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THERMODYNAMIC PARAMETERS DURING THE EXTRACTION OF ESSENTIAL OIL BEARING AND PHARMACEUTICAL PLANTS. ORIENTAL TOBACCO – CONCENTRATED AROMATIC PRODUCTS

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The thermodynamic parameters characterizing the extraction of tobacco leaves (Oriental type, grown in Bulgaria) for obtaining the commercially-ready concentrated aromatic products concrete and resinoid have been determined – Gibbs free energy, activation energy, entropy and enthalpy of the process.

Introduction

Essential oil bearing and medicinal plants, either in fresh or dried form, are processed in various ways for obtaining aromatic products – by distillation, extraction, enfleurage, pressing, depending on their glands structure, position and basic properties (volatility, solubility, adsorption, viscosity, etc.). A single plant material is often processed in a number of ways, to obtain various aromatic products – concrete, resinoid, absolute, liquid or concentrated extracts [12]. Concrete is a product obtained by extraction with non-polar volatile solvents, often at room temperature, followed by low-temperature vacuum evaporation of the solvent. On its turn, resinoid is obtained by hot extraction with polar solvents and further concentrated by a more intensive solvent vacuum evaporation. The two concentrated aromatic products differ in physical and chemical properties, as well as in chemical composition [12]. All extraction aromatic products contain a number of partly volatile or non-volatile substances that are not found in the essential oil – waxes, resins, tannins, flavonoids, phenolic acids, etc. [2, 3, 12].

Tobacco (*Nicotiana tabacum* L.), beside its basic role as a material for the manufacture of smoking and smokeless products for human consumption, is a typical essential oil bearing plant and as such – a valuable source for obtaining aromatic products [11].

Materials and methods of analysis

Cured leaves from Oriental tobacco (ecotype Basma – Krumovgrad), grown in Bulgaria have been used as plant raw material [8, 9]. All technological investigations have been conducted in laboratory conditions. Prior to extraction, tobacco leaves have been dried, ground in a laboratory mill and sieved (mesh 0,11 cm). The coefficients of molecular diffusion of the respective aromatic products have been calculated [9], under the following extraction conditions: raw material: solvent ratio = 1 : 10; duration = 1 h; at each10 min interval the extract being removed by filtration and the remaining raw material extracted with a new portion of fresh solvent. The respective aromatic products have been obtained by extraction with: petroleum ether, temperature range 20÷40 °C – for concrete; and 95 % ethanol, temperature range 20÷70 °C – for resinoid. The solvents have been removed by evaporation on a rotary vacuum evaporator at water bath temperature 35 °C (concrete) and 70 °C (resinoid) [8, 9].

On the basis of aromatic products yields, the equilibrium constant of the process has been determined and the thermodynamic parameters calculated – Gibbs free energy, activation energy, entropy and enthalpy of the process. All experiments have been carried out in triplicate and average values are presented.

Gibbs free energy is determined by the equation [1, 4, 5, 10, 13, 14]

$$\Delta G = -RT \ln K, \qquad (1)$$

where ΔG – Gibbs free energy, J/mol;
R – universal gas constant, J/(K·mol);
T – absolute temperature, K;
K – equilibrium constant of the process.

The activation energy of the process is determined by the equation [1, 4, 10, 13, 14, 15]:

$$E_{act} = 2{,}3RTtg\alpha \tag{2}$$

The entropy is defined by the equation [4, 15]:

$$\Delta S = \frac{(E_{act} + \Delta G)}{T} \tag{3}$$

The enthalpy is determined by the equation [1, 10]:

$$\Delta H = \Delta G + T\Delta S \tag{4}$$

Results and discussion

Figures 1–4 present the change of the thermodynamic parameters characterizing the extraction of concrete from Oriental tobacco leaves – Gibbs energy, activation energy, entropy and enthalpy.

