

ORGANIC RANKINE CYCLE WITH ZEOTROPIC MIXTURES OF ALKANES AS WORKING FLUIDS FOR COGENERATION

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ABSTRACT

Organic Rankine Cycles for the utilisation of low-temperature heat sources suffer from inherently low efficiency due to Carnot limitations, with first law efficiencies of 10-15% for heat source temperatures below 200°C. The large amount of heat rejection in the condenser that this entails means that they are potentially ideal candidates for combined heat and power schemes. This paper analyses the performance of a cycle with a recirculating heat source, using a zeotropic mixture of alkanes as the working fluid. Changing the mixture composition changes the bubble and dew points of the cycle, and introduces a temperature change during phase change, known as “glide”. As the condenser outlet temperature is determined by the pinch point at the condensation temperature, the introduction of glide can increase the condenser and evaporator loading for a given condenser outlet temperature for cogeneration supply. This can work against any added benefit gained by creating a working fluid blend tailored to a specific heat source and sink. When the temperature glide is small, there is a smooth drop in condenser pressure and associated smooth increase in efficiency, When the glide is larger, the change in efficiency happens more abruptly at either end of the transition from one fluid to another, with a period of more gentle change in efficiency in between. The effect these changes have on the performance of the cycle and possible applications in cycle optimisation are an exciting area for future research.

1. INTRODUCTION

Much current research focuses on the development of systems to generate electricity from lower-quality heat sources, with temperatures of less than 250°C. However, the actual proportion of energy demand accounted for by electricity is relatively small. Figure 1, adapted from (UK DECC, 2014a), shows that only 22.8% of non-transport energy usage in the UK is accounted for by electricity.

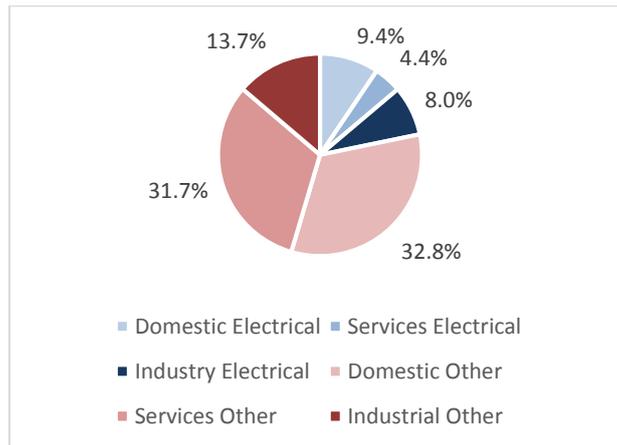


Figure 1: 2013 UK Energy Usage by Fuel and Sector (UK DECC, 2014a)

Table 1: 2013 UK Energy Usage divided into Heating and Other (UK DECC, 2014a)

Space and Water Heating	Domestic	41.9%	
	Service	13.9%	
	Industry	2.8%	58.7%
Other	Domestic	8.8%	
	Service	9.3%	
	Industry	23.2%	41.3%

Table 1, also adapted from (UK DECC, 2014a), shows the breakdown of 2013 UK non-transport energy usage into space and water heating, and other. Although this data does not account for “crossover” usage of energy, such as electric space and water heaters, or heat used for things other than space heating, for example, preheating feedstock in the chemical industry, its implications are clear; there is a large potential market for waste heat, such as that developed by power generation. This is borne out by the UK Department of Energy and Climate Change who, in their report on waste heat utilisation, estimate that there is a demand for 18.7 TWh/yr of low-grade heat (<250°C) for industrial processes (UK DECC, 2014b).

Previous research indicates that small-scale Organic Rankine Cycle systems are capable of efficiencies of the order of 10% (Fu, et al., 2005), (Shu, et al., 2014), (Kang, May 2012). The remaining ~90% of the heat that enters the system is rejected to the environment in the condenser. If this heat can be recovered and used for space and water heating, ORC systems could be ideal for CHP purposes.

This is contingent on the water outflow from the condenser being of sufficient temperature for space or water heating applications. Water heating for washing, for example, requires a temperature of 40°C (UK DECC, n.d.). Underfloor heating requires a temperature of 35-50°C (UK DECC, May 2012) (UK DECC, 2012b) (UK DECC, 2012a). Radiators may require a temperature of 60°C (Institution of Civil Engineers, 2012). To achieve this, district heating schemes usually provide heat at 90-100°C (UK DECC, 2012c) (Poyry Energy Consulting, 2009).

