Calculation of the operating mode of the mixing refrigerator

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Abstract. This article considers the calculation of a mixing refrigerator (contact refrigerator) taking into account the absorption of gaseous components. Calculation of operating mode and definition of optimal operating conditions of the machine that provides the given final gas temperature is carried out.

1. Introduction
The surface heat exchangers are widely used in the industry. At the same time, contact refrigerators and condensers are used mainly in those cases where it is possible to mix hot and cold coolants. Similar machines can be used if the technological scheme provides the subsequent separation of the cold coolant from the main flow. However, contact refrigerators can be used in cases where it is necessary to quickly cool the gas flow, a flow containing solid particles (dust, coke particles) or it is required to absorb a number of gaseous components. This type of machines has a number of advantages: low cost, high heat exchange surface, simple construction, low hydraulic resistance. So, when the regeneration gas of the reforming or dehydrogenation catalyst is cooled, it is necessary to quickly reduce the temperature from 450 ... 500 °C to about 60 ... 70 °C [1] without significant resistance to a gas flow. The regeneration gas or waste gas contains harmful components: chlorine, hydrogen chloride, sulfur dioxide and other. Consequently, a desirable aspect during cooling will be partial absorption of harmful substances. Unfortunately, the calculation of contact refrigerators cannot always be carried out accurately. As a result, we can see both insufficient cooling of the gas (which entails a decrease in the efficiency of the trapping of harmful substances in subsequent machines) and an excess of temperature in the machine that can lead to an emergency. The methods of calculating contact refrigerators that are used for reducing the temperature of waste gases often do not allow foreseeing possible modes of operation of the apparatus (including critical thermal loads) [2]. Also in a number of sources approximate calculation methods are given that do not have sufficient flexibility and completeness and that allow a number of approximations and assumptions [3].

In this paper the calculation of the operation modes of mixing refrigerator of spray type including absorption processes is given. The method of obtaining the curves of the operating modes of the apparatus and finding the optimal operating conditions are considered.

2. Research objective
The aim of this paper is to calculate a spraying type mixing refrigerator made to reduce the temperature of the waste gas in the regeneration processes of the reforming and dehydrogenation catalyst proceeding continuously - Continuous Catalyst Regeneration (CCR). Data on the composition of the waste gas are
taken from the patent literature, for example [4]. When solving the problem, the following conditions are accepted:

1. The absorption of all components contained in the gas, depending on their solubility in the cold coolant is possible

2. The neutralization reactions of the components are described by a number of chemical reactions proceeding mainly in the straight direction.

Assumptions are also made:

1. The cold coolant is first heated to the final temperature and then part of it is vaporized in order to reach the given final temperature of the gas;

2. The thermal effect of the chemisorption reactions is taken into account integrally, regardless of the height of the apparatus.

Thus, in the following version of the calculation of the contact refrigerator, assumptions having an insignificant error are accepted.

3. Results and discussion

The initial data for the calculation are given in Table 1. At the same time, the waste gas consumption is assumed equal to 1000 kg/h with a probable increase to 1100 kg/h (project safety factor) [1]. As a cold coolant, a soda-alkaline solution is adopted, which ensures a more complete absorption of harmful substances compared to water. The remaining salts that are in the solution are the products of the reactions of soda and alkali with the components of the waste gas. As mixing refrigerators have low hydraulic resistance (usually not more than 1 kPa), the pressure change in the system can be neglected.

|                | Waste gas (hot coolant) | Soda-alkaline solution (cold coolant) |
|----------------|-------------------------|---------------------------------------|
| Parameter      | Value                   | Parameter                              | Value                   |
| 1 Temperature, °C | 470                     | Temperature, °C                        | 50…60                   |
| Absolute pressure, MPa | 0.101325               | Absolute pressure, MPa                | 0.101325                |
| Composition, % mass.: |                       | Composition, % mass.:                 |                         |
| N₂             | 63.38                   | H₂O                                   | 90.42                   |
| H₂O            | 13.18                   | Na₂CO₃ и NaHCO₃                       | 4.99                    |
| CO₂            | 19.07                   | NaCl                                 | 2.00                    |
| O₂             | 3.30                    | Na₂SO₃ и Na₂SO₄                       | 0.30                    |
| HCl            | 0.62                    | NaClO                                | 0.30                    |
| SO₂            | 0.10                    | NaOH                                 | 2.00                    |
| Cl₂            | 0.35                    | -                                    | -                       |
| Total:         | 100.00                  | Total:                                | 100.00                  |

In order to simplify the processing of information, all the physical properties of the components are described by the general formula (1):

\[ A_t = a_5 \cdot t^5 + a_4 \cdot t^4 + a_3 \cdot t^3 + a_2 \cdot t^2 + a_1 \cdot t + a_0, \]

(1)

where \( A_t \) – the defined property of substance or mixture

\( a_5, a_4, a_3, a_2, a_1, a_0 \) – coefficients of equation (are not given in the article).

