



**KTH Industrial Engineering
and Management**

Comparative studies and analyses of working fluids for Organic Rankine Cycles - ORC

Jamal Nouman

Master of Science Thesis

KTH School of Industrial Engineering and Management

Energy Technology EGI-2012-086MSC

Division of Thermodynamics and Refrigeration

SE-100 44 STOCKHOLM



**KTH Industrial Engineerir
and Management**

Master of Science Thesis EGI-2012-086MSC

**Comparative studies and analyses of
working fluids for Organic Rankine Cycles –
ORC**

Jamal Nouman

Approved	Examiner	Supervisor
2012-09-17	Per Lundqvist	Per Lundqvist
	Commissioner	Contact person

Abstract

This thesis work investigates the optimal working fluids for Organic Rankine Cycles ORC with focus on thermo-physical, environmental and safety aspects. The choice of the working fluid is of key importance for the cycle efficiency and the Net Work Out. In this study more than 100 pure fluids are investigated from many different perspectives. REFPROP 9 was used as the main source for the thermo-physical data of working fluids. The data in REFPROP 9 were connected to MatLab and different dynamical models were built for simulations and numerical analysis.

To determine what is the optimal working fluid for Organic Rankine Cycle is not easy process, there are many different criteria to deal with. These criteria mainly has to do with working fluids' thermodynamic and heat transfer properties from a side and safety and environmental aspects from other side. To study the working fluids thermodynamically, the process needs building accurate thermodynamic models and running numerical calculations in MatLab. In this work several simulation scenarios with different boundary conditions are done. For every heat source and heat sink there is a series of working fluid candidates. The temperature profile in evaporator and condenser is of key importance for exergy losses and best energy utilization. Sometimes the condenser and evaporator pressure limits the using of some working fluids. A very high evaporator pressure needs more advanced equipment and stronger materials and subsequently increase costs. A very low condenser pressure involves air infiltration problems and needs expensive and special vacuum equipment to reject air from the cycle.

It is hard to find all the needed information about environmental and safety data for some working fluids and it is harder to find the prices. Appendix 1 shows the pure working fluids which exist in NIST REFPROP 9. The environmental and safety data for some working fluids are completed with help of "Physical, Safety and Environmental data" by J. M. Calm (2011)[1].

Acknowledgments

I am very grateful to professor Per Lundqvist for his support during the whole period of this work. I would like to thank him for the guiding and all valuable discussions we had.

Special thank goes to Henrik Öhman, Director New Business Incubation and Manager Opcon Marin for his support and constructive suggestion and I really appreciate his practical experience.

I also would like to thank all the colleges in The Department of Energy Technology for the nice discussions and moments we had together.

Special thanks go to Professor Jurek Pyrko, Bert Sjöberg and Gunilla Persson, Faculty of Engineering (LTH), Lund University for all support and facilities they offered me in order to do my thesis at The Royal Institute of Technology (KTH).

Furthermore, I would like to thank my family and friends for their encouragement, support, love and care.

Table of contents

1 Introduction	1
1.1 History.....	2
1.2 Refrigerant progress.....	3
1.3 Worldwide Organic Rankine Cycle Installation	4
2 Objectives.....	5
3 Low grade temperature heat recovery cycles.....	7
3.1 Kalina Cycle.....	7
3.2 Goswami Cycle	8
3.3 Trilateral Flash Cycle.....	8
3.4 Organic Rankine Cycles	9
4 Organic Rankine Cycle ORC	11
4.1 Comparison between Organic Rankine Cycle and Rankine Cycle.....	11
4.1.1 Working fluids.....	11
4.1.2 Normal Boiling Point and T-S diagram	11
4.1.3 Cycle architecture.....	12
4.1.4 Condenser pressure	13
4.1.5 Environmental and safety aspects.....	13
4.2 Applications.....	13
4.2.1 Waste heat recovery.....	13
4.2.2 Solar thermal power	13
4.2.3 Geothermal power plants.....	14
4.3 The thermodynamics of Organic Rankine Cycle and working principles.....	15
4.4 System equations and theoretical analysis	16
4.5 System improvement	20

4.6	Recuperator or Internal Heat Exchanger IHE.....	21
5	Working fluid selection	23
5.1	Thermodynamic properties.....	23
5.2	Heat transfer properties	24
5.3	Environmental and Safety Criteria	24
5.3.1	Environmental data	24
5.3.2	Safety data	25
5.5	Chemical trends	26
5.6	The influence of overheat on cycle efficiency	27
5.7	Saturation vapor line in T-S diagram.....	29
5.8	The effect of normal boiling point on evaporator and condenser pressure	30
6	Simulation scenarios	33
6.1	Scenario 1.....	35
6.1.1	Flow chart	36
6.1.2	Simulation assumptions.....	37
6.1.3	Simulation results.....	39
6.2	Scenario 2.....	49
6.2.1	Simulation assumptions	49
6.2.2	Simulation results	50
6.3	Scenario 3.....	55
6.3.1	Flow chart.....	57
6.3.2	Simulation assumptions	58
6.3.3	Simulation results.....	58
	Thermal efficiency improvement.....	63
6.4	Scenario 4.....	65

6.4.1 Flow chart.....	66
6.4.2 Simulation assumptions.....	67
6.4.3 Simulation results.....	68
6.5 Thermal conductivity and viscosity.....	73
7 Conclusions.....	75
8 Recommendations for future works.....	77
References.....	79
Appendix 1.....	83
Appendix 2.....	89
Scenario 1.....	89
Scenario 2.....	103
Scenario 3.....	117
Scenario 4.....	143

List of figures

Figure 1 An article about the naphtha engine was published in 1890	2
Figure 2 The naphtha engine.....	2
Figure 3 Worldwide Organic Rankine Cycle Installation.....	4
Figure 4 Kalina Cycle.....	7
Figure 5 Goswami Cycle for cooling and power generation.....	8
Figure 6 Trilateral Flash Cycle.....	9
Figure 7 The T-S diagram for water and some organic working fluids.....	12
Figure 8 Geothermal in Europe, rock temperature at 5 km depth	14
Figure 9 The ideal and the real Organic Rankine Cycle.....	15
Figure 10 T-S diagram for an ideal Organic Rankine Cycle	16
Figure 11 Organic Rankine Cycle, basic layout	17
Figure 12 Cycle layout for an ORC using recuperator	20
Figure 13 T-S diagram for an ORC using recuperator.....	21
Figure 14 Recuperator or Internal Heat Exchanger IHE.....	22
Figure 15 The effect of superheat on thermal efficiency for dry and wet fluids.....	27
Figure 16 The vapor quality at expander outlet.....	28
Figure 17 Saturation liquid and vapor lines for some working fluids.....	28
Figure 18 the T-S diagram for dry, isentropic and wet working.....	29
Figure 19 The percentage of dry, isentropic and wet working fluid in NIST REFPROP 9.....	30
Figure 20 influence of Normal Boiling Point NBP on evaporator and condenser pressure.....	31
Figure 21 Overheat process in scenario 1	35
Figure 22 Relation between NBP and pressure ratio	39
Figure 23 The volumetric flow rate and expansion ratio for ammonia, cyclopropane, R152a, SO ₂ and R21	41
Figure 24 The Net Work Out for ammonia, cyclopropane, R152a, SO ₂ and R21	42

Figure 25 The thermal efficiency versus expander inlet temperature	43
Figure 26 The effect of superheat on heat source temperature at heat exchanger outlet	45
Figure 27 The second law efficiency versus expander inlet temperature	46
Figure 28 The heat addition and heat rejection rates for ammonia, cyclopropane, R152a, SO ₂ and R21	47
Figure 29 The volumetric flow rate and expansion ratio for D ₂ O, toluene, water, methanol and acetone	51
Figure 30 The Net Work Out versus expander inlet temperature	52
Figure 31 The thermal efficiency versus expander inlet temperature	53
Figure 32 The second law efficiency versus expander inlet temperature	53
Figure 33 The heat addition and heat rejection rates for D ₂ O, toluene, water, methanol and acetone	54
Figure 34 The working process and pressure increase loops in scenario 3 (dry fluid).....	55
Figure 35 The working process and pressure increase loops in scenario 3 (wet fluid).....	56
Figure 36 The Net Work Out (kJ/kg) versus expander inlet temperature	59
Figure 37 The Net Work Out (kJ/m ³) versus expander inlet temperature.....	60
Figure 38 The volumetric flow rate versus expander inlet temperature.....	60
Figure 39 The heat added to evaporator versus expander inlet temperature	61
Figure 40 The thermal efficiency for cis-butene, trans-butene, butane, SO ₂ and butene.....	62
Figure 41 The second law efficiency for cis-butene, trans-butene, butane, SO ₂ and butene.....	62
Figure 42 The thermal efficiency for the best wet working fluids in scenario 3.....	63
Figure 43 Thermal efficiency improvement after superheat	64
Figure 44 The working process and expansion in scenario 4	65
Figure 45 The volumetric flow rate and expansion ratio versus expander inlet temperature.....	69
Figure 46 The Net Work Out versus expander inlet temperature	70
Figure 47 The thermal efficiency for SO ₂ , R11, R21, ammonia and cyclopropane.....	71
Figure 48 The second law efficiency for SO ₂ , R11, R21, ammonia and cyclopropane.....	72

Figure 49 The heat addition and heat rejection rates for SO₂, R11, R21, ammonia and cyclopropane72

Figure 50 The thermal conductivity for the working fluids which give the highest thermal efficiency in simulation scenarios.....73

Figure 51 The viscosity for the working fluids which give the highest thermal efficiency in simulation scenarios74

1 Introduction

Energy conservation in the world is becoming very important in recent years, especially the use of low grade temperature and small-scale heat sources. Energy extraction from industrial waste heat, biomass energy, solar energy, and turbine exhaust heat is becoming more popular. Organic Rankine Cycle is an effective way to convert these heat sources into electrical power. Organic Rankine Cycle offers the ability to deal with low temperature heat to generate power. The traditional Rankine Cycle which uses water as the working fluid needs much higher temperature heat source while Organic Rankine Cycle ORC can generate power at a much lower temperature. The heat source temperature can vary from 50 to over 250°C. In recent years a lot of research has been conducted around the world and many ORC systems have been successfully installed in different countries, especially in USA, Canada, Germany and Italy.

Organic Rankine Cycles offer power production from renewable, waste heat and low-grade heat sources like, geothermal energy, biomass, solar energy and waste heat from industry and thermal power plants. Furthermore, Organic Rankine Cycle can be used to recover energy from exhaust gases from power trains, improving the fuel consumption and reducing their impact on climate changes.

Organic Rankine Cycle and working fluids have been widely studied in different scientific articles [2-5]. Some papers widely studied the usage of Organic Rankine Cycle ORC in different applications like waste heat recovery [6-10], geothermal power plants [11], biomass power plants [12] and solar thermal power plants [13,15].

According to Roadmap 2050 from the European Climate Foundation 2010, the greenhouse emissions can be reduced by 80% in 2050 [15]. This target can be achieved through the modification of the current energy system and the following modifications should be accomplished by 2050:

- Increase effectiveness and reduce energy intensity of buildings by 950 TWh/year and of Energy industry by 450 TWh/year.
- Use electricity instead of fossil fuels for transportation and space heating.
- Shift to renewable energies and clean power generation (Wind energy 25%, PV¹ 19%, CSP² 5%, Biomass 12%, Geothermal 2% and Large hydro 12%).
- Increase the grid capacity and reinforce the inter-regional transmission lines.

The Organic Rankine Cycle can play a major roll to achieve objectives 1 and 3[15].

¹ Photovoltaics (PV) is a method of generating electrical power by converting solar radiation into direct current electricity using semiconductors that exhibit the photovoltaic effect.

² Concentrating Solar Power (CSP) systems use mirrors or lenses to concentrate a large area of sunlight, or solar thermal energy, onto a small area.

1.1 History

The first Organic Rankine Cycle implementation was in 1883 when a naphtha engine was patented by Frank W Ofledt. The engine used naphtha instead of water as working fluid in order to replace steam engines on boats [16].



Figure 1 An article about the naphtha engine was published in 1890

The clear liquid hydrocarbon Naphtha can be produced during the fractional distillation of coal tar or crude petroleum oil. The heat of vaporization for naphtha is lower than water and it is obvious that a given amount of heat input will give more vapor if naphtha is used instead of water and then more work out can be achieved by the engine. Naphtha engines became popular after steamboats got a reputation of carrying a high risk of explosions and the Coast Guards made it compulsory for operators to carry licenses. Frank W. Ofeldt's patented discovery was an alternative to steam engines. The patented naphtha engine had essentially the same loop as a steam engine, but used naphtha instead of water. The Gas Engine and Power Company of Morris Heights in New York developed the engine and a few years later, the company started production to meet the urgent market needs after steam engines were phased-out. The new engines were operated by owners themselves without any need for licensed engineers [17].

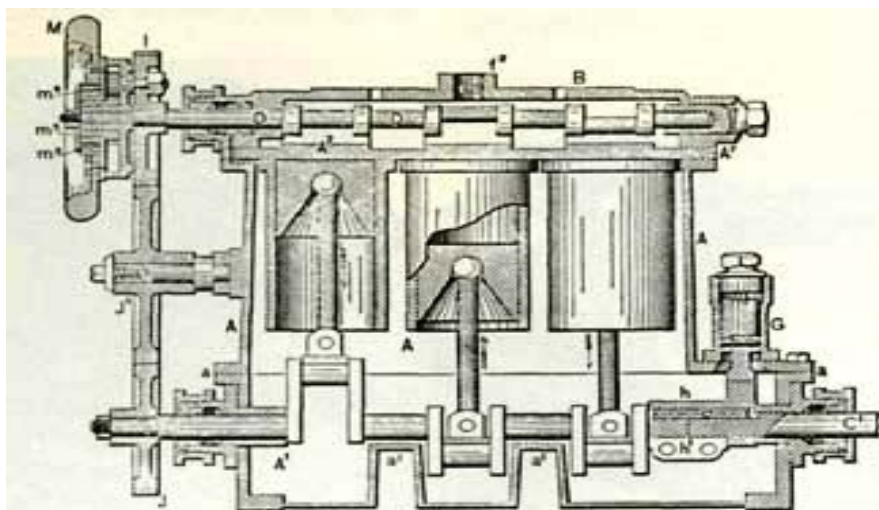


Figure 2 The naphtha engine

In the early 1960s Harry Zvi Tabor prototyped and developed an Organic Rankine Cycle to recover heat from low temperature sources like solar energy and convert it to electricity. Tabor also tried to develop a turbine for Organic Rankine Cycle and the turbine was capable of operating at a relatively low temperature (below 100 C). In 1965 an Israeli company, Ormat privatized this invention and converted the laboratory model into a commercial product [18].

1.2 Refrigerant progress

According to J. M. Calm (2008) there are four generations of refrigerants according to their defining selection criteria [1].

1. **Whatever worked (1830 – 1930)**

Under this period some familiar solvents and volatile fluids had been used. Some common refrigerants were ethers, carbon dioxide, ammonia, sulfur dioxide, methyl formate, HCs, water, carbon tetrachloride and hydro chlorocarbons HCCs. Today many of these refrigerants are considered “natural refrigerants”.

2. **Safety and durability (1931 - 1990)**

This period includes refrigerants like chlorofluorocarbons CFCs, HCFCs, ammonia and water.

3. **Stratospheric ozone protection (1990 – 2010)**

Common refrigerants are HCFCs for transition use, HFCs, ammonia, water, hydrocarbons and carbon dioxide.

4. **Global warming mitigation (2011 - ?)**

The refrigerants to be used under this period are still unknown and to be determined. Typical refrigerants for this period should have very low or no ozone depletion potential ODP, low global warming potential GWP and high efficiency. Potential candidates are:

- Low-GWP HFCs
- Natural refrigerants like ammonia, carbon dioxide, hydrocarbons and water
- Unsaturated hydrofluorochemicals like hydrochlorofluoro-olefins HCFOs and hydrofluoro-olefins HFOs.

The production and development of new working fluids for Organic Rankine Cycle and high temperature cooling systems wasn't profitable until 1990. The chemical companies started the production of such working fluids after the regulations about phasing out the refrigerants with high ozone depletion potential ODP [2].

1.3 Worldwide Organic Rankine Cycle Installation

Organic Rankine Systems have been successfully installed in many countries in the world. Figure (3) shows some countries which are already using ORC system for waste heat recovery. It is obvious that most of the units exist in USA, Canada, Italy and Germany while there is a single unit in each of Finland, Belgium, Swaziland, Austria, Russia, Romania, India and Morocco. Some of ORC equipment suppliers are Ormat, Turboden, ABB and Tas Energy. The units are used to recover wasted heat for some typical industries like oil and gas, biomass, energy, packaging, cement and glass industry [19]. Opcon AB and Entrans are two active Swedish companies. Several Organic Rankine Cycles have been installed by Opcon AB in Sweden in recent years. The company Opcon AB has developed a technology called Opcon PowerBox, this technology extract electrical power from waste heat.



Figure 3 Worldwide Organic Rankine Cycle Installation

2 Objectives

This study aims to determine the optimal working fluids for Organic Rankine Cycles. The focus of this study is on the thermodynamic, environmental and safety aspects, rather than the economics of the system.

In this study several simulation scenarios are created with different boundary conditions covering as much working fluids as possible. Organic Rankine Cycle converts thermal energy from low grade heat source to electricity. Heat source temperature and heat sink temperature are two important parameters needed to determine the optimal working fluids.

There are two main objectives targeted in this study.

1. The first objective is to find the optimal working fluids from a thermodynamic perspective, regarding thermal efficiency, second law efficiency, Net Work Out, etc.
2. The second objective is to assess the importance of the environmental and safety criteria. Attention should be paid to working fluids' impact on Ozone depletion potential ODP and global warming potential GWP. Attention should also be paid to working fluids' flammability and toxicity.

3 Low grade temperature heat recovery cycles

Recovering thermal energy from low-grade energy sources and converting it to electrical power is not profitable in ordinary Steam Rankine Cycles, especially when the heat source temperature is quite low. In order to recover energy from low-grade heat sources many cycles have been developed. The developed cycles like Organic Rankine cycle, Kalina cycle, Goswami cycle, and trilateral flash cycle offer lower equipment costs and higher profitability using other working fluids than pure water.

3.1 Kalina Cycle

The Kalina Cycle is one of the cycles which were successfully developed and used to convert low-grade heat into electrical power. It was first developed in late 1970s and early 1980s by Aleksander Kalina. The working fluid consists of two different components, typically water and ammonia in order to reduce the thermodynamic irreversibility and increase cycle efficiency. Using binary fluids in Kalina Cycle gives a good thermal match due to non-isothermal boiling. Some studies have been done on Kalina Cycle and these studies show that it performs substantially better than Steam Rankine Cycle [20 - 22]. Figure (4) shows the temperature-enthalpy diagram for Kalina Cycle and the non-isothermal evaporation reducing exergy losses.

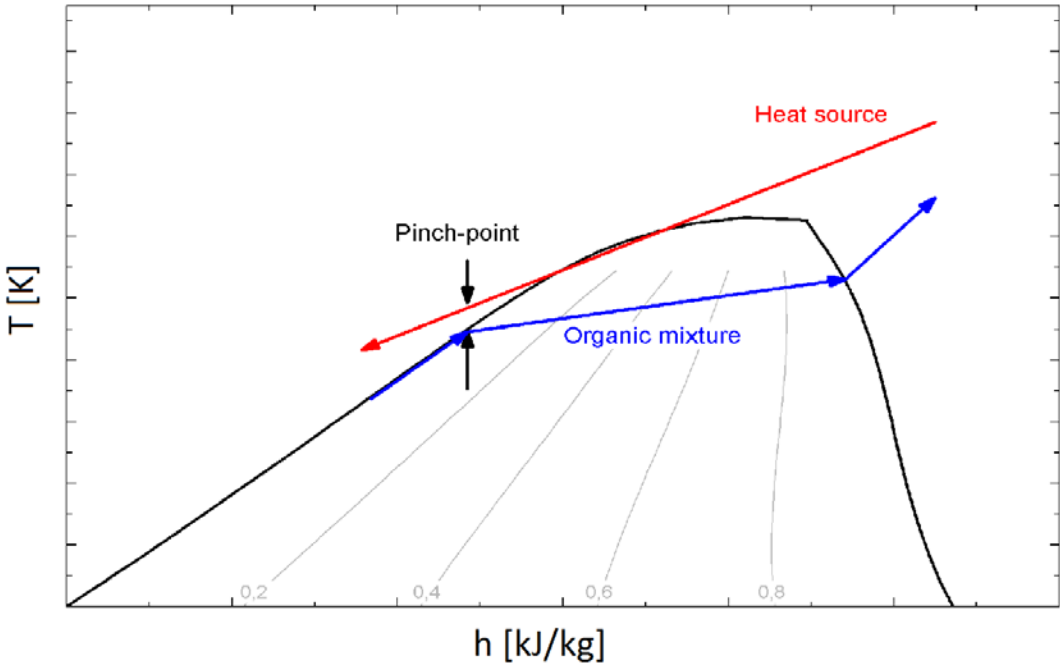


Figure 4 Kalina Cycle

3.2 Goswami Cycle

The Goswami Cycle is a novel thermodynamic cycle used to produce both electrical power and refrigeration in one loop at the same time. The cycle was proposed by Dr. Yogi Goswami in 1998 and it uses binary mixture. The Goswami Cycle is a combination of an absorption cooling cycle and a Rankine Cycle [23].

The binary mixture consists of water and ammonia and it has the advantages of

- Producing cooling and electrical power in the same loop
- The system has flexibility of any combination of this two products, that means it is possible to increase the electrical power produced but the cooling have to be reduced and vice versa
- Efficient conversion of moderate temperature heat source
- Better energy source utilization if the cooling and power are produced separately

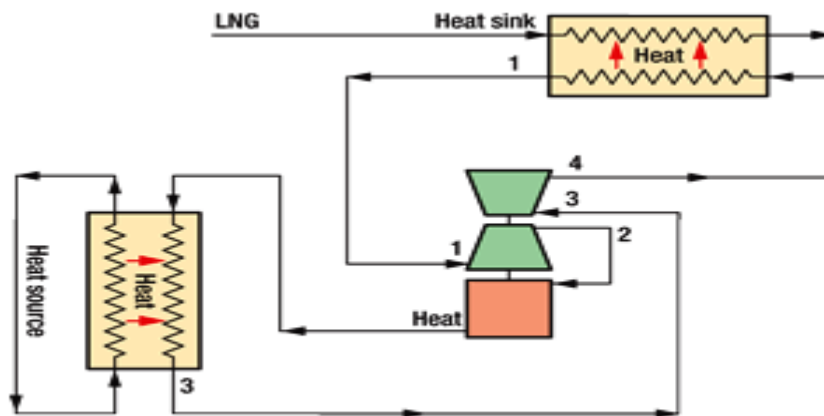


Figure 5 Goswami Cycle for cooling and power generation

3.3 Trilateral Flash Cycle

The uniqueness of this thermodynamic cycle resides in the fact that the expansion starts from the saturated liquid line and not from the vapor phase. The main benefit is avoiding the boiling part of the thermodynamic cycle and decreasing the irreversibility. In this cycle the heat transfer between heat source and the liquid working fluid has a perfect temperature matching. According to some scientific articles, the Trilateral Flash Cycle has a higher power recovery potential than the Organic Rankine Cycle or the flash steam system [24].

The main challenge for this technology is the lack of suitable expanders which can deal with a two phases flow and a high adiabatic efficiency.

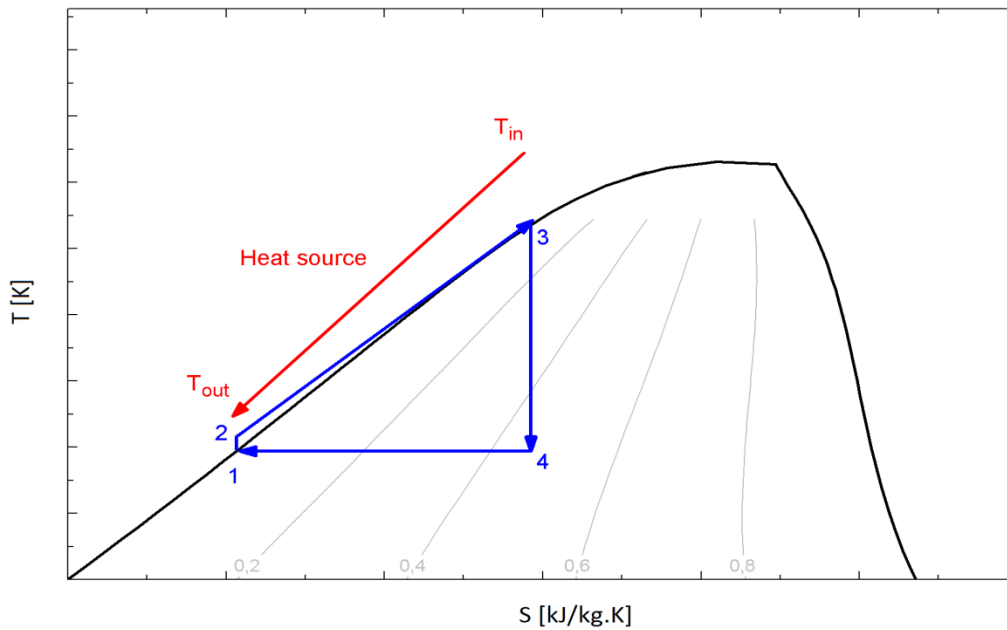


Figure 6 Trilateral Flash Cycle

3.4 Organic Rankine Cycles

There are three types of Organic cycles depending on where the four thermodynamic processes (compression, heat addition, expansion and heat rejection) occur.

Subcritical Organic Rankine Cycle

In this cycle the four processes occur at pressures lower than the critical pressures for the working fluid.

Trans-critical Organic Rankine Cycle

In this cycle the process of heat addition occurs at a pressure higher than the critical pressure for the working fluid. The heat rejection process occurs at a pressure lower than the critical pressure for the working fluid. The compression and expansion processes occur between the two pressure levels.

Supercritical Organic Rankine Cycle

In this cycle the four processes occur at pressures higher than the critical pressures for the working fluid.

4 Organic Rankine Cycle ORC

The Organic Rankine Cycle has the same working principles and main components (evaporator, condenser, expander and pump) as the Steam Rankine Cycle. At the same time, there are some major differences between the two cycles. The differences are mainly related to the used working fluid in the cycle, the working fluid's thermo-physical properties, the heat source temperature and the cycle architecture. Organic Rankine Cycle can extract energy and generate power from much lower heat source temperature than traditional Rankine cycle.

4.1 Comparison between Organic Rankine Cycle and Rankine Cycle

To discuss the comparison between Organic Rankine Cycle and traditional Rankine Cycle several important aspects are highlighted below

4.1.1 Working fluids

The main difference between the two cycles is the working fluid used in each cycle. Water is the only used working fluid in Steam Rankine Cycle while there are hundreds of different working fluids which can be used in Organic Rankine Cycles. The designing and discovering of new working fluids is a continuous process. The cycle architecture, components size and shape, and economics are highly dependent on the chosen working fluid's thermo-physical properties. The thermo-physical, safety and environmental properties vary from one working fluid to another. The environmental and safety data are not available for many working fluids. The choice of the right working fluid is of key importance for the cycle efficiency, Net Work Out and etc.

Water properties and behaviors are well known under different cycle conditions. For Organic Rankine Cycle, especially if we deal with working fluid mixtures there are uncertainties in data bases and subsequently this leads to uncertainty in calculations and results. Under help files in NIST REFPROP 9 we can read following;

“The NIST REFPROP program is designed to provide the most accurate thermophysical properties currently available for pure fluids and their mixtures. The present version is limited to vapor-liquid equilibrium (VLE) only and does not address liquid-liquid equilibrium (LLE), vapor-liquid-liquid equilibrium (VLLE) or other complex forms of phase equilibrium. The program does not know the location of the freezing line for mixtures. Certain mixtures can potentially enter into these areas without giving warnings to the user.”

4.1.2 Normal Boiling Point and T-S diagram

Most of organic fluids have a lower normal boiling point NBP than water. This property make organic fluids need a lower heat source temperature than water to evaporate and recover thermal energy from low grade heat sources. Figure (7) shows the T-S diagram for water and some other working fluids which can be used in Organic Rankine Cycles. The slope of saturation vapor line for organic fluids can be negative, positive or infinite while water has a negative slope. The positive and infinite slopes have enormous advantages for turbo machinery expanders. These working fluids leave the expander as superheated vapor and eliminate the corrosion risk in case of using turbo machinery expanders. Furthermore, there is no need for overheating the vapor before entering the expander, and a smaller and cheaper heat exchanger (evaporator) can be used.

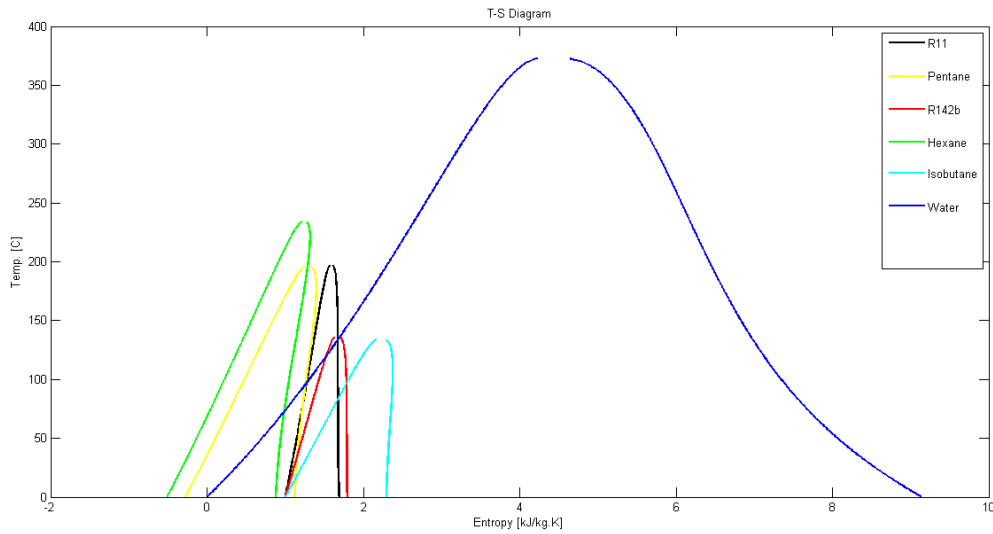


Figure 7 The T-S diagram for water and some organic working fluids

A remarkable difference in figure (7) is the entropy difference between the saturation liquid line and the saturation vapor line. Organic working fluids have a very low entropy change compared with water. Water as working fluid needs more thermal energy to change phase from saturated liquid to saturated vapor and can carry out more thermal energy per kg of water. The advantage of this property is that water needs a much lower mass flow rate than organic fluids to absorb the same amount of thermal power from a certain heat source. A higher mass flow rate leads to higher power consumption by pump and a higher piping system diameter should be used to overcome pressure losses related to high Reynolds number[15]. A higher mass flow means also higher components size and pressure losses.

Some organic fluids have a very low freezing temperature (due to low triple point) and the freezing problem in the condenser is eliminated even at extremely low ambient temperatures [19].

4.1.3 Cycle architecture

The density of the organic fluid is of key importance for sizing cycle components which are highly dependent on the volumetric flow rate. Higher density means lower specific volume, lower volumetric flow rate and subsequently smaller component size.

The pressure ratio, the density and the enthalpy change affect the design of expanders or turbines. In steam cycles the pressure ratio and enthalpy change over the expander is very high. This leads to using expanders with several expansion stages to reduce exergy losses and produce more work out. The pressure ratio and enthalpy change in ORC is lower and one or two stages expansion expanders are needed for many working fluids. Organic fluids offer less costly cycles and small sized piping system (due to high fluids density in evaporator and condenser). Organic Rankine Cycle has some other advantages compared to the conventional Steam cycle: a simple control system and a cheap and simple turbine are some of the advantages related to the cycle architecture [15].

A very common and typical problem in Steam cycles is drop formation at the end of expansion stages. These drops damage turbine blades and reduce the expander's life time and efficiency. To overcome this problem superheat is needed. The boiler in Rankine Cycle usually consists of three

separate heat exchangers (preheater, evaporator and superheater). In Organic Rankine Cycle the boiler consists of one or two heat exchangers.

Many ORC cycles use dry or isentropic fluids and there is no need for superheat. The expansion process can start directly from the saturation vapor line and working fluids leave the expander as superheated vapor. No attention needs to be paid to vapor quality at the end of the expansion process. Sometimes the recuperator or Internal Heat Exchanger IHE is not needed, especially when the working fluid leaves the expander at temperature much lower than the temperature at pump outlet.

4.1.4 Condenser pressure

The condenser pressure in many ORC is higher than the atmospheric pressure. This is a desirable property because a condensing pressure lower than the atmospheric pressure involves air infiltration problems in the cycle and reduce the cycle efficiency [14]. The water condensing pressure at 298 K is 3.15 kPa, at the same time it is 105.49 kPa for R11, 349.14 kPa for Isobutane, 586.67 for DME and 271.04 for R236fa.

4.1.5 Environmental and safety aspects

Water as working fluid is environmentally friendly, non-flammable, non-toxic, has no ozone depletion potential ODP and no global warming potential GWP. Many of the organic fluids have a high negative impact on the greenhouse effect and ozone depletion problems. At the same time these organic fluids can be flammable and toxic. Unknown safety and environmental data is another problem connected to some organic fluids.

4.2 Applications

Organic Rankine Cycle can efficiently be used in many applications in order to generate mechanical work or electrical power and following are some of the applications.

4.2.1 Waste heat recovery

Waste heat recovery is a process in which the energy is extracted from waste heat which comes from many processes, especially in industrial applications. In some applications waste heat boilers, recuperators and regenerators are used in order to directly recover and redirect heat to the process itself [24]. In steam cycles the economics of waste heat recovery don't justify when the temperature of the wasted heat is low. The Organic Rankine Cycle can be used to produce electricity from low grade heat sources.

4.2.2 Solar thermal power

The solar thermal power is a well-proven technology. The parabolic dish, the solar tower and the parabolic trough are three different technologies used to extract power from solar thermal. The parabolic tower can work at a temperature range of 300 °C – 400 °C. For a long time this technology was linked to the traditional Steam Rankine Cycle for power generation. The Organic Rankine Cycle seems to be a more promising technology. However, the Steam Rankine Cycle needs higher temperature and a higher installed power in order to be profitable. The Organic Rankine Cycle can work at lower temperatures, offers a smaller component size and needs much lower investment cost compared to steam cycles. The installed power can be reduced to kW scale [25].

4.2.3 Geothermal power plants

The geothermal power has the potential to supply renewable electricity to a large number of communities. In 2007 was 1% of world's electricity supplied by geothermal sources. This source of energy is clean and renewable and the production can be highly efficient. Dry steam power plants, flash steam power plants and binary cycle power plants are three different technologies used to extract power in geothermal power plants [26].

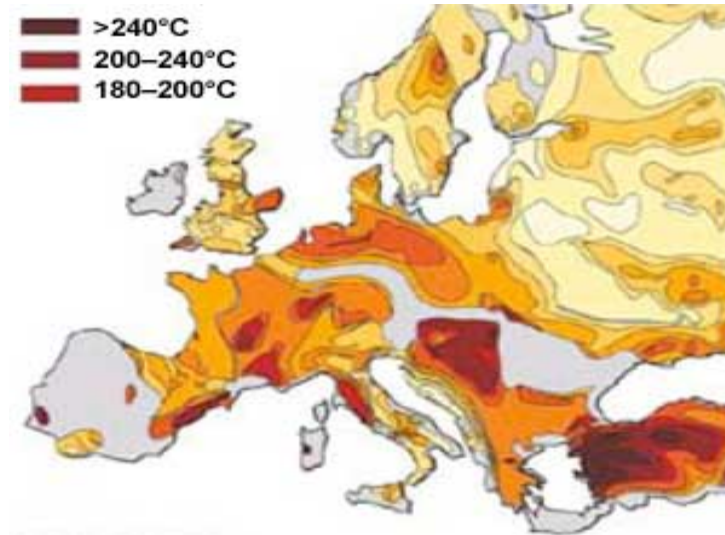


Figure 8 Geothermal in Europe, rock temperature at 5 km depth

4.2.4 Biomass power plants

The traditional fossil fuels are expensive and have a huge impact on climate change and the greenhouse effect. Biomass is a cheap and environmentally friendly energy source and is experiencing a strong market growth. It can be used efficiently to produce both heat and power by fueling a combined heat and power CHP system. Biomass fuels exist in many forms:

- Wood and wood wastes and combustible agriculture wastes
- Biogas from organic materials such as farm waste or wastewater sludge
- Black liquor which is a byproduct of the pulping process.

Trees, energy crops, agriculture residues, food waste and industrial waste and their co-products are some of the typical sources of biomass. Utilizing biomass fuels has many valuable benefits in regard to mitigating global warming, climate changes and economics associated with fuel prices. Biomass displaces purchased fossil fuel, decreasing tipping fees associated with waste disposal and freeing up landfill space. The most important difference between biomass and fossil fuels is that biomass takes carbon out of atmosphere while it is growing and returns it as it burns [27].

4.3 The thermodynamics of Organic Rankine Cycle and working principles

The working principles for the ideal Organic Rankine Cycle are similar to the ideal Rankine Cycle. The condensate working fluid is pumped from the condenser where the pressure is low to the evaporator where the pressure is high. The process takes place at constant entropy. The high pressure liquid enters the evaporator and absorbs the thermal energy from heat source at constant pressure. In this process the refrigerant changes the phase from saturated liquid to saturated or superheated vapor. The external heat source can be waste heat from industry, geothermal heat, solar heat, biomass etc. The high pressure saturated or superheated vapor leaves the evaporator and expands through an expander at constant entropy to produce mechanical work. Under the expansion process, the pressure decreases to condenser pressure. After expansion process the working fluid leaves the expander and enters the condenser as unsaturated, saturated or superheated vapor depending on working conditions and the type of used working fluid. In the condenser, the working fluid condensates and changes phase to saturated or undercooled liquid with the help of a heat sink, and then the cycle is repeated.

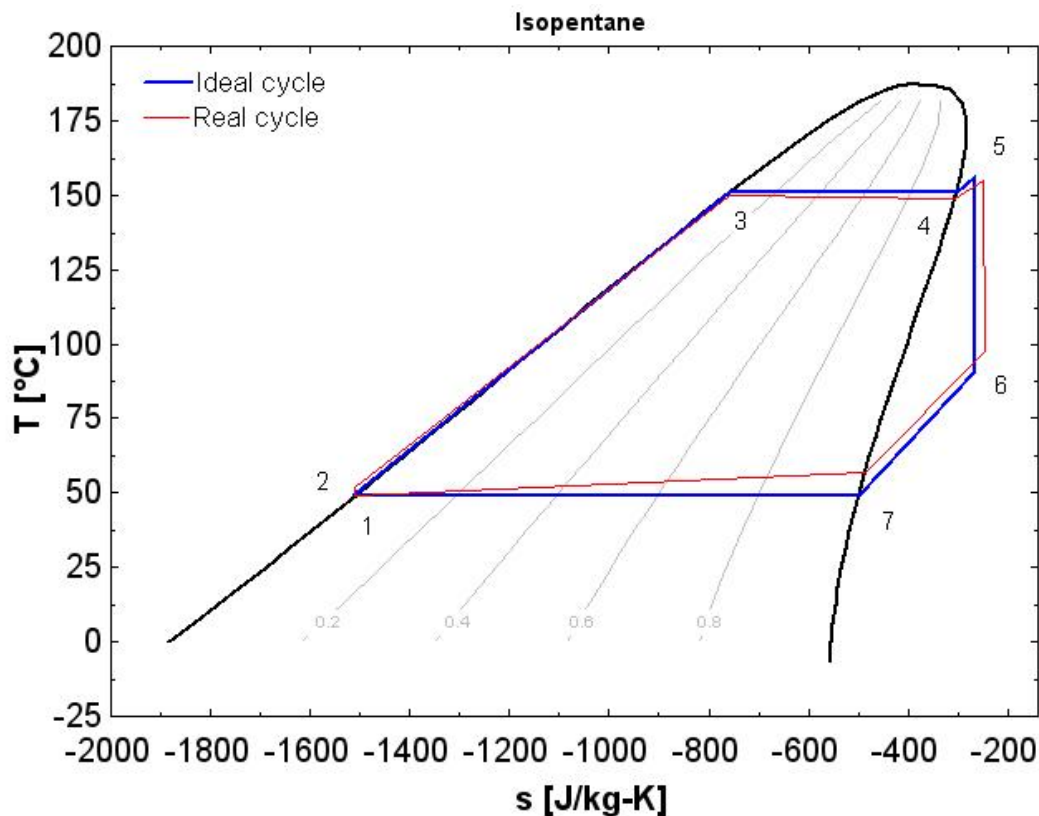


Figure 9 The ideal and the real Organic Rankine Cycle

In the real cycle the compression and expansion processes are not isentropic and there are always some losses in the pump and the expander. The heat addition and heat rejection processes are not isobaric and there are always pressure losses in the piping system. The irreversibility affects very much the performance of the thermodynamic system.

In a real cycle, there are two main sources for entropy generation and these sources are external and internal. The internal entropy generation occurs due to [28]:

- Pressure drop because of friction in the system associated pipes
- Un-isentropic compression and expansion in the compressor or expander
- Internal transfer of energy over a finite temperature difference in the components.

And the external entropy generation occurs due to:

- The mechanical losses during work transfer
- Heat transfer over the finite temperature difference

4.4 System equations and theoretical analysis

The Organic Rankine Cycle has the same working principles and main components (evaporator, condenser, expander and pump) as the Steam Rankine Cycle. The main difference between the two cycles is the working fluid utilized. Figure (10) shows the T-S diagram for a basic Organic Rankine Cycle and figure (11) shows the cycle layout.

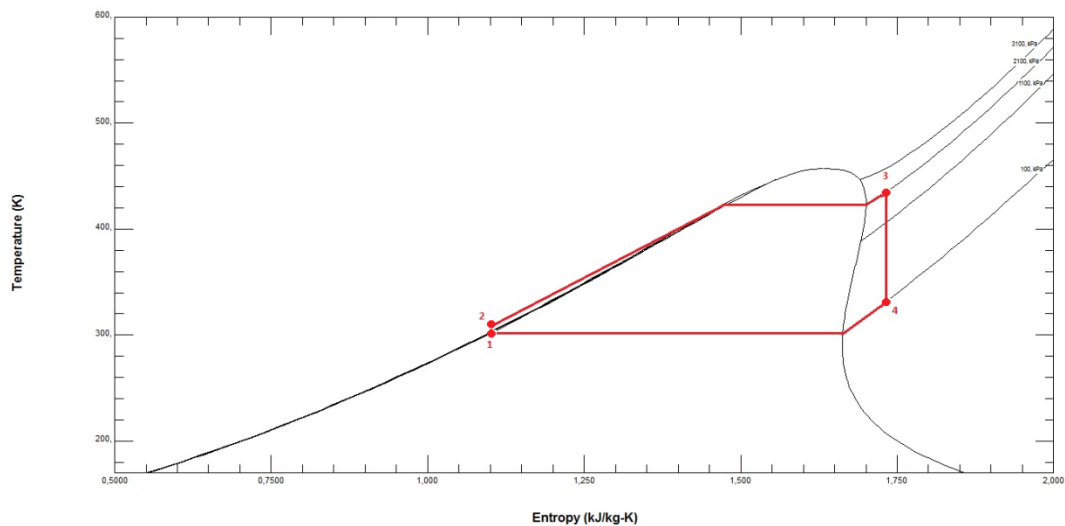


Figure 10 T-S diagram for an ideal Organic Rankine Cycle

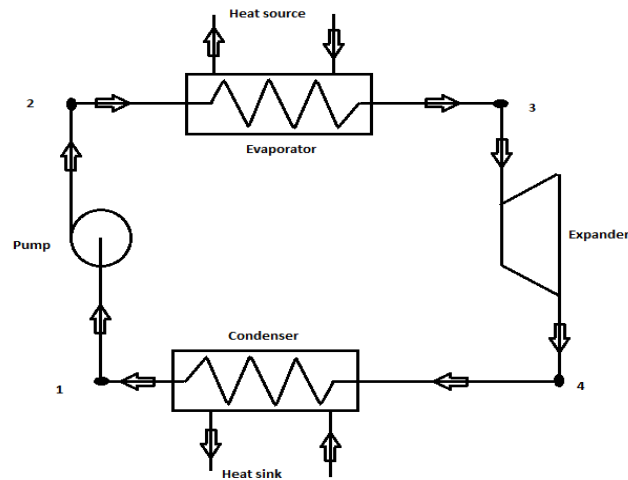


Figure 11 Organic Rankine Cycle, basic layout

The working fluid passes through four main processes in order to complete one cycle. The following are the four processes for the ideal cycle.

Process (1 – 2) Compression

The working fluid leaves the condenser as saturated liquid and then it is pumped to the evaporator pressure at constant entropy. The process is ideal however the efficiency of energy transformation never reaches 100%. The state of the working fluid at pump inlet is indicated by point 1 and at pump outlet by point 2 (figure 11). The power absorbed by the pump is estimated by equation (1).

$$W_{1-2} = \dot{m} * (h_2 - h_1) \quad (1)$$

Where

W_{1-2} is the work consumption by pump

\dot{m} is the mass flow rate

h_1 enthalpy at pump inlet

h_2 enthalpy at pump outlet

The exergy destruction rate in the pump is given by equation (2)

$$\dot{i}_{1-2} = \dot{m} T_0 [(s_2 - s_1)] \quad (2)$$

Where

\dot{I}_{1-2} is the exergy destruction rate in the pump

T_0 ambient temperature in K

s_1 entropy at pump inlet

s_2 entropy at pump outlet

Process (2-3) Heat addition

In this process heat is added to the working fluid at constant pressure, the process can be considered isobaric although the slight pressure drop in the evaporator pipes. The working fluid's state out of the evaporator is indicated by point 3 and the heat added to the working fluid can be calculated by equation (3).

$$Q_{2-3} = \dot{m} * (h_3 - h_2) \quad (3)$$

Where

Q_{2-3} refers to the heat added to the working fluid

h_3 refers to the vapor enthalpy out of the evaporator and into the expander.

The temperature of the heat source decreases through the evaporator. Taking the arithmetic mean temperature (T_H) between inlet and outlet temperature, $T_H = (T_{in} + T_{out})/2$ [28], the energy destruction in evaporator can be estimated by equation (4).

$$\dot{I}_{2-3} = \dot{m} T_0 \left[(s_3 - s_2) - \frac{(h_3 - h_2)}{T_H} \right] \quad (4)$$

Where

\dot{I}_{2-3} is the exergy destruction rate in the evaporator

s_3 is the vapor entropy at evaporator outlet

Process (3-4) Expansion

This is an expansion process and the absorbed energy at the evaporator is converted to useful mechanical work by an expander or a turbine. The process is considered to be isentropic although the expander efficiency can never reach 100%. The state of the working fluid out of the expander is indicated by point 4 and the useful work out can be estimated by equation (5).

$$W_{3-4} = \dot{m} * (h_3 - h_4) \quad (5)$$

Where

W_{3-4} is the useful work produced by the turbine

h_4 is the vapor enthalpy at turbine outlet

Equation (6) gives the exergy destruction rate in the expander.

$$\dot{I}_{3-4} = \dot{m} T_0 [(s_4 - s_3)] \quad (6)$$

\dot{I}_{3-4} is the exergy destruction rate in turbine

s_4 is the vapor entropy at turbine outlet

Process (4-1) Heat rejection

In this process the heat is rejected in condenser in order to condensate the working fluid and recirculates it in the cycle. The heat rejection process is considered to be isobaric despite pressure drops through the condenser due to friction losses in condenser pipes. The working fluid leaves the condenser as saturated or undercooled liquid. Point 1 refers to the working fluid at condenser outlet and pump inlet in T-S diagram. The amount of heat rejected can be estimated by equation (7).

$$Q_{4-1} = \dot{m} * (h_4 - h_1) \quad (7)$$

Where

Q_{4-1} stands for the heat rejected heat in condenser

Since heat sink temperature increases continuously from condenser inlet to condenser outlet, the arithmetic mean temperature, $T_L = (T_{in} + T_{out})/2$ can be used to estimate the exergy destruction in the condenser [13]. Equation (8) gives the exergy destruction in the condenser.

$$\dot{I}_{4-1} = \dot{m} T_0 \left[(s_1 - s_4) - \frac{(h_1 - h_4)}{T_L} \right] \quad (8)$$

Where

\dot{I}_{4-1} refers to the exergy destruction rate in condenser

The net thermal efficiency is defined as

$$\eta_{\text{thermal}} = \frac{W_{3-4} - W_{1-2}}{Q_{2-3}} \quad (9)$$

The thermal efficiency is the ration of the Net Work Out to heat absorbed in the evaporator.

The system's total energy destruction can be calculated by combining equations 2, 4, 6 and 8.

$$\dot{I}_{system} = \dot{I}_{1-2} + \dot{I}_{2-3} + \dot{I}_{3-4} + \dot{I}_{4-1} \quad (10)$$

Which gives

$$\dot{I}_{system} = \dot{m} T_0 \left[\frac{(h_3 - h_2)}{T_H} - \frac{(h_1 - h_4)}{T_L} \right] \quad (11)$$

4.5 System improvement

Unlike Steam Rankine Cycle, the optimization of the Organic Rankine Cycle is quite limited. The limitations are mainly affected by the low heat source temperature. Using isentropic and dry fluids in ORC, the working fluid leaves the expander as superheated vapor and no attention is paid to the vapor quality at the end of the expander. The superheated vapor has a great advantage for turbo machine expanders which always get damages due to low vapor quality. The turbo machines expanders in ORC systems can have a much longer life span than in steam cycles. To overcome the low vapor quality at the expander outlet, screw and scroll expanders can be used instead of turbo machinery expanders. Screw and scroll expanders have much better resistance for vapor quality than turbo machinery expanders. It follows that superheat is not recommended in cycles using dry and isentropic fluids [15]. To overcome the low vapor quality in last expansion stages in Rankine Cycle the superheat is recommended.

The layout of the Organic Rankine Cycle is much simpler than that of the Rankine Cycle. In the Organic Rankine Cycles, the water-steam drum is eliminated and a single heat exchanger can be used instead of the three-part heat exchanger (economizer, preheater and superheater). Reheating and turbine bleeding are not recommended for some working fluids while a recuperator can work as a preheater and be installed between the expander outlet and the pump outlet [15]. Figure (11) shows the cycle layout for an ORC using a recuperator and figure (12) illustrates the cycle layout and figure (13) shows the T-S diagram for ORC.

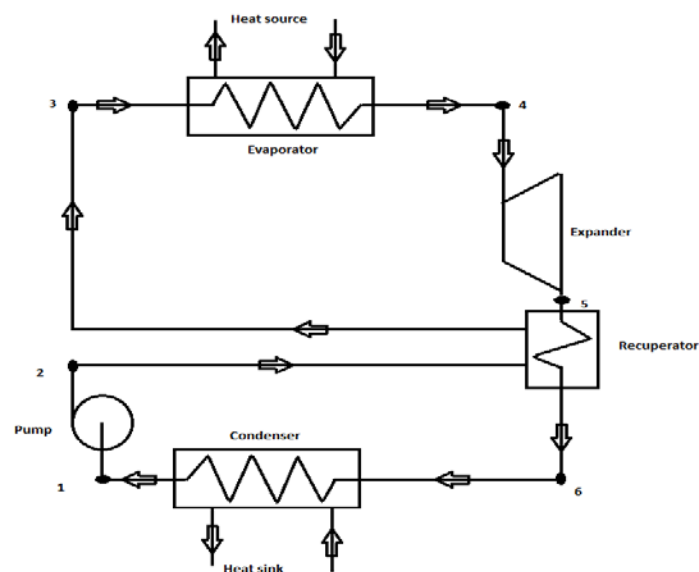


Figure 12 Cycle layout for an ORC using recuperator

Following are the six main thermodynamic processes for an Organic Rankine Cycle uses a recuperator (internal heat exchanger IHE).

Process (1-2) Pump: the condensate working fluid is pumped from condenser pressure to evaporator pressure.

Process (2-3) Recuperator: heat transfer process between undercooled working fluid at pump outlet and superheated vapor at expander outlet.

Process (3-4) Evaporator: after the working fluid leaves the recuperator enters the evaporator to absorb more thermal energy from heat source. Here the working fluid changes the phase from undercooled liquid to saturated or superheated vapor.

Process (4-5) Expander: the saturated or superheated vapor enters the expander and the absorbed thermal energy in recuperator and evaporator converts to useful work. The working fluid leaves the expander as superheated vapor.

Process (5-6) Recuperator: heat transfer occurs between the high temperature vapor at expander outlet and low temperature fluid at pump outlet.

Process (6-1) Condenser: the cooled working fluid at recuperator outlet enters the condenser. The working fluid starts condensation and more heat is rejected with help of a heat sink.

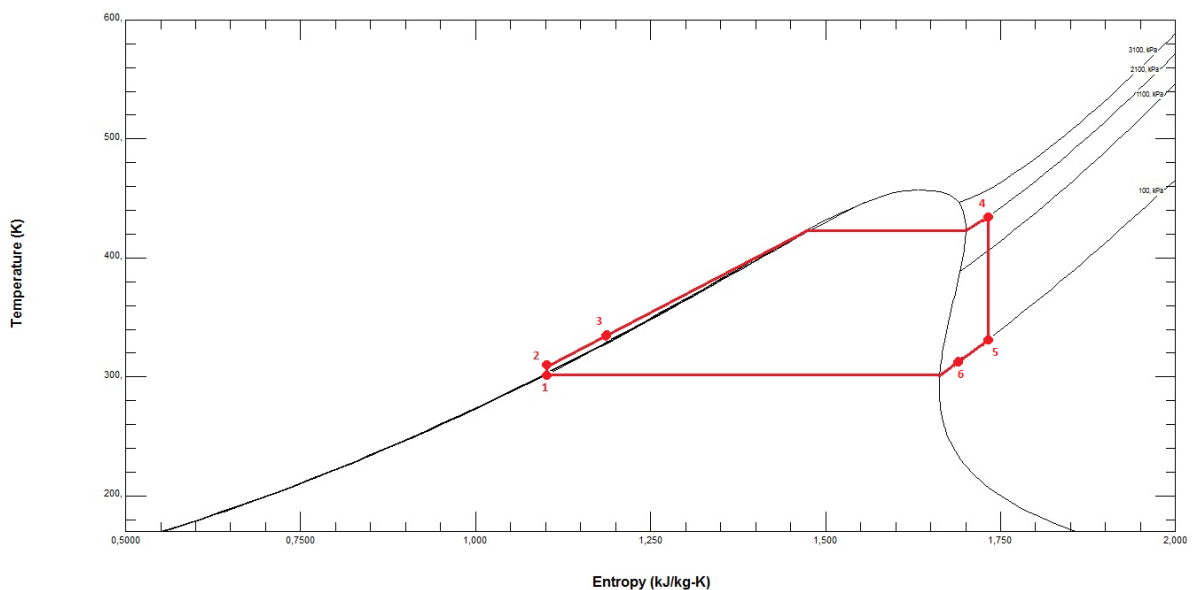


Figure 13 T-S diagram for an ORC using recuperator

4.6 Recuperator or Internal Heat Exchanger IHE

When the working fluid leaves the turbine at a temperature higher than the temperature at the pump outlet, a recuperator can be introduced in the cycle to recover the thermal energy from the working fluid at expander outlet. Here the recuperator can play a major role to increase the thermal efficiency and the second law efficiency by reducing the exergy losses. The recuperator raises the liquid temperature when it leaves the pump and the working fluid preheats before entering

evaporator. In this process the wasted thermal energy which would be rejected by the condenser is extracted and supplied again to the working fluid when it leaves the pump. The heat rejection by the condenser and the condenser size can be reduced.

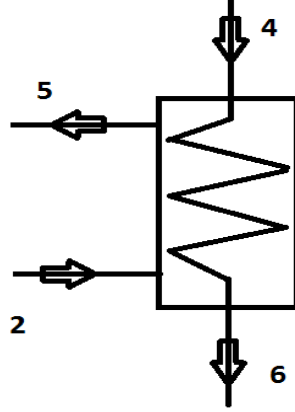


Figure 14 Recuperator or Internal Heat Exchanger IHE

The fundamental process is that the hot stream (4-6) rejects heat at the rate of $\dot{m}_{hot} * (h_4 - h_6)$ while the cold stream (2-5) receives heat at rate of $\dot{m}_{cold} * (h_5 - h_2)$. The heat transfer in IHX can be expressed as

$$Q_{IHE} = \dot{m}_{hot} * (h_4 - h_6) = \dot{m}_{cold} * (h_5 - h_2) \quad (12)$$

Where \dot{m}_{hot} and \dot{m}_{cold} refers to the mass flow rate for hot and cold streams. Assuming the mass flow rates \dot{m}_{hot} and \dot{m}_{cold} are the same, the conservation of energy will be

$$h_4 - h_6 = h_5 - h_2 \quad (13)$$

h_6 and h_5 are unknown parameters and to estimate them a second equation is needed. A heat exchanger effectiveness equation can be introduced from the fact that the maximum possible value of h_5 can never reach h_4 . A possible method to measure the performance is through calculating recuperator effectiveness $\epsilon_{Recu.}$. Recuperator effectiveness is the ratio between the actual received energy by hot stream to the maximum possible value [30].

$$\epsilon_{Recu.} = \frac{T_4 - T_6}{T_4 - T_2} \quad (14)$$

And it follows that h_5 can be estimated as

$$T_6 = T_4 - \epsilon_{Recu.} * (T_4 - T_2) \quad (15)$$

From equations (13) and (15) h_6 and h_5 can be estimated.

5 Working fluid selection

The working fluid selection has been treated in many papers and scientific articles [2,3,5]. Most of the articles and papers are based on theoretical studies of working fluids using simulations of thermodynamic models. Many scientific articles mainly treat the thermo-physical properties of working fluids with a focus on thermal efficiency, second law efficiency, Net Work Out, etc.

The choice of the optimal working fluid depends basically on the heat source and the heat sink temperature. For any heat temperature level there are a number of candidates which show a good match between heat source and heat sink temperatures and cycles boundary conditions. The choice the right working fluid is not an easy process. The fluid selection process is a trade-off between thermodynamic specifications, safety, environmental and economy aspects. The following criteria should be taken in consideration in order to figure out the best candidates [15].

