THERMODYNAMIC STUDY OF INFLECTION POINT OF SATURATED VAPOR CURVE FOR DRY AND ISENTROPIC WORKING FLUIDS

Xinxin ZHANG[1]*, Congtian Zhang[1], Jingfu WANG[1], Maogang HE[2]

[1]Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education
Key Laboratory of Heat Transfer and Energy Conversion, Beijing Municipality
College of Environmental and Energy Engineering, Beijing University of Technology
Beijing 100124, P R China
xinxinzhang@bjut.edu.cn

[2]Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education
School of Energy and Power Engineering, Xi'an Jiaotong University
Xi'an, Shaanxi 710049, P R China
mghe@mail.xjtu.edu.cn

* Corresponding Author Xinxin ZHANG

ABSTRACT

In this paper, the definition of inflection point on saturated vapor curve of dry fluid and isentropic fluid was given according to the shape of the saturated curve of working fluids in a T-s diagram. On this basis, the model of near-critical region triangle was established. Using this model, the effect of inflection point on saturated vapor curve on performance of organic Rankine cycle(ORC) was studied when 38 kinds of dry and isentropic organic working fluids was adopted in ORC. The performance includes relationship between the inflection point temperature and the area of near-critical region triangle, the relationship between the exergy at the inflection point and the area of near-critical region triangle, and the relationship between the area of near-critical region triangle and reciprocal value of slope of saturated vapor curve. On this basis, if the type of heat source is taken into account, the theoretical analysis results show that heptane, cyclohexane, octane, nonane, decane, and dodecane are the suitable working fluids for open-type heat source utilization.

1. INTRODUCTION

The organic Rankine cycle(ORC) which applies the principle of the steam Rankine cycle, but uses organic working fluids with low boiling points was first invented and introduced by Ray and Moss (1966) who used fluorochemicals as working fluid in small Rankine cycle power units. Since then, the ORC technology has become more and more popular in both the waste heat recovery and renewable and sustainable energy utilization field.

As known to all, working fluid plays a very important role in thermodynamic cycle. The efficiency, the operation condition, the impact on the environment, and the economic feasibility of thermodynamic cycle are greatly affected by working fluid selection and the nature of the working fluid. In ORC, organic working fluid plays a decisive role. It is the lower boiling point of organic working fluid compared with water that makes a higher saturation pressure at lower temperatures. Accordingly, work can be produced at a lower temperature because of good thermodynamic performance of organic working fluid.

Organic working fluid can be classified into three categories according to the slope of the saturated vapor curve in a T-s diagram. They are dry fluid with a positive slope(e.g. isopentane), wet fluid with a negative slope(e.g. R22), and isentropic fluid with a vertical slope(e.g. R11)(Hung, 2001; Liu *et al.*, 2004; Chen *et al*., 2010). The working fluids of dry or isentropic type are more appropriate for ORC systems(Liu *et al*., 2004). The literature shows extensive researches on organic working fluid selection under certain predefined temperature conditions and certain operation conditions. If we observe the shape of saturated vapor curve of dry and isentropic fluid in a T-s diagram, we will find an inflection point on saturated vapor curve. In this paper, we defined this inflection point and established a model of near-critical region triangle. Using this model, the effect of inflection point on saturated vapor curve on performance of organic Rankine cycle(ORC) was studied when 38 kinds of dry and isentropic organic working fluids was adopted in ORC. On this basis, taking the type of heat sources into account, the suitable working fluid was analyzed and selected through theoretical calculation.

2. DEFINITION OF INFLECTION POINT ON SATURATED VAPOR CURVE

2.1 Type of Working fluid

As mentioned in Section 1, a working fluid can be classified as a wet, dry, or isentropic fluid according to the slope of the saturated vapor curve ($\mathrm{d}T/\mathrm{d}s$) in its T-s diagram as depicted in Figure 1. Considering the value of $\mathrm{d}T/\mathrm{d}s$ is infinity for an isentropic fluid, the reciprocal value of the slope(e.g $\mathrm{d}s/\mathrm{d}T$) is used to judge the type of a working fluid. Here we define $\xi = \mathrm{d}s/\mathrm{d}T$, if $\xi>0$, then it is a dry fluid, and $\xi\approx 0$ for an isentropic fluid and $\xi<0$ for a wet fluid. Near critical point, there is an inflection point on saturated vapor curve of dry and isentropic working fluid. In order to study the effect of this inflection point on the performance of organic Rankine cycle for waste heat recovery, first we have to judge the type of a working fluid according to its value of ξ and the shape of its T-s diagram.

