

PAPER • OPEN ACCESS

New working fluids for the use of heat secondary sources in mining technologies

To cite this article: Mykhailo Kirsanov *et al* 2023 *IOP Conf. Ser.: Earth Environ. Sci.* **1156** 012028

View the [article online](#) for updates and enhancements.

You may also like

- [Anomalous transport of subdiffusing cargos by single kinesin motors: the role of mechano-chemical coupling and anharmonicity of tether](#)
Igor Goychuk
- [Triode Fuel Cells and Batteries](#)
Stella P. Balomenou and Constantinos G. Vayenas
- [Techno-economic efficiencies and environmental criteria of Ocean Thermal Energy Conversion closed Rankine cycle using different working fluids](#)
N Samsuri, N Sazali, A S Jamaludin et al.



Connect with decision-makers at ECS

Accelerate sales with ECS exhibits, sponsorships, and advertising!

▶ Learn more and engage at the 244th ECS Meeting!

New working fluids for the use of heat secondary sources in mining technologies

Mykhailo Kirsanov^{1,3}, Olena Gupalo^{1,2} and Kostiantyn Podoliak¹

¹Institute of Geotechnical Mechanics named by N. Poljakov of National Academy of Sciences of Ukraine, Simferopolska Str., 2a, Dnipro, 49005, Ukraine

²Ukrainian State University of Science and Technologies, Lazaryana Str., 2, Dnipro, 49010, Ukraine

³Corresponding author: mvksvd1704@gmail.com

Abstract. Production cost of mining enterprises can be significantly reduced when using secondary heat. A large volume of secondary heat sources has a temperature potential of no higher than 50°C. To generate additional electricity using secondary heat it has been proposed to use installations with the Rankine thermodynamic cycle in mining enterprises. The paper aim is to study the thermodynamic efficiency of using R-1234yf and R-744 in the equipment, which uses the secondary heat of mining technologies for evaporation of these working fluids. R-1234yf is a freon that belongs to the class of hydrofluoroolefins and has a much lower level of global warming potential than other ozone-depleting substances. R-744 is carbon dioxide, which belongs to a natural, non-toxic and non-flammable working substance. It has been determined that the thermodynamic efficiencies of using R-1234yf and R-744 are 10% and 6.3%, respectively. The thermodynamic efficiency has been calculated for the temperature range from 50° to 20°C, which is typical for a large volume of secondary heat sources in mining technologies.

1. Introduction

In the last 10-15 years, the mining industry, engineering and energy consume a large amount of organic fossil fuels. At the same time, the limitations of using the organic fuel resources are rising due to harmful impact on the environment. The mining industry extracts organic fuels and consumes a lot of them. In this regard, technologies and equipment designed to reduce the consumption of organic fuel in the mining industry are of practical interest. Reducing the organic fuel consumption can be achieved through more efficient use of secondary energy resources (SER), which are by-product of mining and processing technologies [1]. A significant volume of SER in the mining industry is secondary heat. Due to its beneficial use, additional electricity can be generated. This reduces the consumption of electricity for the production of 1 ton of organic fuel, that leads to reduction of organic fuel consumption during the production of electricity for the mining industry. In this paper, it is proposed to use freon steam turbine (FST) with the Rankine thermodynamic cycle in mining enterprise equipment to generate additional electricity.

The Rankine cycle consists of heating the working fluid in the heat exchanger, adiabatic expansion in the turbine with the return of useful mechanical work to the electric generator, and subsequent condensation of freon to a saturated liquid, which is pumped back into the heat exchanger. The freons are evaporated due to the use of low-potential heat - a secondary product of mining technologies.



Thermodynamic analysis [2-4] of FST for energy utilization of low-potential sources of mining enterprises showed high level of efficiency. To evaluate the effectiveness, the thermodynamic efficiency of the Rankine cycle was calculated with the heating temperature $T_2 = 323$ K (50°C) and the cooling temperature $T_1 = 293$ K (20°C) when the turbine was operating on ozone-safe freons R-125, R-236ea, R-32, R-152a, which belong to the class of hydrofluorocarbons (HFCs). However, the choice of freons as working fluids for FST should be based not only on the analysis of thermophysical properties of these substances, but also on meeting the requirements of international environmental regulation [5,6].