5.1 Thermodynamic properties

Thermodynamic properties are of key importance in the design process of Organic Rankine Cycles, regarding optimal energy utilization and reducing exergy losses. The following are some important thermodynamic properties for working fluids:

- For a certain heat sink and heat source the Net Power Out, the thermal efficiency and the second law efficiency should be as high as possible.
- The condensing pressure should be higher than the atmospheric pressure to avoid leakage issues.
- In sub-critical cycles the critical pressure for the working fluid must be higher than the pressure in the evaporator.
- Vapor density
The higher the density, the lower the specific volume and volumetric flow rate. Low volumetric flow is desirable to achieve smaller component and more compact machines. Low density fluids have high specific volume and need bigger components (heat exchangers and expander). A bigger component size leads to more expensive units and more costly systems. Furthermore, a high specific volume increases the pressure drop in the heat exchangers and needs higher pump work.
- Saturation vapor line
Regarding saturation vapor line, there are three kinds of working fluids which are dry, isentropic and wet working fluids.
Using wet fluid may lead to drop formation at the end of expansion process. The drop formation can lead to serious damages in turbo machinery expanders. To avoid drop formation, superheat is necessary but it needs a bigger and more expensive evaporator. By using dry or isentropic fluids, the problems associated to drop formation can be eliminated.
- Large enthalpy variation in the turbine leads to high Net Work Out.
- Higher convective heat coefficient and high-thermal conductivity increases the heat transfer process between the heat source, the heat sink and the working fluid.
- High heat capacity (C_p) of the liquid leads to better energy recovery from the heat source and decrease the mass flow rate of the working fluid.
- The working fluid should be thermally and chemically stable.

5.2 Heat transfer properties

Heat transfer properties are of key importance and a very important parameter in sizing heat exchangers. High C_p value makes working fluid absorbs efficiently the thermal energy from heat source. High C_p allows a better temperature profile approaches in the heat exchangers and improves efficiencies. There are many factors affecting the heat transfer process. Some factors are related to the cycle architecture including piping design, flow rates (Reynolds number) and material selection. Other factors are related to the working fluid properties and affect the overall heat transfer capability. The working fluid thermal conductivity (k), specific heat (C_p) and viscosity (μ) are three key properties used to calculate Prandtl numbers ($Pr = \mu \cdot C_p / k$) which are widely used in heat exchanger design. It is desirable to have a working fluid with a viscosity as low as possible, and a specific heat and thermal conductivity as high as possible [31].

5.3 Environmental and Safety Criteria

Environmental and safety criteria are of key importance in working fluid selection however many working are phased out or on the way to be. The phased out working fluids have high ozone depletion potential ODP and global warming potential GWP. Some working fluids have good thermodynamic properties but at the same time have undesirable environmental and safety effects [2].

According to EC Regulation 2037/2000, many working fluids like CFC, CFCs and HCFCs refrigerant are already phased out. These refrigerants are banned due to their ozone depletion potential ODP and global warming potential GWP.

The EC Regulation 2037/2000 affects users, producers, suppliers, maintenance and servicing engineers, and those involved in the disposal of all ozone depletion substances ODS. The new regulation includes chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, 1,1,1 trichloroethane, carbon tetrachloride and bromochloromethane (CBM). These refrigerants are mainly used in refrigeration, air-conditioning, foam blowing, as solvents and in fire fighting.

5.3.1 Environmental data

The environmental data includes global warming potential GWP and ozone depilation potential ODP. In this thesis, the environmental data are mainly taken from the physical, safety and environmental data by James M. Calm[1].

5.3.1.1 Global Warming Potential (GWP)

The number of Global Warming Potential (GWP) refers to the amount of global warming caused by a certain working fluid relative to CO_2 for a 100 year time-frame. Or in other words, the GWP is the ratio of the warming caused by a substance to the warming caused by a similar mass of carbon dioxide. Thus, the GWP of CO_2 is defined to be 1.0. Water has a GWP of 0. Carbon dioxide is used as reference because it has the greatest net impact on global warming. There are some other refrigerants which typically have a higher GWP than carbon dioxide but they are available in much smaller quantities [1,2,30,31].

It is worth here to mention that some GWP values like (~ 20) or (<20) reflect uncertainty in calculations and there is no scientific consensus at this time [1].

5.3.2.2 Ozone Depletion Potential (ODP)

The Ozone Depletion Potential (ODP) refers to refrigerants' and other chemicals' ability to destroy stratospheric ozone relative to R11 [1]. According to the United States Environmental Protection Agency EPA the Ozone Depletion Potential ODP is: "The ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11. Thus, the ODP of CFC-11 is defined to be 1.0. Other CFCs and HCFCs have ODPs that range from 0.01 to 1.0. The halons have ODPs ranging up to 10. Carbon tetrachloride has an ODP of 1.2, and methyl chloroform's ODP is 0.11. HFCs have zero ODP because they do not contain chlorine" [16].

The Ozone Depletion Potential ODP is a very important issue in working fluid selection. The selected working fluids shouldn't have a very low or zero Ozone Depletion Potential ODP. Working fluids with any ODP have been or will be phased out, as required by the Montreal Protocol [31].

5.3.2 Safety data

The safety data in this thesis includes the lower flammability level LFL and safety classification of working fluids and refrigerants. The safety data are mainly taken from The Physical, Safety and Environmental Data by James M. Calm[1].

5.3.2.1 Lower flammability limit (LFL)

The lower flammability limit LFL is usually measured in volume percent and refers to the lower end concentration of a flammable solvent in ambient air when the mixture can ignite in a given temperature and pressure. There is a variation in LFL values among separate laboratories and that is because they use different vessels or ignition sources or different evaluation standards [1][32].

5.3.2.2 Safety classification

According to ASHRAE standard 34 (ASHRAE, 2010a and 2010b) the letters A refers to "lower" toxicity while the letter B means higher toxicity. The numbers 1,2 and 3 refer to flame propagation, number 1 means no flame propagation, number 2 means lower flammability and number 3 means higher flammability. The shortening "wwf" indicates the worse case of fraction of flammability or worse case of formulation, and it means that the working fluid is flammable in either vapor or liquid phase. In some cases group 2 is signified with letter L (like A2L and B2L) and here the letter L means more difficult to ignite [1].

Table 1 Safety classification

	Lower toxicity	Higher toxicity
Higher flammability	A3	B3
Lower flammability	A2	B2
No flame propagation	A1	B1

5.5 Chemical trends

According to the Application Guide AG 31-007 (2002) from McQuay International the following trends occur with use of various elements.

“The trends are:

- *Increasing carbon generally increases the molecular weight and the boiling point.*
- *Increasing nitrogen generally makes the compound more reactive. This can lead to toxicity and instability issues.*
- *Increasing oxygen generally reduces atmospheric stability, which is good for GWP and ODP but may lead to toxicity, flammability and reactivity issues.*
- *Increasing sulfur generally increases toxicity and decreases stability.*
- *Increasing hydrogen generally reduces atmospheric lifetime, which is good for GWP and ODP but increases flammability.*
- *Increasing fluorine attached to carbon increases GWP.*
- *Increasing chlorine improves lubricant miscibility but also increases ODP and toxicity.*
- *Increasing bromine increases ODP but lowers flammability.*
- *Using boron in lieu of carbon creates chemicals that are reactive and generally toxic.*
- *Using silicon in lieu of carbon creates substances that adversely react with water and have not performed well thermodynamically.”*

According to McQuay International the trends above were presented by Calm, J., David D. Didion, in ASHRAE/NIST Refrigeration Conference, Oct 6-7, 1997 Atlanta, Ga³.

³ Calm, J., David D. Didion, Oct 6-7, 1996. *Tradeoffs in Refrigerant Selections: Past, Present and Future*. Refrigerants for the 21st Century, ASHRAE/NIST Refrigeration Conference. ASHRAE, Atlanta, Ga.

5.6 The influence of overheat on cycle efficiency

In many scientific articles it is mentioned that super heat is not necessary for organic fluids as it is necessary for steam in the Rankine Cycle [15]. Superheat is used in Steam Rankine Cycle mainly in order to improve the vapor quality when it leaves the expander. Low vapor quality leads to drop formation in the final stages of the expansion. The superheat in Steam Rankine Cycle can also improve the thermal efficiency of the cycle.

To study superheat impact on organic fluids, two groups of working fluid have been chosen. The first group consists of five dry fluids (R236fa, R236ea, RC318, R245fa and Butane) and the second group consists of five wet fluids (H2S, Ammonia, SO2, R152a and R134a).

In this study the same boundary conditions are applied for both groups. The evaporation temperature is set to 363K and then the working fluid is superheated to 403K. The condensing temperature is set to 298K. The pump turbine efficiency is set to 0.7 and no Internal Heat Exchanger IHE is used.

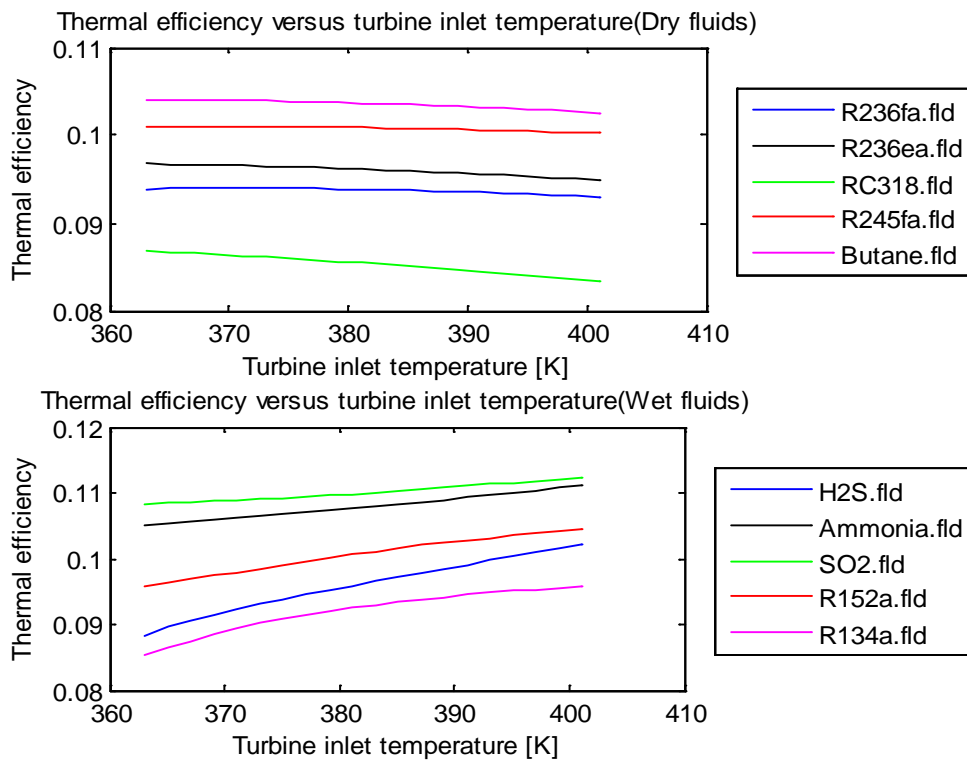


Figure 15 The effect of superheat on thermal efficiency for dry and wet fluids

Figure (15) shows that the thermal efficiency for dry fluids decreases by increasing the superheat rate. This means that the superheat is not recommended for dry fluid and it increases the exergy losses. At the same time wet fluid shows improved thermal efficiency by increasing superheat. Dry fluids already leave expanders as superheated vapor and therefore no attention needs to be paid to vapor quality. But for wet fluids the case is different. However some wet fluids may leave the expander as unsaturated vapor.

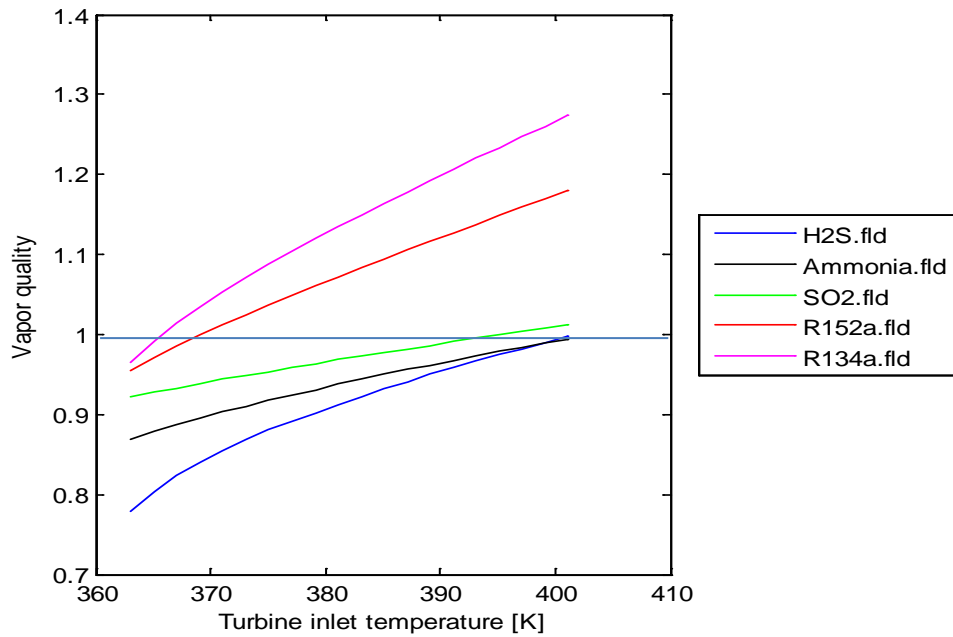


Figure 16 The vapor quality at expander outlet

Figure (16) shows the vapor quality at the end of the expansion process. All studied wet fluids seem to leave the expander as unsaturated vapor when they expand directly from the saturation vapor line (at 363K). R134a and R152a show good vapor quality and reach saturated vapor rapidly after only few degrees of superheat. SO₂, Ammonia and H₂S are far away from reaching saturation vapor and they need more superheat than R134a and R152a. H₂S has the worse vapor quality, followed by ammonia and then SO₂.

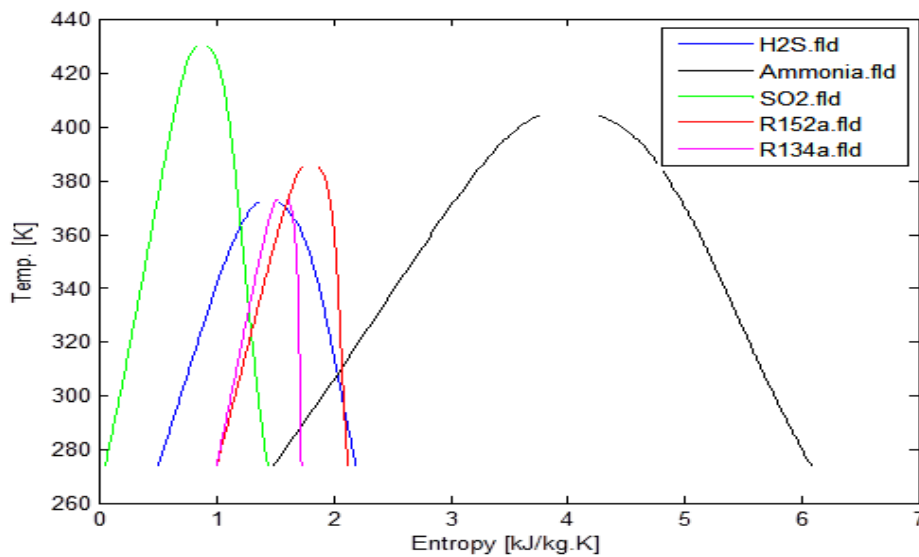


Figure 17 Saturation liquid and vapor lines for some working fluids

Figure(17) is showing the T-S diagram for studied working fluids and it is clear that there is a direct relation between liquid quality and the slope (dS/dT) of the saturation vapor line. The lower the the value of (dS/dT) slope, the better the vapor quality at expander outlet.

This study leads to the conclusion that superheat is desirable for wet fluids because it improves thermal efficiency and vapor quality. At the same time superheat is not recommended for dry fluids because it decreases the thermal efficiency and increase evaporator size and costs.

5.7 Saturation vapor line in T-S diagram

An important characteristic to take into account during the working fluid selection is the slope of the saturation vapor line in the T-S diagram. When it comes to the saturation vapor line, the working fluids can be sorted in three different categories:

- Dry fluids which have positive ds/dt slopes. This category includes working fluids such as Decane, Nonane, Octane, Toluene, Heptane, Cyclohexane, Hexane, R113, R365mfc, etc.
- Wet fluids which have negative ds/dt slopes. Common working fluids in this category are Heavy water, Ethanol, Methanol, R21, Sulfur dioxide, DME, etc.
- Isentropic fluids with infinitely ds/dt slopes. Such common working fluids are R142b, Cis-butene, R11, R141b, Acetone, etc.

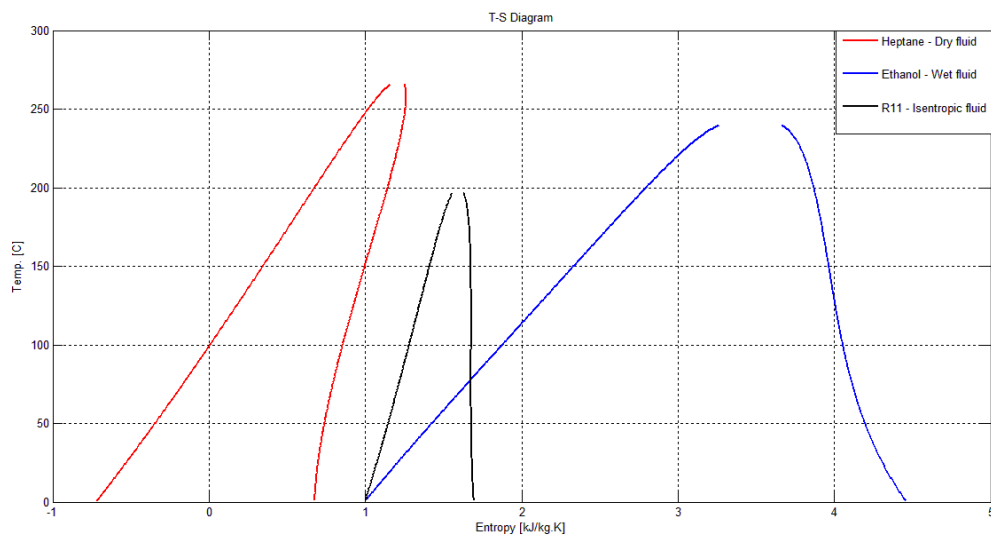


Figure 18 the T-S diagram for dry, isentropic and wet working

There are 104 pure working fluids are investigated in this thesis. The data source for investigated working fluids is NIST REFPROP 9. The figure below shows the percentage of dry, isentropic and wet working fluids to the number of total working fluids.

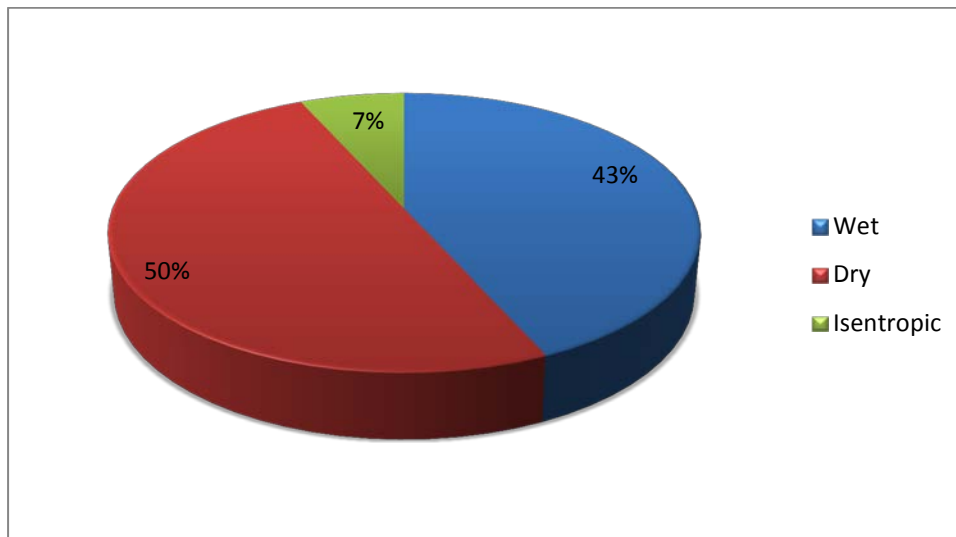


Figure 19 The procentage of dry, isentropic and wet working fluid in NIST REFPROP 9

5.8 The effect of normal boiling point on evaporator and condenser pressure

Figure (20) demonstrates the influence of Normal Boiling Point NBP on evaporator and condenser pressure⁴. In this figure 51 refrigerants (their NBP between 446.27K (decane) and 248.37K (DME)) were investigated. It is obvious that a higher NBP gives a lower evaporator and condenser pressure at a certain evaporator and condenser temperature. If we set the evaporator temperature to 363K and the condenser temperature to 298K, the evaporator and condenser pressures for decane will be 0.18 and 6.3Kpa respectively. The pressure in both evaporator and condenser is lower than the atmospheric pressure. At the same time the evaporator and condenser pressure for DME will be 587.7 and 2712.6kPa respectively. These pressures are much higher than the atmospheric pressure. To increase the pressure levels for decane, both evaporation and condensation temperatures should be increased. Otherwise decane can't be used in Organic Rankine Cycle due to the very low pressure in both evaporator and condenser and air infiltration problems to the cycle.

⁴ In this figure the condenser and evaporator pressure are assumed according to condensing temperature=298K and evaporating temperature=363K.

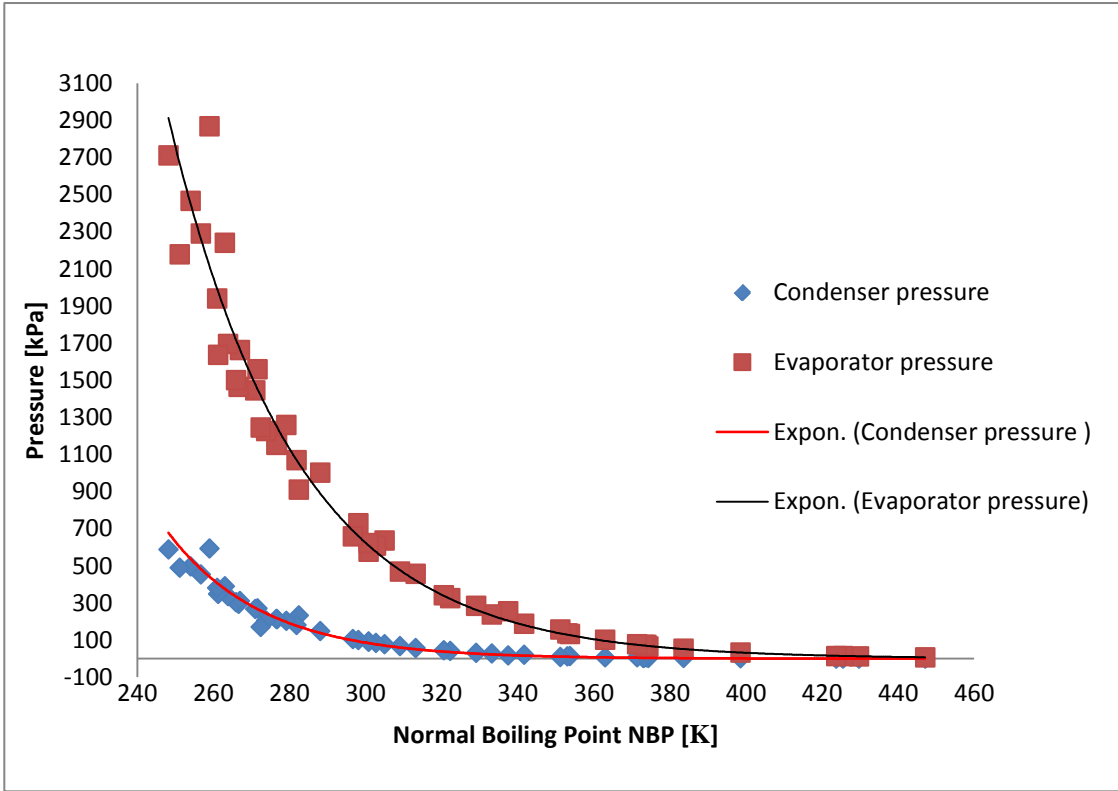


Figure 20 influence of Normal Boiling Point NBP on evaporator and condenser pressure

6 Simulation scenarios

In this section some thermodynamic models have been created in MatLab and linked to the working fluids data base in NIST REFPROP 9. The thermodynamic models are created in MatLab in order to run numerical calculations, simulations and compare the working fluids from a thermo-physical perspective. To complete the selection process the safety and environmental criteria were taken into consideration.

In this thesis 104 working fluids supposed to be simulated and investigated in different scenarios and by applying different boundary. The studied working fluids are listed in appendix 1. Some working fluids have very high or extremely low normal boiling point NBP. This kind of working fluids is not suitable for Organic Rankine Cycle when the heat source temperature can vary between 323 - 523K. The high NBP working fluids need very high condensation and evaporation temperature to keep the pressure in condenser and evaporator over atmospheric pressure. The low NBP working fluids need extremely low heat source and heat sink temperature. The problem here is the heat sink when the temperature in condenser should be under 273K For these reasons, some working fluids can't be used in the simulations.

Every scenario covers a number of working fluids and it is impossible to apply a single scenario to a very wide range of working fluids. The purpose is that the available data in NIST REFPROP 9 are limited and not available for a very wide range of temperature and pressure. To give an example, methyl stearate which has the highest NBP, which has a moderate NBP and helium which has the lowest NBP are compared in the table below.

Table 2 The upper and lower temperature limits for methyl stearate, DME and helium

Working fluid's name	Normal boiling point NBP [K]	Critical temperature [K]	Critical pressure [kPa]	Lower temperature limit [K]	upper temperature limit [K]
methyl stearate	629,56	775	1239	311,84	1000
DME	248,37	400,38	5336,85	131,65	450
helium	4,22	5,2	227,6	2,18	2000

Lower and upper temperature limits in table above refers to the range of available data in NIST REFPROP 9. To study a working fluid, the boundary conditions of the thermodynamic model should be within the upper and lower temperature limits for that working fluid to perform the numerical calculations.

In every scenario two different cycles with same assumptions are investigated. The first cycle is without Internal Heat Exchanger IHE while the second cycle has an IHE. Here the target is to study the influence of IHE on cycle performance and efficiencies. Some working fluids show interesting improvement in terms of thermal efficiency and second law efficiency when IHE is introduced to the cycle. The efficiency improvement is strongly dependent on the fluid temperature at turbine outlet. IHE can be introduced when the vapor temperature at turbine outlet is much higher than the liquid temperature at pump outlet. Dry and isentropic fluids show a better efficiency improvement than the wet fluids when IHE is introduced in the cycle. In case of using wet fluids, the working fluid may leave the expander as unsaturated vapor and at a temperature lower than the fluid temperature at pump outlet. When using dry or isentropic working fluids, the working fluid leaves the expander as superheated vapor. Expander efficiency and superheat rate are some of the factors which can affect the vapor temperature at expander outlet. The lower the expander efficiency and the higher the superheat rate, the higher the vapor temperature at expander

outlet. IHE extracts the thermal energy from the superheated vapor and supply it to the working fluid at pump outlet. IHE reduces exergy losses and increases thermal and second law efficiencies.

6.1 Scenario 1

Scenario 1 is a case study of superheat impact on cycle performance. The condenser and evaporator temperatures are set to 298K and 363K respectively. After the working fluid evaporates in the evaporator and reaches the saturated vapor line, it is subjected to extra thermal energy in order to be superheated. When the working fluid is superheated, it leaves the evaporator and enters the expander to produce useful work. The numerical calculations consist of 20 loops. In the first loop the working fluid leaves the evaporator at saturation vapor line and enters the expander. In the following loops the working fluid is subjected to extra thermal energy until it is superheated by 40K higher than evaporator temperature. The superheating process takes place in 20 loops and in every new loop the working fluid temperature is exceeded by extra 2K than the. The figure below shows the process in scenario 1.

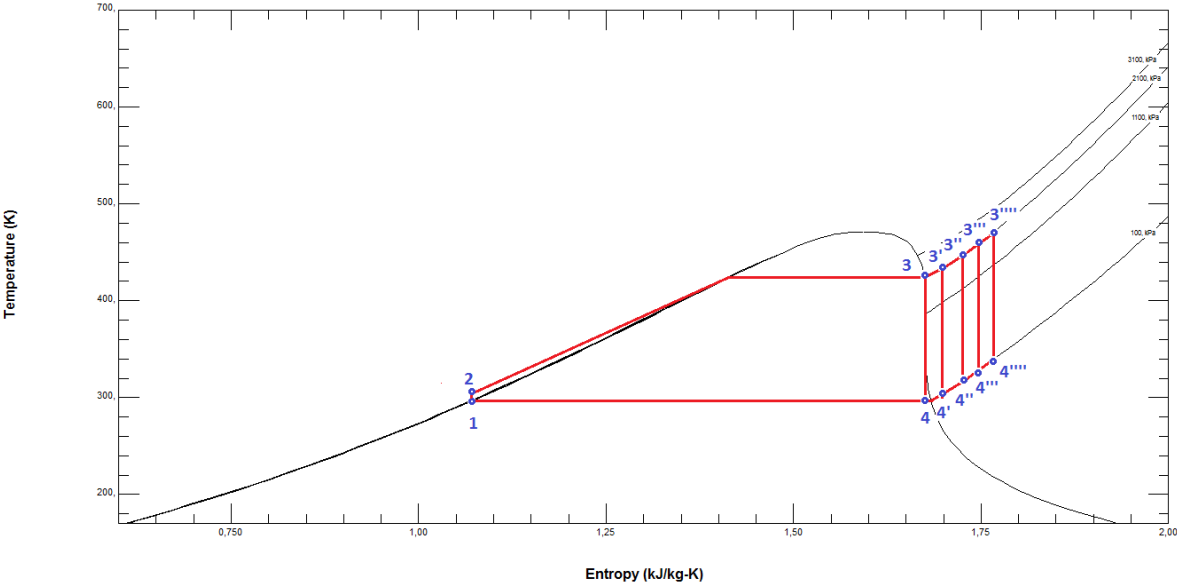
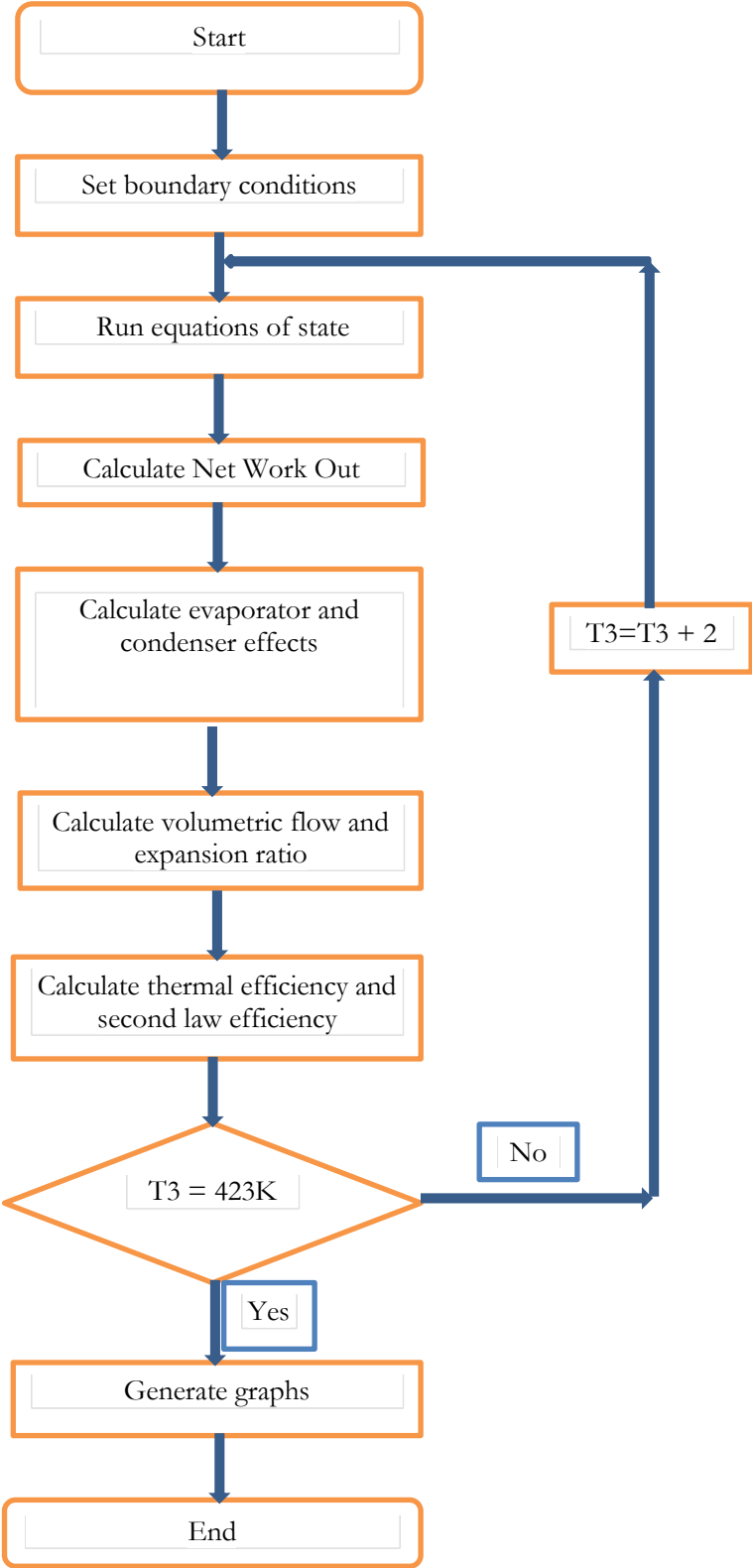


Figure 21 Overheat process in scenario 1

6.1.1 Flow chart



6.1.2 Simulation assumptions

- The cycle is considered to work in a steady state
- Pressure drop in heat exchangers is neglected
- Isentropic efficiency for pump and expander assumed to be 0.7
- Mass flow rate $\dot{m} = 1 \text{ kg/s}$
- Ambient temperature $T_{\text{Amb}} = 298 \text{ K}$
- Heat sinks temperature $T_{\text{Sink}} = 288 \text{ K}$
- Condensing temperature $T_{\text{Cond.}} = 298 \text{ K}$
- Evaporating temperature $T_{\text{Evap.}} = 363 \text{ K}$
- Heat source temperature
 $T_{\text{in}} = 423 \text{ K}$
 T_{out} varies depending on the selected working fluid and the amount of superheat.
- Pinch points for evaporator and condenser 10K and 5K respectively
- Condensing and evaporating pressure can be estimated from saturation liquid and respective temperature in condensing and evaporating temperature; this pressure can vary from one working fluid to another
- The temperature at turbine inlet starts at 363K which is the evaporating temperature; overheating takes place in 20 stages of 2K until the 40 K overheating is reached
- Recuperator or Internal Heat Exchanger (IHE) efficiency is set to 0.8.

Scenario 1 can only cover a number of working fluids in appendix 1 and not all of them. Many working fluids have very high or very low critical temperature. When the critical temperature is too high, the pressure in condenser becomes very low and much lower than atmospheric pressure. When the critical temperature is lower than 363K, it is impossible to perform a subcritical cycle because the evaporator temperature will be higher than the critical temperature for the working fluid. The critical temperature should be enough higher than evaporation pressure to avoid very low pressure in condenser an evaporator temperature higher than critical pressure. To deal with working fluids with high critical temperature and to overcome the low condensing pressure problems, condensing temperature can be raised (see scenario 2). To deal with working fluids which have quite low critical temperature trans-critical or supercritical cycles can be performed. Using working fluid with very high critical pressure, the condensing pressure becomes very low if condensing temperature is set 298K. The working fluids in scenario 1 are chosen according to the following criteria:

- The condenser pressure is higher than the atmospheric pressure at condenser temperature which is 298K.
- The critical temperature is higher than 363K which is the evaporation temperature

Table 3 Selected working fluids in scenario 1

	Name or Number	NBP [K]	Critical temp. [K]	Critical pr. [kPa]	Safety group	Atm. life time	ODP	GWP (100 yr)	Expansion
1	R245ca	298,13	447,42	3925	-	6,5	0	726	dry
2	R11	296,708	470,96	4407,6	A1	45	1	4750	isotropic
3	R245fa	288,14	427	3651	B1	7,7	0	1050	dry
4	R601b Neopentane	282,5	433,6	3196			0	20	dry
5	R21	281,86	451,33	5181	B1	1,7	0,04	151	wet
6	R236ea	279,2	412,29	3502		11	0	1410	dry
7	Cis-butene	276,72	435,6	4225,5					isotropic
8	R114	276,6	427,7	3257	A1	190	0,58	9180	dry
9	Trans-butene	273,88	428,46	4027	A3	0,018	0	20	dry
10	R600 BUTANE	272,5	425	3800	A3	0,018	0	20	dry
11	R236fa	271,6	397,9	3200	A1	242	0	9820	dry
12	Perfluorobutane	270,99	386,18	2323					dry
13	RC318	267	388,2	2780	A1	3200	0	10300	dry
14	Butene	266,69	419,14	4005					dry
15	Isobutene	266	506,96	4010					dry
16	R142b	263,9	410,1	4060	A2	17,2	0,06	2220	isotropic
17	Sulfur dioxide	263	430,5	7090	B1		0		wet
18	Isobutane	261,3	407,7	3630	A3	0,016	0	20	dry
19	R124	261	395,3	3062	A1	5,9	0,02	619	dry
20	R152a	258,98	386,26	4517	A2	1,5	0	140	wet
21	R227ea	256,7	374,8	2930	A1	38,9	0	3580	dry
22	R1234ze [E]	254	382,4	3640		0,045	0	6	dry
23	CF3i	251,15	396,29	3953					wet
24	DME	248,2	400,23	5340	A3	0,015	0		wet
25	R134a	247	374	4059	A1	14,6	0	1300	wet
26	R1234yf	243,5	367,7	3380	A2L	0,029	0	4,4	dry
27	R12	243,2	385	414	A1	100	0,82	10900	wet
28	C270 Cyclopropane	241,8	398,2	5580		0,44	0	20	wet
29	Ammonia	239,7	405,25	11333	B2L	0,02	0	1	wet
30	R161	235,4	375,2	5090		0,18	0	12	wet
31	R22	232,2	369,1	4990	A1	11,9	0,04	1790	wet
32	R290 Propane	231	369,7	4247	A3				wet
33	R1270 Propylene	225,4	364,1	4560	A3	0,001	0	20	wet
34	Carbonyl sulfide	222,84	378,62	6370					wet
35	Hydrogen sulfide	212,7	372,95	9000					wet

Table 3 shows the selected working fluids for scenario 1. The table contains 35 working fluids which are arranged according to their NBP. R11 has the highest NBP = 296.7K and hydrogen has the lowest NBP = 212.7K.

Figure (22) shows the relation between NBP and pressure ratio in for the working fluids in scenario 1. It is obvious that the higher the NBP, the higher the pressure ratio. Most of working fluids are fitting very well with exponential relation between NBP and pressure ratio. The working fluids which are far away from the exponential trend-line (points inside ellipse) present heavy water D2O, water, ethanol and methanol which all are wet fluids. These wet fluids have much higher pressure ratio than other refrigerants with similar NBP. These working fluids and R21 are the only wet fluids having NBP higher than 273K.

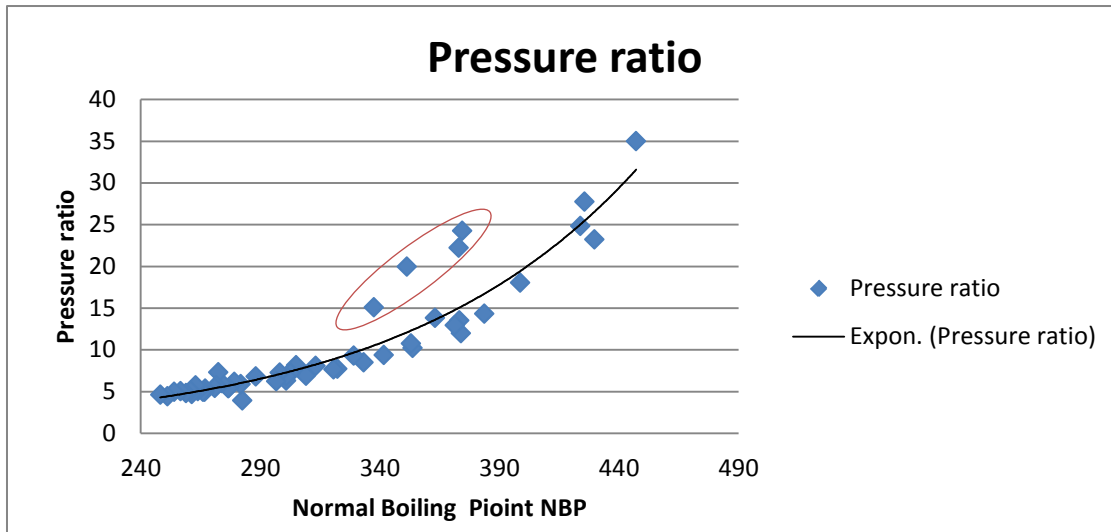


Figure 22 Relation between NBP and pressure ratio

6.1.3 Simulation results

Under this section simulation results are presented for the top 5 working fluids which show the highest thermal efficiencies among the studied working fluids. The working fluids are listed in the table below and have no or very low ODP, very low GWP, very low atmospheric life, low toxicity (except ammonia) and low flammability. SO₂ can be very harmful if any moisture exists in the cycle. A reaction between SO₂ and water may take place and result H₂SO₃ which is a corrosive acid.

Table 4 The best working fluids in scenario 1

Name or number	Safety group	Atmospheric life	Ozone depletion potential ODP	Global warming potential GWP (100 year)
Ammonia	B2L	0.02	0	1
Cyclopropane	n.a.	0.44	0	~20 ⁵
R152a	A2	1.5	0	140
Sulfur dioxide SO ₂	B1	n.a. ⁶	0	n.a.
R21	B1	1.7	0.04	151

Simulation results for other working fluids in scenario 1 are presented in appendix 2 – scenario 1.

6.1.3.1 Volumetric flow rate and expansion ratio

The volumetric flow rate is an important parameter in Organic Rankine Cycle design and component sizing. The higher the volumetric flow rate, the bigger the component size and the higher the work absorbed by the fluid circulation pump. Volumetric flow rate at turbine inlet

⁵ (~) refers to approximated value with some uncertainty in calculations according to [1]

⁶ Information not available

together with expansion ratio gives important information about expander design. Volumetric flow rate at expander inlet can be calculated by dividing mass flow rate to the density at expander inlet.

$$\dot{V}_{inlet} = \frac{\dot{m}}{\rho_{inlet}}$$

Where

\dot{V}_{inlet} is volumetric flow rate at expander inlet

\dot{m} is mass flow rate

ρ_{inlet} is working fluid density at expander inlet

Expansion ratio can be calculated by the following formula:

$$expansion\ ratio = \frac{\rho_{inlet}}{\rho_{outlet}} = \frac{\dot{V}_{outlet}}{\dot{V}_{inlet}}$$

Where

ρ_{inlet} is working fluid density at expander inlet

ρ_{outlet} is working fluid density at expander outlet

\dot{V}_{outlet} is volumetric flow rate at expander outlet

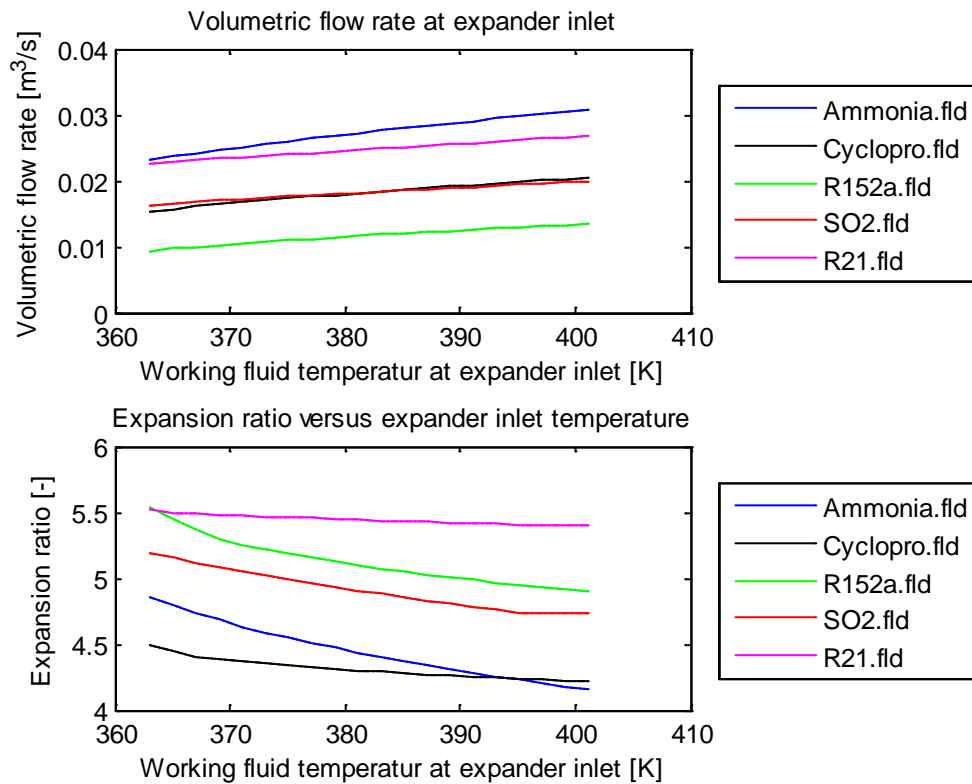


Figure 23 The volumetric flow rate and expansion ratio for ammonia, cyclopropane, R152a, SO2 and R21

Figure (23) shows that the volumetric flow rate increases and expansion ratio decreases for all working fluids with increasing superheat. Ammonia has the highest volumetric flow rate while R152a has the lowest. R21 has high volumetric flow rate at turbine inlet and high expansion ratio resulting in high expander dimensions. To design two expanders, one for ammonia and the other for R21, according to figure above the designed expander for ammonia will have higher inlet area than the one designed for R21. At the same time, the designed expander for R21 will have higher outlet area than the one designed for ammonia.

6.1.3.2 Net Work Out

The Net Work Out represents the difference between the expander power out and the power absorbed by the fluid circulation pump.

$$Net\ Work\ Out = W_{expander} - W_{pump}$$

Where

$W_{expander}$ stands for the work produced by expander

W_{pump} stands for the work absorbed by the circulation pump

Net Work Out per kg working fluid shows how good the working fluid is to convert absorbed thermal energy from a certain heat source to useful mechanical work. It is desirable that the working fluid shows high Net Work Out per 1 kg/s mass flow rate.

Ammonia shows the highest Net Work Out (over 120 kJ/kg) while other working fluids show much lower Net Work Out (less than 50 kJ/kg before superheat).

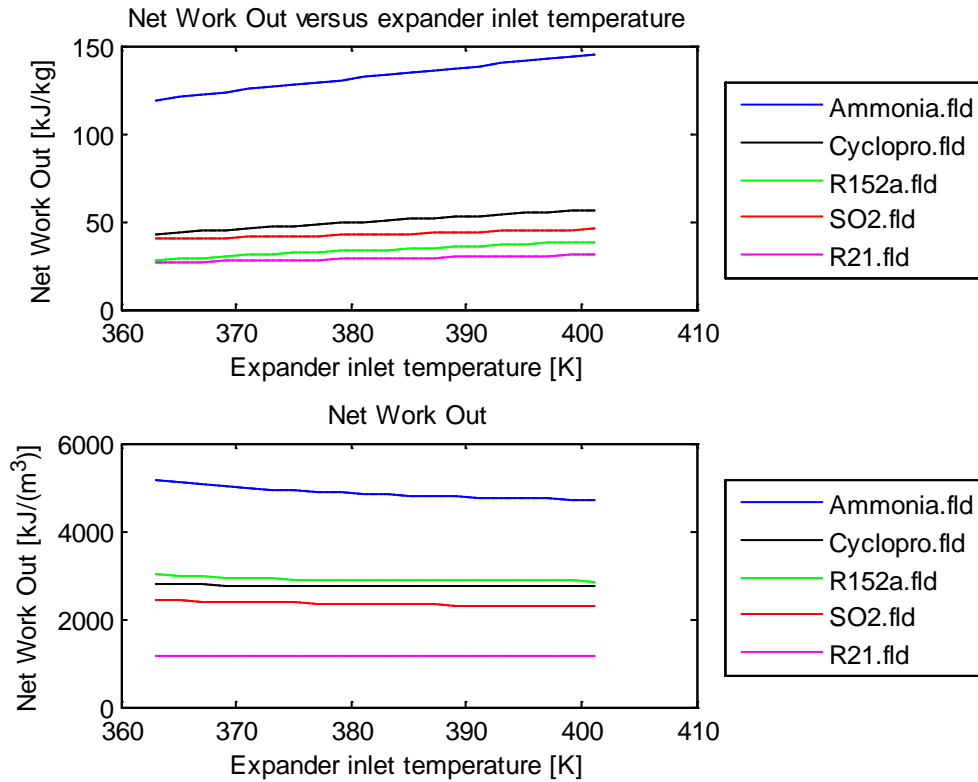


Figure 24 The Net Work Out for ammonia, cyclopropane, R152a, SO2 and R21

Figure (24) shows that Net Work Out increases for all working fluids by increasing superheat but ammonia shows a better response to superheat compared to other working fluids. The lower part of figure (24) represents the achieved Net Work Out per one cubic meter of working fluid at expander inlet. The value of Net Work Out per cubic meter at expander inlet is directly related to the working fluid density at that point. The density of working fluid decrease by increasing temperature and keeping the pressure constant. It is obvious that when the fluid density decreases, its specific volume increases and that is why the Net Work Out per cubic meter working fluid decreases.

6.1.3.3 Thermal efficiency

Thermal efficiency is the ratio between the Net Work Out the absorbed thermal energy in evaporator. The Net Work Out is the difference between expander work out and the work absorbed by the circulation pump.

$$\eta_{thermal} = \frac{Energy_{out}}{Energy_{in}} = \frac{W_{net}}{Q_{evaporator}} = \frac{W_{expander} - W_{pump}}{Q_{evaporator}}$$

According to the first law of thermodynamics, the thermal efficiency can never exceed 100% because energy output never exceeds energy input and there is always irreversibility in the cycle.

$$0\% \leq \eta_{thermal} \leq 100\%$$

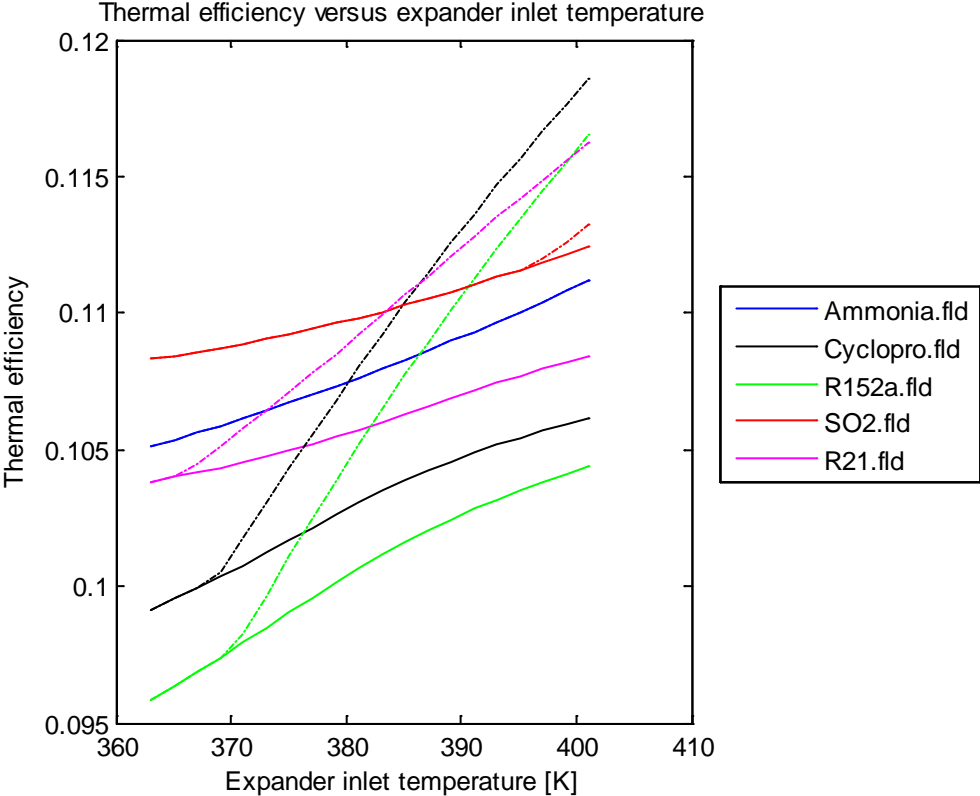


Figure 25 The thermal efficiency versus expander inlet temperature

Figure (25) illustrates the thermal efficiencies for Ammonia, Cyclopropane, R152a, SO2, and R21. The solid lines refer to the cycle without an internal heat exchanger IHE and the dashed lines refer to the cycle which has an internal heat exchanger IHE. When no IHE is introduced in the cycle, SO2 has the highest thermal efficiency and R152a has the lowest among the illustrated working fluids. IHE improves the thermal efficiency for Cyclopropane, R21 and R152a, and the difference between the solid and dashed lines represents IHE’s impact on cycle efficiency. Ammonia is not showing any improvement and an explanation can be that Ammonias temperature in unsaturated region is the same as condensing temperature (298K), which is lower than the temperature at pump outlet. For other working fluids in figure (25) IHE can be used when the fluid temperature at expander outlet is higher enough than the temperature at pump outlet.

6.1.3.4 Second law efficiency

The second law efficiency (or exergy efficiency) represents the ratio of the total exergy output to exergy input. The exergy is defined as the maximum work potential of a system or component at a given state in a specified environment. Exergy efficiency is a very useful tool which can be used to investigate and compare working fluids with each other. The importance of second law efficiency resides in its ability to give a clearer picture about system losses, performance and potential

improvements. The second law efficiency is an important parameter to assess which working fluid is better for a given heat source and heat sink temperature.

According to D.Y. Wang the exergy efficiency evaluates the proximity of the real and Carnot cycle [18].

$$\eta_{II} = \frac{\eta_{thermal}}{\eta_{Carnot}} = \frac{W_{net}}{Q_{evaporator} * (1 - \frac{T_L}{T_H})}$$

Where

T_L is the arithmetic mean temperature between heat sink inlet and outlet temperature in condenser

T_H is the arithmetic mean temperature between heat source inlet and outlet temperature in evaporator

The temperature of heat source decrease in evaporator while the temperature of heat sink increase in condenser and T_L and T_H becomes [14],

$$T_L = \frac{T_{sink\ out} - T_{sink\ in}}{2}$$

Where $T_{sink\ out}$ and $T_{sink\ in}$ represent the heat sink temperature at condenser outlet and inlet respectively.

$$T_H = \frac{T_{source\ in} - T_{source\ out}}{2}$$

Where $T_{source\ in}$ and $T_{source\ out}$ represent the heat source temperature at heat exchanger's inlet and outlet respectively. $T_{source\ out}$ varies with superheat and the higher the superheat, the higher the heat source temperature at heat exchanger's outlet.

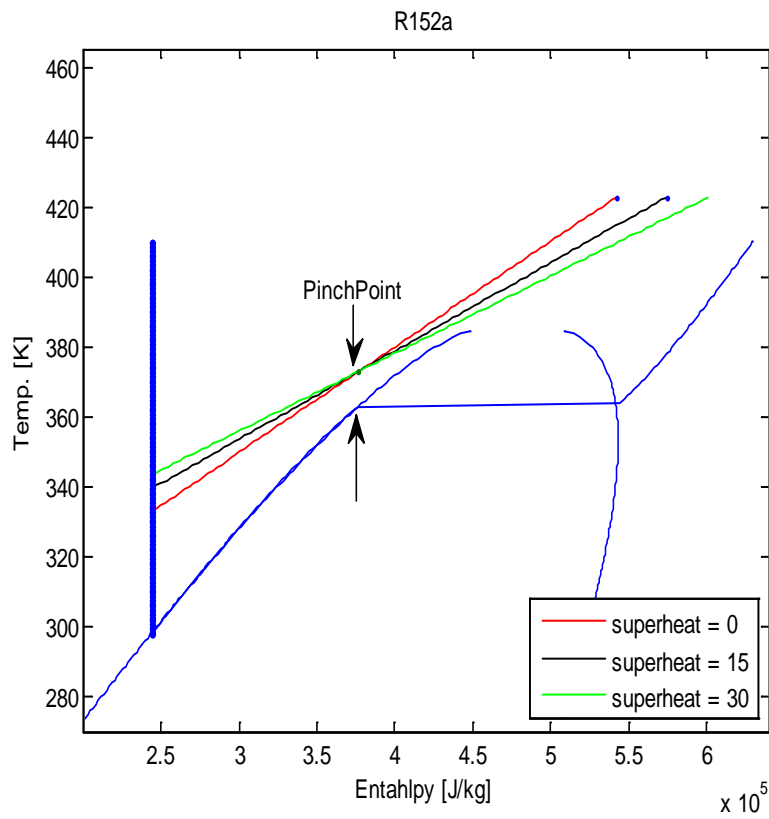


Figure 26 The effect of superheat on heat source temperature at heat exchanger outlet

Figure (26) shows three cases where the superheat is 0K, 15K and 30K respectively. The heat source temperature at heat exchanger inlet is set to 423K. At heat exchanger outlet, the heat source temperature varies between 330K and 345K as working fluid temperature at expander inlet varies from 363K to 393K due to superheat.

