Thermodynamic Analysis of Organic Rankine Cycles

Jaiyejeje Sunday Obafunmi

Submitted to the
Institute of Graduate Studies and Research
in partial fulfillment of the requirements for the Degree of

Master of Science
in
Mechanical Engineering

Eastern Mediterranean University
July 2014
Gazimağusa, North Cyprus

Approval of the Institute of Graduate Studies and Research

Prof. Dr. Elvan Yilmaz
Director

I certify that this thesis satisfies the requirements as a thesis for the degree of Master of Science in Mechanical Engineering.

Prof. Dr. Uğur Atikol
Chair, Department of Mechanical Engineering

We certify that we have read this thesis and that in our opinion it is fully adequate in scope and quality as a thesis for the degree of Master of Science in Mechanical Engineering.

Prof. Dr. Fuat Egelioğlu
Supervisor

Examining Committee

1. Prof. Dr. Uğur Atikol
2. Prof. Dr. Hikmet Aybar
3. Prof. Dr. Fuat Egelioğlu

ABSTRACT

In this thesis, investigations are carried out in order to find the best suitable working fluid for a given temperature limits of Organic Rankine Cycles (ORCs) with the focus on thermodynamic analysis, safety and environmental aspect. Making a suitable choice of working fluid for the ORC is of vital importance for the cycle efficiency and net work output. In this study only the dry and isentropic working fluids are investigated from different perspectives. Engineering Equation Solver (EES) software package was used as the main source to find thermo-physical properties of the working fluids. The data from EES were transferred to the VisSim software package and different block models were developed for the simulation of ORCs.

Five organic working fluids used for this study are Butane, Isobutane, R245fa, R236fa and R124. The cycle operating parameters are varied and the effect of these parameters on the cycle performance and net work produced are investigated. Based on the simulations utilizing VisSim software, the cycle using butane as working fluid achieved the highest thermal efficiency (21.42%). The thermal efficiencies obtained for the ORCs using R245fa, Isobutane, R236fa and R124 as working fluids are 21.09, 20.87, 20.37 and 19.6% respectively. Although the thermal performance of the ORC utilizing R245fa is higher than the cycle utilizing Isobutane, specific net work produced by the cycle using isobutane is higher than the cycle using R245fa.

Butane has better thermodynamic properties but it is not environmentally friendly because it is highly flammable and highly toxic with no ozone depletion potential (ODP) but with a global warming potential (GWP) of 20. The R245fa which also has good thermodynamic properties is not flammable and nearly non-toxic with no ODP and a GWP of 950.

The five working fluids are investigated and the choice of the working fluid is based on the safety and its environmental characteristics. The R245fa is found to be the most suitable organic working fluid compared with the other four working fluids.

Keywords: Organic Rankine Cycle, Low grade heat, Simulation

ÖZ

Bu tezde, Organik Rankine Çevrimlerinde (ORÇ) belirli bir sıcaklık sınırları içerisinde en iyi çalışma akışkanını bulmak için termodinamik analiz, güvenlik ve çevresel yönü üzerinde odaklanarak araştırmalar yürütüldü. ORÇ için uygun çalışma akışkanının seçimi çevrimin ısıl verimliliği yanında net iş üretimi de hayati önem taşımaktadır. Bu çalışmada sadece kuru ve izentropik çalışma akışkanları farklı açılardan incelenmiştir. Mühendislik Denklem Çözücüsü (EES) yazılım paketi çalışma sıvılarının termo-fiziksel özelliklerini bulmak için ana kaynak olarak kullanılmıştır. EES'den alınan termo-fiziksel özellikler VisSim yazılım paketine aktarılmış ve ORÇ'nin simülasyonu için farklı blok modelleri geliştirilmiştir. Bu çalışmada kullanılan beş organik çalışma akışkanı bütan, izobütan, R245fa, R236fa ve R124'tür. Çevrimin çalışma parametreleri değiştirilerek bu parametrelerin çevrimin performansı ve net iş üretimi üzerindeki etkileri araştırıldı. VisSim simülasyonları neticesinde, çalışma sıvısı olarak bütan kullanıldığında çevrimde en yüksek ısıl verimlilik elde edildi (%21.42). ORÇ'lerde R245fa, izobütan, R236fa ve R124 çalışma akışkanları kullanıldığında elde edilen ısıl verimlilik sırasıyla, 21.09, 20.87, 20.37 ve%19.6 olarak bulundu. ORÇ'de isobütan kullanıldığında net iş üretimi R245fa akışkanını kullanıldığından daha yüksek olmasına rağmen R245fa akışkanı kullanan ORÇ'nin ısıl verimliliği daha yüksektir.

Bütanın termo-fiziksel özellikleri diğer akışkanlara göre daha iyidir ancak son derece yanıcı ve yüksek derecede toksik oluşu ozon tüketme potansiyeli olmayan ancak 20 küresel ısınma potansiyeli ile de çevre dostu değildir. Termo-fiziksel özellikleri iyi olan R245fa akışkanı yanıcı ve toksik değildir, ozon tüketme potansiyeli yoktur ve küresel ısınma potansiyeli 950 dir.

Beş çalışma akışkanı incelenmiş ve çalışma akışkanının seçimi, çevrimin performansı ve akışkanın güvenlik ve çevre özellikleri de dikkate alınarak yapıldı. R245fa diğer dört çalışma akışkanına kıyasla en uygun organik çalışma akışkanı olduğu bulunmuştur.

Anahtarkelimeler: Organik Rankine Çevrimi, organik akışkanlar, simülasyon, ısıl verimlilik

Dedicated to God Almighty

ACKNOWLEDGEMENT

My sincere gratitude and appreciation goes to my supervisor Prof. Dr. Fuat Egelioğlu for his guidance and thorough supervision towards the successful completion of this thesis. Working with my supervisor has improved my knowledge in this field tremendously.

I would like to show my debt immense of endless appreciation to my Dad and Mum, Mr M. O. Obafunmi and Mrs Victoria for their encouragement, financial support and prayers. Thank you for not giving up on me even for a second.

My special gratitude goes to my Brother and Sisters: Oluwaseyi, Tonidunni, Oluwaseun, Uncles: Mr Julius Olowosaiye, Mr ikupolati Alexander, and also my Aunt: Rhoda Olowosaiye. I appreciate the love and care you have always shown me.

My special thanks and appreciation also goes to my friends: Ayoola Afolayan, Sama, Besong, Sahar, Mohammed, Jahad, Abdelsalam and Walid for their great support and encouragement.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ORC	Organic Rankine Cycle
GWP	Global Warming Potential
ODP	Ozone Depletion Potential
VisSim	Visual simulation Software package
EES	Engineering Equation Solver
IHX	Internal Heat Exchanger
CFC	Chlorofluorocarbons
HCFC	Hydro chlorofluorocarbons
MW	Mega Watt
NBP	Normal Boiling Point

NOMENCLATURES

w	Work done (kJ/kg)
h	Enthalpy (kJ/kg)
s	Entropy (kJ/kg ºC)
q	Heat transfer (kJ/kg)
T	Temperature (ºC)
P	Pressure (kPa)

Substript

Cond	condenser
Evap	evaporator

Greek symbol

η	Cycle efficiency (%)

Chapter 1

INTRODUCTION

1.1 Overview

The development of the world today has largely been achieved through the increasingly efficient and extensive use of various forms of energy. Over the past decades, the growth in energy consumption around the world has shown that fossil fuel energy source alone will not be capable of meeting future energy demands.

With the increase in fossil fuel consumptions, more and more industrial activities produce increasing amount of waste heat. Energy generated as a result of industrial activities that are not practically utilized is referred to as industrial waste heat. Several studies have shown that the specific amount of industrial waste heat is poorly measured, it is estimated that 25 to 55% of the input energy in industries are actually used while the remaining are discharged as waste heat [1]. While it is almost impossible to avoid waste heat losses from industrial activities, some facilities and heat recovery technologies can be put in place to reduce these waste heats by improving equipment efficiency and energy utilization. The extraction of energy from waste heat, turbine exhaust, solar energy and biomass energy is becoming a popular means of generating alternative energy for most industries. Low grade heat sources can be converted into electrical power and these can be achieved using an ORC system. The basic principles of the ORCs are very much like those of the conventional Rankine cycle. However, the main difference is that the ORC uses an organic working fluid which has a higher vapor pressure and lower boiling point compared to water. These properties of organic fluids boost the cycle efficiency of the ORCs considerably compared to the conventional Rankine cycle. There have been several successful installations of the ORCs around the world and more research is still being carried out to improve the ORC system.

1.2 Motivation

The increase in the energy consumption by burning of fossil fuel has lead to several conflicts around the world, global warming and environmental pollution such as soil, water, air and acid rain pollution. Besides the adverse environmental effects, the prices of fossil fuels are not consistent but usually going up most of the time. The cost of liquid hydrocarbon in the United States is said to be USD 4/gallon and probably more expensive in other countries [2]. Petroleum and natural gas and coal are fossil fuels and are non renewable. Several countries today have been investing money to get new and efficient energy technologies that are alternative for fossil fuels to generate power. Low grade heat is largely available in renewable energy sources and in industrial waste. Utilizing this type of sustainable energy could help reduce the use of non-renewable energy, thus reducing the environmental impacts of non-renewable energy sources. Development of efficient and effective technologies is required to generate useful work by using these low grade heat sources. An ORC is a suitable means of carrying out this purpose. The ORC works with a high molecular mass organic working fluid with the characteristic of having a phase change of liquid to vapor occurring at a temperature which is lower than the phase change of water to steam for a given pressure. The recovery of low grade heat can be achieved using organic fluids. These low grade heat sources can be from biomass energy, solar energy, geothermal energy and industrial waste. The ORC converts the low grade heat into work and finally into electricity.

1.3 Thesis objectives

ORCs modules are built having capacities up to few MWs. For example, Siemens utilized its first ORC module capable to generate power output from 300 kW to 2 MW in 2013. As ORCs are capable of using low grade heat from industrial waste heat, fossil fuels used as primary energy in industry will be more efficiently utilized if an ORC system is employed (i.e., power generation without extra fuel). The need for new ORCs working fluids is growing as the ORC industry is expanding. For example Siemens used chlorine free, non-toxic, substance with a zero ozone depletion potential as the working fluid [3]. Honeywell is working on new working fluids as alternatives to 134a and 245fa that will offer; ultra low- Global-Warming-Potential, increase in system performance, safety and reduced cost [4].

The choice of the working fluid is of primary importance in the ORCs. Selecting an appropriate working fluid for the ORC system is vital for better cycle efficiency, higher net-work output, safety and more environmentally friendly. The aim of this study is to compare the performance of five different organic working fluids operating between the same temperature limits in the ORC system. The aspect that will be focused on when choosing a suitable working fluid for the ORC cycle will be based on the thermodynamic analysis, safety and environmental data of the working fluids.

.

.

Chapter 2

LITERATURE REVIEW

Over the past years, the interest in recovering low grade heat has grown rapidly. Many researchers have come up with several ways of generating electrical power from low temperature heat sources available in solar energy, domestic boilers, biomass and industrial waste heat. Among all these the ORC is considered to be the most suitable due to its simple design and availability of components.

The ORCs use organic working fluids which are more suitable than water in the context of using heat source with low temperatures. The ORC cycle unlike conventional steam cycles is an attractive yardstick for local and small scale power generation.

2.1 History

Frank W. Ofledt patented the naphtha engine in 1883 which has the same application as the ORC. The naphtha was used in place of water as working fluid so as to replace the steam engine on boat [5].

During fractional distillation of crude petroleum oil, distinct liquid hydrocarbon naphtha is produced. Since the heat of vaporization for naphtha is lower compared to water, it was seen that if a certain amount of heat is added to the naphtha it produces more vapor and therefore, more work output could be realized from the engine if water is used. There was a high risk of explosion when steam boats started using naphtha engine, for this reason the coast guides made it mandatory for operators to have licenses which later resulted in the population growth of the naphtha engine [6]. The discovery by Frank W Ofledt was a substitute for using steam engines. Figure 2.1 shows an article about naphtha engine (1890) while figure 2.2 shows a simple design of naphtha engine.

THE ONLY NAPHTHA LAUNCH.

Over 500 now in Successful Operation.

Easy and Safe to Manage.

CLEANLY and ECONOMICAL.

GAS ENGINE and POWER Co., Morris Dock Station, New York City.

The Rudder, July 1890

Figure 2.1: An article on naphtha engine [7]

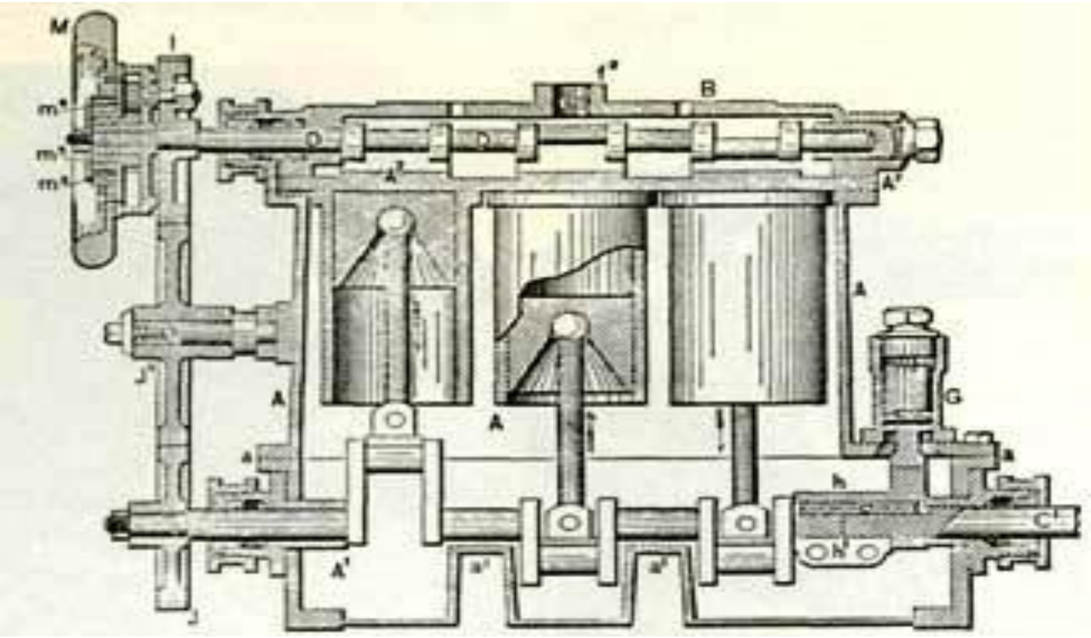


Figure 2.2: Sample design of naphtha engine [8]

The first prototype of the ORC system was first developed by Harry Zvi in the early 1960s [9]. This prototype was mainly used to recover low grade heat which is similar to the solar energy used to convert low temperature sources to electrical power. A turbine capable of working and operating at a comparatively low temperature was also developed by Harry Zvi. This invention was later privatized in 1965 by an Israeli company [10].

