Synthesis of 1,12-Dodecanedioic Acid by Combining Chemocatalysis and Biocatalysis – A Marriage of Convenience or Necessity?

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Introduction

Carboxylic acids, particularly dicarboxylic acids, are commercially important intermediates utilized in the production of polymers, adhesives, perfumes, and antibiotics. Aliphatic dicarboxylic acids or long chain diacids (LCDAs) such as, 1,12-dodecanedioic acid (DDDA) is used as a comonomer in Nylon-6,12. While chemical routes for the synthesis of LCDAs from petrochemical feedstocks using traditional chemocatalysts are known and practiced commercially, the synthesis is complicated and results in mixtures containing various impurities, which require extensive and expensive purification steps. Similarly, production of LCDAs by fermentation with various microorganisms, e.g., yeasts, using alkanes or fatty acids are also known in the literature [1]. Unfortunately, most of these reactions are not practiced commercially due to the limited efficacy of the biocatalysts necessary in commercial processes. It must be noted, however, that in recent years, biotechnology has made significant progress in terms of economics and efficacy, and can compete with some of the traditional commercial chemical processes [2]. Such advances have led scientists from these two disciplines to explore the possibility of combining the benefits of biocatalysis and traditional chemocatalysis to come up with new, cost-advantaged, and transformational processes. Hence, it begs the question, as to whether combining these two unique yet synergistically similar processes make this "a marriage of convenience or necessity?"

Thermochemical processes currently used to prepare DDDA and other LCDAs have several limitations, including a restricted product range, use of multi-step conversion processes, and generation of significant amount of side products. Furthermore, petroleum feedstock is almost exclusively used to produce DDDA, which makes it vulnerable to higher feedstock prices and, from time to time, scarcity in feedstock availability. A more transformational and sustainable process for producing DDDA and other LCDAs would involve hydrodeoxygenation (HDO) of renewably resourced vegetable oils, animal fats and oils, fatty acids, fatty acid methyl ester (FAME), and palm fatty acid distillate (PFAD), etc. to LCAs, followed by microbial oxidation of the latter to LCDAs.

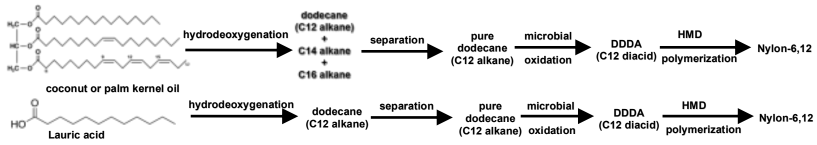

Figure 1. Reaction Scheme to produce 1,12-dodecanedioic acid from renewable feedstock.

The objective of this paper is to delineate a commercially viable process to convert vegetable oils and free fatty acids to polymer grade DDDA via hydrodeoxygenation and microbial oxidation. The paper will also compare the physical and chemical properties of Nylon-6,12 prepared from bio-based DDDA with that of petro-based DDDA.

Materials and Methods

In accordance with the purpose of this study, vegetable oils, such as palm kernel oil and coconut oil, and free fatty acids, such as lauric acid were chosen as the renewable feeds. Various supported base metals (e.g., alumina supported, pre-sulfided Co/Mo/Ni hydrotreating catalyst, CRI DC2318, commercially available from Criterion Catalysts and Technologies, Houston, TX) and precious metal catalysts (Pt/WO_x supported on titania, silica, and alumina) were used for the HDO of vegetable oils and free fatty acids. The reactions were performed in batch and continuous fixed bed reactors in the presence of hydrogen at a temperature and pressure ranging from 225 to 350°C and 500 to 2000 psig (3,450 to 13,900 kPa), respectively. The hydrodeoxygenation product comprising dodecane was vacuum-distilled at 50 torr (absolute) pressure in a vacuum jacketed Oldershaw column. Pure dodecane, thus obtained, was oxidized to DDDA using *Candida Tropicalis* or *Candida Moltosa* yeasts. Last but not the least, polymerization of the pure bio-DDDA with hexamethylene diamine (HMD) was performed in a batch autoclave.

Results and Discussion

Selective HDO of renewably resourced vegetable oils, such as coconut oil and palm kernel oil, and free fatty acids, such as lauric acid, was carried out in the presence of supported base and precious metals catalysts, to produce long chain alkanes in batch and continuous reactors. HDO of palm kernel oil, for example, carried out in a batch reactor at a temperature and pressure of 325°C and 2000 psig (13,900 kPa) for 5 hours in the presence of a sulfided $Co/Ni/Mo/Al_2O_3$ (CRI DC2318), as delineated in Table 1, shows the efficacy of hydrotreating catalyst [3]. Similar results have been obtained for HDO of other vegetable oils and fatty acids in the presence of precious metal catalysts (e.g. $Pt/WO_x/Al_2O_3$) at relatively lower temperature and pressure. The process was scaled up in batch and flow reactors and pure dodecane (ca 99% purity), obtained by distillation, was subjected to microbial oxidation using *Candida Tropicalis*. Dodecane was quantitatively converted to DDDA. Pure DDDA (ca 99.86%) was isolated from the fermentation broth by double crystallization. It was successfully polymerized with HMD to produce Nylon-6,12 and its properties were compared to that of petroleum-based Nylon-6,12. The results indicated that the properties of the bio-based Nylon-6,12 were identical to those of petro-based Nylon-6,12.

Component	C8-	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C18+	Mass Balance
Palm Kernel Oil (wt%)	-	3.5	-	3.4	-	46.2	-	17	-	8.8	-	21.1		100
Hydrodeoxygenated Palm Kernel Oil (wt%)	0.4	3.2	0.4	3	4.6	40.2	2	15	1.1	7.9	2.5	19.3	0.4	100

Table 1. Hydrodeoxygenation of palm kernel oil.

The results of extensive screening of supported base and precious metal catalysts for the HDO of vegetable oils and fatty acids, scale-up in batch and continuous reactors, purification of dodecane, synthesis of DDDA by microbial oxidation, and comparison of bio-based vs petro-based DDDA will be discussed.

Significance

A sustainable and transformational process has been developed to produce 1,12-dodecanedioic acid, a comonomer of Nylon-6,12, from renewable feedstocks by using a unique combination of chemocatalyst and biocatalyst, making it a "marriage of necessity."

References

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