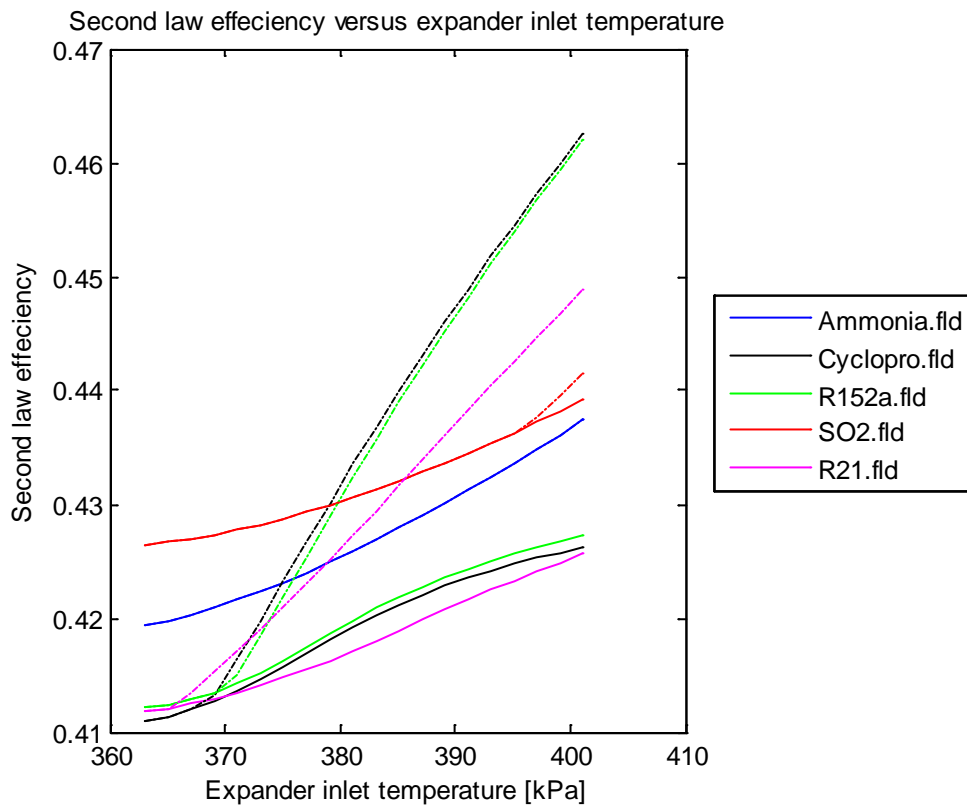


Figure 27 The second law efficiency versus expander inlet temperature

Figure (27) shows the second law efficiency for Ammonia, Cyclopropane, R152a, SO₂ and R21. It is clear that the second law efficiency increases with the superheat for all working fluids. In cycles without IHE, SO₂ and ammonia show high efficiency (solid lines) but by introducing an IHE to the cycle, the highest efficiency can be achieved by Cyclopropane and R152a. In this scenario ammonia doesn't need IHE because the vapor temperature at expander outlet is lower than the fluid temperature at pump outlet. SO₂ has a very low potential compared with R152a and Cyclopropane.

6.1.3.5 Evaporator and condenser load

In this section the heat added to evaporators and the heat rejected from condensers are studied. This parameter is of key importance in the design of heat exchangers. It is also important to figure out the influence of IHE on the needed heat to be supplied to the evaporator and rejected from the condenser. The extra costs for investing and introducing an IHE in the cycle can be compensated by the reduction in evaporator's and condenser's load and size. Figure (28) shows the evaporators' and condensers' load as a function of expander inlet and outlet temperature.

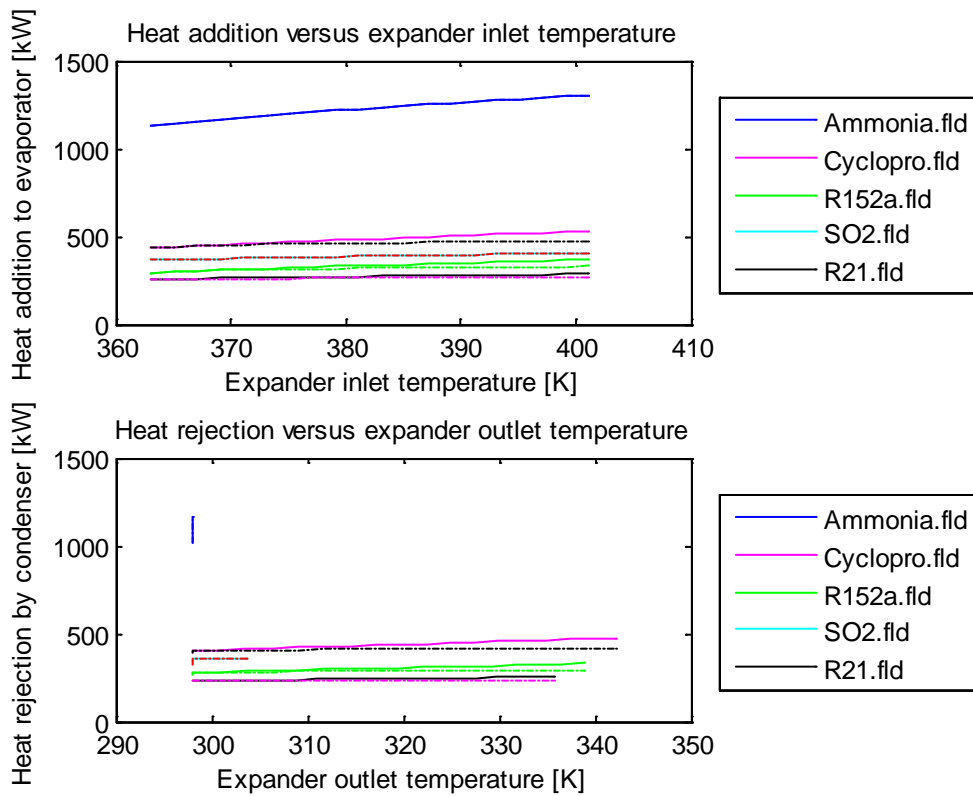


Figure 28 The heat addition and heat rejection rates for ammonia, cyclopropane, R152a, SO2 and R21

The difference between the solid and the dashed lines represents the amount of energy which can be extracted from the working fluid at expander outlet and be added to the working fluid at pump outlet. Solid lines refer to cycle without internal heat exchanger IHE and dashed lines refer to cycle including IHE.

6.2 Scenario 2

The idea behind scenario 2 is the same as the one in scenario 1 with some simple differences like heat source, condensing and evaporating temperatures. These temperatures are quite higher than in scenario 1 in order to investigate and cover more working fluids which weren't included in scenario 1. The low condensing temperature in scenario 1 was leading to low condensing pressure and in some cases a pressure lower than the atmospheric pressure. Subsequently many working fluids were abandoned in order to avoid air infiltration into the system. In scenario 2 the condensing temperature is much higher and many new working fluids with high NBP and critical temperature can be investigated. The heat sink source can be a district heating system which can extract heat from the working fluid in the condenser and use it for heating a building, offices, etc.

6.2.1 Simulation assumptions

Following are the assumption for scenario 2

- The cycle is considered to work at steady state
- Pressure drop in heat exchangers is neglected
- Isentropic efficiency for pump and expander is assumed to be 0.7
- Mass flow rate $\dot{m} = 1 \text{ kg/s}$
- Ambient temperature $T_{\text{Amb}} = 298 \text{ K}$
- Heat sinks temperature $T_{\text{Sink}} = 333 \text{ K}$
- Condensing temperature $T_{\text{Cond.}} = 373 \text{ K}$
- Evaporating temperature $T_{\text{Evap.}} = 473 \text{ K}$
- Heat source temperature.
 $T_{\text{in}} = 533 \text{ K}$
 T_{out} varies depending on the selected working fluid and the amount of superheat.
- Pinch points for evaporator and condenser are 10K
- Condensing and evaporating pressures can be estimated from the saturation liquid and from the respective condensing and evaporating temperatures. These pressures can vary from one working fluid to another
- The temperature at expander inlet starts at 473K which is the evaporation temperature and overheating takes place in 20 stages of 2K until 40 K overheating is reached
- Recuperator or Internal Heat Exchanger (IHE) efficiency is set to 0.8

The condensation and evaporation temperatures are too high in this scenario and much higher than the critical temperature for many working fluids. For this reason, many working fluid with low critical temperature can't be used in this scenario.

The chosen working fluids in scenario 2 have critical temperatures higher than 463K which is the evaporation temperature and the condenser temperature is set to 373K. Table (5) shows the investigated working fluids in scenario 2 and their environmental and safety data are not available.

Table 5 The suitable working fluids for scenario 2

	Name or Number	NBP [K]	Critical temp [K]	Critical Pr. [kPa]	Safety group	Atm. life (yr)	ODP	GWP (100 yr)	Expansion
1	Methyl stearate MSTEARAT	638,41	774,85	1239					dry
2	Methyl linolenate MLINOLEN	628,98	771,85	1369					dry
3	Methyl oleate MOLEATE	627,03	781,85	1246					dry
4	Methyl palmitate MPALMITA	602,15	754,85	1350					dry
5	MD4M	533,75	653,05	877					dry
6	Methyl linoleate MLINOLEA	528,69	798,85	1341					dry
7	D6	517,96	645,63	961					dry
8	MD3M	502,87	628,21	945					dry
9	Dodecane C12	489,15	657,95	1817					dry
10	D5	483,9	619	1160					dry
11	MD2M	467,36	599,25	1227					dry
12	D4	448,35	586,35	1332					dry
13	Decane	447,12	617,55	2103					dry
14	Propylcyclohexane C3CC6	429,75	630,65	2860					dry
15	MDM	425,51	563,94	1415					dry
16	Nonane	423,76	594,4	2281					dry
17	Octane	398,6	569,17	2497					dry
18	Toluene	383,6	591,6	4126,3					dry
19	Heavy water D2O	374,4	643,7	21671					wet
20	Methylcyclohexane C1CC6	373,85	572	3470					dry
21	MM	373,25	518,6	1939					dry
22	Water H2O	373	647	22064					wet
23	Heptane	371,38	540,36	26698					dry
24	Dimethyl carbonate DMC	363	557,23	4835,1					dry
25	Cyclohexane	353,736	553,5	4075					dry
26	Benzene	353,07	561,87	4906,3					dry
27	Hexane	341,71	507,67	3034					dry
28	Methanol	337,5	512,5	8104					wet
29	Isohexane	333,21	497,55	3040					dry
30	Acetone	329,07	507,95	4700					is entropic

It is worth here to mention that water is used in this scenario just to compare its performance with other working fluids. It is clear that using water in this cycle will lead to performing a Stem Rankine Cycle and not Organic Rankine Cycle.

6.2.2 Simulation results

The table below shows the working fluids that show the highest thermal efficiency in scenario 2.

Table 6 The best working fluids in scenario 2

Name or number	Safety group	Atmospheric life	Ozone depletion potential ODP	Global warming potential GWP (100 year)
Heavy water D2O	n.a.	n.a.	n.a.	n.a.
Toluene	n.a.	n.a.	n.a.	n.a.
Water	n.a.	n.a.	n.a.	n.a.
Methanol	n.a.	n.a.	n.a.	n.a.
Acetone	n.a.	n.a.	n.a.	n.a.

Simulation results for other working fluids in scenario 2 are presented in appendix 2 – scenario 2

Methanol, toluene and acetone are known as a flammable working fluids and it is clear that water has the best environmental and safety data like non-flammability, non-toxicity, etc.

6.2.2.1 Volumetric flow rate and expansion ratio

The volumetric flow rate is a significant parameter in sizing components and system design. A low volumetric flow rate is desirable to reduce components' size and material costs when a new system is being designed and built. Figure (29) shows that water has the highest volumetric flow rate at expander inlet while acetone has the lowest. This is due to Acetone has a higher density than water at expander inlet. The expansion ratio together with the volumetric flow rate at expander inlet gives value information for sizing the expander and determining how big the expander outlet will be. Increasing the superheat rate increases the volumetric flow rate and decreases the expansion ratio.

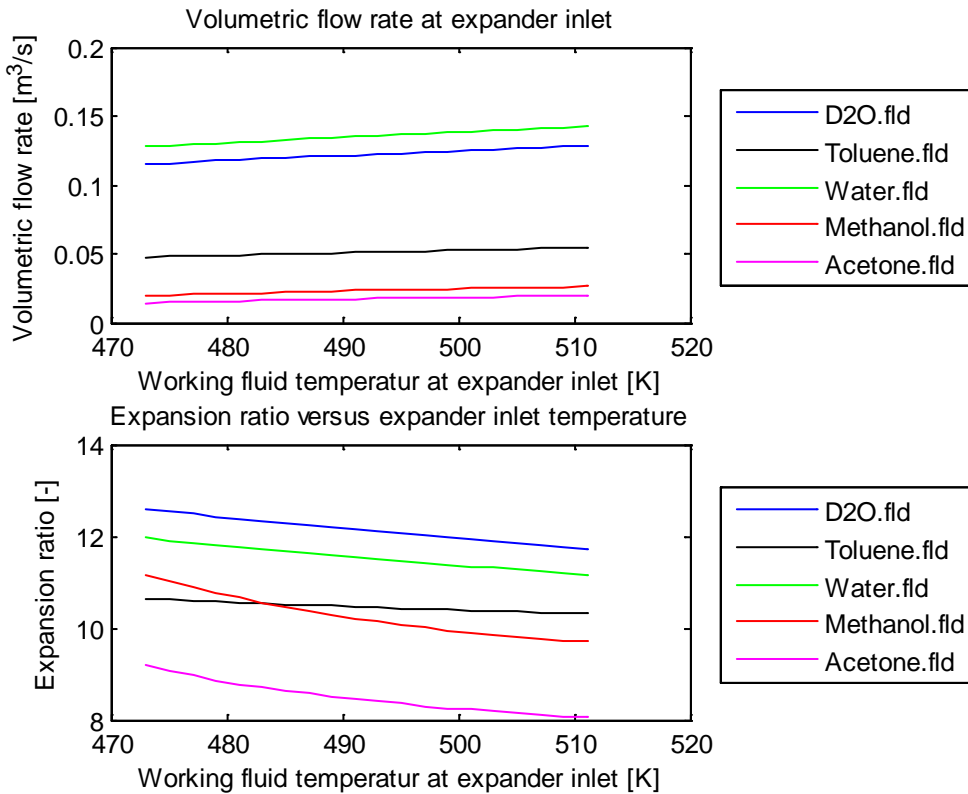


Figure 29 The volumetric flow rate and expansion ratio for D2O, toluene, water, methanol and acetone

Heavy water D2O and water have the highest expansion ratio and together with their high volumetric flow rate, the components' size will be huge compared with acetone. Acetone has the lowest volumetric flow rate and expansion ratio. Using acetone as a working fluid leads to designing a very compact Organic Rankine cycle system. The expansion process seems to be liner for Heavy water D2O, water and toluene while it is non-liner for methanol and acetone.

6.2.2.2 Net Work Out

Figure (30) below shows that water gives the highest Net Work Out per kg working fluid. The next highest Net Work Out is achieved by heavy water D2O, and methanol gives over 110 kJ/ kg before overheat, while acetone and toluene give the lowest Net Work Out per kg working fluid. The Net Work Out increases for all working fluids with the increasing of the superheat rate, and the Net Work Out achieved by acetone exceeds that of toluene when the superheat rate increases.

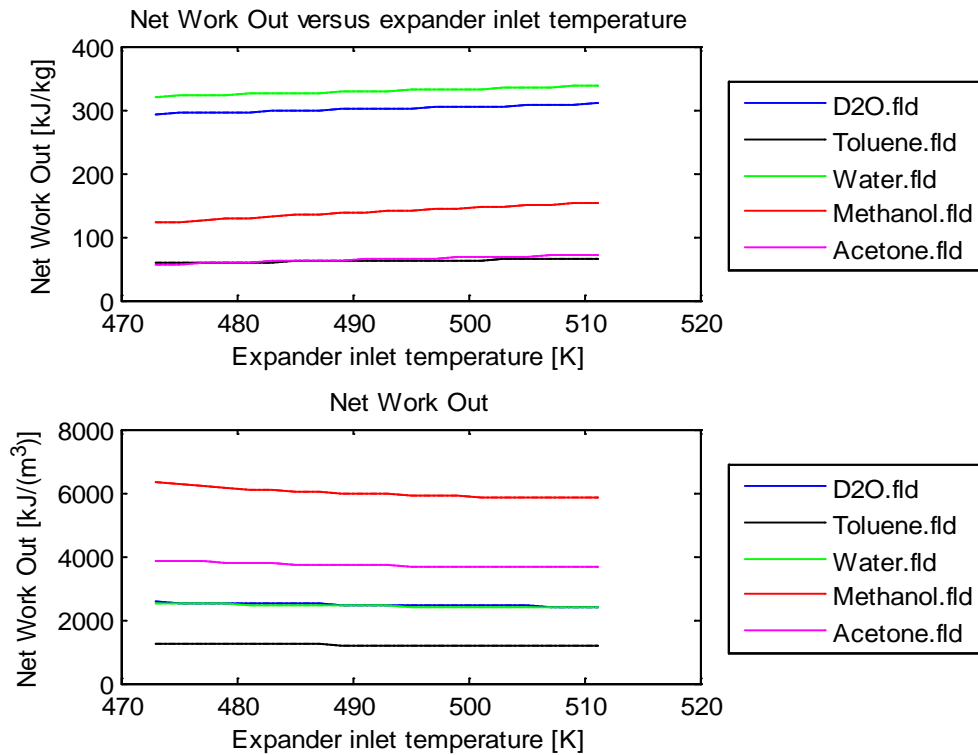


Figure 30 The Net Work Out versus expander inlet temperature

Regarding the Net Work Out per volumetric flow rate at expander inlet (lower graph of figure (30)), methanol gives the highest value and the next highest value is given by acetone. Water and heavy water D2O give almost the same value and toluene has the lowest value. Here the working fluid density is affecting the Net Work Out in kJ/m^3 . The higher the working fluid density, the lower the volumetric flow rate and the higher the Net Work Out in kJ/m^3 .

6.2.2.3 Thermal efficiency

Water and heavy water D2O has the highest thermal efficiency when no IHE is introduced to the cycle and acetone has the lowest (solid lines). The thermal efficiency increases by increasing superheat for all working fluids except toluene which is the only dry fluid. Introducing IHE (dashed lines) to the cycle improves the thermal efficiency for toluene and acetone. The thermal efficiency for toluene becomes higher than that for water and heavy water when enough superheat is applied. Water and heavy water are wet fluids and introducing IHE in the cycle doesn't improve their thermal efficiency because they leave the expander at a temperature lower than the fluid temperature at pump outlet. Methanol is also a wet working fluid and shows a slight efficiency improvement when fluid temperature exceeds 510K at expander inlet.

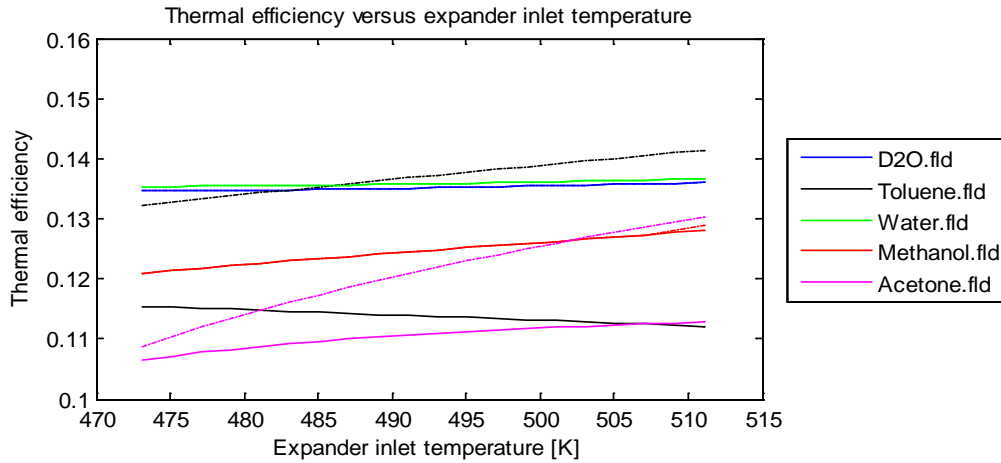


Figure 31 The thermal efficiency versus expander inlet temperature

6.2.2.4 Second law efficiency

The behavior of second law efficiency is quite similar to that of thermal efficiency. Without introducing IHE (solid lines), water and heavy water D2O give the highest second law efficiency and acetone gives the lowest. The second law efficiency increases by increasing superheat rate for all working fluids except toluene. Introducing IHE (dashed lines) improves dramatically the second law efficiency for toluene and acetone and slightly for methanol. The second law efficiency for toluene becomes higher than water and heavy water D2O as soon as IHE introduced. Figure (32) shows how dramatically the second law efficiency changes for toluene and acetone.

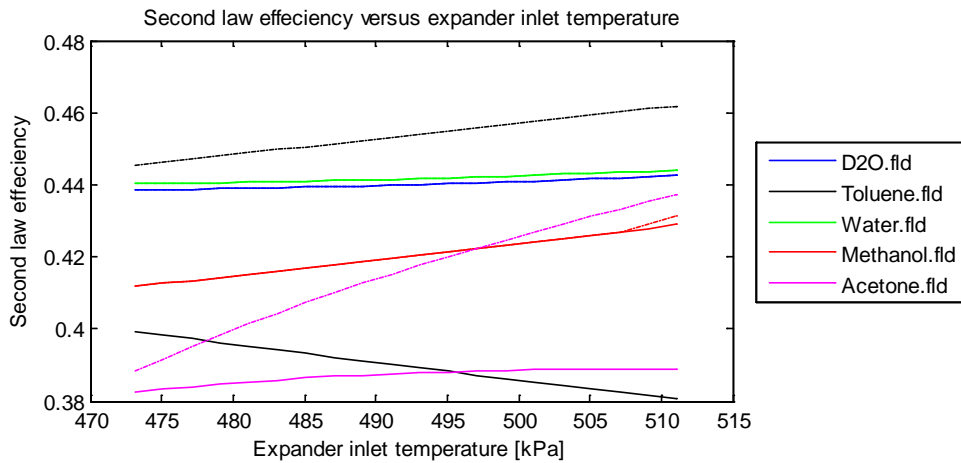


Figure 32 The second law efficiency versus expander inlet temperature

6.2.2.5 Heat addition and heat rejection rates

Figure (33) shows that wet working fluids have high heat addition and heat rejection rates. Acetone (isentropic fluid) and toluene have lower heat addition and heat rejection rates and their rates decrease when IHE is introduced.

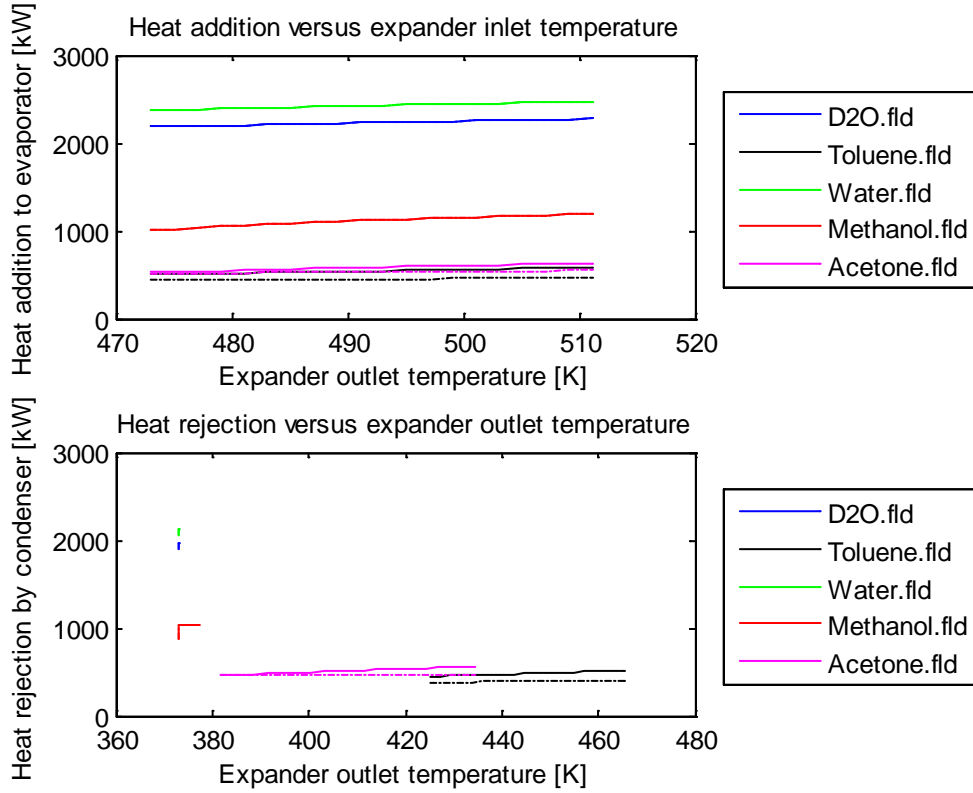


Figure 33 The heat addition and heat rejection rates for D2O, toluene, water, methanol and acetone

6.3 Scenario 3

In this scenario the evaporator pressure is raised to different levels in order to investigate its impact on the Net Work Out, the cycle efficiency and the cycle performance. It is clear that a higher evaporator pressure needs a higher pump work and requires a higher evaporation temperature. Figure (34) shows that a higher evaporator pressure leads also to a higher heat rejection rate by the condenser if no IHE is introduced. By varying evaporator pressure, the Organic Rankine Cycle can be adjusted to deal with different heat source temperature levels. The higher the evaporator pressure, the higher the temperature at which heat added to the working fluid.

Vapor quality significantly varies depending on the used working fluid. The vapor quality at expander outlet for dry and isentropic fluids increases by increasing the evaporation pressure while the expansion process starts directly from saturation vapor line. At the same time the vapor quality for wet fluids may decrease depending on the slope of saturation vapor line and expander efficiency. Figures (34) and (35) show the process on T-S diagrams for dry, respectively wet working fluids.

The expansion process starts from the saturation vapor line and at evaporator pressure and ends at condenser pressure. Using isentropic or dry fluids, the working fluid leaves the expander as superheated vapor (points 4, 4', 4'' and 4''' Figures (34)) and this represents a good advantage for turbo machinery expanders.

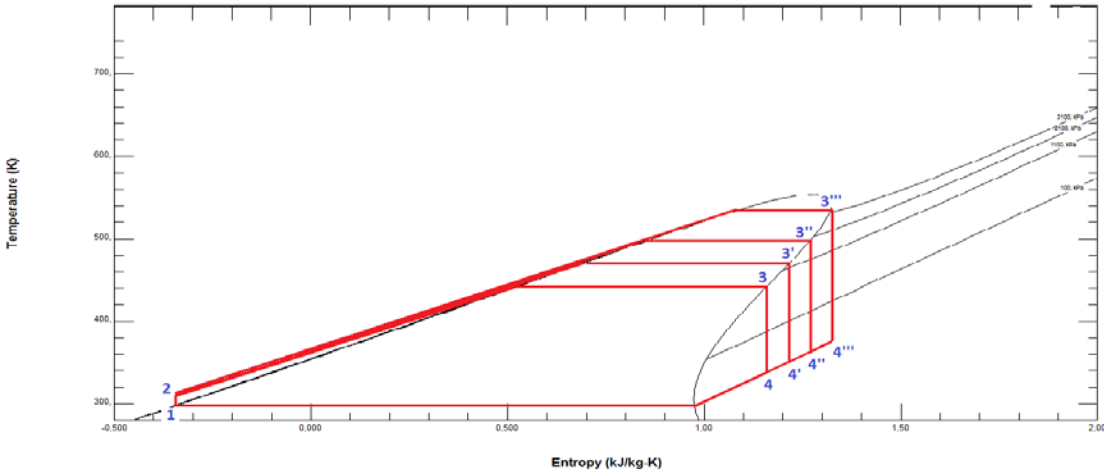


Figure 34 The working process and pressure increase loops in scenario 3 (dry fluid)

For wet fluids, the working fluid may leave the expander as unsaturated vapor. The vapor quality decreases by increasing evaporator pressure figure (35). To avoid drop formation and improve vapor quality, superheat can be used. Drops formation can induce serious damages in the expander blades in turbo machinery expanders. Screw and scroll expanders can deal with low vapor quality and can be used instead of turbo machinery expanders. Figure (35) shows the expansion processes using wet fluids.

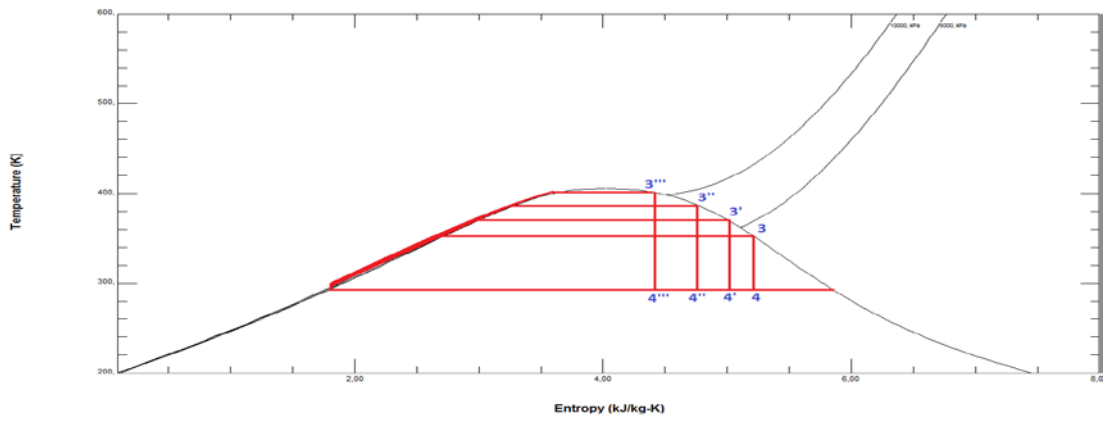
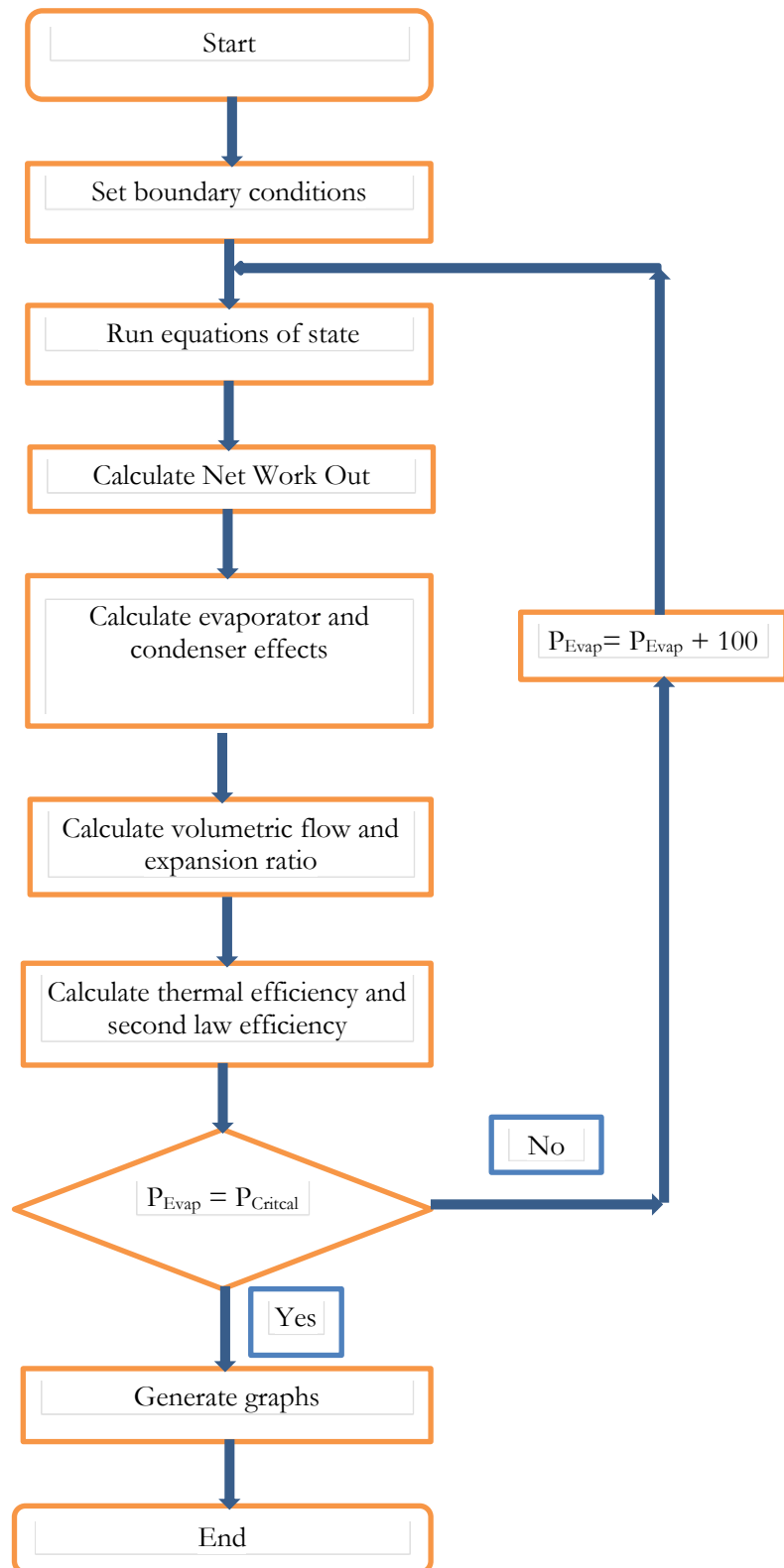


Figure 35 The working process and pressure increase loops in scenario 3 (wet fluid)

6.3.1 Flow chart



6.3.2 Simulation assumptions

Following assumptions are applied in scenario 3

- The cycle is considered to work in a steady state
- Pressure drop in heat exchangers is neglected
- Isentropic efficiency for pump and expander is assumed to be 0.7
- Mass flow rate $m = 1 \text{ kg/s}$
- Ambient temperature $T_{\text{Amb}} = 298 \text{ K}$
- Heat sinks temperature $T_{\text{Sink}} = 288 \text{ K}$
- Condensing temperature $T_{\text{Cond.}} = 298 \text{ K}$
- Source temperature is considered to be 20 K higher than the temperature at expander inlet.
- The mass flow rates of the heat source and the heat sink fluids are considered to be large enough so that the temperature between inlet and outlet is 20K and 5K respectively
- Pinch-point for condenser is set to 5K
- Recuperator or IHE efficiency is 0.8

The suitable working fluids for scenario 3 are the same as the investigated working fluids in scenario 1 due condensation temperature is the same.

6.3.3 Simulation results

The following table shows the working fluids which demonstrated the highest thermal efficiency in scenario 3.

Table 7 The working fluids which have the highest thermal efficiency in scenario 3

Name or number	Safety group	Atmospheric life (year)	Ozone depletion potential ODP	Global warming potential GWP (100 year)
Trans-butene	A3	0.018	0	~20
Cis-butene	n.a. ⁷	n.a.	n.a.	n.a.
Butene	n.a.	n.a.	n.a.	n.a.
Sulfur dioxide SO ₂	B1	n.a.	0	n.a.
Butane	A3	0.018	0	~20

Simulation results for other working fluids in scenario 3 are presented in appendix 2 – scenario 3

Environmental and safety data are not available for Cis-butene and Butene. Trans-butene and Butane are highly flammable, Sulfur dioxide is a toxic working fluid and can be very corrosive if any moisture exists in the system.

6.3.3.1 Net Work Out

Figure (36) shows that Cis-butene has the highest Net Work Out and it increases when the expander inlet temperature increases. The optimal expander inlet temperature for Cis-butene is

⁷ Not available

around 422K and at this temperature the Net Work Out reaches its highest value. The equivalent evaporator pressure at 422K is 3410kPa. A further pressure increase leads to a reduction in Net Work Out. Sulfur dioxide has the lowest Net Work Out and its optimal temperature at expander inlet is around 405K.

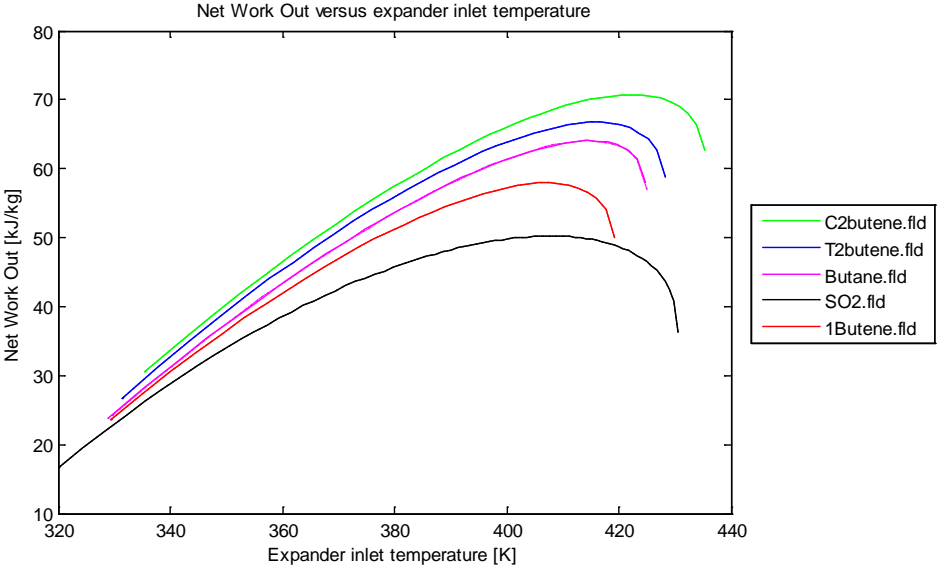


Figure 36 The Net Work Out (kJ/kg) versus expander inlet temperature

Figure (37) shows the Net Work Out in terms of kJ/m³. Here m³ refers to the volume of working fluid at expander inlet. The working fluid density at expander inlet increases with evaporator pressure and subsequently the specific volume of working fluid decrease. SO2 has the highest Net Work Out in kJ/m³ while it has the lowest in kJ/kg. The explanation is that SO2 compared to other working fluids, has much higher density and low specific volume at expander inlet. The relation for Cis-butene is different; it has the highest Net Work Out in kJ/kg and the lowest Net Work Out in kJ/m³. This is because Cis-butene’s density is too low and its specific volume is too high at expander inlet. The Net Work Out in kJ/m³ increases very rapidly when the evaporator pressure increases approaches pressure (right side of figure (37)).

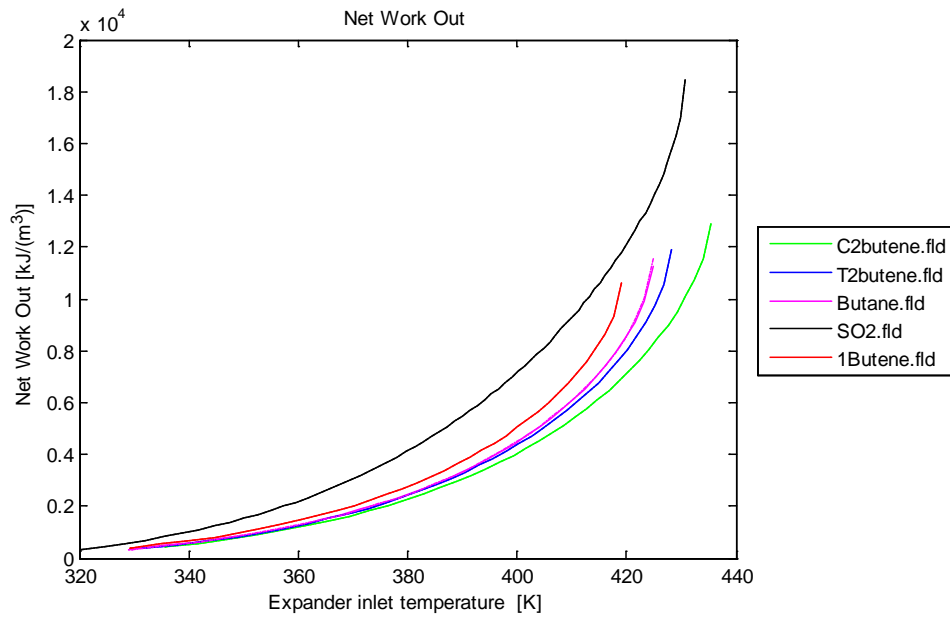


Figure 37 The Net Work Out (kJ/m³) versus expander inlet temperature

6.3.3.2 Volumetric flow rate

The volumetric flow rate is directly proportional to specific volume and inversely proportional to fluid density. Cis-butene has the highest volumetric flow rate at expander inlet and it is slightly higher than the volumetric flow rate for Trans-butene. SO₂ has the lowest volumetric flow rate. The volumetric flow rates decrease dramatically when the expander pressure approaches the critical pressure (right side of figure (38)).

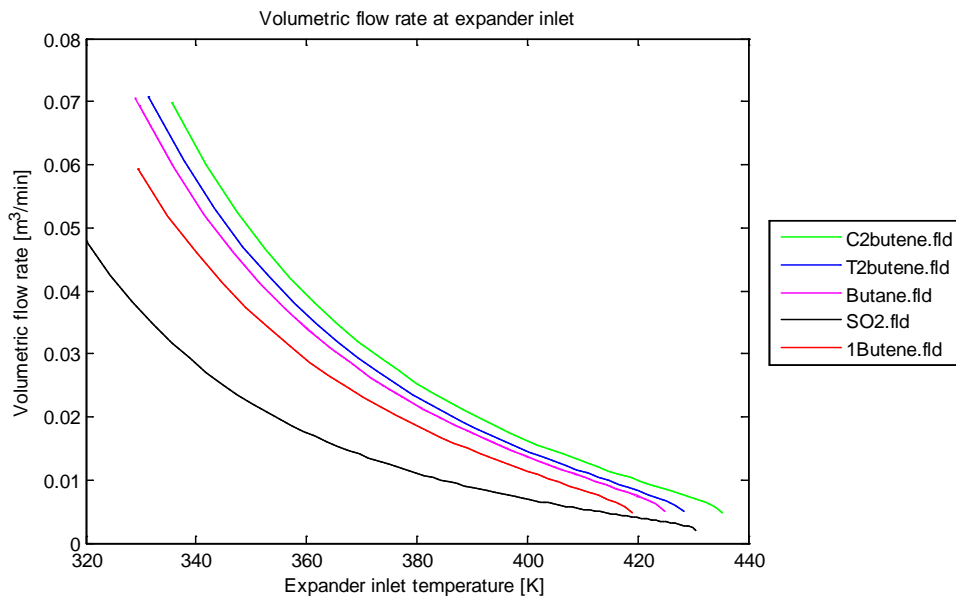


Figure 38 The volumetric flow rate versus expander inlet temperature

6.3.3.3 Evaporator load

Figure (39) represents the heat absorbed by evaporator versus expander inlet temperature. The expander inlet temperature increases as result of increasing the evaporator pressure. The solid lines represent cycles without IHE and the dashed lines present cycles with IHE. The use of IHE leads to a reduction in heat requirements from the heat source. IHE recovers the heat energy from the working fluid when it leaves the expander at a temperature higher than the one at pump outlet. SO2 doesn't need IHE because it is a wet fluid and it leaves the expander at a temperature lower than the one at pump outlet. SO2 may leave the expander as unsaturated vapor while other working fluids are dry fluids and leave the expander as superheated vapor, and at a temperature higher than the temperature at pump outlet.

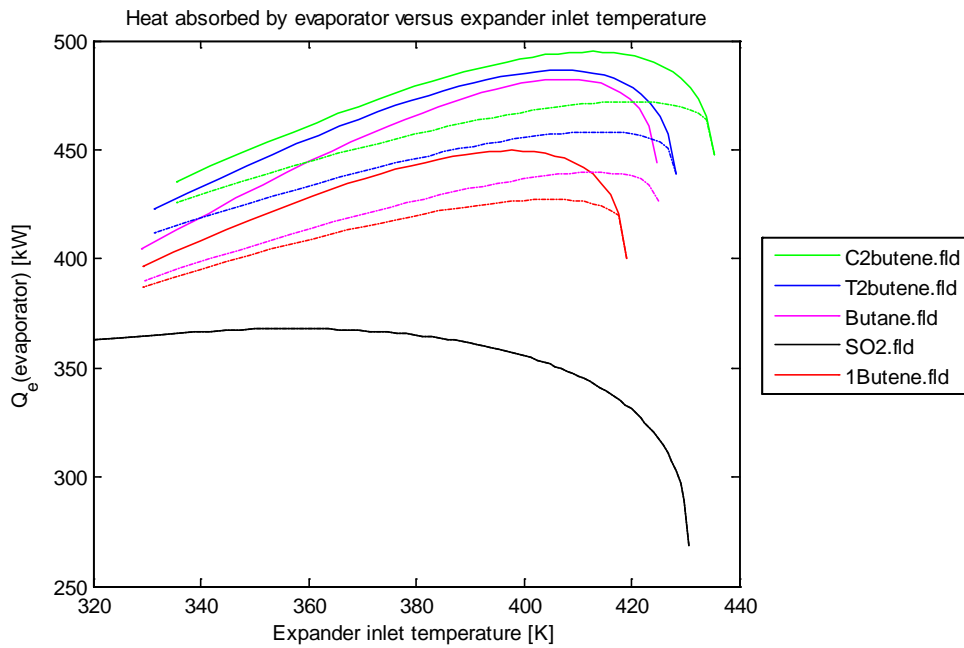


Figure 39 The heat added to evaporator versus expander inlet temperature

6.3.3.4 Thermal efficiency

The highest thermal efficiency is achieved by sulfur dioxide SO2 when no IHE is introduced in the cycle (solid lines). Cis-butene gives a higher thermal efficiency than Sulfur dioxide if IHE is introduced in the cycle (dashed lines). Butene gives the lowest thermal efficiency. The thermal efficiency for all working fluids increases when the expander inlet temperature increases. Figure (40) shows that every working fluid has its optimal expander inlet pressure and the equivalent temperatures vary between 405K – 430K. Further increasing in pressure leads higher expander inlet temperature and reduction in thermal efficiency. The increased temperature is achieved by increasing evaporator pressure.

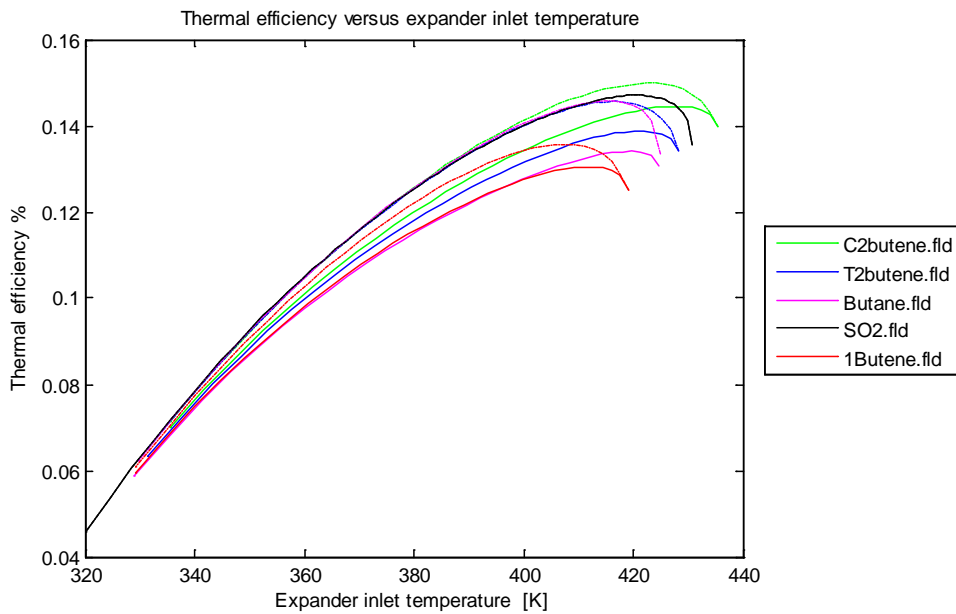


Figure 40 The thermal efficiency for cis-butene, trans-butene, butane, SO2 and butene

6.3.3.5 Second law efficiency

When no IHE is introduced to the cycle (solid lines), the highest second law efficiency is achieved by SO₂ while Cis-butene shows the next highest one. Introducing IHE to the cycle (dashed lines) makes Cis-butene and Butane give higher efficiency than SO₂ figure (41). The second law efficiency for all working fluids is increased until the expander inlet temperature reaches 370K. In the range of 370K – 390K all working fluids show the highest second law efficiency. When the expander inlet temperature exceeds 390K, the second law efficiency decreases for all working fluids.

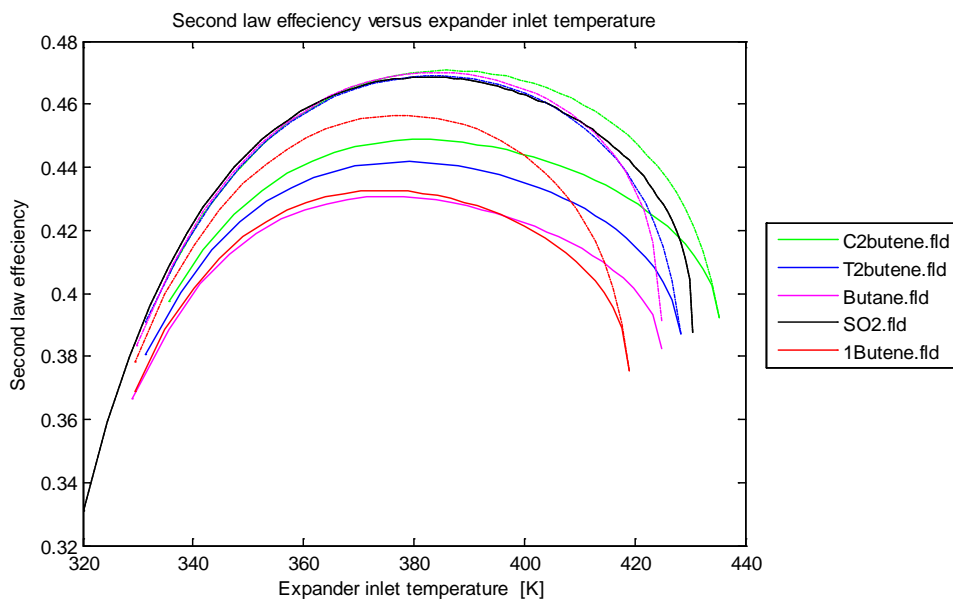


Figure 41 The second law efficiency for cis-butene, trans-butene, butane, SO2 and butene

Thermal efficiency improvement

The best wet fluids in scenario 3 are SO₂, R152a, DME, cyclopropane and ammonia. Simulating these working fluids in scenario 3 will give the optimal evaporator pressure for the best thermal efficiency. Simulating these working fluids in scenario 1 and applying the optimal evaporator pressure and then applying superheat can increase the efficiency further more.

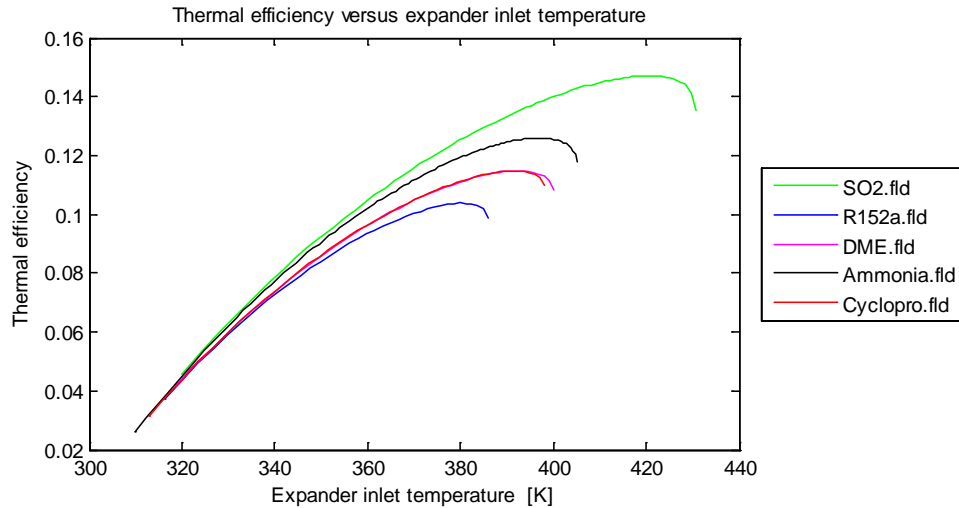


Figure 42 The thermal efficiency for the best wet working fluids in scenario 3

SO₂ has the best thermal efficiency and ammonia has the next best. DME and cyclopropane has almost the same thermal efficiency while R152a has the lowest. The optimal pressures and equivalent temperatures for these working fluids are listed in the following table.

Table 8 The optimal pressure and maximum efficiency for SO₂, R152a, DME, ammonia and cyclopropane (wet fluids)

Working fluid	Optimal evaporator pressure [kPa]	Equivalent evaporator temperature [K]	Maximum efficiency %
Sulfur dioxide SO ₂	6574 – 6774	419,9 – 421,6	14,71
R152a	3987 - 4087	379,87 – 381,17	10,38
DME	4527 – 4729	390,91 – 393,39	11,48
Ammonia	9623 – 9823	396,17 – 397,32	12,60
Cyclopropane	4960 – 5060	391,22 – 392,44	11,48

Figure (43) illustrate the thermal efficiency improvement by using the optimal evaporator pressure and the subjecting the working fluid to 40K superheat. In this investigation, the same

thermodynamic model as the one in scenario 1 is used. Only change is made to the old model, the evaporator pressure is set the optimal pressure for every working fluid.

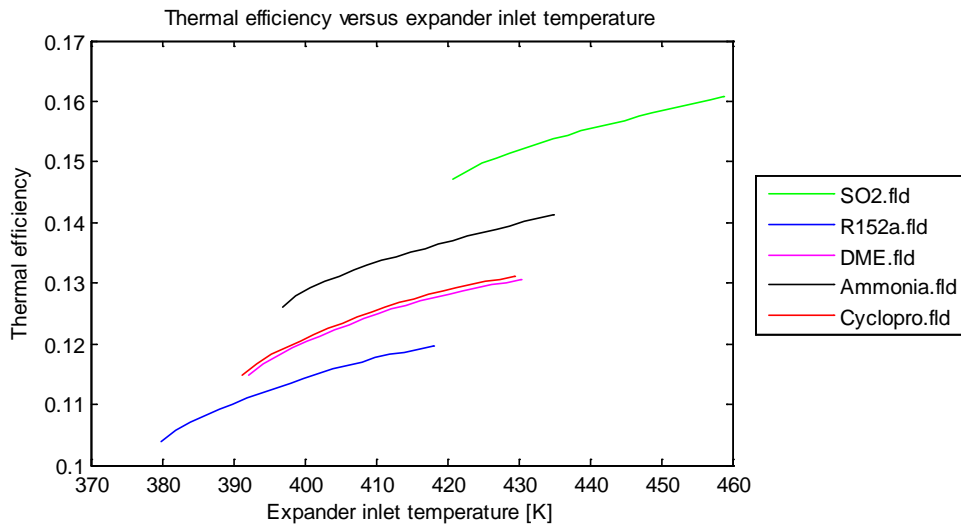


Figure 43 Thermal efficiency improvement after superheat

Figure (43) shows that the thermal efficiency for all working fluids has been improved. The change in thermal efficiency is listed in the table below.

Table 9 The thermal efficiency improvement

Working fluid	Thermal efficiency before overhear %	Thermal efficiency after superheat %	Thermal efficiency improvement %
Sulfur dioxide SO2	14,71	16,08	9,31
R152a	10,38	11,96	15,22
DME	11,48	13,05	13,68
Ammonia	12,60	14,13	12,14
Cyclopropane	11,48	13,11	14,20

Sulfur dioxide SO2 still has the highest thermal efficiency among the investigated working fluids. The trend here is that the working fluids which already have a high thermal efficiency shows lower efficiency improvement than working fluids with low thermal efficiency. R152a has the lowest thermal efficiency before superheating (10,38%) but its efficiency improvement is the highest (15,22%).

6.4 Scenario 4

A super- or trans-critical cycle is another possible solution for some system configurations to recover thermal heat from low grade temperature heat source and convert it to electrical power. In these cycles working fluids with low normal boiling NBP can be used. The system may operate under a very high evaporator or both evaporator and condenser pressures. High pressure means a stronger material should be used to withstand mechanical stresses in heat exchangers and the piping system. On the other hand the high pressure in the system triggers a higher working fluid density and a lower volumetric flow rate. Subsequently more compact machines can be built with a smaller component size.

In scenario 4 the working fluid is pressurized to a pressure higher than the critical pressure. The heat is supplied to the working fluid at a constant pressure in the evaporator. The expansion process is considered to start at an entropy rate given by condenser pressure and a vapor quality equal to 0.9. Figure (44) shows the process in T-S diagram for a wet working fluid. The blue line in T-S shows how the expansion process occurs. Points 3, 3', 3'', 3''' refer to different pressure levels in the evaporator.

