Chemical Engineering Science 143 (2016) 256–269

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Process development for the synthesis of saturated branched fatty derivatives: Combination of homogeneous and heterogeneous catalysis in miniplant scale

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HIGHLIGHTS

- Process with consecutive combination of homo- and heterogeneous catalysis.
- Synthesis of saturated branched fatty derivatives from renewable resources.
- Optimization of liquid distribution by packing dilution with SiC.
- Long-term stability of heterogeneous Pd-catalyst successfully tested (> 100 h).
- No palladium leaching to liquid phase observed.

GRAPHICAL ABSTRACT

Saturated branched fatty derivatives are interesting products for the lubricant and cosmetics industry. The described process combines the homogeneously rhodium catalyzed co-oligomerization of fatty acid methyl esters and ethene with further heterogeneously catalyzed hydrogenation. This paper focusses on the hydrogenation in a trickle bed reactor and presents experimental investigations on operation conditions as well as optimization of packings and liquid distribution.

ARTICLE INFO

Article history:
Received 17 September 2015
Received in revised form
30 November 2015
Accepted 1 December 2015
Available online 23 December 2015

Keywords:
Homogeneous catalysis
Heterogeneous catalysis
Renewables
Co-oligomerization
Hydrogenation
Trickle bed reactor

ABSTRACT

Saturated branched fatty derivatives find application in lubricant and cosmetic industry due to the decisive advantages in temperature and viscosity behavior compared to their linear homologs. Thus, finding new synthesis routes, particularly based on renewable resources, is of great industrial interest. This work covers a new synthesis route for production of such saturated branched derivatives based on linoleic methyl ester. The developed process combines homogeneously rhodium catalyzed co-oligomerization of linoleic methyl ester with ethylene and heterogeneously catalyzed hydrogenation of the co-oligomers in miniplant scale. The paper focuses on the hydrogenation in trickle bed reactor and optimization of operation conditions as well as optimization of packings and liquid distribution. Saturated branched derivatives with very low iodine values have been produced in miniplant scale using a diluted catalyst packing consisting of large Pd/C catalyst pellets and small SiC particles. Different SiC fractions have been tested to investigate the effect on liquid distribution. Additionally long term stability of the heterogeneous Pd/C catalyst has been successfully tested for more than 100 h. Simultaneous adsorption of the used homogenous rhodium catalyst on the fixed bed was analyzed by XPS. Additionally this paper discusses the general transferability of the process combination consisting of homogeneous and heterogeneous reaction steps to other synthesis route and product groups.

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http://dx.doi.org/10.1016/j.ces.2015.12.007
0009-2509/

1. Introduction

Saturated branched fatty derivatives often find application as lubricants and in cosmetics due to the decisive advantages compared to their linear homologs especially in terms of their low temperatures behavior and viscosity index (Kinsman, 1989; Wagner et al., 2001; Willing, 2001; Weitzel and Fretzdorff, 1961) Besides, there are various other beneficial properties of saturated branched fatty derivatives, among those: High thermal and oxidative stability, low surface tension (high wettability), high solubility of corresponding salts in organic solvents, low packing density (high water vapor permeability) and high spreadability (Haase et al., 1988; Ngo et al., 2011; Haase et al., 1989). Looking ahead, finding rapidly biodegrade alternatives is of great interest, especially for use in high-loss lubrication systems and high-risk hydraulic systems.

Behr et al. (Behr et al., 2014, 2013; Behr and Miao, 2004; Behr and Fängewisch, 2003; Behr and Handwerk, 1993; Behr and Laufenberg, 1991) described a new synthesis route to unsaturated branched fatty derivatives based on renewable resources. In this reaction sequence linoleic acid or its methyl ester is converted by a homogeneously catalyzed tandem reaction consisting of consecutive conjugation and co-oligomerization steps with ethylene to form the 1:1-, 2:1- and 3:1 adducts (**1** to **3**), using $RhCl_3{}^*3H_2O$ as catalyst precursor (see Fig. 1). Several different transition metals and precursors have been investigated for the two reaction steps but only $RhCl_3{}^*3H_2O$ has shown potential for the tandem reaction. Although it is only moderately active in the isolated conjugation, the $RhCl_3{}^*3H_2O$ precursor is highly active in the co-oligomerization. Since the conjugation is an equilibrium reaction it can be shifted by the conversion of conjugated linoleic methyl ester during the consecutive co-oligomerization which leads to high yields of the branched fatty products. In a separated step these unsaturated branched fatty compounds are hydrogenated in presence of a heterogeneous Pd/C catalyst to yield the derived saturated branched fatty compounds (**4** to **6**).