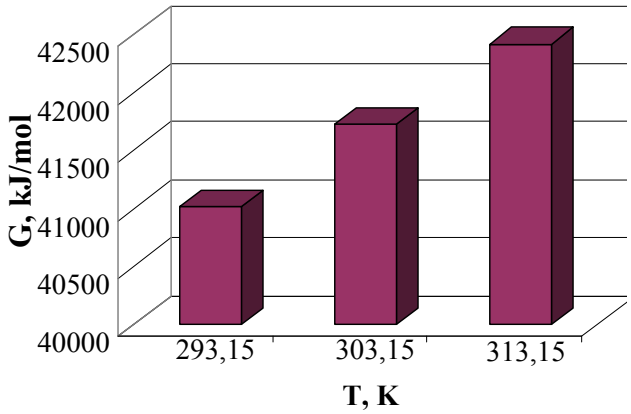

Figure 1 – Change of Gibbs free energy in dependence on temperature

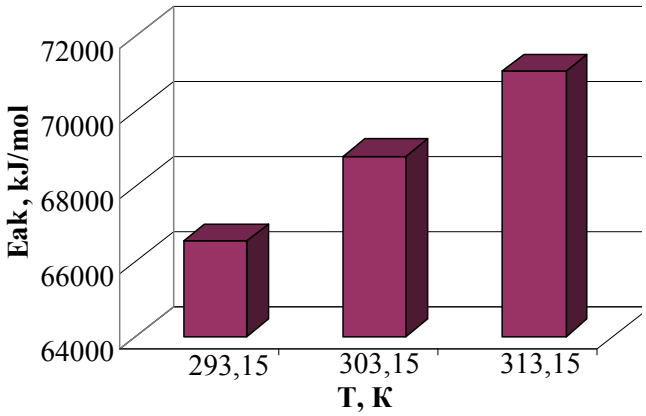

Figure 2 – Change of activation energy in dependence of temperature

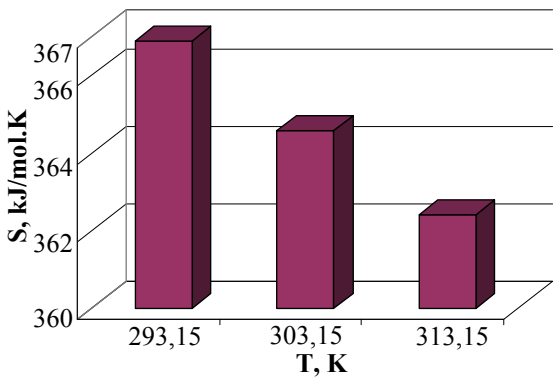

Figure 3 – Change of entropy in dependence of temperature

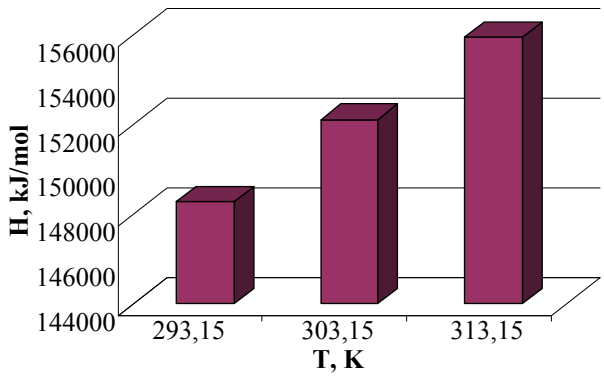

Figure 4 – Change of enthalpy in dependence of temperature

Considering data displayed on the figures it can be seen that the smallest values of three of the studied thermodynamic parameters during the extraction of concrete from Oriental tobacco leaves – Gibbs energy, activation energy and enthalpy, are obtained at temperature 20 °C. At the same temperature, entropy achieves its maximal value. These findings lead to the conclusion that the process of Oriental tobacco leaves extraction with the specified solvent would be most effective at that temperature, since it would require minimum amount of heat for its completion, supplemented at the same time by maximal entropy.

