THE USE OF ORGANIC ZEOTROPIC MIXTURE WITH HIGH TEMPERATURE GLIDE AS A WORKING FLUID IN MEDIUM-TEMPERATURE VAPOR POWER PLANT

by

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The paper presents the idea of using organic substances as working fluids in vapor power plants, in order to convert the low and medium temperature thermal energy sources into electrical energy. The calculation results of the power plant efficiency for butane-ethane zeotropic mixtures of different mass compositions, for the power plant supplied with hot water having a temperature of 120 °C. Based on the results of thermal-flow calculations it was found that the use of zeotropic mixture does not allow to increase the efficiency and output of the power plant (these values appeared as slightly lower ones). However, it was found that, through the selection of a mixture of sufficiently large temperature glide, the heat exchange surface of the condenser can be reduced or a co-generation system can be implemented.

Key words: *organic Rankine cycle, zeotropic mixture, high temperature glide*

Introduction

Energy, except at food production and medicine, is the most important aspect of human development, having a direct impact on quality of life. The search for new sources of energy, especially from renewables and waste, and more efficient ways of energy conversion into usable forms are all currently under intensive development. However, the characteristics of these sources are specific – there is usually a small heat flux/amount of energy from distributed sources, at rather not too high temperature. These aspects, as well as the global trend of increasing of fossil fuel prices have both contributed to the intensive development of organic Rankine cycle (ORC) technology *i. e.* to vapor power plant in which the working fluid is other than water, usually one with organic origin. The main reason for the use of organic substances is in the possibility to generate vapor at a relatively low temperature, without necessity of applying pressure that, in any of the system component, is lower than the ambient pressure. Until recently, natural and synthetic mono-component fluids have been used as the working fluids in the ORC power plants. The principle upon such systems work is similar to that of the classical Clausius--Rankine vapor power plants. The ORC power plant, in the basic version, is composed of heat exchangers: heater, evaporator, and condenser, and of circulation pump and turbo-generator. However, the shape of the saturation curves for the majority of organic substances (particularly the curve $x = 1$) differs from that for water. This is schematically presented in fig. 1.

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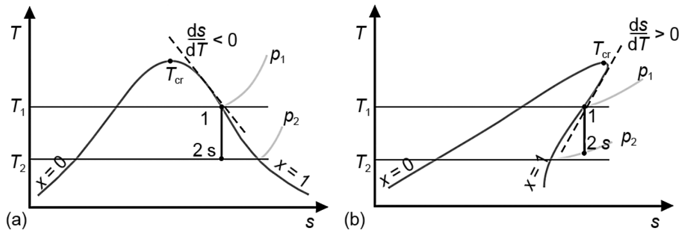

Figure 1. Saturation curves shape for various working fluids and the process of isentropic vapor expansion in the turbine (1-2 s) when using the so-called wet fluid *e. g.* water (a) and dry fluid (b)

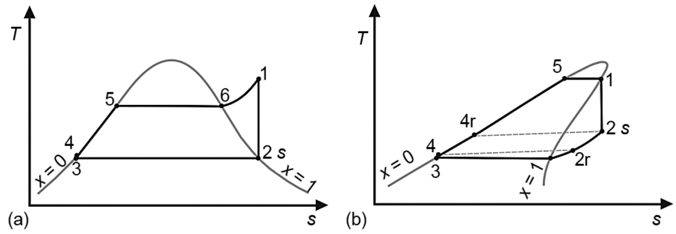

Figure 2. The cycle of thermodynamic changes of vapor power plant cycle implemented by using (a) wet fluid and (b) dry fluid

For the so-called wet substances (*e. g.* water) the working medium should be superheated before being directed to the turbine, process 6-1 in fig. 2(a), in order to avoid the expansion of vapor in the wet vapor area. A characteristic feature of the so-called dry fluids appears as no need to overheat them in order to implement the process of expansion in the superheated vapor area. Furthermore, in power plants with dry fluids, the internal regeneration may be used – the energy of the turbine outlet vapor, in the temperature range from T_{2s} to T_{2r}, can be used to heat the liquid medium in the temperature range from T_{4s} to T_{4r}, as indicated in fig. 2(b). The power plant schemes for different types of fluids are shown in fig. 3.

