

# ABSTRACT

In this doctoral thesis, a new flow type of catalytic membrane reactor with recycle of the liquid phase, as an alternative for operating catalyzed reactions in the three-phase systems, is presented.

The first part of the dissertation focuses on the development of the mathematical model for the studied membrane reactor with recycle of the liquid phase. The results served as a basic guidance for further work, while at the same time presented a clearer picture of the phenomena taking place inside the membrane reactor and of the parameter sensitivity itself.

The second part of the thesis shows that by using sufficiently high levels of overpressure of the gas phase, we are able to displace the liquid phase from the membrane walls and thus control the position of the interface between the two reactants. In this context, the numerous flaws in the structure of the membrane were revealed as the main problem, which are reflected in the very low values of the first bubble pressure phenomenon and as such severely restrict the usefulness and the value of the operating range for the overpressure of the gas phase. The position of the gas-liquid interface within the membrane at various values of overpressure on the gas side has also been experimentally determined. For this purpose, a precipitation method of calcium carbonate was used at the gas-liquid interface within the membrane. During the process in the membrane reactor with the recycle of the liquid phase, the instability at higher levels of the overpressure on the gas side was exposed.

The third part of the dissertation is aimed towards studying the influence of the overpressure on the gas side on the mass transfer gas-liquid and on the process of selected model reactions. In a catalytic membrane reactor, the mass transfer of oxygen and carbon dioxide into the aqueous medium was studied. For different operating pressures and overpressures of the gas phase, findings regarding the operational stability of the experimental apparatus resulting from the reaction of precipitation of calcium carbonate were confirmed. With different values of the recirculation flow of the liquid phase the validity of existing correlations for prediction of mass transfer in the range of laminar flow ( $Re \leq 2100$ ) was verified. Due to the geometry of the experimental apparatus itself, the laminar flow profile conditions within the tube could not be fully administered. For further purposes the Lévêque correlation was corrected because

of the observed discrepancies in the predictions of the output concentrations in the membrane reactor with the recycle of the liquid phase. A new correlation was proposed to predict the mass transfer coefficient on the liquid side. This correlation was used in the subsequent prognosis of the mass transfer and for the productivity of a membrane reactor in order to better match the measurements and at the same time avoid doubt that the observed deviations between measurements and predictions were due to incorrect calculations of mass transfer with a basic Lévêque equation.

In the final, fourth part, the reactor apparatus with further catalytic oxidation of formic acid and catalytic oxidation of oxalic acid was studied. For this case a catalytic membrane with a Pt metal phase as a catalyst, prepared according to the method of »evaporation-crystallisation«, was used. The performed experiments have shown that changing the position of the gas-liquid interface between the reactants in the wall of the membrane has a strong influence on the efficiency of the membrane reactor. The results obtained by the catalytic oxidation of formic acid were verified with the results from other researchers who were dealing with the same catalytic reaction system in the membrane reactors of different configurations, but under comparable operating conditions. While performing the catalytic oxidation of formic acid, it has been shown that the rate of disappearance of the formic acid on one hand, depends on the diffusion of formic acid through the filtration layer and the intermediate layers to the reaction zone, and on the other hand, it was shown that the measured rate was not influenced by the oxygen concentration at the interface between the gas and liquid phase inside the wetted part of the membrane in the reaction zone. The results obtained show that the performance of the catalytic membrane reactor with recycle can be improved by operating at higher linear velocities of the liquid phase, which means that the external resistance to the mass transfer also has a strong influence on the productivity of this type of reactor.

Similar conclusions from the results of the catalytic oxidation of oxalic acid were established. In this case, the results also showed that the rate of disappearance of oxalic acid is determined largely by the mass transfer of oxalic acid from the main recycled flow into the membrane. In both cases, it was observed that in the region of low concentration values of the liquid reactant, the partition coefficient of the reactant in the filter layers is greater than 1.

At the end of the dissertation, the comparison between the measured and calculated results obtained by the mathematical model, based on a maximum mass flow approach, which was used to predict the diffusion paths of the two reactants and the position of the reaction zone within the membrane, is presented.

*Keywords:* catalytic membrane reactor; ceramic membrane; interface between gas and liquid; catalytic oxidation; formic acid; wet air oxidation.