The application of Organic Rankine Cycle for cogeneration has attracted considerable attentions. Twomey et al (Twomey, et al., 2013) considered a solar-powered ORC system providing water heated by the condenser at 65°C, and using a scroll device as their expander. They showed electrical efficiency of 3.47%. Stoppato (Stoppato, 2012) performed an energetic and economic investigation of an existing ORC cogeneration plant in Italy, providing district heating water at 80°C from a 310°C heat source. This cycle aims to increase exergy efficiency by splitting the flow between a regenerative heat exchanger and a fluid preheater using the primary heat source, and achieves an electrical efficiency of 18.6%, modelling the cycle components as black boxes with performance varying based

on empirical data. Uris et al (Uris, et al., 2014) performed an analysis of a biomass cogeneration plant with a 300°C heat source providing heat from 65-90°C, using various sub- and supercritical working fluids. This showed a maximum first law thermal efficiency of 22.62% for a subcritical recuperative cycle.

Typical sources of heat for ORC systems include solar thermal, geothermal, and waste heat from industry. The UK contains several potential geothermal resources with temperatures of up to 180°C (UK DECC, 2013a). Unlike geothermal resources, solar thermal resources vary in temperature depending on the incident radiation and the degree of concentration. Temperatures in excess of 700°C have been generated in practice (Deutsches Zentrum für Luft- und Raumfahrt, n.d.). For industrial waste heat, most high-temperature sources are in the solid phase (steel billets, etc.) which is hard to effectively recover energy from. If these are excluded, 88.9% of easily-utilised waste heat, i.e. that which is available in sources in the liquid or gaseous phase, are at low temperatures, less than 250°C (UK DECC, 2014b).

So far, most research and development of ORC systems has considered single-component organic working fluids. This has several shortcomings: (i) There is always a mismatch of temperature profiles between heat transfer fluid and the working fluid because the single working fluid evaporates and condenses at fixed temperatures while the heat transfer fluid changes temperature during heat transfer. This mismatch leads to irreversibility and reduces the cycle efficiency (Chys, et al., 2012). (ii) An ORC power plant is currently designed by selecting a working fluid to match the heat source and sink temperatures. Considering that these temperatures differ from one customer to another, and the design options are limited by the availability of suitable organic fluids, installation costs are high. A wider choice of working fluids is desirable to reduce installation and operating costs (Chys, et al., 2012).

It is proposed here that these challenges can all be addressed by using zeotropic mixtures, which have the following advantages: (i) A zeotropic mixture has a variable temperature during phase change. **Figure 2** shows the bubble and dew lines of a zeotropic mixture formed by Butane and Heptane. For example, for a mixture with 20% of the high-boiling-point component Heptane, the evaporation starts at the temperature T_{bubble} and ends at T_{dew} . The differential ($T_{\text{bubble}} - T_{\text{dew}}$) is the temperature 'glide' of this mixture, which can be used to match the temperature change of heat transfer fluid in counter flow heat exchangers, so that the irreversibility can be reduced (Rajapaksha, n.d.). The use of suitable zeotropic mixtures as working fluids can increase cycle efficiency and power production of ORC systems, especially for lower temperature applications (<250 °C) [22]. (ii) Zeotropic mixtures display bubble- and dew-point temperatures between those of the two member components, and this varies predictably with mixture percentage. This allows the formation of a mixture with a particular composition to match heat sink temperatures so that more options of working fluids are available.