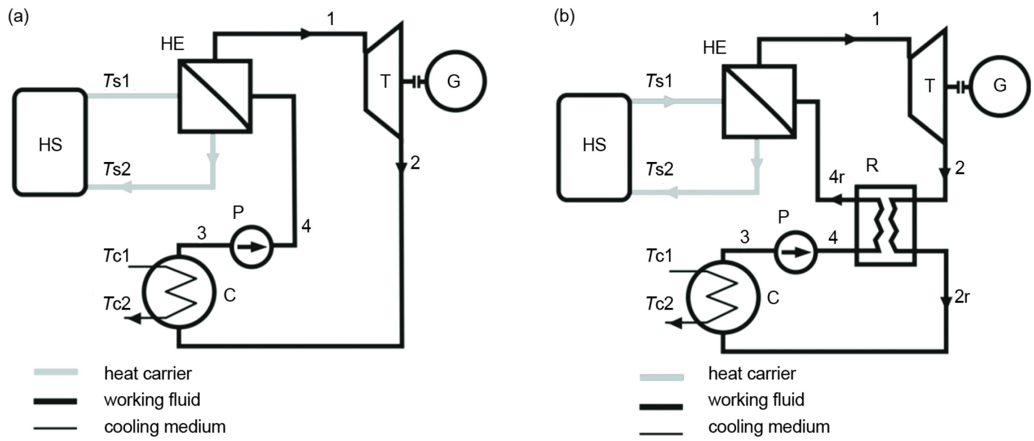

Figure 3. Installation diagram of ORC power plant supplied with saturated dry vapor with (a) wet or dry fluid, without internal regeneration and (b) dry fluid, using internal regeneration

The first experimental ORC type power plants with unary halogen-derivatives factors (R12, R22) were already used in the last century, mainly for geothermal applications [1, 2]. Recently, the energy from biomass combustion [3], the energy obtained in focusing solar collectors [4], and the waste energy from technological processes [5] have all been used to supply the ORC power plant. The work towards searching for new, more environmentally friendly working fluids that meet thermodynamic and operational requirements is continuously in progress. It should be emphasized that the use of any fluid (other than water) is associated with the work on optimizing the structure of the turbine, pump and heat exchanger, and on appropriate choice of the material system. Due to the nature of the working substances used in ORC power plants the latter have to be provided with a hermetic design.

Zeotropic mixtures as working fluids

Zeotropic mixtures are the substances of two or more components characterized in that that during the process of phase transition at evaporation as well as at condensation, both carried out at a constant pressure, the temperature of the mixture changes. The property of the temperature change in the isobaric process of the phase transition is called a temperature glide. That phenomenon has an influence on the shape of the comparative Clausius-Rankine cycle, as shown in fig. 4. The temperature difference in points 6 and 5 is a temperature glide in the evaporator, while that in points 2s and 3 is a temperature glide in the condenser. Figure 5 shows the evaporation process at constant pressure, for zeotropic mixture of 50/50 butane-ethane composition. As it can be seen from fig. 5, the change of the mixture composition affects the extend of the temperature glide.

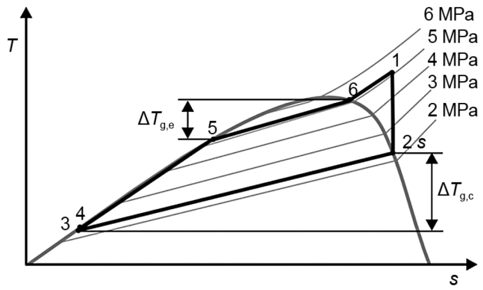

Figure 4. Isobars course for zeotropic wet working fluid (based on 50/50 butane-ethane mixture) and the cycle of thermodynamic changes of the vapor power plant cycle implemented with the use of this working fluid