Comparing the results about the calculated thermodynamic parameters obtained for Burley light air-cured [6] and Virginia flue-cured tobaccos [7] it becomes obvious that the activation energy of the process takes minimal values at temperature 20 °C, but there is considerable deviation in Gibbs energy, entropy and enthalpy values. These variations reflect the differences in the chemical composition of the used raw materials and the interactions occurring during the extraction of concrete. Generally, it could be concluded that the most appropriate extraction temperature for obtaining concrete from tobacco (regardless of tobacco type) with 95 % ethanol as a solvent is 20 °C.

Figures 5–8 present the change of the studied thermodynamic parameters – Gibbs energy, activation energy, entropy and enthalpy of the process, during the extraction of resinoid from Oriental tobacco leaves.

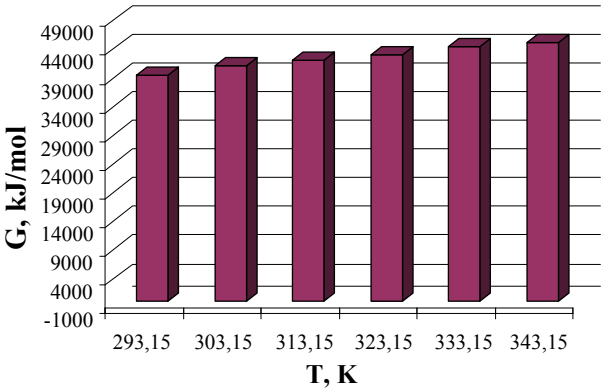

Figure 5 – Change of Gibbs free energy in dependence on temperature

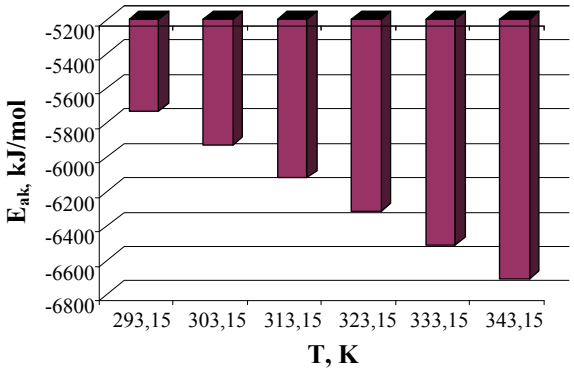

Figure 6 – Change of activation energy in dependence of temperature

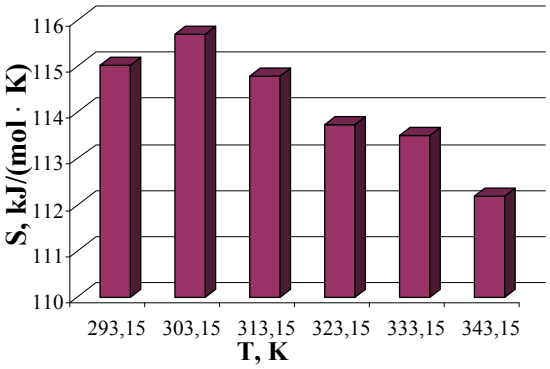

Figure 7 – Change of entropy in dependence of temperature

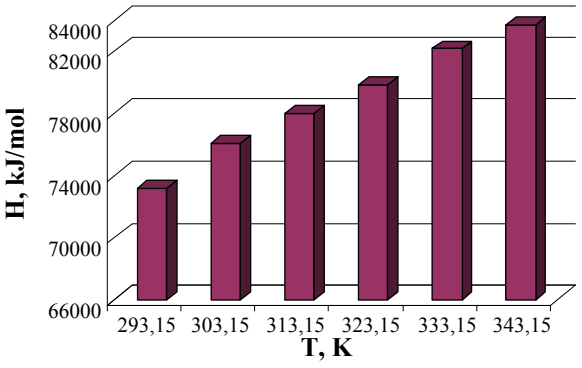

Figure 8 – Change of enthalpy in dependence of temperature

Data show that the values of Gibbs energy, activation energy and enthalpy characterizing the obtaining of resinoid from Oriental tobacco leaves are the smallest at temperature 20 °C, while that of entropy – at 40 °C. The calculated maximal values of the studied thermodynamic parameters are as follows: Gibbs energy – at temperature 70 °C, entropy – at 30 °C, and enthalpy – at 70 °C. The negative values registered for the activation energy suggest that there are certain chemical interactions occurring between the extracted raw material and the solvent.

