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MINIREVIEW

Advances in nanocatalysts design for biofuels production

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Abstract: The exploitation of nanocatalysts, at the boundary between homogeneous and heterogeneous catalysis, is tracking new efficient ways to produce renewable biofuels in environmentally friendly conditions. Their solid state makes them recyclable, and their nanometric particle size enables high activities approaching those offered by homogeneous catalysts, as well as novel and unique catalytic behaviors not accessible to solids above the nanometer range. Furthermore, the use of magnetically active materials has led to the development of nanocatalysts easily recoverable through the application of magnetic fields. In this mini-review, latest achievements in the production of advanced biofuels using stable, highly active, cheap and reusable nanocatalysts are described. Specifically, biodiesel and high density fuels have been chosen as major topics of research for the design of catalytic nanomaterials.

1. Introduction

Biofuels, generally defined as any energy-enriched chemical derived from biomass, represent an alternative to the steady depletion of fossil fuel resources. Indeed, biofuels bring together unique characteristics such as renewable energy sources, biodegradability, low toxicity, diversity and an easy and locally controllable availability. Moreover, while the combustion processes of fossil fuels produce the majority of CO₂ emissions in the Earth's atmosphere, the combustion of biofuels is considered to be carbon neutral.^[1-3] Nevertheless, the production of biofuels has to be responsibly planned and handled since the uncontrolled exploitation of plants as biomass source might lead to massive deforestations or to the consumption of soils used for edible crops. In this way, the eco-friendly and sustainability scope of biofuels as energy resource depends on the class and the nature of biomass employed as feedstock, as well as on the characteristics of the production processes, which include reaction conditions, reagents, the use of catalytic or non-catalytic reactions and the type of catalyst employed.^[4, 5]

The most general categorization of biofuels is made in terms of the direct or indirect production of energy. Thus, the first category,

or primary biofuels, are organic materials used in an unprocessed form, such as wood fuel or dried animal dung fuel, to directly produce heat or electricity. These primary biofuels have been the energy engine for the human development up to the rise of fossil fuels. Although utilizing primary biofuels for everyday use as fuel is no longer accepted in terms of environmental sustainability, it is still the main source of energy, especially for cooking and heating, in a large number of communities in developing countries. The second category, or secondary biofuels, are those indirectly obtained from organic material, either of plant or animal origin, that requires advanced and efficient conversion technologies from which solid, liquid or gaseous biofuels are produced depending on the specific characteristics of the process.

The main technologies for biomass conversion can be divided in thermochemical, biochemical and extraction methods. Although the processes for upgrading biomass are also employed to obtain fine-chemical products, in this review we will focus and refer just to biofuel production. Thus, thermochemical processes are the ones attracting major research attention and the most common methodologies for biomass conversion into biofuels, with the broader range of developed technologies.^[6] Thermochemical methods can be subdivided into gasification and direct liquefaction methods. Gasification is mainly used to produce syngas (mixture of CO and H₂, primarily used for methanol or Fisher-Tropsch hydrocarbons synthesis) from biomass conversion at low- (LTG) or high-temperature (HTG) in the presence of oxidant gases (mainly O₂, CO₂, steam and air). Direct liquefaction is employed to produce liquid biofuels (e.g. biodiesel, bio-methanol, bio-oil) and can be subdivided in hydrothermal and catalytic liquefaction, and pyrolysis (thermal biomass decomposition in absence of oxygen) methods.^[7]

On the other hand, biochemical processes consist on biomass conversion through fermentation or anaerobic digestion, using alive microorganisms or enzymes, to produce liquid or gaseous biofuels.

Finally, the extraction methodology is based on physical methods (sonication, microwaves, bead beating, autoclaving, grinding, osmotic shock, etc.) and/or chemical methods in the form of solvent extraction (e.g. using ionic liquids, Soxhlet, Blighand Dyer's or supercritical CO₂ extraction).

Depending on the nature of the biomass feedstock, secondary biofuels are subdivided into three different classes: i) first generation biofuels, obtained from food crops; ii) second generation biofuels, derived from non-food biomass crops, no longer edible food derived materials (e.g. wasted oils) as well as agriculture, urban and industrial organic waste; and iii) third generation biofuels, which consist of biofuels derived from microalgae. Figure 1 schematically shows the classification of biofuels into categories and classes.