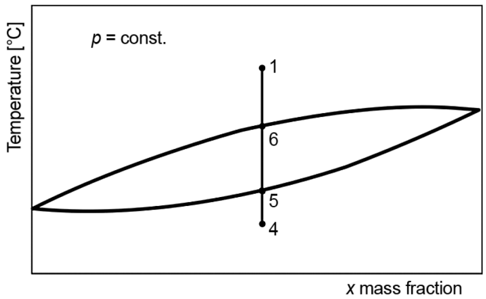

Figure 5. Isobaric process of boiling of a zeotropic working fluid

Table 1 shows the temperature values at the border lines for various compositions of the ethane-butane mixture at the pressure of 5.2 MPa and the temperature glide value for the evaporation process $\Delta T_{g,e}$ [6]. It should be clarified that for ethane/butane compositions 0.2/0.8, 0.1/0.9, and for pure components the pressure of 5.2 MPa exceeds the critical pressure, therefore for these cases it is not possible to implement the subcritical cycle for the evaporation pressure of 5.2 MPa.

Table 1. Saturation temperatures for various compositions of the ethane/butane mixture (for $p_5 = p_6 = 5.2$ MPa)

Ethane/butane mass fraction	0.8/ /0.2	0.7/ /0.3	0.6/ /0.4	0.5/ /0.5	0.4/ /0.6	0.3/ /0.7
T_5	48.2	55.2	63.4	73.5	86.4	103.3
T_6	58.6	71.3	83.5	95.3	106.9	118.3
$\Delta T_{g,e}$	10.4	16.1	20.1	21.8	20.5	15

The possibility to apply the zeotropic mixtures in the Rankine cycle is the subject of several publications. It is worth quoting the work of [7], which presents the results of calculations performed using the Stan Mix program for calculating thermodynamic properties of mixtures. This paper examines the efficiency of utilization of the butane (50%) + n-hexane (50%) mixture in the ORC power plant supplied with geothermal water having a temperature of 140 °C and cooled with air at 12 °C. Utilization of the butane/hexane mixture allowed obtaining thermal efficiency at 10.2% as compared to the efficiency equal to 9.3% for the unary pentane. The paper also explores the possibility of using a multicomponent mixture: MM (3.18%) + MDM (34.14%), MD2M (45.51%) + MD3M (16.17%) + MD4M (1%) in the ORC power plant supplied with heat carrier at a temperature of 400 °C. This work includes the possibility of using an internal heat recovery, but mainly in the recovery of heat from the turbine outlet vapor, as the fluids chosen for calculation are characterized by a high value of the d*s*/d*T* derivative. The work [8] presents the results of experimental studies of the ORC system that utilizes R245fa and a mixture of R245fa/R152a (0.9/0.1 and 0.7/0.3%), and is powered by the solar energy from a liquid manifold. It is the only work containing the results of experimental studies to which the author of the present paper managed to reach, but that experimental system did not include a turbo-generator (only the expansion valve) thus no values of the Rankine cycle efficiency could be obtained, which for pure R245fa amount to 4.16%, for the mixture with a composition of 0.9/0.1 amount to 4.29%, while for the mixture 0.7/0.3 – 5.59%. These are the values calculated assuming the 75% internal efficiency of the turbine. In [9], the use of a zeotropic mixture in supercritical cycle was proposed. The possibility of using a mixture of R134a/R32 (mass fractions of 0.7/0.3) was analysed and the results of a comparative analysis were referenced to the system with R134a fluid. Vapor power plants with working fluids available for the highest temperature in the cycle in the range of 120 to 200 °C (without considering the heat source) were analysed. The obtained values of efficiency for power plant with R134a fluid (9.70-10.13%) are lower than those for the power plant with a mixture of (10.77-13.55%). The internal heat recovery has not been considered also in that work, as the mixture selected for the calculation is characterized by low temperatures glide and the process is not likely to be realized. The use of mixtures in the vapor power plant cycle undoubtedly involves some difficulties, especially when working fluid leaks and the need to supplement a mixture with relevant components fractions appears as a consequence. However, with the development of technology in the field of refrigeration and air conditioning, the process of supplementing the equipment with zeotropic mixtures seems to be no longer a major obstacle restricting their use. In case of the vapor power plant a much more fundamental problem arises in the process of selection of a suitable mixture and its composition, in view of the power plant thermodynamic performance and operation terms.

