別紙様式８

研　究　主　論　文　抄　録

論文題目　　（種々の有機化合物の化学変換のための亜臨界水中での電気分解）
(Electrolysis in Sub-critical Water for the Chemical Conversion of Various Organic Compounds)

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主論文要旨

Electrochemical methods for the oxidation of organic compounds and treatment of industrial wastewaters have recently attracted increasing attention. In this project, we propose a novel environmentally friendly process called “hydrothermal electrolysis” that offers promise for the treatment of organic wastes and their conversion into more valuable chemicals.

A general overview of wastewater treatment, the importance and recent commercial applications as well as hydrothermal electrolysis, which was proposed in this work, for the treatment of organic wastes were described in more detail. In this project, two hydrothermal electrolysis systems were used: specially designed batch reactor and continuous flow reactor. In the following sections, hydrothermal electrolysis technique was applied on basis for 1-butanol as a starting material and glycerol which is generated as main by-product from biodiesel production processes. For better understanding, model biodiesel wastewater was prepared and treated by both batch and continuous flow reactors. Moreover, as carrying crucial importance to clarify the reaction mechanism, electrolysis reaction pathway of lactic acid which is generated as main product after hydrothermal electrolysis of glycerol, has been studied in following chapters. Finally, application of hydrothermal electrolysis technique for complete mineralization of nitrogen containing organic compounds (1,8–Diazabicyclo[5.4.0]undec-7-ene (DBU) and some azo-dyes) has been investigated in separate chapters.

Being one of the objectives of this work, electrochemical reaction experiments on 1-butanol under hydrothermal conditions has been conducted to produce fuel sources from biomass resources. Experiments were carried out at pressures of 8-10 MPa and temperatures of 200-250 °C by batch reactor with and without applying currents. More than 70% of

1-butanol was mainly converted to butanal and then butyric acid was formed from oxidation of butanal.

In another chapter, conditions under which glycerol could be converted into valuable chemicals such as lactic acid, formic acid were investigated by hydrothermal electrolysis with both batch and continuous flow reactors. For these purposes, 0.1 M glycerol and varying concentrations of NaOH (10, 25, 50, and 100 mM) were used as feed materials. Reaction temperature and pressure were kept constant at 280°C and 10 MPa, respectively. Various current values (0-2.0 A) were passed through the electrodes for 30-120 min. With a batch reactor, maximum glycerol conversion of 84% was achieved whereas by continuous flow reactor more than 92% of glycerol could be decomposed under the same conditions. Increasing the concentration of NaOH led to a great increase in the amount of lactic acid which was the main product, with a yield of 34.7%.

After understanding the basic concepts of hydrothermal electrolysis technique and the reaction behavior of pure glycerol, for further investment, a model biodiesel wastewater was prepared and tried to be decomposed by using both batch and continuous flow reactors. During the hydrothermal electrolysis with batch reactor, the maximum conversion was recorded as 83% by applying 1 A current at 250 °C, whereas by using continuous flow reactor, maximum 75% of glycerol was converted into gas and liquid products at 1 A current during 60. In the case of total organic carbon removal, under same conditions, it was found that 23% and 15.9% TOC conversions were achieved by batch and continuous flow reactors, respectively.

For further investment, lactic acid was also used as feed material and hydrothermal electrolysis experiments were conducted under alkaline conditions by continuous flow reactor. Acrylic acid, acetaldehyde and acetic acid were formed as main products. The applied current greatly affected the conversion of lactic acid (max.55%). However, further increases in the pH of the solution, up to 13, resulted in difficulty in degrading the lactic acid. In a sub-critical reaction medium after hydrothermal electrolysis, decomposition of lactic acid may follow two major pathways, dehydration and decarboxylation.

Finally, application of hydrothermal electrolysis technique to nitrogen containing organic compounds was investigated by continuous flow reactor. For this purpose, DBU as a model compound for industrial wastewaters containing heteroatoms, was investigated using hydrothermal electrolysis and then continued with some azo- dyes (orange G, acid orange 7 and congo red). In most cases, more than 93% of DBU and azo-dyes were degraded.

These results indicate that hydrothermal electrolysis can be applied for the successful treatment of various types of organic compounds. It might be possible to carry out hydrothermal electrolysis without the need for an additional electrolyte, thereby simplifying the process and possibly making it more economical.