An agreement on the phased reduction of HFC consumption was reached at the 28th Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer in Kigali, the capital of Rwanda (October 2016). HFCs are used as an alternative to ozone-depleting substances (ODS). Not being ODS, HFC are greenhouse gases that have a high or very high global warming potential (GWP) in the range of 121-14800. In the series of R-125, R-236ea, R-32, R-152a, freon R-152a has a minimum GWP value of 140. Therefore, it is advisable to consider freons, for example, R-1234yf (GWP=4) from the class of hydrofluoroolefins (HFO), which are characterized by a much lower level of HFC. In addition, at the meeting in Kigali, a recommendation was adopted for the wider use of natural (non-toxic, non-flammable) working substances, for example, R-744 (carbon dioxide, for carbon dioxide GWP =1). The greenhouse properties of carbon dioxide are accepted as a standard or a unit of the GWP scale of various working fluids.

This paper is devoted to the evaluation of the effectiveness of the use of R-1234yf and R-744 in installations for additional electricity production using the secondary heat of mining technologies. The mathematical apparatus of the methodology previously presented in [2] was improved [3]. In this regard, the purpose of the article is to calculate the thermodynamic efficiency of the use of R-1234yf and R-744 in equipment for using the secondary heat of mining technologies and to verify the operation of the proposed mathematical apparatus for these freons.

2. Methods

The paper is based on the use of fundamental laws and equations of thermodynamics. In [3], a classification of thermodynamic working substances, including freons, was proposed depending on the behavior of the entropy function of the saturated vapor of the substance as a function of temperature. Depending on this property of freons, the line of adiabatic expansion in the turbine can be located in two ways on the diagram of the Rankine cycle in the "pressure p - specific volume v " coordinates.

In the [2], the cycle efficiency calculation method is developed for the location option on the Rankine cycle diagram (figure 1) of line "5-6" of freon expansion, when in order to close the loop of the cycle on line "4-5", freon must be overheated. Freon or other working fluids (water, carbon dioxide), for which the Rankine cycle in the "pressure p - specific volume v " coordinates shown in figure 1, is characterized by the following property. The entropy of the saturated vapor of such freon decreases with temperature increasing. Let's call such working fluids, including freons, working fluids of the first type. Freons of this type include R-125, R-236ea, R-32, R-152a.

However, there are also working fluids (substances) in which the property regarding the change in entropy with temperature is formulated in the opposite way. In particular, the entropy of saturated freon vapor increases with increasing temperature. Such freons include R-1234yf. Let's call them working fluids of the second type. The geometric form of the Rankine cycle diagram for the second type freons is shown in figure 2. It shows that the change in the dependence of the entropy of a saturated vapor of freon (of the second type) on temperature changes the Rankine cycle diagram for freons of this type. In figure 2, point "5" is located on the isobar p_1 , which corresponds to the condensation pressure at temperature T_1 (cooling temperature of the working fluid in the Rankine cycle). This means that to close the Rankine cycle, the expansion of freon vapor in the turbine ends in the region of superheated vapor parameters relative to the saturation state at temperature T_1 . Figures 1 and 2 were given in the paper [3] in connection with the proposed classification of freons. In this paper, we provide these figures to explain the numbering of the

calculation points of the cycle. A certain difference in the geometric shape of the figure "1-2-3-4-5-6-1", the area of which is numerically equal to the useful work of the Rankine cycle [7], in figures 1 and 2 entails a corresponding difference in the mathematical apparatus for calculating efficiency the use of freons of the two specified types. Freon R-1234yf belongs to the second type, and freon R-744 (carbon dioxide) to the first one. To calculate the efficiency, useful work of the Rankine cycle is required.

