 matrix
x0 = reshape(x,[],1)';
% liquid composition, 3 X 10 matrix

y = Data((2:NC),(2:end));
% vapor compostion from Hysys Flash, 3 X 10 matrix
y0 = reshape(y,[],1)';
% vapor composition, 1 x 10 matrix

xin = Data((NC+1:2*NC-1),1)';
% inlet liquid compostion from Hysys
yin = Data(2:NC,1)';
% inlet vapor composition from Hysys

xout = Data((NC+1:2*NC-1),end)';                              % outlet liquid compostion fron
yout = Data(2:NC,end)';                                       % outlet vapor composition fron

v = FlashResults(:,2*NC);
% vapor phase from Hysys for inlet/outlet streams
ZG = FlashResults(:,end-1);
% vapor compresibility for inlet/outlet streams
ZL = FlashResults(:,end);
```

```
% liquid compresibiliti for inlet/outlet streams

%initial conditions for MR temperature
Tin = -65+273;         %MR inlet temperature, K
Tout = -180+273;       %MR outlet temperature, K
T0 = FlashResults(2:end,1)'+273;
% Initial Temperature conditions Hysys flash calculation

% initial conditions for total holdup
V = 10;                                                        %volume, m3
Vcell = V/N;                                                   %Volume of one cell, m3

[~,HGin,VGm_in,~,~ ] = srkHEXV3(ZG(1),[yin, 1-sum(yin)],T0(1),Pin);
[~,HGout,VGm_out,~,~ ] = srkHEXV3(ZG(end),[yout, 1-sum(yout)] ,T0(end),Pout);

[~,HLin,VLm_in,~,~ ] = srkHEXV3(ZL(1),[xin, 1-sum(xin)],T0(1),Pin);
[~,HLout,VLm_out,~,~ ] = srkHEXV3(ZL(end),[xout, 1-sum(xout)] ,T0(end),Pout);

Hin = v(1)*HGin + (1-v(1))*HLin;                       % spefific enthalpy for inlet assuming
[kJ/kmol]
Hout = v(end)*HGout + (1-v(end))*HLout;                % specific enthalpy for outlet assuminc

Vm_in = v(1)*VGm_in + (1-v(1))*VLm_in;                 % inlet molar volume assuming perfect m
Vm_out = v(end)*VGm_out + (1-v(2))*VLm_out;            % outlet molar volume assuming perfect
Vm_avg = (Vm_in+Vm_out)/2;


P0 = linspace(Pin,Pout,N);                              % pressure, kPa
nT0 = linspace(Vcell/Vm_in, Vcell/Vm_out, N);           % total holdup, assuming linear change

% Initial condition for internal energy, [kJ]
U0 = linspace(Hin,Hout,N).*nT0-Pin*Vcell;

% Initial condition for component holdup
n0 = zeros(1,(NC-1)*N);
for j=1:N
    n0((NC-1)*j-2:(NC-1)*j) = nT0(j).*z0;
end

Zg0 = ZG(2:end)';        % vapor compressibility
Zl0 = ZL(2:end)';        % liquid comrpesibility
v0 = v(2:end)';
VL0 = Vcell.*(1-v0);
```

```
w0 = [nT0,n0,U0,T0,x0,y0,VL0,Zg0,Zl0,P0 ]; % vector of initial condition

%ODE solver options**********************************************************
nrDyn = NC-1+2; %number of dynamic equations per cell
nrAlg = 2*(NC-1)+5; %number of algebraic eq per cell

d1 = ones(1,nrDyn*N);
d2 = zeros(1,nrAlg*N);
Mass = diag([d1,d2]);

options = odeset('RelTol',1e-8,'mass',Mass, 'MaxStep',1e-5);
%ODE solver
[t,w]=ode15s(@HEXV16,[0 1],w0,options);       % integrate

T = w(:,(2*N+(NC-1)*N+1:3*N+N*(NC-1)));
figure
plot(t,T)
xlabel('Cell #')
ylabel('Temperature [^oC]')
legend('N = 10')

T2 = T(end,:)-273;
figure
stairs([1:N],T2)
xlabel('Cell #')
ylabel('Temperature [^oC]')
```