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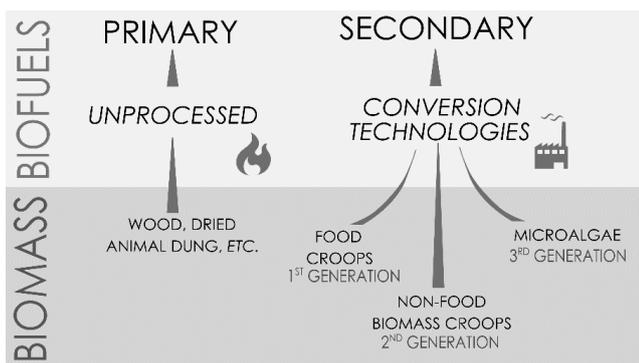


Figure 1. Classification of biofuels.

The definition for second generation biofuels is also shared by the third generation, as biomass sources from both generations do not directly compete with the food supply. In fact, only the first two generations existed initially to classify secondary biofuels, and those from microalgae were originally included as second generation. However, the special characteristics of biofuel production from microalgae, potentially capable of much higher yields (up to 300 times) with lower land requirement than any other feedstock, made them worthy of their own category. The extraordinary photosynthesis efficiency of microalgae (high capacity for CO₂ capture) is mainly responsible for some of their unique characteristics as high both adaptability and growth rate (above 50 times faster than land based plants). Notwithstanding, third generation biofuels are more expensive than those from other biomass sources due to the high cost for the large amount of water, nitrogen and phosphorous (the latter two in terms of fertilizer) required for the microalgae to grow, which in addition brings a negative balance of greenhouse gases emissions for the global process as including the fertilizer production.^[8] Furthermore, from a strictly logistic view, microalgae cultures need the combination of large cultivation areas, sunlight, water and a source of CO₂ in the same place. As far as now, this utopic place does not exist on our planet. Therefore, despite the advantages, third generation biofuels will not become a commercial reality soon, and nowadays these are rather restricted at small scale.

With respect to the other biofuel sources, first generation was the earliest class of secondary biofuels, produced using potentially edible biomass feedstock which is considered as not sustainable, since, if massively exploited, would have a serious impact on the world food supply. On the contrary, second generation biofuels use a more sustainable biomass in terms of availability, waste recycling potential and less impact of their use on food supply, greenhouse gas emissions, biodiversity, and exploitation of agricultural land (linked to food and water supply). However, biomass source for second generation biofuels use to be more difficult to convert than food feedstock, due to the lower reactivity of the former ones as well as increased structural and composition complexity. Nowadays biofuel production is faster, easier and cheaper from highly pure oils and lipids than production from non-food crops and other biomass sources from waste residues.

Therefore, first generation still constitutes the majority of biofuels currently manufactured, while most of second generation fuels are still at the development stage and not widely available for commercial use.^[9, 10]

In most of the cases, biofuels are still not cost-competitive with fossil fuels. Apart from waste derived biomass, the rest of biomass feedstock can account up to 60-80% of the total cost of biofuel production, mainly due to the high costs for biomass collection and transportation compared to those for fossil fuels extraction and delivery to centralized processing stations.^[9, 10] Regardless of the economic issue, commercial production and use of biofuels have progressively been scaled up during last decades, mostly because of the prospective threat of fossil fuels shortage together with the challenging international commitments to reduce greenhouse gases emission standards. Accordingly, the research efforts on biofuels technology have been intensified in order to reduce production costs. The main approach has been to develop more efficient, environmentally friendly and economically viable novel processes, in order to move from the first to the second generation of biofuels.

Some methodologies successfully use homogeneous catalysis to speeding reaction rates up, increasing conversion and selectivity, minimizing side reactions and by-products. However, homogeneous catalysts cannot be recovered and reused. They must be neutralized at the end of the reaction, producing vast quantities of undesired waste chemicals that have to be separated, and limiting implementation of continuous downstream processes. Moreover, corrosion is especially favored in homogeneous catalysis.

Alternatively, heterogeneous catalysis offers, in addition to the aforementioned advantages inherent to a catalytic reaction, the possibility of recycling the solid catalyst and, if using liquid or dissolved biomass, operating processes under continuous flow conditions, with reduced corrosion problems compared to homogeneously catalyzed reactions. Moreover, the use of solid catalysts opens the chance for multifunctionality, consequently decreasing the number of steps in a biomass upgrading process, towards even higher both energy and cost efficiency.

Nevertheless, mass transfer effects are mostly negligible in homogeneous catalysis, where reactants, products, and catalysts are in the same phase. On the contrary, typical liquid-solid heterogeneously catalyzed reactions for biomass conversion are limited by mass transfer or diffusion processes between solid phase of catalyst and liquid phase of reactants, leading to long reaction rates and low efficiency.^[11] Therefore, heterogeneous catalysis research has focused on developing solid catalysts in the nanometer-size scale (nanocatalysts), where mass transfer resistance is minimized by the intrinsic large surface to volume ratios.