2.2 Worldwide ORC Installation

At present the installations of ORCs have been successful in many countries. Several countries are now using the ORCs to utilize waste heat. Most ORC systems exist in Germany, Italy, Canada and the USA while in other countries like Belgium, Austria, Romania, Russia, Finland, Swaziland, Morocco and India have just installed a single unit of the ORC system [11]. The major companies that supplies ORC equipment are Tas Energy, Ormat and Turboden [12]. Most of the industries that use the ORC system to recover waste heat in different countries are the gas, glass and cement industries.

2.3 Low grade temperature heat recovery cycles

It is not cost effective to use conventional Rankine cycles to convert thermal energy from low grade heat source to electricity especially when the temperature is extremely low. Several cycles have been developed so that energy from low grade heat source can be utilized properly. Some of the developed cycles like Goswami cycle, Kalina cycle, trilateral flash and ORC provide higher benefits and low price of components since organic working fluids are used instead of water [13]. Kalina cycle, Goswami cycle, Trilateral flash cycle and the Organic Rankine cycle are briefly discussed in the following sub-section.

2.3.1 The Kalina Cycle

The Kalina cycle was successfully developed to convert low grade heat to electrical power. Aleksander Kalina developed the first cycle in the late 1970s [14]. In order to boost the cycle efficiency and also to minimize the irreversibility, water and ammonia were used as working fluid. Kalina cycle uses two different fluids which are thermally matched. Researches carried out on this cycle showed that it performs better to a large extent than conventional Rankine cycle. Figure 2.3 shows the diagram of the Kalina cycle.

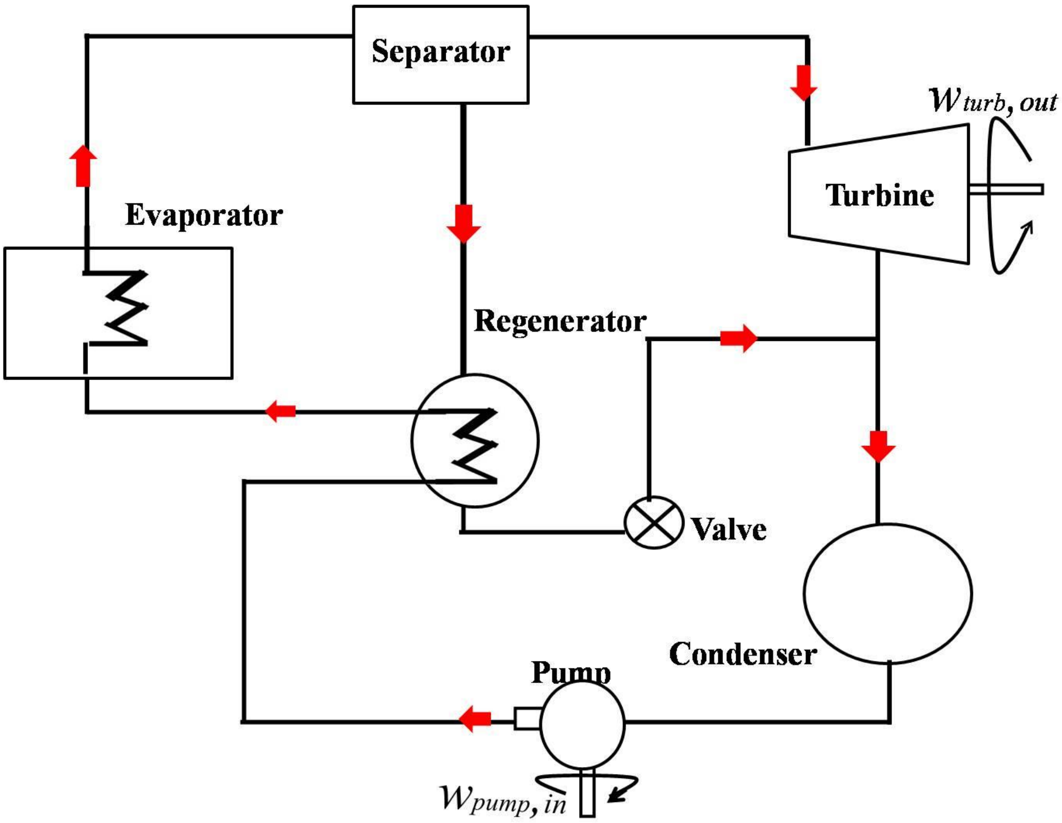


Figure 2.3: Kalina Cycle

2.3.2 Goswami Cycle

The Goswami cycle was first projected by Dr. Yogi Goswami in 1998 [15]. This peculiar thermodynamic cycle uses a binary mixture to produce both electricity and refrigeration in one loop simultaneously. The binary mixture consists of ammonia and water which increases energy source utilization of the cycle. The system allows efficient conversion of low grade heat source into electrical power and it is flexible to produce any combination of electrical power and refrigeration. This means that the electrical power produced can be increased while the cooling is reduced. Figure 2.4 shows the Goswami cycle.

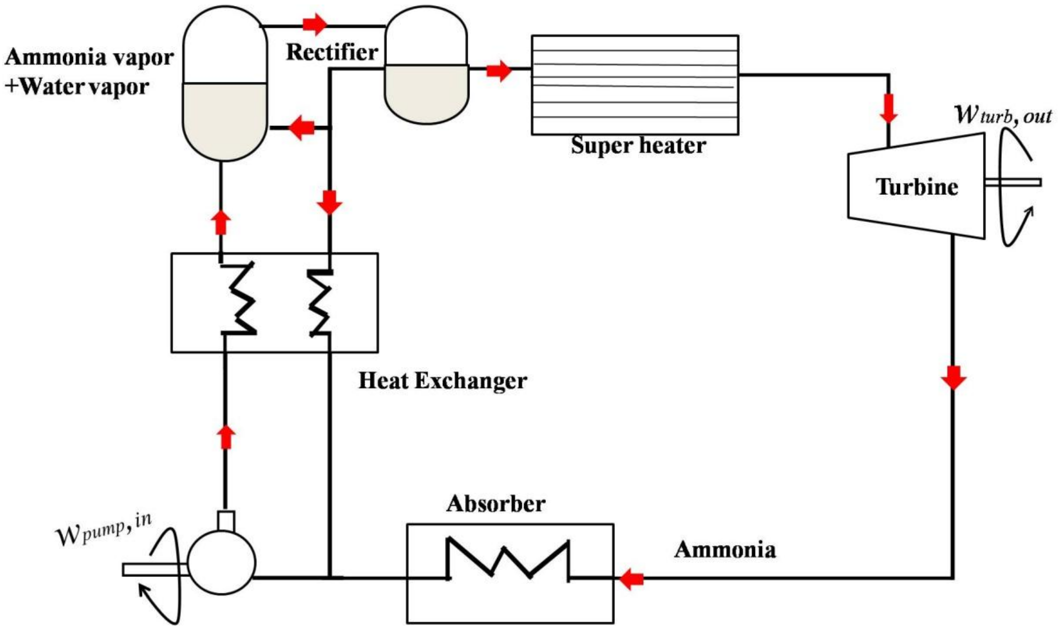


Figure 2.4: Goswami cycle

2.3.3 Trilateral Flash Cycle

The expansion process in this unique thermodynamic cycle does not start from the vapor phase rather it begins from the saturated liquid line. Based on some scientific papers, this cycle is said to have greater power when it comes to recovering waste heat than flash steam system and probably the ORC system [16]. The major setback for this system is the difficulty to find appropriate expanders that can handle the high adiabatic efficiency and also the two phase flow. Figure 2.5 shows the trilateral flash cycle.

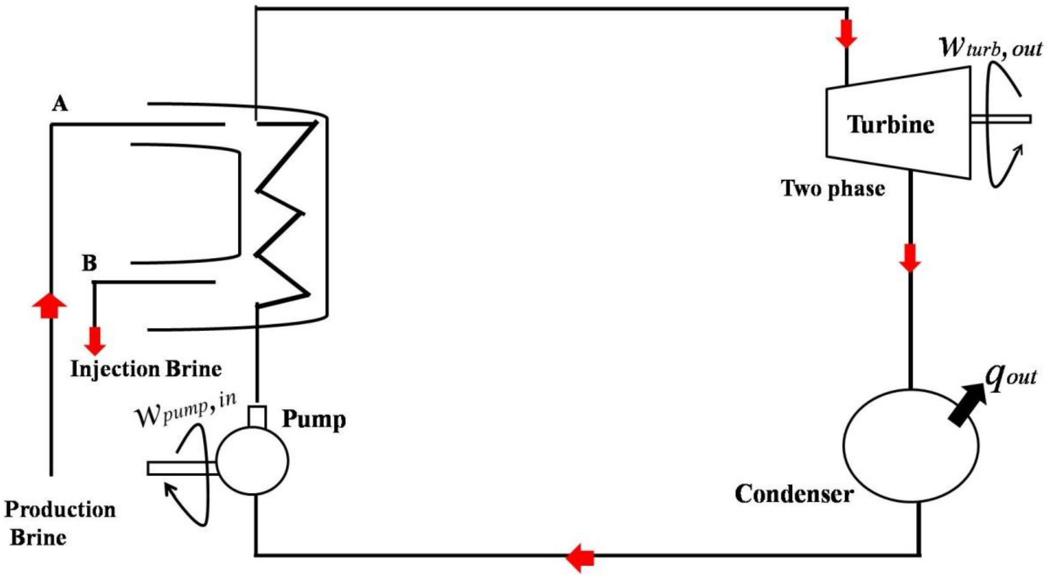


Figure 2.5: Trilateral flash cycle

2.3.4 Organic Rankine Cycle

As mentioned earlier the ORC and conventional Rankine cycle have the same working principles. They also have similar components like the condenser, pump, evaporator (boiler), and expander (turbine). However, there is a difference related to the kind of working fluid that is used in the cycles. The ORC extract and generate electrical power from low grade heat compared to the conventional Rankine cycle.

2.4 Applications of ORCs

The applications of the ORC to generate mechanical and electrical power are as follows:

2.4.1 Waste heat recovery

The extraction process of energy from waste heat as a result of numerous industrial activities is called waste heat recovery process. In some applications, regenerators and waste heat boilers are used to redirect and recover heat into their own system. The economics of waste heat recovery in steam cycle do not support when the waste heat temperature is low. The production of electrical power using low grade heat source can be done easily using an ORC cycle. Figure 2.6 shows the application of ORC in waste heat recovery.

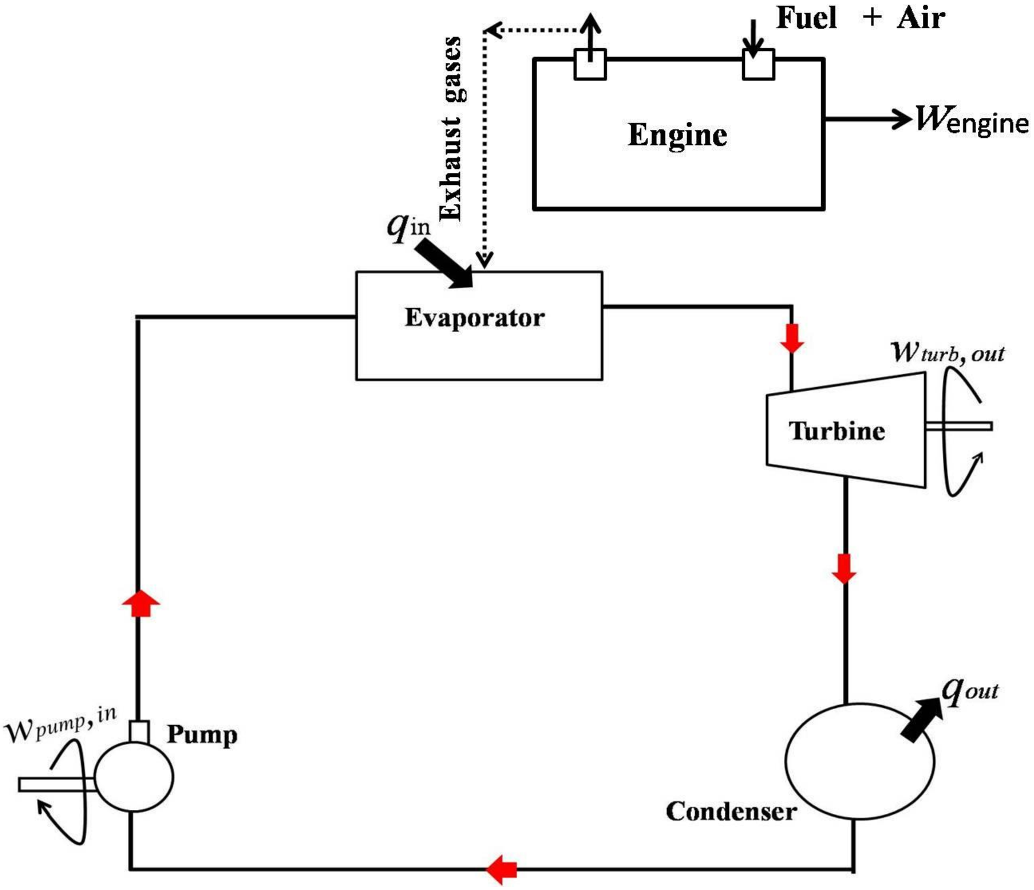


Figure 2.6: ORC in waste heat recovery

2.4.2 Solar thermal power

Solar thermal power generation is a well established technology. The extraction of solar thermal energy can be achieved using different components such as the parabolic dish, the parabolic trough and the solar tower. The working temperature of the parabolic dish ranges from 300ºC-400ºC [17]. Several years ago the generation of electrical power from steam was connected to this technology. However, in order for the conventional Rankine cycle to be economically attractive, it requires a high source temperature and a high installation power capacity. The ORC works at a much lower temperature limits and is less capital intensive. The ORC requires and accepts smaller component size compared to the conventional Rankine cycle. Figure 2.7 shows a typical solar thermal power plant.

