

SPECIFIC FEATURES OF THERMAL ISOMERIZATION OF VERBENOL IN SUPERCRITICAL ALCOHOL

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Verbenol is produced by direct oxidation of α -pinene, that is a monoterpene compound of vegetal origin. Being the main component of insect-pest pheromone compositions, verbenol is used for synthesis of aromatic and medicinal substances, such as citral and menthol.

Methods for thermal isomerization of verbenol in the gas and liquid phases are known. Thermal isomerization of verbenol in the liquid phase yields (iso)piperitenol as the main product. The gas-phase thermal isomerization of verbenol leads not only to (iso)piperitenol, but also to geranial (trans-citral) and neral (cis-citral), the amount of two latter products not exceeding ~25 wt %. Complete conversion of verbenol at the gas-phase isomerization is not attained even at temperatures above 600°C and contact time ~9 min.

New method for thermal isomerization of verbenol in supercritical ethanol as the reaction medium is suggested in present report. The conversion of verbenol was studied at 120 atm pressure in the temperature range 280–440°C and at residence time ≤ 2 min. Geranial (trans-citral) and neral (cis-citral) were found to be main products of the reaction (see figure below), their amount comprising ~30 wt %, which indicates that in supercritical ethanol the selectivity to these products is two times higher as compared to the gas- and liquid-phase processes. It was shown that the resultant amount of citrals (a mixture of its cis- and trans-isomers) reaches a maximum at elevated reaction temperature. In this case, the maximum content of the indicated citrals (35%) was observed at complete conversion of verbenol, namely, at temperature ~380°C and contact time of ca. 70 sec.