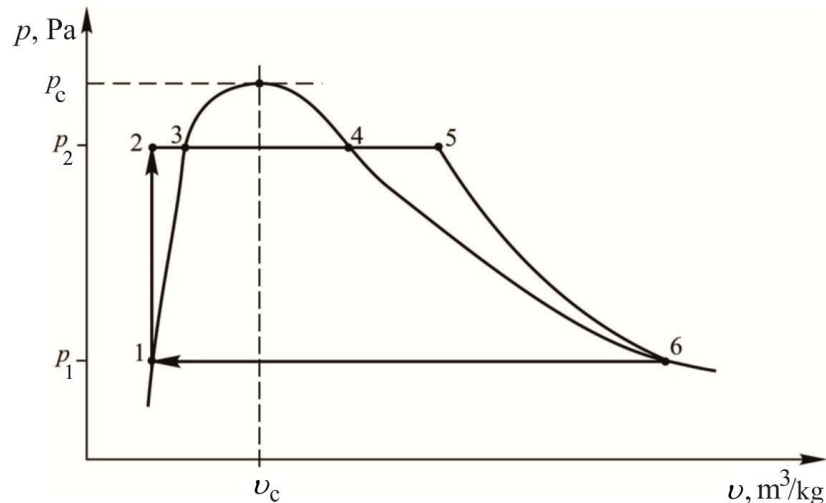


Figure 1. Rankine cycle in "pressure p - specific volume v " coordinates, where p_1, p_2 - freon pressure on lines "6-1" and "2-5", respectively, Pa; p_c, v_c - pressure (Pa) and specific volume (m^3/kg) at the critical point.

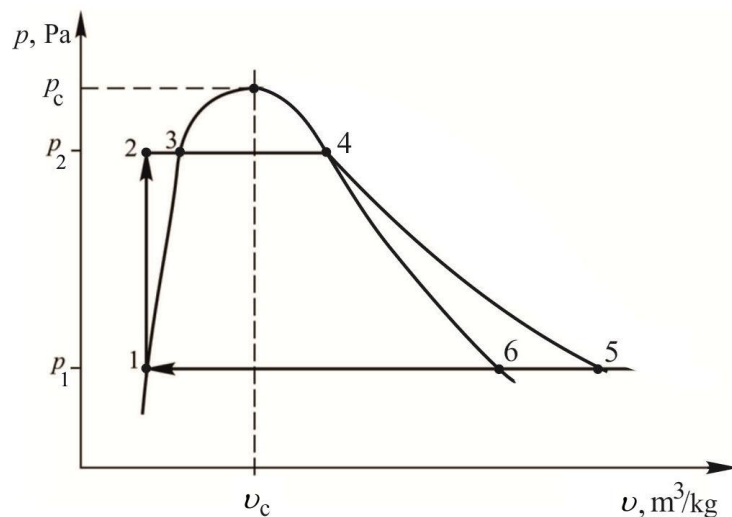


Figure 2. Rankine cycle in "pressure p - specific volume v " coordinates, where p_1, p_2 - freon pressure on lines "6-1" and "2-5", respectively, Pa; p_c, v_c - pressure (Pa) and specific volume (m^3/kg) at the critical point.

For freon of the first type (Rankin cycle diagram - figure 1), the expression for useful work has the following form

$$U_{R,1} = (p_2 - p_1) \cdot \left[(v_5 - v_1) + \left(\frac{v_6 - v_5}{2} \right) \right], \quad (1)$$

where p_1, p_2 are freon pressures on lines "2 – 5" and "6 – 1" (figure 1), respectively, Pa; v_1, v_5, v_6 are specific volumes of freon at points "1", "5", "6" (figure 1), respectively, m³/kg.

For freon of the second type (Rankin cycle diagram - figure 2), the expression for the useful work is as follows

$$U_{R,2} = (p_2 - p_1) \cdot \left[(v_4 - v_1) + \left(\frac{v_5 - v_4}{2} \right) \right], \quad (2)$$

where p_1, p_2 are freon pressures on lines "2 – 5" and "6 – 1" (figure 2), respectively, Pa; v_1, v_4, v_5 are specific volumes of freon at points "1", "4", "5" (figure 1), respectively, m³/kg.