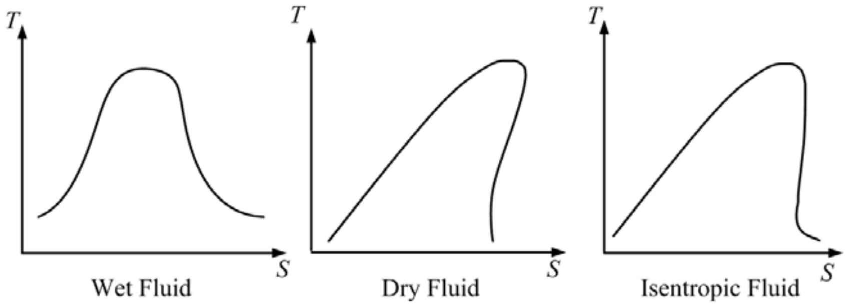

Figure 1: Temperature-entropy (T-s) diagrams of different fluids

Liu *et al.*(2004) introduced an equation for calculating the value of ξ, which is:

$$\xi = \frac{c_\mathrm{p}}{T_\mathrm{H}} - \frac{[(n \cdot T_\mathrm{rH})/(1-T_\mathrm{rH})]+1}{T_\mathrm{H}^2} \Delta H_\mathrm{H} \tag{1}$$

where, ξ ($\mathrm{d}s/\mathrm{d}T$) denotes the reciprocal value of the slope of saturated vapor curve in a T-s diagram, n is suggested to be 0.375 or 0.38(Poling *et al*., 2001), T_rH($=T_\mathrm{H}/T_\mathrm{c}$) denotes the reduced evaporation temperature, and ΔH_H is the enthalpy of vaporization.

The calculation value of ξ according to Equation (1) and corresponding type of a working fluid is listed in Table 1. The calculation values have a good agreement with the shape of saturated vapor curves in a T-s diagram.

2.2 Definition and Determination of Inflection Point on Saturated Vapor Curve

From the classification of working fluid introduced in the last subsection, it can be seen that in a T-s diagram, a significant difference between dry(or isentropic) fluid and wet fluid is the existence of a point on its saturated vapor curve on which the entropy value reaches the maximum. This point is located near the critical point. After passing this point, the entropy value on saturated vapor curve of dry fluid decreases. For isentropic fluid, the entropy value basically keeps unchanged. However, we cannot find out such a point on saturated vapor curve of wet fluid.

Table 1: The calculation value of ξ and corresponding type of a working fluid

Working Fluid	Calculation Value of ξ	Fluid Type
Water	-13.1818	Wet
Ethanol	-5.4299	Wet
R11	-0.3903	Isentropic
R123	0.1202	Isentropic
HFE7100	1.8252	Dry
n-Pentane	1.2835	Dry
Iso-pentane	1.1801	Dry
Benzene	0.3316	Isentropic
Toluene	1.0600	Dry
p-Xylene	1.5390	Dry
butane	0.0083	Dry
butene	0.0065	Dry
cis-butene	0.0059	Dry
cyclohexane	0.0112	Dry
decane	0.0146	Dry
dodecane	0.0149	Dry
heptane	0.0121	Dry
hexane	0.0106	Dry
isobutane	0.0083	Dry
isobutene	0.0071	Dry
isohexane	0.0113	Dry
nonane	0.0124	Dry
octane	0.0121	Dry
pentane	0.0098	Dry
perfluorobutane	0.0051	Dry
perfluoropentane	0.0056	Dry
R113	0.0030	Isentropic
R114	0.0033	Isentropic
R115	0.0032	Isentropic
R124	0.0030	Isentropic
R141b	0.0030	Isentropic
R142b	0.0029	Isentropic
R218	0.0045	Isentropic
R227ea	0.0042	Isentropic
R236ea	0.0043	Isentropic
R236fa	0.0038	Isentropic
R245ca	0.0046	Isentropic
R245fa	0.0044	Isentropic
R365mfc	0.0056	Dry
RC318	0.0043	Isentropic
trans-butene	0.0067	Dry

Considering this unique characteristic of dry and isentropic fluid, here we define an inflection point on saturated vapor curve of dry or isentropic fluid as a point whose entropic reaches the maximum value ranging from freezing point to critical point. Figure 2 illustrates the inflection point on saturated vapor curve of dry and isentropic fluid.