Description of the working cycle variants and the most important relations

In the present study, the thermodynamic efficiency has been analysed for the power plant powered by hot water with the temperature of T_{s1} = 120 °C and pressure of 0.2 MPa (in order to avoid phase transition of the energy carrier), and for which the heat flux supplied to the working fluid was Q_s = 100 kW. The choice of the source parameters is not accidental. Such parameters are characteristic for the power plant energy carriers in case of the low temperature combustion of biomass, of the waste energy, *e. g.* energy recovered from the exhaust gas (gas turbine, *etc.*) [10], or in case of energy from the cooling system of the cogenerative piston engines that are powered by gas or biogas [11]. For the energy carriers previously listed, the energy carrier exit temperature T_{s2}, that is the temperature the energy carrier should have when leaving the ORC system, appears as an important parameter. This analysis assumes that the energy carrier has its exit temperature at T_{s2} = 80 °C.

The possibility of using a mixture of butane+ethane with varying compositions was examined and, for comparison, reference of the results was made to those obtained for pure butane. It is assumed that the vapor temperature of the working fluid at the inlet to the turbine is T_1 = 115 °C and, therefore, the vapor pressure at this point of the cycle will differ for varying compositions of the working fluid mixture. The assumed temperature at the inlet of the vapor turbine to be at 115 °C caused that for the compositions of the working fluid mixture of 0,2 butane, 0,3 butane, and 0,4 butane the ORC is supercritical, while for the working fluid mixture with composition of 0,5, 0,6, and 0.7 butane the implemented thermodynamic cycle is subcritical.

Butane is a component belonging to the group of dry fluids, so for the respective mono-component case the calculations of the cycle variant with the internal regeneration has been performed. A mixture of ethane+butane belongs to a group of wet fluids. However, due to the occurrence of the temperature glide in the condenser, it is possible also in such case to provide internal regeneration by using a portion of the condensation heat to preheat the liquid downstream of the cycle pump. The respective cycles are shown in figs. 6(a) – subcritical cycle for the mixture composition of 0.5, 0.6, and 0.7 butane, and 6(b) – supercritical cycle for the mixture composition of 0.2, 0.3, and 0.4 butane, while the cycle implemented with the use of pure butane is shown in fig. 2(b).

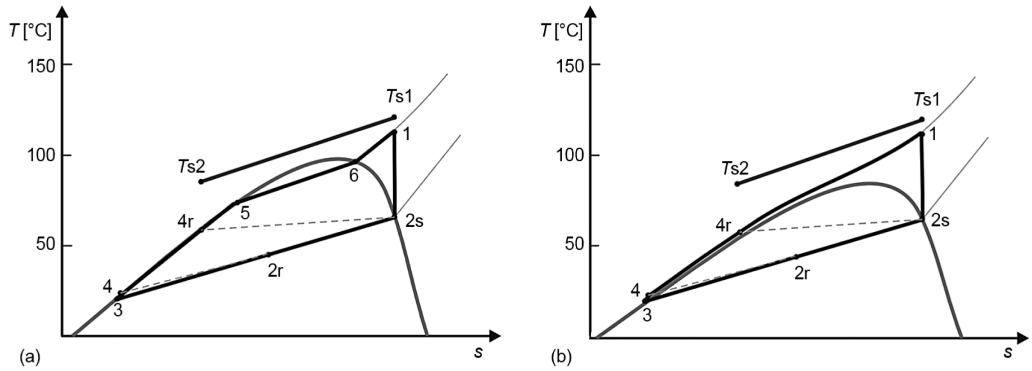

Figure 6. The ORC (a) subcritical cycle for the mixture composition of 0.5, 0.6, and 0.7 butane and (b) supercritical cycle for the mixture composition of 0.2, 0.3, and 0.4 butane

Additional assumptions used in calculations are adopted as: the temperature of the condenser cooling air T_{c1}= 15 °C, the temperature difference at the pinch point ΔT_{pp} = 5 K, the internal efficiency of the turbine η_t = 0.8 and of the pump η_p = 0.7.

