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Competition of free radical and ionic reaction pathways during the decomposition of glycerol in near- and supercritical water.

A.Kruse, W. Bühler, E. Dinjus, H. Ederer, C. Mas

Institut für Technische Chemie, Bereich Chemisch-Physikalische Verfahren
Forschungszentrum Karlsruhe

Experimental results of the reaction of glycerol in near- and supercritical water in the temperature range of 622-748 K, at pressure between 25 and 45 MPa, reaction times from 32 to 165 seconds and different concentrations are presented. The reaction has been carried out in a tubular reactor and the conversion is between 0.4 and 31%. The main products of the glycerol degradation are methanol, acetaldehyde, propionaldehyde, acroleine, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide, and hydrogen. The results are compared with the studies of other working groups.

The non-Arrhenius behaviour, pressure dependence of the reaction rate and product distribution indicates the occurrence of two competing reaction pathways. One pathway consists of ionic reaction steps and is preferred at higher pressures and lower temperatures. The second reaction pathway is a free radical degradation and dominates at lower pressures and higher temperatures.

For modelling this, two mechanisms, an ionic and a free radical reaction network are compiled to one reaction model. Using the computer package CHEMKIN the reaction model and the kinetic parameters are optimised. The reaction rates for the glycerol degradation and the product formations are calculated using this reaction model. The calculated results are compared with the experimental results. The calculated and experimental reaction rates are in good accordance. This means that the reaction network of the model, considering an ionic and a free radical contribution satisfactorily describes the complex reaction.