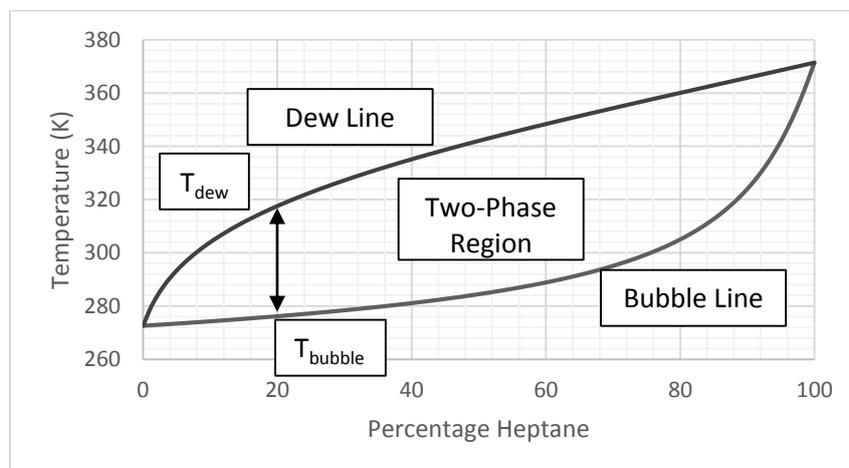


Figure 2: Glide curve of a mixture of Heptane and Butane at 1 bar

In this research, the working fluids selected for the cycle were zeotropic mixtures of alkanes. Specifically pentane, hexane and heptane, and their mixtures with butane. These substances are thermodynamically and chemically quite similar, being non-polar, dry fluids, minimising the number of independent variables to be considered when comparing results.

2. THEORY

The coolant outlet temperature from the condenser is primarily determined by the dew point of the working fluid at condenser pressure. If the dew point is at a lower temperature, or a higher enthalpy, the flow rate of coolant required to maintain the pinch point temperature difference will be greater.

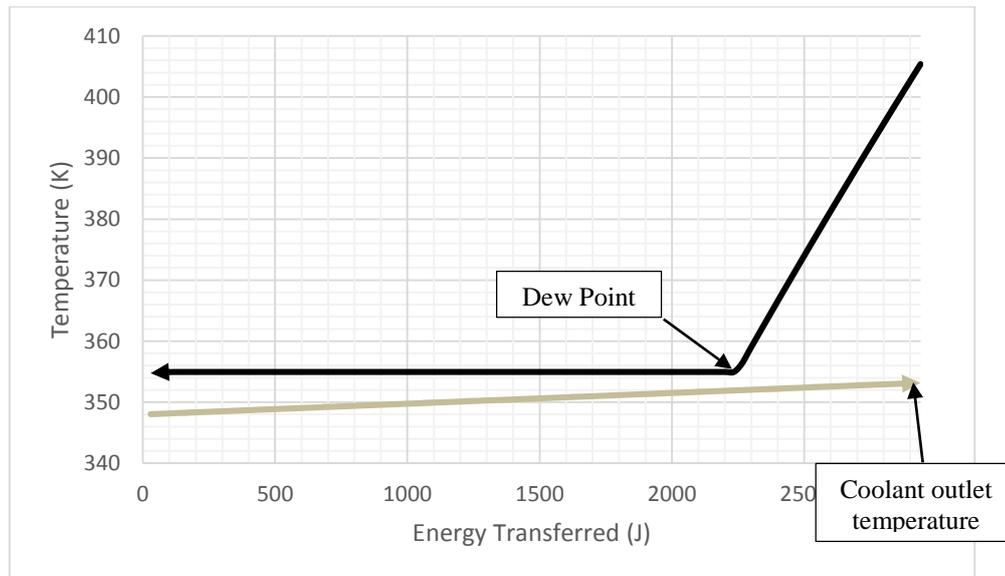


Figure 3: Condenser Temperature Profile for Heptane

Figure 3 demonstrates this principle. The pinch point in the condenser occurs at the dew point. If the dew point moves downwards (lower temperature) or to the right (higher enthalpy), the slope of the lower line must decrease in order for it to maintain the temperature gap at the pinch point. Decreasing the slope results in a lower coolant outlet temperature. In physical terms, this can be achieved by increasing the flow rate of coolant through the condenser.

When a fluid with a lower boiling point is added to one with a higher boiling point, two primary effects occur. One is that the bubble and dew points of the fluid are decreased, the other is that a degree of glide, or temperature change during phase change, is introduced. This means that the dew point increases more quickly than the bubble point. The aim of this paper is to investigate the effects these changes in bubble and dew points have on the required condenser pressures and efficiency of an Organic Rankine Cycle used for cogeneration.

