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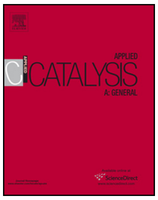

Green oxidation of fatty alcohols: Challenges and opportunities

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ABSTRACT

Selective oxidation of the so-called fatty alcohols, aliphatic long chain alcohols that are present in vegetable waxes, forestry residues and pulping industry subproducts, could be used to obtain the corresponding aldehydes, acids and esters, widely used in pharmaceutical and cosmetic applications and as emulsifiers. The physico-chemical characteristics of this type of alcohols entail specific challenges for the reaction. This work is aimed to review and evaluate the state-of-art of catalytic selective oxidation of the higher fatty alcohols (C_{10+}), to assess the feasibility of new "green" processes using biomass for the production of fine chemicals. Due to the scarcity of information available on these reactions, the scope was extended to all C_{8+} primary alkanols, to identify trends and characteristics of the oxidation of longer chain aliphatic alcohols, as well as suitable process conditions.

The critical evaluation of available literature allows to conclude that the oxidation of higher alcohols is feasible using non enzymatic heterogeneous catalysts, either without solvent or with solvents miscible with both polar and nonpolar media (depending on the alcohol chain length), and using clean oxidants such as H_2O_2, molecular oxygen or air. The appropriate selection of the catalytic system and solvent may allow directing the reaction selectively to production of the aldehyde, the acid or the ester. These features would allow the implementation of small-scale processes, well in accordance with the principles of "green chemistry".

1. Introduction: motivation and opportunities

The sustained growth of population, as well as the exponential growth of their quality of life, has resulted in increased demand for fuels and chemicals. Currently the main raw material for their production is crude oil. Environmental concerns, together with the need to reduce the society's dependence on oil, and the possibility to diversify resources and their location have boosted the interest in biomass as a source for chemicals production. The industrial application of feedstock from renewable resources requires new processes, that could also be useful for valorizing wastes from some economic sectors (such as forestry, agriculture and the paper industry), by using them as raw materials.

The higher alcohols (monohydric aliphatic alcohols of six or more carbon atoms) with long carbon chains are generally denoted as fatty alcohols, because historically they were mostly derived from fats, oils and waxes [1], though nowadays are also produced by chemical synthesis. Those of natural origin are unbranched. Fatty alcohols are also present in forestry wastes, such as beech or Douglas-fir barks, in tall oil, the third largest subproduct of the Kraft pulping process of wood mainly from coniferous trees [2], and in pulps from several non woody species (flax, hemp, sisal and abaca) by alkaline pulping [3]. Selective oxidation of these alcohols could allow to using them as a new resource for producing desired aldehyde, ketone, ester and fatty acid products that are valuable intermediates for the fine chemical, pharmaceutical [4] and agrochemical sectors. For instance, behenic acid ($C_{22}H_{43}O_2H$) is used in cosmetics, hair conditioners and creams, due to its high wettability [5], and lignoceric acid ($C_{24}H_{48}O_2$) is used in pharmaceutical [6,7] and health-care preparations [8] and as additives in foods [9].

At present, natural fats and oils are the main source of fatty acids. They are composed of triglycerides of even numbered carbon fatty acids having a chain length in the diesel oil range, which explains the large effort devoted in the past few years to the conversion of fats into fuels [10]. But now there is a shift from triglycerides toward lignocellulose as raw material for the future development for large-scale production of biofuels. This may increase the availability of some fatty acids (especially, those edible ones) and open opportunities for synthesizing products with a higher added value [11]. It should be noted, however, that: (a) the preponderant number of technically available triglycerides consists particularly of C_{16} and C_{18} fatty acids with one or more insaturations [1]; and (b) that fatty acids with twenty or more carbon atoms are extremely scarce

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in nature. New ways to produce them, as well as other acids less available, would be of great applied interest.

Many aldehydes and ketones with a lineal, aliphatic carbon chain, found in natural products (essential oils and fruits of plants) or made synthetically, have desirable olfactory properties. Examples of these odoriferous aldehydes include n-valeraldehyde (C_5) (occurring in musk, herbs), n-octanal (occurring in lemon oil, lemongrass oil), n-nonanal (occurring in mandarin, orris root, Ceylon cinnamon), n-capraldehyde (C_{10}) (occurring in sweet orange, lemongrass, mandarin neroli, coriander), n-dodecanal (occurring in oils of silver fir, lemon and rue), n-tetradecanal (occurring in ocotea, pinus, and Formosan camphor oils), n-hexadecanal and n-octadecanal, as well as those not naturally occurring with odd carbon atom numbers n-heptanal, n-undecanal and n-tridecanal [12]. These odoriferous aldehydes are so potent that they markedly affect the character of a perfume or formulation to which they are incorporated. When prepared synthetically, the purity of the aldehydes or ketones is a controlling factor in their commercial use, as the presence of unpleasant by-odors resulting from by-products formed during the synthesis can make their use in perfume formulations totally unacceptable. Thus, methods of preparing odoriferous aldehydes synthetically that minimize or eliminate objectionable by-products are needed. Selective oxidation of fatty alcohols to the corresponding aldehydes would contribute to this goal.