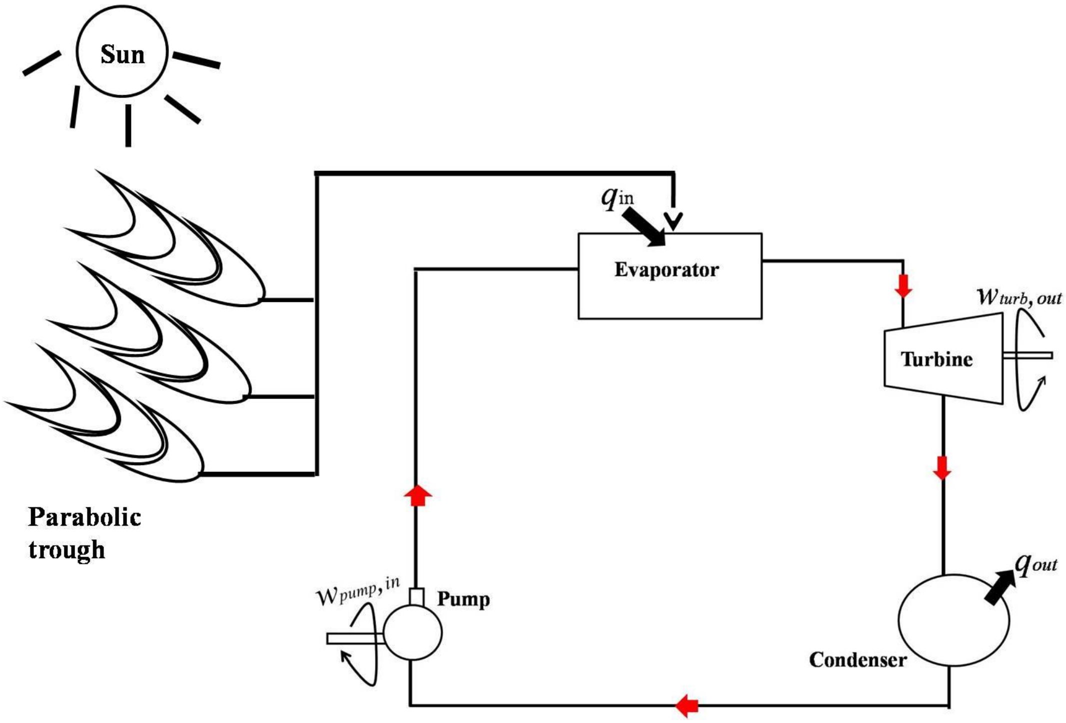


Figure 2.7: Solar thermal power plant

2.4.3 Geothermal power plants

Geothermal power plant has the capability to supply a lot of communities with renewable electrical power. In 2008 the geothermal sources supplied 1% of world´s electrical power [18]. Geothermal power plant energy source is renewable and also clean. The power generation in a geothermal power plant can be achieved by using three different technologies; these are the flash steam power plants, the binary cycle power plants and the dry steam power plants. Figure 2.8 shows the geothermal electric generation for the dry steam and flash steam system.

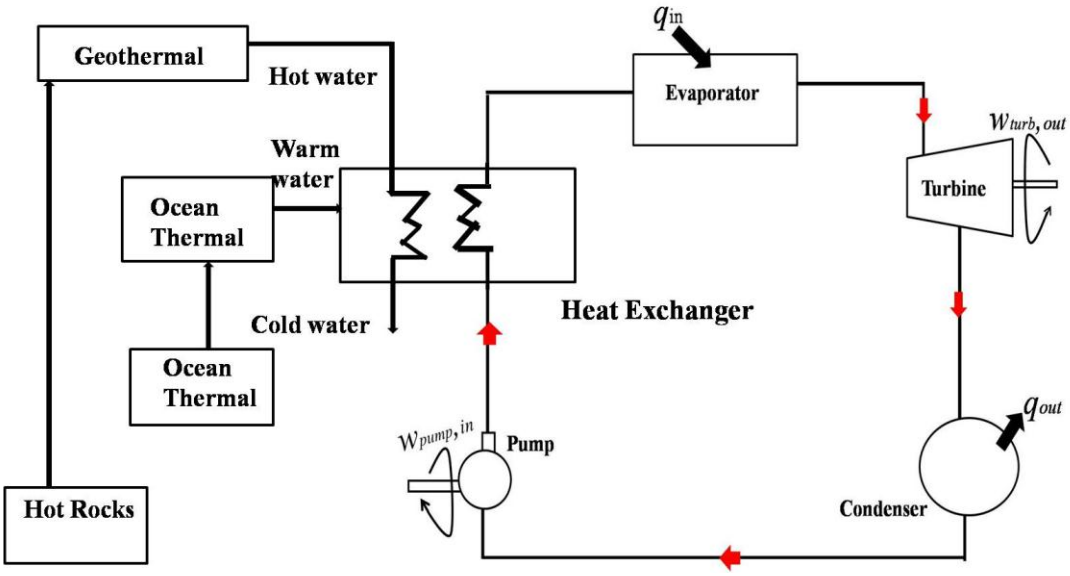


Figure 2.8: Geothermal electric generation system

2.4.4 Biomass power plant

The price and use of conventional fossil fuel is continuously increasing. Fossil fuel consumption largely affects the environment; causing a change in the climate conditions and pollution as a result of exhaust gases. Presently, biomass energy resources are experiencing an increase in market growth due to the fact that it is cheaper and environmentally more friendly compared to fossil fuels [19]. There are many forms in which biomass fuels exist, examples are the biogas from wood wastes and combustible agriculture wastes. Using biomass fuels has a lot of advantage when it comes to the reduction in prices of fuel and global warming potential. Figure 2.9 shows the application of the ORC using biomass.

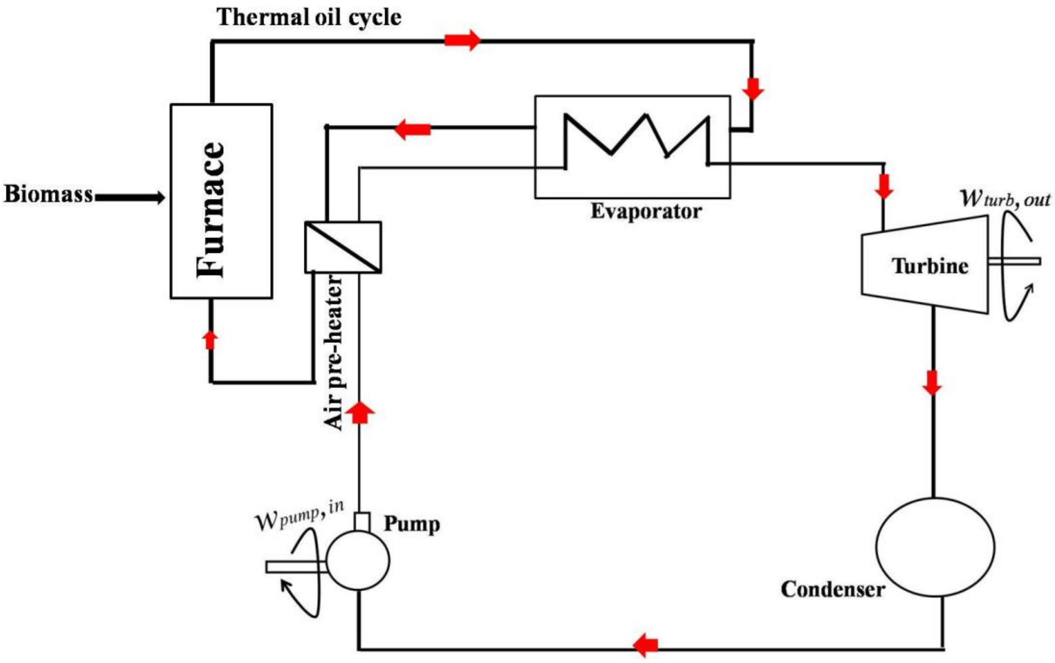


Figure 2.9: Biomass ORC

2.5 ORC market share for different heat source

Currently the Biomass ORC market share is the largest. The Geothermal ORC which is now in second position was known to play the major part in market share source [20]. Waste heat recovery which is currently in the third position has 20 % of the ORC market share and can be applied to many industrial processes. The solar ORC due to lack of awareness, is currently at the fourth position with only 1% of the ORC market share and still have a huge potential to grow. Figure 2.10 shows the market share for different heat sources. The application of biomass based ORC is the highest because it is the only proven technology to generate up to 1MWel for decentralized applications from solid fuels like biomass [21].

Since 1980s when ORC have been available in the market, more than 200 projects with total power of about 2000 MW of electricity have been installed [20]. This is one of the major reasons for the exceptional growth in the usage of ORC in recent years. This shows that the ORC market has a bright future.

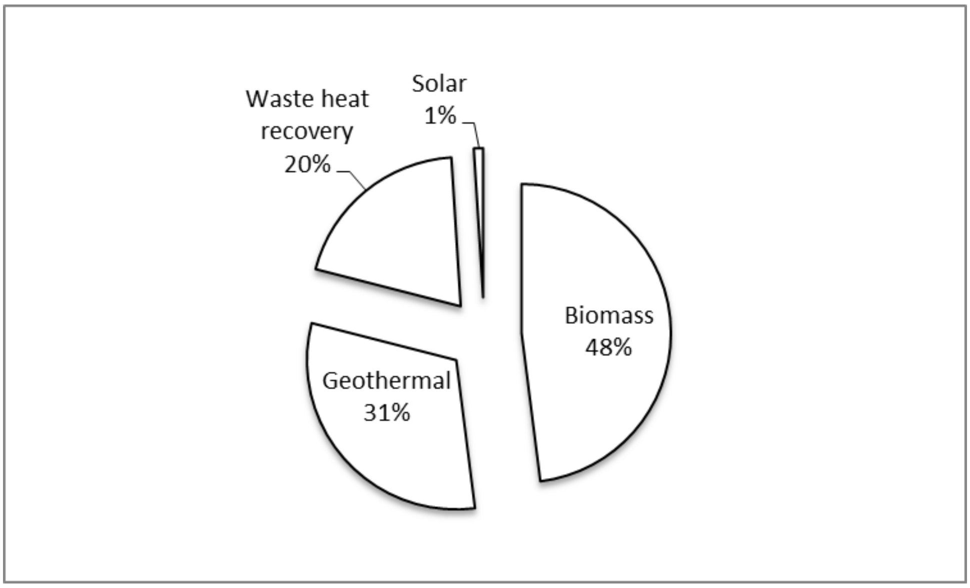


Figure 2.10: The ORC market share for different heat sources [22]

Chapter 3

THE ORGANIC RANKINE CYCLE

3.1 The ORC and the Conventional Rankine Cycle

The major differences between the ORC and Conventional Rankine cycle are as follows:

3.1.1 Working fluids

Apart from the operating parameters such as temperature and pressure; the major difference between the ORC and the conventional steam Rankine cycle is the working fluid used in each cycle. In the conventional Rankine cycle water is the only working fluid that can be used while in an ORC there are over a hundred different working fluids that can be used. The discovering of new working fluids for the ORC system is a continuous process. The components sizes of an ORC system depends on the thermodynamic property of the working fluid. The thermodynamic, environmental and safety properties of each working fluid are different. Safety and environmental data for most working fluids are not readily available [23]. Selecting an appropriate working fluid for the ORC system is vital for better cycle efficiencies and higher net work outputs.

3.1.2 Environmental and safety properties

Working fluid like water does not pose any danger to the environment because it is non-toxic, non-flammable, has no global warming potential and no ozone depletion potential. Many organic working fluids are not environmentally friendly because they have ozone depletion potential and also some are causing green house effect which is harmful to the environment. Some organic working fluids have the characteristic of high toxicity and high flammability [24].

3.1.3 Normal Boiling Point (NBP)

Majority of ORC fluids when compared to water have low NBP. Due to low NBP the ORC working fluid requires a low grade heat source than water to evaporate and recover low thermal energy from heat sources. Figure 3.1 compares the saturation properties of selected organic fluids with that of water on a T-s diagram. Water has a negative saturation vapor line slope on a T-s diagram, while the organic working fluids have three different saturation vapor line slopes namely; infinite, positive and negative vapor line slope. A turbo expander has more advantages when the employed working fluid has either a positive or infinite vapor line slope. One of the advantages of the positive and infinite slope is that working fluids in both leave turbo expanders as superheated vapor thereby eliminating the risk of corrosion. In addition when the working fluid has a positive or infinite slope the vapor in the evaporator do not require superheating and for this reason smaller and cheaper ORC components can be used [24].