According to the definition of inflection point on saturated vapor curve, its location is determined by the entropic value of dry or isentropic fluid given by REFPROP 8.0 software developed by the National Institute of Standards and Technology Laboratories (NIST)(Lemmon et al., 2007). Dry and isentropic working fluids are selected from all the working fluids in REFROP 8.0 according to the calculation value of ξ. The *T*-*s* diagrams of these two types of working fluids are made by software. Observe the shape of saturated vapor curve in *T*-*s* diagram, and obtain the entropy value under each temperature from the critical point to freezing point using 0.5K as a step. For dry fluid, it can be seen that on saturated vapor curve the entropy value increases with the temperature decrease from critical point until inflection point. As for isentropic fluid, the entropy value basically keeps constant when temperature is around the inflection point. Therefore, we define the inflection point of isentropic fluid as the closest point to critical point with the maximum entropy value on saturated vapor curve. Table 2 lists the temperature on inflection point of 38 working fluids(dry and isentropic) studied in this paper.

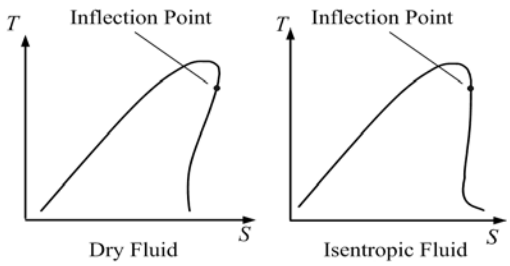

Figure 2: Inflection point on saturated vapor curve of dry and isentropic fluid

3. DEFINITION AND AREA OF NEAR-CRITICAL REGION TRIANGLE

Figure. 3 describes the typical process(1-2s-2'-3-4-5) of an organic Rankine cycle with dry working fluids. The thermal efficiency of an ideal ORC can be calculated from the following equation.

$$\eta_{\mathrm{i}} = \frac{w}{q_1} = \frac{w - w_{\mathrm{p}}}{h_1 - h_4} = \frac{h_1 - h_{2\mathrm{s}} - \left(h_4 - h_3\right)}{h_1 - h_4} \tag{2}$$

where, *h* denotes enthalpy value, *w* denotes work, and *q* denotes heat. The number on subscript stands for the state point of the ORC.

The thermal efficiency of a practical ORC can be calculated from the following equation.

$$\eta_{\mathrm{r}} = \frac{w}{q_1} = \frac{w_{\mathrm{r}} - w_{\mathrm{p}}}{h_1 - h_4} = \frac{h_1 - h_2 - \left(h_4 - h_3\right)}{h_1 - h_4} \tag{3}$$

From the above two equations, it can be seen that the enthalpy value of point 1 significantly effects the thermal efficiency of an ORC. Therefore, the inflection point introduced in this paper focuses on the characteristics of point 1 in an ORC. The inflection point usually has a relatively high temperature. Moreover, latent heat of vaporization reaches the maximum value at the inflection point for dry and isentropic fluid(In the range between critical point and inflection point). However, the temperature between critical point and inflection point doesn't offer any help for improving the thermal efficiency of an ORC. In order to study the effect of inflection point on saturated vapor curve on the thermal efficiency of an ORC, we have to define a parameter to measure the meaningless part surrounded by saturated curve of dry or isentropic fluid for improving the cycle thermal efficiency. This meaningless part will be described by the area of near-critical region triangle.

In *T*-*s* diagram, draw a line through the inflection point and make it parallel to the *s* axis. This straight line will make two intersections with the saturated liquid curve and saturated vapor curve. These two intersections, with the critical point, make a triangle. This triangle is defined as the near-critical region triangle. The base of the near-critical region triangle stands for the entropy difference between the saturated liquid state and the saturated vapor state at the inflection point temperature. The height of the near-critical region triangle stands for the temperature difference between the critical point and the inflection point. Figure. 4 illustrates the near-critical region triangle of dry and isentropic fluid. The unit of entropy difference is kJ/kg·K(triangle base), and that of temperature difference is K(triangle height), therefore, the area of near-critical region triangle has a unit of kJ/kg which is the same as the unit of enthalpy.