It is known [7] that the efficiency of the Rankine cycle determines the ratio of useful work to the heat given off by the working fluid on the cooling line "6-1" in figure 1 or on the cooling line "5-6-1" in figure 2. Then the efficiency of the Rankine cycle for freon of the first type is determined by the expression

$$\eta_{R,1} = \frac{U_{R,1}}{L(T_1)}, \quad (3)$$

where $L(T_1)$ is the specific heat of the " evaporation -condensation" phase transition, J/kg.

When using freon of the second type, the heat given off by the working fluid on the cooling line "5-6-1" in figure 2 consists of the specific heat of condensation $L(T_1)$ on the line "1-6" at temperature T_1 and the cooling heat of the freon vapor from points "5" to points "6". That is, the efficiency of the Rankine cycle for freon of the second type has the form

$$\eta_{R,2} = \frac{U_{R,2}}{L(T_1) + q_1}, \quad (4)$$

where q_1 is the cooling heat of freon vapor from point "5" to point "6", J/kg.

The expression for the q_1 of the cooling heat can be obtained after introducing the coefficients included in the approximation of the specific isochoric heat capacity of R-1234yf depending on the temperature. To model the thermophysical properties of working fluids, it is proposed [8, 2] to use the Redlich-Kwong thermal equation of state:

$$p_{RK}(v, T) = \frac{R_{gf} T}{v - b} - \frac{a}{v(v + b)\sqrt{T}}, \quad (5)$$

where T is temperature, K; v is specific volume, m³/kg; b is the constant of the Redlich-Kwong equation, which characterizes the forces of intermolecular repulsion (m³/kg); a is the constant of the Redlich-Kwong equation, which characterizes the forces of intermolecular attraction, (Pa·m⁶·K^{0.5}/kg²), R_{gf} is the gas constant of freon, J/(kg·K), which is determined by the expression

$$R_{gf} = \frac{R_{gu}}{M_f}, \quad (6)$$

where $R_{gu} = 8.314$ J/(mol·K), the universal gas constant; M_f – molecular weight of freon, kg/mol.

When determining the efficiency of the use of a specific working fluid (freon) in the Rankine cycle, it is necessary to have an expression for the entropy of this freon, the thermal properties of which are given by the Redlich-Kwong equation. In the [1], the expression for the entropy of the working fluid according to Redlich-Kwong was obtained

$$S_R(v, T) = A_S(v, T) - A_S(v_0, T_0), \quad (7)$$

where $S_R(v, T)$ is the specific entropy of freon, the thermal properties of which are modeled by the

Redlich-Kwong equation, $J/(kg \cdot K)$; v_0 is the specific volume at some point, which is taken as the initial state of the adiabatic process, m^3/kg ; T_0 is the temperature at some point, which is taken as the initial state of the adiabatic process, K ; $A_S(v, T)$ is a function whose dimension coincides with the dimension of the specific entropy of freon $J/(kg \cdot K)$ and which has the following form

$$A_S(v, T) = \ln \left[(v - T)^{R_{gf}} \right] + \left(\frac{a}{b \cdot T^{1.5}} \right) \cdot \ln \left(\frac{v}{v - b} \right) + c \ln(T) + d \cdot T + \frac{k \cdot T^2}{2}, \quad (8)$$

where c , d , k are constants of the polynomial approximation of the dependence of the isochoric heat capacity (in the ideal gas state) of freon on temperature [7], which have the dimensions respectively $J/(kg \cdot K)$, $J/(kg \cdot K^2)$, $J/(kg \cdot K^3)$.

The isochoric heat capacity of the working fluid in the ideal gas state has the form of a quadratic polynomial [9]:

$$C_v^0(v, T) = c + dT + k \cdot T^2, \quad (9)$$

where $C_v^0(v, T)$ is the specific isochoric heat capacity of freon in the ideal gas state, $J/(kg \cdot K)$.

