ABSTRACT OF THE DOCTORAL DISSERTATION

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Badania reakcji utleniającego rozszczepienia podwójnego wiązania węgiel-węgiel z wykorzystaniem nadtlenku wodoru i tlenu jako czynników utleniających

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The objective of this dissertation was to develop a two-step oxidative cleavage methodology with demonstrable application potential, employing environmentally sustainable oxidizing agents. The literature review encompassed industrially relevant oxidants, with particular emphasis on hydrogen peroxide and molecular oxygen, as well as the mechanisms, conditions, and catalytic systems employed in oxidative cleavage reactions. Furthermore, previously reported processes involving the oxidative cleavage of selected substrates - long-chain olefins and cyclohexene were examined.

The experimental section presents the development of a green, two-step oxidative cleavage protocol. For investigations involving linear alkenes, a C30+ olefinic fraction originating from ethylene oligomerization and comprising linear α-olefins with 28–36 carbon atoms was selected. This fraction represents a low-value industrial by-product with limited commercial utility; its oxidative functionalization yields a diverse range of polar waxes with high added value.

Cyclohexene was investigated as a second model substrate due to its capacity to yield adipic acid—a compound of significant industrial relevance used in the manufacture of nylon 6,6, polyurethanes, plasticizers, and as an acidulant.

For each substrate, the developed methodology was implemented in two sequential stages:

I. Oxidation of the substrate with hydrogen peroxide

II. Subsequent oxidation of the intermediate product using molecular oxygen

Owing to its structural simplicity and well-defined reactivity, dodec-1-ene was employed as a model substrate in preliminary investigations, enabling detailed monitoring of reaction intermediates and product composition.

The study successfully established a method for obtaining long-chain carboxylic acids with prospective industrial applicability. It was demonstrated that the consumption of hydrogen peroxide during epoxidation can be significantly reduced without compromising reaction efficiency. Novel catalytic systems were developed for the second-stage oxidation using molecular oxygen. In consideration of process safety, oxidation of long-chain waxes was also investigated in the presence of solvents an approach not previously described in the literature. From an environmental perspective, only solvents with minimal ecological impact were employed, specifically water and supercritical carbon dioxide ($scCO_2$).

The results indicate that, through appropriate optimization of reaction parameters, the resulting products can be tailored to exhibit predictable physicochemical properties. This aspect is particularly significant in the context of C30+ olefin oxidation, given the technological potential of the process. Preliminary assumptions for a scalable oxidation technology converting AlphaPlus C30+ into polar waxes were formulated, achieving a technology readiness level (TRL) of 4. The resulting materials may serve as components in stable emulsions or be used directly as functional end products.

The proposed method is broadly applicable and may be extended to the synthesis of other industrially valuable carboxylic acids from structurally suitable olefins—for example, the preparation of adipic acid from cyclohexene, or azelaic and pelargonic acids from oleic acid.