3. NUMERICAL SIMULATION

There was assumed to be no pressure or heat loss from piping or heat exchangers, and no significant effects from velocity, momentum, change in elevation, or compressibility in the flow. A numerical simulation in MATLAB using REFPROP 9.1 (Lemmon, et al., 2013) was developed to analyse a cogeneration system using zeotropic working fluids. The naming convention for points in the cycle was as shown in figure 4:

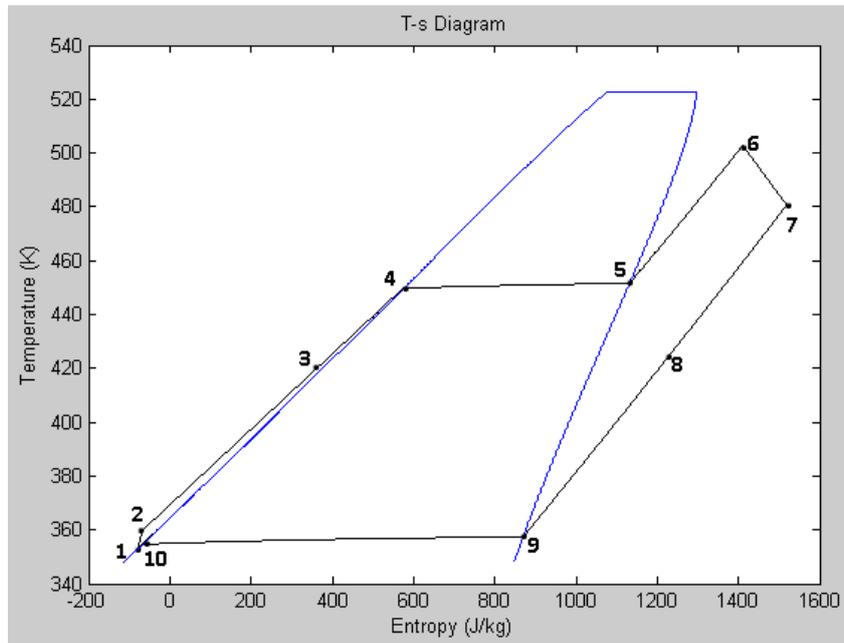


Figure 4: Cycle Diagram, with numbered points.

The pinch point temperature difference in the condenser was taken to be 5°C, which is consistent with previous research (Liu, et al., 2014), (Stefano Clemente, 2012). The coolant inlet temperature was taken to be 80°C, to represent mains water, and the outlet temperature to be 90°C, to represent a district heating scheme. The condenser pressure was then increased from an initial value of 10kPa until the pinch point opened up to the desired 5°C.

REFPROP allows for the calculation of each of the fluid properties on its extensive list given any two other properties, so temperature and pressure information is sufficient to also calculate the enthalpy and entropy of the fluid at this point.

The heat source temperature was taken to be 250°C, and the condenser pressure set to 1600kPa, which was low enough to ensure that the highest boiling point fluid, heptane, would fully vaporise at this temperature.

$$T_6 = 250^{\circ}\text{C} \quad (4)$$

$$P_{evap} = 1600\text{kPa} \quad (5)$$

The isentropic efficiency of the pump and the expander were taken to be 90% and 70% respectively. Assuming isentropic pumping and expansion, $h_{2,isentropic}$ and $h_{7,isentropic}$ can then be obtained from REFPROP, and used to calculate the actual values, using the equations:

$$h_2 = h_1 + \eta_{pump} * (h_{2,isentropic} - h_1) \quad (6)$$

$$h_7 = h_6 - \eta_{expander} * (h_6 - h_{7,isentropic}) \quad (7)$$

Once this has been done, two properties are known for each of the four key points in the cycle; pump outlet, evaporator outlet, expander outlet and condenser outlet, and so equation 8 can be used to calculate the efficiency of the cycle.

$$\eta_{cycle} = \left(\frac{(h_6 - h_7) - (h_2 - h_1)}{h_6 - h_2} \right) \quad (8)$$

This allowed for the efficiency of the cycle to be calculated.

Keeping the evaporator pressure the same for comparability, the process was then repeated as the second fluid was added to the base fluid of butane in 10% increments of mass fraction. Limiting the evaporator pressure reflects the design considerations in real-world ORC plants, where higher pressures increase the cost and suffer from diminishing returns in efficiency.