Now the second addend q_1 of the heat of cooling in (4) taking into account (9) is determined by the expression

$$q_1 = (T_5 - T_6) \cdot \left[c + \frac{d}{2} \cdot (T_5 - T_6) + \frac{k}{3} \cdot (T_5 - T_6)^2 \right]. \quad (10)$$

The content of the technique [3] consists of determining v_5 and T_5 by solving the equation

$$A_S(v_5, T_5) = A_S(v_6, T_6), \quad (11)$$

and Redlich-Kwong equation (5) and on the basis of data on v_5 calculation of the thermal efficiency of the use of this freon in the Rankine cycle. It is necessary to analyze the possibility of applying the technique for the use of R-1234yf, for which the Rankine cycle diagram is presented in figure 2.

3. Results and discussion

The parameters of R-1234yf ($CH_2 = CFCF_3$) at point "6" are tabular data of its thermophysical properties [10]. In the conditions of our calculation example, these properties are taken at temperature $T_1 = 293$ K ($20^\circ C$) of freon condensation in the Rankine cycle on line "1-6", figure 2. The Redlich-Kwong equation (5) with respect to $(\sqrt{T_5})$ is a cubic equation. The paper [3] proposed approximations for solving the Redlich-Kwong equation for T_5 as a function of v_5 . These approximations also simplify the solution (11) by Newton's method [11]. Since the change in the parameters of the R-1234yf (tetrafluoropropene) freon, compared to the previously considered freons, does not affect the approximation algorithm, the technique can be used for tetrafluoropropene as well. Thermodynamic parameters were calculated for tetrafluoropropene at key points of the Rankine cycle according to the method [3], the results are presented in table 2. For carbon dioxide (R-744), which belongs to the working fluids of the first type, the method [3] of calculating the thermodynamic parameters of the Rankine cycle must be specified taking into account parameters near the critical point of carbon dioxide. The peculiarity of this case is that equation (11) is also valid for the line "5-6" in figure 1. But in this case, only v_5 is unknown in equation (11). The temperature T_5 is known because it corresponds to the temperature T_2 of evaporation of R-744. The temperature T_2 is $50^\circ C$ in the conditions of our calculation example. The solution of equation (11) with respect to v_5 can also be carried out by Newton's method [11]. When v_5 is calculated for R-744 according to (11), we determine the pressure p_2 of injection of carbon dioxide into the heat exchanger of evaporation of carbon dioxide due to the secondary heat of mining technologies using the Redlich-Kwong equation

$$p_2 = \frac{R_{gf} T_5}{v_5 - b} - \frac{a}{v_5 \cdot (v_5 + b) \cdot \sqrt{T_5}}. \quad (12)$$

Thermodynamic parameters of R-1234yf and R-744 with a low GWP value as working fluids for the use of secondary heat of mining technologies are shown in table 1.

Table 1. Constants of the Redlich-Kwong equation and isochoric heat capacity for R-1234yf and R-744 freons [9, 10].

Parameter, unit	Freon class	
	R-1234yf	R-744
R_{gf} , J/(kg·K)	72.9	188.91
a , (N·m ⁴ ·K ^{0.5})/ kg ²	1739.8	3331.2
b , m ³ /kg	6.896·10 ⁻⁴	6.675·10 ⁻⁴
c , J/(kg·K)	174.95	1003
d , J/(kg·K ²)	2.649	0.205
k , J/(kg·K ³)	-6.694·10 ⁻⁴	-8.54·10 ⁻⁵

The data obtained using the methods described above for determining the thermodynamic parameters of R-1234yf and R-744 at the calculation points of the Rankine cycle (figures 1 and 2) are presented in the table. 2.

Table 2. Parameters of R-1234yf and R-744 freons at the calculation points of the Rankine cycle.