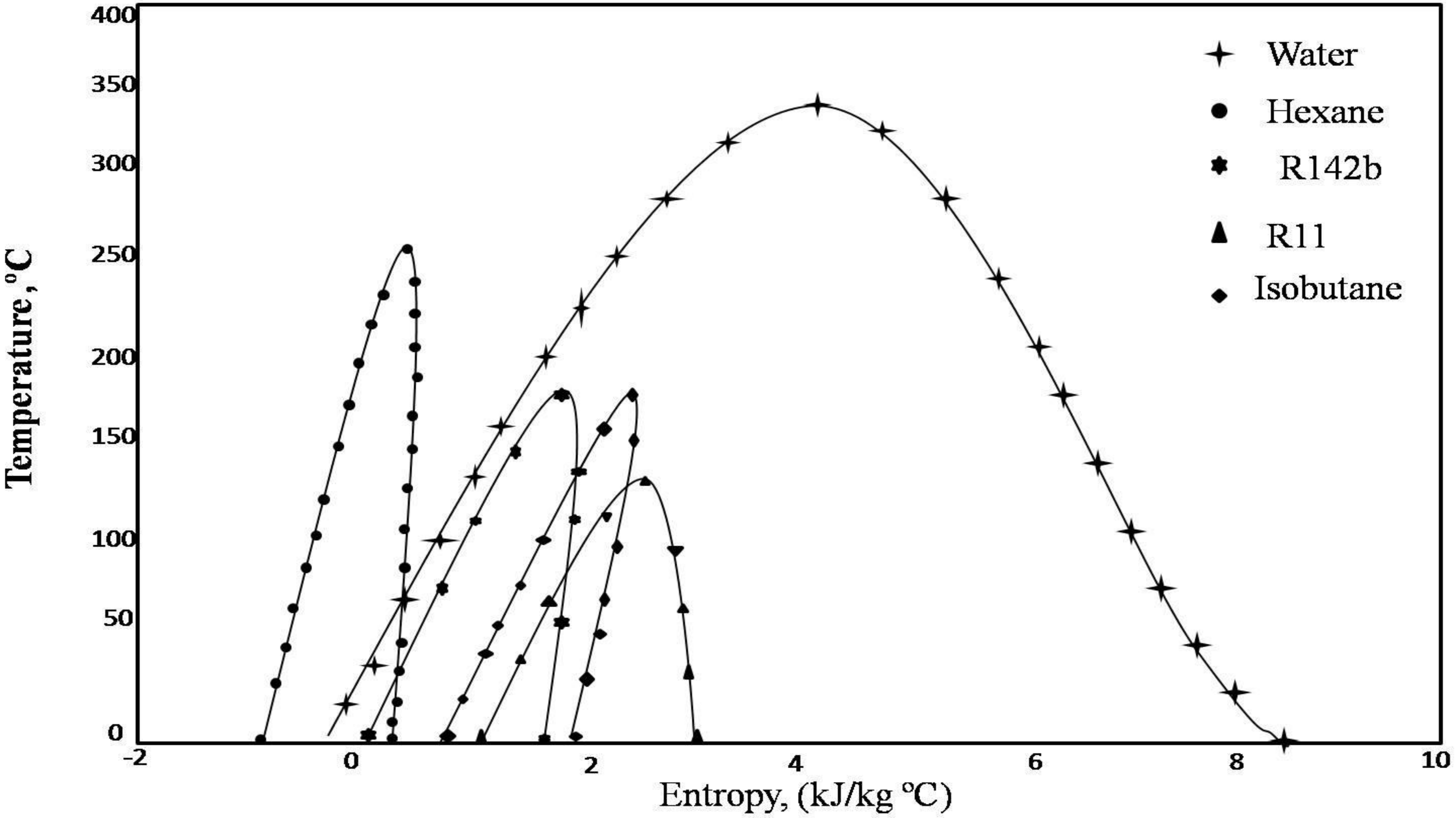


Figure 3.1: The T-S diagram for comparing selected organic fluids and water [25]

A noticeable difference in Fig. 3.1is the entropy difference between saturation liquid line and saturated vapor. Organic fluids have a very low entropy change compared with water. Using water as working fluid needs more thermal energy to change phase from saturated liquid to saturated vapor. A higher mass flow rate leads to higher power consumption by the pump so therefore, to eliminate the risk of high pressure losses a high pressure piping system (steam system pipes designed to operate more than 15 p.s.i) is used [26]. In addition, as mass flow rate increases the component sizes of the system also need to be increased and vice versa.

3.1.4 Condenser pressure

The condensing pressures in most ORCs are higher than the atmospheric pressure Patm. It is very important that the condensing pressure is higher than the atmospheric pressure because it avoids any form of infiltration problem which may occur in the system and also avoid efficiency decrease in the cycle. The condensing pressures at a temperature of 298 K for some organic fluids such as R11, Isobutane and R236fa are 105.49, 349.14 and 271.04kPa respectively and water at the same temperature has a condensing pressure lower than Patm, which is of 3.15kPa [27].

3.1.5 Cycle architecture

When considering the design and size of an ORC component, the density of the organic working fluid is very important. When the density of the working fluid is high, the specific volume and volumetric flow is subsequently low and smaller size components can be used for the ORC system. Density, enthalpy change and pressure ratio influences the cycle architecture of the expander. In steam cycles the enthalpy change and pressure ratio over the expander is very high. The expander undergoes several stages of expansion to produce more work output. The enthalpy change and pressure ratio in ORC is low making the expansion stages in ORC system less for most working fluids (one or two expansion stages). Due to high density in the condenser and evaporator, the organic fluids gives smaller size piping system and offer a less capital intensive cycle. Some other advantages of the ORC is that they require a less complicated control system and also their components are a lot cheaper when compared to the conventional Rankine cycle [28].

The droplet formation is one major problem encountered at the end of expansion process in the expander when using Steam Rankine cycle. When these droplets are formed they cause corrosion to the turbine blades which reduces the life cycle and thermal efficiency of the expander. Superheating the steam in the steam generator avoids the formation of liquid droplets in the system. The preheater, evaporator and superheater are three heat exchangers required in the boiler of a steam Rankine cycle while the ORC system requires one or two simple heat exchangers. Most ORCs use isentropic and dry working fluids therefore, there is no need for superheating. For dry and isentropic working fluids the expansion of the saturated vapor eventually leaves the expander at a superheated temperature thereby reducing the risk of liquid droplet formation in the expander. An addition of an internal heat exchanger where dry and isentropic organic fluids are employed improves the cycle efficiency.

3. 2 working fluid selection

Heat source and heat sink temperatures are very important when selecting a suitable working fluid for the ORC system. There are different organic fluids that have a good match between the heat source and heat sink temperature for different operating parameters. Choosing a suitable working fluid for the ORC system is not an easy task. The fluid selection process basically depends on thermodynamic, safety and environmental properties of the working fluid. Some criteria should be taken into consideration when selecting a suitable working fluid for ORCs. These criteria are as follows:

3.2.1 Thermodynamic properties

In the design process of the ORCs, the thermodynamic properties are of key importance. Factors affecting the ORC design are discussed below

- There should be a high thermal efficiency and net work out for any specific heat source and heat sink temperature.
- There should be an increase in the heat transfer between the organic working fluid, heat source and heat sink temperature.
- To avoid leakage problems, the atmospheric pressure should be lower than the condensing pressure.
- When there is a large variation of enthalpy, the network out in the expander is high.
- There should be stability in the fluid both chemically and thermally.
- With regards to saturation vapor line slope; Isentropic, wet and dry are three different organic working fluids used in ORCs. When wet fluids are used in ORCs, they tend to have a negative saturation vapor line slope causing the formation of liquid droplets which may damage and also reduces the efficiency of the turbine blades. When dry and isentropic working fluids are used in ORCs having positive and infinite saturation vapor line slope respectively, they do not form liquid droplet since they leave the evaporator exit as superheated vapor. Figures 3.2 - 3.4 show the T-s diagram for isentropic, wet and dry fluids [29].

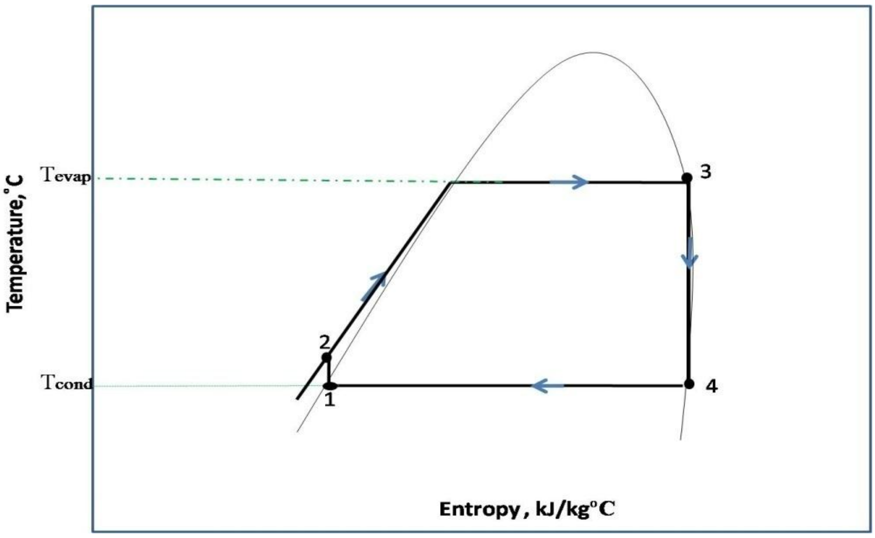


Figure 3.2: Isentropic working fluid T-s diagram

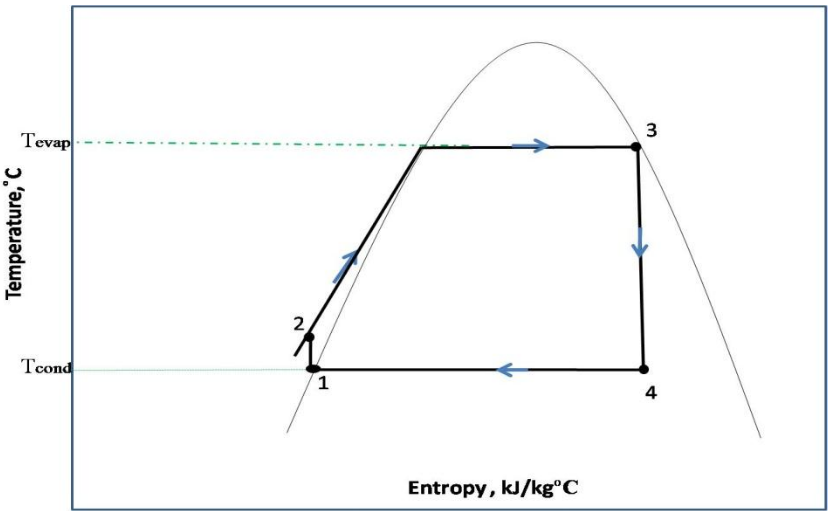


Figure 3.3: Wet working fluid T-s diagram

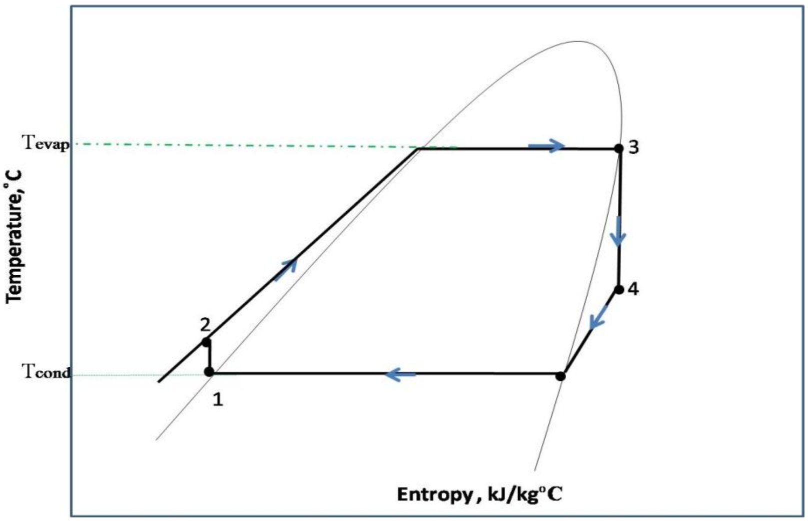


Figure 3.4: Dry working fluid T-s diagram

3.2.2 Safety and Environmental Criteria

When selecting a working fluid the safety and environmental impact are major aspects which should be taken into consideration. Over the past years, a lot of working fluids have been phased out due to their unfriendly characteristics in the environment and more working fluids are still being phased out. Most of the working fluids phased out are due to their high global warming potential and ozone depletion potential. It is important to note that while some working fluids have very good thermodynamic properties they may not be suitable when taking the safety and environmental aspects into consideration. Examples of working fluids that have been phased out are some CFCs and HCFs [30]. The major reasons why these working fluids were banned were their global warming potential and/or ozone depletion potential. Safety and environmental criteria that should be considered when selecting a suitable working fluid are discussed below:

The environmental and safety data for this study are taken from physical, safety and environmental data by James M. Calm [31].

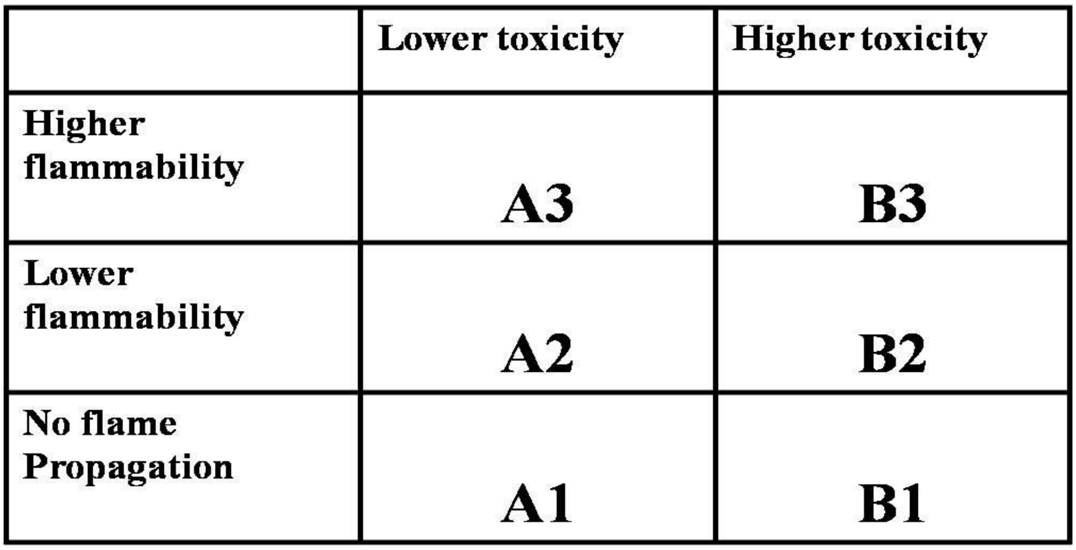
- **Global Warming Potential (GWP)**: The amount of GWP refers to the global warming caused by a particular working fluid relative to CO_2 for a 100 year time frame. Water has zero GWP and CO_2 has GWP of 1. Carbon dioxide has a large net impact on global warming that is why it is used as a reference point. Some working fluids which are available in smaller quantities have higher global warming potential when compared to CO_2 but they are disregarded.
- **Ozone Depletion Potential (ODP)**: The Ozone Depletion Potential refers to the working fluid ability to destroy the ozone layer above the earth surface relative to tri-chlorofluoro-methane (R11). CFC-11 has ozone depletion potential to be

one while other CFCs and HCFCs have ozone depletion potential ranging from 0.01 to 1.0. Ozone depletion potential in halons (synthetic chemical compound containing one or two carbon atoms and bromine) are very high getting up to 10. In working fluid selection the ODP is a very important factor that needs to be put into high consideration. A lot of working fluids have been phased out by the Montreal Protocol due to their high ODP. Therefore any working fluid that is selected should have a very low ODP.