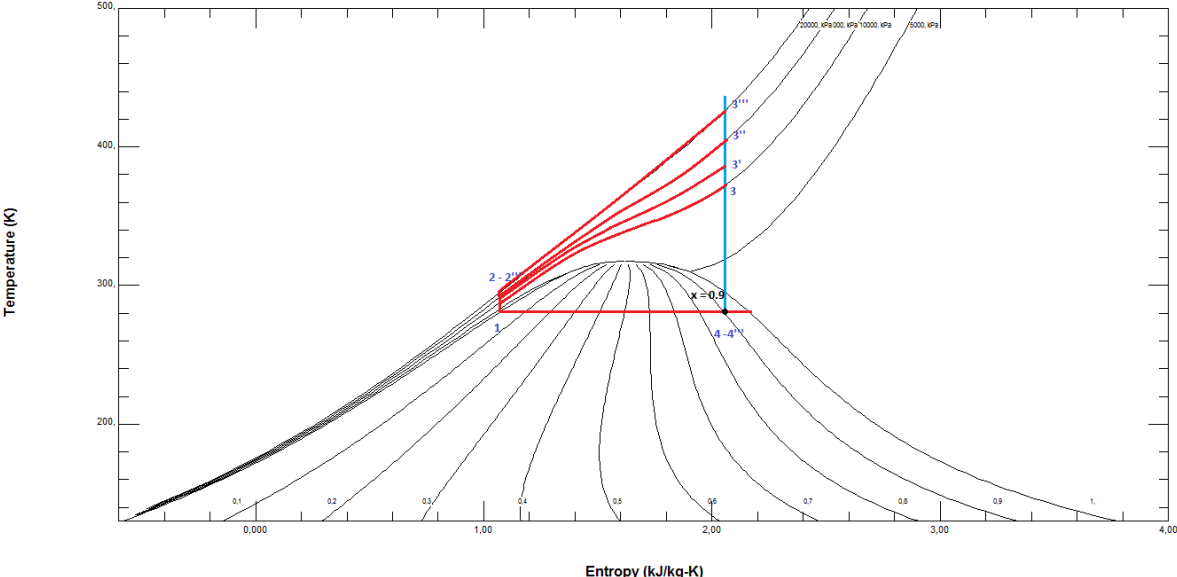
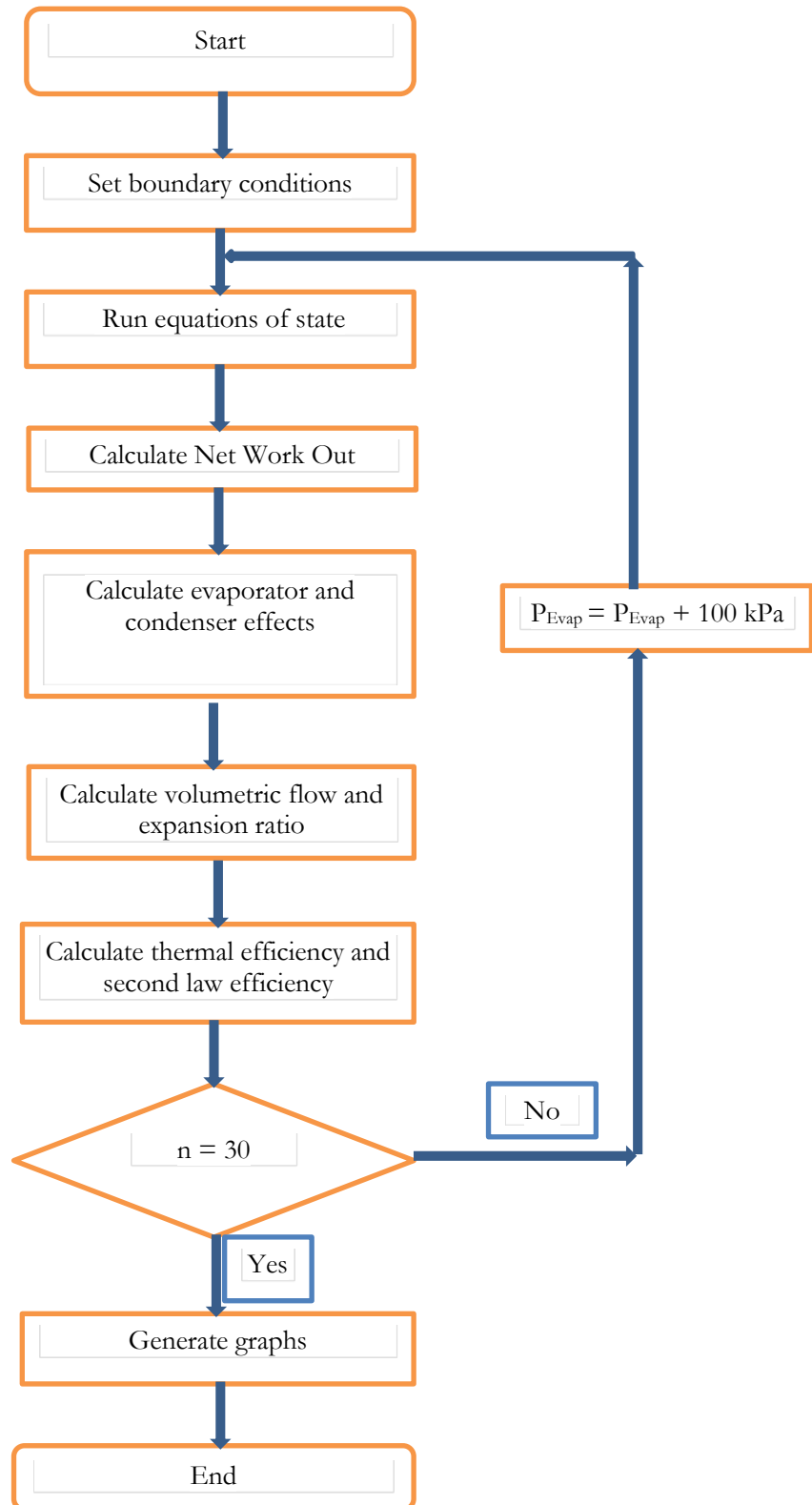


Figure 44 The working process and expansion in scenario 4

6.4.1 Flow chart



6.4.2 Simulation assumptions

- The cycle is considered to work in a steady state
- Pressure drop in heat exchangers is neglected
- Isentropic efficiency for pump and expander is assumed to be 0.7
- Mass flow rate $m = 1 \text{ kg/s}$
- Ambient temperature $T_{\text{Amb}} = 298 \text{ K}$
- Heat sinks temperature $T_{\text{Sink}} = 288 \text{ K}$
- Condensing temperature $T_{\text{Cond.}} = 298 \text{ K}$
- Source temperature is considered to be higher than the temperature at expander inlet by 20K.
- The mass flow rates of the heat source and the heat sink fluids are considered to be large enough, so that the temperature difference between inlet and outlet is 5K
- Pinch-points for condenser set to 5K
- The efficiency of the recuperator or IHE efficiency is set to 0.8
- For each working fluid, the evaporator pressure for the first loop starts at a level higher by 100 kPa than that of the critical pressure. For the following loops the evaporator pressure increases by 100 kPa in every loop. The pressure increase takes place in stages of 100 kPa in 30 loops until the evaporator pressure becomes higher than the critical pressure by 3000 kPa
- The temperature at expander inlet increases with evaporator pressure.

The working fluids are chosen according to the following criteria:

- The condenser pressure is higher than the atmospheric pressure at condenser temperature which is 298K.
- The critical temperature is higher than the condensing temperature which is 298K.
- The evaporator pressure is higher than the critical pressure.

The suitable working fluids for scenario 4 are listed according to their critical temperature in table (10).

The thermo-physical data for R21 at pressure higher than its critical pressure are very limited. Because of this limitation the evaporator pressure could be raised just until 500 kPa higher than the critical pressure.

Table 10 The investigated working fluids in scenario 4

	Name or number	NBP [K]	Critical temp. [K]	Critical pr. [kPa]	Safety gr.	Atm. life (yr)	ODP	GWP (100 yr)	Expansion
1	R11	296,7	471	3034	A1	45	1	4750	isentropic
2	R21	281,86	451,31	5181	B1	1,7	0,04	150	wet
3	Sulfur dioxide SO2	269	430,5	7090	B1		0		wet
4	Butene	272,69	419,14	4005					dry
5	Isobutene	272	418,1	4010					dry
6	R142b	269,9	410,1	4060	A2	17,2	0,06	2220	isentropic
7	Isobutane	267,3	407,7	3630	A3	0,016	0	20	dry
8	Ammonia NH3	245,7	405,25	11333	B2L r	0,02	0	1	wet
9	DME	254,2	400,23	5340	A3	0,015	0		wet
10	C270 Cyclopropane	247,8	398,2	5580	n.a.	0,44	0	20	wet
11	R236fa	277,6	397,9	3200	A1	242	0	9820	dry
12	CF3I	257,15	396,29	3953					wet
13	R124	267	395,3	3062	A1	5,9	0,02	619	dry
14	R152a	264,98	386,26	4517	A2	1,5	0	140	wet
15	Perfluorobutane C4F10	276,99	386,18	2323					dry
16	R1234ze [E]	260	382,4	3640		0,045	0	6	dry
17	Carbonyl sulfide COS	228,84	378,62	6370					wet
18	R161	241,4	375,2	5090		0,18	0	12	wet
19	R227ea	262,7	374,8	2930	A1	38,9	0	3580	dry
20	R134a	253	374	4059	A1	14,6	0	1300	wet
21	H2S Hydrogen sulfide	339,3	372,95	9000					wet
22	R290 Propane	236,9	369,7	4250	A3	0,041	0	20	wet
23	R22	238,2	369,1	4990	A1	11,9	0,04	1790	wet
24	R1234yf	249,5	367,7	3380	A2L r	0,029	0	4,4	dry
25	1270 Propylene	231,4	364,1	4560	A3	0,001	0	20	wet
26	R115	239,8	352,95	3130	A1	1020	0,6	7230	dry
27	R143a	231,76	345,71	3761	A2	48,3	0	3800	wet
28	R218	242,17	345	2671	A1				dry
29	R32	227,3	351,1	5780	A2L r	5,2	0	716	wet
30	R125	230,9	339	3618	A1	32,6	0	2800	wet
31	Sulfur hexafluoride SF6	210,75	318,573	3755					wet
32	R41	200,7	317,1	5900	A1	2,8	0	107	wet
33	Nitrus oxide N2O	190,53	309,37	7245					wet
34	R170 ethane	190,4	305,2	4870	A3	0,21	0	20	wet
35	Carbon dioxide CO2	357,465	303,978	7377,3					wet

6.4.3 Simulation results

The following table shows the working fluids that demonstrated the highest thermal efficiency in scenario 4.

Table 11 The working fluids which have the highest thermal efficiency in scenario 4

Name or number	Safety group	Atmospheric life (year)	Ozone depletion potential ODP	Global warming potential GWP (100 year)
R11	A1	45	1	4750
R21	B1	17	0,04	150
Sulfur dioxide SO2	B1	n.a.	0	n.a.
Ammonia	B2L	0,02	0	~1
Cyclopropane	n.a.	0,44	0	~20

Simulation results for other working fluids in scenario 4 are presented in appendix 2 – scenario 4

R11 is a non-flammable and non-toxic working fluid but it has a high atmospheric life, ODP and GWP. R21 is non-flammable but it is a toxic working fluid and has a high atmospheric life and low ODP and GWP. Sulfur dioxide is also non-flammable but is a toxic working fluid. The atmospheric life and the GWP for sulfur dioxide are not available, but this working fluid has a low ODP. Ammonia is more toxic than sulfur dioxide and 21 and it is also flammable, but difficult to ignite. Ammonia has a very low atmospheric life, no ODP and a negligible GWP. The safety group for Cyclopropane is not available and it has a low atmospheric life time, no ODP and a very low GWP.

6.4.3.1 Volumetric flow rate and expansion ratio

The figure below shows that ammonia has the highest volumetric flow rate and R11 has the lowest. The figure also shows that the volumetric flow rate for all working fluids decreases when the temperature increases. It is worth here to mention that the temperature increases as result of pressure raise which increase by 100 kPa in every loop. So the volumetric flow rate decreases mainly because of the increasing evaporator pressure and not because of the increase in expander inlet temperature. The lower part of figure (45) shows the expansion ratios for working fluids. R11 has the highest expansion ratio compared to other working fluids. Ammonia has the lowest expansion ratio and it has the highest volumetric flow rate.

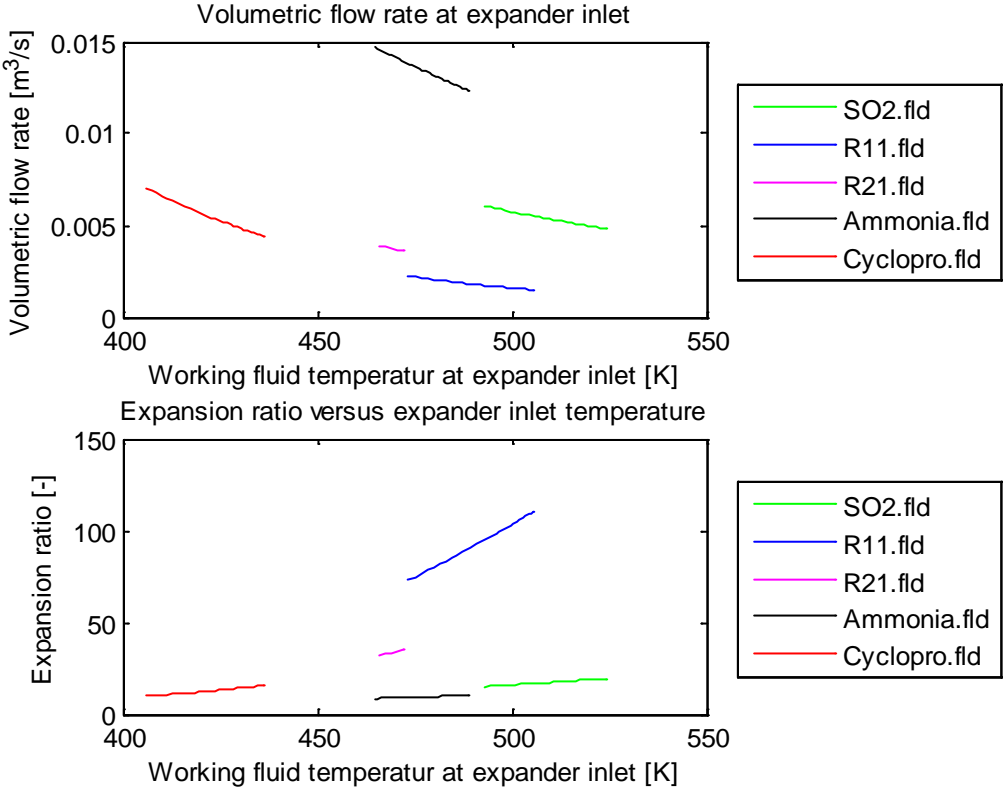


Figure 45 The volumetric flow rate and expansion ratio versus expander inlet temperature

The lower part of figure (45) shows that the expansion ratio increases with expander inlet temperature (or evaporator pressure). The expansion ratio is highly dependent on pressure ratio between evaporator and condenser. Higher pressure ratio leads to higher expansion ratio.

6.4.3.2 Net Work Out

The upper part of figure (46) shows that ammonia has the highest Net Work Out per kg of working fluid and R11 has the lowest. The lower part of figure (46) shows the Net Work Out in kJ/m^3 and here m^3 refers to the volume of the working fluid at expander inlet. R11 has the highest Net Work Out per m^3 due to its extremely low volumetric flow rate. Ammonia has the highest Net Work Out in kJ/kg and apparently R11 has much higher density than ammonia. That is why R11 shows higher Net Work Out in kJ/m^3 . The Net Work Out per kg of working fluid remains constant for R21 and R11 and increases for ammonia, sulfur dioxide and cyclopropane when the evaporator pressure increases. The Net Work Out per m^3 of working fluid at expander inlet increases for all working fluids when increasing evaporator pressure.

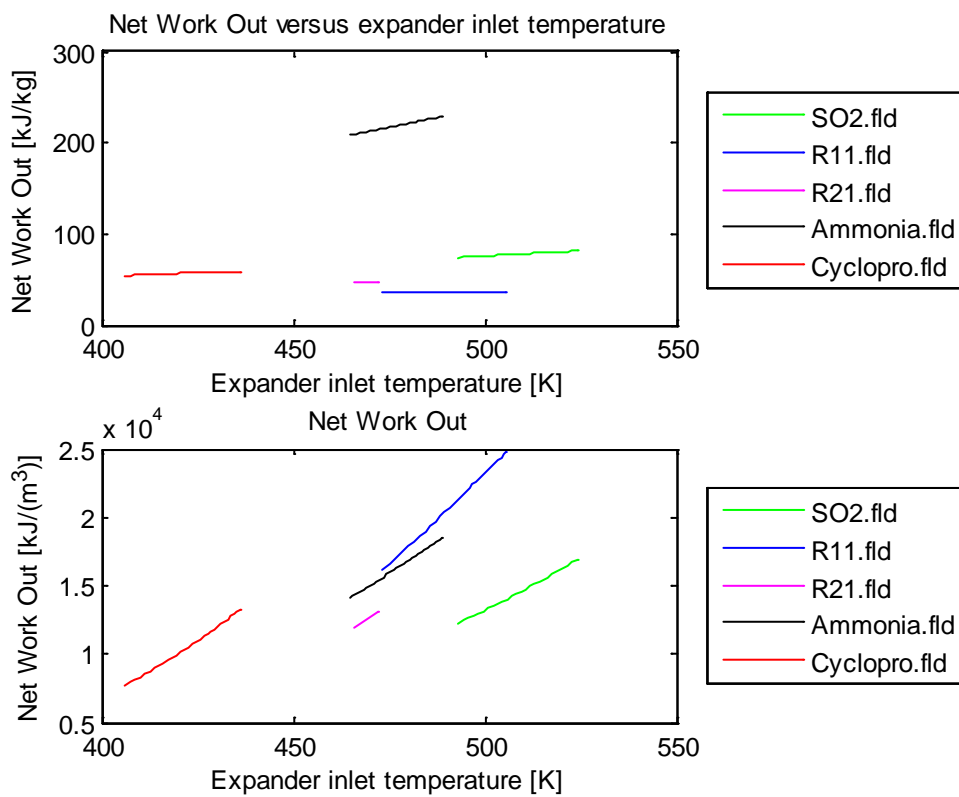


Figure 46 The Net Work Out versus expander inlet temperature

6.4.3.3 Thermal efficiency

Sulfur dioxide SO₂ has the highest thermal efficiency. R11 and R21 have almost the same value and cyclopropane has the lowest value. The thermal efficiency for all working fluids improves by increasing the evaporator pressure and subsequently expander inlet temperature. Introducing IHE to the cycle in this scenario doesn't improve the thermal and second law efficiency because the temperature at expander inlet is lower than the temperature at pump outlet. The vapor quality lies between 0.9 and 1 for most of working fluids and can hardly exceed 1. IHE can be used when vapor temperature at expander outlet is higher than the fluid temperature at pump outlet.

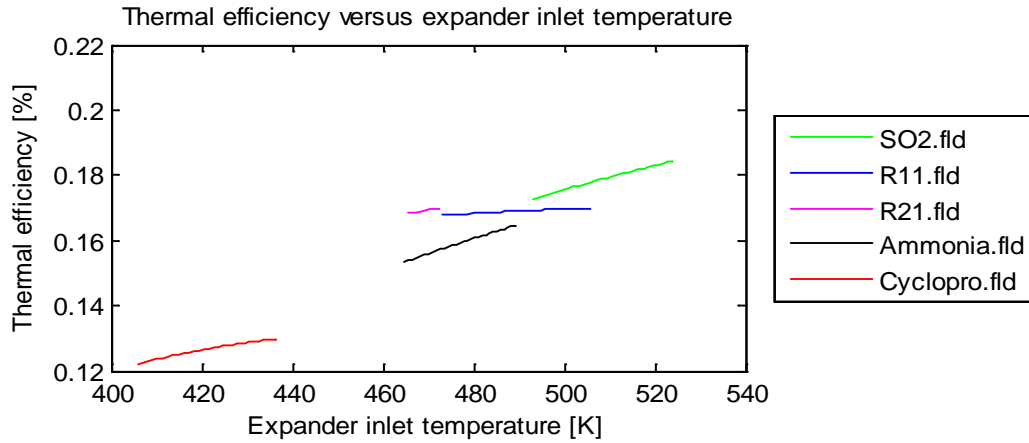


Figure 47 The thermal efficiency for SO₂, R11, R21, ammonia and cyclopropane

6.4.3.4 Second law efficiency

Figure (48) below illustrates how the second law efficiency varies with the evaporator pressure and subsequently with the expander inlet temperature. R21 has the highest second law efficiency while cyclopropane and R11 have lower one. R11 and cyclopropane have almost the same second law efficiency despite the difference in their temperature ranges at expander inlet. The second law efficiency decrease for all working fluids by increasing the evaporator pressure. The efficiency reduction occurs dramatically for R11 and cyclopropane.

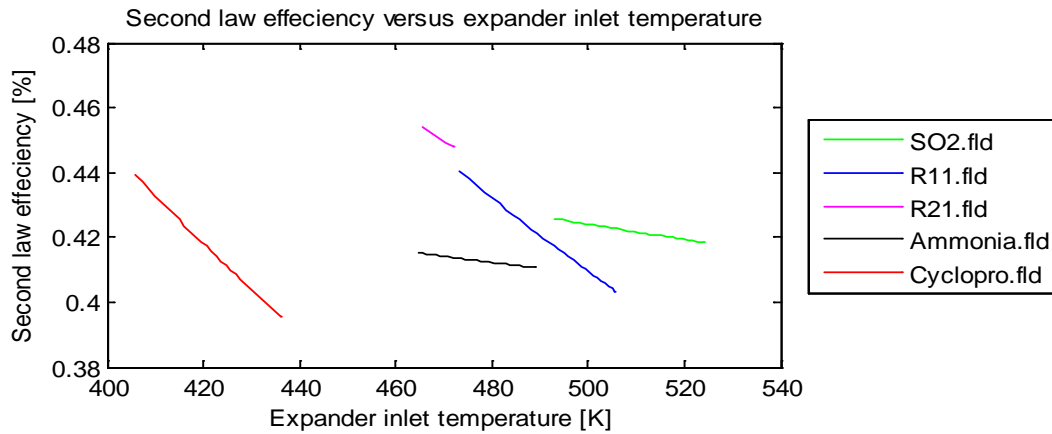


Figure 48 The second law efficiency for SO2, R11, R21, ammonia and cyclopropane

6.4.3.5 Heat addition and heat rejection

The amount of heat added to ammonia is very high and it is much higher than the amount heat needed for other working fluids (upper part of figure (49)). SO2 and cyclopropane need almost the same amount of heat but at different temperature levels. The heat rejection rate is the highest for ammonia and it increases with increasing the evaporator pressure and subsequently expander inlet temperature (lower part of figure (49)). R11 has the lowest heat rejection rate. Heat rejection rates for all working fluids seem to be constant increasing expander inlet temperature. These working fluids leave the expander outlet as unsaturated vapor or at temperature slightly higher than condensing temperature.

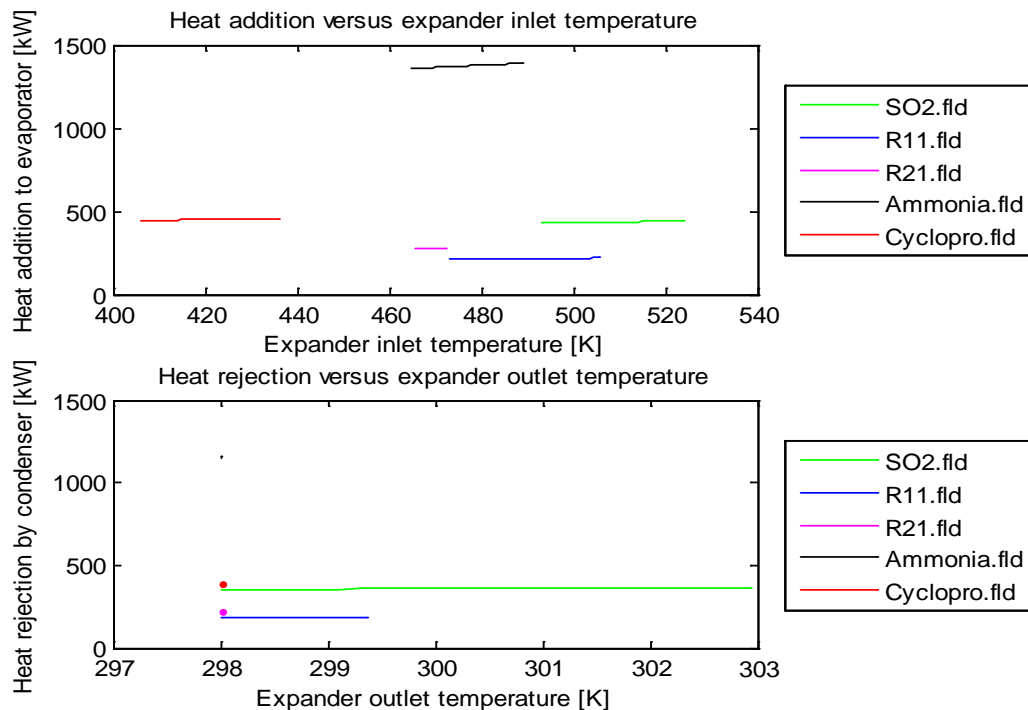


Figure 49 The heat addition and heat rejection rates for SO2, R11, R21, ammonia and cyclopropane

6.5 Thermal conductivity and viscosity

The thermal conductivity and viscosity of working fluids are two very important parameters in the design of heat exchanger and other Organic Rankine Cycle equipment. The knowledge of thermal conductivity is necessary to estimate the size of heat exchanger while the knowledge of viscosity is required to determine the required work for pumping the working fluid. High thermal conductivity and low viscosity is desirable in order to keep down heat exchangers size and to reduce the needed work for pumping the working fluid. Figures (50 & 51) show the thermal conductivity and viscosity for the working fluids which give the highest thermal efficiency in simulation scenarios. The thermal conductivity is estimated at 373K and saturation liquid while the viscosity is estimated at 298K and saturation liquid. The thermal conductivity and viscosity data are not available for sulfur dioxide SO₂. Water is not considered a working fluid for Organic Rankine Cycle and it is added to these figures just to compare its properties to the properties for other working fluids [35-36].

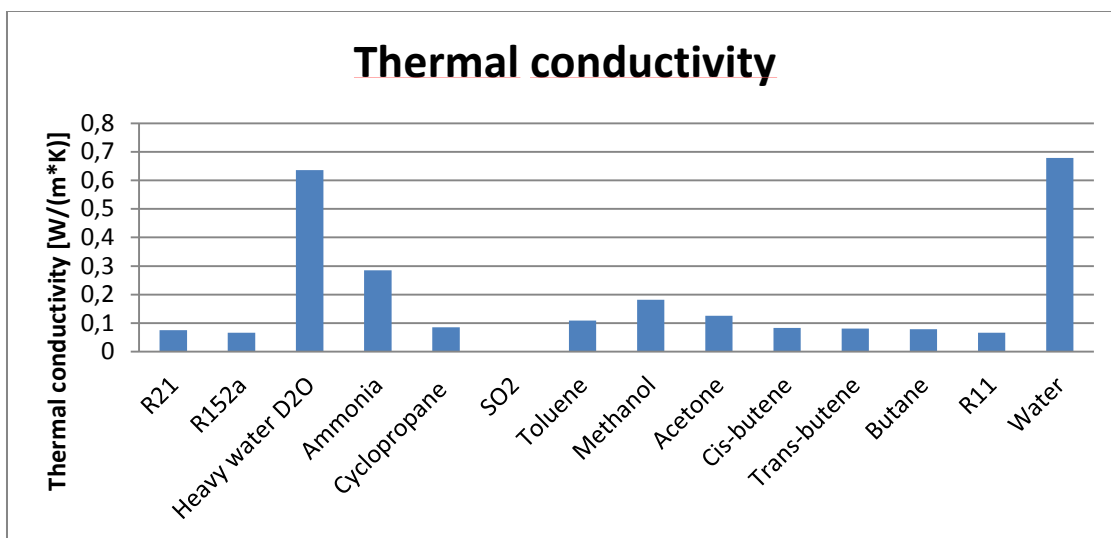


Figure 50 The thermal conductivity for the working fluids which give the highest thermal efficiency in simulation scenarios

Figure (50) shows the water and heavy water has the highest thermal conductivity while R11, R21 and R152a has the lowest. Ammonia has the highest thermal conductivity among working fluids with normal boiling point lower than 373K.

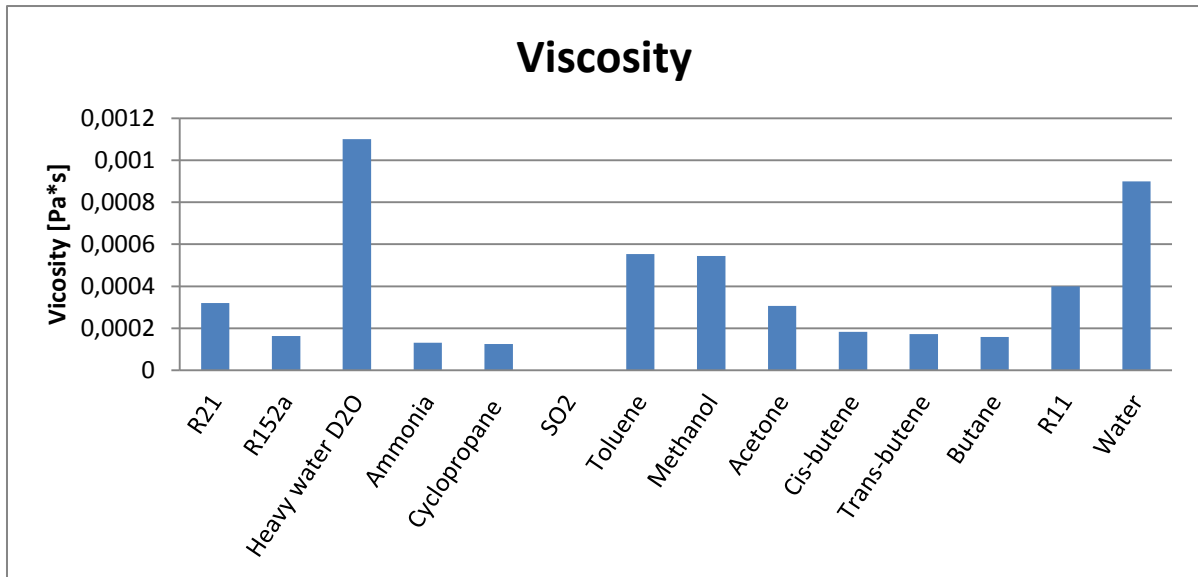


Figure 51 The viscosity for the working fluids which give the highest thermal efficiency in simulation scenarios

Figure (51) shows heavy water and water has the highest viscosity while ammonia and cyclopropane has the lowest. Ammonia has interesting properties like high thermal conductivity, low viscosity, high thermal efficiency and Net Work Out.

7 Conclusions

The selection of optimal working fluid for Organic Rankine Cycle is not an easy process. There are many different working fluids to choose among and many criteria should be taken in consideration. Some working fluids have good thermodynamic properties but at the same time have undesirable environmental and safety data. Other fluids have a good environmental and safety data but they are not efficient thermodynamically. There is no ideal working fluid can achieve all the desired criteria and the fluid selection process is a trade-off between thermodynamic, environmental and safety properties.

From a thermodynamic perspective, the selection of the optimal working fluid depends basically on the heat source and the heat sink temperatures. For every heat source and heat sink temperature there are a number of working fluid candidates. The most selected working fluids should have good thermodynamic properties like high thermal efficiency, second law efficiency and Net Work Out. The volumetric flow rate and the working fluid viscosity should be as low as possible to reduce the components size, pressure losses and the work needed for pumping. The thermal conductivity of working fluid is another important aspect that should be taken in consideration in working fluid selection process.

Regarding evaporation and condensation pressures in the cycle, three different cycle layouts are possible.

- **Subcritical Organic Rankine Cycle:** the evaporation and condensation pressures are lower than the critical pressure for the selected working fluid, and the evaporation temperature should be lower than the critical temperature. The working fluid candidates for subcritical Organic Rankine Cycles have high critical pressure. Heptane, ethanol, methanol and ammonia are some of the many working fluids which can be used for subcritical cycles.
- **Trans-critical Organic Rankine Cycles:** the evaporation pressure is higher than the critical pressure and the condensation pressure is lower. Suitable working fluid candidates have a moderate critical pressure and temperature. R152a, DME, R134a and cyclopropane are some of these suitable candidates.
- **Supercritical Organic Rankine Cycle:** the evaporator and condenser pressures are higher than the critical pressure. Suitable candidates have low critical pressure and temperature. Carbon dioxide, Xenon and nitrus oxide are some of the suitable candidates.

In Trans-critical and supercritical cycles the temperature profile between heat source fluid and working fluid shows a very good match compared with subcritical cycles. This match decreases exergy losses and increases thermal efficiency and second law efficiency. In such cycles the pressure level is high in the just evaporator or in both evaporator and condenser. Higher pressure means stronger and more expensive materials are needed to withstand mechanical stresses. On the other hand a higher pressure leads to a higher working fluid density and a lower volumetric flow rate. By low volumetric flow rate, the component size can be dramatically reduced, leading to the creation of more compact machines.

According to results from simulation in scenarios (1,2 and 3) and regarding thermal efficiency, the best working fluids for subcritical cycles are: ammonia, cyclopropane, R152a, sulfur dioxide SO₂, R21, heavy water, toluene, methanol, acetone, cis-butene, trans-butene, butane and R11. Furthermore the best working fluids for trans-critical cycles (scenario 4) are: R11, R21, ammonia, cyclopropane and SO₂.

Regarding the environmental and safety criteria, the selected working fluid should have zero ozone depletion potential ODP, non-flammable, non-toxic and global warming potential should be very low. Taking all these criteria in consideration, following working fluids are not optimal: ammonia (flammable and toxic), SO₂ (toxic), R21 (flammable, toxic and ODP=0,04), methanol (flammable), acetone (flammable), trans-butene (highly toxic), butane (highly toxic), R152a (toxic), and R11 (ODP=1 and GWP=4750). The environmental and safety data are not available for toluene and heavy water and the safety group for cyclopropane is also not available. Here the conclusion is that there is no ideal working fluid which can have all desirable criteria and properties at the same time. The trade-off is between high thermodynamic performance and environmental and safety criteria. There are some safe and environmental friendly working fluids like R124, but their thermodynamic performance is quite low.

The conclusions of this thesis can be abstracted in following points:

1. The fluid selection process is a trade-off between thermodynamic, environmental and safety properties
2. The selection of the optimal working fluid depends basically on the available heat source and the heat sink temperatures
3. Superheat is not recommended for dry working fluids
4. The selected working fluid should have good thermodynamic properties like high thermal efficiency, second law efficiency and Net Work Out
5. The volumetric flow rate and the working fluid viscosity should be as low as possible
6. GWP and ODP as low as possible
7. Toluene is an interesting working fluid especially when an IHE is introduced to the cycle
8. Ammonia is another interesting working fluid and has high Net Work Out, high thermal conductivity and low viscosity
9. The simulations shows that the best working fluids are the wet working fluids if no IHE is introduced
10. Introducing the IHE is very necessary for dry and isentropic working fluids because it rapidly increases the thermal and second law efficiencies.
11. IHE is not always recommended for wet fluids
12. The thermal efficiency for wet fluids can be improved by first estimating the optimal pressure and then applying super heat
13. Regarding the thermal efficiency, the best working fluids for subcritical cycles (scenario 1 – 3) are: ammonia, cyclopropane, R152a, sulfur dioxide SO₂, R21, heavy water, toluene, methanol, acetone, cis-butene, trans-butene, butane and R11. The best working fluids for trans-critical cycles (scenario 4) are: R11, R21, ammonia, cyclopropane and SO₂
14. No working fluid is ideal!

8 Recommendations for future works

The environmental and safety data for many working fluids in this thesis were not available during the time period when this study was conducted and completed. Working fluid prices, stability and availability are other issues which should be investigated. Many working fluids show interesting thermodynamic properties and in order to take the right decision whether these working fluids can be used or not in ORC, the environmental and safety data should be available and taken into consideration.

- Furthermore future work should include an investigation of the supercritical cycles for which it is possible to use working fluids with low critical pressure and temperature. In such way many other working fluids can be investigated. CO₂ is a very interesting working fluid for such applications!
 - Performing overcritical cycles leads to low volumetric flow rate and keeps down component size.
 - Furthermore overcritical cycles offer a better temperature profile match in evaporator. This reduces the exergy losses and increases the second law efficiency.

This thesis is focusing on pure working fluids, but it is also recommended and desirable to further investigate fluid mixtures or the so-called “zeotropic mixtures”. Zeotropic mixtures can be used in subcritical, trans-critical and super critical cycles. Some advantages provided by the zeotropic mixtures are:

- Zeotropic mixtures allow a good temperature profile match between the heat source and the working fluid in the evaporator.
- The flammability and toxicity of some working fluids can be reduced by mixing flammable and toxic working fluids with other fluids.
- The ODP and GWP also can be reduced by mixing working fluids.
- Zeotropic mixtures offer new working fluids with new thermodynamic properties. The properties can be adjusted by changing the mixture contents and fractions.

Zeotropic mixtures have the disadvantage of not allowing for an accurate estimation of the environmental and safety data concerned. The mixture’s stability under different working conditions is another problem which rises when some zeotropic mixtures are used.

Future works should also focus on studying the two-phase expansion where the working fluid enters the expander before reaching the saturation vapor line. In such way the exergy losses can be dramatically reduced in subcritical cycles.

Finally, the future work should include practical studies for most interesting working fluids in order to compare the theoretical and practical results. The practical testing is a necessary issue however there is uncertainty in databases for some working fluids.

References

- [1] J. M. Calm, G. C. Hourahan (2011). Physical, Safety and Environmental data for current and alternative Refrigerants, ICR 2011, August 21 – 26 – Prague, Czech Republic
- [2] Per Lundqvist, Working fluids for Organic Rankine Cycle.
- [3] B. Saleh, G. Koglbauer, M. Wendland, J. Fischer, Working fluids for low-temperature Organic Rankine Cycles. *Energy*, 32 (2007), pp. 1210–1221.
- [4] Bahaa S, Koglbauer G, Wendland M, Fischer J. Working fluids for low temperature organic Rankine Cycles. *Energy* 2007;32(7):1210–21.
- [5] Karellas S, Schuster A. Supercritical fluid parameters in Organic Rankine Cycle applications. *International Journal of Thermodynamics* 2008;11(3):101–8.
- [6] E.H. Wang, H.G. Zhang, B.Y. Fan, M.G. Ouyang, Y. Zhao, Q.H. Mu. Study of working fluid selection of Organic Rankine Cycle (ORC) for engine waste heat recovery. *Energy*, 36 (2011), pp. 3406–3418.
- [7] T.C. Hung, T.Y. Shai, S.K. Wang, A review of Organic Rankine Cycles (ORCs) for the recovery of low grade waste heat. *Energy*, 22 (1997), pp. 661–666.
- [8] C.J. Butcher, B.V. Reddy, Second law analysis of a waste heat recovery based power generation system. *International Journal of Heat and Mass Transfer*, 50 (2007), pp. 2355–2363.
- [9] D. Wei, X. Lu, Z. Lu, J. Gu, Performance analysis and optimization of Organic Rankine Cycle (ORC) for waste heat recovery, *Energy Conversion and Management* 48 (2007) 1113–1119.
- [10] Adrienne B. Little, Srinivas Garimella, Comparative assessment of alternative cycles for waste heat recovery and upgrade. *Energy*, 36 (2011), pp. 4492–4504.
- [11] H.D.M. Hettiarachchi, M. Golubovic, W.M. Worek, Y. Ikegami, Optimum design criteria for an Organic Rankine Cycle using low-temperature geothermal heat sources. *Energy*, 32 (2007), pp. 1698–1706.
- [12] U. Drischer, D. Bruggemann, Fluid selection for the Organic Rankine Cycle (ORC) in biomass power and heat plants. *Applied Thermal Engineering*, 27 (2007), pp. 223–228.
- [13] J.C. Bruno, J. Lopez-Villada, E. Letelier, S. Romera, A. Coronas, Modelling and optimisation of solar Organic Rankine Cycle engines for reverse osmosis desalination. *Applied Thermal Engineering*, 28 (2008), pp. 2212–2226.
- [14] A.M. Delgado-Torres, L. Garcia-Rodriguez, Analysis and optimization of the low temperature solar Organic Rankine Cycle (ORC). *Energy Conversion and Management*, 51 (2010), pp. 2846–2856.

- [15] Sylvain Quoilin (2011). Sustainable Energy Conversion Through the Use of Organic Rankine Cycles for Waste Heat Recovery and Solar Applications. Presented to the Faculty of Applied Science of the University of Liège, Belgium.
- [16] <http://www.kgraenergy.com/technical/organic-rankine-cycle-history>
- [17] <http://gasengine.farmcollector.com/Gas-Engines/The-Naphtha-Engine.aspx>
- [18] <http://theenergylibrary.com/node/10537>
- [19] <http://www.kgraenergy.com/projects/worldwide-orc-installations>
- [20] M.B. Ibrahim and R.M. Kovach, A Kalina cycle application for power generation, *Energy*, vol. 18, Sep. 1993, pp. 961-969.
- [21] P. Lolos and E. Rogdakis, A Kalina power cycle driven by renewable energy sources, *Energy*, vol. 34, Apr. 2009, pp. 457-464.
- [22] C. Dejfors, E. Thorin, and G. Svedberg, Ammonia-water power cycles for direct-fired cogeneration applications, *Energy Conversion and Management*, vol. 39, 1998, pp. 1675-1681.
- [23] <http://www.eng.usf.edu/~hchen4/Goswami%20Cycle.htm>
- [24] <http://www.wasteheatrecovery.com>
- [25] Sylvain Quoilin (2009). Technological and Economical Survey of Organic Rankine Cycle Systems. 5th European Conference, Economics and Managements of Energy Technology
- [26] http://www.clean-energy-ideas.com/geothermal_power.html
- [27] <http://www.biomassenergycentre.org.uk>
- [28] Wei D, Lu X, Lu Z, Gu J. Performance analysis and optimization of organic Rankine cycle (ORC) for waste heat recovery. *Energy Convers Manage* 2007;48:1113–9.
- [29] J.P. Roy, M.K. Mishra, Ashok Misra, Performance analysis of an Organic Rankine Cycle with superheating under different heat source temperature conditions. *Applied Energy* 88 (2011) 2995–3004.
- [30] Gas Turbine Theory
- [31] http://www.mcquay.com/mcquaybiz/literature/lit_ch_wc/AppGuide/AG31-006.pdf
- [32] <http://www.epa.gov/ozone/defns.html#odp>
- [33] <http://www.astm.org/Standards/E681.htm>
- [34] D.Y. Wang (2011), Analysis of Working Fluid for Organic Rankine Cycle, Department of Thermal Science and Energy Engineering, University of Science and Technology of China.

[35] Marcia L. Huber. Model for the Viscosity and Thermal Conductivity of Refrigerants, including a New Correlation for the Viscosity of R134a. *Ind. Eng. Chem. Res.* 2003, 42, 3163-3178

[36] Tayebah Hosseinnejad, Viscosity and thermal conductivity of some refrigerants at moderate and high densities on the basis of Rainwater–Friend theory and the corresponding states principle. *Fluid Phase Equilibria*, Volume 263, Issue 1, 15 January 2008, Pages 85–95

Appendix 1

Refrigerants		Physical data			Safety data			Environmental data			Expansion
Number or name		NBP	TC	PC	OEL	LFL	Safty	Atmospheric	ODP	GWP	
		[°C]	[°C]	[kPa]	(ppMv)		Group	Life Time		(100 yr)	
1	Methyl stearate	365,41	501,85	12,39							dry
2	Methyl linolenate	355,98	498,85	13,69							dry
3	Methyl olenate	354,03	508,85	12,46							dry
4	Methyl palmitate	329,15	481,85	13,5							dry
5	MD4M	260,75	380,05	8,77							dry
6	Methyl linoleate	255,69	525,85	13,41							dry
7	D6	244,96	372,63	9,61							dry
8	MD3M	229,87	355,21	9,45							dry
9	Dodecane	216,15	384,95	18,17							wet
10	D5	210,9	346	11,6							dry
11	MD2M	194,36	326,25	12,27							dry
12	D4	175,35	313,35	13,32							dry
13	Decane	174,12	344,55	21,03							dry
14	Propylcyclohexane	156,75	357,65	28,6							dry
15	MDM	152,51	290,94	14,15							dry
16	Nonane	150,76	321,4	22,81							dry
17	Octane	125,6	296,17	24,97							dry
18	Toluene	110,6	318,6	41,263							dry
19	Heavy water D2O	101,4	370,7	216,71							wet
20	Methylcyclohexane	100,85	299	34,7							dry
21	MM	100,25	245,6	19,39							dry
22	Water	100	374	220,64			A1		0	<1	wet

Refrigerants		Physical data			Safety data			Environmental data			Expansion
Number or name		NBP	T _c	P _c	OEL	LFL	Safety	Atmospheric	ODP	GWP	
		[°C]	[°C]	[kPa]	(ppMv)		Group	Life Time		(100 yr)	
23	Heptane	98,38	27,36	266,98							dry
24	Dimethyl carbonate	90	284,23	48,351							dry
25	Cyclohexane	80,736	280,5	40,75							dry
26	Benzene	80,07	288,87	49,063							dry
27	Ethanol	78,24	61,48	240,75							wet
28	Hexane	68,71	234,67	30,34							dry
29	Methanol	64,5	239,5	81,04							wet
30	Isohexane	60,21	224,55	30,4							dry
31	Acetone	56,07	234,95	47							isentropic
32	Cyclopentane	49,25	238,54	45,15	600	1,1		0,007	0	11	dry
33	R113	47,6	214,1	33,92	1000	none	A1	85	0,85	6130	dry
34	R365mfc	40,15	186,85	32,66							dry
35	Pentane	36,1	196,55	33,7	600	1,2	A3	0,009	0	20	dry
36	R141b	32	204,35	42,12	500	5,8		9,2	0,12	717	isentropic
37	Perfluoropentane	29,75	147,4	20,45							dry
38	Isopentane	27,8	187,2	33,78	600	1,3	A3	0,009	0	20	dry
39	R123	27,8	183,68	36,67	50	none	B1	1,3	0,01	77	dry
40	R245ca	25,13	174,42	39,25		7,1		6,5	0	726	dry
41	R11	23,708	197,96	44,076	C1000	none	A1	45	1	4750	isentropic
42	R245fa	15,14	154	36,51	300	none	B1	7,7	0	1050	dry
43	R601b Neopentane	9,5	160,6	31,96	600	1,4			0	20	dry

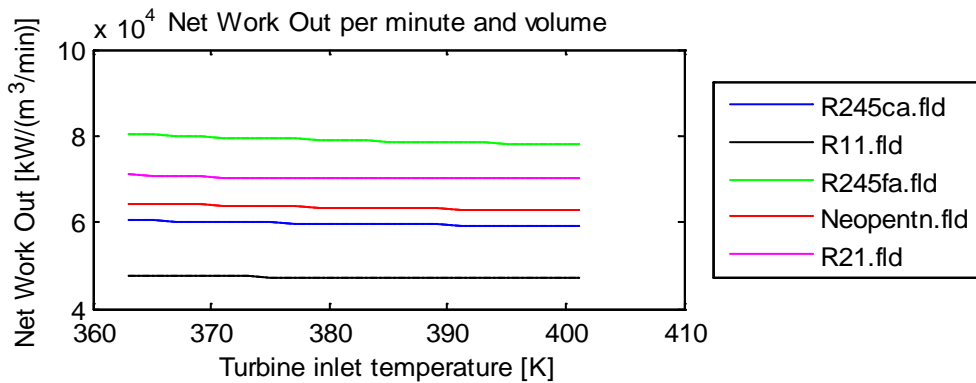
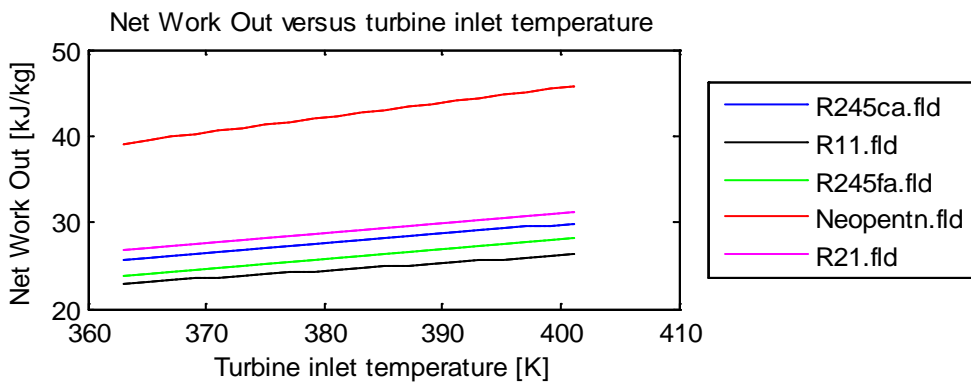
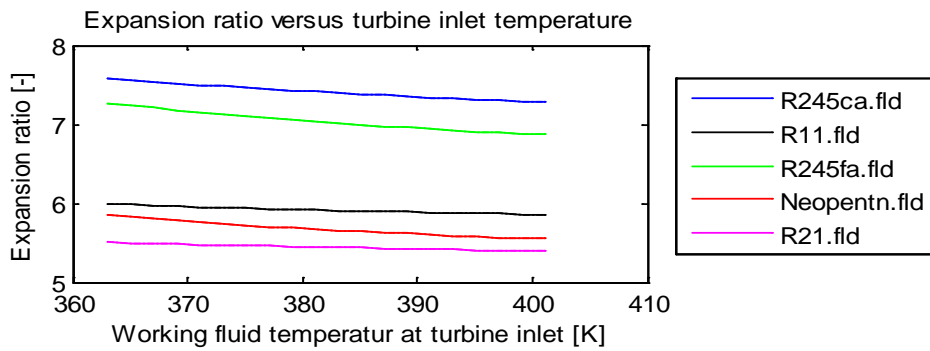
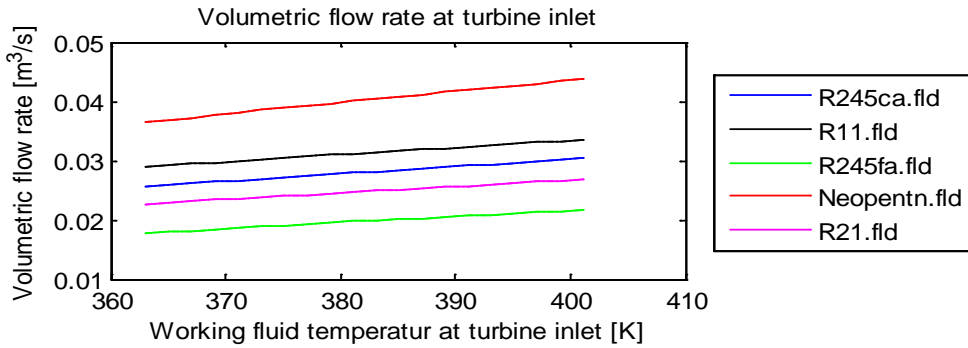
Refrigerants		Physical data			Safety data			Environmental data			Expansion
Number or name		NBP	TC	PC	OEL	LFL	Safty	Atmospheric	ODP	GWP	
		[°C]	[°C]	[kPa]	(ppMv)		Group	Life Time		(100 yr)	
44	R21	8,86	178,33	51,81	10	none	B1	1,7	0,04	151	wet
45	R236ea	6,2	139,29	35,02	1000	none	n.a.	11	0	1410	dry
46	Cis-butene	3,72	162,6	42,255							isentropic
47	R114	3,6	154,7	32,57	1000	none	A1	190	0,58	9180	dry
48	Trans-butene	0,88	155,46	40,27	1000	2	A3	0,018	0	20	dry
49	R600 BUTANE	-0,5	152	38	1000	2	A3	0,018	0	20	dry
50	R236fa	-1,4	124,9	32	1000	none	A1	242	0	9820	dry
51	Perflourobutane C4F10	-2,01	113,18	23,23							dry
52	RC318	-6	115,2	27,8	1000	none	A1	3200	0	10300	dry
53	Butene	-6,31	146,14	40,05							dry
54	Isobutene	-7	233,96	40,1							dry
55	R142b	-9,1	137,1	40,6	1000	8	A2	17,2	0,06	2220	isentropic
56	Sulfur dioxide	-10	157,5	70,9	2	none	B1		0		wet
57	Isobutane	-11,7	134,7	36,3	1000	1,6	A3	0,016	0	20	dry
58	R124	-12	122,3	30,62	1000	none	A1	5,9	0,02	619	dry
59	R152a	-14,02	113,26	45,17			A2	1,5	0	140	wet
60	R227ea	-16,3	101,8	29,3	1000	none	A1	38,9	0	3580	dry
61	R1234ze [E]	-19	109,4	36,4	1000	7,6		0,045	0	6	dry
62	CF3I	-21,85	123,29	39,53							wet
63	DME	-24,8	127,23	53,4	1000	3,4	A3	0,015	0		wet
64	R134a	-26	101	40,59			A1	14,6	0	1300	wet
65	R1234yf	-29,5	94,7	33,8	500	6,2	A2L r	0,029	0	4,4	dry

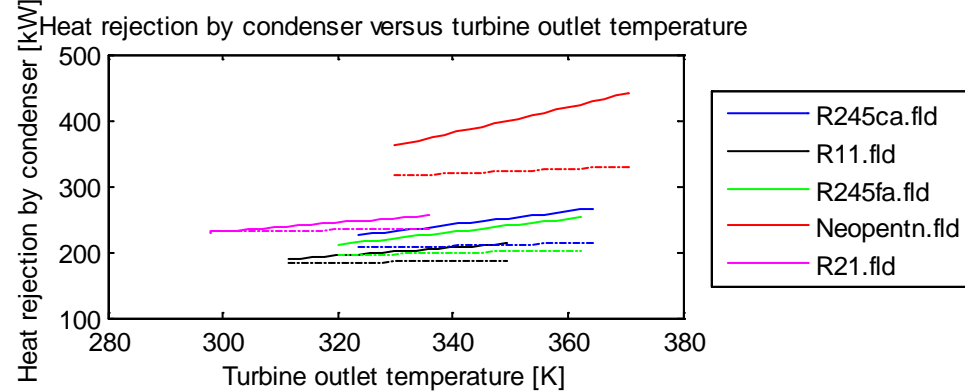
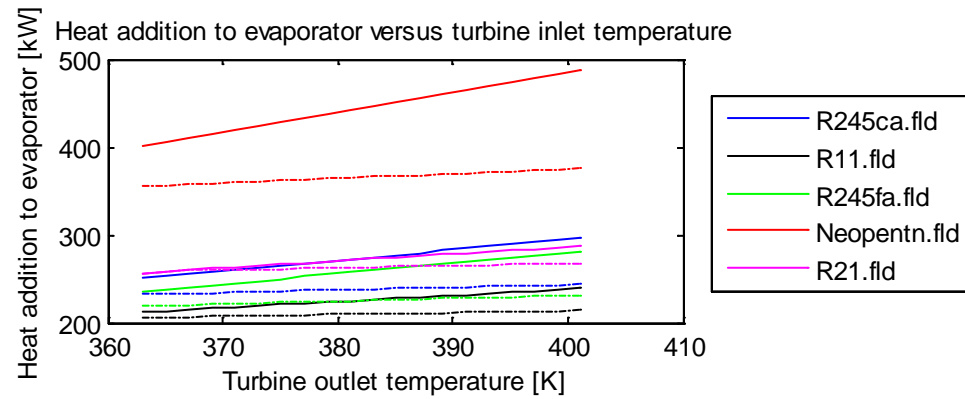
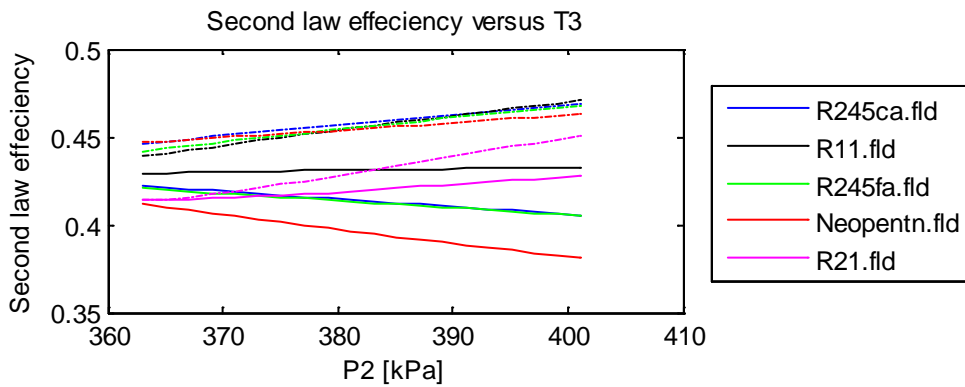
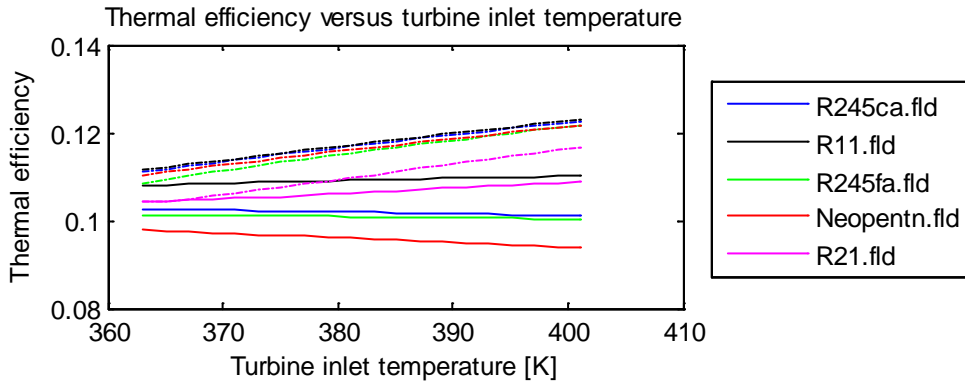
Refrigerants		Physical data			Safety data			Environmental data			Expansion
Number or name		NBP	TC	PC	OEL	LFL	Safty	Atmospheric	ODP	GWP	
		[°C]	[°C]	[kPa]	(ppMv)		Group	Life Time		(100 yr)	
66	R12	-29,8	112	4,14	1000	none	A1	100	0,82	10900	wet
67	C270 Cyclopropane	-31,2	125,2	55,8		2,4		0,44	0	20	wet
68	Ammonia	-33,3	132,25	113,33	25	16,7	B2L r	0,02	0	1	wet
69	R218	-36,83	72	26,71			A1				dry
70	R161	-37,6	102,2	50,9		3,8		0,18	0	12	wet
71	R115	-39,2	79,95	31,3	1000	none	A1	1020	0,6	7230	dry
72	R22	-40,8	96,1	49,9	1000	none	A1	11,9	0,04	1790	wet
73	Propane	-42	96,7	42,47			A3				wet
74	R290 Propane	-42,1	96,7	42,5	1000	2,1	A3	0,041	0	20	wet
75	R143a	-47,24	72,71	37,61			A2	48,3	0	3800	wet
76	1270 Propylene	-47,6	91,1	45,6	500	2,7	A3	0,001	0	20	wet
77	R125	-48,1	66	36,18	1000	none	A1	32,6	0	2800	wet
78	Carbonyl sulfide	-50,16	105,62	63,7							wet
79	R32	-51,7	78,1	57,8	1000	14,4	A2L r	5,2	0	716	wet
80	H2S Hydrogen sulfide	60,3	99,95	90							wet
81	Sulfur hexafluoride	-68,25	45,573	37,55							wet
82	R116	-78,1	19,9	30,5	1000	none	A1	10000	0	12200	isentropic
83	R41	-78,3	44,1	59			A1	2,8	0	107	wet
84	Carbon dioxide	78,465	30,978	73,773							wet
85	R13	-81,5	28,9	38,8	1000	none	A1	640	1	14400	wet
86	R23	-82	26,1	48,3	1000	none	A1	222	0	14200	isentropic
87	Nitrus oxide	-88,47	36,37	72,45							wet