Most of the research has focused on developing nanocatalysts for biomass conversion into biodiesel, with proportionally meaningless number of studies for upgrading biomass to other liquid biofuels. Accordingly, the aim of this work is to provide an overview of the ultimate advances in nanocatalysts for biodiesel production. In addition, progresses in the use of nanocatalysts to

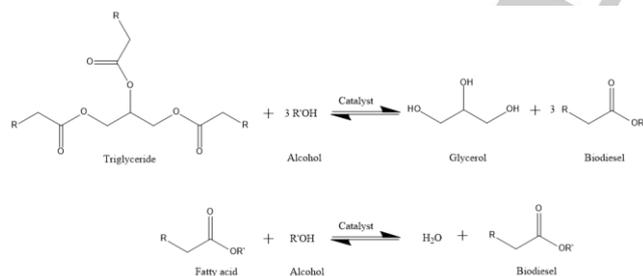
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produce high density eco-fuels, including those produced from biomass and from plastic waste, will be also summarized.

2. Biodiesel

The most common biofuels produced include bio-alcohols, biodiesel, bio-ethers, biogas (mainly a mixture of CH₄ and CO₂), bio-syngas (mixture of CO and H₂) and high density biofuels.^[12] Among all those, biodiesel has attracted by far the major attention from the industrial and research sectors, due to its multiple and well-known advantages.^[13] In addition to the benefits related to sustainability such as renewable source, biodegradability and low toxicity, biodiesel is fully compatible with conventional diesel fuel engines without any modification.

Biodiesel is composed of mono-alkyl esters of long chain fatty acids (fatty acid alkyl esters, FFAE) derived from natural and renewable lipid feedstock, such as vegetable oil or animal fats. The direct use of oils and fats as diesel is in fact hindered by the high kinematic viscosity of the feedstock and by the carbon deposition. Hence, oils and fats must be processed to be compatible with existing engines.^[4] There are two primary conversion methodologies for producing biodiesels: pyrolysis and transesterification. As introduced above, the pyrolysis is a thermal treatment which needs high temperature and is extremely energy-consuming.^[14] Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. The transesterification of TAGs (triacylglycerol) and esterification of FFAs (free fatty acids), illustrated in Scheme 1 and also defined as alcoholysis of plant oils or animal fats, is the most common technology to produce biodiesel.^[15]



Scheme 1. Schematic illustration of transesterification of triglyceride and esterification of free fatty acids.

There are different transesterification processes that can be applied to synthesize biodiesel: (a) base-catalyzed transesterification, (b) acid-catalyzed transesterification, (c) enzyme-catalyzed transesterification, and (d) supercritical alcohol transesterification. The most common method is homogeneously base-catalyzed transesterification, which is much faster than any of the others (e.g. 4000 times faster than homogeneous acid catalysis reaction), in addition to be easier and cheaper.^[16-23] Nowadays more than 95% of the world total biodiesel is produced from highly pure edible oil feedstock, entailing the increasing of

food prices and deforestation. On the other hand, non-edible oils have gained attention because of their elevated oil content and the possibility to be grown in territories not suitable for agriculture with reduced cultivation costs. Residual cooking oils are also considered as possible feedstock for biodiesel production due to the low costs, but they are composed mainly of free fatty acids (FFAs), which strongly influence the yield and purity of the biodiesel.^[24] Although base-catalyzed transesterification is a simple process, it is very sensitive to the presence of free fatty acids which leads to undesired saponification reactions of pursued products. Consequently, it requires high cost virgin oil (high grade) as feedstock, highly increasing the production cost as compared to the acid-catalyzed transesterification.

Nevertheless, regardless of the acid or base reaction mechanism, homogeneous catalysis for biodiesel production has some important limitations, despite its attractive characteristics. Thus, to avoid saponification and hydrolysis of esters, sodium hydroxide is used only with high purity edible oils. On the other hand, sulfuric acid can be used with low grade feedstock, but it needs longer time of reaction. Lastly, the post-reaction treatment required for the removal of the residual catalysts is costly, difficult and generate a large waste water stream. Considering also that the catalysts are consumed during the process, it's obvious and clear the need for a more promising alternative.^[4]

