The Method of Carbon-Dioxide Recovery in Fish-Processing Industry

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Abstract. The article introduces one of the methods of carbon-dioxide recovery at alcohol-processing plants. It also analyses how to use carbon dioxide in combination with the binary mixture for trout cooling and shows some technological advantages of this technology usage. The article presents the results of the experiments in trout cooling with the help of water ice, the combination of water ice and snowlike carbon dioxide, and snowlike pure CO₂. Basing on the experiments and their analysis we have drawn the isotherms of cooling medium temperature changing for trout cooling and for the duration of trout cooling with different carbon dioxide concentrations.

Introduction

In recent times different factors have led to the prominent growth of interest to some technologies of using carbon dioxide (CO₂) as a coolant. High potential of carbon dioxide usage in refrigeration systems is due to its effectiveness and safety for the environment, which other refrigerants cannot do. The use of many coolants is restricted by many different ecological standards, besides, there is a great tendency to make these standards stricter. That is why the use of natural coolants is getting more and more popular.[1]

Carbon dioxide belongs to the group of natural coolants (ammonia, propane, butane, water, etc.), it has zero ozone depleting potential (ODP=0) and is a standard unit of calculating global warming potential (GWP=1). However, natural coolants have their own drawbacks: ammonia is poisonous, propane is flammable, the use of water is restricted because of impossibility to use it at low temperatures. CO₂ is neither poisonous nor flammable. But in spite of the fact that carbon dioxide is a part of the air and is necessary for different bioprocedures, high concentration of CO₂ in the air is considered to be one of the reasons of global warming. That is why carbon dioxide influence on the environment is not obvious.

The technology we develop perfectly suits the new agreement coming into operation in 2022. The aim of the agreement is to prevent the 2°C growth of a global average temperature. One of the measures the Russian delegation suggested is to introduce some economical tools including the inner “carbon price”, which means necessity to pay for carbon dioxide emissions. They also discuss to begin industrial emission monitoring since 2019, which is supposed to consist of three preparatory stages. Firstly, Ministry of Natural Resources is to develop the methods of an enterprise report on greenhouse gases emission, and Ministry of Economic Development is to prepare the draft law making such reports obligatory. Then, up to the end of 2019 companies, firms, enterprises and the like are to give the information of the emissions which go beyond 150 000 tons of CO₂ - equivalent per year. By the beginning of 2020 these reports are to be given by all companies if their emissions are more than 50 000 tons. As soon as the system of such reports and emission data checking are developed, the authorities will be ready to discuss the introduction of the “carbon price”, i.e. emission fee, in Russia [2].

Thus in the future we may expect industrial enterprises to require different possible ways how to recover waste greenhouse gases including carbon dioxide. To introduce this method as one of the industrial ways of recovery of carbon dioxide which is a waste product of alcohol-processing plants we have undertaken a series of studies of trout cooling with the help of CO₂.
On the world's markets chilled fish is in great demand and the industrial sector of its production is one of quickly-growing. It is important for a prominent group of customers to have such a product easy and quick to cook: choosing chilled food a customer saves time while defrosting it, thus having a finer product. Also this method based on carbon dioxide usage has some advantages over traditional methods of cooling [3].

There are some traditional ways of fish cooling: by cold air, by cold liquid, by ice, by carbon dioxide. For air cooling there is used modern technological equipment with use of coolants e.g. cabinets, chest freezers, etc. The way of fish cooling in cold water is rather simple and it doesn’t require any commercial expenses, but fish of fine texture is poorly kept in sea water: it can swell and get oversalted. It loses water-soluble proteins, extractive nitrogen compounds.

The most popular way of fish cooling is that by water ice. We can use either natural ice taken from waterbodies in winter or artificial ice made by ice machines from fresh town water. To prepare a stock of natural ice is rather hard, its sanitary state is not very good, it is difficult to keep it in summer as about its 40% is being lost. Artificial ice may be of different forms (cubes, tubes, scales) depending on ice machines [4].

Nowadays in fish-processing industry it is innovative to use a “binary mixture” having ice crystal of very little size as cooling medium. It makes possible to eliminate fish mechanical damage, to provide high ability of the mixture to penetrate between fish trunks, and to create large ice-product contact surface [5]. Traditional ways of fish cooling have some drawbacks; ice cooling is used for short storage before fish processing, the speed of fish cooling is low, cooling is inhomogeneous, a container volume is not used effectively, a great amount of ice is lost because of melting, fish trunks can be damaged while contacting with ice. Besides, all kinds of ice except of cube form are produced at the moment of ice usage. It is not possible to keep this ice as its great amounts can flow into an indiscrete mass because of pressure. To balance these drawbacks we suggest the technology of fish (trout) cooling using “water ice and CO2” medium as an additional cooling agent [6].