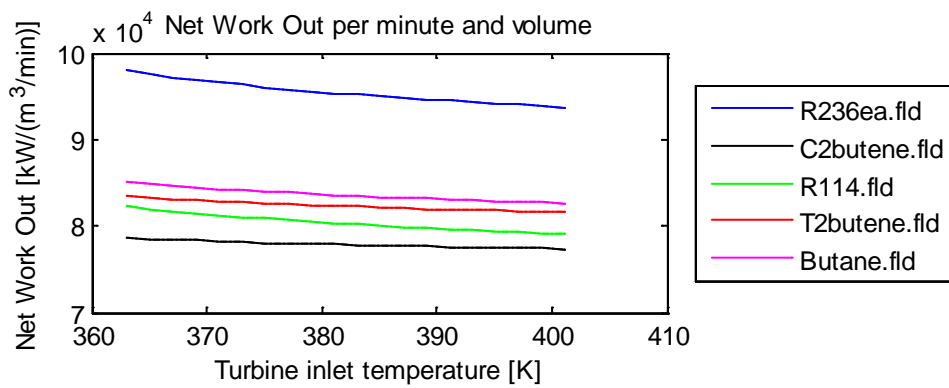
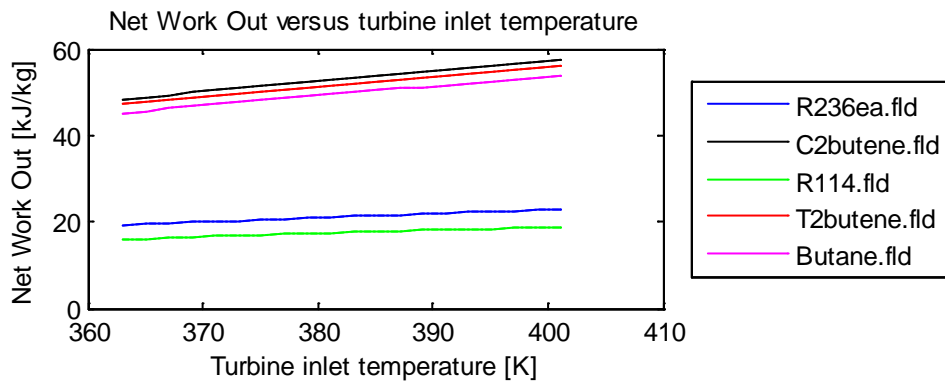
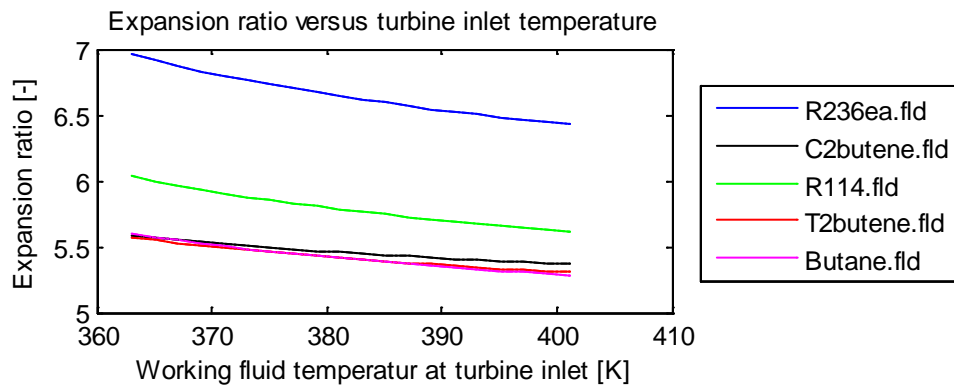
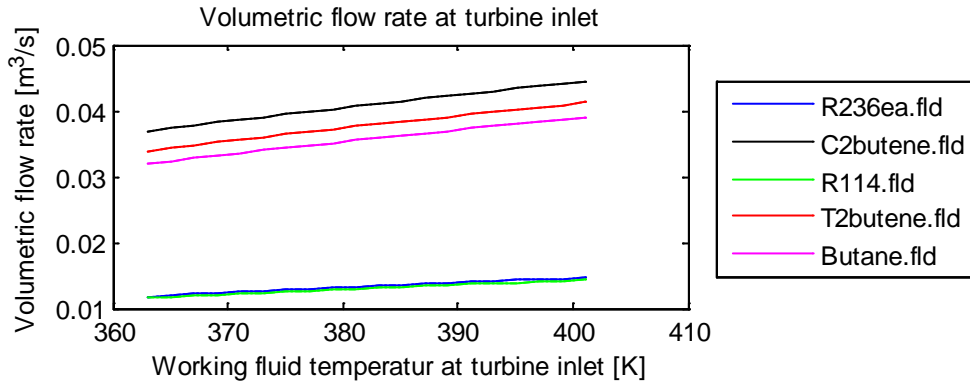
Refrigerants		Physical data			Safety data			Environmental data			Expansion
Number or name		NBP	TC	PC	OEL	LFL	Safty	Atmospheric	ODP	GWP	
		[°C]	[°C]	[kPa]	(ppMv)		Group	Life Time		(100 yr)	
88	R170 ethane	-88,6	32,2	48,7	1000	3,1	A3	0,21	0	20	wet
89	Ethylene	-103,77	9,2	50,418							wet
90	Xenon	-108,1	16,583	58,42							wet
91	R14	-128	-45,6	37,5	1000	none	A1	50000	0	7390	wet
92	Nitrogen trifluoride	-129	-39,15	44,6							wet
93	R784 Kr-Krypton	-153,4	-63,7	55,3		none			0		wet
94	R50 - Methane	-161,5	-82,6	46	1000	4,8	A3	12	0	23	wet
95	Oxygen	-182,96	-118,57	50,43							wet
96	R740 Ar - Argon	-185,8	-122,5	48,6		none	A1		0		wet
97	Fluorine	-188,11	-128,74	51,724							wet
98	Carbon monoxide	-191,51	-140,29	34,94							wet
99	R728 N2 - Nitrogen	-195,8	-147	34		none			0		wet
100	R720 Ne - Neon	-246	-228	26		none	A1		0		wet
101	D2 Deuterium	-249,84	-234,81	16,65							wet
102	Orthohydrogen	-252,77	-293,93	13,107							wet
103	R702 H2 - Normal hydrogen	-252,8	-240	13		4	A3		0		wet
104	Parahydrogen	-252,88	-240,21	12,858							wet
105	R704 Helium	-268,9	-268	2,3		none	A1		0		wet

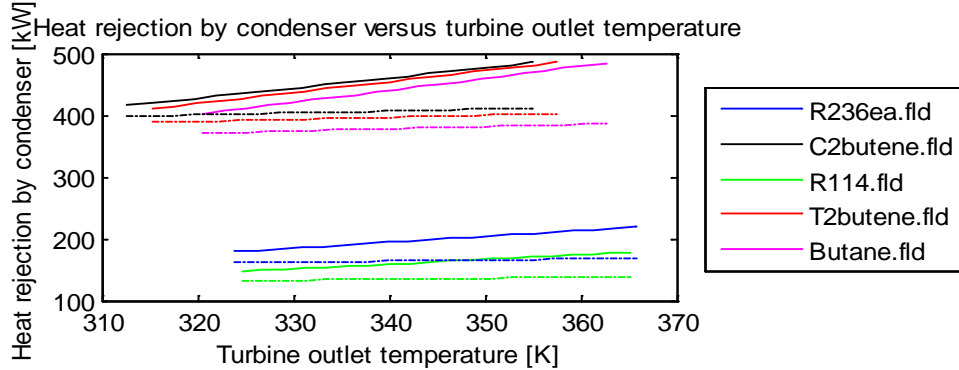
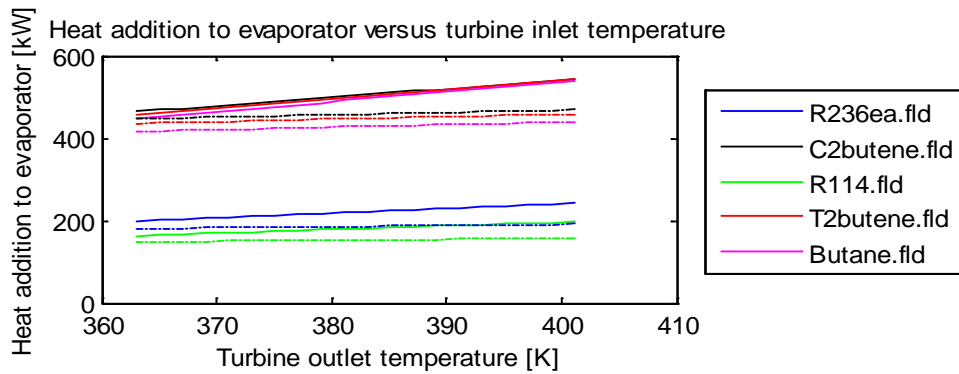
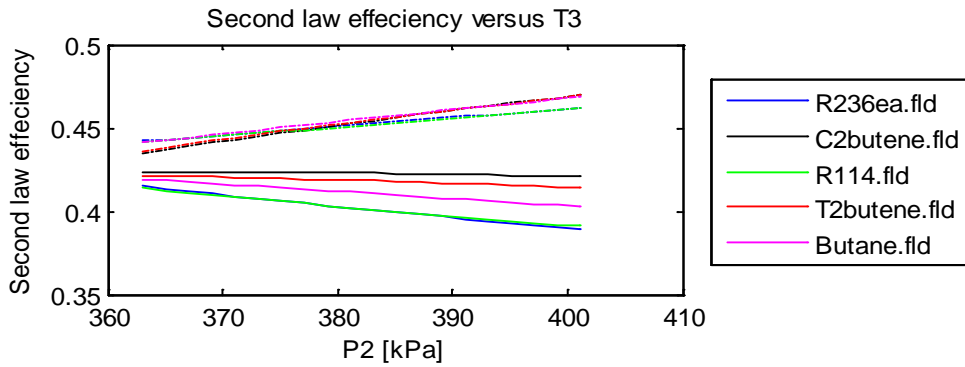
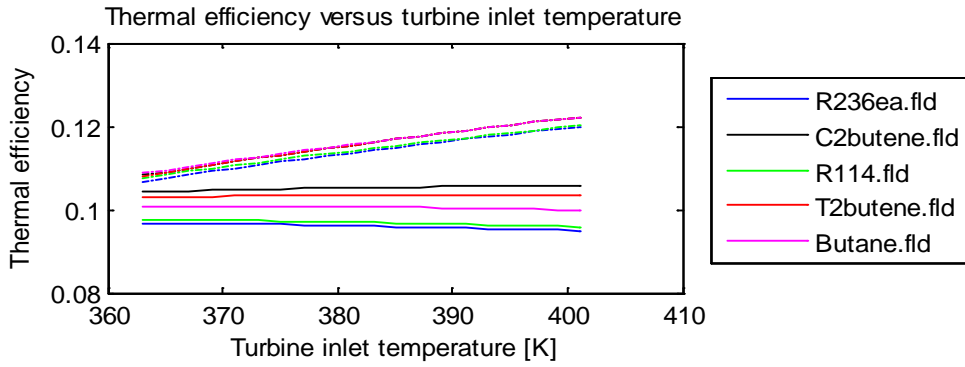
Appendix 2

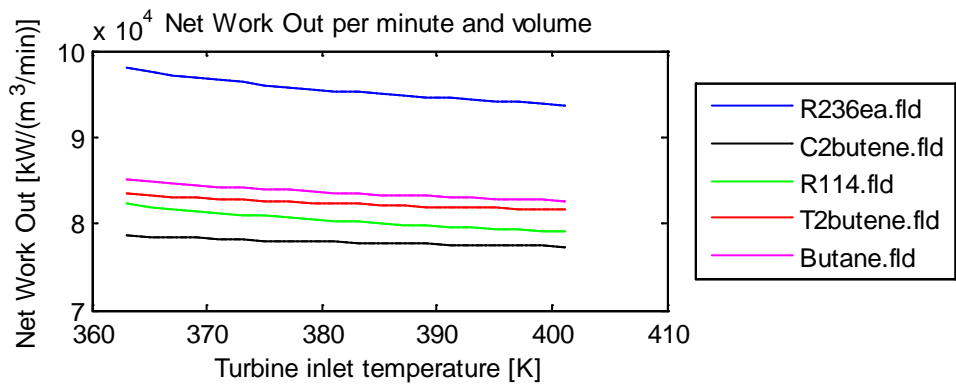
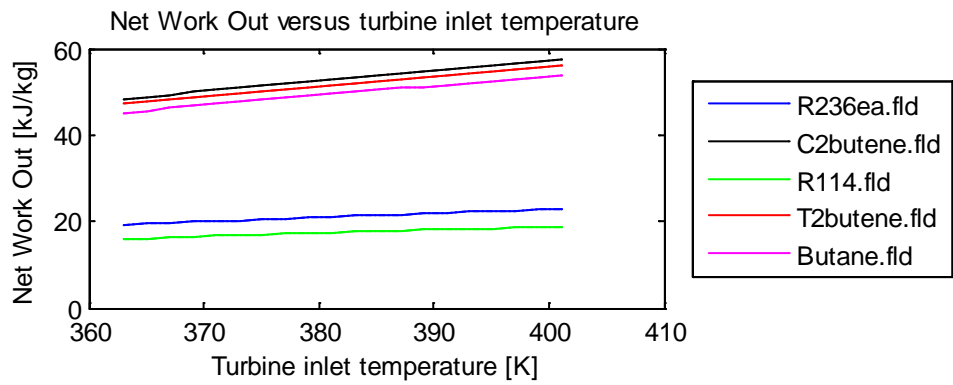
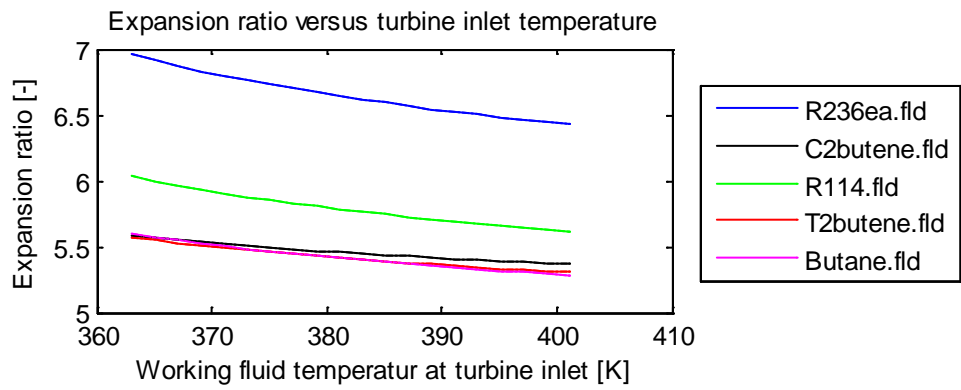
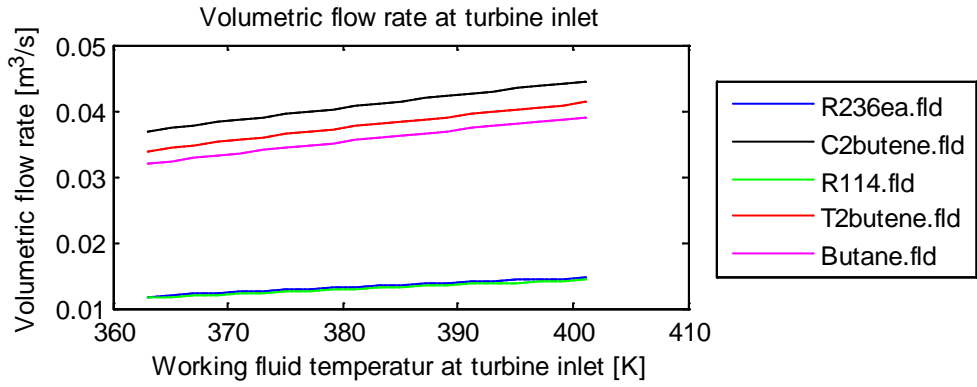
Scenario 1

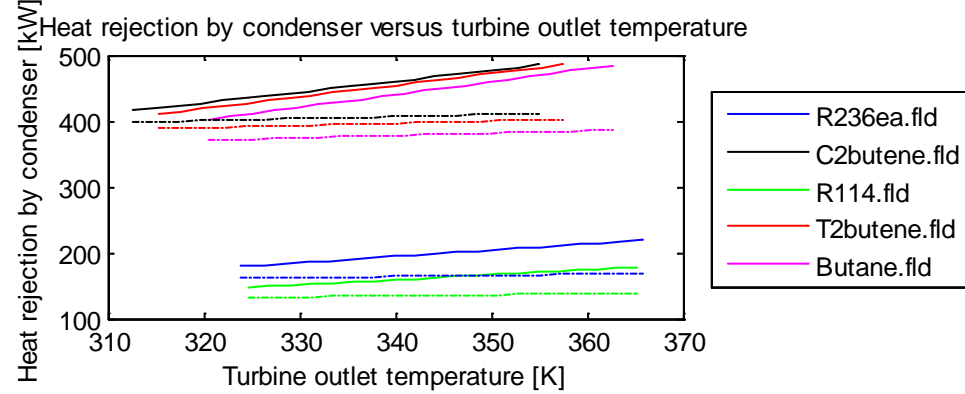
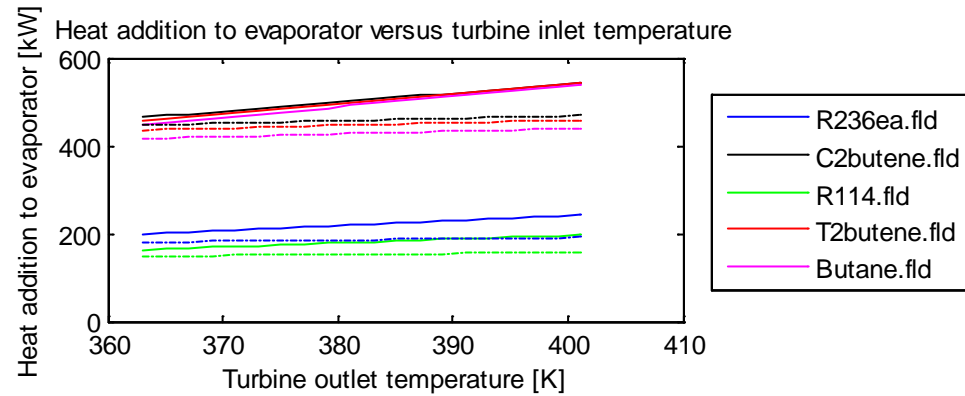
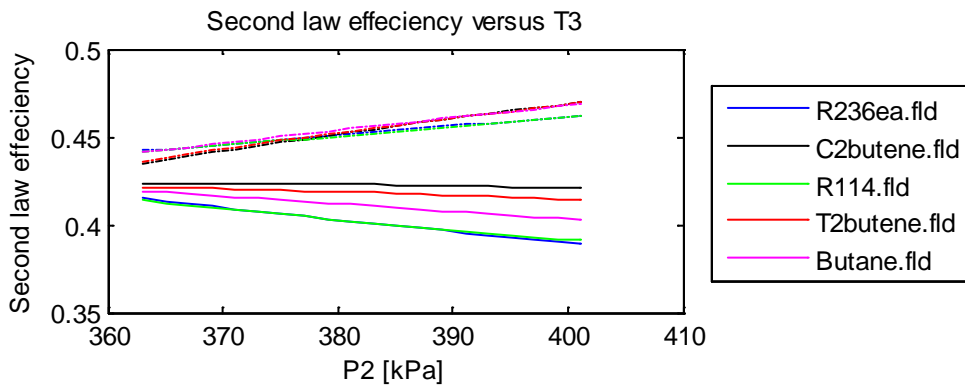
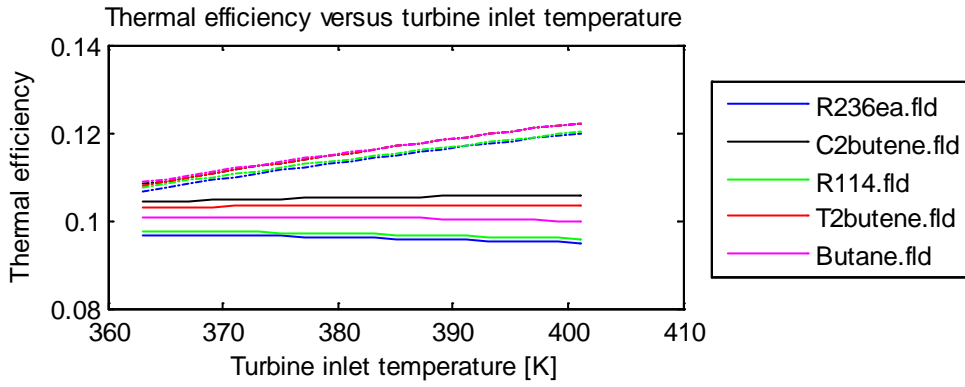


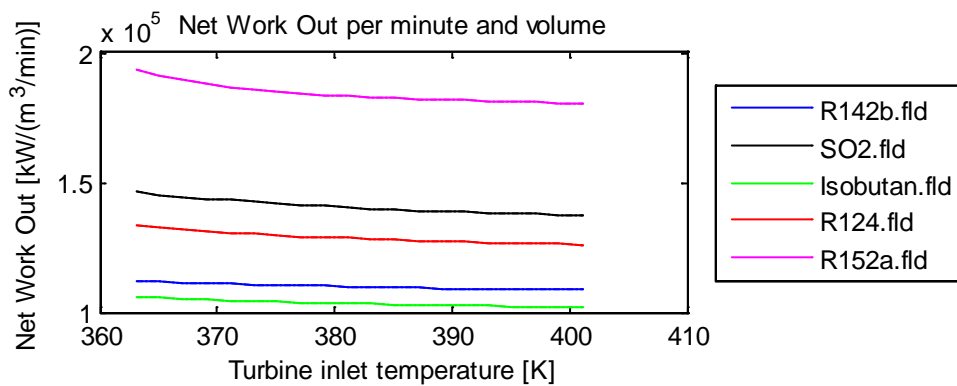
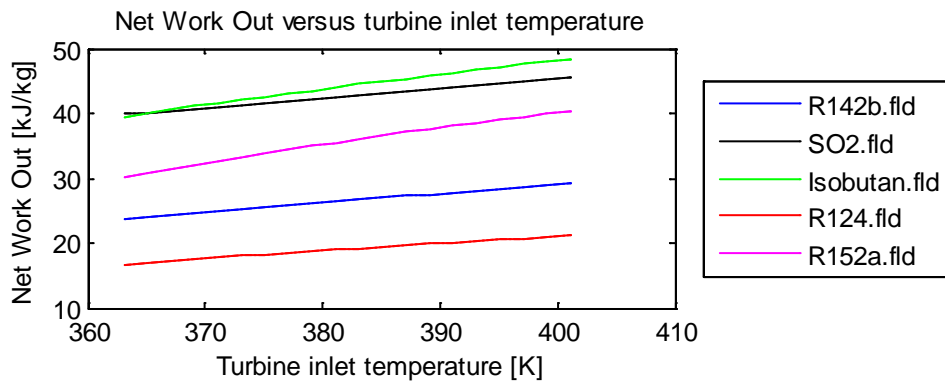
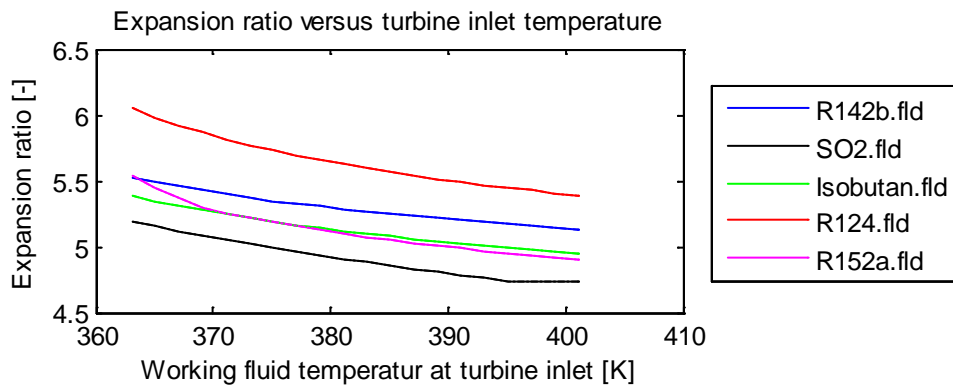
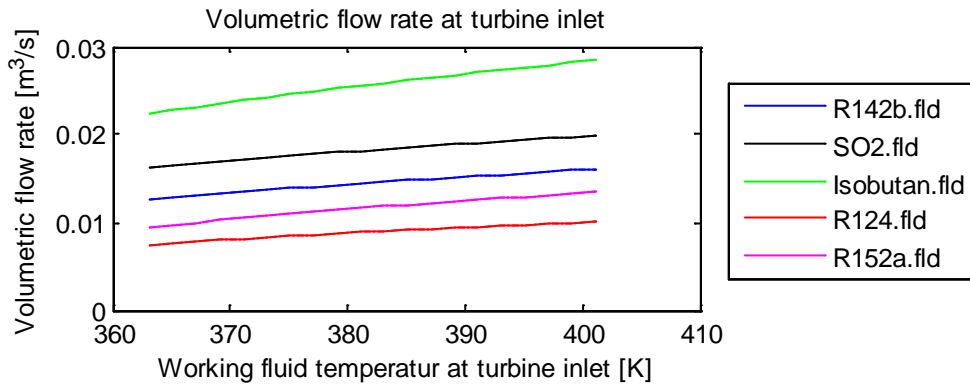


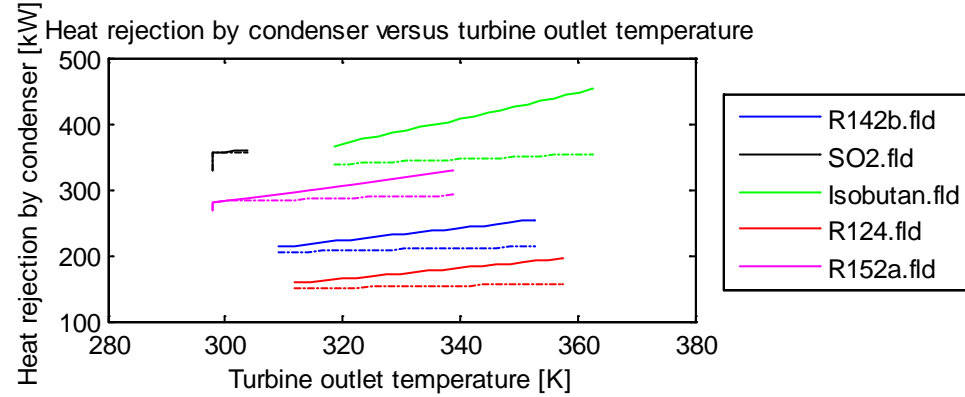
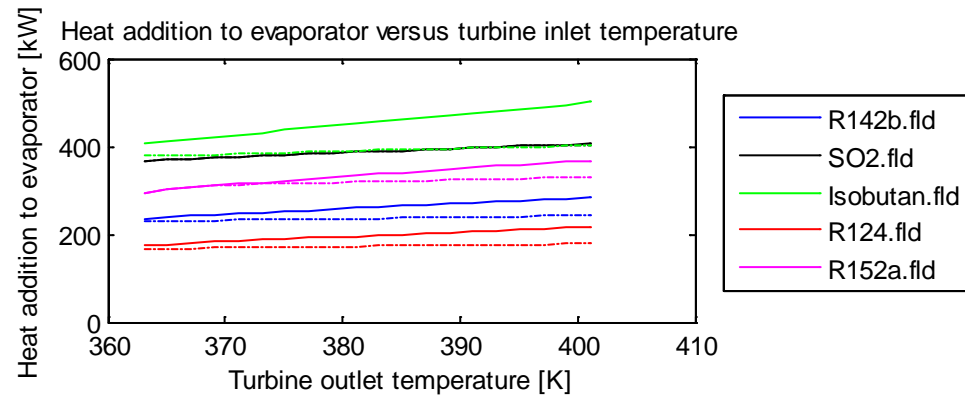
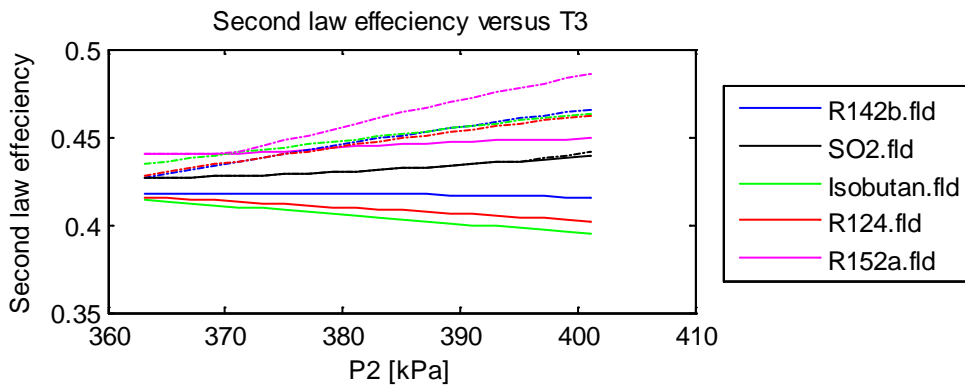
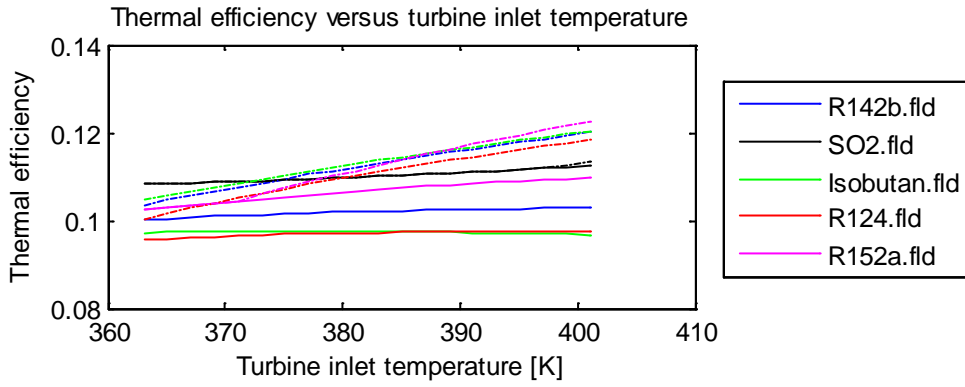


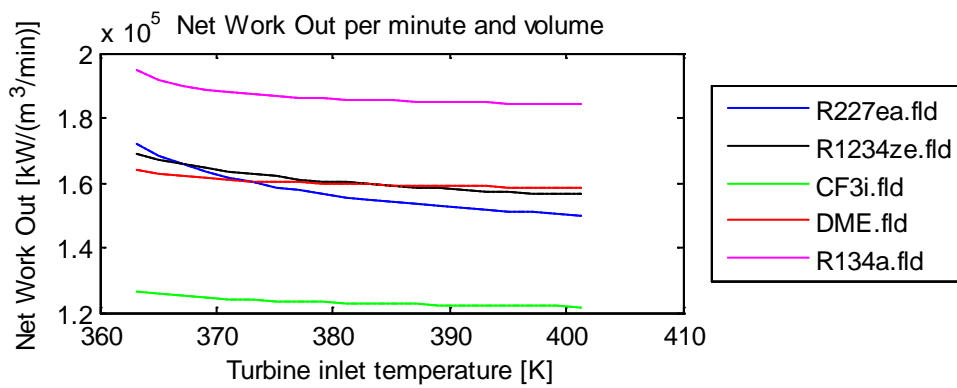
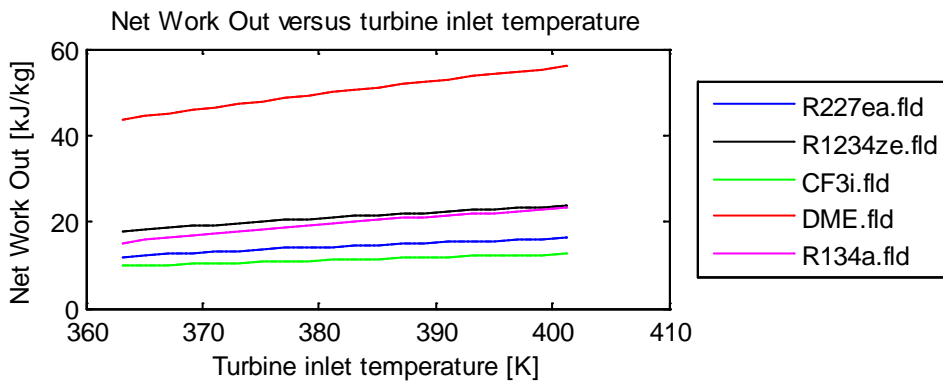
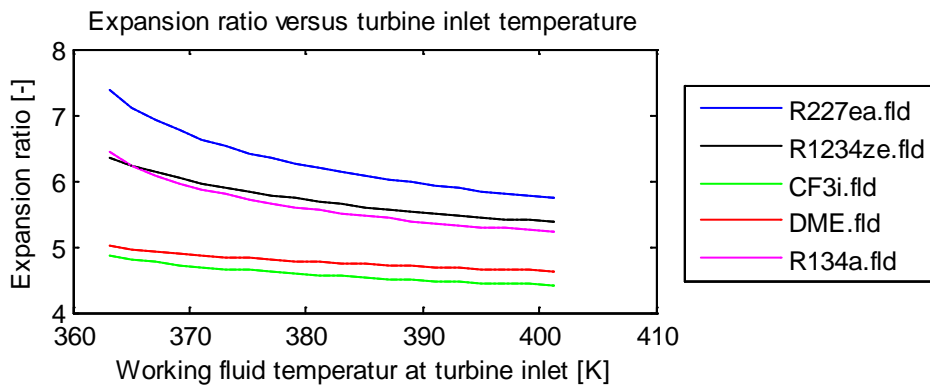
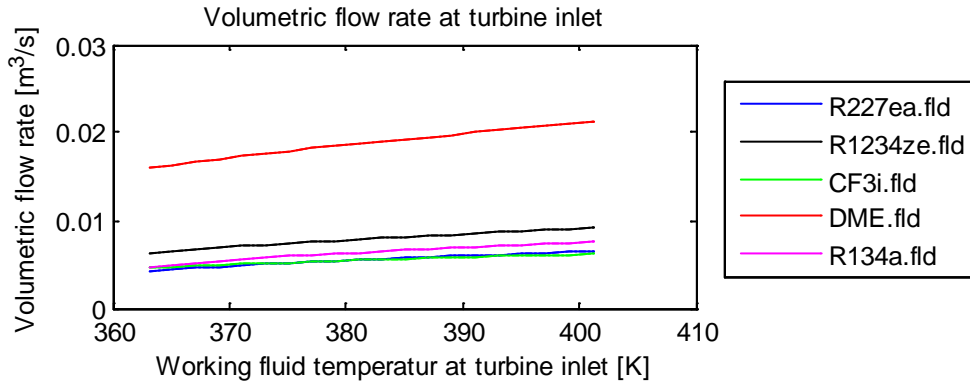


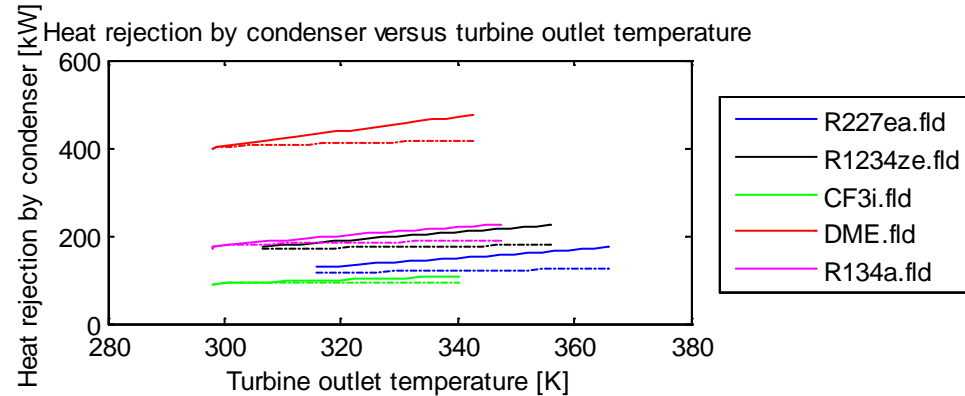
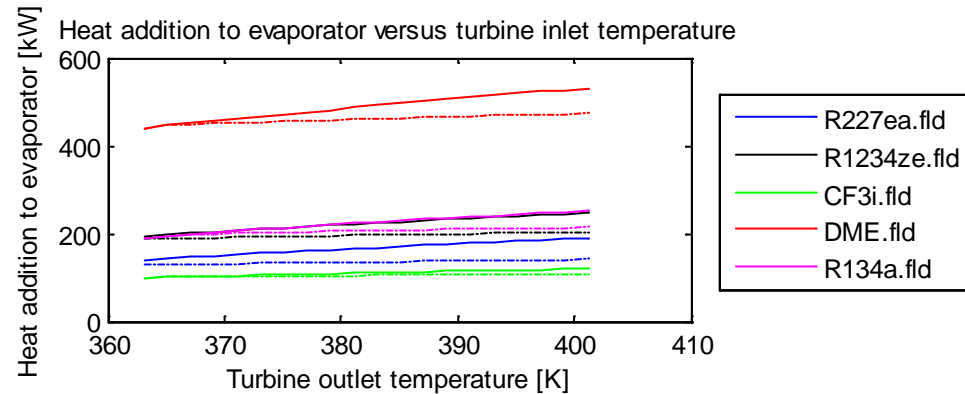
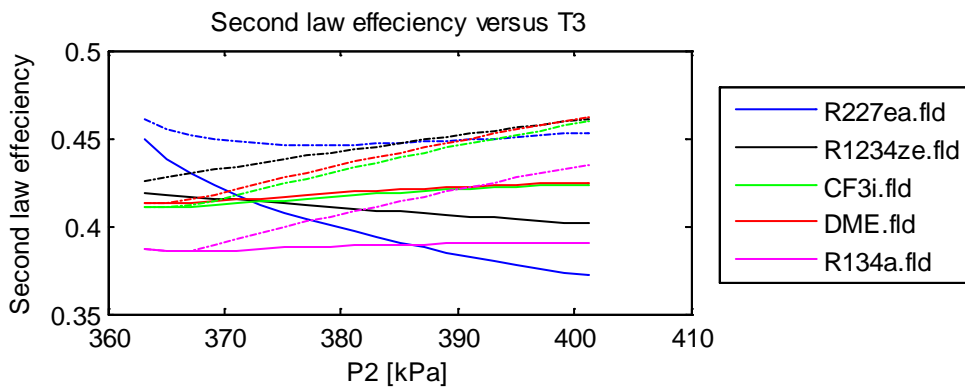
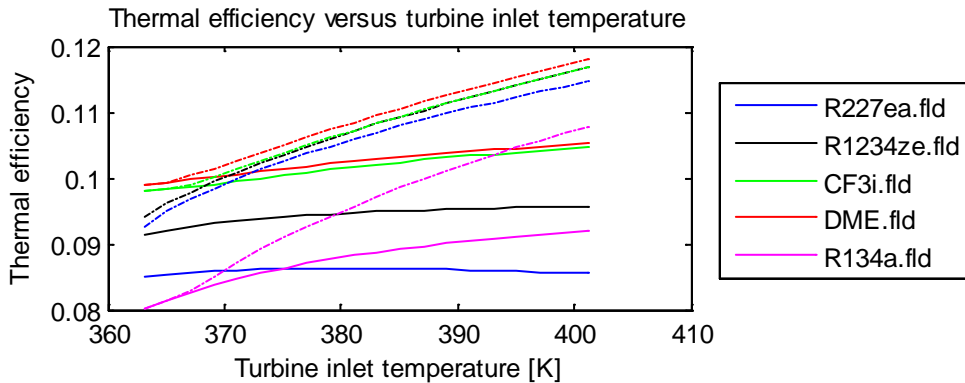


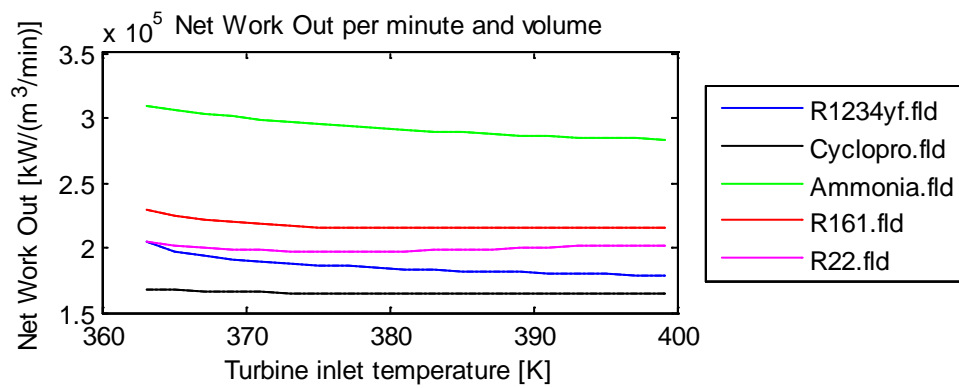
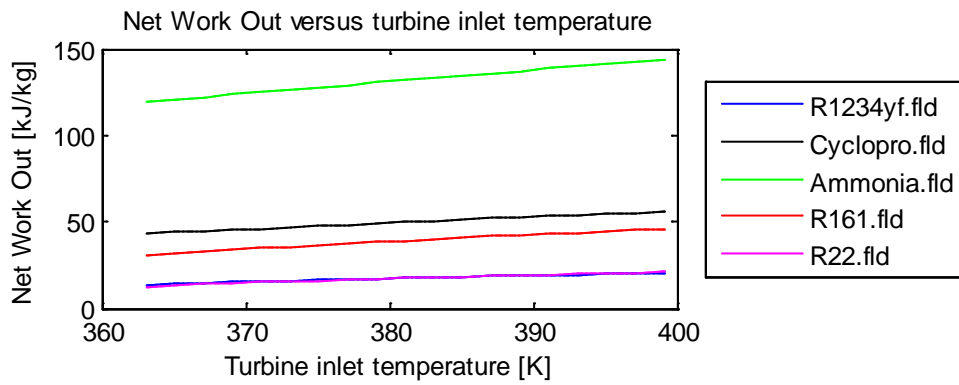
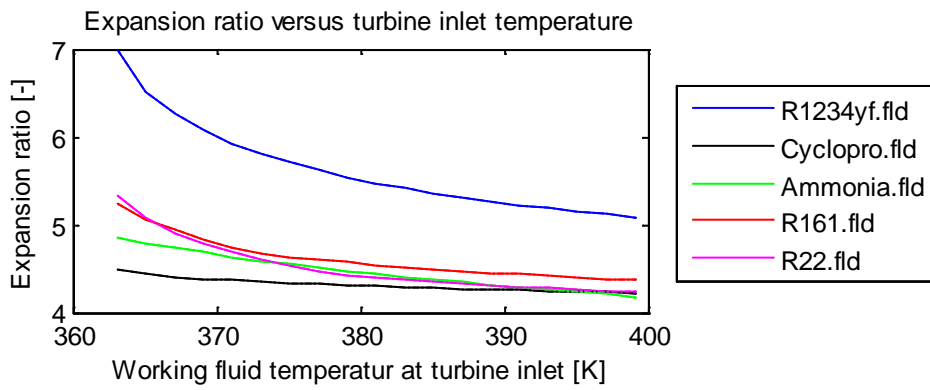
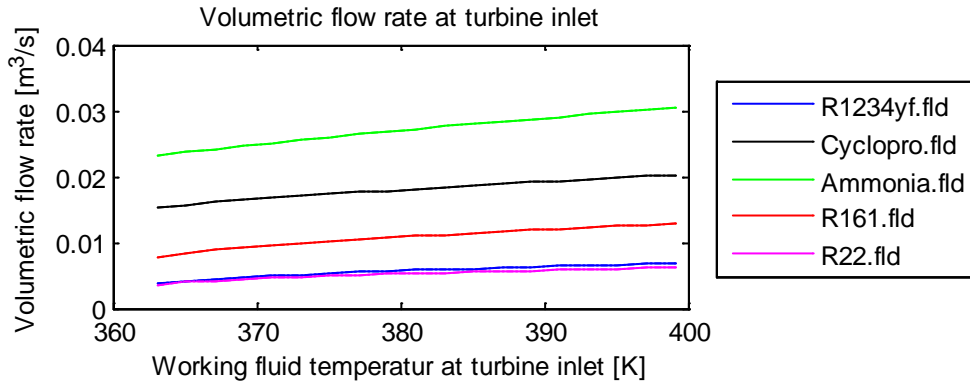


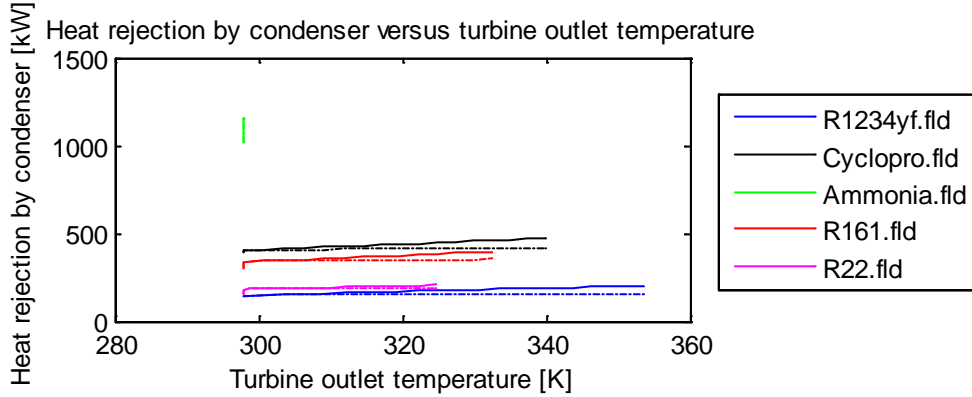
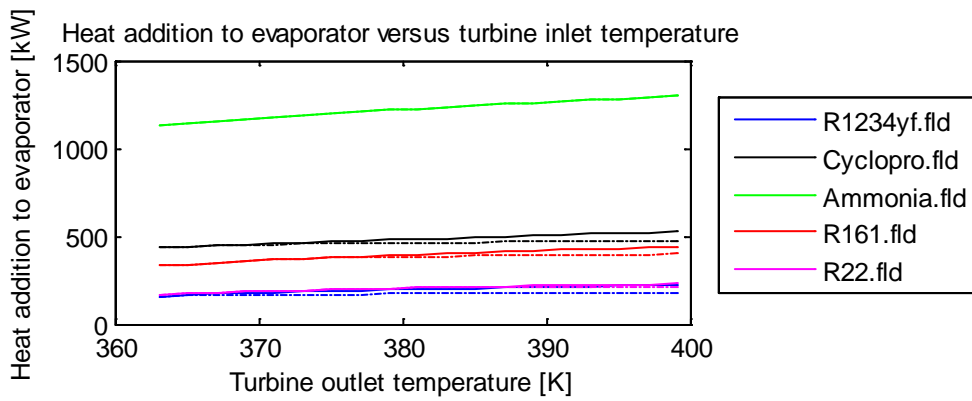
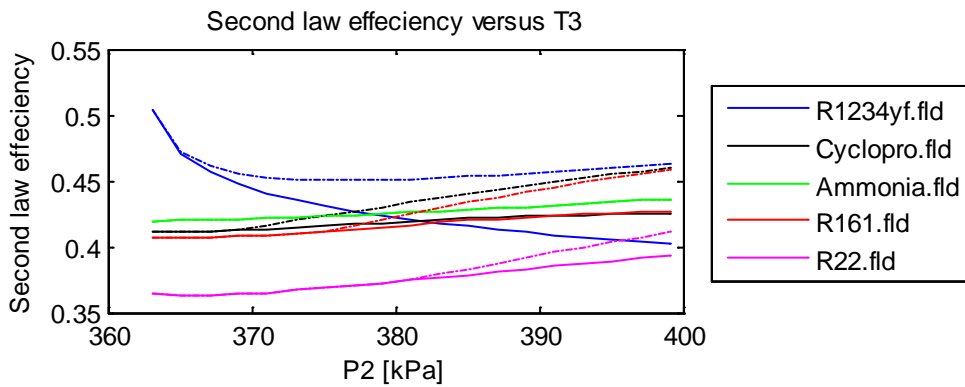
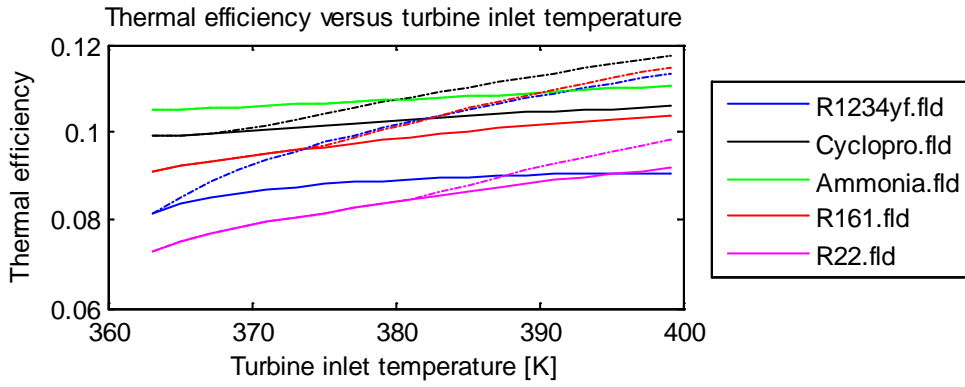


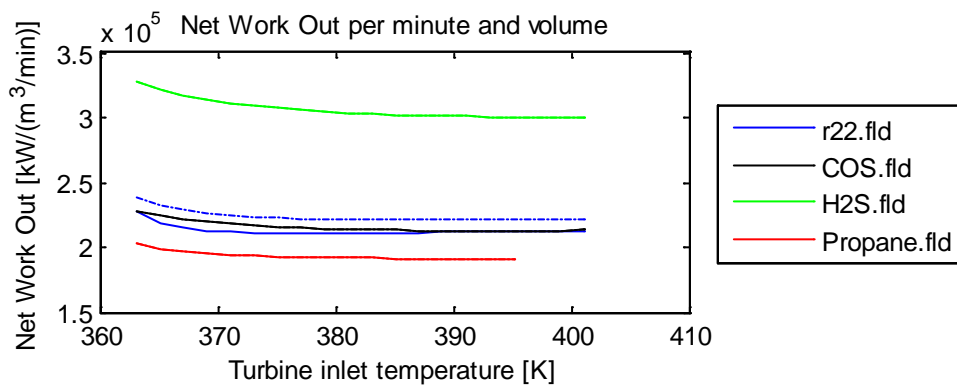
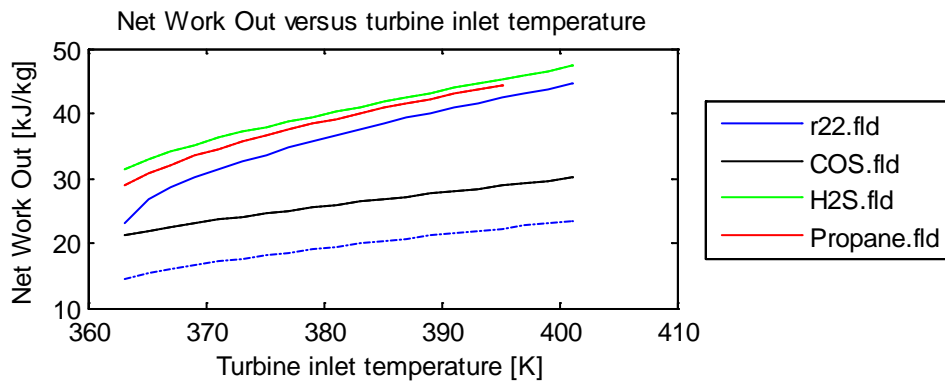
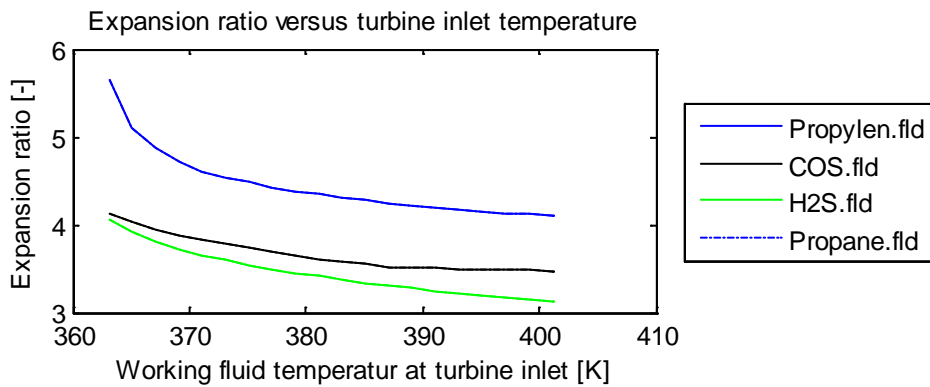
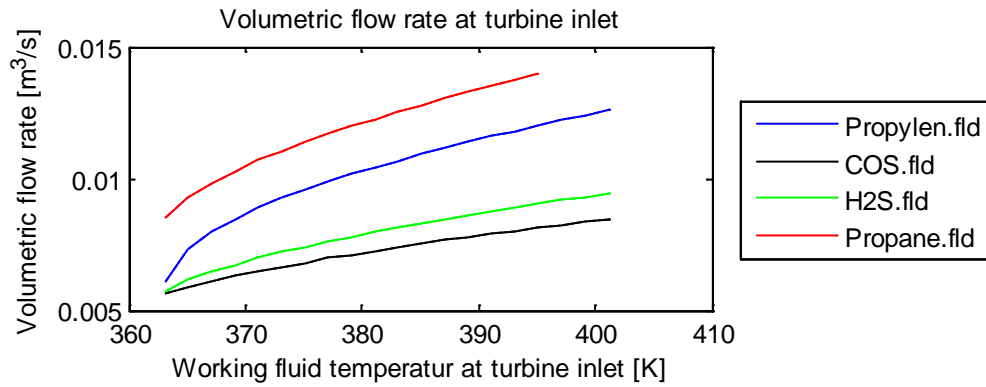


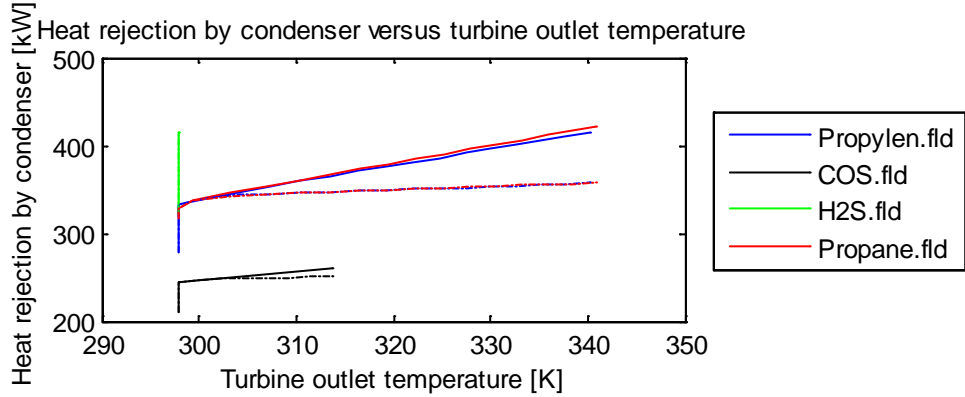
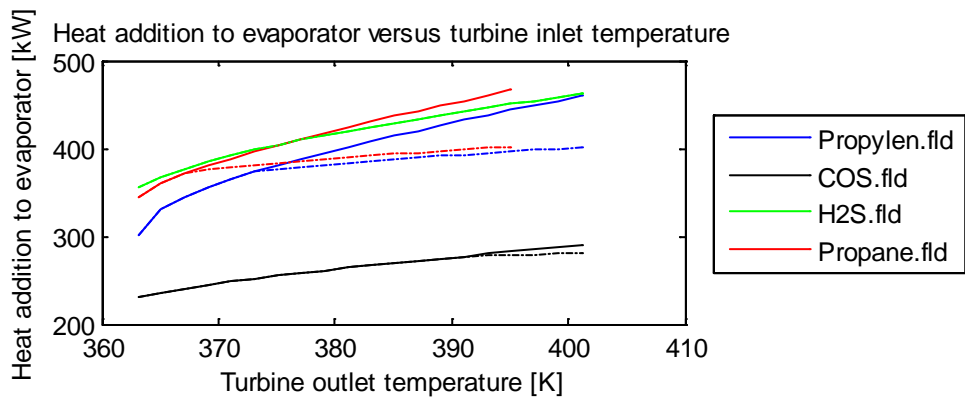
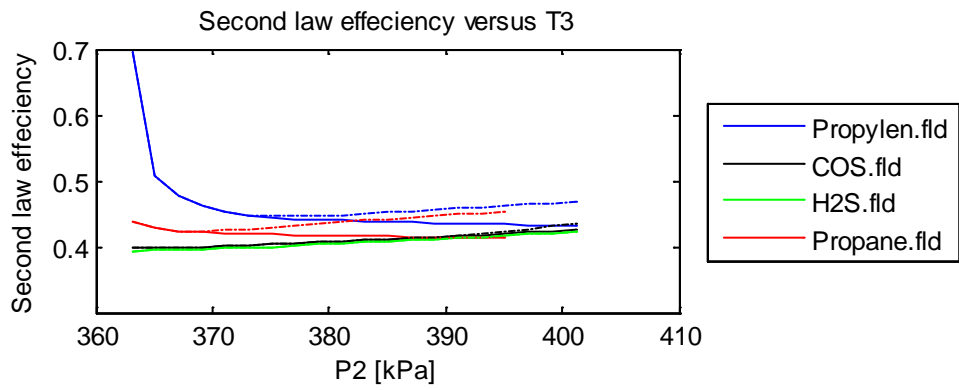
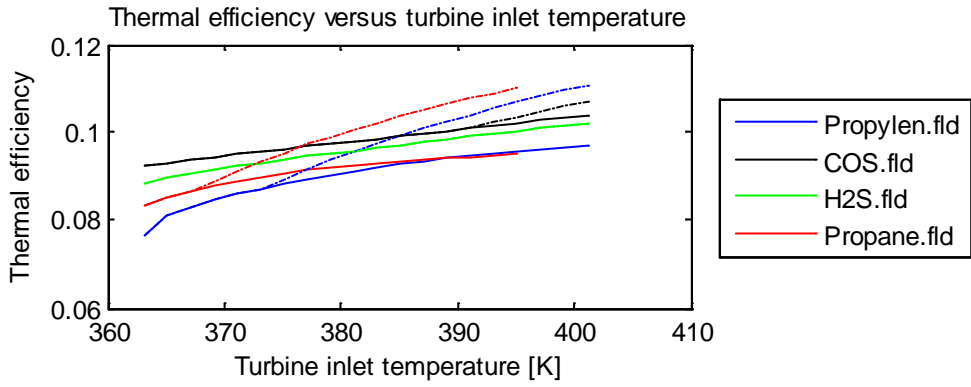