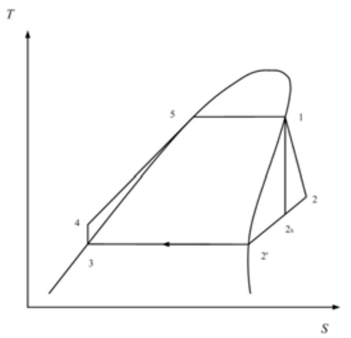

Figure 3: Typical process of an organic Rankine cycle with dry working fluids

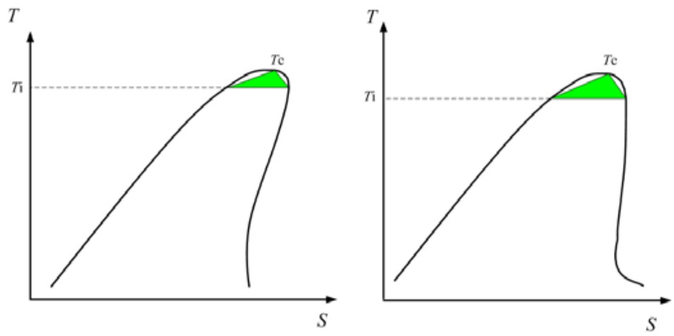

Figure 4: Near-critical region triangle of dry and isentropic fluid

From the database of REFPROP 8.0 software, 38 kinds of dry and isentropic fluids are selected for calculation and analysis. Table 2 lists the basic thermophysical characteristics of these 38 kinds of fluids. According to these parameters and the definition of near-critical region triangle, the areas of near-critical region triangle of these 38 kinds of working fluids were calculated. Figure 5 depicts the relation between the inflection point temperature and the area of near-critical region triangle. From the figure, it can be seen that dodecane and perfluoropentane has the smallest area of near-critical region triangle. However, dodecane has the highest inflection point temperature among these 38 kinds of working fluids. Most of working fluids have inflection point temperatures ranging from 350K to 500K. Here it has to be mentioned that the critical temperature of R116(hexafluoroethane) is 293.03K which is much lower than the operation temperature of an ORC which is from 353K to 673K. Therefore, R116 will not be included in the following analysis.

