System analysis and safety of the process to obtain CO$_2$-extracts from plants

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Abstract. Systematization and analysis experience in the field of value extraction from plant material using liquid carbon dioxide is allowed modernizing the extraction unit to include additional operations. The results of studies performed by the extraction unit are also scheme modernization comprising the steps of removing air from the raw material by using a vacuum pump and organization low-frequency pulsating extraction mode by using a special apparatus-pulsator. The sequence of technological processes to extract extractives from various plant materials were tested. The safety of the extraction unit operated under the saturated vapour pressure of carbon dioxide to 7.0 MPa was discussed. The studies of system analysis methods for preparing highly concentrated extracts with liquid carbon dioxide was performed in an improved extraction system. The object of research was olive and spicy raw materials, with different contents of extractives: apricot, clove buds, ginger rhizome, the fruit of coriander and cumin seeds. The liquid carbon dioxide that exhibits high extraction properties of +10 °C to +25 °C temperature range and pressure from 4499 kPa to 6436 kPa was selected as the solvent. The calculation of the evaporator, which is one of the primary devices for the extraction unit, was done.

1. Introduction

Complex The complex optimization problem of the process to extract valuable components from vegetable or animal raw material with liquefied carbon dioxide became possible through the use of modern system analysis means. Unstructured approach to the decision to reduce extraction duration depends on the methods and materials processing modes. So when extraction experiment planned some information about significant indicators, not only about the content of the individual components but also their antioxidant properties must be taken into consideration [1].

The qualitative composition of the herbal extract is entirely dependent on the raw material starting characteristics. This illustrative example for this case is element selenium content in the extract of essential selenium obtained from raw materials with high selenium content as a result of agrochemical cultivation [2]. The authors developed the extraction mode to increase the yield of selenium-containing extracts from Chinese cabbage and amaranth seed.
Several inventions related to improvement for CO₂ extracts methods and apparatuses are known [3, 4, 6]. Described settings are distinguished by different communication shut-off equipment and raw material for research. A relatively new type of food additives to enrich bread composition is finely ground seed meal, amaranth, after removal from the raw CO₂ extractives [5]. It is possible to obtain bakery products of high quality when amaranth meal is used. The technology and software methods of raw materials dehydration during the preparation period for extraction are very interesting [7]. The authors use supercritical CO₂ and vacuum microwave drying of fruit and berries in preparation for extraction for the first time.

Using methods and means of system analysis allowed setting process mode extraction company to create the best conditions to extract target components from plant matrices [8, 9]. Physical, chemical and biological laws which were discussed by the authors, allowed creating a mathematical model of the extraction process in the formal numerical form. The scale transition from laboratory studies was carried out. This process was for extracting β-carotene from plants to a countercurrent multistage extraction. The scale transition was carried out by simulating the conditions experienced in the production [10]. For this process, the supercritical carbon dioxide ability to extract the valuable component at a temperature from 40 to 90 °C is crucial [11, 13]. Opportunities to optimize this process were identified by screening assay components extraction process from seeds Gmelin beans [12]. Constant speed extraction process substances from the beans 1.26*10¹¹ (dm³/mol)-1s⁻¹, the definition of physical and chemical parameters – humidity viscosity, pH, and others were set.

Review of scientific, technical and patent literature showed the usefulness of the system elements analysis to optimize process conditions of modernizing the plant to produce Herbal CO₂-extracts.

2. Materials and methods
Realization with obligatory safety requirements to use of CO₂-extraction unit begins with control over the physical condition of the container with carbon dioxide. This action takes place before starting work on installation at least once a year. The container must be black and without damage. The yellow inscription "Carbon dioxide" on the lateral surface of the Russian cylinder (container) is wrong because it is not carbonic in the cylinder. But you can find liquefied carbon dioxide or carbon dioxide there. The rest of the installation apparatus operating under pressure up to 7 MPa (evaporator, condenser, collector and extractor), must have hydraulic test under the pressure of 10 MPa and have state supervision certificate of labour protection.