The work objective
The work objective is to develop the methods of snowlike CO2 usage with the purpose of its recovery in combination with water ice for trout cooling, to make a comparative analysis of trout cooling in the media “water ice” and “water ice and snowlike CO2”

Results and discussion
The main experimental material was thermograms of processes and curves of density variation of heat current over time.

Using thermograms of trout cooling process we defined the temperature drop in fish trunk layers and the time length of snowlike carbon dioxide sublimation.

Heat exchange coefficient is defined by Newton – Richmann formula on the basis of experientially reported values of heat current density.

Cooling treatment of a trout trunk lasted to reach the rated temperature in all layers of fish trunks [7].

A trout trunk of 0.8±0.05kg was cooled in a standard container of maximum capacity of 50 l. In the former case we used water ice of the mass weight of 2 kg, in the later case we used water ice of the mass weight of 1.6 kg and snowlike CO2 480g (30% of ice mass). Boundary dimensions of the container were 0.9 x 0.6 x 0.4m. The mass of cooled fish was defined by weighing. Temperature changing in fish and in a cabinet was controlled with the help of Chromel-Copel thermocouples put in a trout trunk under its scale to the depth of 3mm and in the fattest part of the trunk (close to its backbone) to the depth of 0.002 and 0.004m. The thermocouple signal goes to the temperature controller. Measurement of density variation of heat current on the outer surface was taken with the help of a heat current probe unit whose signal goes to a heat current indicator. Throughout the process the fish temperature and the temperature in the container was regularly measured with the temperature controller (TPM-138).
Fig. 1 shows the thermogram of process of trout cooling by water ice at an environment temperature of 20±2°C and the cooling medium temperature of about 0±2°C. The trout weight is 0.8±0.05kg.

Analysing the obtained diagrams we can state the following: the cooling process of the trunk outer layer is more intensive as the outer surface is in an immediate contact with ice. Then we see temperature equalization on the surface and its approaching to the cooling medium temperature.

The trunk central part (in the distance of 20 mm from the backbone) is cooled owing to heat removing from the outer surface, which comes in contact with ice.

The process of the inner layer cooling (in the distance of 40 mm from the backbone) is much less intensive as the body cavity heat removing is throughout all the layers to the water ice on the surface. In the end of the cooling process the temperature of the layers equalizes and comes to the cooling medium temperature.

On the whole the process of cooling of all layers of a fish trunk by water ice lasted for 195 min and showed a low rate of cooling. Water ice expenditure was 0.9kg.

The diagram of heat current density on the trout trunk outer surface if cooled by ice is shown in Fig. 2. The environment temperature during that experiment was 20±2°C.
Figure 2. Density variation of heat current for trout cooling in the medium “water ice”

On the basis of the obtained experimental data the average integral value of heat current density on the trunk outer surface is about $q_{\text{avg}} = 200 \text{ W/m}^2$, the maximum value of heat current density on the trunk outer surface is $q_{\text{max}} = 1100 \text{ W/m}^2$.

At the initial time when the temperature difference between the trunk and the ice is a maximum we can observe the most intensive process of heat removing and, consequently, heat current density is a maximum. Further temperature drop leads to reduction of heat current density, at the end of the process the density approaches to zero value.[8, 9]

On the basis of the obtained experimental data the average integral value of the heat exchange coefficient for the trunk outer surface is $\alpha_{\text{avg}} = 5.1 \text{ W/(m}^2\text{K)}$, the maximum value of the heat exchange coefficient is $\alpha_{\text{max}} = 19.1 \text{ W/(m}^2\text{K)}$.

As the cooling rate is low and consequently, the duration of cooling grows, water ice expenditure is prominent. To find the most effective and rational way of fish cooling we undertook a number of studies with the use of carbon dioxide. During the experiments we used roundfish, trout of 0.8±0.05kg weight. Water ice expenditure was 0.9kg.