Characteristic parameters for which the comparative analysis of the power plants variants has been conducted include:

– the net output power of the ORC plant, N_{ORC}, which is a difference of the turbine power, N_T, and pump power, N_P, where:

$$N_T = \dot{m}_n (h_1 - h_{2s}) \eta_T \tag{1}$$

$$N_P = \frac{\dot{m}_n (h_{4s} - h_3)}{\eta_P} \tag{2}$$

– thermal efficiency η_I

$$\eta_I^{ORC} = \frac{N_T - N_P}{\dot{Q}_s} \tag{3}$$

– exergy efficiency η_{II}

$$\eta_{\mathrm{II}}^{\mathrm{ORC}} = \frac{N_{\mathrm{T}} - N_{\mathrm{P}}}{\dot{B}_{\mathrm{s}}} \tag{4}$$

where in the exergy source was determined from the dependence:

$$\dot{B}_{\mathrm{s}} = \dot{B}_{\mathrm{s1}} - \dot{B}_{\mathrm{s2}} \tag{5}$$

and the logarithmic mean temperature drop in the condenser ΔT_{c}:

$$\Delta T_{\mathrm{c}} = \frac{(T_{2\mathrm{r}} - T_{\mathrm{c2}}) - (T_3 - T_{\mathrm{c1}})}{\ln \dfrac{T_{2\mathrm{r}} - T_{\mathrm{c2}}}{T_3 - T_{\mathrm{c1}}}} \tag{6}$$

Calculation results and their analysis

Thermodynamic analysis of the ORC systems with different compositions of working mixture showed that the application of zeotropic ethane/butane mixture does not allow for higher cycle efficiency than that with the use of pure butane. This results due to the fact that the pressure difference, Δp, between the upper pressure (upstream of the turbine p_1) and the lower pressure of the mixture (in the condenser p_3), regardless of its composition, is significantly higher than that for the pure butane and leads to much higher values of the pumping power. The respective results of the calculations are presented in tab. 2.

Table 2. Summary of the calculations results for different variants of the ORC system

Ethane/butane mass fraction		0.8/0.2	0.7/0.3	0.6/0.4	0.5/0.5	0.4/0.6	0.3/0.7	Butane
N_{T}	kW	15.6	14.4	13.3	12.1	11.0	10.4	11.4
N_{P}	kW	6.9	5.1	3.9	3.0	2.3	1.8	0.5
N_{ORC}	kW	8.7	9.3	9.4	9.1	8.8	8.6	10.8
$\eta_{\mathrm{I}}^{\mathrm{ORC}}$	%	8.7	9.3	9.4	9.1	8.8	8.6	10.8
$\eta_{\mathrm{II}}^{\mathrm{ORC}}$	%	38.2	40.9	41.2	40.1	38.5	38.0	47.9
p_1	MPa	9.3442	7.5693	6.2532	5.2091	4.3584	3.6618	1.1741
p_3	MPa	3.1473	2.8549	2.5568	2.2446	1.9101	1.5453	0.2834
$\Delta p = p_1 - p_3$	MPa	6.1969	4.7144	3.6964	2.9645	2.4483	2.1165	0.8907

The pumping power in the ORC power plant with the ethane/butane mixture of 0.8/0.2 is more than 13 times higher than that for the system with pure butane, and the turbine power is only by 36% higher. There were noted, however, the benefits resulted from using a zeotropic mixture with a fairly large temperature glide. Figure 7(a) shows the temperature distribution in the condenser for the power plant with pure butane as the working fluid. The calculation assumes that the cooling medium at the inlet to the condenser is at a temperature of T_{c1} = 15 °C while at the outlet T_{c2} = 25 °C. Thus, the condensation temperature of the working medium is T_3 = 30 °C. The pinch point for this variant is present in the condenser outlet area of the cooling medium. The use of zeotropic liquids, which is characteristic by the temperature change at the phase transition realized at the constant pressure, lowers the condensing temperature. The pinch point for the heat exchanger occurs then at the inlet of the cooling fluid to the condenser, fig. 7(b).