Wax esters (esters of long-chain fatty acids esterified with long-chain fatty alcohols) have a variety of uses in many industries, as high pressure lubricants, replacing hydraulic oil, and in the pharmaceutical, cosmetic, printing and leather industries. For instance, myristyl myristate (tetradecyl tetradecanoate) is an appreciated emollient used in lotions and creams. Though wax esters are widespread in nature, as common components of the waxy cuticle on aerial surfaces of higher plants [13], but they are usually found in low concentrations. The only known exception among plants is jojoba (*Simmondsia chinensis*) which seeds contain up to 60% of the dry weight of their cotyledons of wax esters composed of very-long-chain (C_{20}, C_{22}, and C_{24}) monounsaturated fatty acids and alcohols [14]. Besides from jojoba oil, wax esters were obtained from spermaceti oil [15], not longer available after the demise of commercial whaling. They also can be found in some deep water fishes, but New Zealand is currently the only country extracting wax esters from fish oil [16].

It seems evident that selective oxidation of fatty alcohols shows potential as one technological option for producing fatty acids with very long chain or odd carbon atoms number, rare aldehydes, and wax esters, which are high value chemicals nowadays scarce.

2. Scope and aim of this review

Selective alcohol oxidation is one of the key transformations in organic synthesis and in industrial practice. By the last turn of century the world-wide annual production of carbonyl compounds was over 10^7 tonnes and many of these compounds are produced from the oxidation of alcohols [17]. Conventional methods were based in the use of stoichiometric oxidants, mostly noxious transition metal oxides and salts, halogenated compounds or sulfur oxides, which produce great amounts of undesirable subproducts, a nightmare from the environmental point of view. So, it is not surprising the considerable effort made to comply the principles of green chemistry, by implementing processes based on catalysis and non-toxic oxidants: the number of papers on catalytic selective oxidation of alcohols increased linearly almost tenfold in the last years: from 24 in 1998 to 221 in 2011 [18]. Selective oxidation of alcohols in general have been object of several specific reviews [19–26] and it is also examined inside reviews devoted to some catalytic systems used for it, such as those based on gold [27,28], ruthenium [29] or heteropolycompounds [30].

However, none of these addresses the specific issues of fatty alcohols oxidation. In fact, most of the published research deals with activated alcohols, such as allylic, benzylic and polyfunctional alcohols, and much less with the aliphatic alcohols (alkanols). More specifically, there are very few papers devoted to selective oxidation of the higher alcohols. The only exception is the oxidation of 1-octanol, usually reported jointly with that of more active alcohols of similar number of carbon atoms for comparison purposes. As a consequence, this information is rather scattered.

This paper is aimed to review and evaluate critically the state-of-art of selective oxidation of the fatty alcohols with the longer carbon chains, and to assess the feasibility of making it by processes in accordance with “green chemistry” principles: economy of atoms, reaction with low toxicity compounds, decreased use of solvents and co-solvents, use of renewable resources, avoiding derivatization, production of biodegradable products and use of catalysis [31].

However, as the information available on the oxidation of those alcohols is very scarce, the scope is extended to all primary alkanols with eight or more carbon atoms (C_{8+}), looking for to identify trends and characteristics of the oxidation of long chain aliphatic alcohols, as well as suitable process conditions. Such processes should overcome the specific challenges caused by the chemical and physical properties of these compounds, quite different from those of activated alcohols, and even from those of short chain aliphatic alcohols.

3. Fatty alcohols characteristics: the challenges

The first challenge is that chemical reactivity of aliphatic alcohols is much lower than that of benzylic, allylic or functionalized alcohols. For instance, the turnover frequencies (TOF, h^{-1}) of the solvent-free oxidation of different types of C_8 primary alcohols to aldehydes using Au–Pd/TiO_2 catalysts (with oxygen at 160 °C) are: 269,000 for 1-phenylethanol, 86,500 for benzyl alcohol, 10,630 for 3-octanol and just only 2000 for 1-octanol [32]; this evidences clearly the higher difficulty of oxidizing the non-activated aliphatic alcohols, such as fatty alcohols. Furthermore, TOF for 1-butanol (5930) was almost threefold that of 1-octanol, which indicates that reactivity decreases with the increase of chain length.

Additional challenges come from some physical properties of primary fatty alcohols, summarized in Table 1. It shows definite trends in physical properties which are of relevance for operative conditions to be used in selective oxidation. Both the melting and the boiling points increase progressively with the increase of the number of carbon atoms. And also hydrophobicity: solubility of fatty alcohols in water decreases exponentially with the chain length increase [33]. In parallel, the viscosity increases with the number of carbon atoms: 8.4, 13.8, 18.8 and 53 cP at 20 °C for the alcohols with 8, 10, 12 and 16 carbon atoms, respectively. These characteristics impose some constraints for the practical reaction conditions.

On one hand, the high boiling points make the operation in the gas phase unpractical and energy costly. On the other, high melting points (and high viscosity of the heavier alcohols) impose progressively higher minimum reaction temperatures (T_R) to operate without solvent, or the use of solvents to operate in the liquid phase. Hydrophobicity of the alcohols with longer chains (and of their oxidation products) conflicts with the use of water as solvent. The limited solubility in water may be overcome by using co-solvents, such as ethers of general formula $R_1O(CH_2CH_2O)_nR_2$ where $n = 1–4$ and R_1, R_2 are alkyl radicals of 1–4 carbon atoms. Thus, aerobic oxidation of 1-octanol over a commercial 5% Pt/C catalyst reaches a 77.4% yield of caprylic acid when dissolved in diglycol dimethyl