The properties of mixtures are calculated by formulas DIPPR. Table 2 shows the equations of chemical reactions between the components of the solution and the absorbed substances.
Chemisorption reactions taking into account two stages - physical absorption and the actual chemical reaction - are given in Table 3 with the indication of the thermal effect per 1 kmol of the absorbed substance. It is necessary to note that in Table 3 the coefficients for equation (1) are given, with the help of which it is possible to calculate the thermal effect of the reaction with a given chemisorption temperature. Absorption of inert components (nitrogen, oxygen) is not considered as the share of absorbing these gases does not exceed 0.01%.

An approximate thermodynamic calculation gives (with rounding up to 0.05) the values of selectivities for the reactions: for the first 0.75; for the second 0.25; for the third 0.75; for the fourth 0.25; for the fifth in sulfur dioxide, 0.50; for the sixth (for the remainder of chlorine) 0.50; for the seventh (for the remainder of chlorine) 0.50; for the eighth 0.50.

The thermal calculation of the mixing refrigerator is based on the solution of the thermal balance equation (2):

Table 2. Chemical reactions equation

| Number of reaction | Equation of summary reaction |
|--------------------|------------------------------|
| 1                  | $CO_2 + NaOH = NaHCO_3$      |
| 2                  | $CO_2 + Na_2CO_3 + H_2O = 2NaHCO_3$ |
| 3                  | $2HCl + Na_2CO_3 + NaOH = 2NaCl + NaHCO_3 + H_2O$ |
| 4                  | $HCl + NaOH = NaCl + H_2O$   |
| 5                  | $Cl_2 + SO_2 + 4NaOH = Na_2SO_4 + 2NaCl + 2H_2O$ |
| 6                  | $Cl_2 + 2NaOH + Na_2SO_3 = Na_2SO_4 + 2NaCl + H_2O$ |
| 7                  | $3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O$ |
| 8                  | $SO_2 + 2NaOH = Na_2SO_3 + H_2O$ |

Chemisorption reactions with the indication of the thermal effect

| Reaction | Coefficients of the polynomial for finding enthalpy, kJ/mol |
|----------|-----------------------------------------------------------|
|          | $a_4$ | $a_3$ | $a_2$ | $a_1$ | $a_0$ |
| Absorption $CO_2$ | $-3.117 \times 10^{-8}$ | $9.256 \times 10^{-6}$ | $-1.065 \times 10^{-3}$ | $1.982 \times 10^{-2}$ | $-24.71$ |
| Absorption $HCl$  | $-2.924 \times 10^{-8}$ | $8.645 \times 10^{-6}$ | $-8.859 \times 10^{-4}$ | $1.228 \times 10^{-2}$ | $-86.28$ |
| Absorption $SO_2$ | $1.708 \times 10^{-12}$ | $6.984 \times 10^{-11}$ | $5.050 \times 10^{-4}$ | $2.463 \times 10^{-2}$ | $-32.67$ |