- **Safety classification** (ASHRAE, 2010a and 2010b)

  Table 3.1 shows the safety classification of organic working fluid according to ASHRAE. The letter A indicates when the working fluids have lower toxicity while the letter B indicates when the working fluids have higher toxicity. The flame propagation of the working fluid are indicated by the numbers 1, 2 and 3. When the flame propagation is 3 it means that the working fluid has a higher flammability potential, when the flame propagation is 2 it means that the working fluid has a lower flammability potential and when the flame propagation is 1 it means that the working fluid has no flammability potential.

Table 3.1: The Safety classification



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

Chapter 4

METHODOLOGY

4.1 The thermodynamics of ORCs

Similar to the conventional steam power cycle, the working fluid in the ORC system is first pumped from a condenser at a low pressure to a high pressure at the evaporator inlet. In an ideal cycle the entropy remains constant throughout the pumping process. Thermal energy is absorbed from a heat source at constant pressure by the high pressure liquid entering the evaporator. During this process a phase change occurs in the organic working fluid from a saturated liquid to a saturated vapor. Waste heat from industrial activities, biomass, solar and geothermal can be a source of external heat for the ORC system. In an ideal cycle, mechanical work is produced in the expander when high pressure saturated vapor leaves the evaporator and expands isentropically. The pressure of the fluid at the exit of the expander decreases to the condenser pressure. The working fluid that leaves the expander after expansion process enters the condenser as either saturated or superheated vapor based on the thermo-physical properties of the employed organic working fluid. There is a change in phase in the organic working fluid as it condenses in the condenser from a saturated vapor to saturated liquid. After all these processes, the cycle repeats the entire procedure again. Figure 4.1 shows a real and ideal T-s diagram of the ORC.

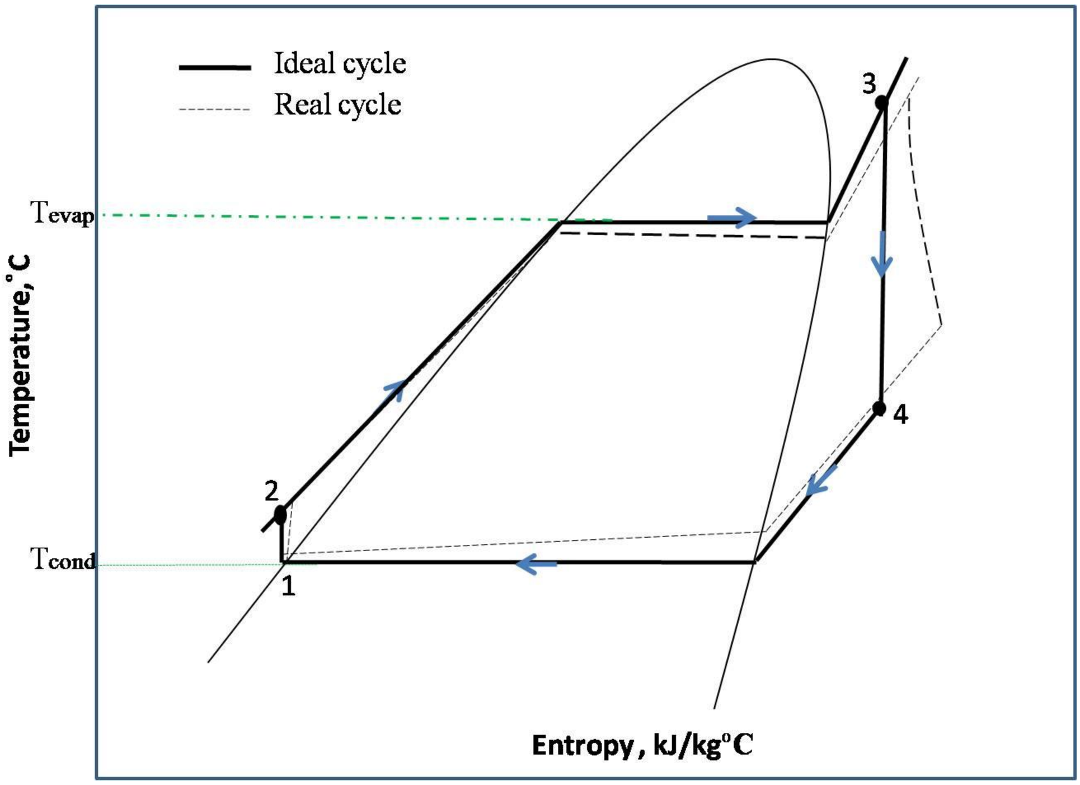


Figure 4.1: Real and ideal T-S diagram of ORC

Some losses occur in an expander and pump in a real cycle during the expansion and pumping of the working fluid. In other words the expander and pump isentropic efficiencies are less than 100 %. The heat addition and rejection in the real process is not isobaric therefore, there are some pressure losses in the piping system. The performance of the thermodynamic system is very much affected by irreversibilities.

4.2 Theoretical analysis of the ORC system

The conventional Rankine cycle have components which are similar to that of the ORC such as pump, evaporator, condenser and expander. As mentioned earlier, they both have the same working principle the only major difference between them is the working fluid employed in the system. Figure 4.2 shows the ORC cycle layout while figure 4.3 shows the T-S diagram for an ideal ORC.

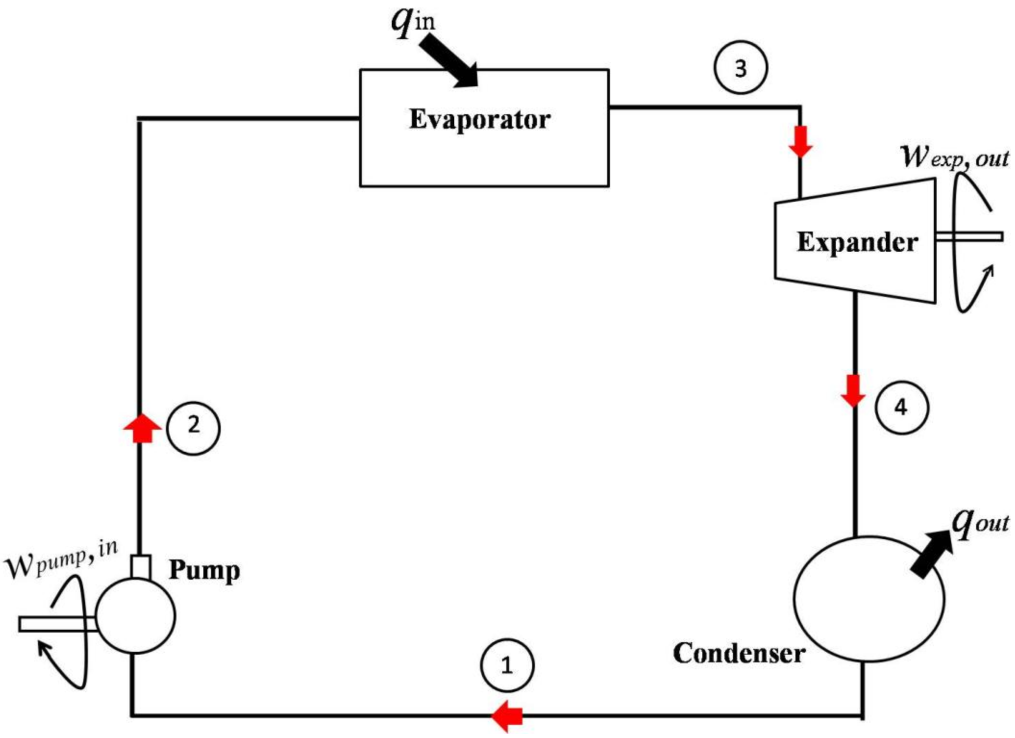


Figure 4.2: ORC basic layouts

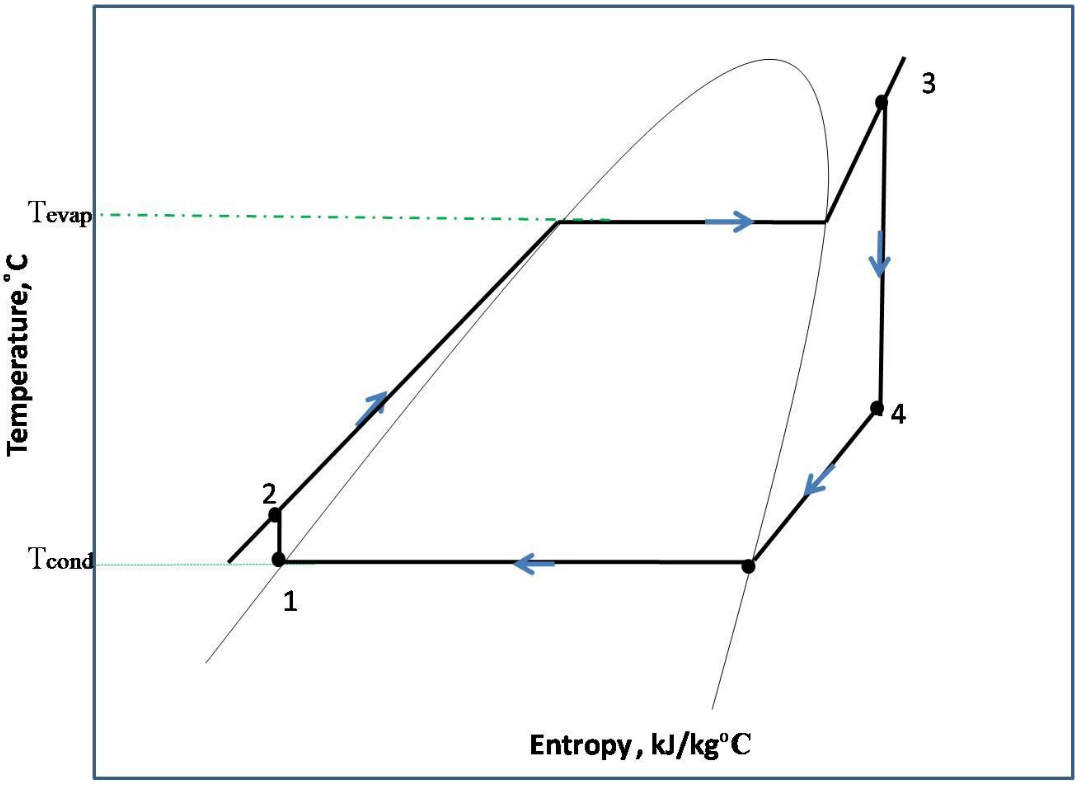


Figure 4.3: T-s diagram for an ideal ORC

For an ideal cycle, there are four major processes the working fluid undergoes before a complete cycle is made. These are as follows:

4.2.1 Process (1 – 2) compression in the pump

In this process the saturated fluid that leaves the condenser is pumped at constant entropy to the evaporator pressure. Energy transformation efficiency never reaches 100% even in an ideal process. As shown in Fig. 4.3, point 1 indicates the state of the working fluid at pump inlet and point 2 indicates the state of working fluid at pump outlet. The specific work input by the pump is calculated by the following equation.

$$w_{1-2} = (h_2 - h_1) \tag{4-1}$$

Where w_{1-2} is the work input of pump (kJ/kg), h_1 is the enthalpy at the pump inlet (kJ/kg) and h_2 is the enthalpy at the pump exit (kJ/kg).

4.2.2 Process (2-3) heat addition in the evaporator

Point 3 indicates the evaporator exit when heat is added to the working fluid and this can be estimated by the following equation.

$$q_{2-3} = (h_3 - h_2) \tag{4-2}$$

Where q_{2-3} is the specific heat added to the working fluid (kJ/kg) and h_3 is the vapor enthalpy at the exit of the evaporator (kJ/kg).

4.2.3 Process (3-4) expansion in the expander

In this process energy is absorbed in the evaporator as the working fluid expands in the expander to produce mechanical work. Point 4 indicates the expander exit where the work is done and this can be calculated as:

$$w_{3-4} = (h_3 - h_4) \tag{4-3}$$

Where w_{3-4} is the work input of the expander (kJ/kg) and h_4 is the vapor enthalpy at the expander exit (kJ/kg).

4.2.4 Process (4-1) heat rejection in the condenser

Heat is rejected in this process as the working fluid in the condenser condenses and is recycled in the system again. Regardless of friction losses in the pipes of the condenser, the heat rejection process is said to be isobaric even though there is pressure drop in the condenser. The working fluid becomes saturated after it leaves the condenser. The state of the working fluid indicated as Point 1 in Fig 4.3 represents the condenser exit and pump inlet. The amount of heat rejected can be calculated as:

$$q_{4-1} = (h_4 - h_1) \tag{4-4}$$

Where q_{4-1} is the specific heat rejected in the condenser (kJ/kg). The cycle thermal efficiency for the entire process can be calculated from the following equation.

$$\eta_{\text{th}} = \frac{w_{3-4} - w_{1-2}}{q_{2-3}} \tag{4-5}$$

The cycle efficiency is the ratio of the net work output to heat that is absorbed in the evaporator.

4.3 ORC system improvement

To improve the ORC efficiency the isentropic and dry working fluid can be employed since they both leave the expander at superheated vapor state. The superheated vapor at the exit of the expander reduces the possible damage on the turbo machine expanders as a result of low vapor quality. In ORCs, the turbo machine expanders have longer life span compared with the conventional Rankine cycle. In an ORC system a scroll and screw expander can be used instead of a turbo machine expander that has low resistance to improve the vapor quality after expansion. Therefore, it is not necessary to superheat the working fluid in the ORC system when dry and isentropic working fluids are used.

4.3.1 The Internal Heat Exchanger

When an internal heat exchanger is introduced to improve the ORC system, the cycle undergoes six major thermodynamic processes. They are as follows:

4.3.1.1 Process (1-2) compression in the pump: the condensing working fluid is pumped from condenser pressure to evaporator pressure.

