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Recent advances in sulfonated resin catalysts for efficient biodiesel and bio-derived additives production

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ABSTRACT

The drive toward greener process chemistry has stimulated the development of strong solid acids to replace traditional catalysts for efficient biodiesel production from free fatty acid (FFA) enriched biomass feedstocks. Notably, heterogeneous systems enable simple product isolation procedures and improve the catalyst recyclability. They may also be used in continuous reactors. Increasing interest is directed toward organic polymer-supported solid acid catalysts, holding the promise of easy incorporation of the catalyst into the support with high density and easy tuning of the support microstructure/morphology. In the present review, the focus is set on the most widely employed members of this class, including cation-exchange resins, micro- and mesoporous acidic resins, as well as supported acidic ionic liquids and ionomeric membranes. Moreover, we present the use of alternative organic polymer-based acidic catalysts (hybrid systems). Attention is paid to correlations between parameters such as catalyst morphology, excess of alcohol required, FFA content in oil feedstock, presence of impurities and the performance of resin-supported acid catalysts, as well as to the catalyst recyclability. Finally, a brief survey illustrates the use of resin-supported acid catalysts for the preparation of biofuel additives alkyl levulinates – structurally quite similar to the biodiesel – starting from biomass derived levulinic acid.

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Contents

Abbreviations: BET, Brunauer, Emmett and Teller method; DVB, 1,4-Divinylbenzene; FA, Fatty Acid; FAME, Fatty Acid Methyl Ester; FFA, Free Fatty Acid; IEC, Ion Exchange Capacity; LA, Levulinic Acid; PDVB, Polydivinylbenzene; PS, Polystyrene; PVA, Polyvinyl Alcohol; TOF, Turnover frequency Number (t^{-1})

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1. Introduction

Process innovation is the front research of the liquid fuel industry. Most of efforts, indeed, are directed toward reframing the way of producing conventional biofuels (e.g. sugar-cane ethanol) as well as their advanced counterpart, i.e. fuels from biomass sources and lands not used for primary production systems, such as food production and farming. Researchers and industry seek for higher process efficiency, improved product purity, lower power consumption and ultimately, reduced operating costs. In addition to process innovation, product innovation is also the subject of further research, by developing new bio-based products that reach ideal conditions for fuel usage [1].

The European Union endorsed a mandatory target of 10% of the transport fuel consumption coming from renewable sources by 2020. Fuel suppliers are also required to reduce the greenhouse gas intensity of the EU fuel mix with 6% by 2020 [2]. To effectively reduce greenhouse gas emissions without adversely affecting environmental social sustainability, biofuels must be produced in a sustainable manner [2]. To start with, sustainable feedstocks must be selected in accordance with the EU Renewable Energy Directive to provide at least 35% net CO_2 emission savings (in comparison to fossil fuels), but at the same time they should benefit local communities in terms of food availability, economical and labor benefits, human and property rights as well as preservance of local biodiversity and soil and water quality used for the biomass production [2]. Sustainable feedstocks typically include lignocellulosic residues from agriculture and forestry, fast-rotation non-edible crops, organic fractions of urban waste and algae [1,3]. However, sustainable biofuel production also implies the use of clean, safe, efficient and viable manufacturing processes [1–3].

1.1. Fatty acid methyl esters

Biodiesel consists of a mixture of long chain C_{10}—C_{22} fatty acid (FA) alkyl esters, generally methyl esters (FAMEs, Fig. 1a). It is a sustainable, low-toxic and biodegradable diesel fuel substitute produced and used worldwide. It has been proved to enable low emissions of particulate matter, CO_2, CO, polycyclic aromatic hydrocarbons, sulfur oxide and nitric polycyclic hydrocarbons. Furthermore, it has superior lubricity, high flash point and cetane number [4–6].