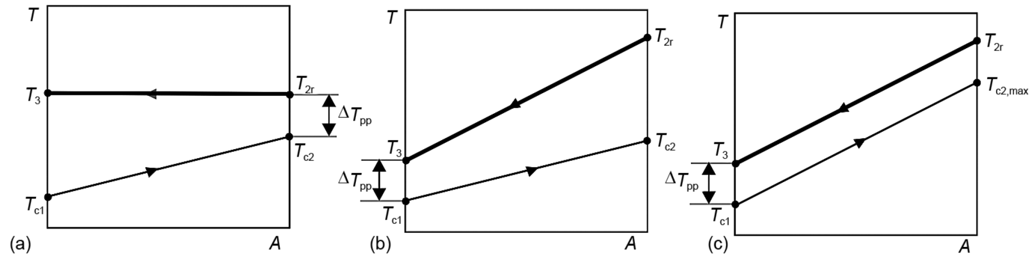

Figure 7. Distribution of the temperature in the condenser for the power plant (a) with pure butane, (b) with a zeotropic mixture – minimization of the heat exchange surface, and (c) with a zeotropic mixture – maximum coolant condenser heating

Temperature of the zeotropic working fluid at the inlet to the condenser T_{2r} is much higher than that for the unary component and depends on the composition of the mixture, as shown in tab. 3.

Table 3. Summary of the working fluid temperatures at the inlet to the condenser T_{2r}, the temperature glide $\Delta T_{g,c}$ and the maximum temperature of the coolant condenser T_{c2},max

Ethane/butane mass fraction		0.8/0.2	0.7/0.3	0.6/0.4	0.5/0.5	0.4/0.6	0.3/0.7	Butane
T_{2r}	°C	39.6	43.4	47.3	51.8	56.5	60.3	30.0
$\Delta T_{g,c}$	K	19.6	23.4	27.3	31.8	36.5	40.3	0
$T_{c2,max}$	°C	34.6	38.4	42.3	46.8	51.5	55.3	25
ΔT_c	K	8.9	10.3	11.6	13.0	14.4	15.5	9.1

In such case, fig. 7(b), the phenomenon of the temperature glide in the condenser can be used to reduce the heat exchange surface of the heat exchanger as the mean temperature drop in the condenser ΔT_c, determined from eq. (6), reaches higher values. Condensation process in the heat exchanger at constant heat capacity values can also be implemented, as shown schematically in fig. 7(c). This option will be applied when the condenser cooling medium is next used for other energy purposes. The values of the maximum temperatures up to which the condenser cooling medium can be heated, $T_{c2,max}$, are presented in tab. 3.

Conclusions

The possibility of using fluid mixtures (and not just zeotropic ones) in the practical power plant applications will become possible only when the practical implementation of the ORC systems with unary cycle fluids is well in command. The mixture of ethane/butane selected and presented in the present work appears not to be the best solution in terms of operational properties of the substance, while the use of such a mixture does not allow to produce more power plant output than that for the pure substance – butane. This results from the power absorbed by the cycle pump that is much higher than that for the system with pure butane.

However, as indicated by the results of the calculations, the proper selection of the zeotropic mixture composition, such with a large temperature glide, allows to reduce the power plant condenser surface or to use heat of condensation for other technological or heating processes.

Nomenclature

h – specific enthalpy, [kJkg^{-1}]
$\dot{m}$ – mass flow rate, [kgs^{-1}]
N – power, [kW]
p – pressure, [bar]
s – specific entropy, [kJkg^{-1}K^{-1}]
T – temperature, [°C]
ΔT_g – temperature glide, [K]

Greek symbols

η – efficiency, [%]
η_I – thermal efficiency, [%]
η_{II} – exergy efficiency, [%]

Subscripts

c – cooling
e – evaporation
n – organic working fluid
s – heat carrier
1, 2, 2s, 2r, 3, 4, 4s, 4r, 5 – characteristic points of cycle

Acronyms (used as subscripts)

C – condenser
G – generator
HE – heat exchanger
HS – heat source
ORC – organic Rankine cycle
P – pump
R – internal regenerator
T – turbine

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