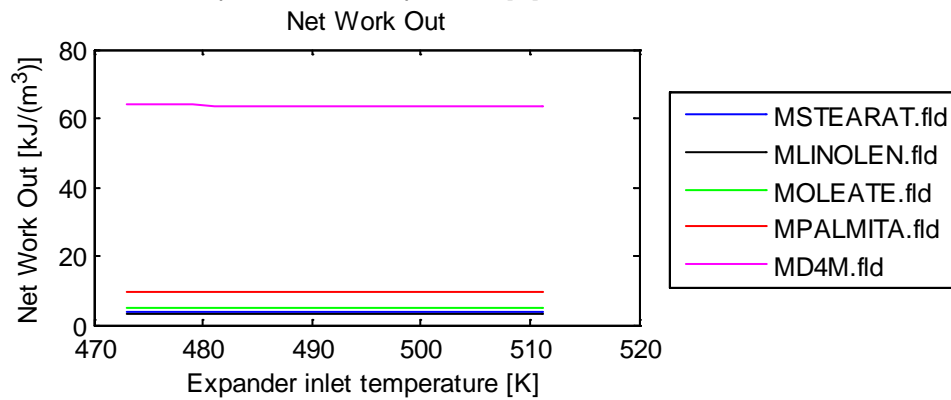
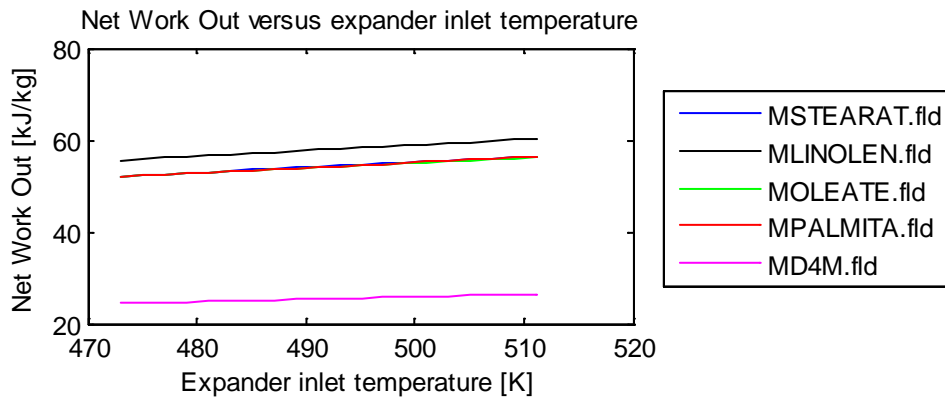
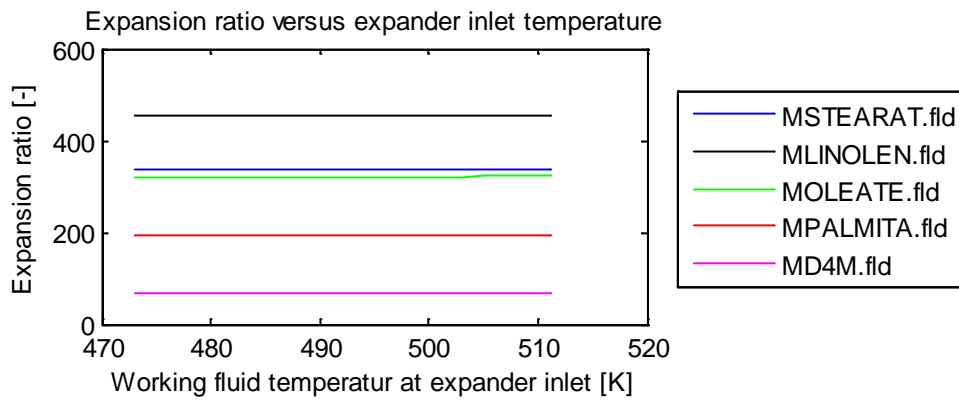
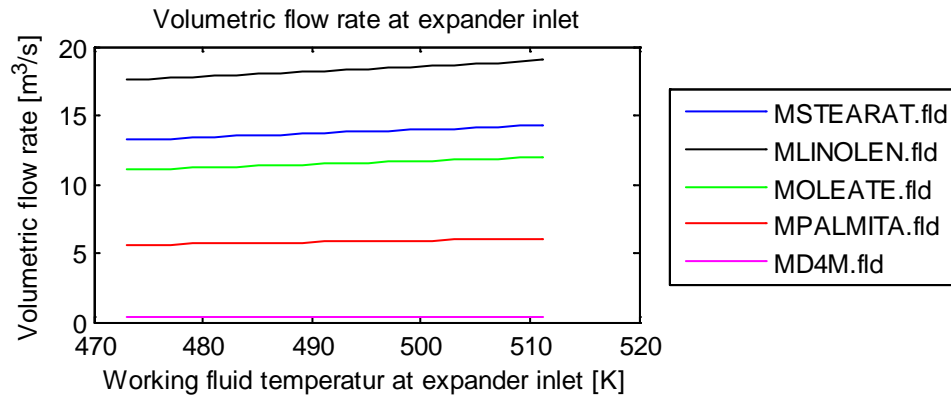


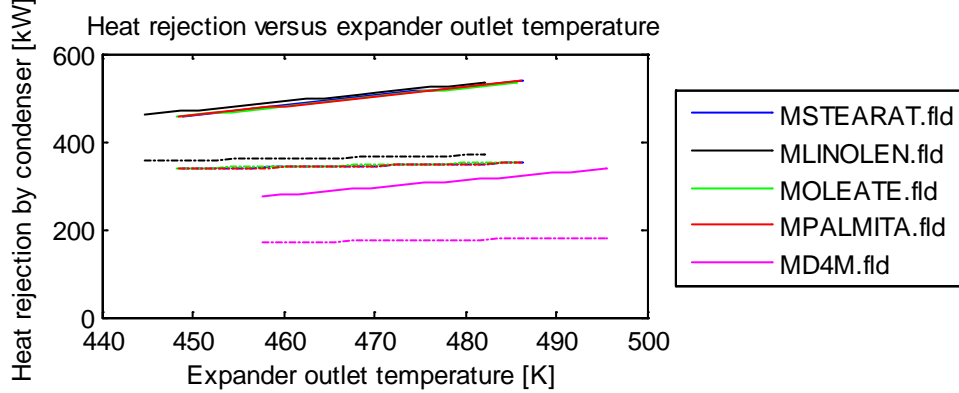
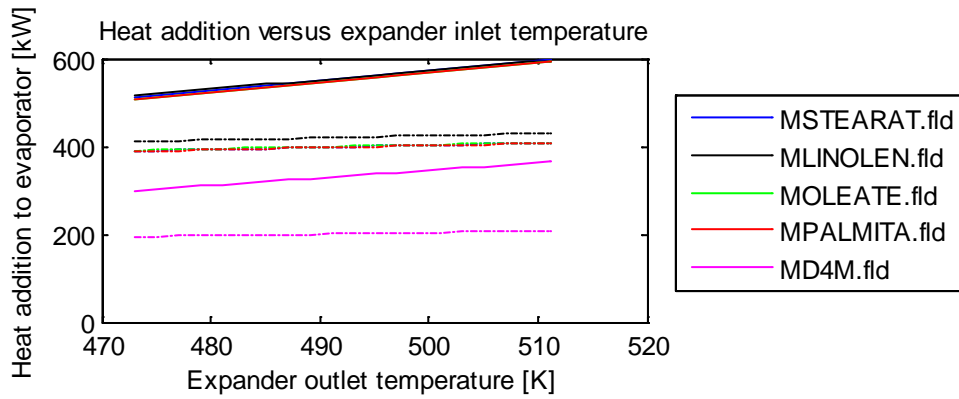
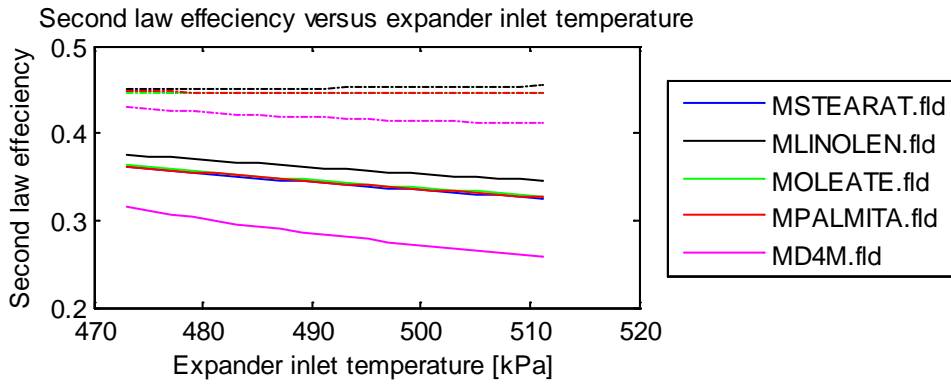
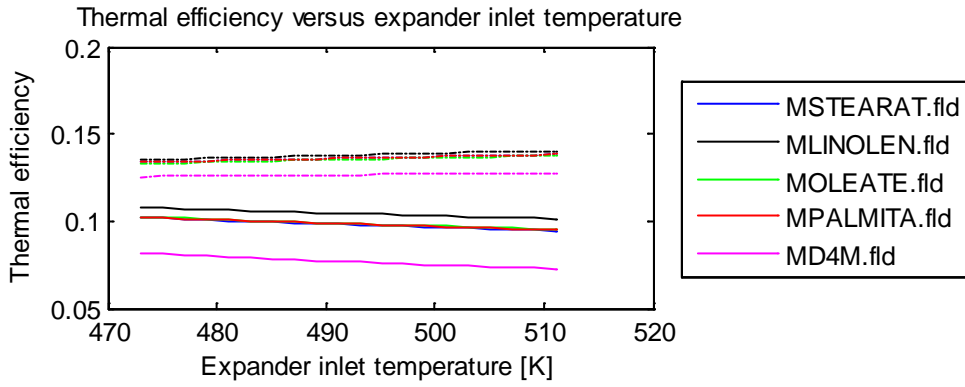


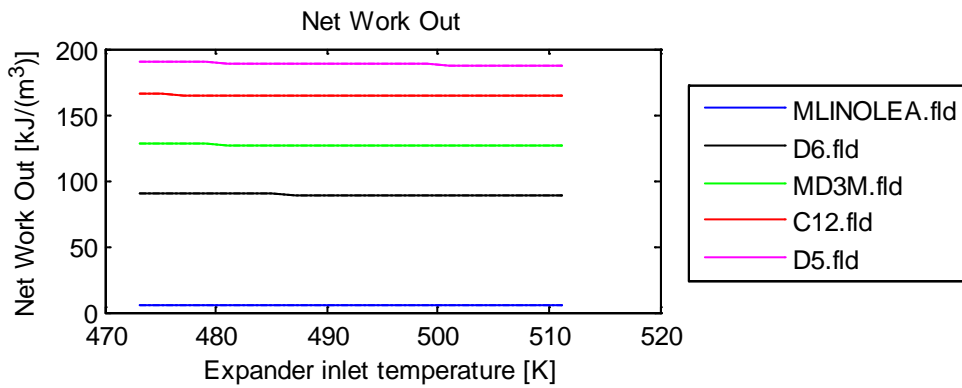
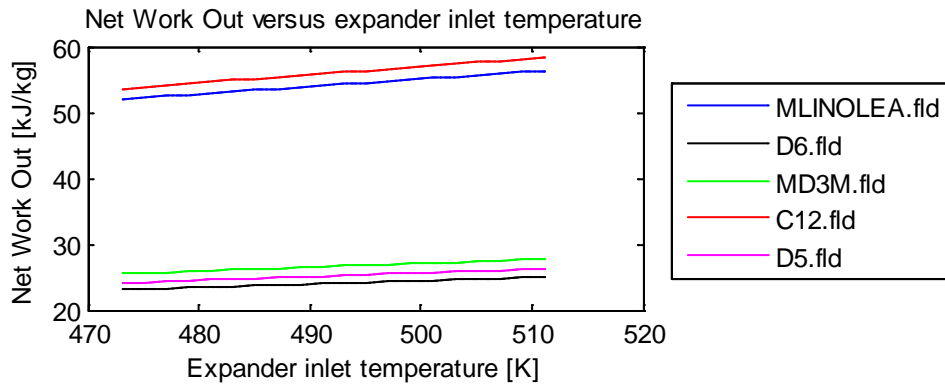
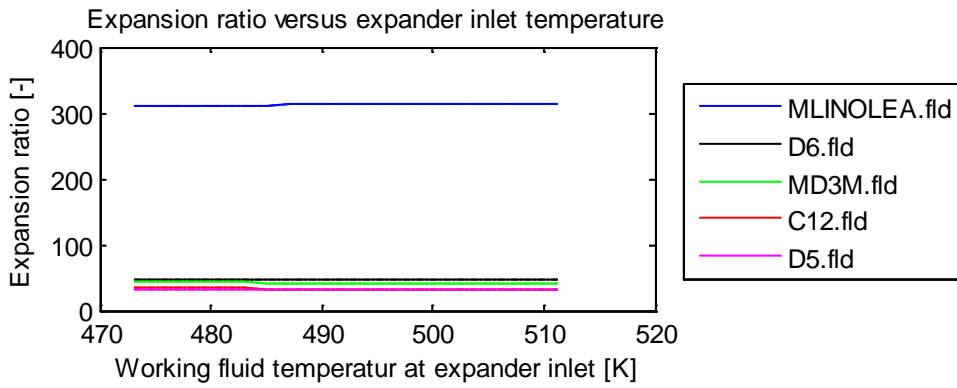
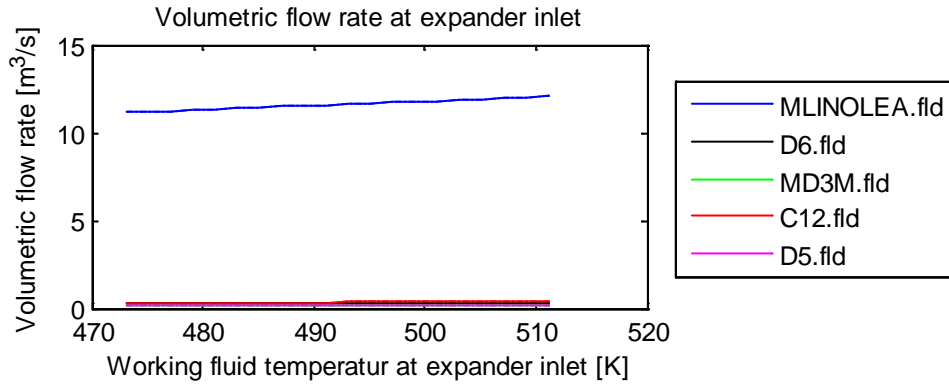


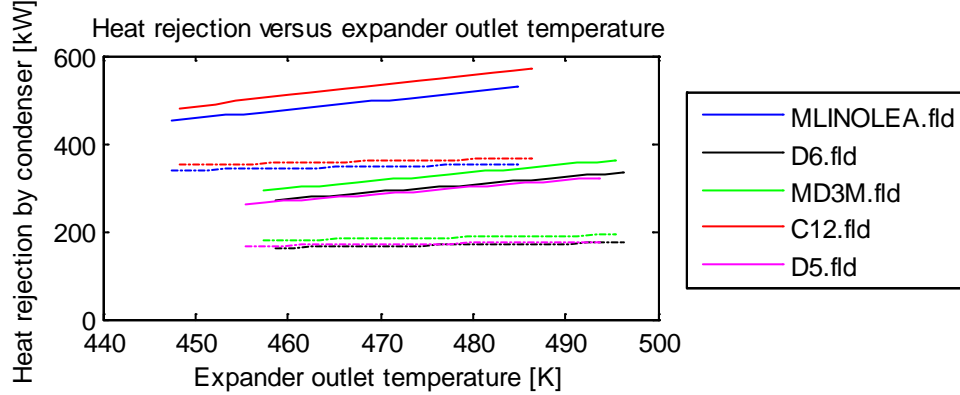
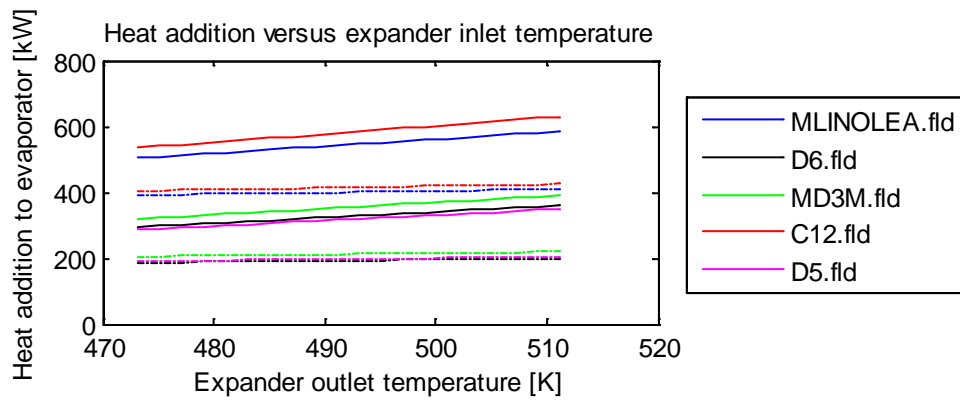
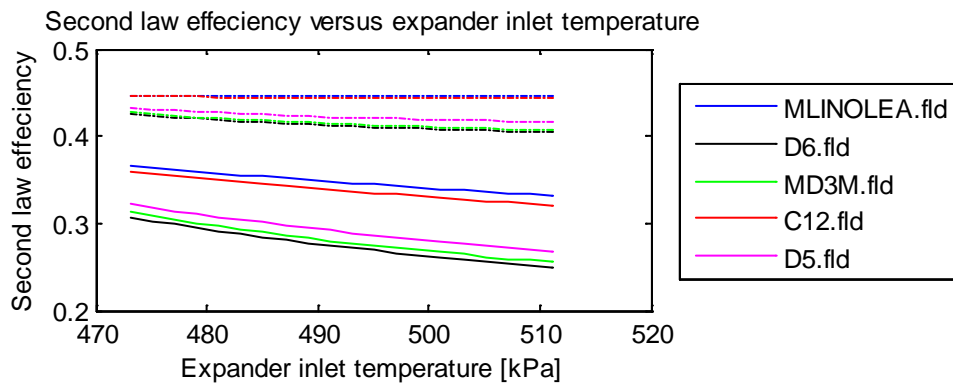
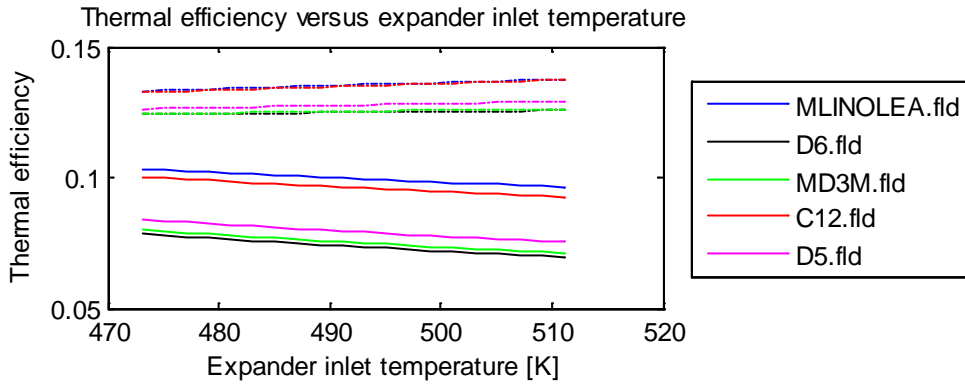


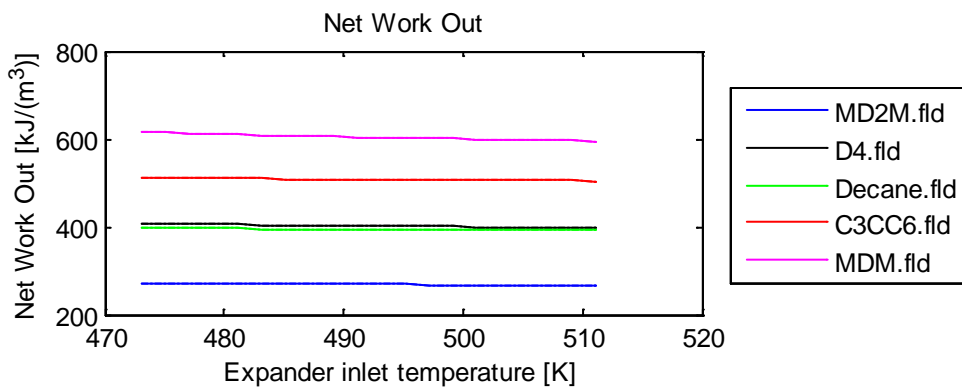
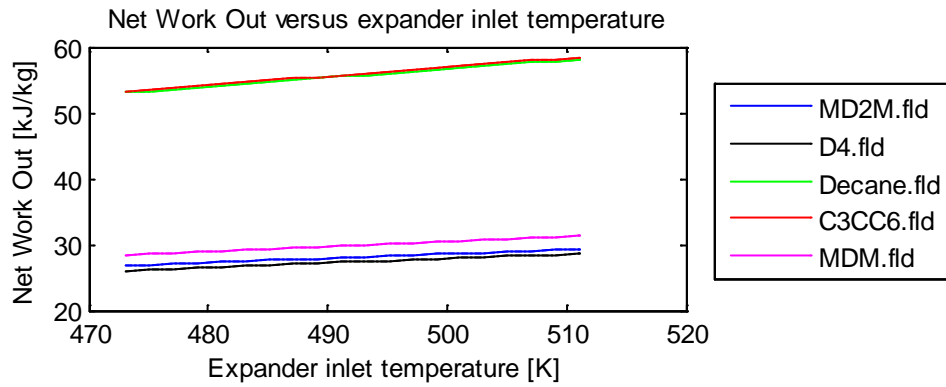
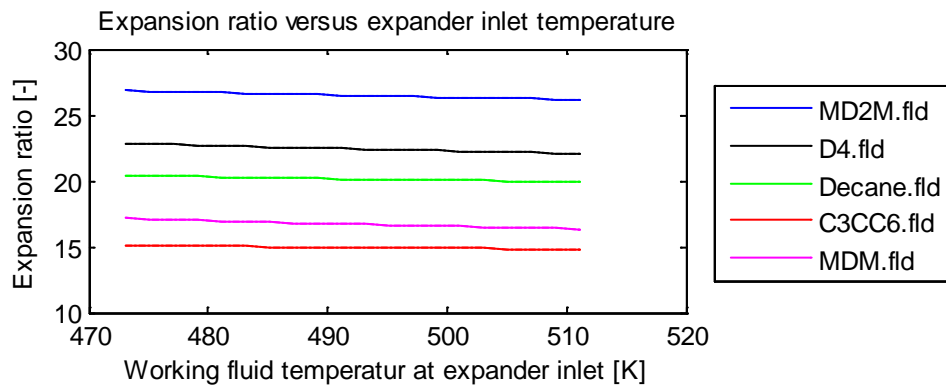
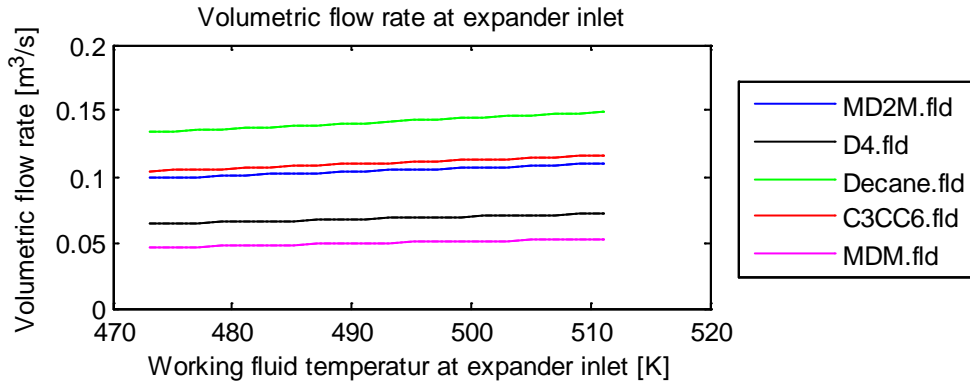
Scenario 2

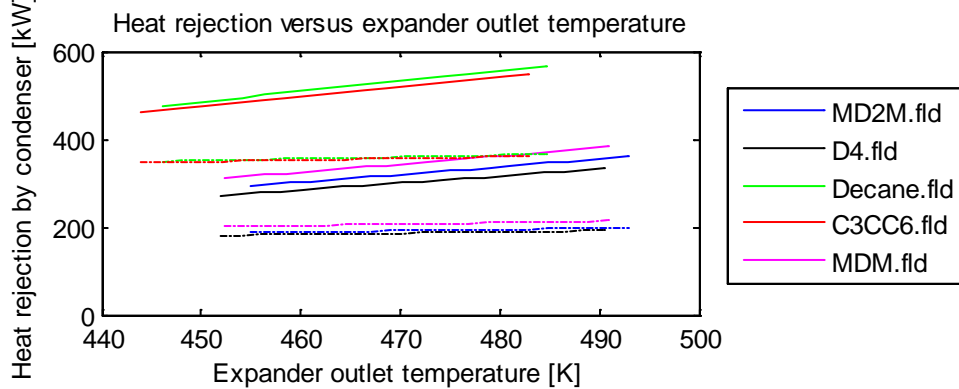
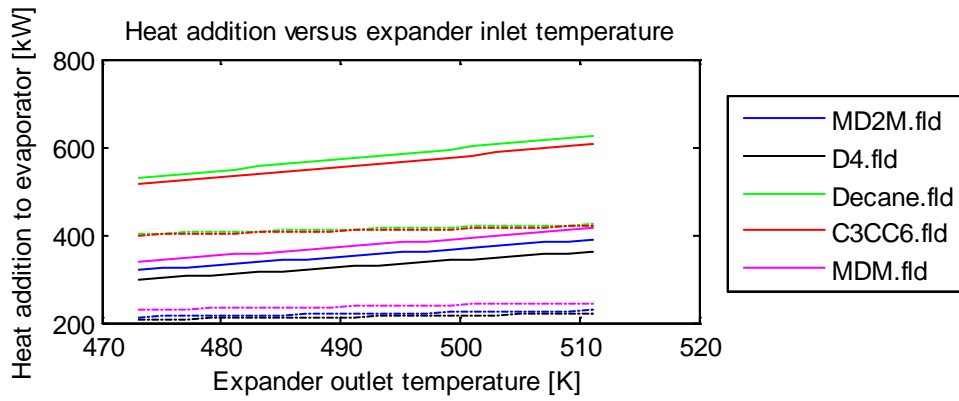
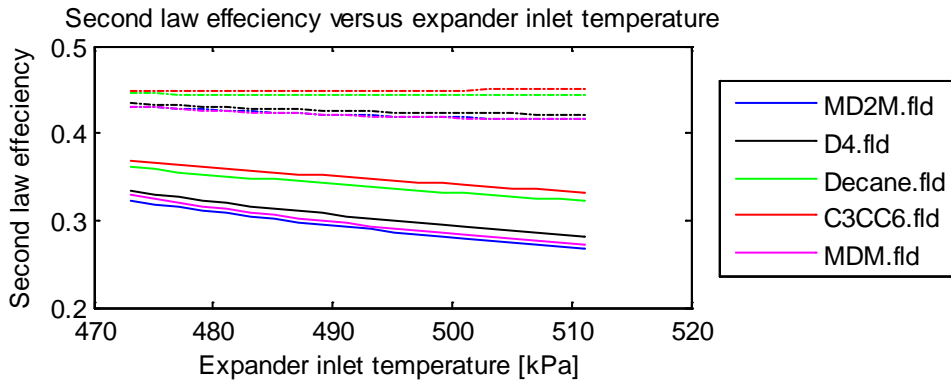
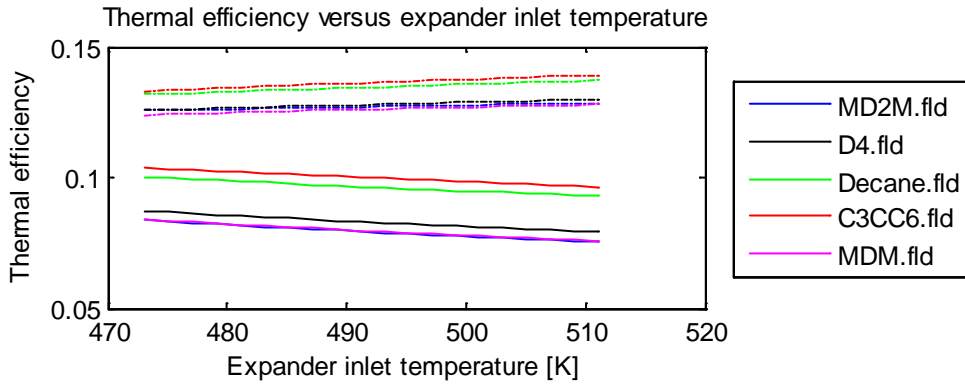


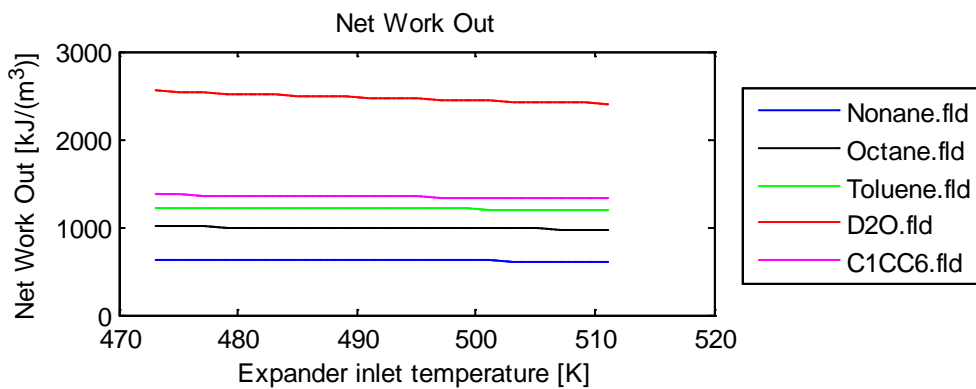
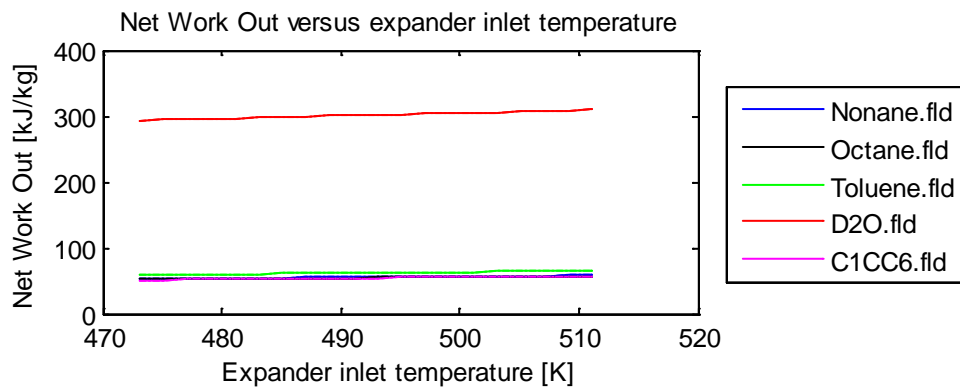
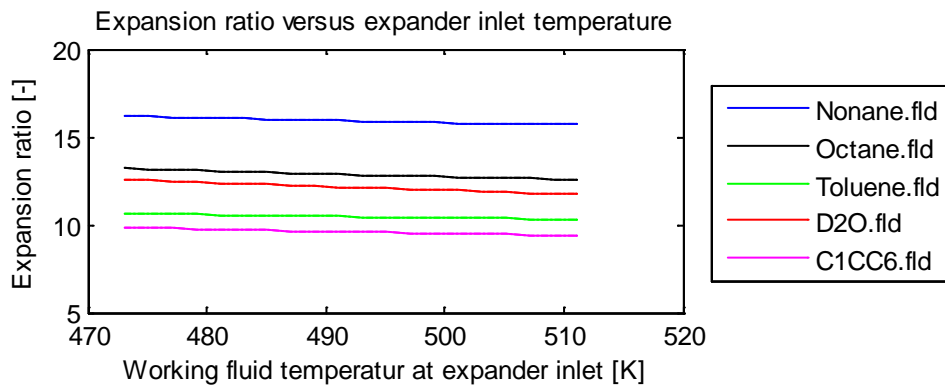
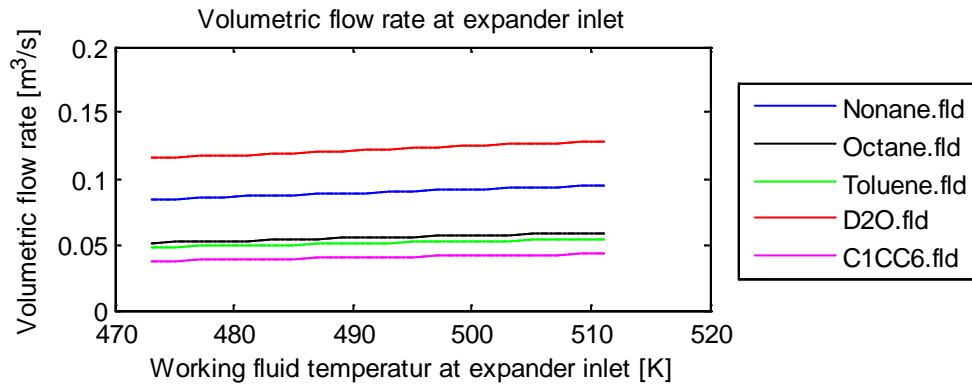


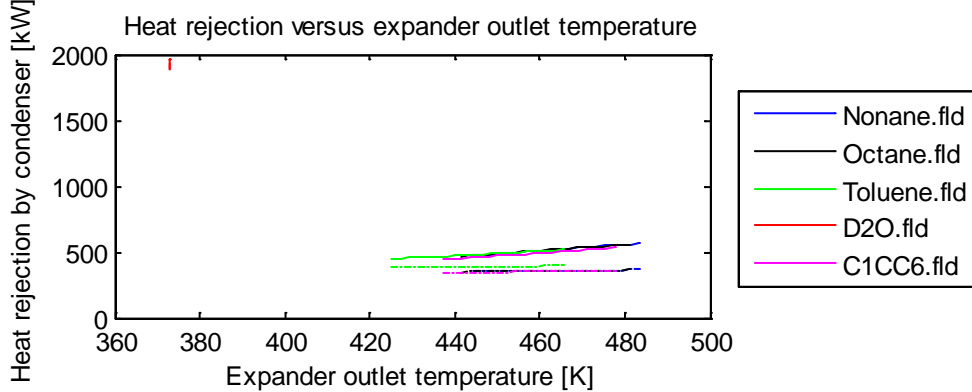
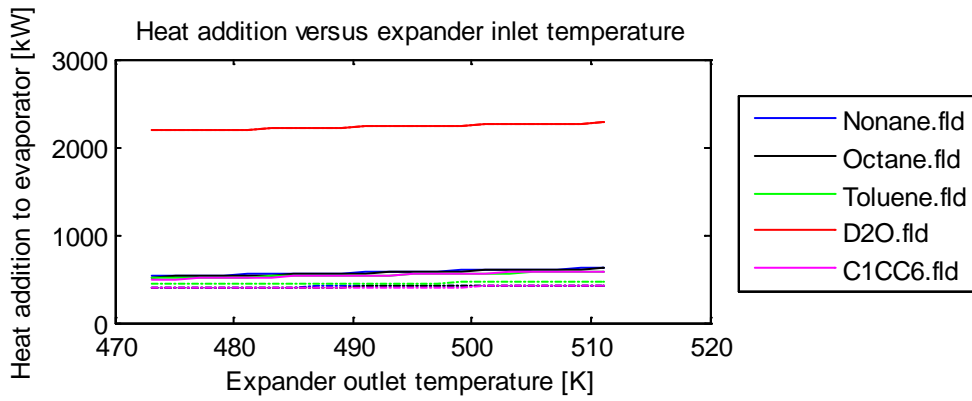
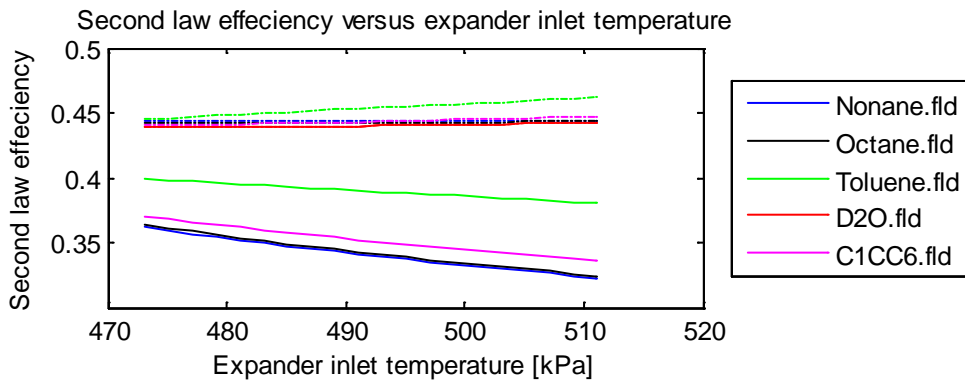
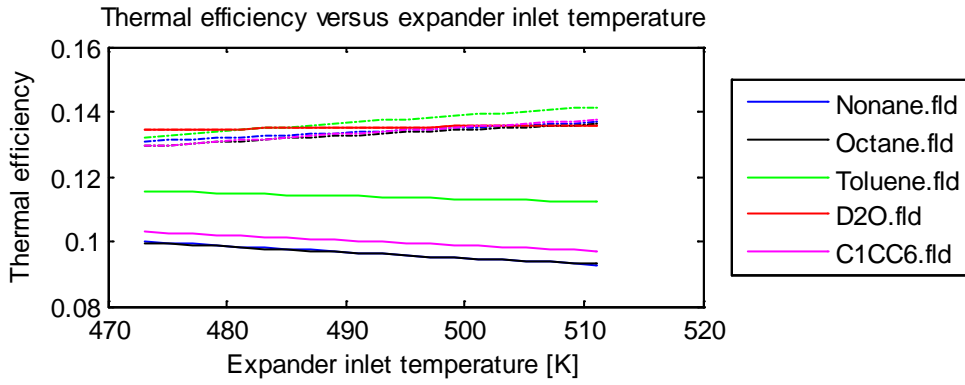


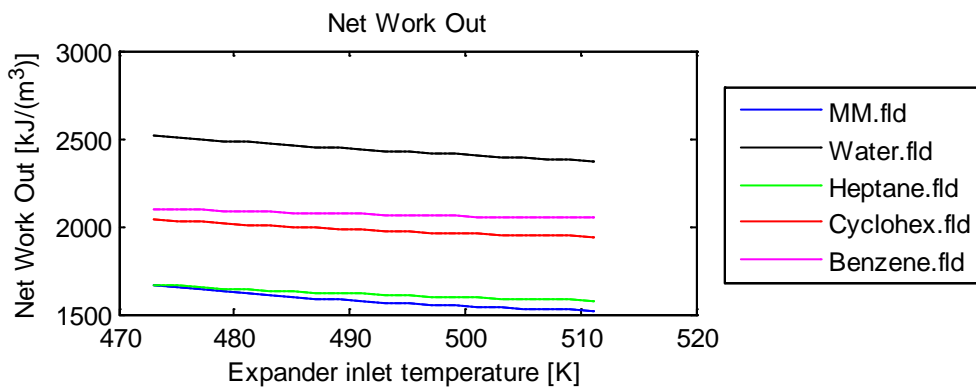
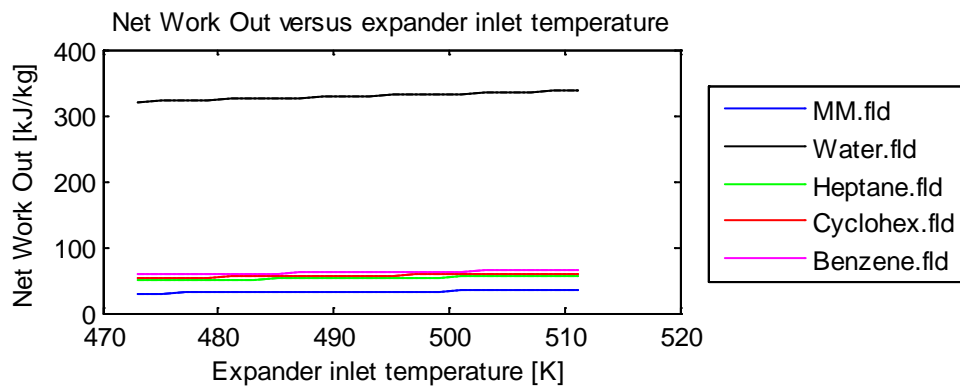
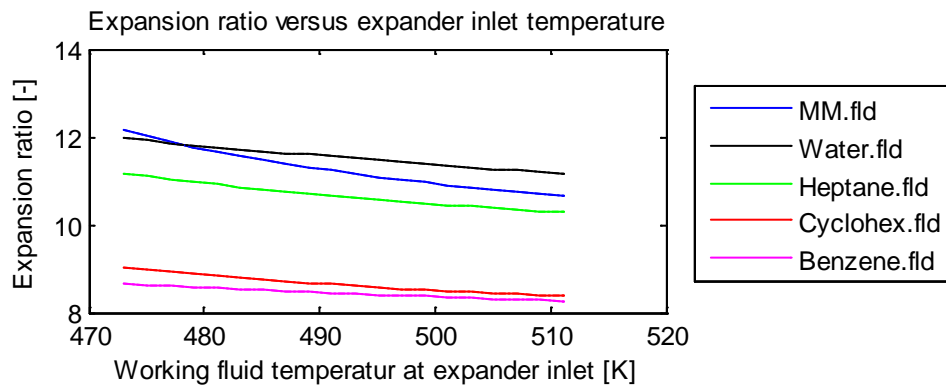
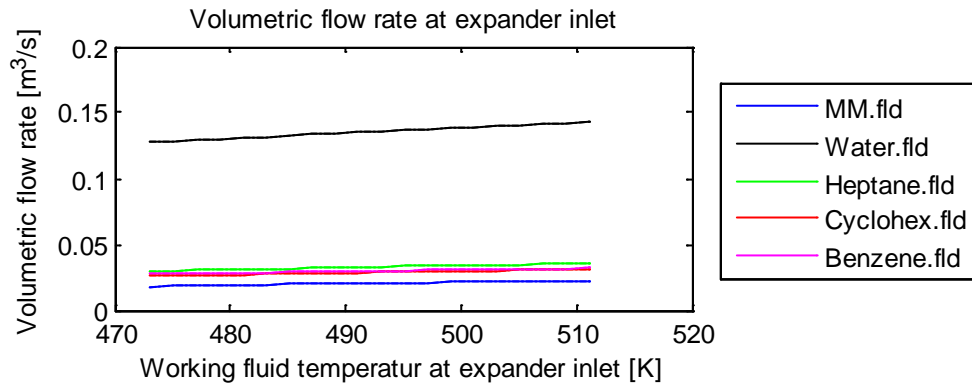


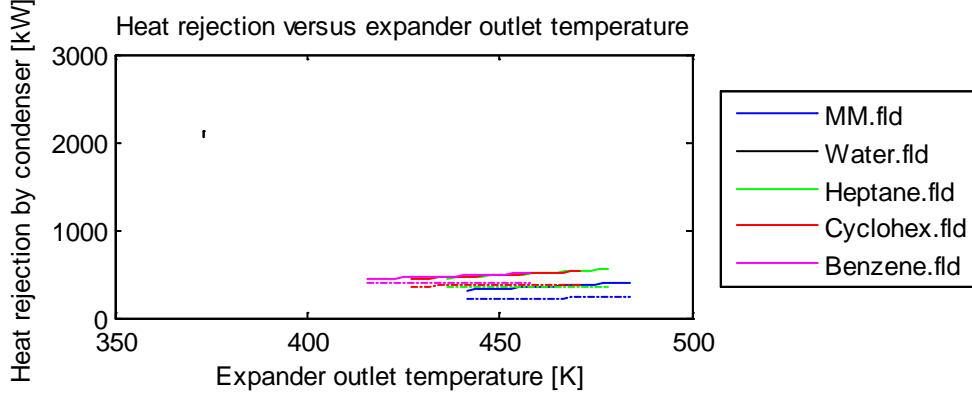
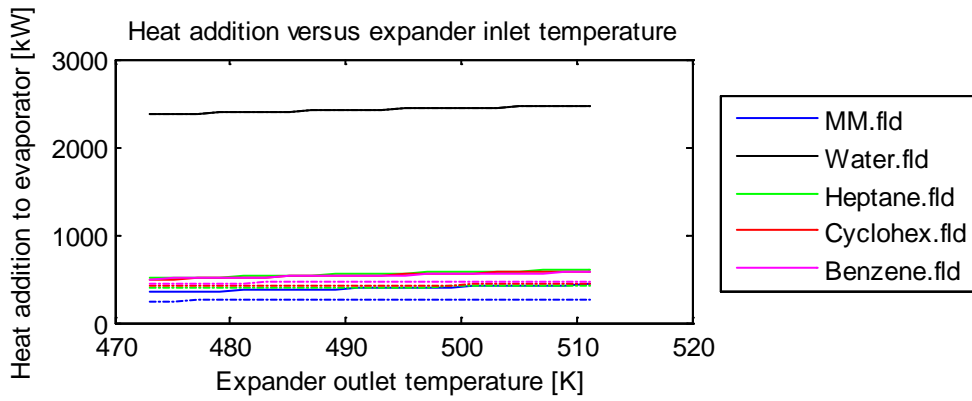
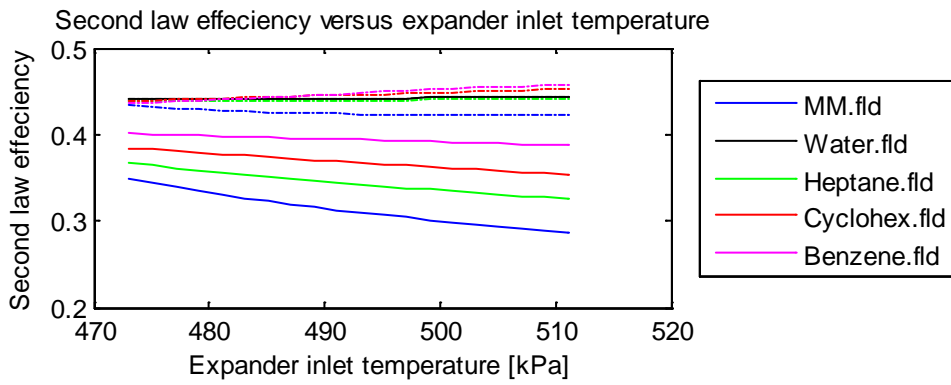
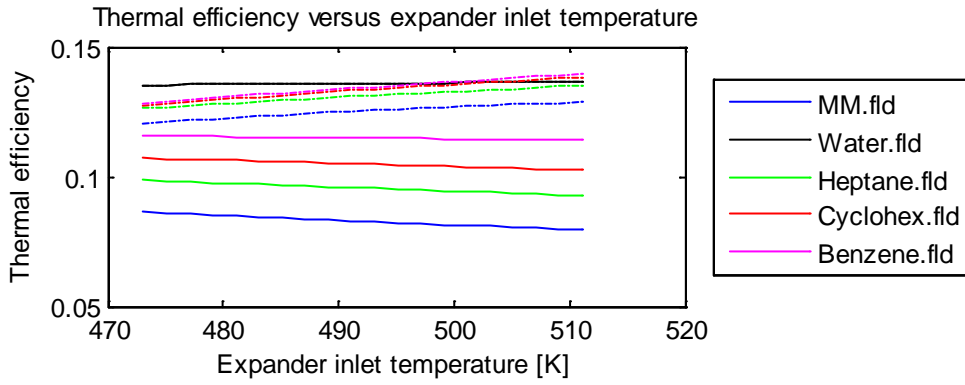


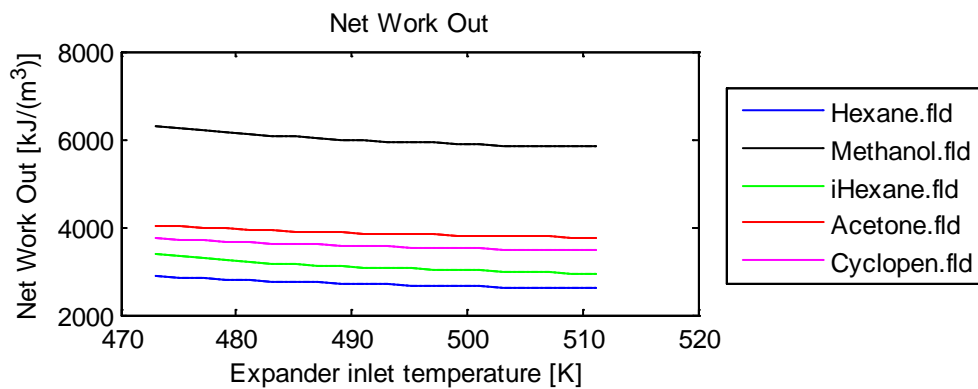
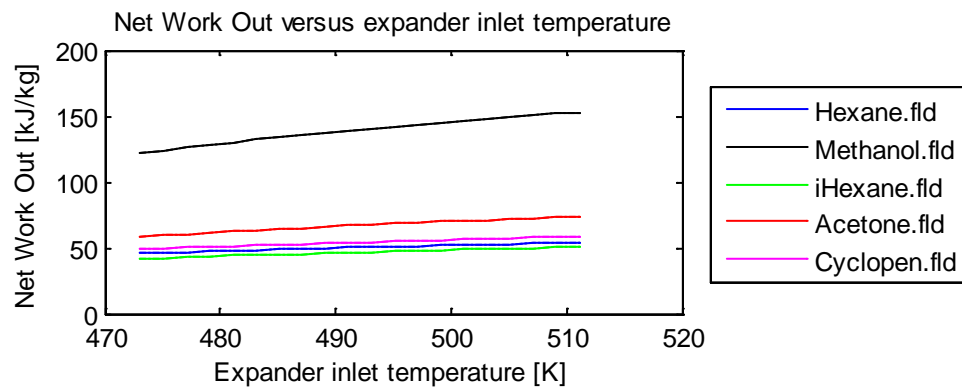
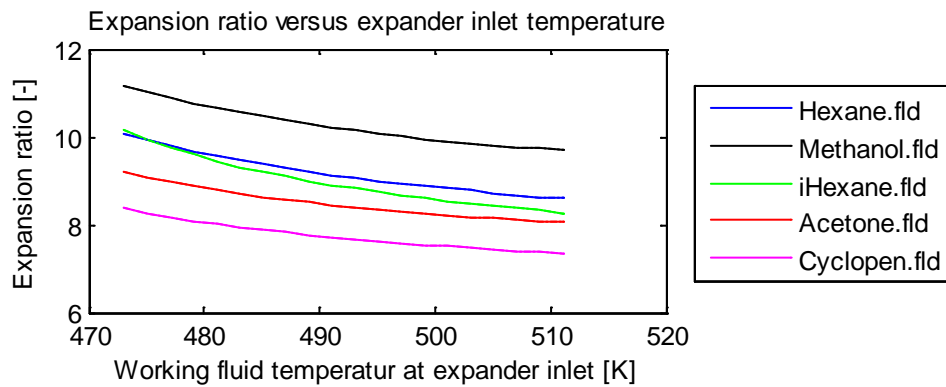
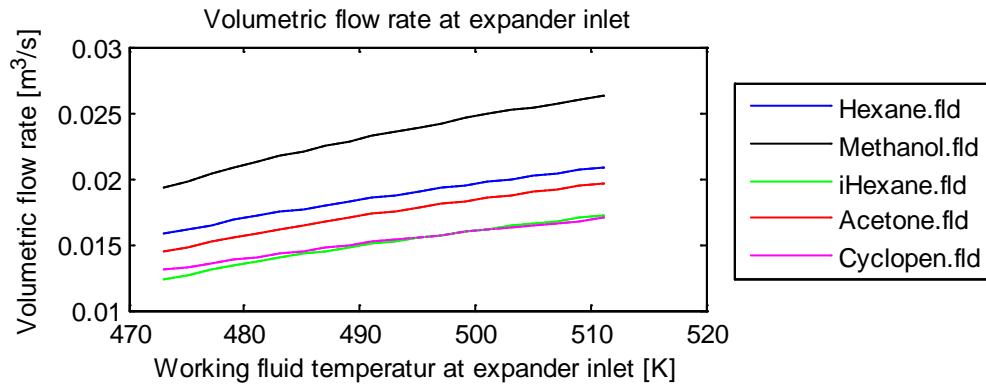


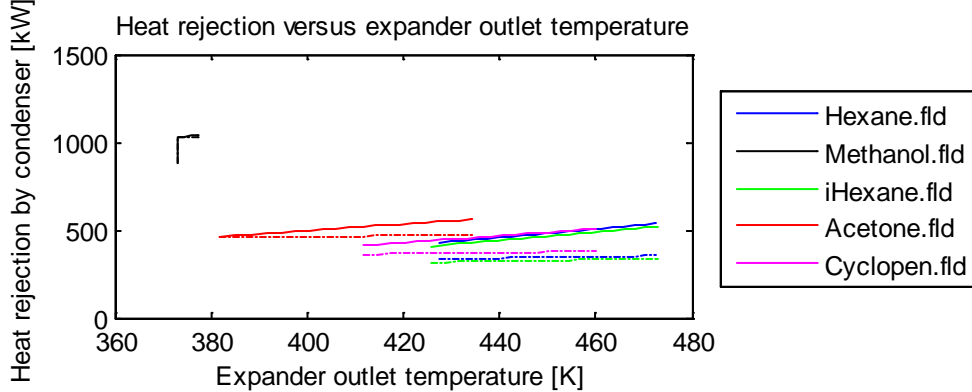
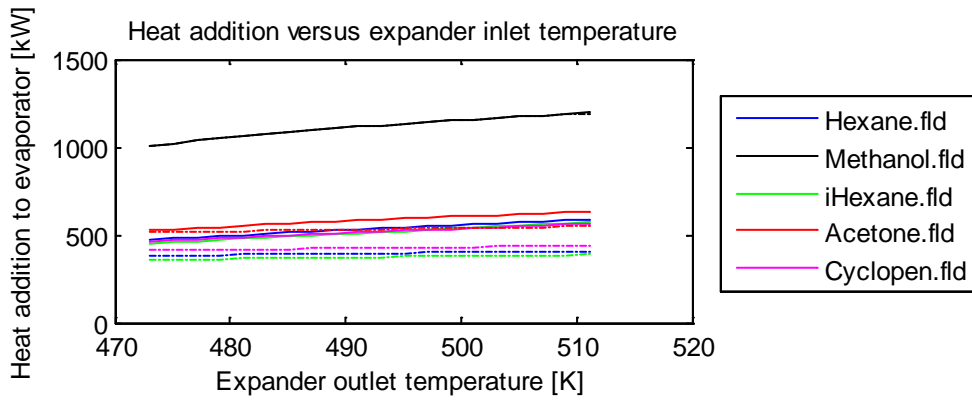
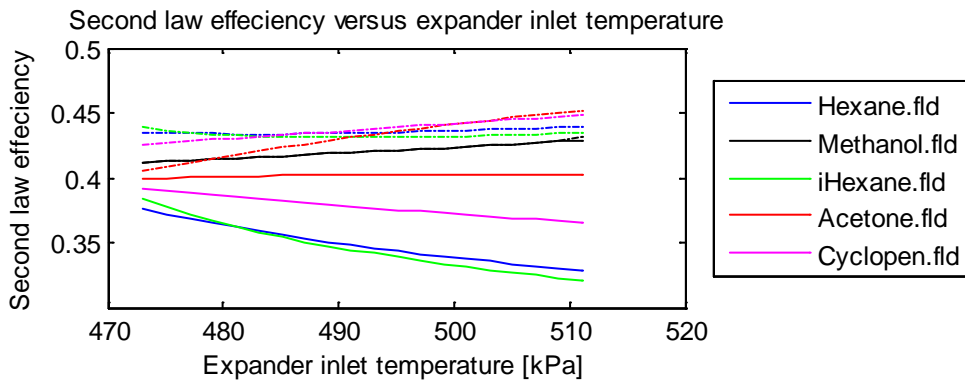
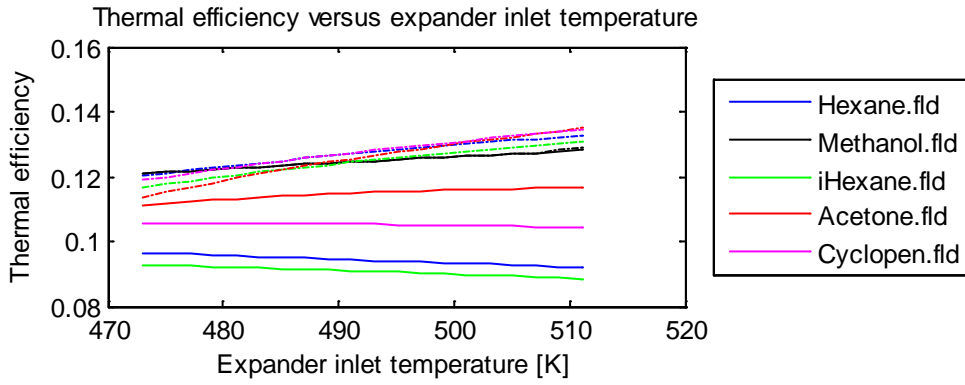