Same indices were determined: thermal characteristics of heat exchange processes in a CO₂-extraction unit: CO₂ pressure in the flow part of the installation $P_r = 6,4$ MPa. This corresponds to the saturation temperature $t_s = 24,7$ °C. Density of the liquid $\rho_l = 718$ kg/m³, vapour density $\rho_v = 240$ kg/m³. Specific heat of vaporization $r = 123,5$ kJ/kg. The dynamic viscosity of the vapour $\nu_v = 2,10^{-3}$ Pa·s, liquid $\nu_l = 6,10^{-3}$ Pa·s. The kinetic viscosity of the pair $\nu = 8,3-10^{-8}$ m²/s. The thermal conductivity of steam $\lambda_v = 35,10^3$ W/(m·K). Prandtl number ($Pr = \frac{C_p \nu}{\lambda}$) steam $Pr_v = 6,0$, liquid $Pr_l = 5,0$.

Specific heat $c_p = 3,3-10^3$ J/(kg·K). Critical parameters CO₂ $P_c = 7,3$ MPa; $T_c = 304$ K. The characteristics of the heating water and cooling brine: density $\rho = 965$ kg/m³, the heat capacity $c_v = 4,2-10^3$ J/(kg·K). The thermal conductivity of water $\lambda_w = 0,65$ W/(m·K), antifreeze $\lambda_a = 0,55$ W/(m·K). Kinematic viscosity of water $\nu = 4,7-10^{-6}$ m²/s, antifreeze $\nu = 1,5-10^{-6}$ m²/s. Prandtl number of water $Pr_w = 3$, antifreeze $Pr_a = 11,4$. The thermal characteristics of heat exchange are calculated without taking into account the influence of local velocities of the liquid and gaseous CO₂ in the boiling and condensation characteristics. It covers only the bulk nature of the boiling and condensing surface in interaction with the heat transfer tube elements.

3. The results of the research
Experimental studies on adaptation system analysis methods to a process to obtain highly concentrated extracts with liquid carbon dioxide was performed in the improved extraction system. The object of research was the olive and spicy raw materials, with different contents of extractives: apricot, clove
buds, ginger rhizome, the fruit of coriander and cumin seeds. The solvent for the components of plant raw material was liquid carbon dioxide. It was selected through its high extraction properties of +10 °C to +25 °C temperature range and pressure from 4499 kPa to 6436 kPa. The figure shows the diagram of the modernized plant to carry out the process of subcritical CO2 extraction of components from the raw material.

Figure 1 illustrates the following point: carbon dioxide in the gaseous state is supplied from cylinder 1 and through the reduction gear 2 and valve. It is supplied in the calm state (it was cooled by tosol) to condenser 3, where it is liquefied at temperature +5...+7 oC. In collector 4, liquid carbon dioxide is collected and thermostated to a predetermined extraction temperature. Intended and prepared raw material for extraction is loaded into the mesh inside extractor 7 and air is removed from it by vacuum pump 5. Then it is impregnated into liquid carbon dioxide from the collector 4 and formed miscella is supplied into a heated vaporizer 8, where liquid CO$_2$ (one component of miscella) rapidly boils, and it is removed into condenser 3 for liquefaction.

**Figure 1.** Scheme of the modernized plant to carry out the process of subcritical components extraction from raw – material: 1 – balloon (container) with CO$_2$, 2 – reducer, 3 – condenser, 4 – collector, 5 – vacuum pump, 6 – pulsator, 7 – extractor, 8 – evaporator, 9 – extract collection.

3.1. Calculation of the capacitor

Vapour temperature CO$_2$ $t_1 = 30$ °C. Chilled brine temperature $t_{b1} = 6$ °C. Coolant flow volume $G_B = 2$ m$^3$/h. Heat exchange surface $F = 4.1$ m$^2$.

We define the power consumed to cool to CO$_2$ to the saturation temperature $t_S = 30$ °C:

$$W' = G_{CO_2} * C_p(t_1 - t_S) = \frac{45}{3600} * 3.6 * 10^3(30 - 24) = 270 W.$$  

To calculate the heat transfer in the annulus using the formula 1 for transverse flow staggered tube bundle:

$$Nu = 0.195 * Re^{0.6} * Re^{0.33},$$  

(1)
Speed is determined by the formula 2:

\[ v_{\text{CO}_2} = \frac{G_{\text{CO}_2}}{\rho'} \cdot \frac{1}{l(D - 8d_n)}, \]

where \( l = 1.490 \) – length capacitor.

