Especially the choice and use of working substances in power plants of small capacity

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Abstract. The issue of the choice of the working fluids for power plants, operating on the basis of (according to the foreign literature sources) the Organic Rankine Cycle – ORC – has multifactorial character, which is first of all imposed by famous international (Montreal, Kyoto, Paris) ozone-hazardous freons application prohibition and greenhouse emissions control agreements. At the analysis of different working fluids implementation prospects also the ecological and technological safety issue has a paramount importance. When all mentioned above factors are taken into account the chosen fluids thermodynamic efficiency and thermal stability issue comes to the fore. The authors justify the use of organofluorine it working substances, is formulated and confirmed by a number of their advantages.

1. Introduction

At the modern stage of development low or distributive power engineering projects became more important. Effective use of energy resources issues, problems of energy costs in the industry and communal services reduction come to a fore, continuous developments of alternative, unconventional energy resources are carrying out. Secondary sources, which recently were considered as waste, are used to replace organic fuel. The majority of technological processes, work of many mechanisms and devices are accompanied by ejection of huge amount of heat, which has no any implementation and dissipates in the environment, in other words, is simply dumped (from this fact is name – “waste heat”). Waste heat often has low temperature potential. Low potential heat sources can be technogenic systems: industrial enterprises, water cooling systems, drains of industrial enterprises and wastewater treatment plants; biogas units, gas-generator units etc. (Calorific value of fuel used in these units). And beside of all mentioned above the sources of natural origin: geothermal sources (Earth’s energy); solar collectors (solar energy). Wide opportunities for utilization of the higher temperature lever heat (about 500 °C level) can be obtained by such sources as exhaust gases after Gas-turbine plants and piston mini power stations, generating gases, flue gases from industrial furnaces and others.
2. Especially the choice and use of working substances in power plants of small capacity

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Transformation of low potential heat energy can be carried out at the different thermodynamic cycles based on organic fluids. Such cycles are often called as ORC (Organic Rankine Cycles). The operation principle of power stations based on pentane technology of more successful producers Turboden (Italy) Ormat (USA), Nuovo Pignone S.p.A. (GE), – is almost similar. Mostly Pentane C5H12 and Pentene C5H10 are used as working fluids. These units have two circuits: the one of them with incombustible coolant transport the heat from waste heat boiler to second turbine circuit with organic flammable working fluid of hydrocarbon composition.

Organic fluids, which have main features such as higher than water’s molecule mass and vaporization heat substantially lower than water’s, are used at the ORC units. Cycle configuration, physical and chemical features of these working fluids get an opportunity to design more effective units, than with water and steam, taking into account such low operation and power features. Steam turbine power stations of this power rang are inferior to power stations based on organic cycle, because of great reduction of Efficiency coefficient and increase of specific indicators of low power steam turbine machines, that’s why at this power rang power stations based on organic cycle come to a fore.

Working fluids of synthetic origin (freons) are used about a half of century at the low and medium power level power engineering units at the systems of low and distributive power engineering. The rang of considered fluids greatly different and wide: carbon dioxide, aqueous ammonia solutions, hydrocarbons, inert gases, fluoroorganic compounds. Taking into account the results of last years research authors formulated the number of technical suggestions to implement fluoroorganic working fluids into heat power circuit of nuclear units based on fast neutrons with fluid metal heat transfer agent and power engineering units of low distributive power engineering systems [1]. Wide rang of limiting ecological, legislative and technological conditions in this multifactorial target made it appropriate and reasonable to apply systematical method to resolve it successfully. An important characteristic of the working fluid, which also affects the overall dimensions of the heat exchange equipment, is the enthalpy Δh triggered at the turbine. The value of Δh is as well larger, as larger the specific volume, that is, the smaller the molecular weight. However, the requirement for the molecular weight of the working fluid is not unambiguous. Thus, as the molecular weight increases, the value of Δh decreases and the flow of the working fluid in the Power Plant increases, and, consequently, the overall dimensions of the heat exchangers. At the same time, the energy loss in the turbine increases with the output speed and the power costs for the drive of the circulating pump, which leads to a decrease in the effective efficiency of the Power Plant. On the other hand, at small Δh, it becomes possible to use relatively cheap one-, three-stage turbines and to achieve their compactness, which helps improve the technical and economic performance of the vocational-
technical school. At small $\Delta h$, it becomes possible to realize the process of intra-cycle regeneration, which makes it possible to increase the average integral temperature of the heat input and the efficiency of the cycle.