This whole process was repeated using pentane, hexane and heptane as the second fluid, and the effects on the performance of the cycle observed.

The model was validated against experimental results obtained by Kang (Kang, May 2012) by using the same initial parameters, and produced results that were within 2% of his values for all points of the cycle as shown previously by the authors (Collings & Yu, 2014). This was considered reasonable in light of the assumptions that had been made in the production of the model, which offered us the confidence to apply this model to cogeneration application as presented in this paper.

4. RESULTS

As described in section 3, the heat source temperature was set to 250°C and the evaporator pressure to 1600kPa. The coolant inlet and outlet temperatures were set to 80 and 90°C respectively.

For all of the fluids under consideration, their addition to butane increased the bubble and dew points of the mixture, and allowed the condenser pressure to be dropped while maintaining the same temperature of water for cogeneration purposes at the condenser outlet, increasing the pressure ratio and therefore the efficiency of the cycle.

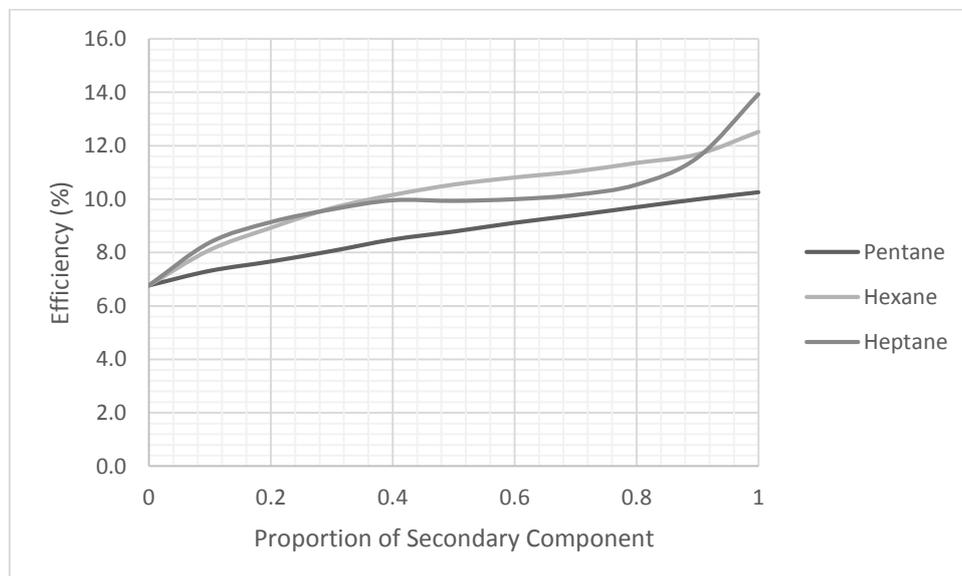


Figure 4: Performance of the system against the proportion of different secondary fluids

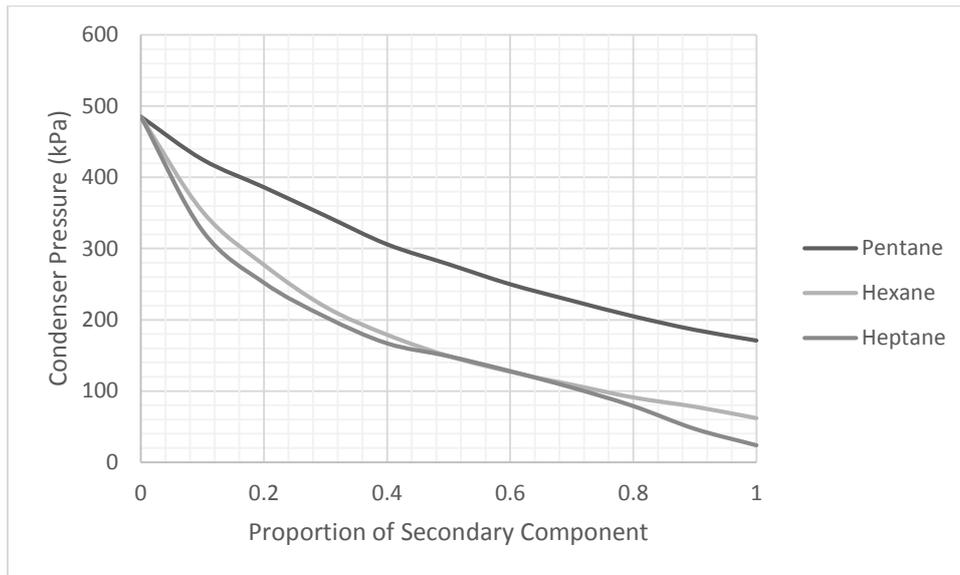


Figure 5: Performance of the system with changing condenser pressure for different secondary fluids

