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Kinetic scheme of apple pectin oxidative transformations under the action of the ozone-oxygen mixture

© **Galiya G. Kutlugil'dina**,[1] **Yury S. Zimin**,[1*+] **Margarita V. Sakhibgareeva**,[2] **Semen I. Spivak**,[3] and **Akhat G. Mustafin**[1]

[1] *Department of Physical Chemistry and Chemical Ecology. Bashkir State University. Zaki Validi St.,32. Ufa, 450074. Republic of Bashkortostan. Russia. Phone: +7 (347) 229-96-94. E-mail: ZiminYuS@mail.ru*

[2] *Department of Ground Infrastructure Information Systems Development. RN-BashNIPIneft. Lenin St., 86. Ufa, 450006. Republic of Bashkortostan. Russia*

[3] *Department of Mathematical Modeling. Bashkir State University. Zaki Validi St.,32. Ufa, 450074. Republic of Bashkortostan. Russia.*

*Supervising author; +Corresponding author

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Abstract

Mathematical modeling of apple pectin oxidative transformations (AP) under the action of the ozone-oxygen mixture in aqueous solutions (the reaction system "AP + O_3 + O_2 + H_2O") has been carried out. The kinetic scheme of the oxidation process was compiled basing on the well-known ideas of liquid-phase oxidation mechanisms of organic compounds (taking into account the currently known experimental results on AP oxidation). Using the "KhimKinOptima" software package for the proposed scheme, the inverse and direct chemical kinetics problems were solved. The well-known literature data on the rate constants of elementary stages were used. The rate constants of the oxidation key stages have been determined after solving the chemical kinetics inverse problem with the index method of the observed and calculated kinetic data global optimization. It turned out that the rate constants of the individual stages obtained by calculation are in good agreement with the values of the rate constants taken from literary sources. The chemical kinetics direct problem has been solved with the found rate constants and allowed obtaining kinetic curves of all participants in the apple pectin ozonized oxidation. It was found that the kinetic curve of the accumulation of carboxyl groups, obtained experimentally, completely coincided with the theoretical dependence. It has been also shown that the proposed apple pectin oxidative conversion scheme in the "AP + O_3 + O_2 + H_2O" reaction system allows one to explain all the currently available experimental results. The apple pectin ozonized oxidation under another initiator (H_2O_2 + $FeSO_4$) has been studied to confirm the kinetic scheme. To do this, 3 new stages has been introduced into the scheme proposed, characterizing the catalytic decomposition of hydrogen peroxide under a transition metal (Fe^{2+}). By solving the chemical kinetics direct problem, the accumulation kinetic curves of the final reaction products were obtained. It has been found that the carboxyl groups accumulation kinetics in the reaction system "AP + O_3 + O_2 + H_2O_2 + $FeSO_4$ + H_2O" after the supplementary experiment coincided with the theoretical kinetic curve. Thereby, the accuracy of the apple pectin proposed oxidative conversion scheme is confirmed.

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