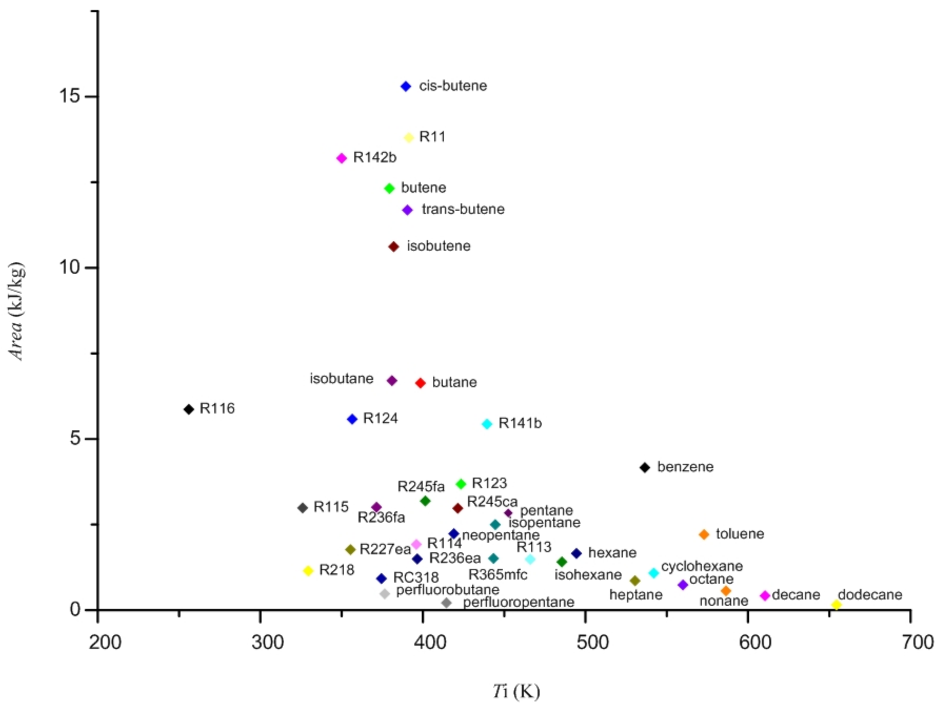

Figure 5: Relation between the inflection point temperature and the area of near-critical region triangle

Table 2: Basic thermophysical characteristics of 38 working fluids

Working Fluid	Critical Temperature/ K	Temperature on inflection point/ K	Vapor entropy on inflection point/ kJ·(kg·K)$^{-1}$	Liquid entropy on inflection point/ kJ·(kg·K)$^{-1}$
benzene	562.05	536.5	1.3865	1.0710
Butane	425.13	398.5	1.357	1.0539
Butene	419.29	379.5	1.1707	1.0303
cis-butene	435.75	389.5	1.2149	1.0565
Cyclohexane	553.64	542	1.4009	1.0711
Decane	617.7	610.5	0.47934	0.3824
Dodecane	658.1	654.5	0.4546	0.3836
Heptane	540.13	530.5	1.6772	1.3305
Hexane	507.82	494.5	1.6776	1.5374
Isobutane	407.81	381	1.5635	1.3951
Isobutene	418.09	382	1.4151	1.1946
Isohexane	497.7	485.5	1.2371	0.9202
Isopentane	460.35	444.5	1.7003	1.4793
Neopentane	433.74	419	1.5991	1.3125
Nonane	594.55	586.5	1.8847	1.5986
Octane	569.32	560	1.7887	1.3505
Pentane	469.7	452.5	1.369	1.2213
perfluorobutane	386.33	376.5	1.5087	1.3263
perfluoropentane	420.56	414.5	1.6921	1.5041
R11	471.11	391.5	1.6371	1.4109
R113	487.21	466	1.8634	1.6349
R114	418.83	396	1.7999	1.5510
R115	353.1	326	1.9259	1.7425
R116	293.03	256	1.5085	1.3759
R123	456.83	423.5	1.2	0.9647
R124	395.43	356.5	1.5067	0.8932
R141b	477.5	439.5	1.3865	1.0710
R142b	410.26	350	1.357	1.0539
R218	345.02	329.5	1.1707	1.0303
R227ea	374.9	355.5	1.2149	1.0565
R236ea	412.44	396.5	1.4009	1.0711
R236fa	398.07	371.5	0.47934	0.3824
R245ca	447.57	421.5	0.4546	0.3836
R245fa	427.16	401.5	1.6772	1.3305
R365mfc	460	443.5	1.6776	1.5374
RC318	388.38	374.5	1.5635	1.3951
Toluene	591.75	573	1.4151	1.1946
trans-butene	428.61	390.5	1.2371	0.9202

4. EFFECT OF INFLECTION POINT ON PERFORMANCE OF AN ORC

Exergy is used to evaluate the quality of energy. Under ambient condition, the energy that can be converted into useful work is called exergy. Through exergy analysis of an ORC, we can find out the part that needs to be improved. As for an ORC, the exergy loss caused by expansion process cannot be ignored. Based on this consideration, the exergy at inflection point temperature of working fluid and its area of near-critical region triangle is compared. Figure. 6 depicts this comparison result. From the figure, it can be seen that heptane, cyclohexane, octane, nonane, decane, and dodecane has a relatively small area of near-critical region triangle but a high exergy.