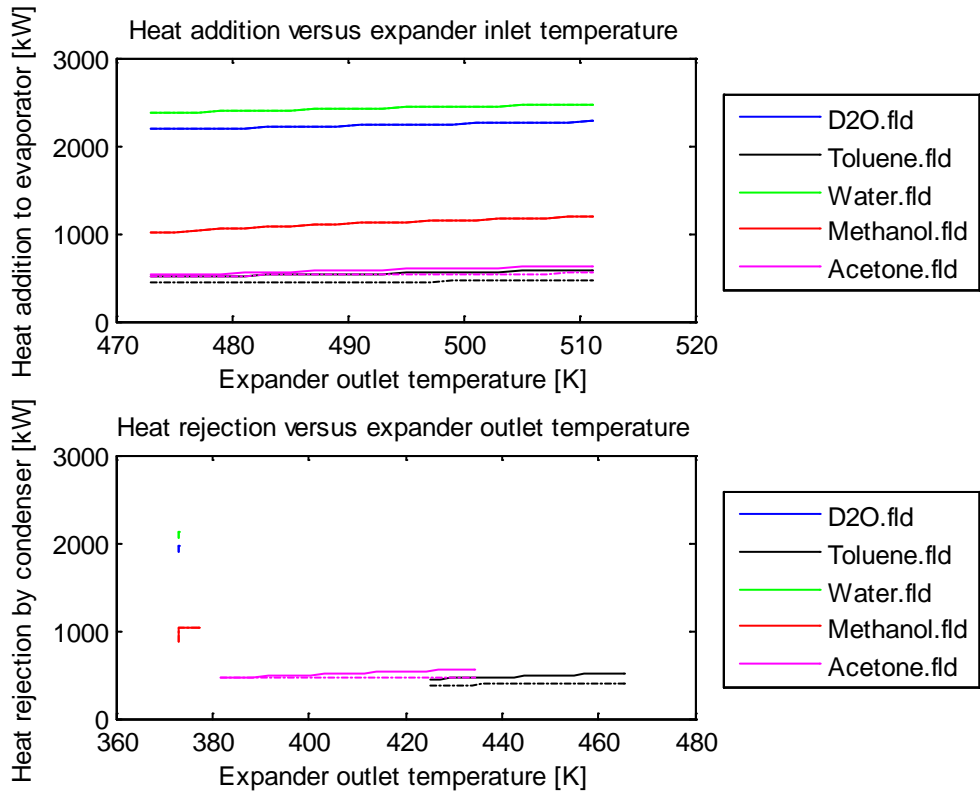




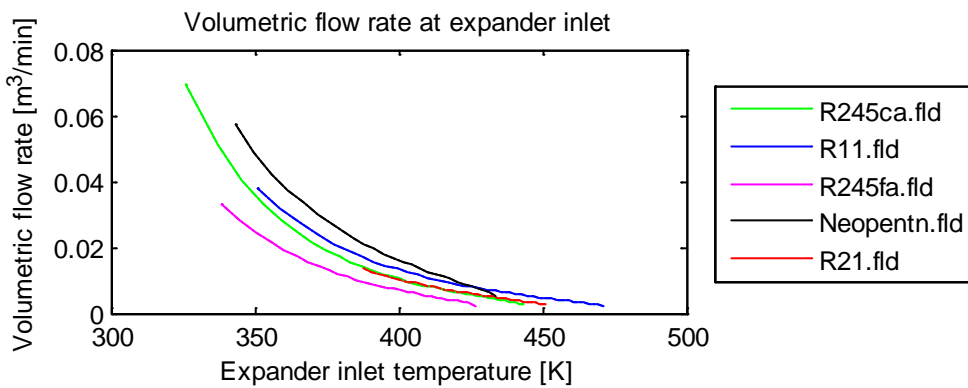
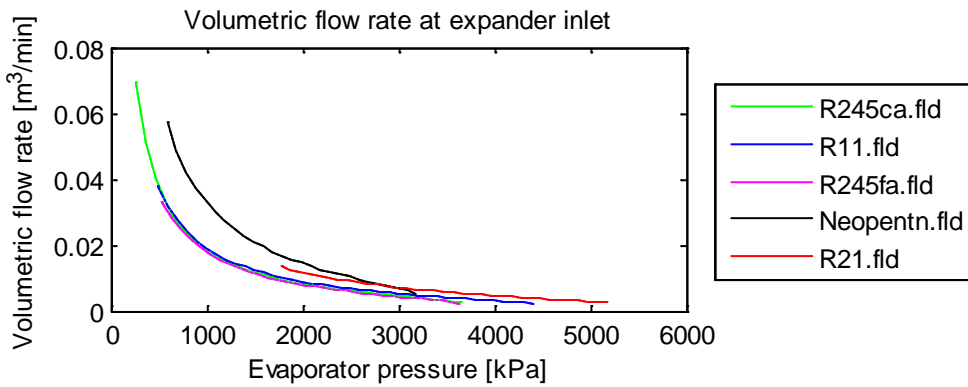
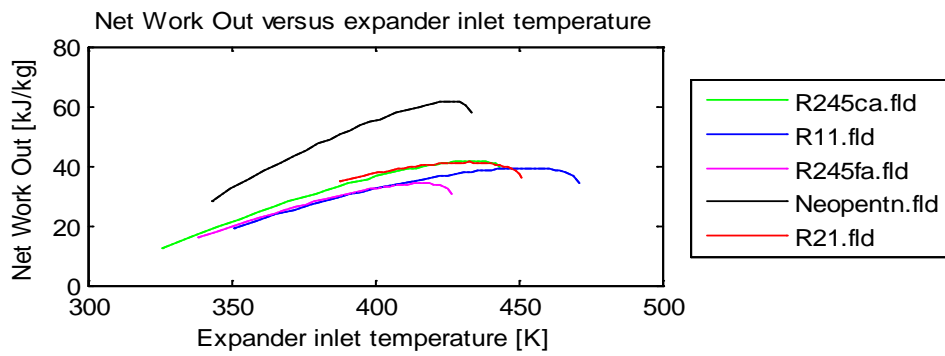
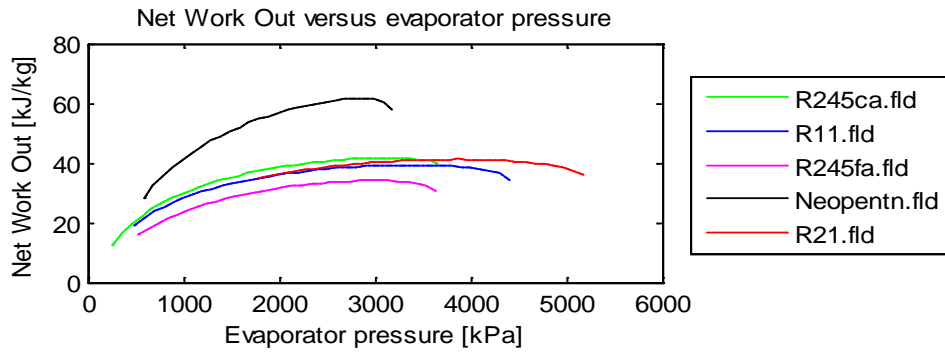


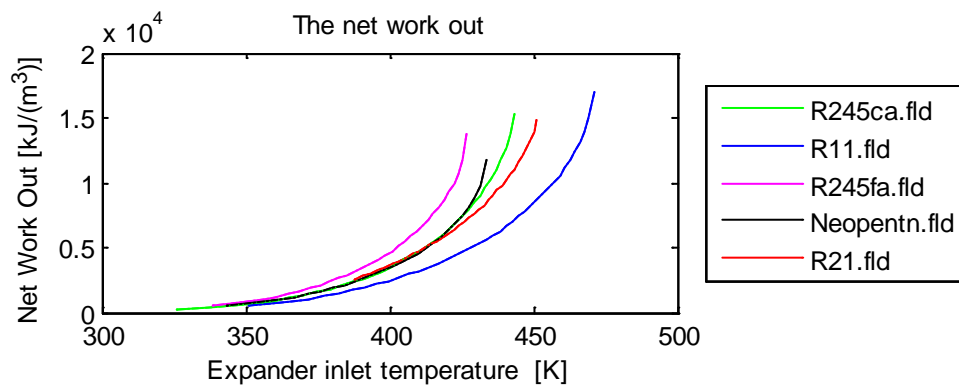
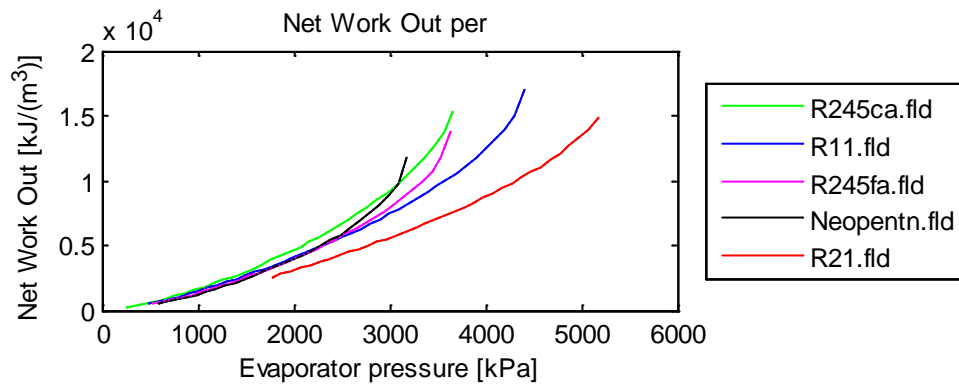
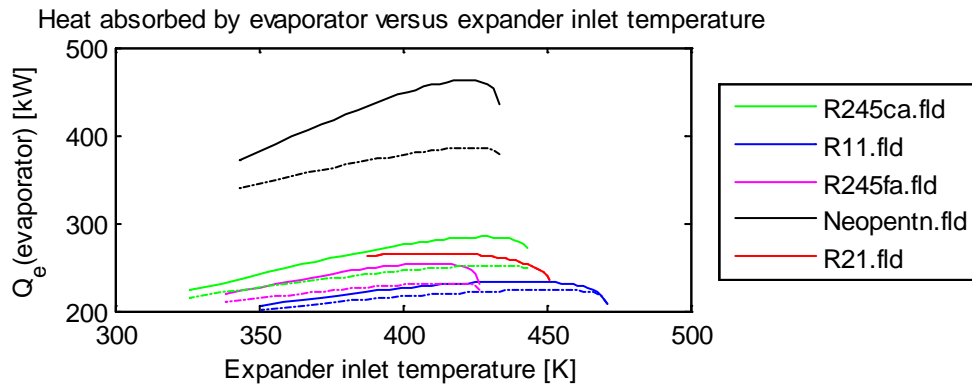
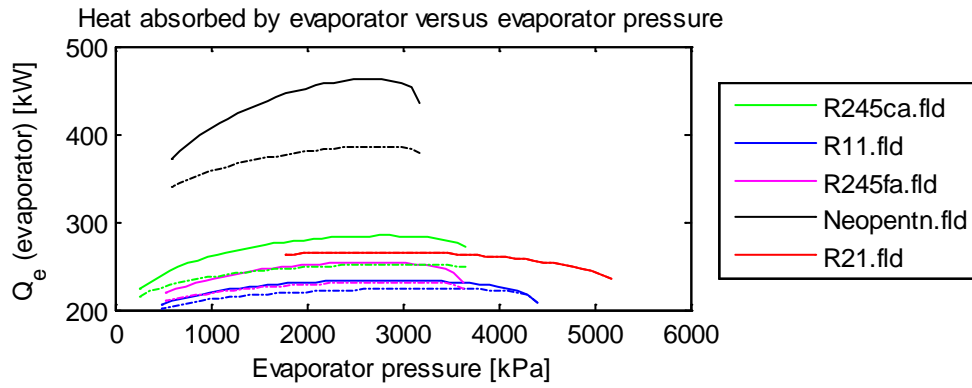


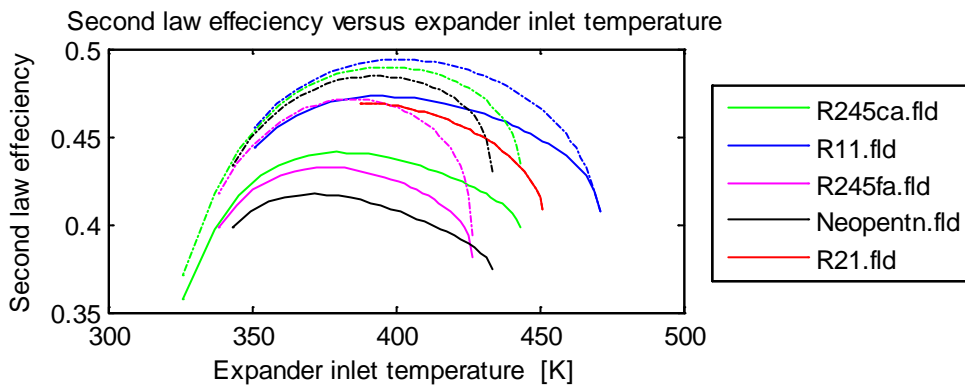
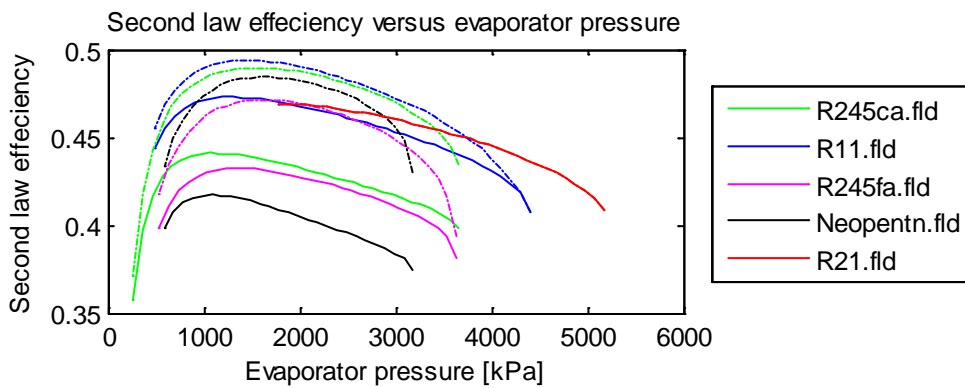
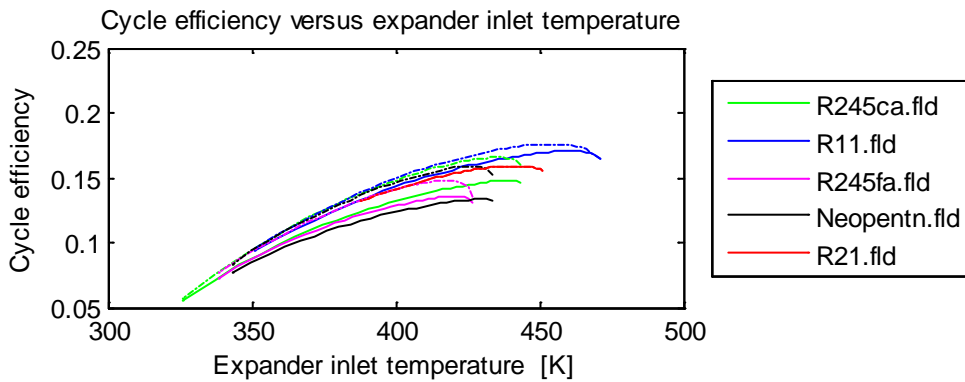
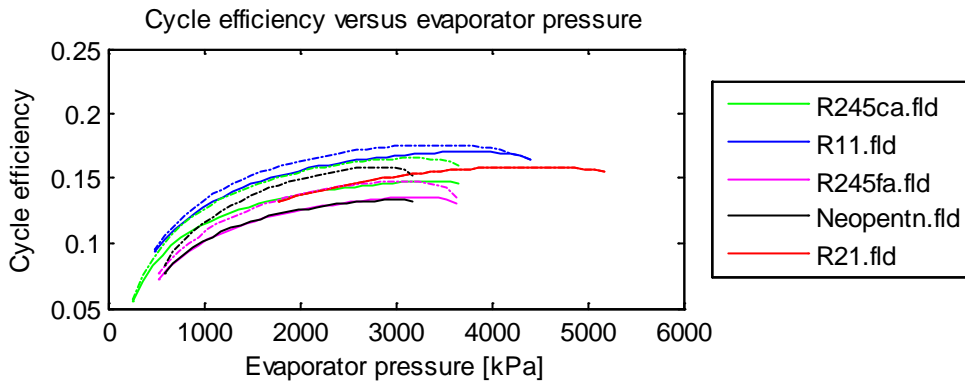


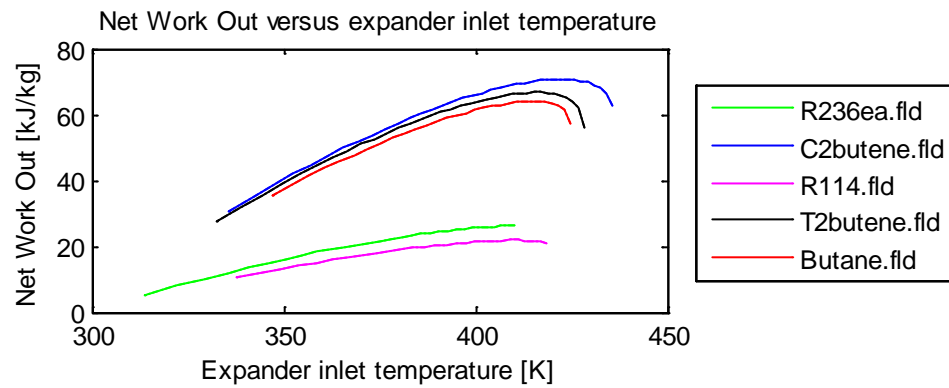
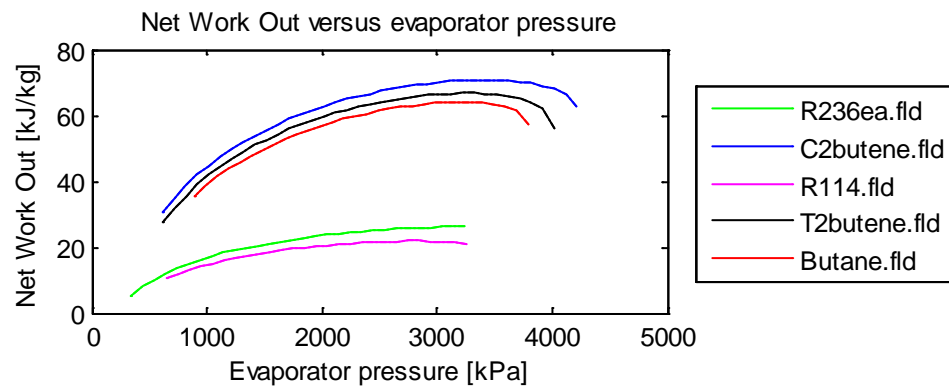
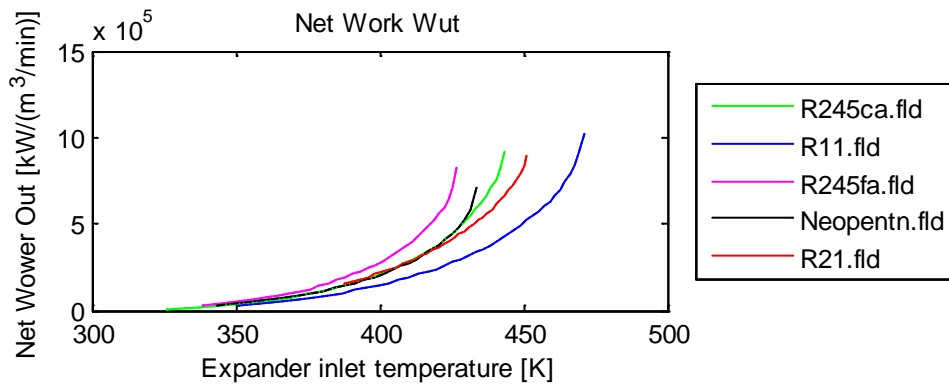
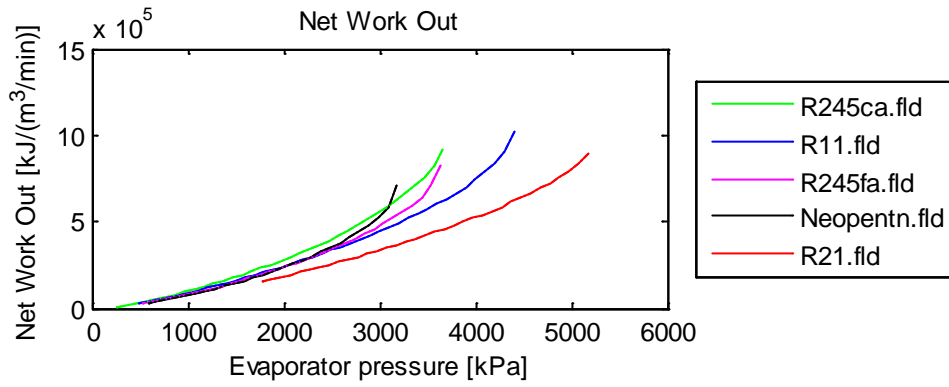


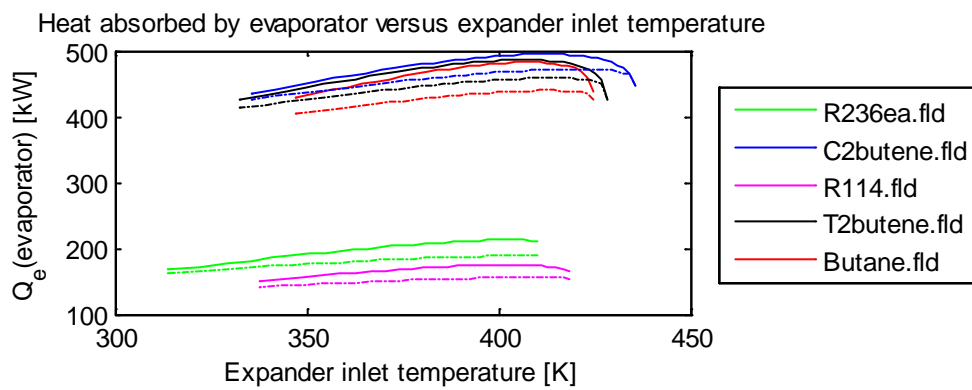
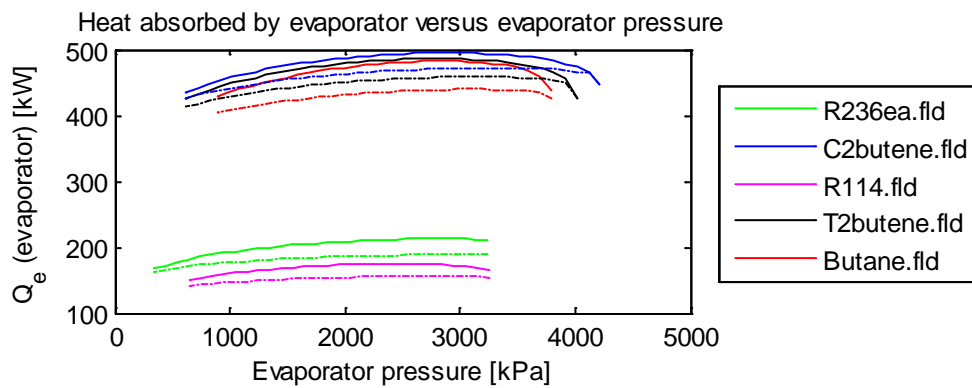
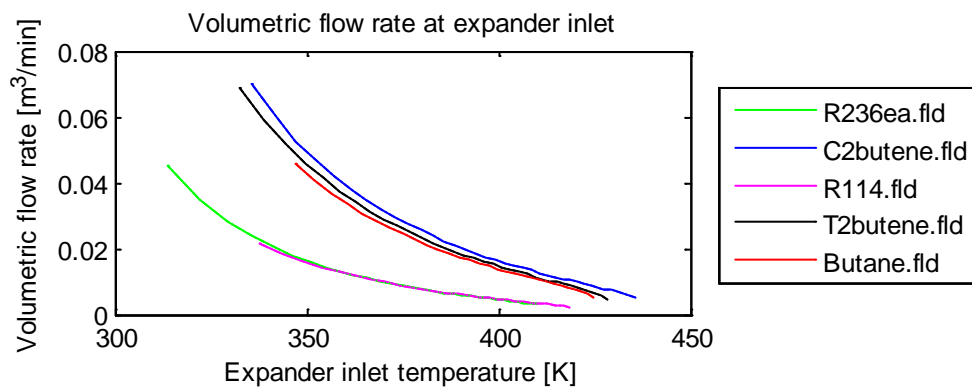
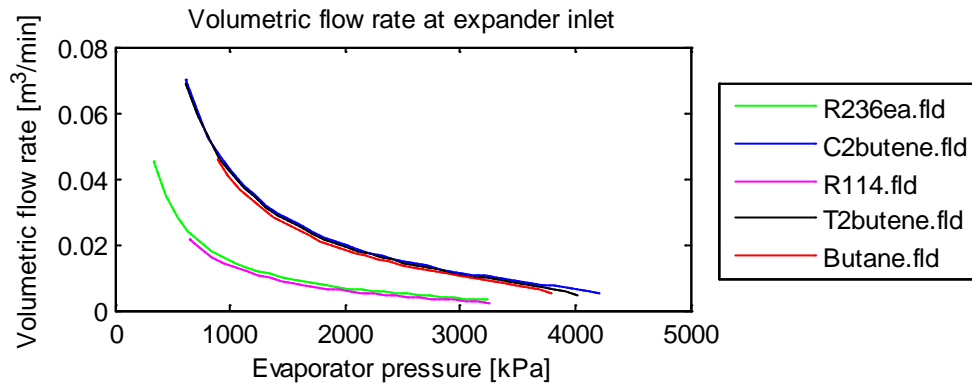
Scenario 3

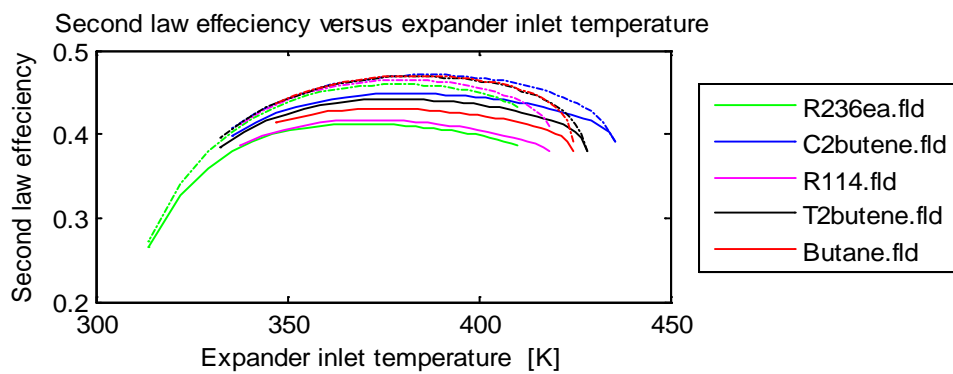
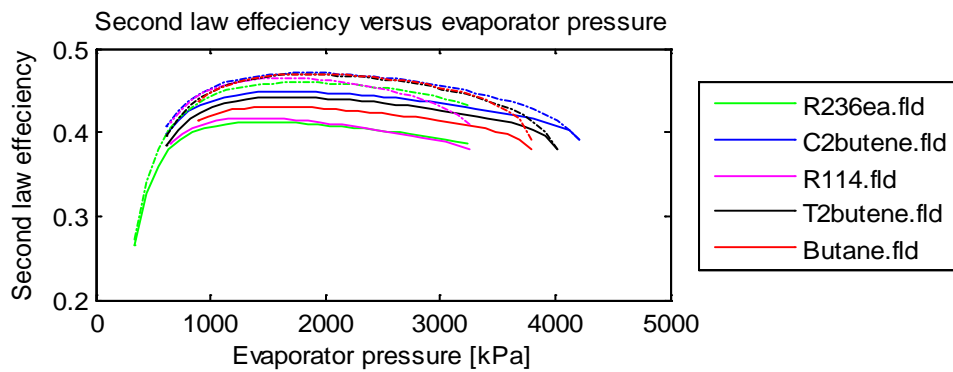
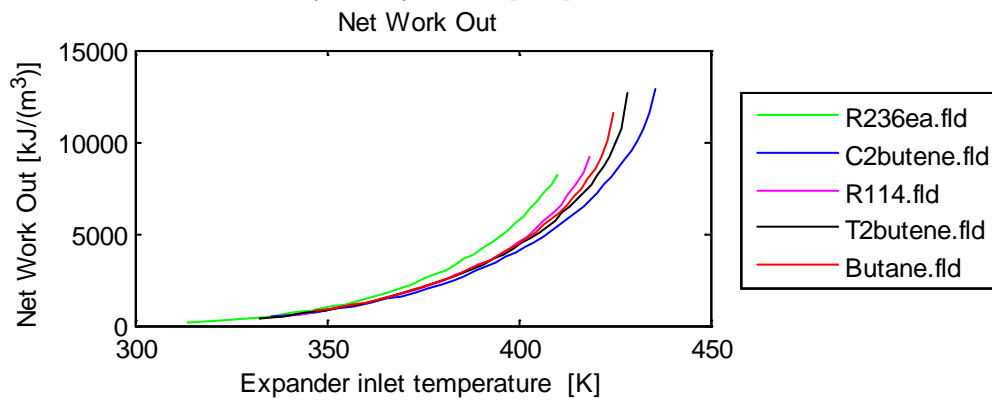
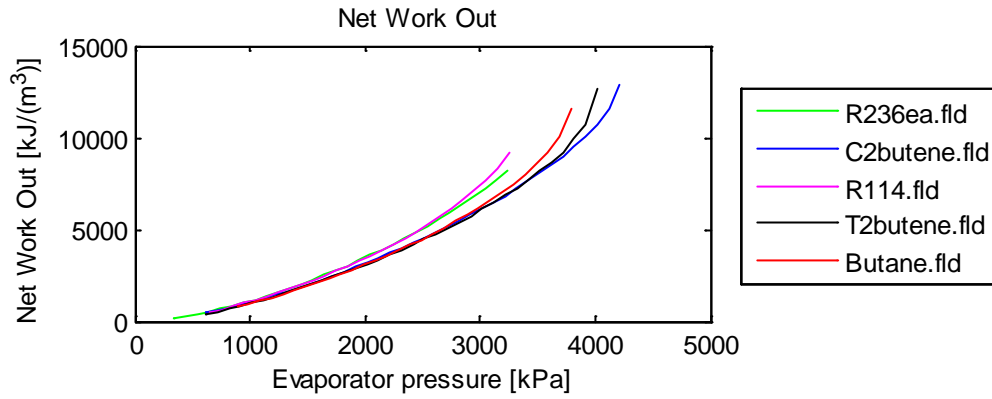


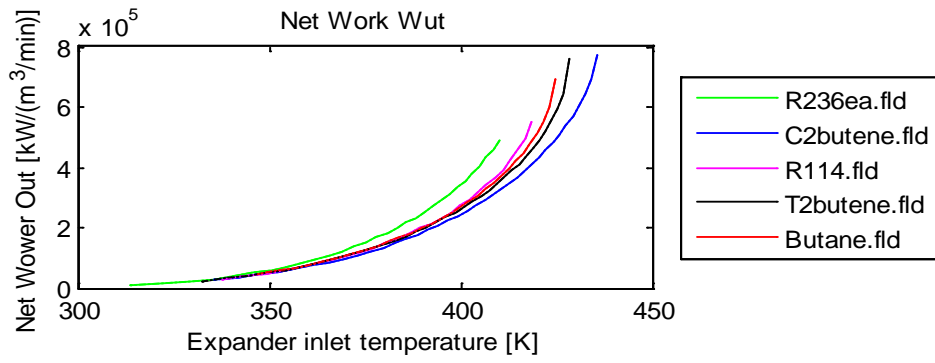
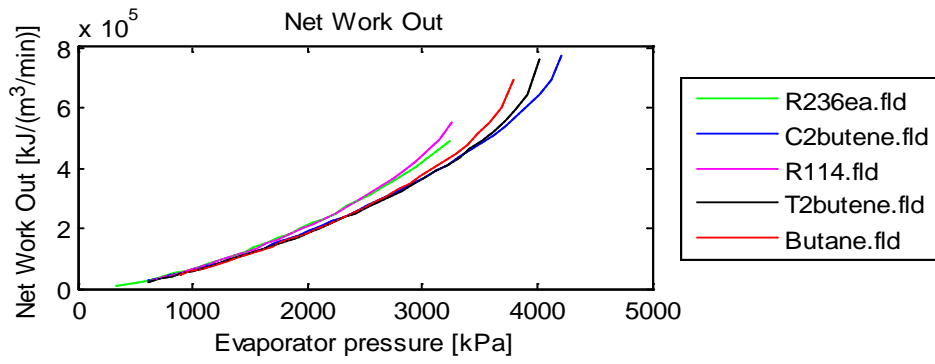


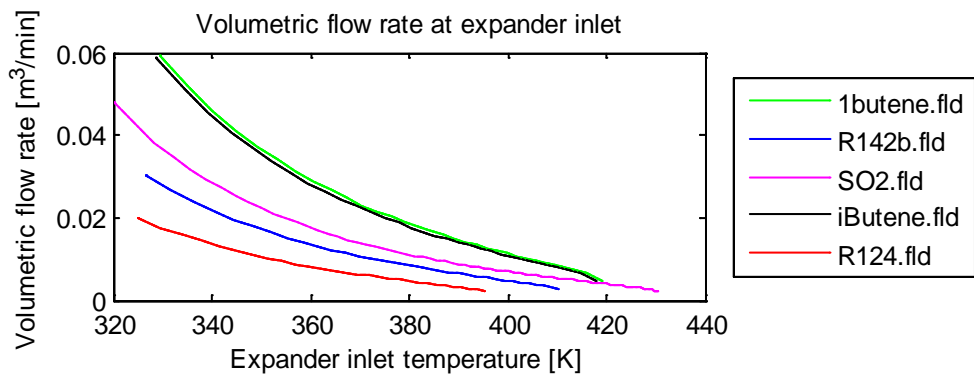
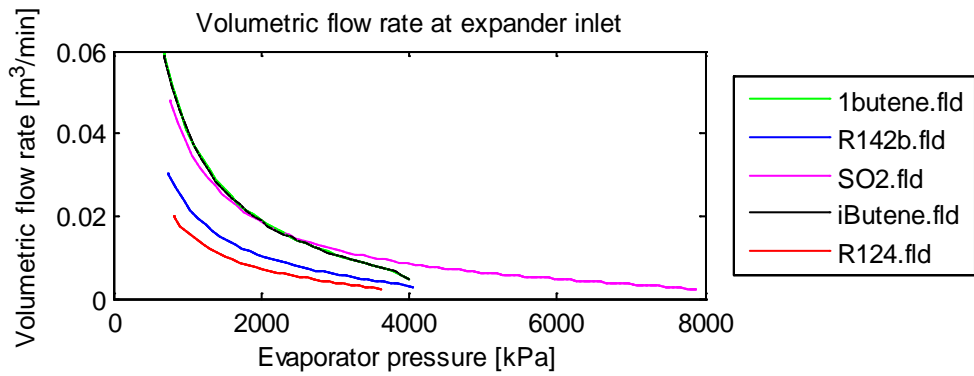
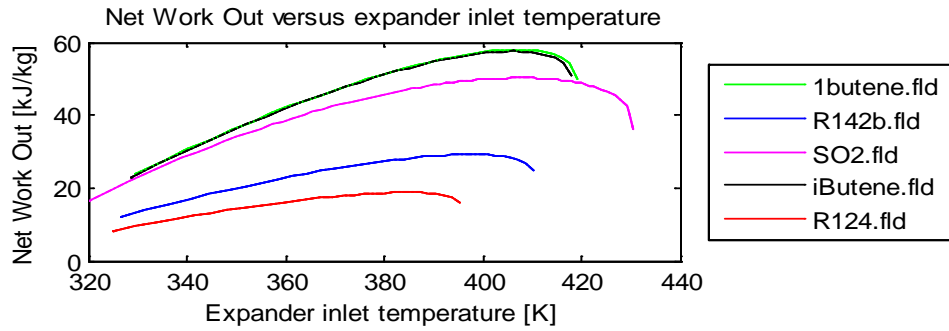
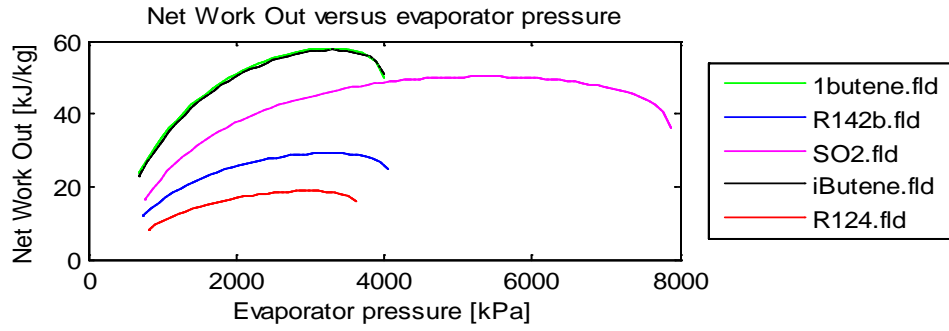


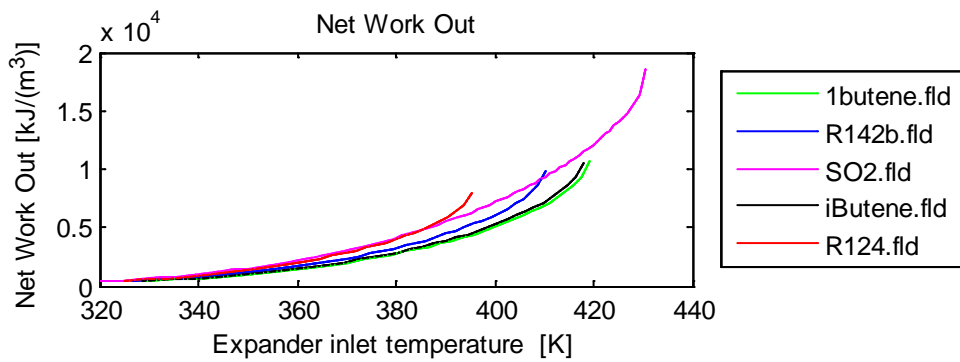
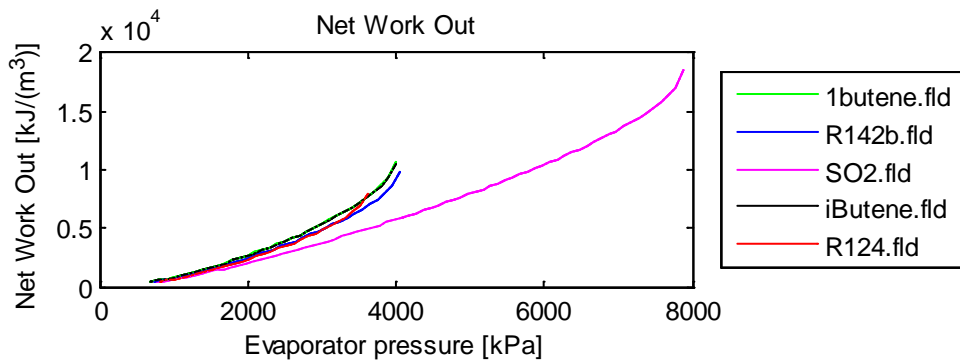
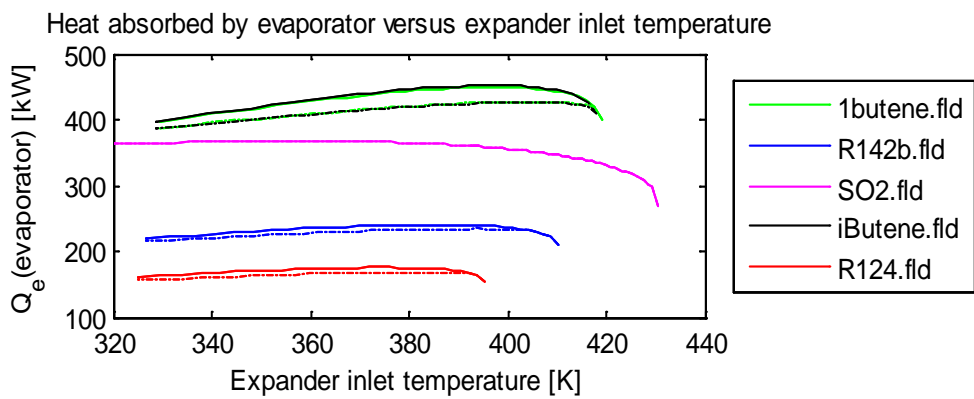
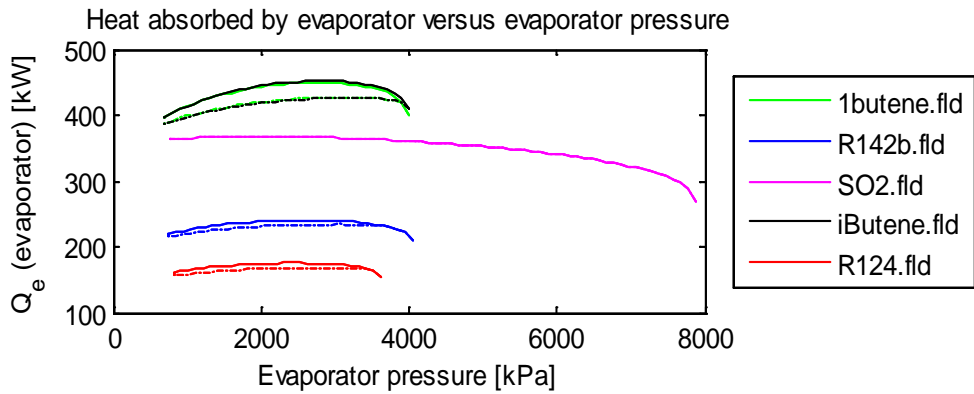


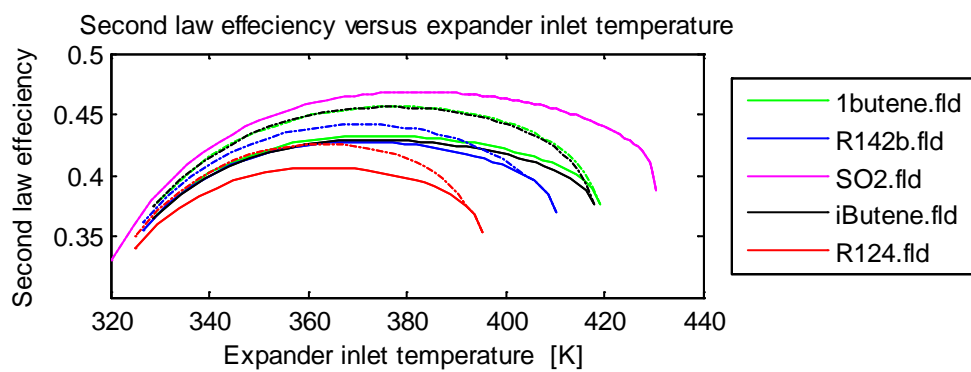
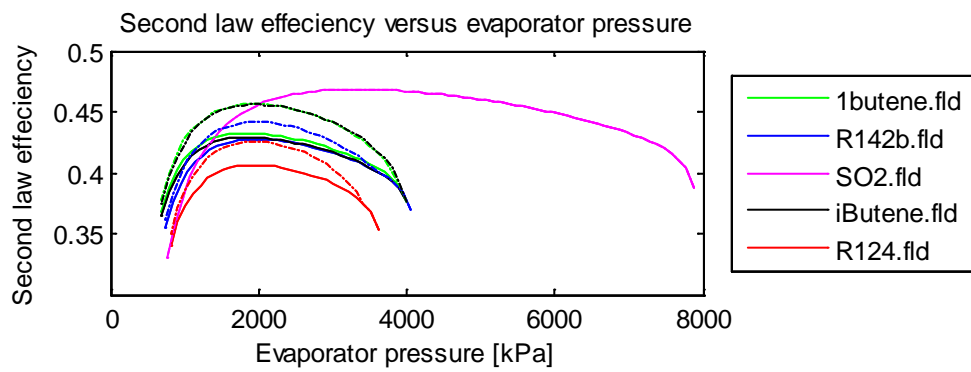
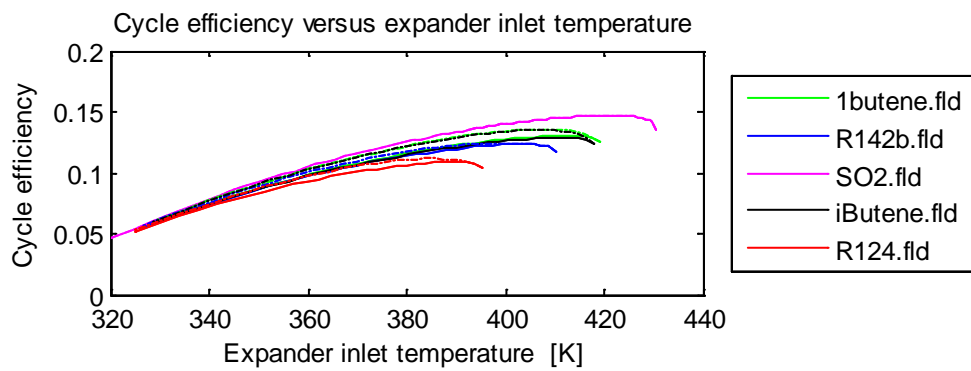
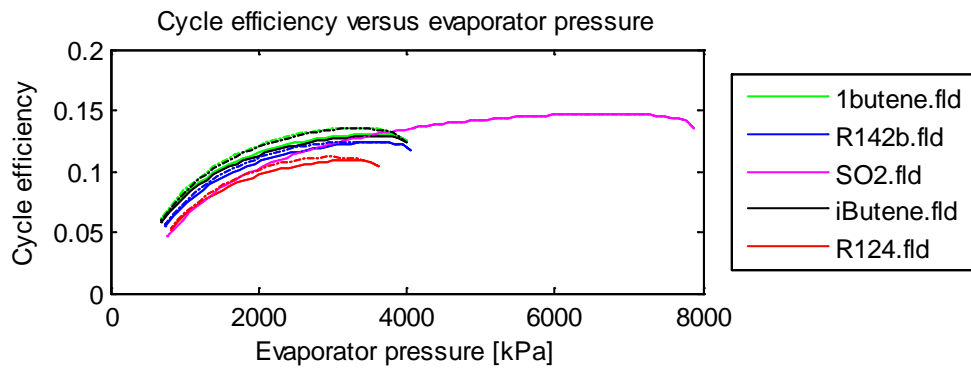


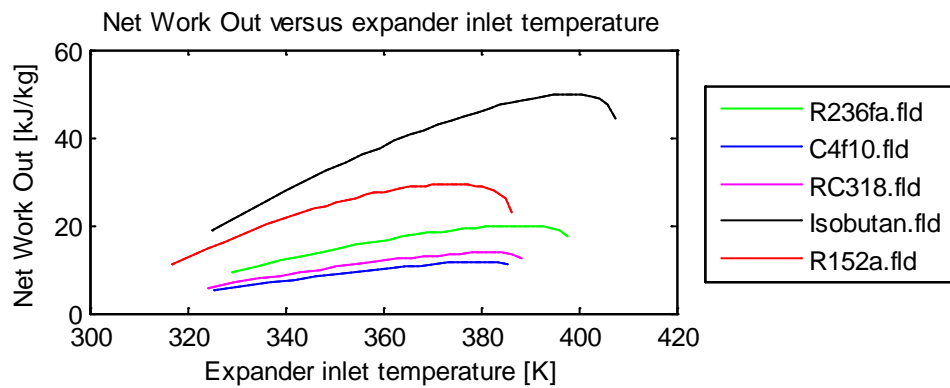
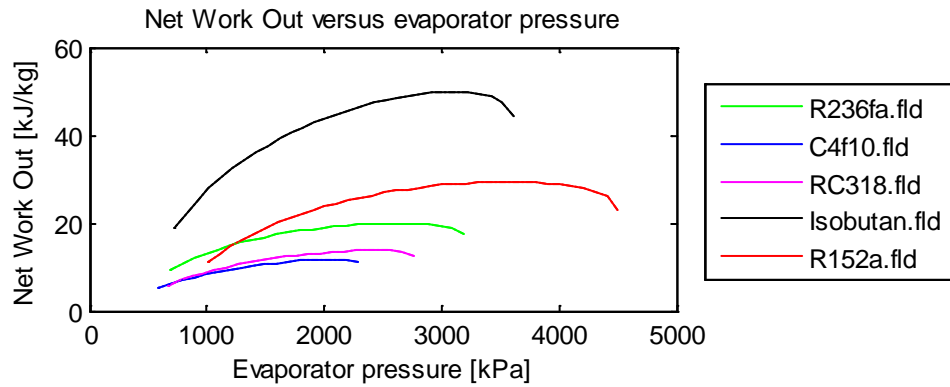
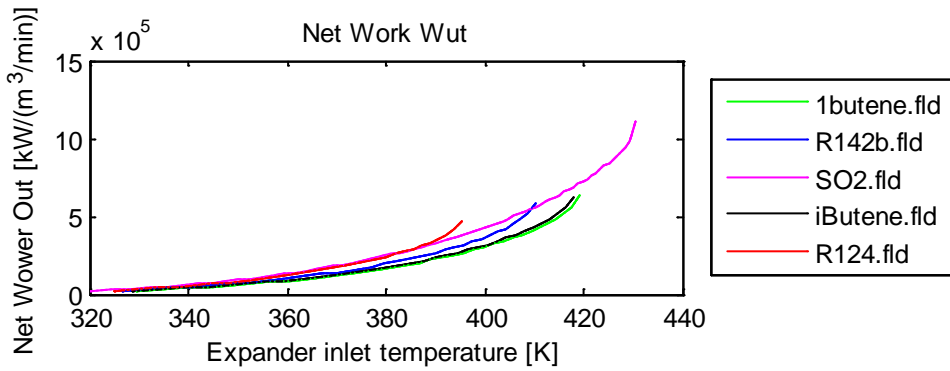
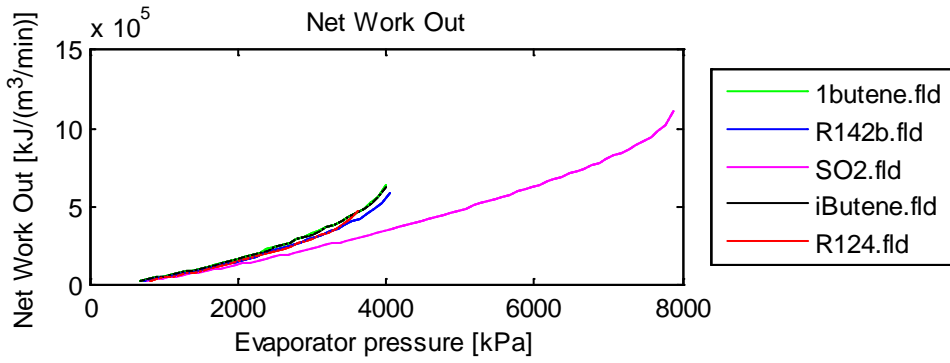


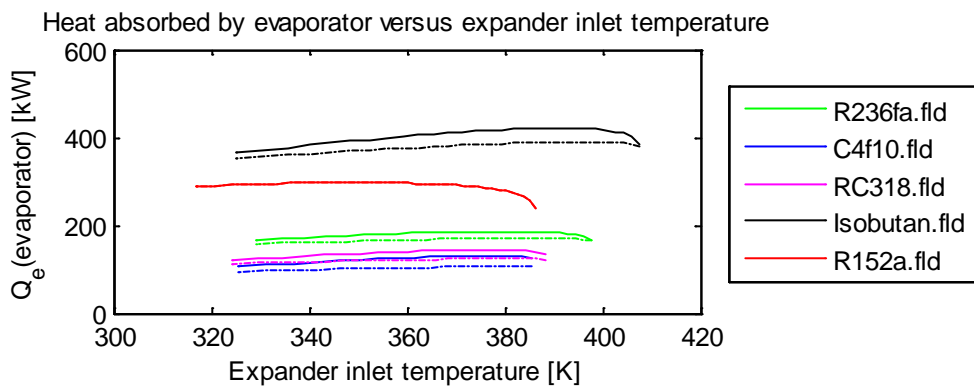
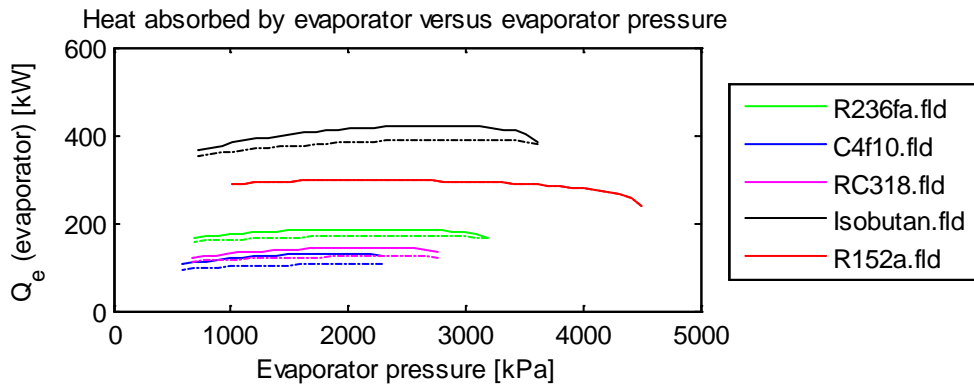
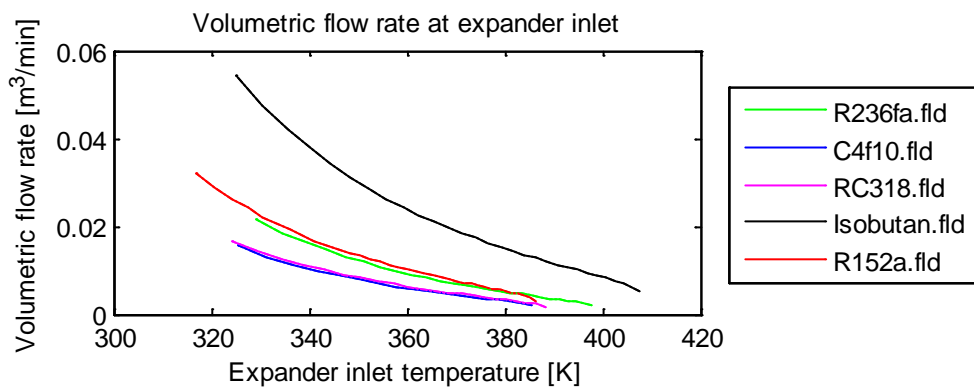
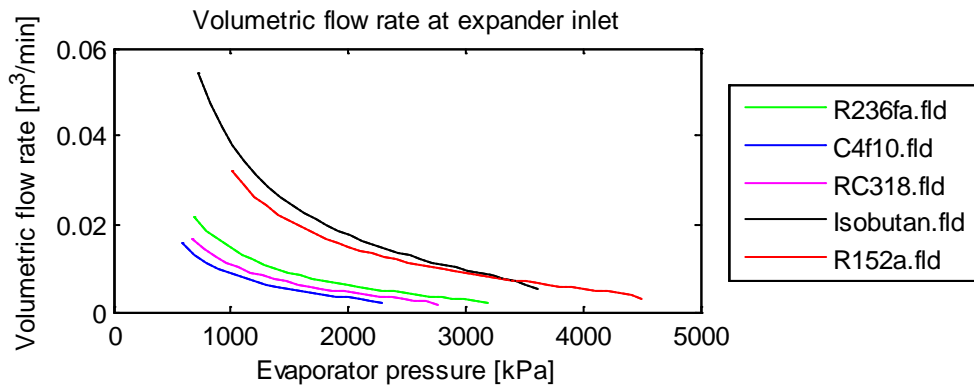


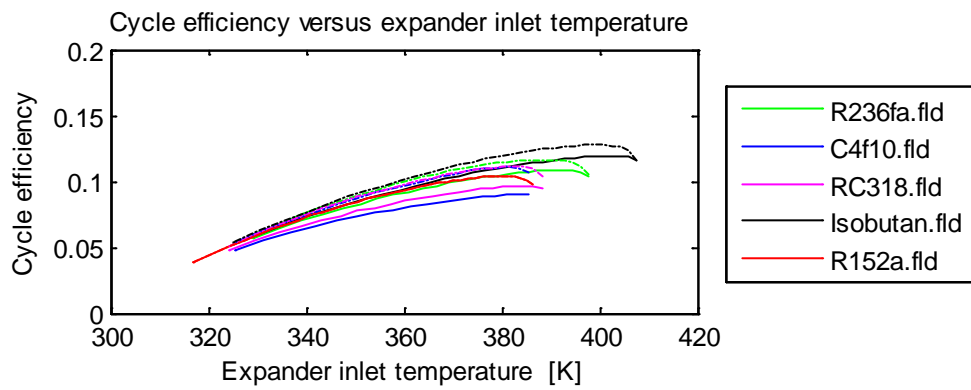
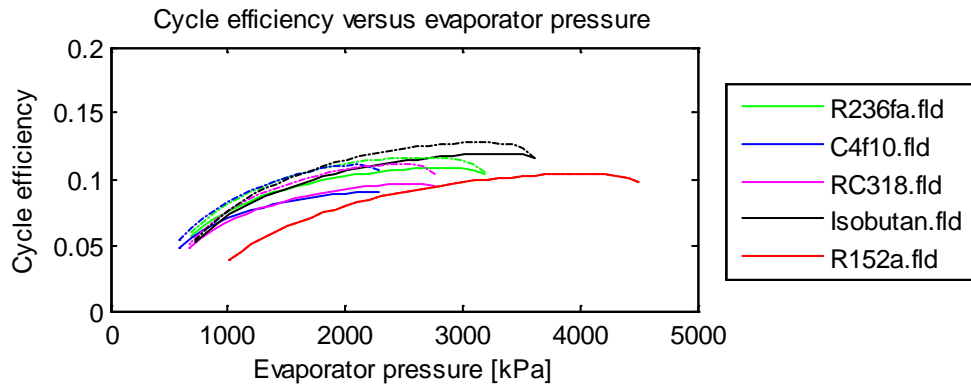
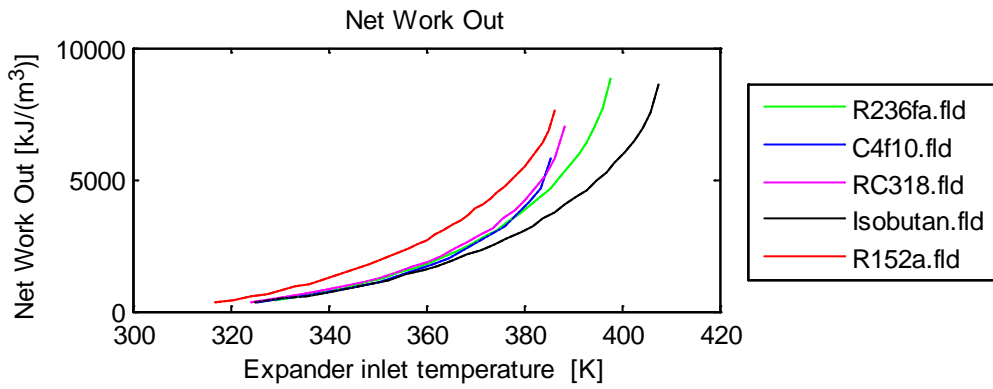
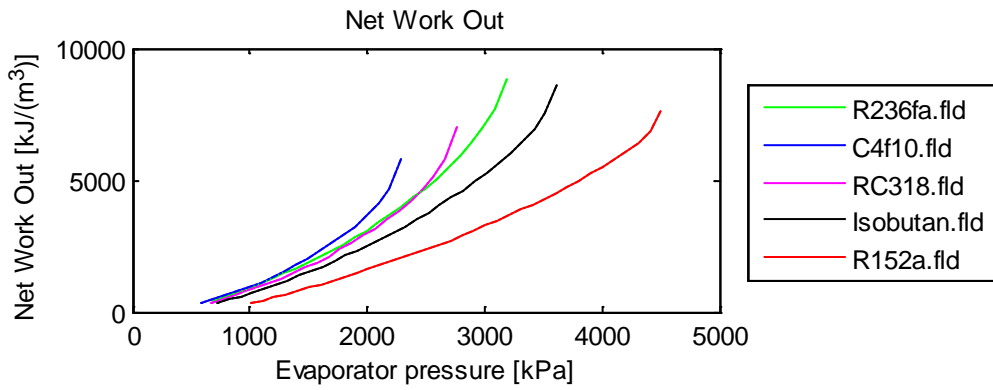