Fig.3 shows the temperature fall changes on the surface and in the deep central part of a fish trunk during the cooling process in the medium “water ice + snowlike CO$_2$ – 20%”. The trout weight is 0.8±0.05kg

The measurements taken were similar to the experiment mentioned above. The temperature field corresponds to the previous experiment of trout cooling with water ice.
Analysing the thermogram we can come to the conclusion that the cooling process in the medium of water ice + snowlike CO₂ with 20% carbon dioxide is more intensive in all layers of a trout trunk than in the previous experiments. It is due to the fact that the temperature of water ice at the initial time of cooling falls prominently to 75°C below zero and gradually rises, but its elevation rate is much lower which allows to reduce the length of cooling process, in this particular case it is 145 min, and additionally to reduce water ice expenses up to 0.4kg.

Fig. 4 reflects the data of heat current density for trout cooling in the medium “water ice + snowlike CO₂ – 20%”.

Figure 3. The thermogram of the trout cooling process in the medium of water ice with addition of 20% of carbon dioxide

Figure 4. Density variation of heat current for trout cooling in the medium of water ice with addition of 20% of carbon dioxide
The maximum value of heat current density is reached during the first minutes of the experiment. As well as in the previous case it may be explained by the fact that at this period of time the difference between the temperature of the trunk and that of the cooling medium is a maximum, and the process of heat removing has its maximum values.

During the experiment we register the maximum value of heat current density which rises up to 1800 W/m², it is higher than during the trout cooling in the previous experiment. It is due to the fact that the difference of temperatures between the product and the heat removing medium is a bit more which leads to more intensive heat removing from the trout trunk. Later the trout trunk temperature begins falling intensively and we register sharp reduction of heat current density, while during the process of cooling with the help of water ice the reduction of heat current density is gradual and lasts longer.[10]

Apart from great temperature difference of cooling media it is due to the fact that CO₂ addition lets to keep the water ice temperature at a low level as long as possible and prevents it from quick melting. The heat exchange coefficient for this method of cooling is $a_{avg}=6.0 \text{ W/(m}^2\text{K)}$, the maximum value of the heat exchange coefficient is $a_{max} = 22.3 \text{ W/(m}^2\text{K)}$.

The further experiments were conducted with increase of carbon dioxide concentration. The scheme of thermocouples position and the thermogram of the trout trunk cooling process by snowlike CO₂ with trunk weight of 1.10±0.05kg is presented in Fig.5. The time of fish cooling is 30.7 min.

Analyzing the thermogram we state that cooling of the fish outer layer is rather intensive. It is connected with the following: the fish outer surface layers contact the snowlike CO₂, through a gas space formed by snowlike CO₂ sublimation there is slight freezing of fish flesh. Then we can state that temperature fall gets less intensive. This fact may be explained by the beginning of the process of phase transition when ice crystals start forming and undetected heat radiation is observed [11].

As the fish internal parts are not deleted the process of cooling of the central part of a trunk goes at the expense of heat conductivity through the outer layers. This process is similar to cooling of surface layers, but the time difference is about 7 min.

Cooling of the internal layers of a trout trunk is less intensive because there is no immediate contact with carbon dioxide and may be explained by the theory of temperature field expansion from the surface to its centre.

The process of density variation of heat current from outer surface of a roundfish trout cooled by snowlike CO₂ is presented by the diagram in Fig.6.
Figure 6. The density variation of heat current on the outer surface of a trout trunk cooled by snowlike CO$_2$

According to experimental data the average integral value of heat current density of the fish outer layers is $q_{avg}=560$ W/m$^2$, the maximum value of heat current density of the trunk outer surface is $q_{max}=2390$ W/m$^2$. These values of heat current density may characterize high intensity of heat exchange at this method of cooling treatment.[12,13]

At the beginning of the experiments we can observe the rise of heat current density up to reaching the maximum, then its fall follows. This is due to the fact that at the beginning of the process the temperature difference between a trunk and snowlike CO$_2$ is a maximum. Later on the temperature gradually decreases as well as a heat current to 10 minute. After completion the temperature becomes steady due to the beginning of crystal formation in the fish outer layers. The average integral value of heat exchange coefficient is $\alpha_{avg}=10.2$ W/(m$^2$K), its maximum value is $\alpha_{max} = 32.1$ W/(m$^2$K).

Fig. 7 presents the graph of temperature changes of the cooling medium during the process of trout cooling.