Another thermodynamic and thermophysical characteristic, important in the choice of the working substance, is the slope of its boundary condensation curve in the T-S diagram. In mathematical terms, the slope of the boundary condensation curve is expressed as the tangent of the slope of the line of the boundary curve or the sign of the differential $\frac{dT}{dS}$. This feature has a specific effect on the main characteristics when using this working substance in thermodynamic cycles (cycle efficiency, heat exchanger dimensions, degree and proportion of necessary regeneration). The slope of the steam saturation curve in the T-S diagram depends on the type of working substance used. Low boiling working substances can be divided into three types according to the slope of the condensation curve: $\frac{dT}{dS} > 0$, $\frac{dT}{dS} = 0$, $\frac{dT}{dS} < 0$. T-S diagrams of cycles on working substances with different slopes of the condensation curve are shown in Figure 1.

![T-S diagrams of cycles on low-boiling working substances with different slopes of the condensation curve](image)

Fig. 1 - T-S diagrams of cycles on low-boiling working substances with different slopes of the condensation curve

With a positive or zero slope of the saturation curve ($\frac{dT}{dS} = 0$, $\frac{dT}{dS} < 0$), the working substances show better thermodynamic efficiency in the expansion devices due to the absence of condensation in the form of liquid droplets in the turbine. From the technical and economic point of view it is desirable to have working bodies with small negative values of $\frac{dT}{dS}$, that is, when the orientation of the condensation line is close to the isentropic one. In this case, the process of adiabatic expansion of the working fluid in the turbine ends in the vapor-liquid region of the state diagram at high degrees of dryness. In this cycle, there is no need to carry out regeneration, and, consequently, to introduce an additional element - regenerator - into the technological scheme of the installation, which contributes to the improvement of its technical and economic characteristics. In addition, at vapor content $x = 0.95 ... 0.97$, the appearance of moisture in the flowing part of the turbine at the end of the expansion process does not have a significant effect on its efficiency and the energy efficiency of the Power Station as a whole. At positive values of $\frac{dT}{dS}$, the expansion process in the turbine ends in the region of superheated steam. This creates very favorable conditions for the operation of the turbine, since it eliminates the appearance of condensation at the end of the expansion process, the corresponding energy losses, and the erosion of the impeller blades, and there is no need to overheat the steam before feeding it to the turbine. However, the superheated steam braking temperature at the outlet of the turbine, determined primarily by the condensation pressure of the cycle, is much higher than the lower cycle temperature, which leads to the need for additional heat removal by means of a regenerator. The appearance of an additional aggregate-regenerator in the technological scheme of the plant somewhat complicates the hydraulic circuit of the circuit, but it allows increasing the average integral
temperature of the heat supply and, consequently, the efficiency of the cycle. At large negative values of $\frac{dT}{d\delta}$ the slope of the saturation curve, in order to reach the values of the degree of dryness of wet steam close to unity at the end of the expansion process in the turbine, the pairs in the cycle of the Power Station have to overheat. The introduction of overheating is always advantageous from a thermodynamic point of view, since this contributes to an increase in the thermal efficiency of the cycle. However, at the same time, the weight and size characteristics of the steam generator deteriorate due to the introduction of an additional element in it - a superheater. In a number of cases this factor has a prevailing influence on technical and economic characteristics of vocational schools and causes their deterioration.

The next important thermotechnical characteristic of the working body is the optimal values of the working medium pressure in the temperature range of the direct cycle. The saturation pressure of the working fluid at ambient temperature is desirable to be slightly above atmospheric in order to prevent air from being sucked into the capacitors. The freezing point of the working fluid should be significantly lower than the temperature at which condensation heat is transferred to the environment. Of great importance from the point of view of energy efficiency is the identification of optimal pressures in front of the turbine. As a rule, the numerical values of the optimum pressures ahead of the turbine installations on the organic Rankin cycle are substantially lower than the corresponding characteristics of steam-water turbines.

Simultaneously with the thermotechnical requirements to the working bodies of the Power Station, operational and technological requirements are also imposed (for example: fire and explosion safety, non-toxicity, low corrosive and erosive activity, high thermal and chemical stability, availability and low cost).

The schematic diagram of the heat-power circuit when introducing these substances as low-boiling working fluids (LBWF) in comparison with steam-water is much simplified (Fig. 2).
Waste heat exchanger Q0; T - turbine; G - generator, generating electric power Ne; RHE - regenerative heat exchanger with thermal power Qp; C is a capacitor of thermal power Qk; P – pump.

Fig.2 - Schematic diagram of an electric generating installation on Organic working fluids

Of particular importance is the fact that, due to the particular configuration of the thermodynamic supercritical cycle on fluorocarbon working fluids (FWF), a high share of heat recovery (in the likeness of gas-turbine cycles) is provided, a high average integral heat input temperature. The configurations of the thermodynamic cycle are shown in Fig. 3.