4.3.1.2 Process (2-3) IHX: heat transfer process in the IHX between saturated working fluid at pump exit and superheated vapor at expander exit.

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

4.3.1.4 Process (4-5) expander: the saturated or superheated vapor enters the expander and the absorbed thermal energy in the IHX and evaporator leaves the expander as superheated vapor.

4.3.1.5 Process (5-6) IHX: heat transfer process in the IHX between the high temperature vapor at expander exit and low temperature at pump exit.

4.3.1.6 Process (6-1) condenser: The saturated vapor at the IHX exit enters the condenser. Here heat is rejected from the working fluid.

When an internal exchanger is introduced into the ORC cycle, it enables the cycle to recover thermal energy from the working fluid at the expander exit which has higher temperature than the condenser temperature. Internal heat exchanger plays a major role in increasing the thermal efficiency [32]. Figure 4.4 show the layout of an internal heat exchanger.

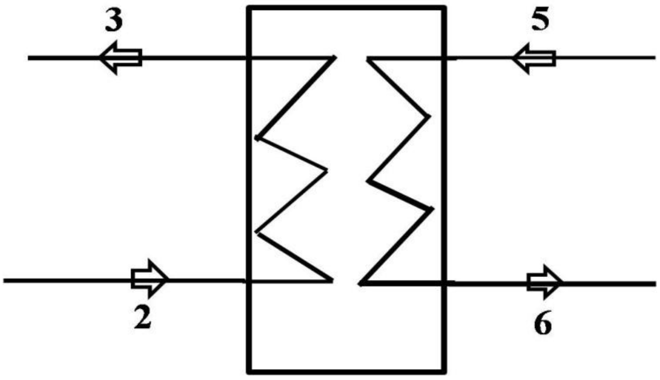


Figure 4.4: Cycle layout of Internal Heat Exchanger

The total heat transfer in the internal heat exchanger can be estimated from the following equation.

$$q_{IHX} = (h_5 - h_6) = (h_3 - h_2) \tag{4-6}$$

4.4 The thermodynamic Model of the ORC

Thermodynamic models have been developed in this study using the Vissim and the EES software packages. The VisSim is a block diagram visual simulation program employed to run simulation, do numerical calculations which enables the analyses of engineering design problems. The Engineering Equation solver (EES) is a general equation solving program that can numerically solve thousands of coupled non-linear algebraic and differential equations. A major feature of EES is the high accuracy thermodynamic property database that is provided for hundreds of substances in a manner that allows it to be used with the equation solving capability [33].

In this study only the selected dry and isentropic working fluids are considered. The selected organic working fluids used in this study are Butane, R245fa, Isobutane, R236fa and R124. To carry out the performance analyses of the ORCs with different working fluids; simulations were performed for different operating parameters. An internal heat exchanger is introduced into the simple ORC system as shown in Fig. 4.5. The cycle consists of an internal heat exchanger, a pump, a condenser, evaporator and an expander. When an internal heat exchanger is introduced into the system, the cycle performance improves. The improvement in the thermal efficiency is strongly dependent on the working fluid temperature at the expander exit. The dry and isentropic working fluids show greater thermal efficiency improvement when an internal heat exchanger is added to the system compared to the wet types. The expander efficiency, evaporator, condenser pressure and the rate of superheating are factors that affect the expander exit vapor temperature. The internal heat exchanger extracts thermal energy from the superheated vapor and supplies it to the working fluid at the pump exit.

To investigate the proposed working fluids the operating parameters of the ORC system are set between two temperature limits i.e, a low temperature at the condenser (T_{cond}) and a high temperature at the evaporator (T_{Evap}). Figure 4.6 shows the ORC T-s diagram used for the investigation. The operating parameters are varied and their effects on the cycle performance and the net work output are investigated. The effect of expander inlet temperature, condenser temperature on the cycle performance and net work output are investigated.

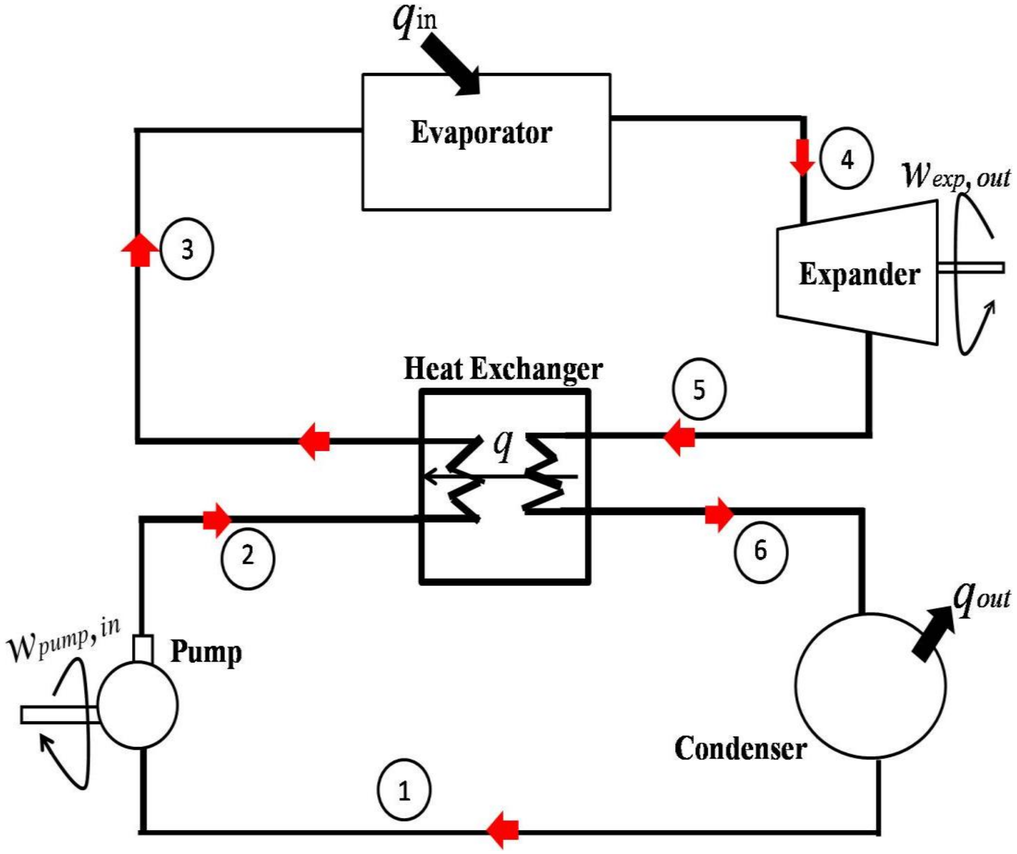


Figure 4.5: ORC system used for investigation

4.5 Simulation assumptions in the analyses

The followings are the assumptions used in the study

- The pressure drops in the heat exchangers are neglected.
- The expander and pump's isentropic efficiencies are considered to be 0.9.
- Condensing temperature $T_{Cond.}$ = 20ºC
- Evaporating temperature $T_{Evap.}$ = 120ºC.
- The mass flow rates of the hot and cold fluid in the internal heat exchanger are assumed to be the same.
- There is no temperature increase or decrease between the evaporator exit temperature and the expander inlet temperature.

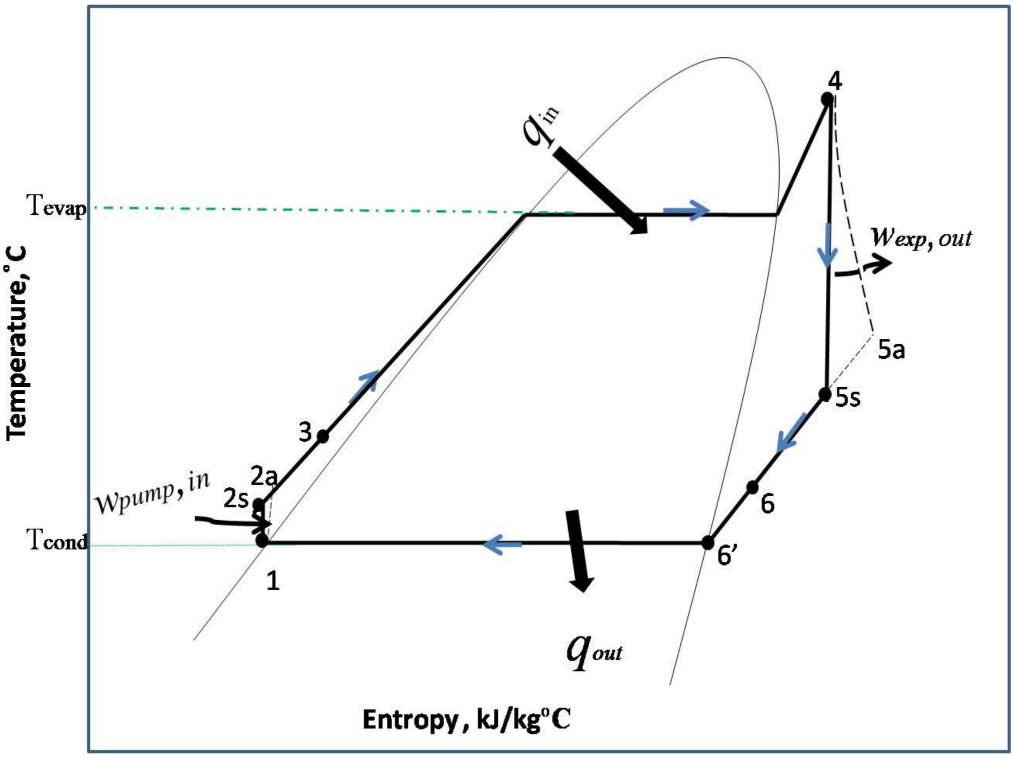


Figure 4.6: T-s ORC diagram for investigation

4.6 Properties of the working fluids used for the investigation

Table 4.1 shows the critical temperature and pressure for some isentropic and dry working fluids and Fig 4.7 shows the T-s diagram of the working fluids. The properties of working fluids used in this study are briefly discussed below:

4.6.1 Butane

Butane is an organic compound with the formula C_4H_{10} that is an alkane with four carbon atoms. It is a gas at atmospheric pressure and room temperature. It is a highly flammable, highly toxic colorless gas. Inhaling of butane can cause drowsiness, narcosis, euphoria and high blood pressure which can eventually lead to death. It is most commonly used in the United Kingdom and was the cause of about 50% of "solvent related" deaths in 2000 [34]. Burning of butane gas produces Nitrogen dioxide, a toxic gas which is very hazardous to human health.

4.6.2 Isobutane

Isobutane which is also known as methyl-propane is a chemical compound with molecular formula C_4H_{10} and is an isomer of butane. Isobutane is the simplest alkane with a tertiary carbon. Using isobutane as refrigerant has hazards associated with explosion risk because of its highly flammable characteristic. Some of the refrigerator explosions reported in the United Kingdom is suspected to have been caused as a result of isobutane leaking into the refrigerator cabinet and being set on fire by sparks in the electrical system [35].

4.6.3 R245fa (1, 1, 1, 3, 3-pentafluoropropane)

R245fa is a hydro fluorocarbon used primarily for closed cell spray foam insulation produced by Honeywell and also in Asia by Sinochem [36]. It has no ozone depletion potential; it is not flammable and nearly non-toxic. Despite the fact that it is intended to remain trapped within the foam insulation, it is practically non-biodegradable with a lifetime of 7.2 years when it eventually escapes into the atmosphere.

4.6.4 R236fa (1, 1, 1, 3, 3, 3-Hexafluoropropane)

R236fa is an organic chemical fluoride. It is a colourless gas usually available in the form of a liquid gas. The global warming potential is 9820 [37]. It is used as a heat transfer medium, fire suppression agent and also as working fluids in thermodynamic cycles.

4.6.5 R124 (1-Chloro-1, 2, 2, 2-tetrafluoroethane)

R-124 is a hydro chlorofluorocarbon used as a refrigerant. It is a colourless gas, non flammable but has an ozone depletion potential of 0.02 and a global warming potential of 619. The chemical is also marketed for use as a gaseous fire suppressant [38].

Table 4.1: Critical temperature and pressure for water and different organic working fluids [39]

S/N	**Short name**	**Full name**	**Critical temp (C)**	**Critical pressure (bars)**	**Working fluid type**
1	Butane	n-Butane	151.975	37.960	dry
2	Isobutane	2-methyl propane	134.66	36.290	dry
3	R113	1,1,2-trichloro-1,2,2-trifluoroethene	214.06	33.922	dry
4	R115	Chloropenta-fluoroethane	80.0	31.200	Isentropic
5	R116	Hexafluroethane	19.88	30.480	isentropic
6	R123	1,1-dichloro-2,2,2 trifluoroethane	183.681	36.618	isentropic
7	R124	1-chloro-1,2,2,2 tetrafluoroethane	122.275	36.242	isentropic
8	R125	Pentafluroethane	66.023	36.177	isentropic
9	R141b	1,1-dichloro-1-fluoroethane	204.4	42.120	dry isent
10	R142b	1-chloro-1,1 difluoroethane	137.11	40.550	isentropic
11	R218	Octafluoropropane	71.87	26.400	dry
12	RC318	Octafluorocycle butane	115.23	27.775	dry
13	R227ea	1,1,1,2,3,3,3-heptafluoropropane	102.80	29.990	dry
14	R236ea	1,1,1,2,3,3-hexafluoropropane	139.29	35.019	dry
15	R236fa	1,1,1,3,3,3-hexafluoropropane	124.92	32.00	dry
16	R245ca	1,1,2,2,3-pentafluoropropane	174.42	39.25	dry
17	R245fa	1,1,1,3,3-pentafluoropropane	154.1	36.40	dry
18	Water	Water	374	220.6	Wet