As a result, \( v_{\text{CO}_2} = \frac{45}{3600 \cdot 240} \cdot \frac{1}{0.151 + 1.49} = 2.2 \cdot 10^{-4} \) m/s.

Reynolds number

\[ \text{Re}_{\text{CO}_2} = \frac{v_{\text{CO}_2} \cdot d}{\theta'} = \frac{2.2 \cdot 10^{-4} \cdot 21 \cdot 10^{-3}}{8.3 \cdot 10^{-8}} = 55. \]

Nusselt number for the annulus

\[ \text{Nu}_A = 0.195 \cdot 55^{0.6} \cdot 6^{0.33} = 3.8 \]

The heat transfer coefficient in the annulus at a steam cooling:

\[ \alpha_A = \text{Nu} \cdot \frac{\lambda'}{d} = 3.8 \cdot \frac{35 \cdot 10^{-3}}{21 \cdot 10^{-3}} = 6.3 \frac{W}{m^2 \cdot K} \]

Speed of movement in the tube cooler is determined by the formula 3:

\[ v_B = \frac{G_B}{n \cdot \pi d^2} \]

wherein \( n = 22 \) – the number of pipes conducting in one direction flow (\( d = 20 \cdot 10^{-3} \) m– the inner diameter of the pipes).

Resulting:

\[ v_B = \frac{2 \cdot 4}{3600 \cdot 22 \cdot 3.14 \cdot (20 \cdot 10^{-3})^2} = 0.08 m/s, \]

Reynolds number as the current similarity criterion miscella:

\[ \text{Re} = \frac{v_B \cdot d}{\theta_B} = \frac{0.08 \cdot 20 \cdot 10^{-3}}{1.5 \cdot 10^{-6}} = 1067. \]

When this is done a laminar flow regime and Nusselt number for the tube space \( \text{Nu}_T = 3.6 \).

As a result, the heat transfer coefficient in the tube \( \alpha_T \) and overall heat transfer coefficient when cooling \( K' \) are:

\[ \alpha_T = \text{Nu}_T \cdot \frac{\lambda_B}{a} = 3.6 \cdot \frac{0.55}{20 \cdot 10^{-3}} = 99 \frac{W}{m^2 \cdot K} \]

\[ K' = \frac{1}{\alpha_A} + \frac{\delta_{CT}}{\lambda_{CT}'} + \frac{1}{\alpha_T} = \frac{1}{6.3} + \frac{10^{-3}}{60} + \frac{1}{99} = 6.2 \frac{W}{m^2 \cdot K}. \]

The area of heat exchange necessary for cooling the \( \text{CO}_2 \) vapour to the condensing temperature:

\[ F' = \frac{W'}{K' \left[ \frac{1}{2} \ast (t_1 - t_s) - t_B \right]} = \frac{270}{6.2 \ast (27 - 6)} = 2.07 m^2. \]
Thus, much of the heat exchanger serves to cool the CO$_2$ vapour. Directly to the condensation area remains: $F'' = F' = 4,1 - 2,07 = 2,03m^2$.

To calculate the condensation process on horizontal tubes is determined by the formula 4 to define condensate film Reynolds number:

$$Re = \frac{\bar{q} \cdot \pi \cdot d_n}{\eta \cdot r''}.$$  \tag{4}

where $\bar{q}$ – some average heat flux:

$$\bar{q} = \frac{W''}{F''} = \frac{2 \cdot G_{CO_2}}{3600 \cdot 2,03} = 760 \frac{W}{m^2}.$$  

Wherein:

$$Re = \frac{760 \cdot 3,14 \cdot 21 \cdot 10^{-3}}{123,5 \cdot 10^3 \cdot 6 \cdot 10^{-5}} = 6,8$$

This number is less than the critical value ($Re_{kv}=50$), corresponding to the transition into a turbulent regime. Coefficient of heat transfer from the condensing CO$_2$ determined for these conditions by formula Nusselt (5):

$$\alpha_K = 0,726 \left[ \frac{\delta'' \rho'' \cdot (\rho'' - \rho') g \cdot r}{\eta' \cdot d_n \cdot (t_s - t_{WT})} \right]^{0.25},$$  \tag{5}

where $t_{WT}$ is an unknown temperature of the pipe wall.