Fig. 3 - Configuration of the thermodynamic supercritical cycle

As a subject for studying the thermodynamic efficiency of Organic working fluids, a wide range of substances was selected: R32, R125, R134a, R141b, RC318, R218, R125, R134a, R143a, R507a, R428A, R422D, R422C, R422B, R422A, R421B, R417A, R227ea, R236ea, R236fa, R245ca, R245fa, R365mfc, R3110, R600 (butane), R601 (pentane), toluene, ethanol, isobutene, isohexane, isopentane, methanol. Figure 4 shows the boundary curves of the investigated working bodies in Ts coordinates, and in Table. 1 shows their critical parameters.
As can be seen from the nature of the boundary curves of the test substances, organic substances with different slopes of the condensation curve were selected for analysis: negative - R32, R125, R134a, ethanol, methanol; "Zero" - R142b; Positive - R123, R141b, R218, RC318, R227ea, R3110, R600, R601, toluene, heptane, isobutene, isohexane, isopentane, neopentane. The substances selected for the initial analysis have different thermodynamic properties: molar mass, critical temperature and critical pressure. The key characteristic when choosing a working substance is the value of the maximum thermal stability of the substance according to the source [3].

**Table 1 - Critical parameters of Organic Working fluids**

| Designation | Full name of organic substance | Chemical formula | \(T_{cr},K\) | \(\rho_{cr},MP\) | Molar mass kg/kmol | ODP | GWP |
|-------------|--------------------------------|------------------|-------------|-----------------|-------------------|-----|-----|
| R32         | Difluoromethane                | \(CH_2F_2\)      | 351.26      | 5.78            | 52,024            | 0   | 650 |
| R125        | Pentfluoroethane               | \(C_2HF_5\)      | 337.17      | 3.62            | 120,02            | 0   | 3400|
| R134a       | Tetrafluoroethane              | \(C_4H_8F_4\)    | 374.21      | 4.06            | 102,03            | 0   | 1300|
| RC318       | Octafluorcyclobutane           | Cyclo-C_4F_8     | 388.38      | 2.7775          | 200.03            | 0   | 102.5|
| R3110       | Decafluorobutane               | \(C_4F_{10}\)    | 386.33      | 2.3234          | 238.03            | 0   | -   |
| R218        | Octafluoropropane              | \(C_8F_8\)       | 345.02      | 2.64            | 188.02            | 0   | 8690|
| ethanol     |                                | \(C_2H_5O\)      | 513.49      | 6.15            | 46,068            | 0   | 1   |
| methanol    |                                | \(CH_2O\)        | 513.62      | 8.22            | 32,042            | n/a | n/a |
The initial analysis consisted mainly of evaluating the thermal efficiency of the organic Rankin cycle on each of the selected working substances. To calculate the Rankin cycle with the subsequent calculation of the thermal efficiency, a number of assumptions were introduced: the calculation was carried out in the MathCad environment using the Refprop data at various pressures at the turbine inlet in the range from 3 to 12 MPa in steps of 0.5 MPa and at a fixed working temperature substances depending on thermal stability; The condensation temperature of the substances is assumed to be 30 °C. Since the process is supercritical for selected liquids, the configuration of the cycle with the regeneration process was chosen. The results of the calculation are presented in Table. 2 and in Fig. 5.

Table 2 - Thermal efficiency of the Organic working substances at a fixed value of the temperatures at the inlet to the turbine T1, K and in the capacitor T4, K