| Reaction | Coefficients of the polynomial for finding enthalpy, kJ/mol |
|----------|-----------------------------------------------------------|
|          | $a_4$ | $a_3$ | $a_2$ | $a_1$ | $a_0$ |
| Absorption $Cl_2$ | $6.961 \times 10^{-8}$ | $-2.028 \times 10^{-5}$ | $2.405 \times 10^{-3}$ | $-9.603 \times 10^{-2}$ | $-22.33$ |
| Reaction 1 | $8.130 \times 10^{-7}$ | $-2.004 \times 10^{-4}$ | $1.720 \times 10^{-2}$ | $-8.553 \times 10^{-2}$ | $5.849$ |
| Reaction 2 | $-7.331 \times 10^{-7}$ | $1.767 \times 10^{-4}$ | $-1.470 \times 10^{-2}$ | $4.133 \times 10^{-2}$ | $-46.83$ |
| Reaction 3 | $-7.737 \times 10^{-7}$ | $1.886 \times 10^{-4}$ | $-1.597 \times 10^{-2}$ | $5.435 \times 10^{-2}$ | $-48.35$ |
| Reaction 4 | $-1.741 \times 10^{-6}$ | $4.334 \times 10^{-4}$ | $-3.895 \times 10^{-2}$ | $1.197$ | $-551.20$ |
| Reaction 5 | $-8.937 \times 10^{-7}$ | $2.236 \times 10^{-4}$ | $-2.011 \times 10^{-2}$ | $7.551 \times 10^{-2}$ | $-410.10$ |
| Reaction 6 | $-2.693 \times 10^{-6}$ | $6.740 \times 10^{-4}$ | $-6.029 \times 10^{-2}$ | $2.476$ | $-356.50$ |
| Reaction 7 | $-8.470 \times 10^{-7}$ | $2.098 \times 10^{-4}$ | $-1.884 \times 10^{-2}$ | $4.411 \times 10^{-1}$ | $-141.00$ |
\[ G_g \cdot (t_{g1}^f - t_{g1}^w) + G_{ww} \cdot (t_{ww}^{i1} - t_{ww}^w) + Q_{chem} = G_l \cdot (t_{l}^w - t_{l}^{i1} + e \cdot r_{l}^w), \]  

where \( G_g, G_{ww}, G_l \) - consumption of dry gas, water vapor and neutralization solution, respectively, kg/h; 
\( t_{g1}^f \) and \( t_{g1}^w \) - enthalpy of dry gas at initial gas temperature \( t_{g1} \) and at a final temperature (the temperature of a wet thermometer at which thermal equilibrium is reached) \( t_w \) respectively, kJ/kg; 
\( t_{ww}^{i1} \) and \( t_{ww}^w \) - enthalpy of water vapor contained in the gas at temperatures \( t_{g1} \) and \( t_w \) respectively, kJ/kg; 
\( t_l^w \) and \( t_l^{i1} \) - the enthalpy of the neutralization solution (cooling liquid) at the initial temperature of the liquid \( t_{l1} \) and \( t_w \), respectively, kJ/kg; 
\( Q_{chem} \) - total heat released during chemisorption, kJ/h; 
\( e \) - mass fraction of liquid evaporated water (liquid); 
\( r_{l}^w \) - specific heat of evaporation of the liquid at a temperature \( t_w \), kJ/kg. 

Calculation is described above.

1. Set the temperature of wet thermometer \( t_w \), °C and the initial flow rate of the neutralization solution \( G_l \), kg/h.
2. Calculate the thermal effect of the reactions taking place in the solution (including the thermal effect of absorption) upon the absorption of carbon dioxide in an amount \( F'_\text{CO}_2 = F_{\text{CO}_2} - F'_{\text{CO}_2} \). For the analysis of the proceeding reactions, it is assumed that the reactions fully proceed. In this case, the data of Tables 2 and 3 are used. Find the thermal absorption effect. Calculate the total heat flux during chemisorption \( Q_{chem} \), kJ/h.
3. Find the value of the left side of the equation (2).
4. With the temperature \( t_w \) define the pressure of saturated water vapor in accordance with the formula (3):
\[ P_{sat} = 1.12 \cdot 10^{-3} \cdot t^4 - 6.43 \cdot 10^{-2} \cdot t^3 + 5.508 \cdot t^2 - 22 \cdot t + 808.6 \], Pa.
5. Find the mass content of water vapor \( y_{H_2O} \) in a gas mixture at the final temperature in accordance with the formula (4):
\[ y_{H_2O} = \frac{P_{sat}}{P_{abs}} \cdot \frac{M_{H_2O}}{M_g} \] 
where \( M_g \) - average molar mass of dry gas which is found in accordance with the formula (5), kg/Kmol:
\[ M_g = \sum y_i' \cdot M_i \] 
where \( y_i' \) - mole fraction of the i-component; 
\( M_i \) - molar mass of the i-component.
6. The mass flow rate of water vapor, converted into the gas is found in accordance with the formula (6):
\[ G_{ww}' = \frac{y_{H_2O}}{1 - y_{H_2O}} \cdot \left( G'_{N_2} + G'_{\text{CO}_2} + G'_{O_2} + G'_{\text{HCl}} + G'_{\text{SO}_2} + G'_{\text{Cl}_2} \right) \] 
where \( G'_{N_2}, G'_{\text{CO}_2}, G'_{O_2}, G'_{\text{HCl}}, G'_{\text{SO}_2}, G'_{\text{Cl}_2} \) - mass flow rates of the relevant components in the output flow, kg/h.
7. Determine the degree of evaporation of water vapor in accordance with the formula (7):
\[ \varepsilon = \frac{G_{ww}' - G_{ww}}{G_l} \] 
8. Choose a value of \( G_l \) such that the right side of equation (2) becomes equal to the left side.
Based on the calculations carried out by the authors of this article, it could be argued that when cooling the gas in the mixing refrigerator, no more than 20 MJ/h of heat will be released during the absorption of the above components. In further calculations in this article, exactly this thermal effect of chemisorption will be used as the maximum. In this case, a margin is provided for the degree of extraction of components of the order of 5 ... 7%. The reader can independently calculate the heat effect of chemisorption in order to have result that is more accurate.