If the results are compared to those referring the extraction of resinoid from the two other tobac-

cos grown in Bulgaria – Burley light air-cured and Virginia flue-cured, it turns out that there is a complete coincidence of process parameters [6, 7]. Therefore, the thermodynamic parameters of the process of extraction of resinoid from cured tobacco leaves show no variation with respect to raw material (tobacco ecotype).

Conclusion

For the first time, there have been defined the thermodynamic parameters – Gibbs free energy, activation energy, entropy and enthalpy, during the extraction of concrete and resinoid from Oriental-type tobacco leaves.

References

1 Damyanov, D. Physic chemistry. – Union of Scientists in Bulgaria – branch Burgas. – vol. 1 and 2. – 1994.
2 Jirovetz, L., Buchbauer G. Processing, analysis and application of essential oils. – HKB&Sons, Dehradun, India. – 2005.
3 Jirovetz, L. Aromatic plants from Asia, their chemistry and application in food and therapy. – HKB&Sons, Dehradun, India. – 2007.
4 Mogaddasi, F. Kinetic and thermodynamic study on the removal of methyl orange from aqueous solution by adsorption onto camel thorn plant // Asian J. Chem. – 2010. – vol. 22. – No. 7. – P. 5093–5100.
5 Nwabanne, J. Kinetics and thermodynamics study of oil extraction from fluted pumpkin seed // Int. J. Multidisciplinary Sci. Eng. – 2012. – vol. 3. – No. 6. – P. 11–15.
6 Popova, V. Thermodynamic parameters during the extraction of essential oil bearing and pharmaceutical plants. 8. Burley light air-cured tobacco – concentrated aromatic products // (in press).
7 Popova, V. Thermodynamic parameters during the extraction of essential oil bearing and pharmaceutical plants. 10. Virginia flue-cured tobacco – concentrated aromatic products // (in press).
8 Popova, V. Chemical composition of aromatic products from tobacco (*N. tabacum* L.). 3. Oriental tobacco // Sci. Works UFT, Plovdiv. – 2010. – vol. 57. – No 1. – P. 391–396.
9 Popova, V. Coefficients of diffusion in the process of obtaining aromatic extraction products from tobacco. 3. Oriental tobacco // Sci. Works “A. Kanchev” University, Ruse. – 2010. – vol. 49. – series 9.2,. – P. 120–123.
10 Quan, X. A thermodynamic analysis for heterogeneous boiling nucleation on a superheated wall // Int. J. Heat and Mass Transfer. – 2011. – vol. 54. – P. 4762–4769.
11 Ross, I. Medicinal plants of the world. Volume 3. Chemical constituents, traditional and modern medicinal uses. – Humana Press Inc., Totowa, NJ. – 2005. – P.271–371.
12 Stoyanova, A. Technology of essential oils. – UFT Academic Publishing House, Plovdiv. – 2007.
13 Tasheva, J. Evaluation of the effectiveness of selective solvents used in the extraction process of middle distillation fractions // Yearbook "Prof. Dr. A. Zlatarov" University, Burgas. – 2004. – vol. 33. – No 1. – P. 129–133.
14 Tasheva, J. Methods for obtaining eco-friendly middle distillation fuels: Dissertation, PhD. – Sofia: BAS. – 2005.
15 Yaqub, A. Biosorption of heavalent chromium by *Spirogyra* spp.: Equilibrium kinetics and thermodynamics // J. Animal Plant Sci. – 2012. – vol. 22. – No 2. – P. 408–415.

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