To recycle the precious homogeneous rhodium catalyst Behr et al. used a thermomorphic multicomponent system (TMS) (Behr et al., 2014; Behr and Miao, 2004; Behr and Fängewisch, 2003), consisting of a medium polar solvent (1,4-dioxane), a polar component (propylene carbonate) and the apolar fatty compounds. With this TMS-technique the reaction can be realized in a single liquid phase, while with temperature decrease two liquid phases are formed in order to separate the polar catalyst from the apolar product phase after the reaction (see Fig. 2). The polar catalyst phase can then be recycled to the reaction.

However, the tests indicated that, after heating up the components to reaction temperature, the rhodium catalyst coordinates to the double bonds of the unsaturated fatty derivatives and cannot be separated completely as a result (Behr et al., 2014). An illustration of this phenomenon, based on model components, can be seen in Fig. 3. The leaching clearly depends on the number and constitution of the oleo components' double bonds.

In order to overcome the problem of catalyst recycling triphenylphosphine (TPP) was used as a ligand for the tandem reaction. As a result, a decrease in rhodium leaching was observed. The reaction system and conditions for the conjugation and co-oligomerization of linoleic acid with ethylene were investigated and the tandem reaction was tested in a continuously operated miniplant for 100 h (Behr et al., 2014). During the miniplant operation the homogeneous rhodium catalyst could be recycled successfully to the reaction. However, using TPP as ligand leads not only to a lower rhodium leaching in the product phase, but also to a dramatic drop at yields to the branched unsaturated fatty derivatives.

The present work uses technical linoleic methyl ester as feedstock. Investigations showed that the optimized reaction conditions and achievable yields in co-oligomerization are comparable to the results with linoleic acid as feedstock (Behr et al., 2014). The scope of this paper is to present a new process for the synthesis of *saturated* branched fatty derivatives. The developed process includes:

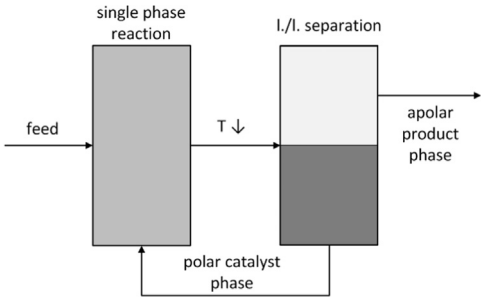

Fig. 2. TMS-technique used for catalyst recycling.

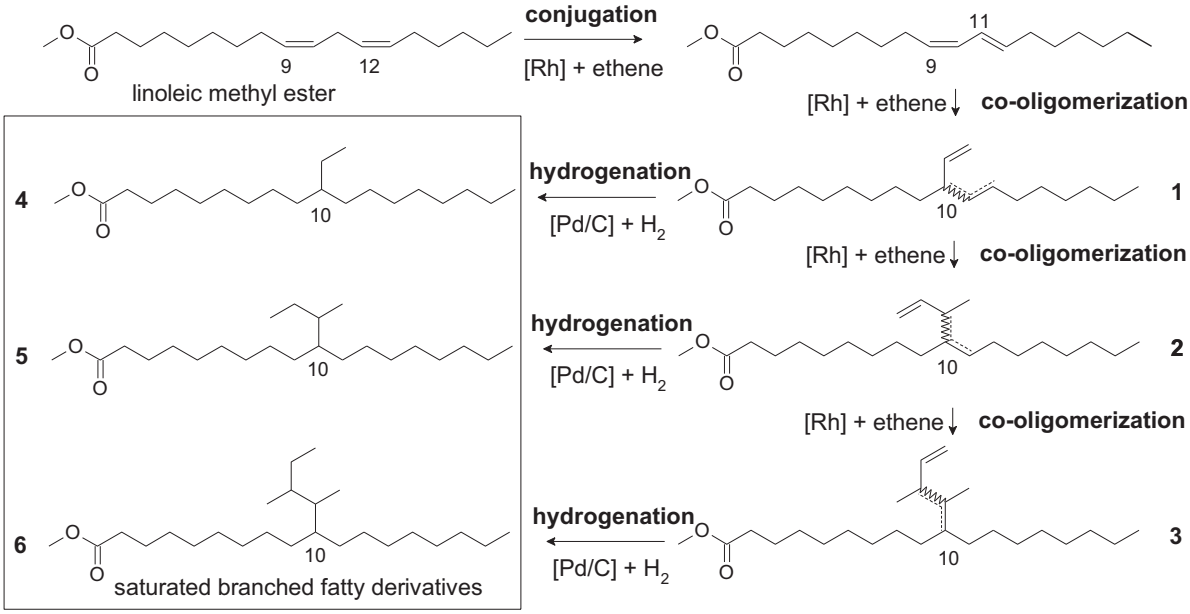

Fig. 1. Conjugation of linoleic methyl ester, further co-oligomerization with ethylene and hydrogenation of the co-oligomers.