



Recent developments in heterogeneous catalysis for the sustainable production of biodiesel



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ABSTRACT

The quest for energy security and widespread acceptance of the anthropogenic origin of rising CO₂ emissions and associated climate change from combusting fossil derived carbon sources, is driving academic and commercial research into new routes to sustainable fuels to meet the demands of a rapidly rising global population. Biodiesel is one of the most readily implemented and low cost, alternative source of transportation fuels to meet future societal demands. However, current practises to produce biodiesel via transesterification employing homogeneous acids and bases result in costly fuel purification processes and undesired pollution. Life-cycle calculations on biodiesel synthesis from soybean feedstock show that the single most energy intensive step is the catalytic conversion of TAGs into biodiesel, *accounting for 87% of the total primary energy input*, which largely arises from the quench and separation steps. The development of solid acid and base catalysts that respectively remove undesired free fatty acid (FFA) impurities, and transform naturally occurring triglycerides found within plant oils into clean biodiesel would be desirable to improve process efficiency. However, the microporous nature of many conventional catalysts limits their ability to convert bulky and viscous feeds typical of plant or algal oils. Here we describe how improved catalyst performance, and overall process efficiency can result from a combination of new synthetic materials based upon templated solid acids and bases with hierarchical structures, tailored surface properties and use of intensified process allowing continuous operation.

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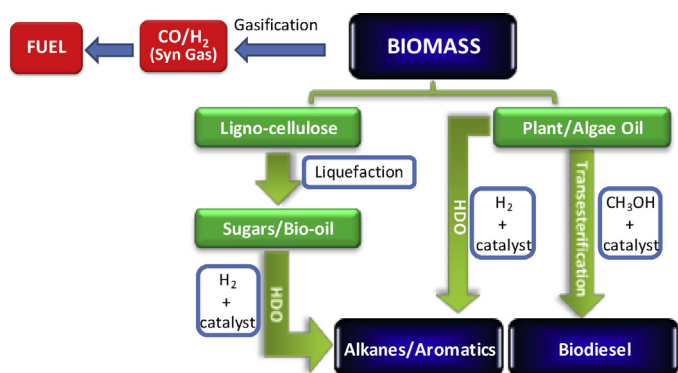
1. Introduction

Tackling the current world energy crisis and increasing environmental concerns over global climate change is a top priority for both developed and developing nations in the 21st century. Sustainability, in essence the development of methodologies to meet the needs of the present without compromising those of future generations, has become a watchword for modern society. In the context of energy, despite significant growth in proven and predicted fossil fuel reserves over the next two decades (e.g. heavy crude oil, tar sands, deepwater wells, and shale oil and gas), there are great uncertainties in the economics of their exploitation via current extraction methodologies, and crucially, an increasing proportion of such carbon resources (estimates vary between 65 and 80% [1,2]) cannot be burned without breaching the UNFCC targets for a 2 °C increase in mean global temperature relative to the pre-industrial level [3,4]. There is clearly a fine balance between

meeting rising energy demands, predicted to rise 50% globally by 2040 [5] and the requirement to mitigate current CO₂ emissions and hence climate change. The quest for sustainable energy to meet the demands of a rapidly rising world population represents one of this century's grand challenges [6,7], with biomass, derived from non-food sources of lignocellulose, sugars, and triglycerides the only sustainable source of carbon that can provide low cost solutions for transportation fuels.

Heterogeneous catalysis has a rich history of facilitating energy efficient selective molecular transformations and contributes to 90% of chemical manufacturing processes and to more than 20% of all industrial products [8,9]. In a post-petroleum era, catalysis will be central to overcoming the engineering and scientific barriers to economically feasible routes to alternative source of both energy and chemicals. While many alternative sources of renewable energy have the potential to meet future demands for stationary power generation, biomass offers the most readily implemented, low cost solution to a drop-in transportation fuel for blending with/replacing conventional diesel [10] via the thermal processing, as illustrated for carbohydrate pyrolysis/hydrodeoxygenation (HDO) [11,12] or lipid transesterification [13,14] to alkanes and

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Scheme 1. Thermal routes to the production of transportation fuels from biomass.

biodiesel respectively in Scheme 1. Indeed recent breakthroughs show the energy quotient for catalytic alkane production from biomass is twice that of fermentation routes to ethanol [15].

First-generation bio-fuels derived from edible plant materials received much criticism over the attendant competition between land usage for fuel crops versus traditional agricultural cultivation [16]. Deforestation practices, notably in Indonesia, wherein vast tracts of rainforest and peat land have been cleared to support palm oil plantations, have also provoked controversy [17]. To be considered sustainable, second generation bio-based fuels and chemicals are sought that use biomass sourced from non-edible components of crops, such as stems, leaves and husks or cellulose from agricultural or forestry waste. Alternative non-food crops such as switchgrass or *Jatropha curcas* [18], which require minimal cultivation and do not compete with traditional arable land or drive deforestation, are other potential candidate biofuel feedstocks. There is also growing interest in extracting bio-oils from aquatic biomass, which can yield 80–180 times the annual volume of oil per hectare than that obtained from plants [19]. Around 9% of transportation energy needs are predicted to be met via liquid biofuels by 2030 [20].