Biodiesel can be manufactured from a variety of feedstocks, ranging from (in)edible vegetal feedstock (e.g., sunflower, rapeseed, *Jatropha curcas*, palm and soybean oil) to animal fats and waste cooking oil [5–7]. Microalgae are also an emerging feedstock, since they hold the promise of cost-competitive biodiesel production, although much work is still required in the field. In fact, algal species can produce biomass very rapidly, and have the capacity to produce energy-rich oil in high yield. They can be grown on marginal or non-arable land and, additionally, they may be efficient in removing nutrients from water, thereby enabling waste stream remediation in the process of culturing these microalgae. [7] The use of inedible vegetal or waste cooking oils is preferred because of their low price and

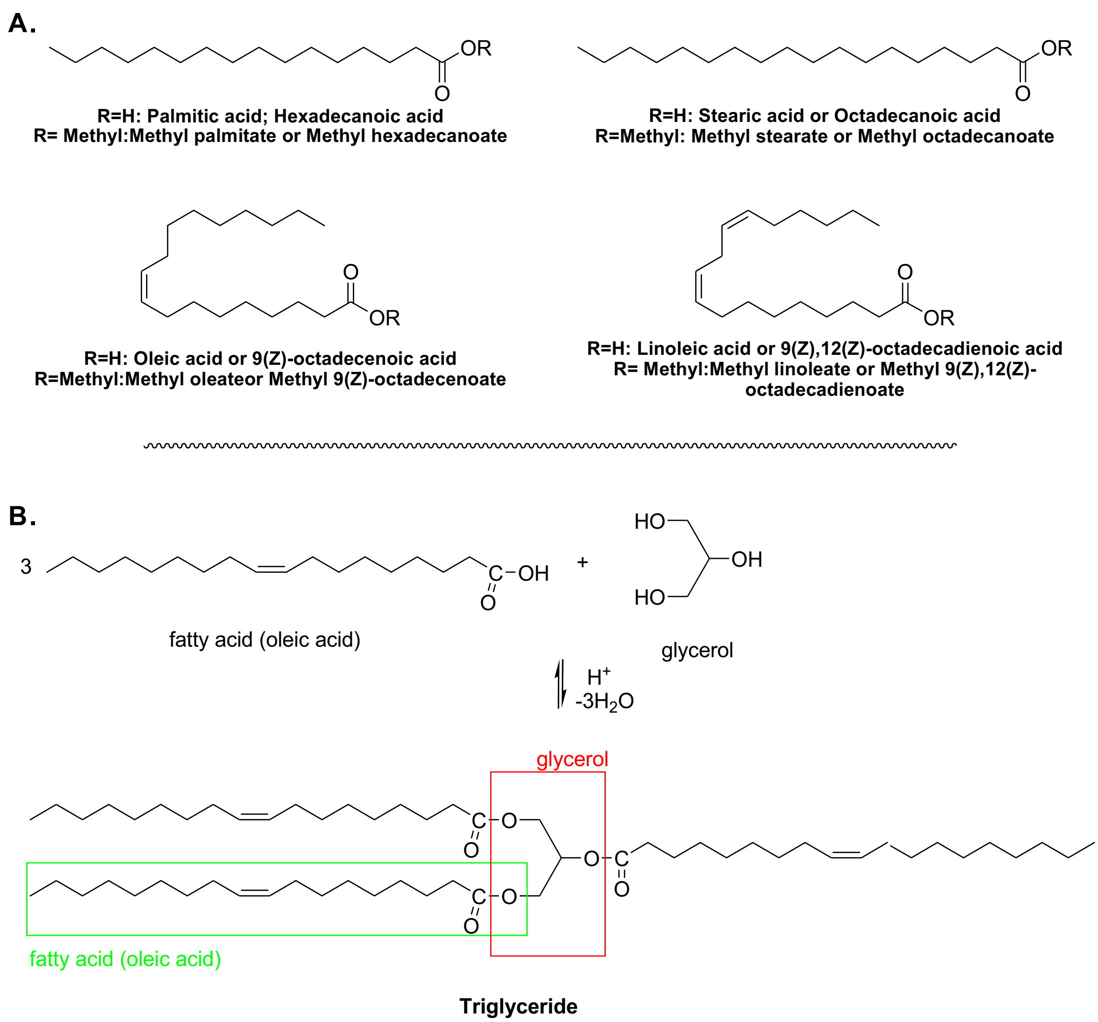

Fig. 1. (a) Chemical structure of common long chain fatty acids and corresponding methyl esters (FAMEs) and (b) Chemical structure of a common triglyceride.

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