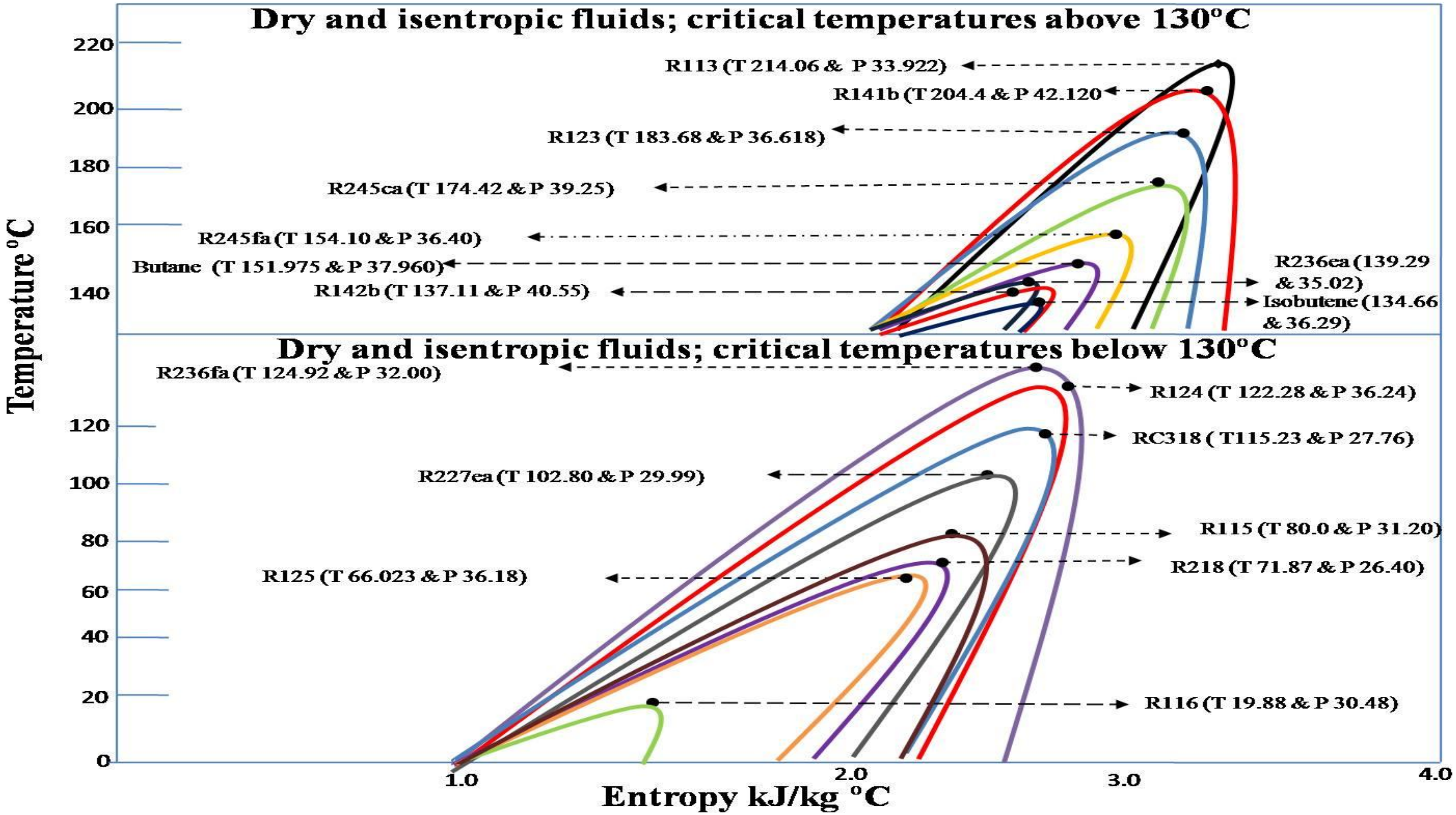


Figure 4.7: T-s diagram for some dry and isentropic working fluids

4.7 Simulation model

In this study, the system modeling has been done using VisSim. All the components of the ORC system (see Fig. 4.5) are modeled separately under compound blocks (i.e modular simulation) and the ORC system modeling are performed by connecting these sub-components. As a result of this, the program blocks developed for the ORC system simulation includes about 600 blocks including the organic working fluid property blocks. The thermodynamic properties of the working fluids were prepared by using the EES software package. These working fluid properties were arranged in various blocks in VisSim to find the state of the working fluids at different points such as the saturation and superheated properties at a given state Figure 4.8 shows a sample block model for butane.

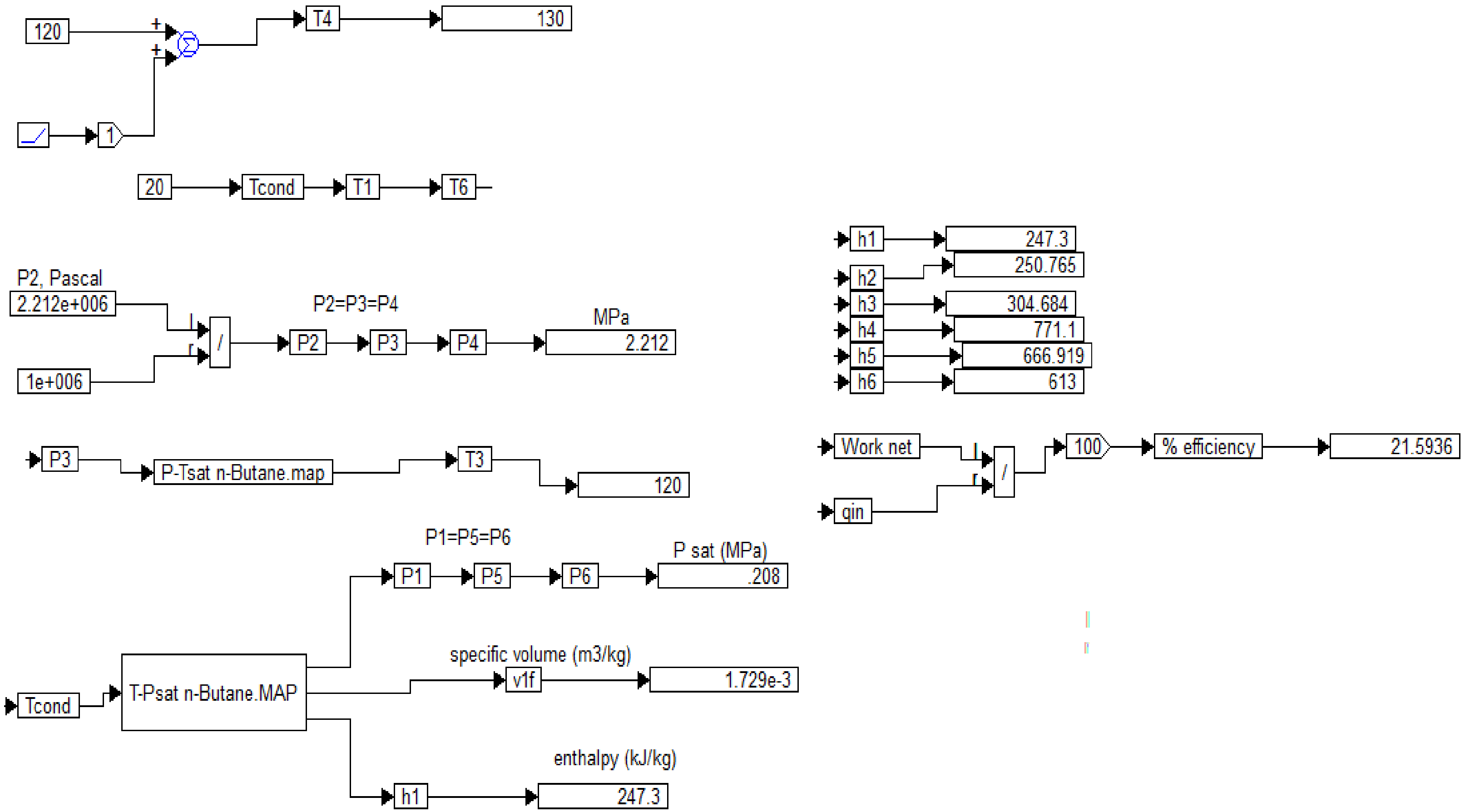


Figure 4.8: A sample simulation model for butane

Chapter 5

RESULT AND DISCUSSION

5.1 Simulation results

In this study the following criteria are used to determine the suitable working fluid in the ORCs based on their thermodynamic, environmental and safety properties.

5.1.1 The effect of superheating on cycle efficiency

Figure 5.1 shows that slightly superheating the dry and isentropic working fluid has negligible impact on the cycle efficiency. The efficiency of the cycle remains almost constant as the fluid is slightly superheated i.e., 10ºC higher from the expander inlet temperature (120ºC) to a superheated temperature at the expander inlet (130ºC). There is a change in entropy when additional heat is added to the working fluid. According to the results obtained from the simulations the best working fluid in this case is Butane having the highest efficiencies between 21.42% and 21.60%, the second is the R245fa having efficiencies between 21.09% and 21.40%, the third is Isobutane having efficiencies between 20.87% and 21.01%, the fourth is R236fa having efficiencies between 20.37% and 20.58% and the fifth is R124 having the lowest thermal efficiency between 19.6% and 19.7%. The result shows that superheating dry and isentropic working fluids are not necessary as they leave the expander exit at a superheated state unlike the wet types.

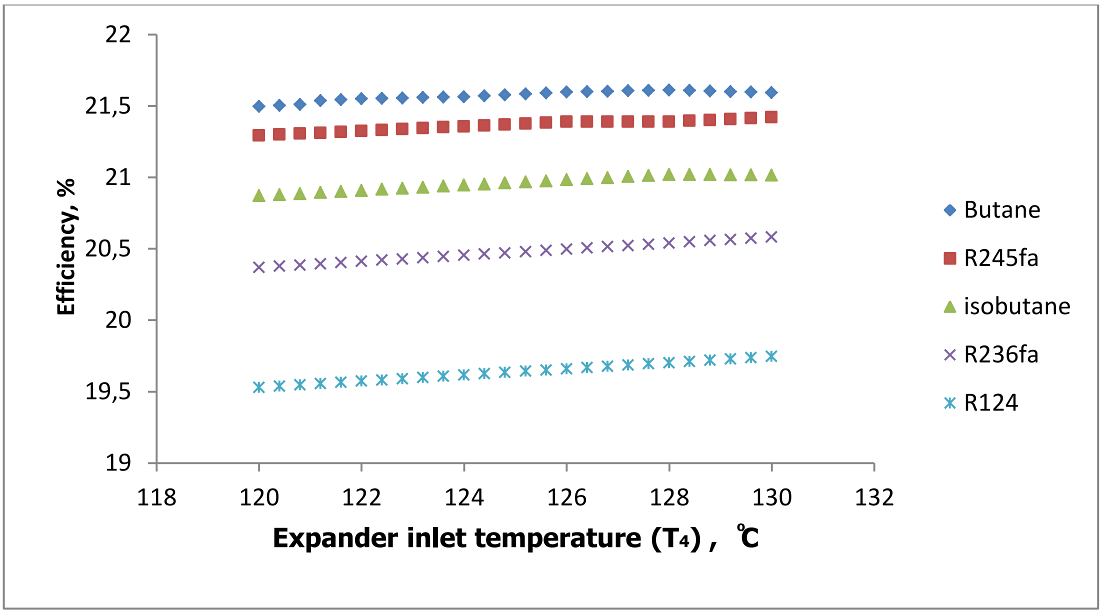


Figure 5.1: The effect of superheating on cycle efficiency

5.1.2 The effect of condenser temperature on cycle efficiency

Figure 5.2 shows that increasing the condenser temperature of the working fluid has a negative impact on the cycle efficiency. If the temperature of the working fluid in the condenser increases, the thermal cycle efficiency of the working fluids linearly decreases. In this case the condenser temperature at 20ºC is increased steadily 10ºC higher to a new condenser temperature at 30ºC. Butane and R245fa show better thermal efficiencies compared with the other working fluids. Increasing the condenser exit temperature is not favorable to the thermal efficiency of the cycle. The results show that the efficiency of the working fluids linearly decreased for butane from 21.60% to 19.66%, for R245fa 21.40% to 19.54%, for isobutene 21.01% to 19.12%, for R236fa 20.58% to 18.74% and for R124 from 19.7% to 17.94% as the condenser temperature increases to 30ºC. This result indicates that ORC systems will be more beneficial in places where lower condenser temperatures are available.

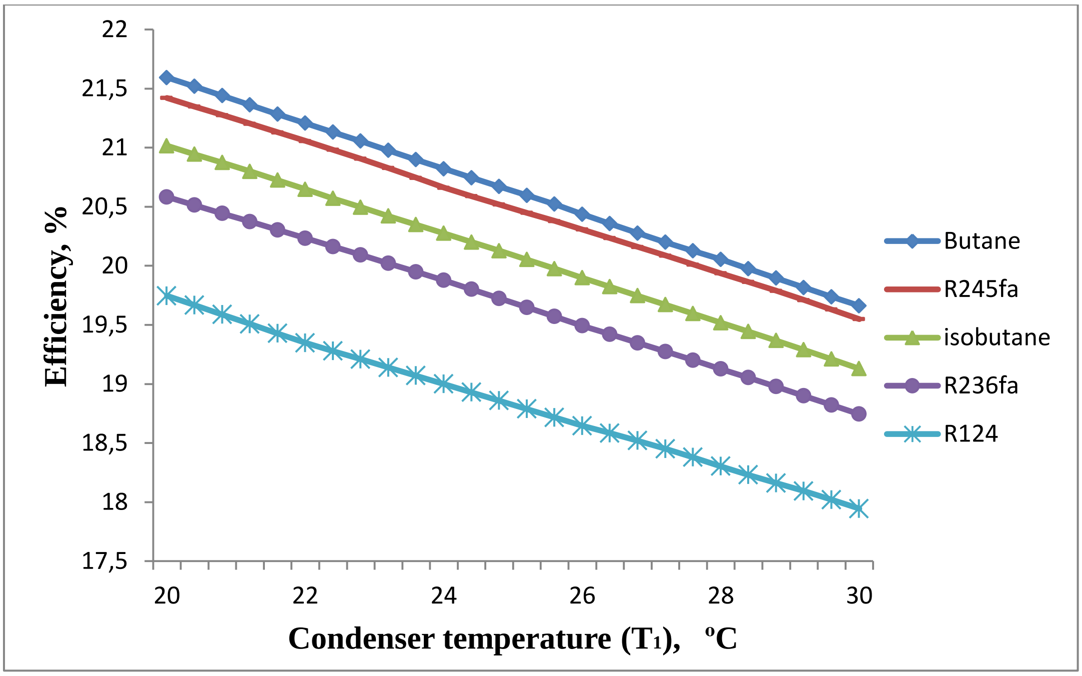


Figure 5.2: The effect of condenser temperature on cycle efficiency

5.1.3 The effect of expander inlet temperature on net work output

Figure 5.3 shows that the specific net work output slightly increased as working fluids are slightly superheated 10ºC higher from the expander inlet temperature. The specific net work output for isobutane increased from 88.2kJ/kg to 89.05kJ/kg which is higher than R245fa which increased from 52.25kJ/kg to 52.66kJ/kg. This is due to large enthalpy variation as the temperature increases. Butane has the highest specific network output of 98.7kJ/kg to 100.7kJ/kg before and after superheating. The working fluids R236fa and R124fa have almost the same specific net work output. Although, the cycle efficiency utilizing R245fa is higher than the cycle utilizing isobutane, the specific net work is higher in the cycle utilizing isobutane as the working fluid. The results show that the specific network output depends largely on enthalpy variation at different temperatures for each working fluid and also the net work output slightly increases when the working fluid is superheated.