Figure 7. The graph of temperature changes of the cooling medium during the process of trout cooling
Analysing these isotherms we can come to the conclusion that when the snowlike carbon dioxide concentration rises, the temperature of cooling ice mixture lowers during the whole period of cooling. It results in a shorter time-period of cooling treatment. But the use of the snowlike carbon dioxide for cooling may result in slight freezing of fish, thus worsening its quality in the storage process.

Fig.8 presents the curve of trout cooling time length for different concentrations of carbon dioxide.

![Graph showing trout cooling time length](image)

**Figure 8.** The time length of trout cooling for different concentrations of carbon dioxide

Analyzing Fig.7 and Fig.8 we can come to the conclusion that with the growth of carbon dioxide concentration the time-length of sublimation considerably increases, which can reduce ice expense during the process of fish cooling with water ice, consequently, it reduces electric power necessary for a compressor engine drive and for a condenser fan of the ice machine freezer, it can also reduce the time-length of trout cooling.

**Conclusion**

The use of carbon dioxide in fish-processing industry lets to recover it effectively in small amounts. The use of carbon dioxide in combination with water ice allows to reduce water ice and carbon dioxide expenses for fish cooling, to avoid slight freezing of trout and to shorten the time period of its cooling. Snowlike CO₂ has high thermophysical characteristics. Besides, it does not cause chilling shrink of products, prevents them from swelling and partial oversalting, from removal of organic and mineral substance out of fish tissue. It lets to save a considerable amount of power necessary for water ice production. That is why it can become an effective cooling medium in a production environment.

**References**

[1] Popov, A.M. Determination of dependence between thermophysical properties and structural-and-phase characteristics of moist materials. / A.M. Popov, D.V. Donia, K.B. Plotnikov // Foods and raw materials – 2017. - Vol. 5, No. 1. – pp. 137-143.

[2] Hrnjak, P.S. In tube heat transfer and pressure drop characteristics of pure NH₃ and CO₂ in refrigeration systems / P.S. Hrnjak, C.Y. Park // IIR Conference: Ammonia Refrigerating Technology for Today and Tomorrow, Ohrid, 2007. P. 48-53.

[3] Energy efficiency analysis of the sea buckthorn (hippophae rhamnoides) fruits quick freezing / E.V. Korotkaya, V.V. Kireev // Foods and Raw Materials. 2016. T. 4. № 1. P. 110-120.
[4] Belozerov G.A. Study of the process of cooling fish using binary ice / G.A. Belozerov, N.M. Mednikova, V.P. Pytchenko, E.N. Serova, E.N. Kharenko, R.V. Artyomov // Refrigeration. - 2012. № 6. p. 37-41.

[5] Kalitin K.V. Cold processing is a guarantee of the quality of the fish. / K.V. Kalitin, A.M. Rukavishnikov // Refrigeration technical. - 2010. No. 1. - pp. 32-35.

[6] Kalnin I.M. Energy efficiency and environmental safety of refrigeration systems / I.M. Kalnin // Refrigeration. 2008. -№3. - p.12-14.

[7] Lisitsyn AB Scientific support of innovative technologies in the production of healthy food products / A.B. Lisitsyn, I.M. Chernukha, N.A. Gorbunova // Storage and processing of agricultural products. 2012. № 10. P. 8-14.

[8] Neverov, Ye.N. Investigation of the cooling process of intact fishing trout with carbon dioxide / E.N. Neverov // Polzunovsky Vestnik. - 2014. –T. 2, No. 4. pp. 132–136.

[9] Neverov, E.N. The use of carbon dioxide for the cold processing of fish / E.N. Neverov // Bulletin of the Krasnoyarsk State Agrarian University. - 2016. - № 4. - P. 125–131.

[10] Artemov R.V., Kharenko E.N. Microbiological studies of fish cooled with “liquid ice” during storage. - Murmansk: MSTU, 2009.

[11] Kharenko E.N., Artemov R.V. Prospects for the use of liquid ice for the production of chilled products. - Kaliningrad: Ed. AtlantNIRO, 2007.

[12] Ballot Miguet B., Rached W. / Revue general du Froid, FR, 6 (2009), vol 99, n.1094; 45 51 / Coulis de glace a –35 ° C: efficacite energetique systemes de refroidissement.

[13] Egolf P. W., Kauffeld M. / International Journal of Refrigeration. 28 (2005), 4 12 pp./ From the physical properties of ice slurries to industrial ice slurry applications.