Substituting the values obtained:

$$\alpha_K = 0,726 \left[ \frac{(85 \cdot 10^{-3}) \cdot 718(718 - 240)9,8 \cdot 123,5 \cdot 10^3}{6 \cdot 10^{-5} \cdot 21 \cdot 10^{-3} \cdot (24,7 - t_{WT})} \right]^{0.25} \approx 2738 \frac{1}{(24,7 - t_{WT})^{0.25}}.$$

The wall temperature is determined from the condition that the heat flows from the cooling liquid and the condensing vapour:

$$\frac{1}{\alpha_T} + \frac{\theta_{CT}}{\lambda_{CT}} (t_{WT} - t_{B_1}) = \alpha_K (t_s - t_{WT})$$

As a result, we obtain the equation

$$99(t_{WT} - 6) = 2738(24,7 - t_{WT})^{0.75}.$$

Solving it, we find the value of $t_{WT}=24,08$ °C and the heat flux $q = 99(t_{WT} - t_{B_1}) = 1797 \frac{W}{m^2}$.

This heat flow is more significant than necessary (760 W/m$^2$). Thus, the remaining area (2,03 m$^2$) condensation takes place completely.

Table 1 shows the results of extraction of CO$_2$-extractives from plant material according to the processing modes.

From Table 1, it is clear that the yield of extractives CO$_2$ is mainly dependent on the kind of raw materials and the conditions of the extraction process.
Table 1. CO2-extraction results in extracts from vegetable raw materials depending on processing conditions

| Type of raw materials for the CO2-extraction | Bulk density, kg/m^3 | Yield extractives, % |
|--------------------------------------------|----------------------|----------------------|
|                                            | P=4499 kPa t=10 °C | P=5085 kPa t=15 °C | P=5729 kPa t=20 °C | P=6436 kPa t=25 °C |
| Apricot (bone)                             | 245±1,22             | 7,6±0,38             | 8,1±0,410          | 8,6±0,43           | 9,1±0,45           |
| Clove (bud)                                | 385±2,01             | 13,5±0,67            | 14,2±0,71          | 17,8±0,85          | 18,6±1,10          |
| Ginger (rhizome)                           | 273±1,32             | 1,3±0,03             | 1,7±0,08           | 2,1±0,01           | 2,6±0,18           |
| Coriander (fruits)                         | 225±1,12             | 1,4±0,07             | 1,9±0,09           | 2,6±0,18           | 2,9±0,12           |
| Caraway (seeds)                            | 210±0,98             | 3,2±0,16             | 3,9±0,01           | 4,5±0,30           | 5,2±0,23           |

4. The discussion of the results
The process extractives intensification plant material using carbon dioxide in a subcritical state from 4499 to 6436 kPa is discussed in this study. Removal of air from vegetable raw materials and the use of the pulsator for increasing the rate of diffusion refers to an innovative manufacturing process. Development of this area is linked with the analysis of systemic deviations from the extraction mode and requires mathematical modelling stages of technological systems. Experimental data on the dependence of the CO2-extractives from the raw material, depending on changes in pressure and temperature in the extractor.

5. Conclusion
Scientific studies performed result extraction unit is a modernization scheme, comprising the steps of removing air from the raw material by using a vacuum pump and a low-frequency pulsating organization extraction mode by using a special apparatus-pulsator. The tested sequence of technological processes of extracting extractives from various plant materials. When calculating the condenser cooling processes considered CO2 vapour condensation and membrane.

To cool the vapours to a condensation temperature 24,7 °C necessary 2,07 m^2 of the heat transfer surface. The directly condensing surface must be 0,82 m^2.

In the considered service requirements for the safety of the extraction unit operate under the saturated vapour pressure of carbon dioxide to 7,0 MPa.

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