The effect of slight superheating of the working fluid on the thermal efficiency compared with the effect of increasing the saturation temperature of the working fluid at the same level (i.e., 130ºC), it was found that slight superheating has higher impact on the cycle efficiency.

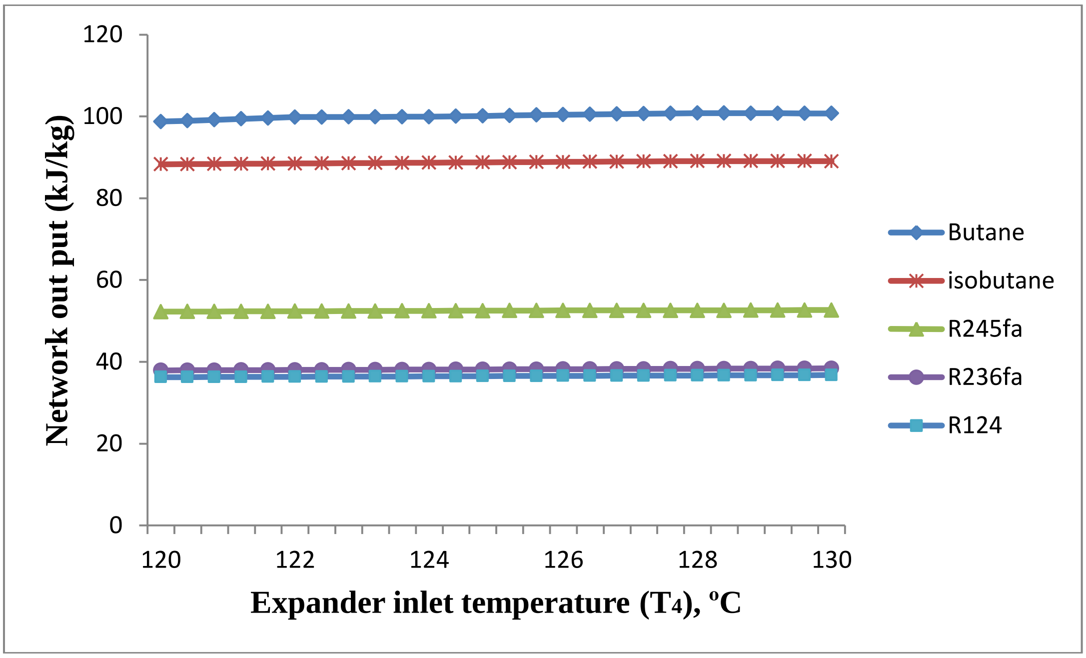


Figure 5.3: The effect of expander inlet temperature on net work output

5.1.4 The effect of condenser temperature on the net work output

Figure 5.4 shows that increasing the condenser temperature of the working fluids has a negative impact on the specific net work output of the ORC. When the temperature of the condenser increases, the net work output of the ORC linearly decreases. Butane and isobutane show better specific net work output compared with the other fluids. The results show that the specific net work output of the working fluids linearly decreases as the condenser temperature at 20ºC is increased steadily 10ºC higher for example for butane the net work decreases from 100.7kJ/kg to 87.05kJ/kg, for isobutane it decreases from 89.05kJ/kg to 76.49 kJ/kg, for R245fa from 52.66kJ/kg to 45.54kJ/kg, for R236fa from 38.40kJ/kg to 32.87kJ/kg and for

R124 from 36.72 kJ/kg to 31.36kJ/kg. Similar to the results presented in Fig. 5.3, even though, R245fa has better cycle efficiency compared to isobutane, the specific net work out produced by ORC employing isobutane as working fluid is higher than R245fa. The results indicate that increasing condenser temperature is not favorable on the specific net work output of the cycle as expected.

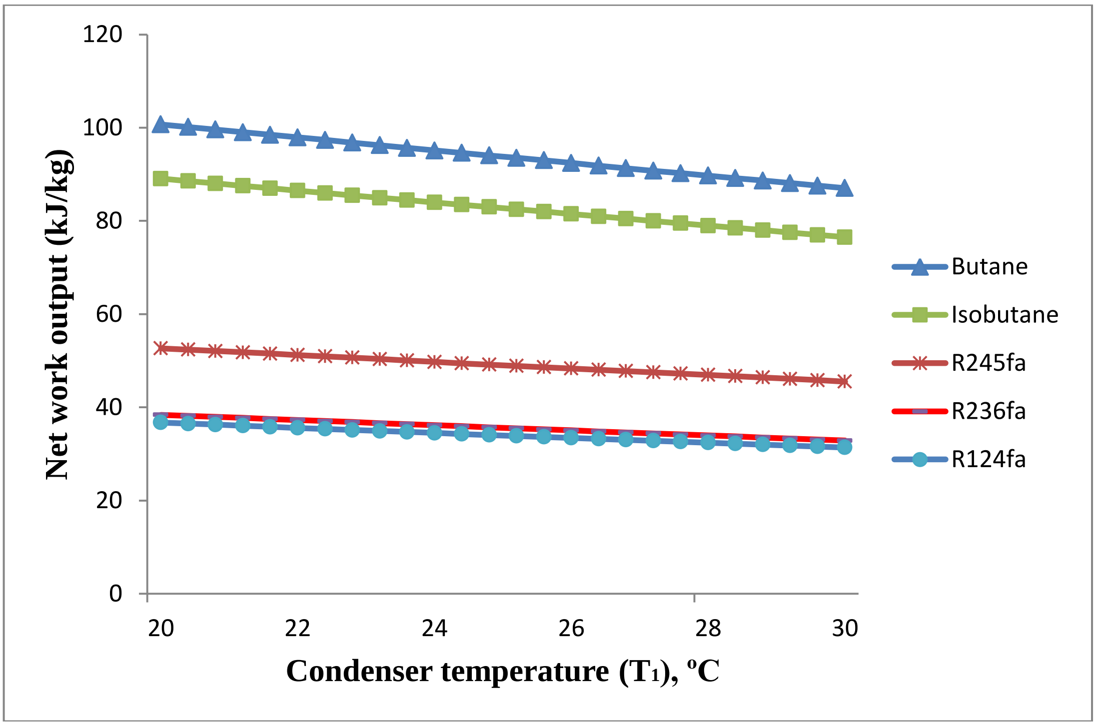


Figure 5.4: The effect of condenser temperature on net work out put

5.1.5 Environmental and Safety Data for the Working fluids

Table 5.1 presents the environmental and safety data for the working fluids investigated. The data show that butane belongs to a safety group A3 which implies that it is highly flammable and highly toxic with no ozone depletion potential and a global warming potential of 20. R245fa belongs to the group B1 which implies that it is non flammable, but toxic with no ozone depletion potential and a Global warming potential of 950. Isobutane belongs to the safety group A3 which implies that it is highly flammable and highly toxic with no ozone depletion potential and a global warming potential of 20. R236fa belongs to the safety group A1 which implies that it is non flammable, has low toxicity with no ozone depletion potential and a global warming potential of 9820. R124 belongs to the safety group A1 which implies that it is non flammable, has lower toxicity with ozone depletion potential of 0.02 and a global warming potential of 619.

Table 5.1: Environmental and safety data for the investigated working fluids taken from physical, safety and environmental data by James M. Calm [43]

Name of working fluids	**Safety group**	**Ozone depletion potential (ODP)**	**Global warming potential (100 years) (GWP)**
Butane	A3	0	20
R245fa	B1	0	950
Isobutane	A3	0	20
R236fa	A1	0	9820
R124	A1	0.02	619

Chapter 6

CONCLUSION

In this thesis simulations were carried out using the VisSim and EES software package to analyze thermodynamically the ORCs utilizing different working fluids. Selecting a suitable working fluid for an ORC system is not an easy task. Only some of the dry and isentropic working fluids are considered and the criteria used to determine which of the working fluid is suitable are based on the thermodynamic analysis, safety and environmental aspects of the working fluids.

From the thermodynamic perspective, it is not necessary to superheat dry and isentropic organic working fluid since they leave the evaporator exit at a superheated vapor state. According to the simulation results for the studied working fluids, butane has the highest thermal efficiency compared with other working fluids studied. The highest thermal efficiency was achieved when butane was slightly superheated and at the 20ºC condenser temperature. The R245fa also shows high thermal efficiency when compared to the remaining organic working fluids i.e, isobutane, R236fa and R124. The specific net work output for butane and isobutane are higher than R245fa because of the large variation in enthalpy as the temperature increases. The R245fa is preferred to isobutane even though isobutane has higher specific net work output as R245fa has higher thermal efficiency compared with isobutane.

Butane has better thermodynamic properties compared with other working fluids, but it is not environmentally friendly because it belongs to the group A3 which is highly flammable and highly toxic with no ozone depletion potential and a global warming potential of 20. The cycle using R245fa has better performance except for butane and it belongs to the safety group B1 which means that it is not flammable but toxic with no ozone depletion potential and a global warming potential of 950. In conclusion the working fluids in this study are investigated based on their thermodynamic performance, safety and environmental characteristics. It is concluded that the R245fa is the most suitable working fluid for an ORC cycle compared to the four working fluids.

.

REFERENCES

[1] BCS Incoporated, Waste Heat Recovery Technology and opportunities in United State industry. (2008), pp. 12-13.

[2] L.Yunfei, Analysis of low temperature Organic Rankine Cycle for solar application. (2012), pp. 20-23.

[3] J. Nouman, Comparative studies and analysis of working fluids for Organic Rankine Cycle. (2012), pp. 4-25.

[4] http://www.energy.siemens.com/hq/en/fossil-power-generation/steam-turbines

[5] S. Emdadul, Experimental Investigation of R134a based Organic Rankine cycle. (2011), p.3.

[6] J. M. Calm, G. C. Hourahan, Physical, Safety and Environmental data for current and alternative Refrigerants, (2011).

[7] B. Saleh, G. Koglbauer, M. Wendland, J. Fischer, Working fluids for low-temperature Organic Rankine Cycles. Energy, 32 (2007), pp. 1210–1221.

[8] S. Bahaa, G. Koglbauer, M. Wendland, J. Fischer. Working fluids for low temperature organic Rankine cycles. (2007), pp.1210–21.

[9] Karellas S, Schuster A. Supercritical fluid parameters in Organic Rankine Cycle applications. International Journal of Thermodynamics 2008; p.101.

[10] 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.

[11] 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.

[12] 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, (2007), pp. 2355–2363.

[13] 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), pp.1113–1119.

[14] 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.

[15] 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.

[16] 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, (2008), pp. 2212–2226.

[17] A.M. Delgado-Torres, L. Garcia-Rodriguez, Analysis and optimization of the low temperature solar Organic Rankine Cycle (ORC). (2010), pp. 2846–2856.

[18] S. Quoilin, Sustainable Energy Conversion through the use of Organic Rankine Cycles for Waste Heat Recovery and Solar Applications. (2011)

[19] http://www.kgraenergy.com/technical/organic-rankine-cycle-history

[20] http://gasengine.farmcollector.com/Gas-Engines/The-Naphtha-Engine.aspx

[21] http://theenergylibrary.com/node/10537

[22] http://www.kgraenergy.com/projects/worldwide-orc-installations

[23] M.B. Ibrahim and R.M. Kovach, A Kalina cycle application for power generation, vol. 18, (1993), pp. 961-969.

[24] P. Lolos and E. Rogdakis, A Kalina power cycle driven by renewable energy sources, vol. 34, (2009), pp. 457-464.

[25] 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.

[26] http://www.eng.usf.edu/~hchen4/Goswami%20Cycle.htm

[27] S. Quoilin, Technological and Economical Survey of Organic Rankine Cycle Systems. (2009)

[28] http://www.clean-energy-ideas.com/geothermal_power.html

[29] http://www.biomassenergycentre.org.uk

[30] Wei D, Lu X, Lu Z, Gu J. Performance analysis and optimization of organic Rankine cycle (ORC) for waste heat recovery. (2009), p.1113

[31] J.P. Roy, M.K. Mishra, A. Misra, Performance analysis of an Organic Rankine Cycle with superheating under different heat source temperature conditions. Applied Energy 88 (2011), pp.2995–3004.

[32] http://www.mcquay.com/mcquaybiz/literature/lit_ch_wc/AppG

[33] h4ttp://www.epa.gov/ozone/defns.html#odp

[34] http://www.astm.org/Standards/E681.htm

[35] D.Y. Wang, Analysis of Working Fluid for Organic Rankine Cycle. (2011).

[36] Marcia L. Huber. Model for the Viscosity and Thermal Conductivity of Refrigerants, including a New Correlation for the Viscosity of R134a. (2003), pp.3163-3178.

[37] http://www.honeywell-orc.com/tomorrows-solutions

[38] T. Hosseinnejad, Viscosity and thermal conductivity of some refrigerants at moderate and high densities on the basis of Rain water Friend theory and the corresponding states principle. (2008), pp.85–95.

[39] http://en.wikipedia.org/wiki/File:Organic_Rankine_Cycle

[40] B. Adrienne, S. Garimella, Comparative assessment of alternative cycles for waste heat recovery and upgrade. Energy, 36 (2011), pp. 4492–4504.

[41].U. Drescher, D. Bruggemann, Fluid selection for the organic Rankine cycle in biomass power and heat plants, (2007) pp.223-228.