In the case of design calculations, the adopted value of the thermal effect is justified by the margin on the machine operation stability.

To find the operating modes of the apparatus (the set of points for plotting the curves), the above calculation is repeated several times for different initial temperatures of the cold coolant and the required final temperatures of the cooled gas. Below is a calculation of one of the options of the operation of the machine.

In the first approximation, we take the temperature of the wet thermometer equal to \( t_w = 65 \, ^{\circ}C \). This temperature is higher than the initial temperature of the liquid which is equal to \( t_{1i} = 50 \, ^{\circ}C \). The initial gas temperature \( t_{g1} = 470 \, ^{\circ}C \). The gas is cooled to the temperature \( t_w = 65 \, ^{\circ}C \).

The heat flow of chemisorption is assumed to be equal to \( Q_{chem} = 20000 \frac{kJ}{h} \).

Enthalpy for dry gas under the given conditions for the initial temperature \( \int _{g_1} = 523,88 \frac{kJ}{kg} \) and for the final \( \int _{g_w} = 65,51 \frac{kJ}{kg} \).

Enthalpy for water vapor under the given conditions for the initial temperature \( \int _{w_1} = 3471,07 \frac{kJ}{kg} \) and for the final \( \int _{w_w} = 2617,96 \frac{kJ}{kg} \).

Enthalpy for neutralization solution under the given conditions for the initial temperature \( \int _{l_1} = 248,65 \frac{kJ}{kg} \) and for the final \( \int _{l_w} = 190,31 \frac{kJ}{kg} \).

The value of the left side of the heat balance equation (2) at a known flowrate of the gas flow (1000 kg/h is assumed):

\[
G_g \cdot (\int _{g_1} - \int _{g_w}) + G_{wv} \cdot (\int _{w_1} - \int _{w_w}) + Q_{chem} =
\]

\[= 868,32 \cdot (523,88 - 65,51) + 131,77 \cdot (3471,07 - 2617,96) = 530429 \frac{kJ}{h}.\]

We find the pressure of saturated water vapor at the temperature of a wet thermometer in accordance with the formula (3):

\[
P_{sat} = 1,12 \cdot 10^{-3} \cdot 65^4 - 6,43 \cdot 10^{-2} \cdot 65^3 + 5,508 \cdot 65^2 -
\]

\[-22 \cdot 65 + 808,6 = 24988,04 \text{ Pa}. \]

Then the water vapor content in the outgoing gas at absolute pressure \( P_{abs} = 101325 \text{ Pa} \) and average molar mass of dry gas \( M_g = 30,7618 \frac{kg}{kmol} \) is equal in accordance with the formula (4):

\[
y_{H_2O} = \frac{24988,04}{101325} \cdot 18,0153 + \left(1 - \frac{24988,04}{101325}\right) \cdot 30,7618 = 0,1609. \]

As the flowrates of components in the gas flow do not change (except for the flowrate of water vapor), the mass flowrate of water vapor in the gas phase in the outgoing gas flow is found as follows:

\[
G_{wv}^"{} = \frac{y_{H_2O}}{1-y_{H_2O}} \cdot G_g = \frac{0,1609}{1-0,1609} \cdot 862,32 = 166,46 \frac{kg}{h}. \]
We take the flowrate of neutralization solution equal to \( G_l = 7697,35 \frac{kg}{h} \).

