POLITECHNIKA ŚLĄSKA
WYDZIAŁ CHEMICZNY
KATEDRA TECHNOLOGII CHEMICZNEJ ORGANICZNEJ I PETROCHEMII

PRACA DOKTORSKA

Badania nad procesami utleniającego rozszczepienia alkenów z wykorzystaniem nadtlenku wodoru lub tlenu

Research on the processes of oxidative cleavage of alkenes with hydrogen peroxide or oxygen

mgr inż. Dariusz Pyszny

Promotor: dr hab. inż. Beata Orlińska, prof. PŚ

GLIWICE 2020

Abstract

As part of this work, research was undertaken into the oxidative cleavage reaction of C=C double bonds in order to determine the possibility of using this method to obtain polar waxes from long chain C30+ α-olefins. Oxidation product of C30+ olefins, containing mainly long-chain (C30+) carboxylic acids and esters of these acids, can be used in the production of stable aqueous emulsions, lubricants, surfactants, polymers and others. The oxidative cleavage of α-olefins with more than 20 carbon atoms has not previously been described in the literature.

In order to select the favorable reaction conditions for the oxidative cleavage of olefins, preliminary tests were performed using 1-dodecene as a model compound. Unlike the higher C30+ α-olefins, it was possible to use gas chromatography to determine the composition of the products. The influence of the type of oxidizer and catalyst as well as process conditions on its course was determined. Based on the results obtained, it has been found that the use of hydrogen peroxide as an oxidant and a tungstic acid as catalyst in combination with phase transfer catalysts (PTC) is preferred.

In further studies on the oxidative cleavage of C=C double bonds with hydrogen peroxide with tungstic acid, a mixture of C30+ α-olefins from Chevron-Philips was used as the raw material. The influence of the type of PTC catalyst, addition of mineral acid and process parameters on the content of carboxyl and ester groups in the oxidation product was determined. Product has high acid number (up to 80 mgKOH/g) and saponification number (up to 100 mgKOH/g) and melting point ca. 83÷86°C. Thermal effects of the process were also determined. On this basis, the most favorable conditions were selected and the initial technological assumptions for the oxidation process of C30+ α-olefins were proposed. In selected conditions, attempts were also made to use the developed method to oxidize polyethylene micro wax (MWPE) derived from the thermal processing of waste polyethylene.

As part of the work, research was also undertaken into the use of oxygen in the oxidative cleavage of olefins. *N*-hydroxyphthalimide (NHPI) was used as a catalyst. NHPI shows high activity in reactions that follow according to the radical mechanism. α-Methylstyrene (AMS) was used as a model raw material. The influence of the catalyst, type of additives (azo-compounds, transition metal compounds, alkylammonium salts), solvent and process conditions on its course was determined. For the first time catalytic activity of NHPI was proved in the aerobic oxidative cleavage of AMS carried out without solvent. Under certain conditions, other unsaturated compounds (with C=C bond) were used instead of AMS, including 1-dodecene.