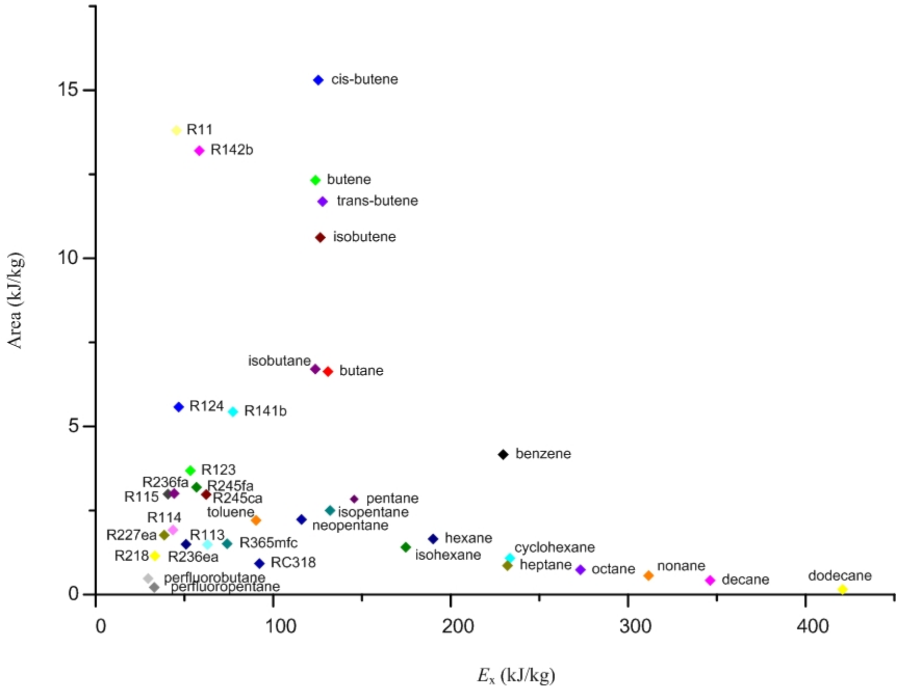

Figure 6: Relation between the area of near-critical region triangle and the exergy at inflection point temperature

From the previous discussion, it is known to all that the drier working fluid is, the more benefit an ORC gets from an expander's perspective. What is the relation between the area of near-critical region triangle of a working fluid and its type. Figure. 7 depicts this relation. The value of ξ can be used to judge the type of a working fluid. The dry fluid has a positive value of ξ. From the figure, it can be seen that compared with other working fluids, decane and dodecane has a relatively big value of ξ and a relatively small area of near-critical region triangle. These two working fluids are good candidates for selection.

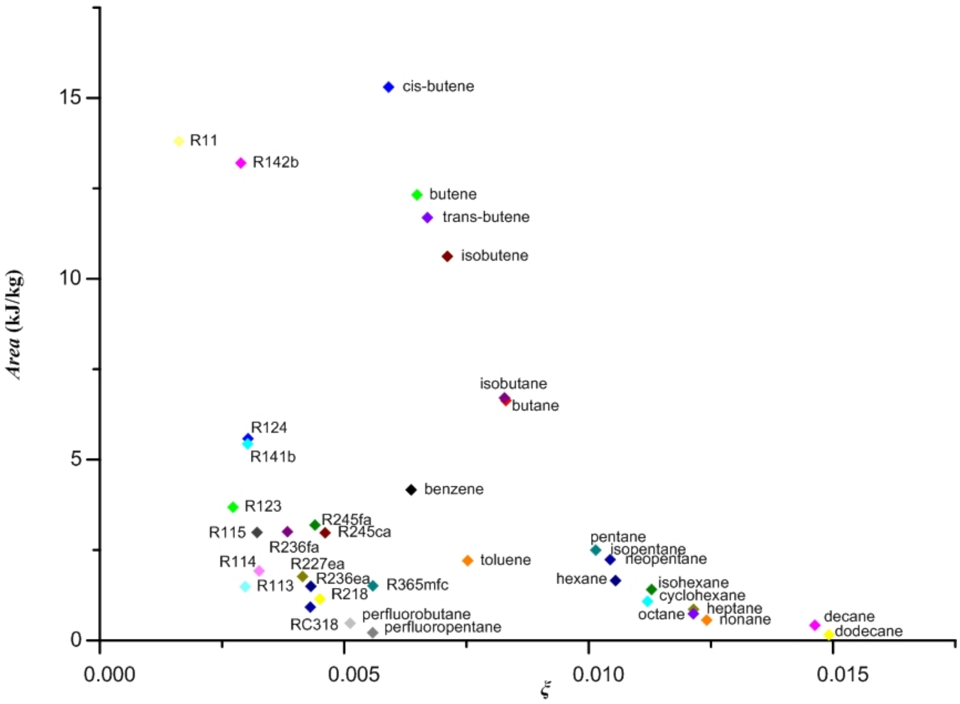

Figure 7: Relation between the area of near-critical region triangle and the type of working fluid