№ point, condition working substance	Pressure, MPa		Specif. volume, m ³ /kg		Temperature, °C	
	R-1234yf	R-744	R-1234yf	R-744	R-1234	R-744
1, saturated freon after condenser	0.592	0.527	9·10 ⁻⁴	0.001	20.0	20.0
2, non- evaporating freon	1.302	1.196	9·10 ⁻⁴	0.0001	50.0	50.0
3, evaporating freon	1.302	1.196	9.1·10 ⁻⁴	0.0012	50.0	50.0
4, dry saturated freon's vapor	1.302	1.196	0.013	0.0269	50.0	50.0
5, superheated vapor or dry saturated vapor	0.592	0.527	0.032	0.0285	25.0	52.4
6, dry saturated freon's vapor	0.592	0.527	0.03	0.0618	20.0	20.0

The data in table 2 allow us to determine the efficiency of the Rankine cycle according to expressions (3) and (4) from the use of the considered fluids. The thermodynamic efficiency of the Rankine cycle when using R-1234yf was 10.2%. For the use of R-744 in this cycle, the efficiency is 6.3%. At the same time, the calculation was carried out for the temperature range from 50°C to 20°C, which is typical for a large volume of secondary heat sources in mining technologies.

4. Conclusion

The efficiency of using R-1234yf and R-744 as working fluids with a low global warming potential for installations for the use of secondary heat of mining technologies was studied.

The previously developed model for calculating the efficiency of freons of first type can also be used for R-1234yf. To calculate thermodynamic efficiency of the use of R-744, mathematical model was refined considering the fact that the critical point of R-744 is within the range of the calculated parameters.

Thermodynamic efficiency of using R-1234yf is 10.2%. Thermodynamic efficiency of R-744yf is

6.3%. The efficiencies were calculated for temperature range from 50°C to 20°C, which is typical for a large volume of secondary heat sources of mining technologies.

The use R-744 is also advisable, considering that the GWP for this working fluid is four times lower than that of R-1234yf. In addition, R-744 is a completely non-combustible gas. It is possible that the efficiency of using R-744 can be increased in the temperature range from 30°C to 12°C. For this, during condensation in the Rankine's cycle with R-744, mine water with a temperature of 8-12°C can be used. Therefore, the proposed temperature range for the use of R-744 is quite realistic.

References

- [1] Bulat A F and Chemeris I F 2006 *Nauchno-technicheskie osnovy sozdaniya shahtnyih kogeneratsionnyih energeticheskikh kompleksov* (Kiev: Naukova dumka).
- [2] Kirsanov M, Diakyn I, Ruban V, Skosyriev V and Zhevzyk O 2020 Estimation of usage efficiency of the freon-steam turbines in mine energy complexes *E3S Web Conf.* **168** 00048 DOI: 10.1051/e3sconf/202016800048
- [3] Semenenko Yu V Kirsanov M V and Ruban V D 2020 Pro otsinku efektyvnosti zastosuvannia freoniv u tsykli Renkinu *Proceedings of the III International Conference "Topical issues of science and practice", UK, London, 02-06 November 2020* pp 736-741.
- [4] Kirsanov M, Slobodiannikova I and Gupalo O (2021) Improving the technology of using freon-steam turbines in mine power complexes *IOP Conf. Ser.: Earth Environ. Sci.* **970** 012019 DOI: 10.1088/1755-1315/970/1/012019
- [5] Ivaniuta S P, Kolomiets O O, Malynovska O A and Yakushenko L M (2020) *Zmina klimatu: naslidky ta zakhody adaptatsii: analitychna dopovid* (Kiev: Natsionalnyi Instytut strategichnykh doslidzhen)
- [6] United Nations Environment Programme 2016 *The Kigali Amendment to the Montreal Protocol: HFC Phase-down*. <https://wedocs.unep.org/20.500.11822/26589>
- [7] Buliandra O F 2021 *Tekhnichna termodynamika* (Kiev: Tekhnika)
- [8] Redlich O 1975 On the Three Parameter Representation of the Equation of State *Industrial and Engineering Chemistry Fundamentals* **44** (1) pp 254-260.
- [9] Reid R, Prausnitz Jh and Shervood T (1977) *The properties of gases and liquids* (New York: McGraw Hill Book Company)
- [10] *Thermodynamic properties of refrigerants: handbook* 2018 (Bristol: Climalife)
- [11] Volontyr L O, Zelinska O V, Potapova N A and Chikov I A 2020 *Chyselni metody* (Vynnytsia: NAU Publ.)