| \( p_2, \text{MPa} \) | Thermal efficiency of ORC \( \eta_T, \% \) |
|------------------|---------------------------------|
|                  | R32 (T1=413 K, T4=303 K) | R125 (T1=473 K, T4=303 K) | R134a (T1=413 K, T4=303 K) | ethanol (T1=573 K, T4=353 K) | methanol (T1=573 K, T4=353 K) | RC318 (T1=473 K, T4=303 K) | R3110 (T1=473 K, T4=303 K) | R218 (T1=473 K, T4=303 K) |
| 3                | 7,8                           | 11,3                          | 24,8                          | 24                           | 22,3                          | 27,2                          | 22,6                          | 22,6                          |
| 3,5              | 9,8                           | 13,3                          | 25,5                          | 24,5                         | 22,8                          | 28,4                          | 23,3                          | 23,3                          |
| 4                | 11,3                          | 14,9                          | 25,9                          | 24,8                         | 23,2                          | 29,3                          | 23,7                          | 23,7                          |
| 4,5              | 12,5                          | 16,2                          | 26,1                          | 25,1                         | 23,5                          | 30                            | 24                            | 24                            |
| 5                | 13,4                          | 17,2                          | 26,1                          | 25,2                         | 23,7                          | 30,6                          | 24,2                          | 24,2                          |
| 5,5              | 14                            | 18,1                          | 25,9                          | 25,3                         | 23,9                          | 31,1                          | 24,3                          | 24,3                          |
| 6                | 14,5                          | 18,8                          | 25,5                          | 25,3                         | 24                            | 31,6                          | 24,3                          | 24,3                          |
| 6,5              | 14,9                          | 19,4                          | 25                            | 25,3                         | 24,1                          | 31,9                          | 24,4                          | 24,4                          |
| 7                | 15,1                          | 19,9                          | 24,5                          | 25,2                         | 24,1                          | 32,3                          | 24,4                          | 24,4                          |
| 7,5              | 15,1                          | 20,3                          | 23,9                          | 25                            | 24,1                          | 32,5                          | 24,4                          | 24,4                          |
| 8                | 15,2                          | 20,7                          | 23,5                          | 24,8                         | 24                            | 32,8                          | 24,4                          | 24,4                          |
| 8,5              | 15,1                          | 21                            | 23,2                          | 24,6                         | 24                            | 33                            | 24,4                          | 24,4                          |
| 9                | 14,9                          | 21,2                          | 22,9                          | 24,3                         | 23,9                          | 33,2                          | 24,4                          | 24,4                          |
| 9,5              | 14,7                          | 21,4                          | 22,7                          | 24                            | 23,7                          | 33,3                          | 24,4                          | 24,4                          |
| 10               | 14,5                          | 21,6                          | 22,6                          | 23,6                          | 23,6                          | 33,5                          | 24,4                          | 24,4                          |
| 10,5             | 14,2                          | 21,7                          | 22,4                          | 23,2                          | 23,4                          | 33,6                          | 24,4                          | 24,4                          |
| 11               | 14                            | 21,9                          | 22,3                          | 22,7                          | 23,2                          | 33,7                          | 24,4                          | 24,4                          |
| 11,5             | 13,6                          | 22                            | 22,2                          | 22,3                          | 23                            | 33,9                          | 24,4                          | 24,4                          |
| 12               | 13,3                          | 22,1                          | 22,1                          | 21,9                          | 22,8                          | 34                            | 24,4                          | 24,4                          |
3. Conclusions

The high thermodynamic efficiency of the use of fluorocarbon composition (octafluoropropane C3F8, cyclofluorobutane C4F8, decafluorobutane C4F10) as working bodies for power plants with binary cycles was first noted in the works of Gokshstein D.P. and co-authors as early as the 60s of the last century [3]. However, calculations of the cycles on these substances with reasonable accuracy can be performed only by the results of thermophysical studies carried out at the Department of Theoretical Foundations of Thermal Engineering MPEI in the period 2006-2014. With undoubted thermodynamic efficiency and zero ozone-depleting potential (ODP = 0), fluorocarbons are considered to be so-called "greenhouse" gases. The question of the lifetime of these substances in the atmosphere becomes the key, and the estimates of the Lifetime for fluorocarbons given in the IPCC reports (IPCC-94, IPCC-2013) without the presentation of the methodology for calculating this important quantity cause valid doubts about their reliability.

The working body chosen for the power plant must have favorable chemical, physical and operational properties under the specified operating conditions, i.e. be stable, non-flammable, explosion-proof, non-toxic, inert to construction materials. The development of converters of thermal energy into electric power in the sphere of small power engineering was based on the use of hydrocarbons. Clearly, the main disadvantage is their flammability, explosiveness and low thermal stability. Such facilities are limited by the temperatures of the recycled streams to 290 °C and have, in addition to the turbine, an additional circuit with a heat-resistant liquid (oil) and an intermediate heat exchanger, which affects the efficiency of the entire system. In [4, 5], density measurements were performed and thermal octafluoropropane (C3F8) up to 550 °C, octafluoroclobutane (C4F8) to 420 °C and decafluorobutane (C4F10) to 520 °C were confirmed.
The performed thermodynamic analysis shows: 1). At the same temperatures in front of the turbine and the conditions for removing heat to the environment, the thermal efficiency of the cycle is higher than the efficiency in the water working body or gas; 2). An increase in the energy efficiency of cycles is achieved by providing a high average integral heat input temperature in supercritical cycles with a large proportion of internal regeneration. Such an advantage in thermodynamic efficiency is most noticeable at low and medium pressures.

In the authors' opinion, the expansion of the temperature range of the use of non-aqueous working bodies, the increase in the energy efficiency of heat-power converters can be achieved through the use of fluorocarbons. Fluorocarbon substances, especially octafluoropropane (C3F8), octafluorocyclobutane (C4F8) and decafluorobutane (C4F10), are of particular interest from the standpoint of the possibility of using them as a working fluid (instead of water) in turbine cycles of thermal energy conversion into electric energy over a wide temperature range of utilizable Heat flux from 100 °C to 550 °C. The application of the hydrocarbon composition most common in the technologies of electrogeneration based on the "organic Rankine cycle" of low-boiling working fluids is limited to 290 °C.

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