There are two types of waste heat(Yan, 1982; Zhao and Qian, 1984; He *et al*. 2014). One is called open type. The other is called closed type. For the open type, the inlet temperature and the mass flow rate are known, and the working mass of the heat source is directly discharged after being used. For the closed type, the heat release is specific and the working mass of the heat source is usually recycled after releasing heat. Therefore, the standards used to measure the waste heat recovery of these two types of heat source are different(Yan, 1982; Zhao and Qian, 1984). For the open type, the maximum net power output is used as the criterion. However, for the closed type, the maximum thermal efficiency is the criterion. Accordingly, the selection principle of working fluid for waste heat recovery with different heat source is different(Yan, 1982; He *et al*. 2014). For the open type, the working fluids with high liquid specific heat and low latent heat of evaporation should be selected as the working fluids. In contrast, the working fluids with low liquid specific heat and the high latent heat of evaporation are better for the closed heat source.

According to the above conclusion, the liquid specific heat at the inflection point temperature and the latent heat of evaporation at the inflection point temperature for 38 kinds of organic working fluids are listed in Table 3. Moreover, Figure 8 depicts the relation between these two parameters.

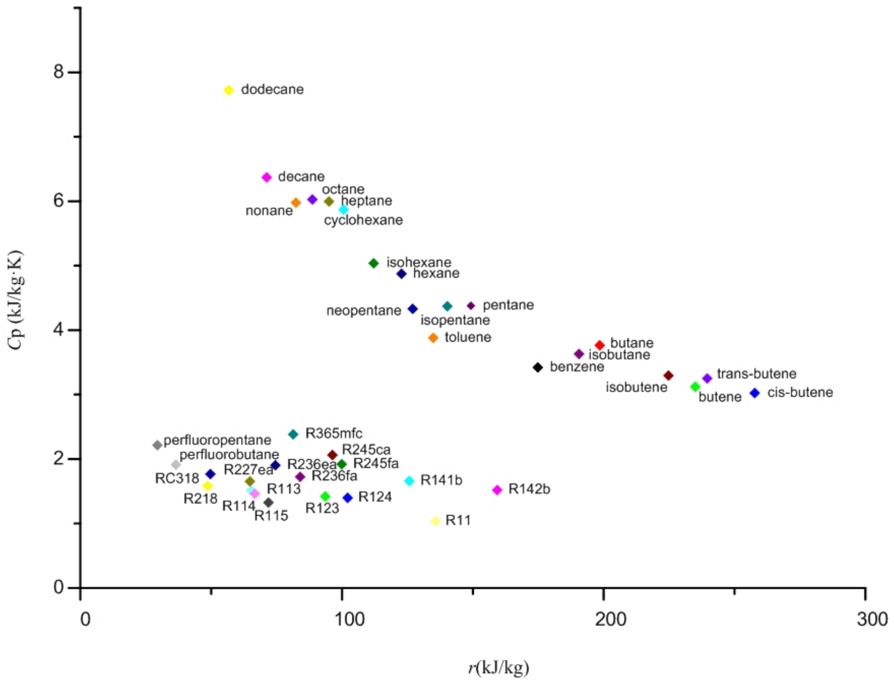

Figure 8: Relation between the liquid specific heat at the inflection point temperature and the latent heat of evaporation at the inflection point temperature

Scanning the figure carefully, it can be seen that the working fluids at the upper left corner should be selected for waste heat recovery of open type heat source. In contrast, the working fluids at the bottom right corner are better for the closed type heat source. The working fluids at the upper left corner (heptane, cyclohexane, octane, nonane, decane, and dodecane) are just the ones we have selected through the previous discussion. However, butene and its isomers which are at the bottom right corner are not selected due to their big areas of near-critical region triangle.

5. CONCLUSIONS

Through scanning the shape of saturated curve of dry and isentropic fluid, it can be seen that there is an inflection point on its saturated vapor curve. We define an inflection point on saturated vapor curve of dry or isentropic fluid as a point whose entropic reaches the maximum value ranging from freezing point to critical point. On this basis, we define the near-critical region triangle which is used to measure the meaningless part surrounded by saturated curve of dry or isentropic fluid.