We find the degree of evaporation of the liquid in accordance with the formula (7):

\[
\epsilon = \frac{166,46 - 131,77}{7697,35} = 0,0045.
\]

We calculate the right side of the heat balance equation (2), knowing the specific heat of evaporation at the temperature of a wet thermometer \( r_{tw} = 2345,73 \frac{kJ}{kg} \):

\[
G_l \cdot (t_{tw}^r - t_{l1}^r + \epsilon \cdot r_{tw}^r) = 7697,35 \cdot (248,65 - 190,31 + 0,0045 \cdot 2345,73) = 530429 \frac{kJ}{h}.
\]

In order to determine the optimal operating conditions of the apparatus, the analysis of the apparatus is carried out with the repetition of the calculation for different modes: different initial liquid temperatures (we take 50, 55, and 60 °C), and also different final temperatures of the cooled gas (in the range of 52 to 76 °C). The results of the analysis are given in Table 4.

It should also be noted, that in order to obtain a better understanding of the operation of the apparatus, the step between the temperatures of the cold coolant must be made less.

**Table 4. Results of the analysis of the operation of the mixing refrigerator**

| Final gas temperature \( t_{w} \), °C | Removable heat \( kW \) | Liquid flow rate at an initial temperature \( t_{l1} \), kg/h |
|--------------------------------------|-------------------------|-----------------------------|
|                                      |                         | 50 °C | 55 °C | 60 °C |
| 52                                   | 151.4                   | 86449 | -     | -     |
| 54                                   | 150.8                   | 41596 | -     | -     |
| 56                                   | 150.2                   | 26533 | 158905| -     |
| 58                                   | 149.5                   | 18906 | 50324 | -     |
| 60                                   | 148.9                   | 14242 | 28432 | -     |
| 62                                   | 148.3                   | 11047 | 18903 | 66041 |
| 64                                   | 147.7                   | 8679  | 13476 | 30266 |
| 66                                   | 147.0                   | 6815  | 9894  | 18107 |
| 68                                   | 146.4                   | 5271  | 7285  | 11818 |
| 70                                   | 145.8                   | 3936  | 5238  | 7843  |
| 72                                   | 145.1                   | 2732  | 3529  | 4990  |
| 74                                   | 144.5                   | 1603  | 2022  | 2739  |
| 76                                   | 143.9                   | 504   | 622   | 816   |

The obtained data are graphically shown in Figure 1.

It is clearly seen that the curves of the flowrate of the liquid at different initial temperatures have a bend which meet a transition to a low-efficiency mode of heat removal when moving from right to left or when the final temperature of the gas decreases. It can also be seen that as the initial temperature of the liquid decreases, the minimum achievable final temperature of the gas decreases.

On the basis of the data obtained, it can be concluded that effective cooling corresponds to a flat curve located in the area of higher final gas temperatures. In our case, at a liquid temperature of 50 °C of such area, the final gas temperature will be above 55-56 °C.

The curves of the operation of the machine have the following boundary conditions:

1. When the final temperature of the cooled gas approaches the final temperature of the cold coolant, the irrigation flow increases significantly, as a result of which the moisture contained in the initial gas starts to condense (the opposite effect is observed – the cold coolant starts evaporating);
2. With a small amount of irrigation, all the coolant coming into the mixing refrigerator completely evaporates; the gas temperature does not decrease to the given temperature.

For other initial conditions (composition and flow parameters), similar curves characterizing the operation of the mixing refrigerator can be obtained.

![Figure 1. Characteristic of operation of the mixing refrigerator.](image)

4. Conclusion

In this paper, a method of calculating a contact refrigerator of a spraying type taking into account the proceeding chemisorption is given. On the basis of the derived equations, the curves characterizing the operation of the apparatus (load irrigation, depending on the initial and final temperatures of coolants) are constructed. An approximate method for estimating the operation’s parameters of the apparatus providing cooling of the gas to a given temperature is proposed. At a higher initial temperature of the cold coolant, the irrigation flowrate is reduced. In order for the final temperature of the gas to be close to the final temperature of the cold coolant, it is required to increase the irrigation flowrate. The optimum irrigation flow is at the lower flat curves until the inflection points clearly visible in Figure 1. Further investigations can be directed to the refined calculation with the use of a differential calculation of the height of the apparatus as well as taking into account the effects of mass transfer.

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