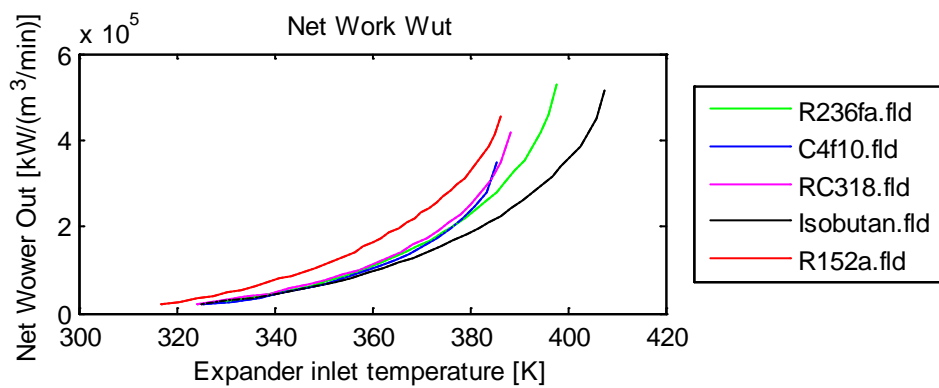
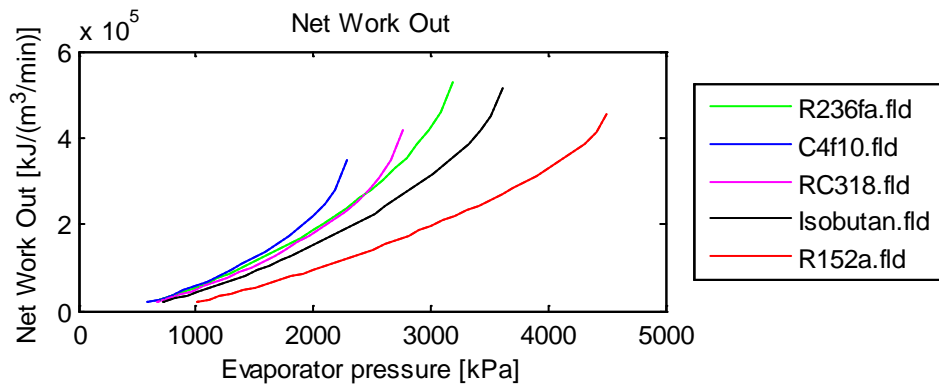
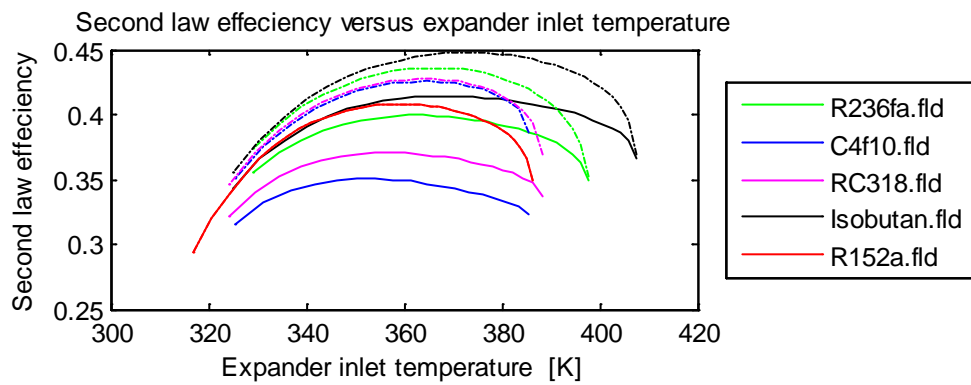
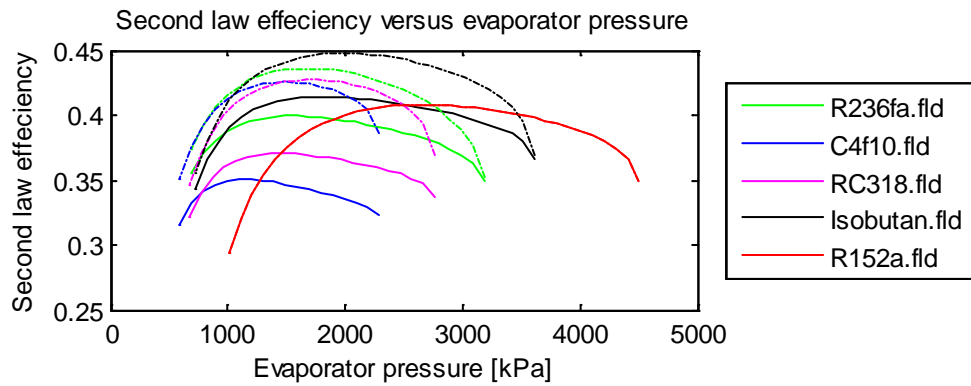


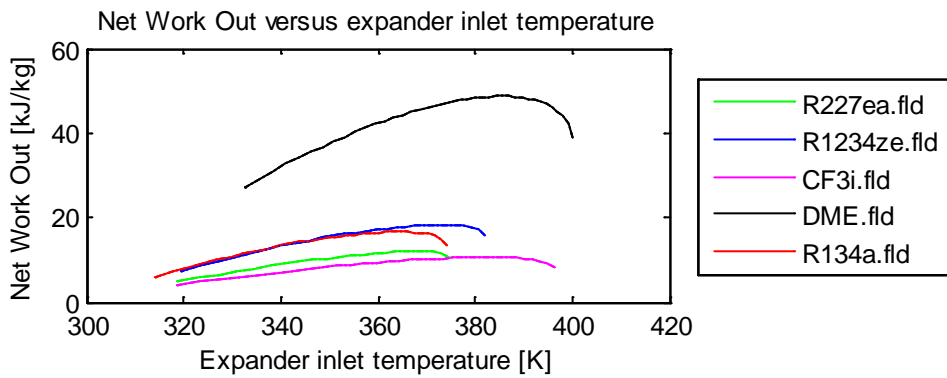
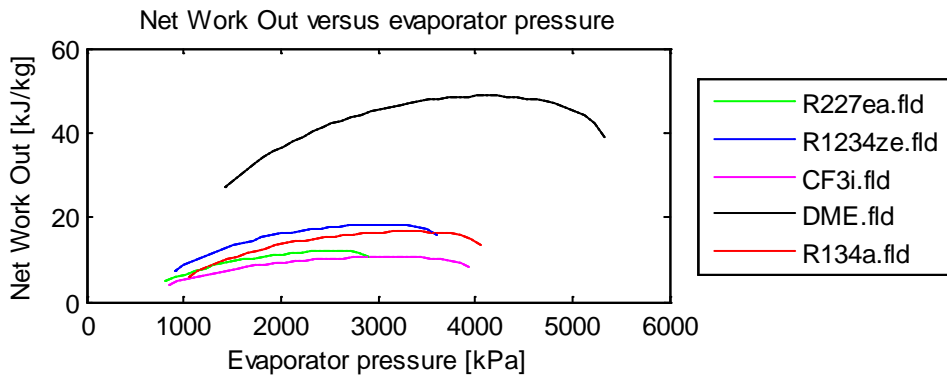
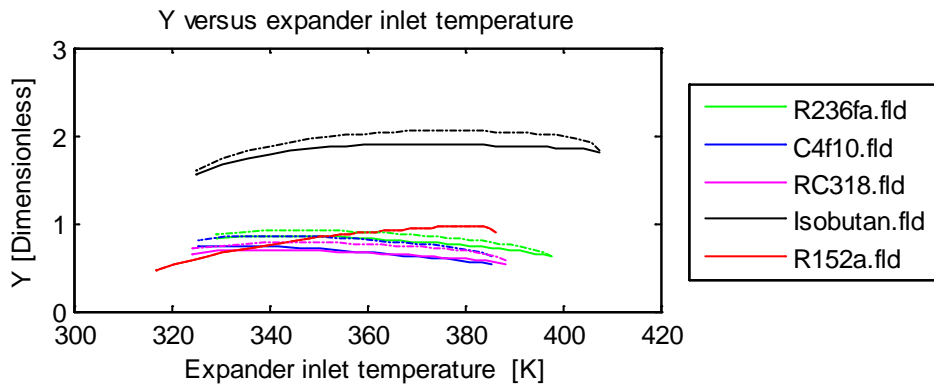
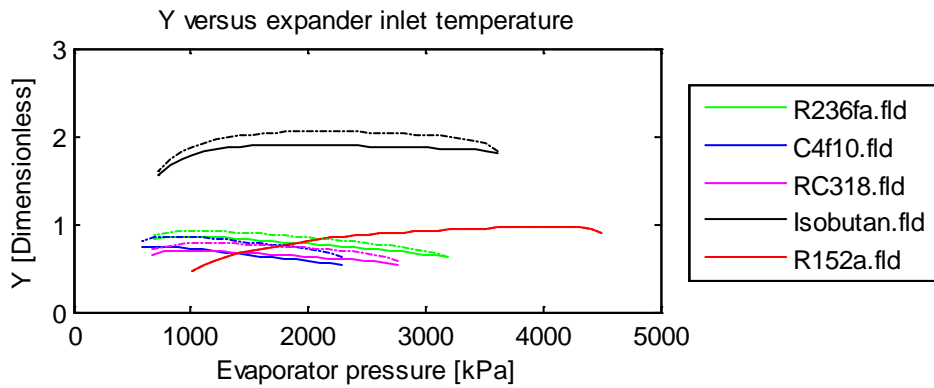


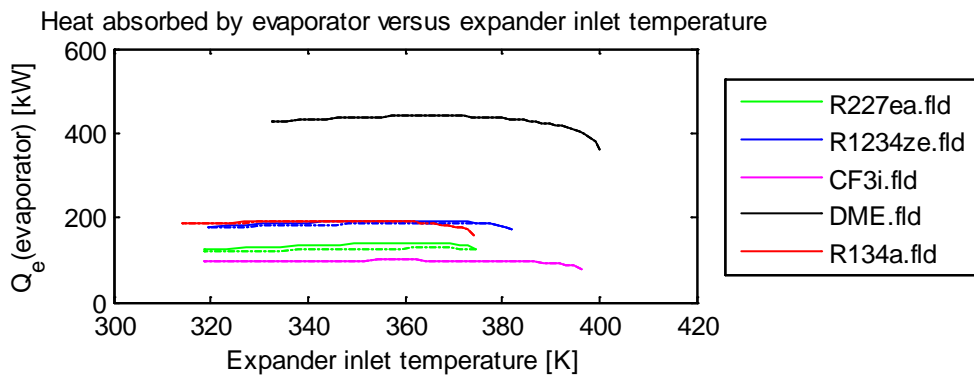
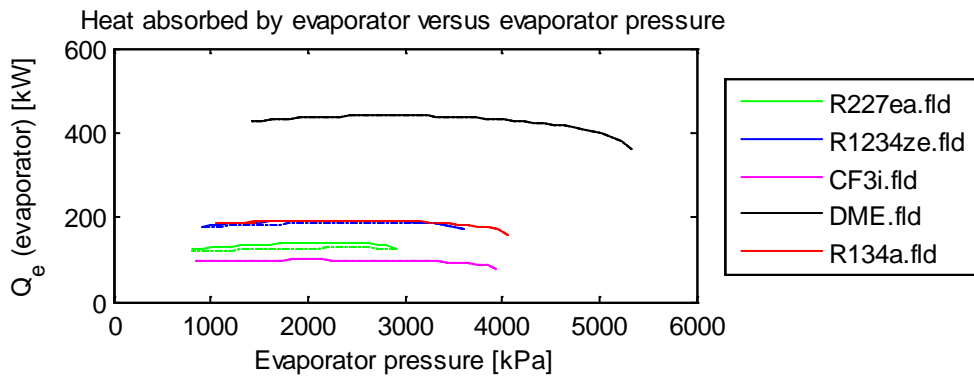
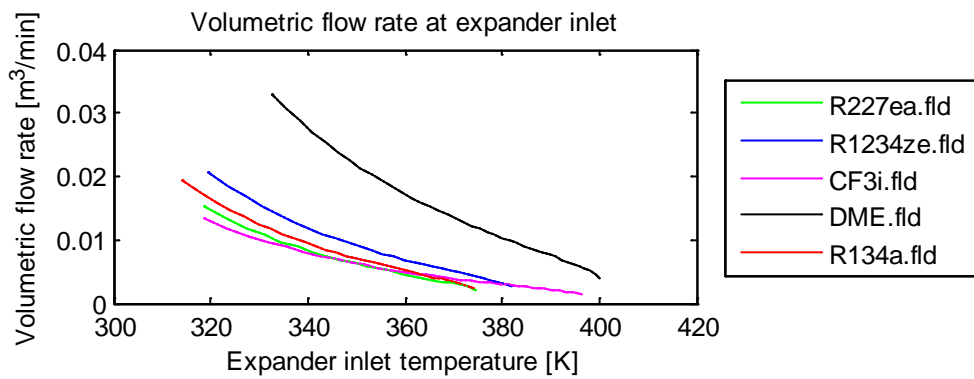
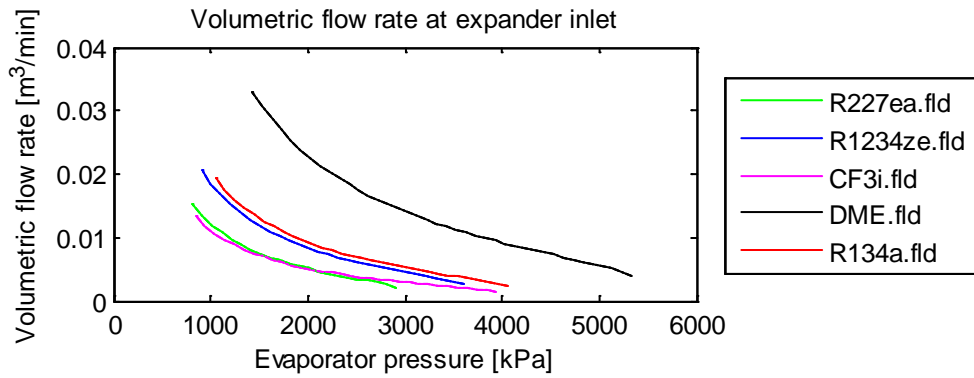


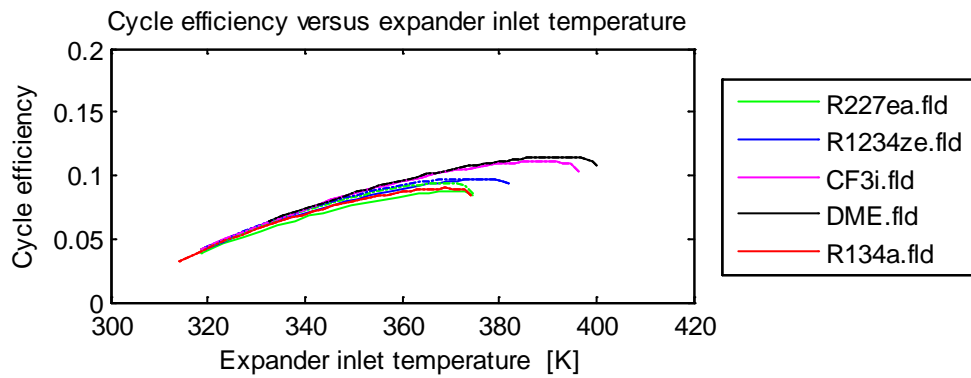
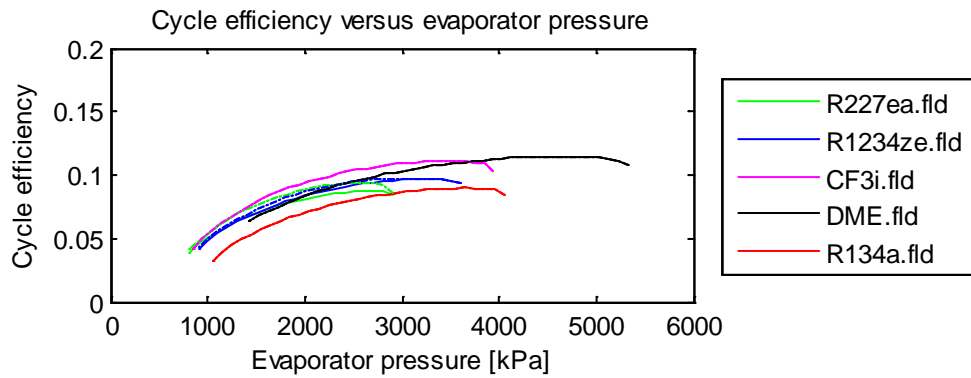
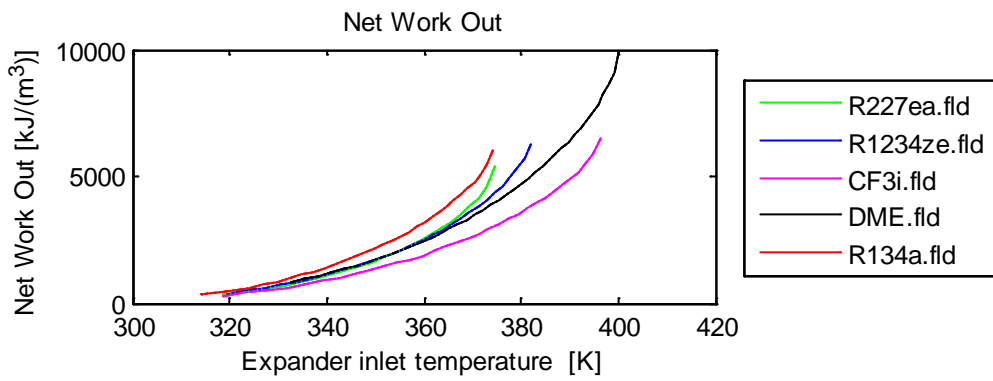
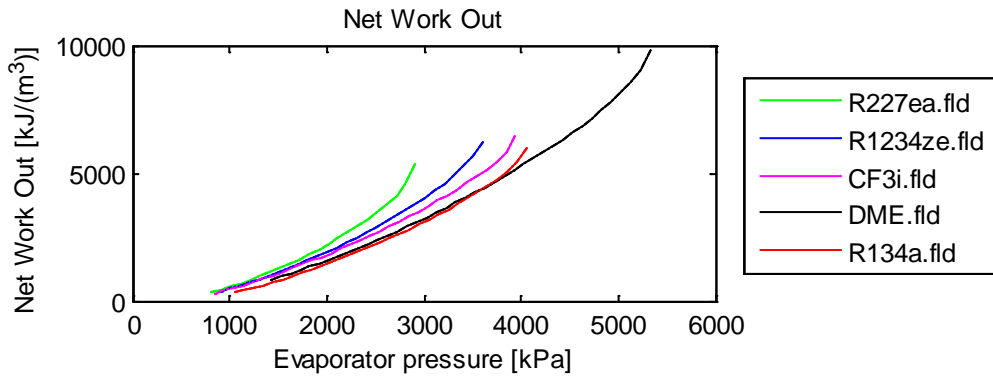


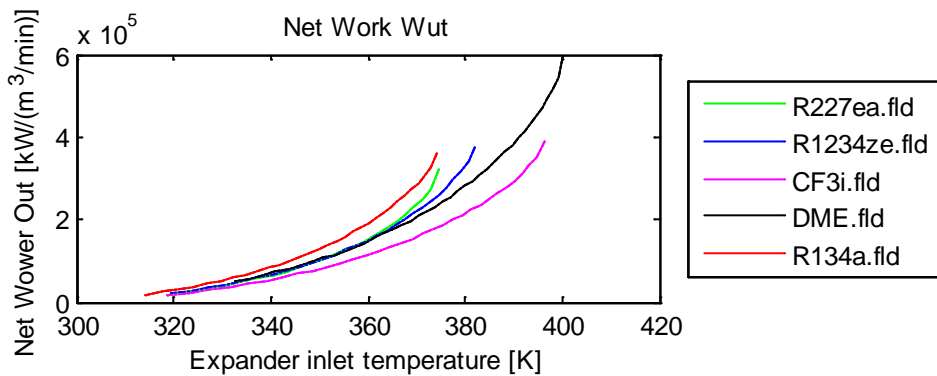
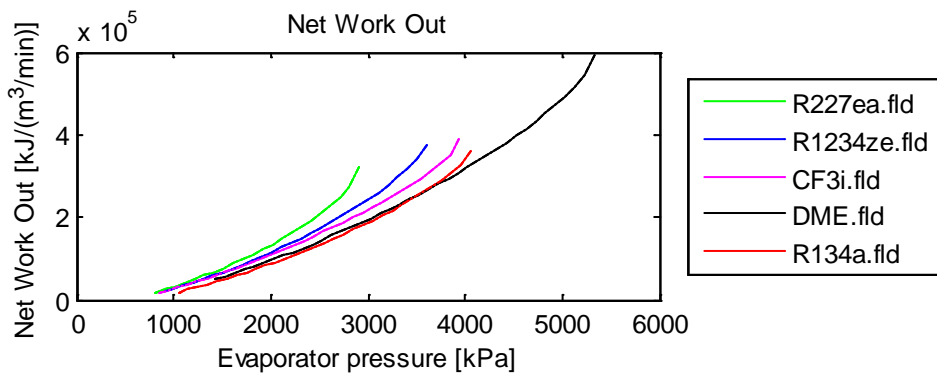
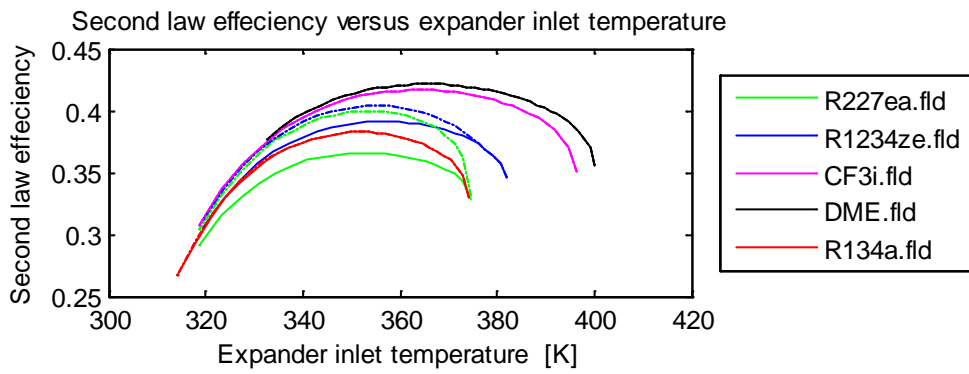
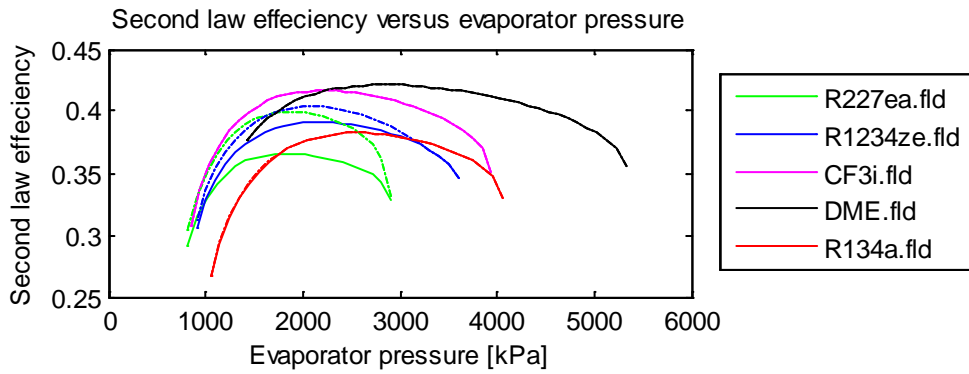


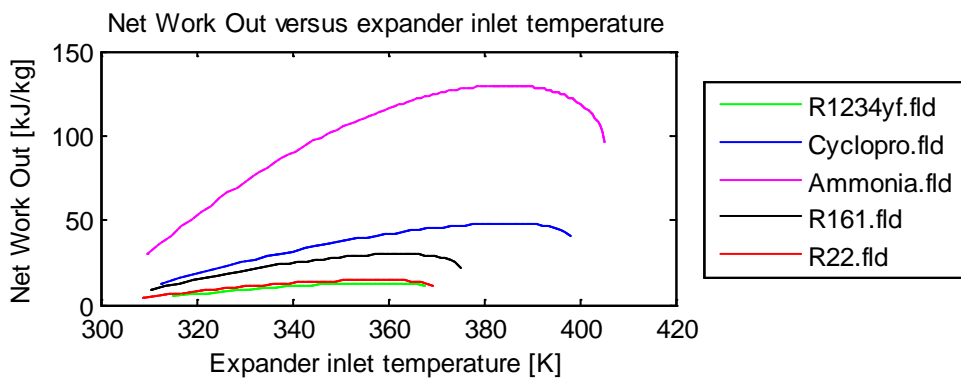
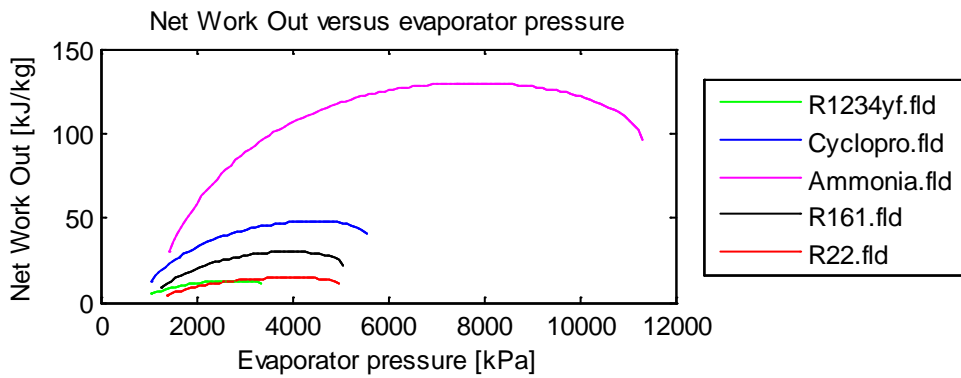
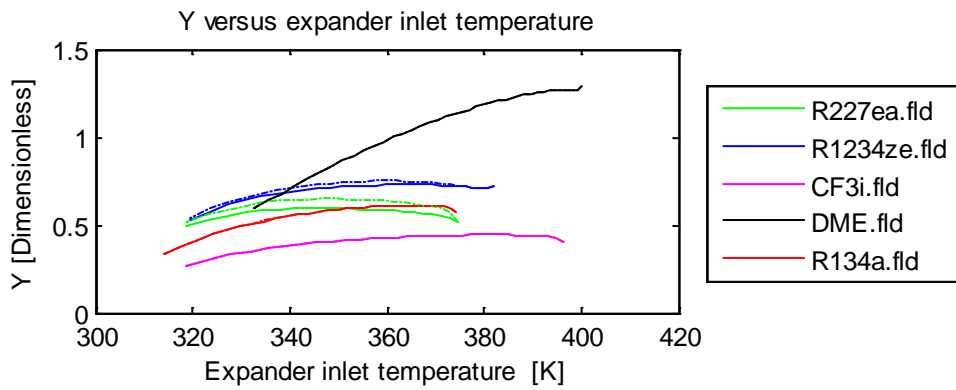
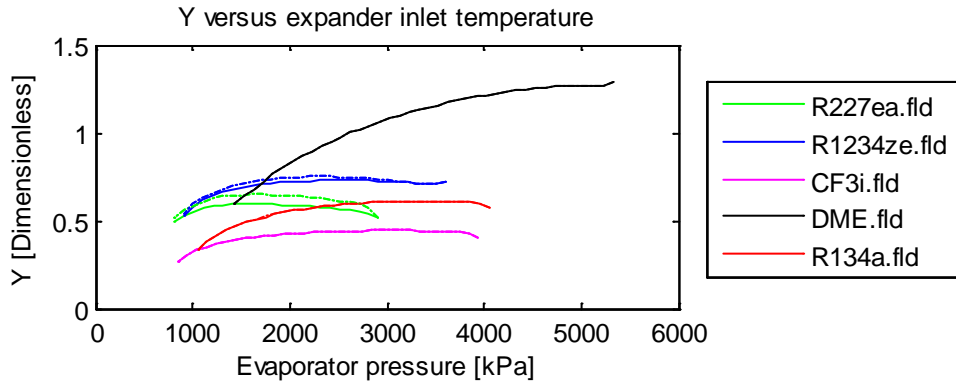


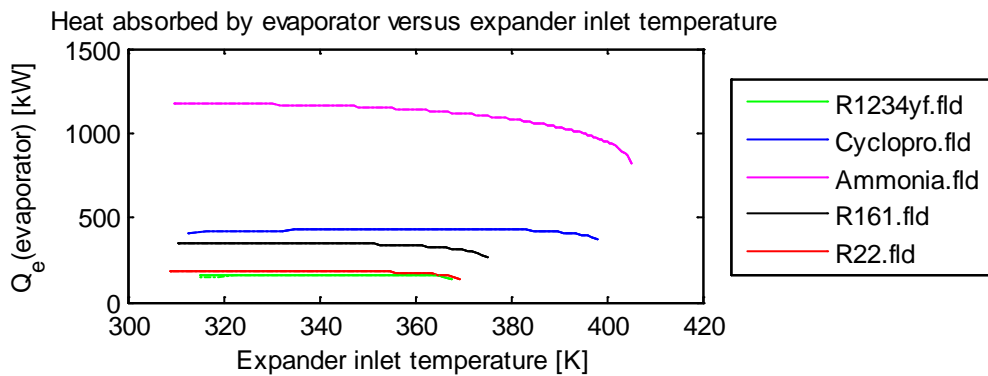
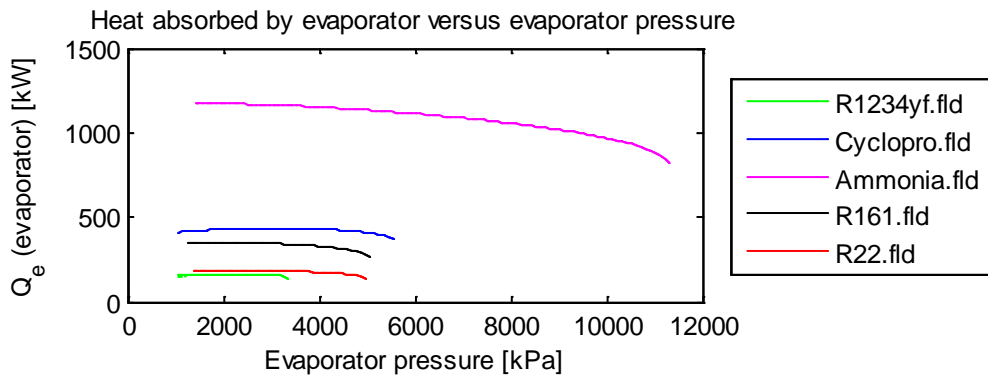
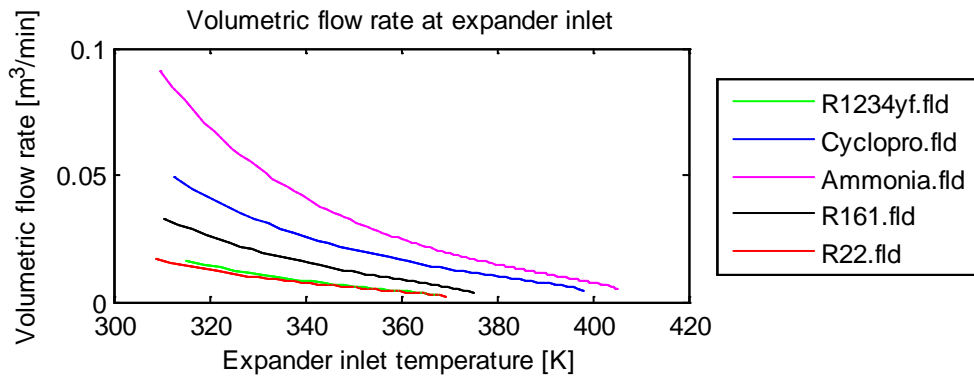
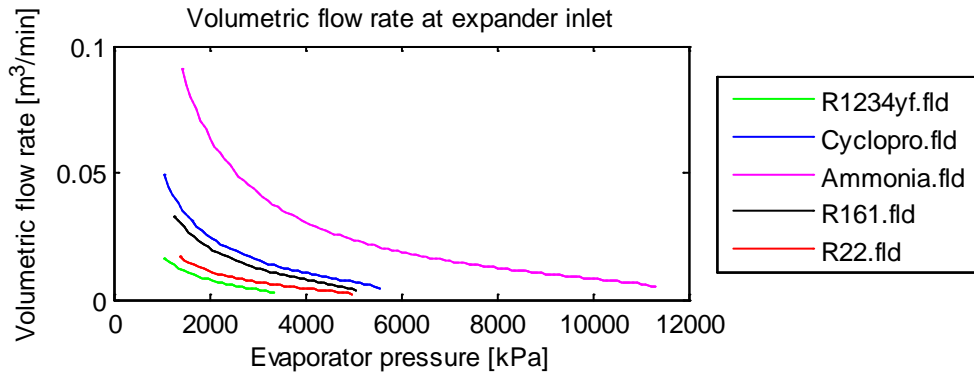


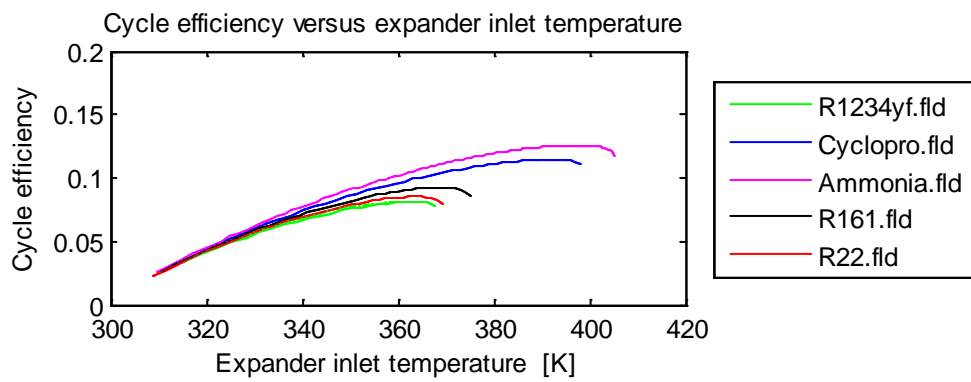
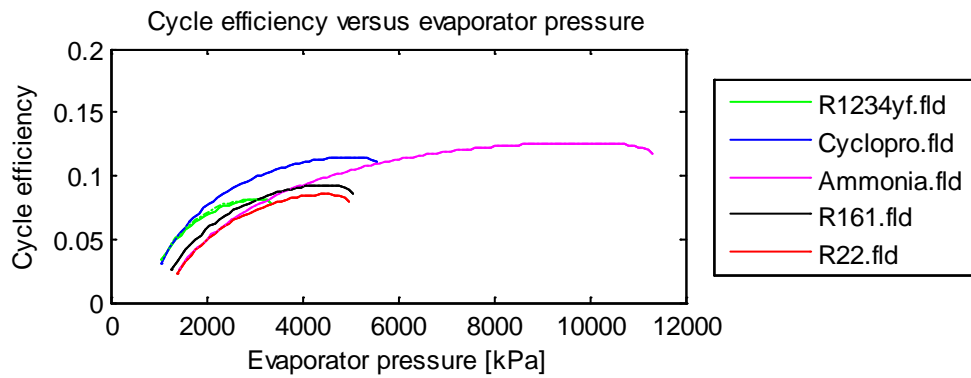
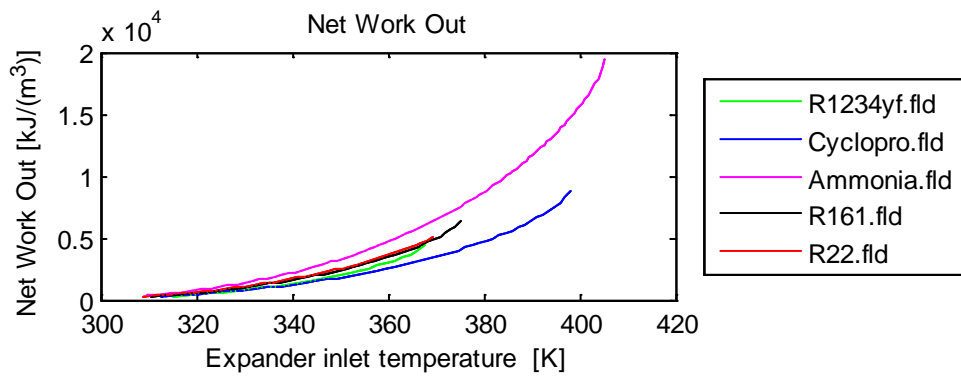
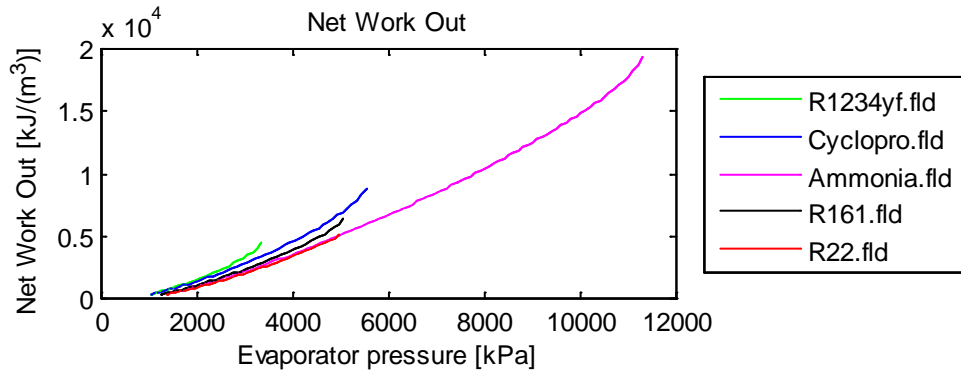


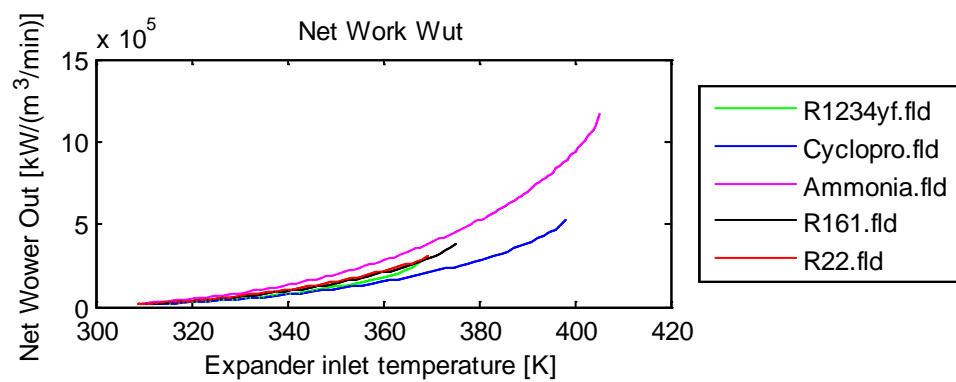
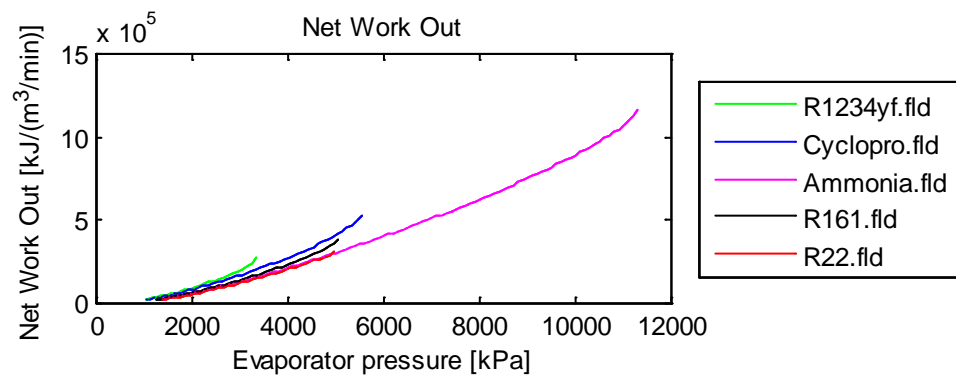
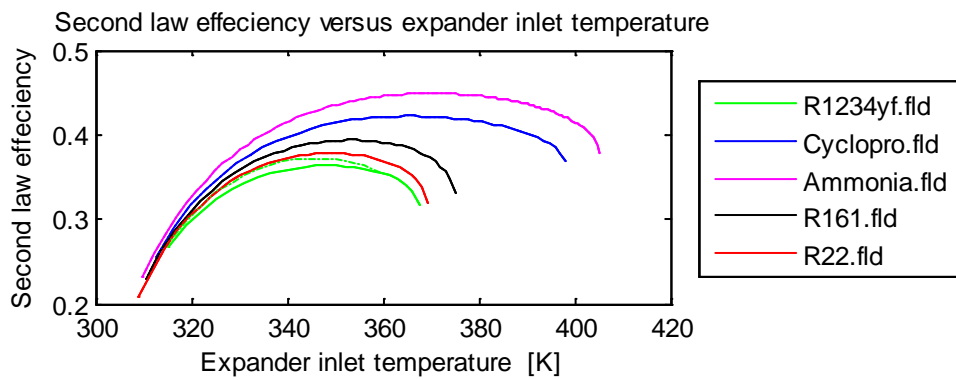
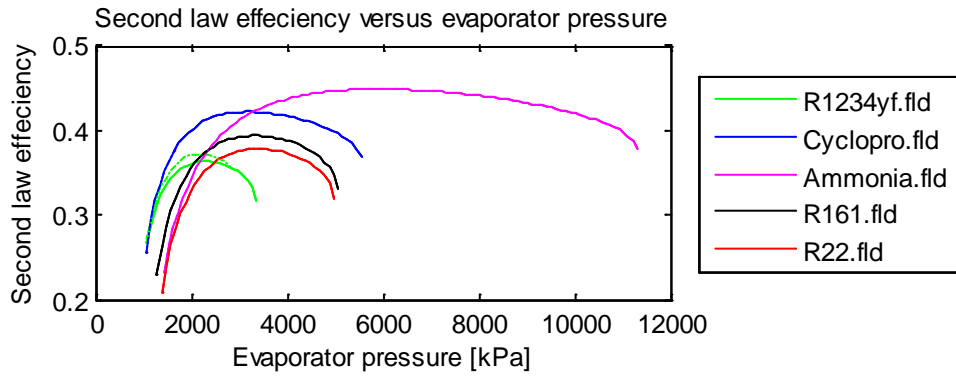


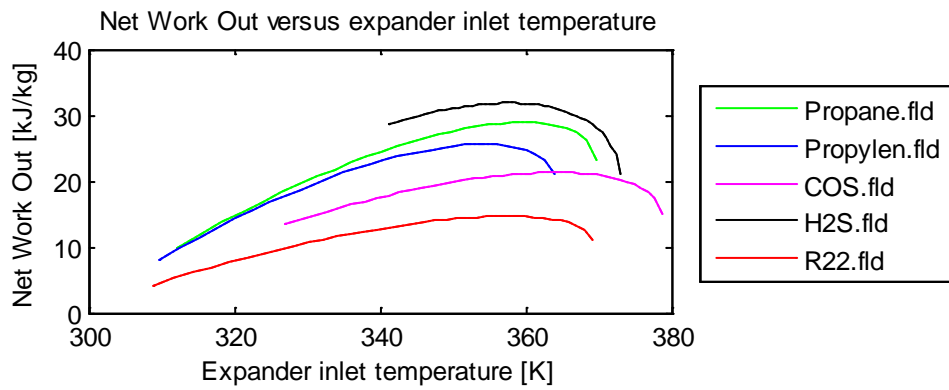
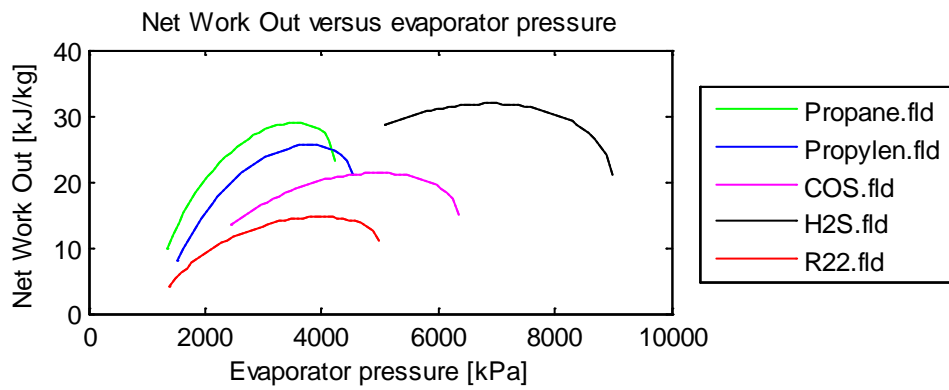
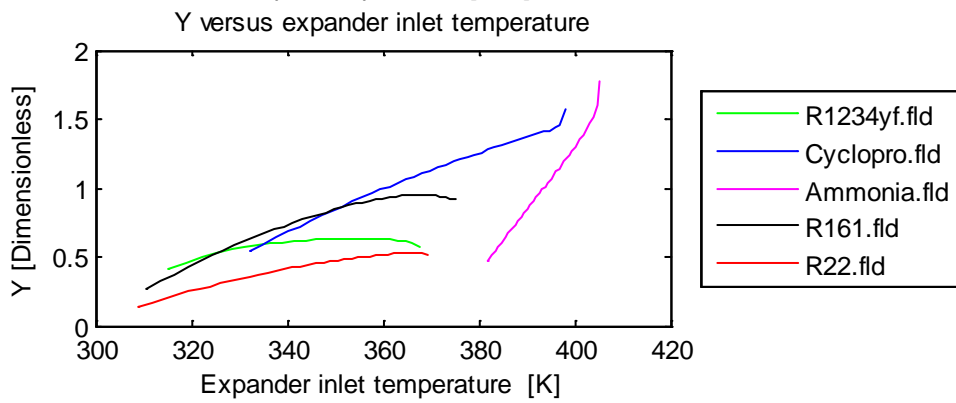
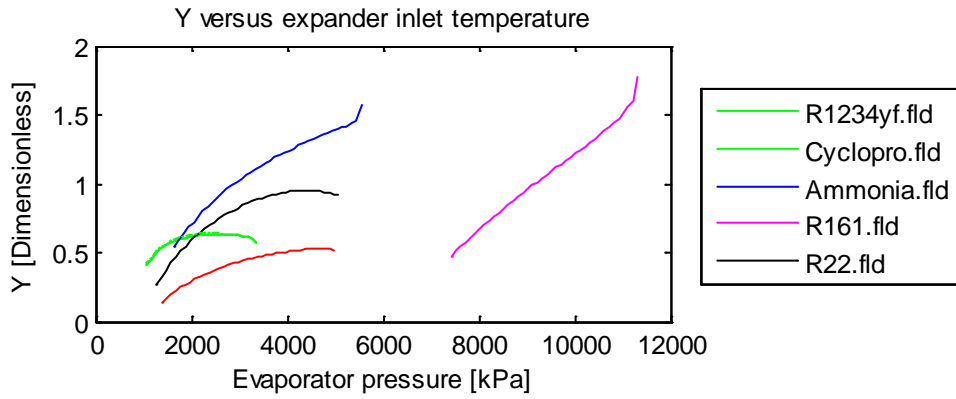


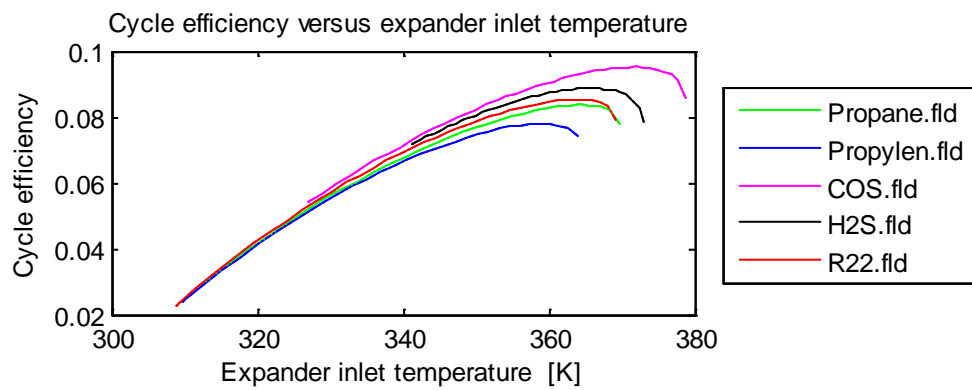
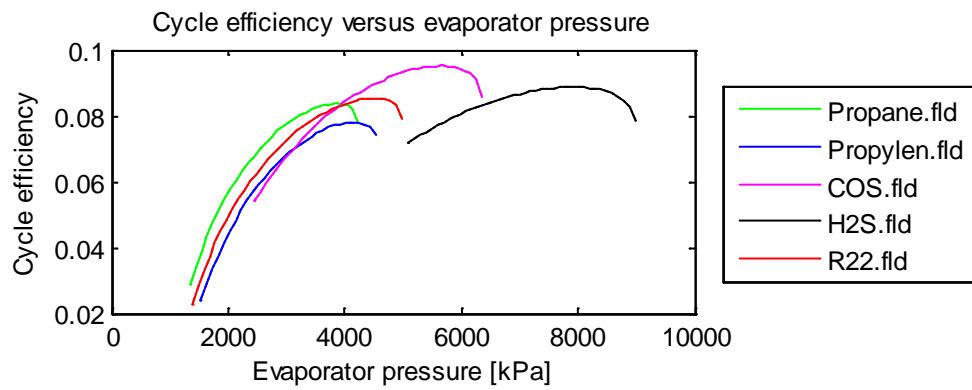
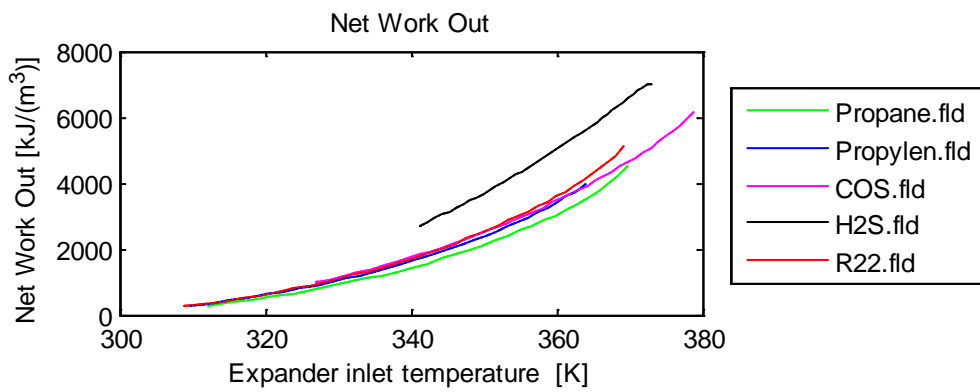
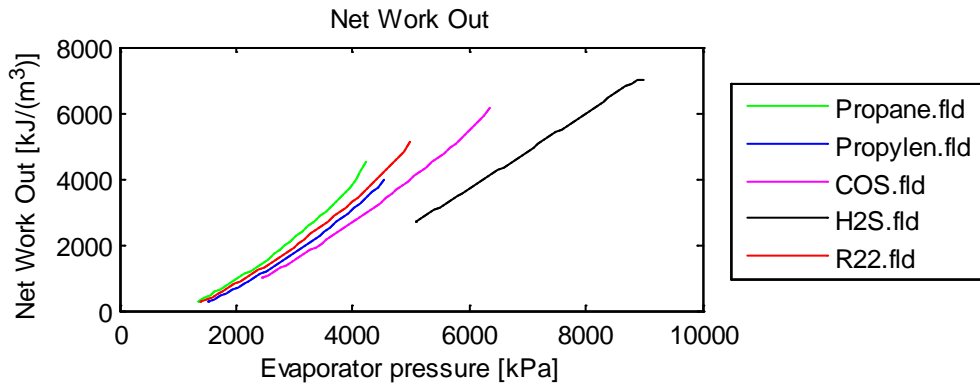


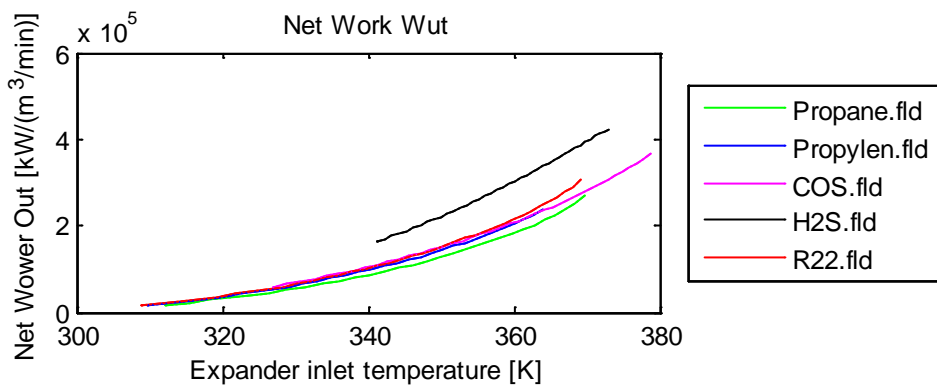
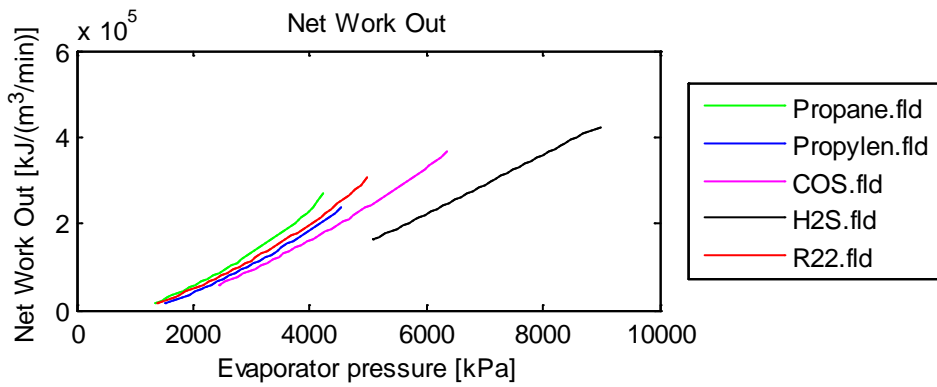
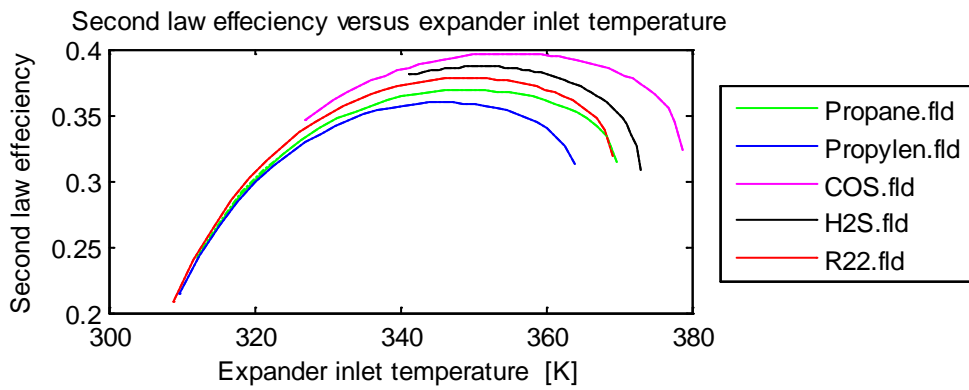
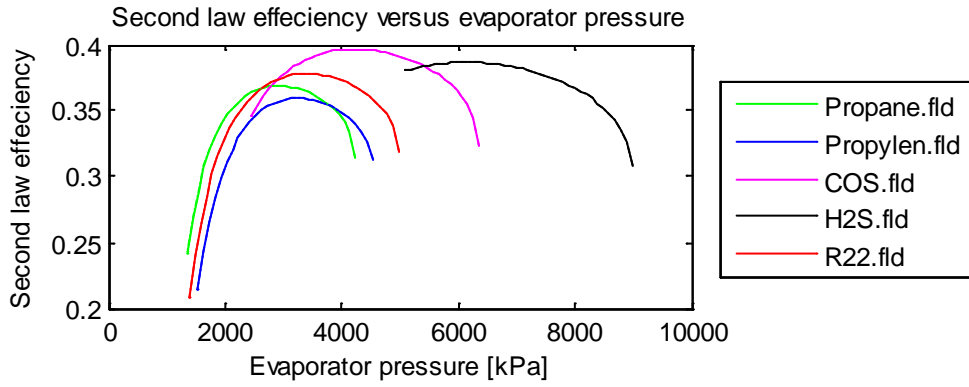


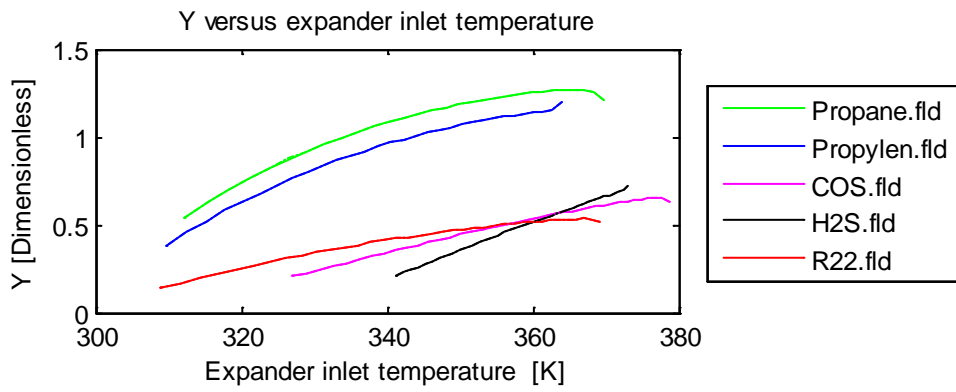
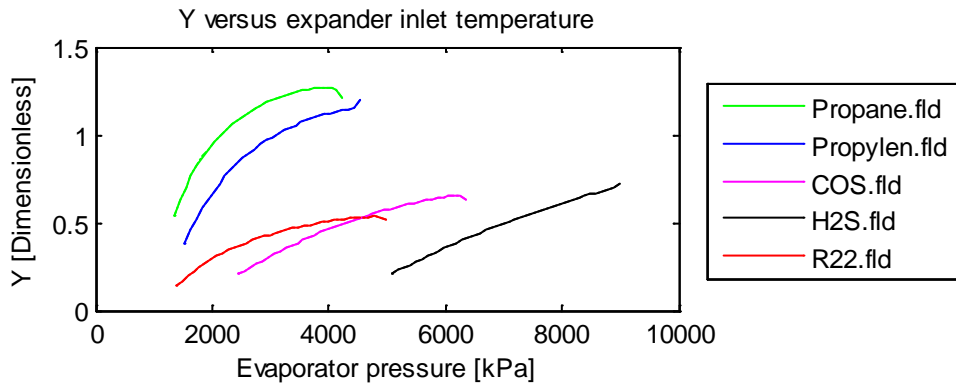












Scenario 4