Table 3: Liquid specific heat and latent heat of evaporation at the inflection point temperature of 38 working fluids

Working Fluid	**Liquid specific heat at the inflection point temperature, C_p / kJ·(kg·K)$^{-1}$**	**Latent heat of evaporation at the inflection point temperature, / kJ·kg^{-1}**
Benzene	3.4216	174.84
Butane	3.7638	198.48
Butene	3.1208	235.01
cis-butene	3.0254	257.72
Cyclohexane	5.8695	100.62
Decane	6.3693	71.25
Dodecane	7.7228	56.71
Heptane	5.9967	95.04
Hexane	4.8754	122.74
Isobutane	3.6316	190.56
Isobutene	3.2953	224.77
Isohexane	5.0375	112.11
Isopentane	4.3709	140.24
Neopentane	4.3319	126.99
Nonane	5.9777	82.37
Octane	6.0278	88.7
Pentane	4.378	149.26
perfluorobutane	1.9117	36.51
perfluoropentane	2.2151	29.42
R11	1.036	135.75
R113	1.5117	65.34
R114	1.4625	66.67
R115	1.3247	71.88
R123	1.419	93.57
R124	1.3982	102.14
R141b	1.6606	125.71
R142b	1.5201	159.3
R218	1.5841	48.68
R227ea	1.6539	64.82
R236ea	1.9049	74.52
R236fa	1.7247	84.03
R245ca	2.0641	96.31
R245fa	1.9207	99.91
R365mfc	2.3851	81.37
RC318	1.7678	49.66
Toluene	3.8798	134.84
trans-butene	3.2499	239.57

Using these two model, the effect of inflection point on saturated vapor curve on performance of organic Rankine cycle(ORC) was studied when 38 kinds of dry and isentropic organic working fluids was adopted in ORC. The analysis results show that heptane, cyclohexane, octane, nonane, decane, and dodecane are the suitable working fluids. On this basis, if the type of heat source is taken into account, a same theoretical analysis results is gotten for open-type heat source utilization. However, for the closed-type heat source, there is no suitable working fluid if using these two models for analysis due to the big areas of near-critical region triangle of butene and its isomers.

REFERENCES

Ray, S.K., Moss, G., 1966, Fluorochemicals as working fluids for small rankine cycle power units, *Adv. Energy. Convers.*, vol. 6, no.2: p. 89-102.

Hung, T. C., 2001, Waste heat recovery of organic Rankine cycle using dry fluids, *Energy. Convers. Manage.,* vol. 42: p. 539-553.

Chen, H., Goswami, D.Y., Stefanakos, E.K., 2010, A review of thermodynamic cycles and working fluids for the conversion of low-grade heat, *Renew. Sust. Energ. Rev.,*vol. 14: p.3059-3067.

Liu, B.T., Chien, K.H., Wang, C.C., 2004, Effect of working fluids on organic Rankine cycle for waste heat recovery, *Energy*, vol.29: p.1207-1217.

Poling, B.E., Prausnitz, J.M., O'Connell, J.P., 2001,The properties of gases and liquids, 5th ed., McGraw-Hill, New York.

Lemmon, E.W., McLinden, M.O., Huber, M.L., 2007, NIST reference fluid thermodynamic and transport properties-REFPROP version8.0, National Institute of Standard Technology, Boulder.

Yan, J.L., 1982, Thermodynamic principles and formulas for choosing working fluids and parameters in designing power plant of low temperature heat. *J. Eng. Thermophys.*, vol. 3, no.1: p.1-7.[In Chinese]

Zhao, G., Qian, L., 1984, Exergy analysis and its application, Higher Education Press, Beijing.[In Chinese]

He, C., Liu C., Zhou, M. et al., 2014, A new selection principle of working fluids for subcritical organic Rankine cycle coupling with different heat sources, *Energy*, vol.68: p. 283-291.

ACKNOWLEDGEMENT

This work was supported by the National Key Basic Research Program of China (973 Program, No.2013CB228306). The authors gratefully acknowledge them for financial support of this work.