As shown in figures 4 and 5, the addition of pentane to butane smoothly decreases the condenser pressure and increases the efficiency, with a slightly more rapid rate of increase for lower mass fractions of butane.

A similar effect can be seen for the addition of hexane and heptane. The addition of hexane reduces the condenser pressure and increases the efficiency of the cycle. However, this change is less smooth, and the increase in the slope of the efficiency-composition line is more pronounced at very high and very low mass fractions of butane. For heptane, the increased slope at either end of the plot is far more obvious in, although the general trend of decreasing condenser pressure and increased efficiency remains.

A possible explanation for the observed shape of plot is that adding a higher-boiling-point component to the working fluid, such as heptane to butane, will tend to increase the dew point of the cycle, while leaving the bubble point largely unchanged. This allows for the condenser pressure to be dropped without closing the pinch point located at the fluid's dew point to unacceptable levels.

The rate of increase moderates between 20% and 70% heptane, due to the fact that in this region, the glide changes far more slowly, and the condenser pressure is able to decrease smoothly. Above 70% hexane, the bubble point begins to increase rapidly, which results in a sharp decrease in evaporator loading while maintaining roughly the same work output in the expander.

For pentane and hexane, these effects are also present, but the lower overall amount of glide means that the slopes of the bubble and dew lines are more similar at all compositions and results in a smoother profile as the composition changes. This is shown in **Figure 6**. The curve for butane-pentane features less glide, and so the bubble and dew curves have more similar slopes, meaning that the initial changes in bubble and dew points at each end of the scale are less drastic. The overall result of this is that the efficiency of the cycle will vary smoothly as the composition is changed, as shown in the earlier figures.