The conversion of oleaginous feedstocks from plant, algal or waste oil sources to fuels by hydrotreating or transesterification (Scheme 2) gives rise to fuels with fundamentally different properties. Hydrotreatment of triglyceride-containing oils proceeds by two reaction pathways [21]: hydrodeoxygenation (HDO) to yield n-alkanes, water and propane or hydrodecarboxylation (HDC) produces hydrocarbons with one carbon atom less than in the original fatty acid forming CO, CO₂ and propane as by-products. Hydrotreating can thus crack the fatty acid chains to yield high grade fuels using existing infrastructure from current petroleum refining processes [22]. While desirable for established petrochemical industry this requires energy intensive operating conditions 250–350 °C and a renewable H₂ source, limiting the potential for localised production of fuels as would be desirable in developing nations. In contrast, commercial biodiesel is currently synthesised via liquid base catalysed transesterification of C₁₄–C₂₀ triacylglyceride (TAG) components of lipids with C₁–C₂ alcohols [23–26] into fatty acid methyl esters (FAMES) which constitute biodiesel as shown in Scheme 2, alongside glycerol as a potentially valuable by-product [27]. Such transesterification routes offer a more energetically economical route for localised fuel production, with processes typically operating <150 °C that are better aligned for small scale production. Biodiesel is thus viewed as a viable alternative (or additive) to current petroleum-derived diesel [28], however, it must be borne in mind that fuel quality is however highly dependent on oil source, with higher chain length (>C₁₈) molecules degrading fuel properties such as the cloud and pour points.

Care must also be taken with purification of biodiesel as unfortunately, contamination from homogeneous acid and base catalysts can corrode reactors and engine manifolds, and their removal from the resulting biofuel is particularly problematic and energy intensive, requiring aqueous quench and neutralisation steps which result in the formation of stable emulsions and soaps [10,29,30]. Life-cycle calculations on biodiesel synthesis from soybean feedstock show that the single most energy intensive step is the catalytic conversion of TAGs into biodiesel, accounting for 87% of the total primary energy input [31], which largely arises from the intermediate quench and separation steps. Such homogeneous approaches also yield the glycerine by-product, of significant potential value to the pharmaceutical and cosmetic industries, in a dilute aqueous phase contaminated by inorganic salts. The utility of solid base and acid catalysts for biodiesel production has been widely reported [13,25,32–34], wherein they offer improved process efficiency by eliminating the need for quenching steps, allowing continuous operation [35], and enhancing the purity of the glycerol by-product. Technical advances in catalyst and reactor design remain essential to utilise non-food based feedstocks and thereby ensure that biodiesel remains a key player in the renewable energy sector for the 21st century. In this review, we highlight our contributions to catalytic biodiesel synthesis via tailored solid acid and base catalysts for TAG transesterification to FAMES and free fatty acid (FFA) esterification with a particular focus on the impact of pore architectures on catalyst performance.

2. Conventional solid acid and base catalysts in biodiesel synthesis

2.1. Solid acids

A wide range of inorganic and polymeric solid acids are commercially available, however, their application for the transesterification of oils into biodiesel is less frequently explored, in part reflecting their lower activity compared with base-catalysed routes [30], in turn necessitating higher reaction temperatures to deliver suitable conversions. Solid acids have the advantage however over solid bases in that they are less sensitive to FFA contaminants than their solid base analogues, and hence can operate with unrefined or waste oil feedstocks containing FFA content [30]. Solid acids can either be used to remove fatty acid impurities by esterification as a pre-treatment, or at higher temperatures, simultaneously esterify FFA and transesterify major TAG components, without soap formation, and thus reduce the number of processing steps to biodiesel [36–38].

While there are a range of potential solid acids, heteropolyacids are an interesting class of well-defined acid catalysts for use in biodiesel synthesis which exhibiting superacidic ($pK_{H^+} > 12$) properties and possess flexible structures [39]. In their native form, heteropolyacids are unsuitable as heterogeneous catalysts for biodiesel applications due to their high solubility in polar media [40]. While, dispersing such polyoxometalate clusters over traditional high area oxide supports can modulate their acid site densities [41,42], this does little to improve their solubility during alcoholysis. Ion-exchanging larger cations into Keggin type phospho- and silicotungstic acids can however increase their stability towards dissolution. For example, Cs salts of phosphotungstic acid (Cs_xH_(3-x)PW₁₂O₄₀ and Cs_yH_(4-y)SiW₁₂O₄₀) are virtually insoluble in water, with proton substitution accompanied by a dramatic increase in surface area of the resulting crystallites [36,43]. As a consequence of these enhanced structural properties, albeit at the expense of losing acidic protons, both Cs_xH_(3-x)PW₁₂O₄₀ and Cs_yH_(4-y)SiW₁₂O₄₀ are active for palmitic acid esterification to methyl palmitate and tributyrin transesterification (Fig. 1). For

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