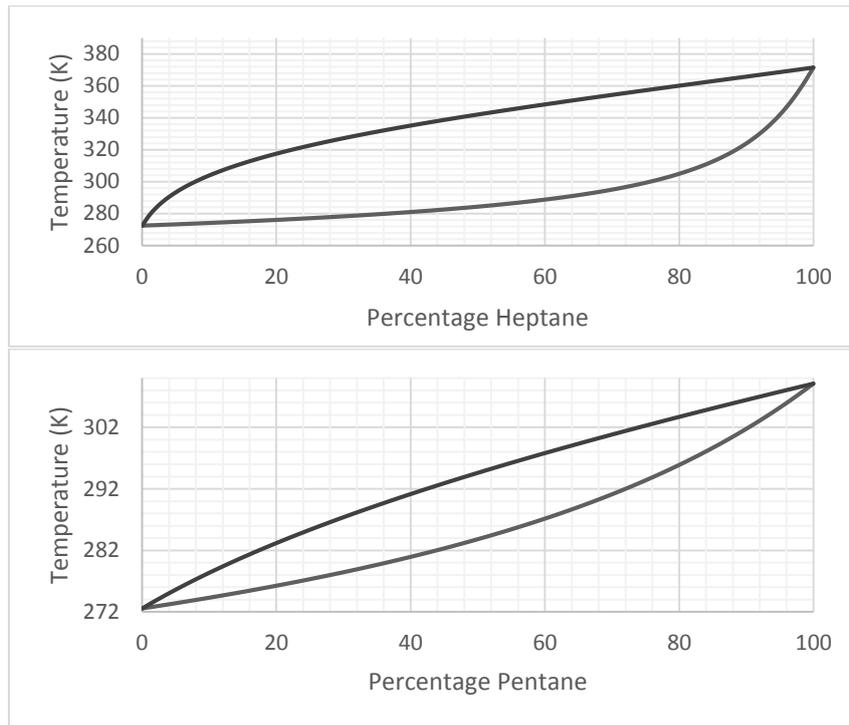


Figure 6: Comparison of glide curves for Butane-Heptane and Butane-Pentane

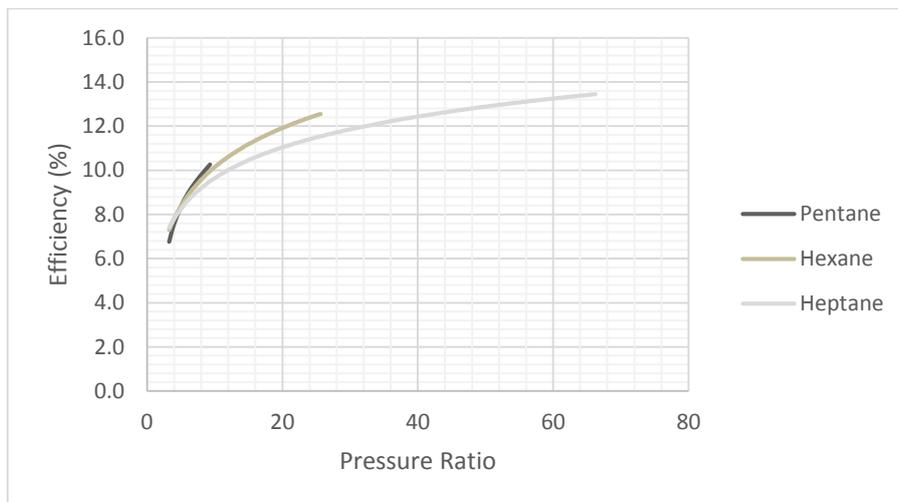


Figure 7: Relationship between pressure ratio and efficiency for different secondary fluids

For all secondary fluids, the efficiency increased as the pressure ratio increased, as shown in

Figure 7, with the increase tapering off, as even an infinitely large pressure ratio will never be able to overcome the Carnot limitation on the cycle.

Figure 7 also shows that the efficiency is higher at lower pressure ratios for lower boiling point secondary components, perhaps because butane-heptane mixtures exhibit higher glide for the same condenser pressure, increasing the condenser and evaporator loading without increasing expander work.

The practical implication of this for the implementation of Organic Rankine Cycles limited by condenser water outlet temperature is that working fluids can be tailored to match heat source and

sink temperatures by mixing them together, but ideally the components of the mixture must be selected to have relatively similar boiling points, otherwise sharp drops in efficiency will be observed as the composition is changed. For situations in which the pressure ratio is limited by any reason, such as the pressure rating of the evaporator and condenser, lower boiling-point secondary components, such as Pentane or Hexane, can be more efficient, however, the use of a higher boiling-point secondary component fluids in a system with a limited evaporator pressure is capable of achieving a higher pressure ratio, as the permitted condenser temperature is lower. In practice, the optimal solution will be determined by the exact configuration and limitations of the system. The higher the achievable pressure ratio, the more likely that Heptane will be the better option.

5. CONCLUSION

It has been shown that zeotropic mixtures can cause changes in the condensing temperature and pressure of a cycle, and that these changes can affect the efficiency of the cycle for a fixed coolant outlet temperature. For zeotropic mixtures consisting of components with relatively similar boiling points, this change in efficiency and condenser pressure is relatively smooth. However, if the temperature glide is too great, the larger changes in bubble and dew point at either end of the scale cause correspondingly abrupt changes in efficiency at these points.

For all mixtures, the benefit in efficiency from tailoring the working fluid to the heat source and sink outweighs the negative effect caused by the increased condenser and expander loading. This benefit is greater for a given pressure ratio when the two components of the working fluid have similar boiling points, as this results in a lower temperature glide, minimizing evaporator and condenser loading.

Potential utilisation of these effects to improve the efficiency of ORCs for cogeneration is a fertile area for future research.

NOMENCLATURE

h	Enthalpy	J/kg
P	Pressure	kPa
s	Entropy	J/kg K
T	Temperature	K
η	Efficiency	%

Subscript

1	Pump Inlet
2	Pump Outlet
3	Regenerator Outlet, cold (unused)
4	Bubble point, evaporator
5	Dew Point, evaporator
6	Expander Inlet
7	Expander Outlet
8	Regenerator Outlet, hot (unused)
9	Dew Point, condenser
10	Bubble Point, condenser
Critical	Property at critical point of the fluid

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