In that sense, in order to improve the transesterification of glycerides, various types of heterogeneous catalysts have been studied. These include solid base catalysts, such as hydrotalcites, metal oxides, metallic salt, supported solid bases and alkali-modified zeolites. Unlike homogeneous catalysis, low-quality oils or fats with FFAs and water can be used with heterogeneous base catalysts, which have been intensively studied over the last decade for transesterification synthesis of biodiesel. However, their catalytic efficiency still needs to be improved. On the other hand, solid acid catalysts, with longer history than solid bases, are especially qualified for low-quality oil feedstocks with high content of FFAs. Acid catalysts can simultaneously catalyze both esterification and transesterification, showing a much higher tolerance to FFAs and water than basic catalysis, but with less activity. Currently developed solid acid catalysts are cation exchange resins (i.e. Amberlyst-15 and NR50), mineral salts (i.e. ferric sulphate, zirconium sulphate, aluminium phosphate and zirconium tungsten), supported solid acids, zeolites and heteropolyacid catalysts.^[25]

Finally, enzyme-catalyzed transesterification has been also reported as an option, since it can avoid saponification, simplifying the purification process and allowing the use of lower pure feedstock as inedible and waste oils. Enzymes can be used in mild reaction condition, consuming low energy, and showing high purity of the products even using high FFAs value feedstock.^[26] The consistent price of the enzymes means the utilization of an immobilizing material to facilitate the recovery of the biocatalyst. With this aim, the integration with magnetic material is an ideal combination.^[27] However, long reaction times and low yields, so far, have to be strongly improved in order to become a feasible commercial application.^[13]

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2.1. Advanced Design of Nanocatalysts for Biodiesel

The research addressed to obtain environmentally friendly and economically viable processes for biomass conversion, moving from first to second generation biofuels, has focused on developing novel heterogeneous catalysts, stable, easy to recycle and with high efficiency and selectivity. As a response to this demanding need for catalyst improvement, especially in production of biodiesel, nano-catalysis has clearly emerged offering unique solutions at the interface between homogeneous and heterogeneous catalysis. In general, the main driving force behind the use of nanocatalysts is their nano-sized solid nature which offers the closest approach to a homogeneous catalyst behavior, with the advantage to be recoverable and recyclable.^[23, 28, 29] Thus, the high activity characteristic of homogeneous systems can be similarly provided by the large specific surface areas intrinsic to solid catalysts consisting of nanometric size particles. Furthermore, beyond displaying benefits from both homogenous and heterogeneous systems, nanomaterials open the way to new properties, which also have the origin in their size. The extent of electronic delocalization in nanometric materials with strong chemical bonding, such as metal nanoparticles, is very sensitive to the particle size. This effect, coupled to structural changes, can lead to size-dependent chemical and physical properties, which cannot be achieved with microscopic particles. The surface reactivity is among these properties, strongly influenced by the atomic coordination at the surface, the latter controlled not only by the nanoparticle size but also by its shape which determines the atomic-level structure of the outer-most exposed planes.^[30] By this way, while the surface of a spherical nanoparticle exposes a wide variety of atomic environments, a cubic nanoparticle exposes just one type of atomic structure. In addition to influence the catalytic activity, the control of the nanoparticle shape leads to the homogeneity of the surface atomic structure which directly translates into high catalytic selectivity.^[31] Therefore, the catalytic properties (activity and selectivity) of nano-catalysts can be tuned by simply changing the shape and size of their active phase.^[32] At this point it must be mentioned that nanocatalysts include either nanometer-sized particles or nanopore-separated materials. Metal, alloy or composite nanoparticles can be free or grafted on supports, such as oxides, zeolites or carbonaceous substrates, the latter preferably with high surface area in order to favor the exposure of the maximum possible surface area of nanoparticles.

Beyond the size and shape of nanoparticles, the acid-base properties, type and content of metal/s and porosity are key parameters for the catalytic performance of nanocatalysts. Additionally, nanomaterials can be used as supports for enzyme biocatalysis. In that sense, nanocatalysts for biodiesel production are typically divided according to their alkali, acid or enzymatic nature as base, acid, and bio-nano-catalysts, respectively, as illustrated in Figure 2. In general, inorganic nanocatalysts reported for synthesis of biodiesel mostly include alkaline earth metal oxides (CaO, MgO)^[33-35], hydrotalcites^[36, 37], zeolites^[38, 39], zirconia^[40] and sulfated oxides.^[41] Most advanced nanocatalysts have been developed to boost the recovery characteristics by exploiting magnetic properties.^[42-44] Thus, combination of some of

these catalysts with magnetic materials has prompted the evolution of magnetically recoverable nanocatalysts.^[45]

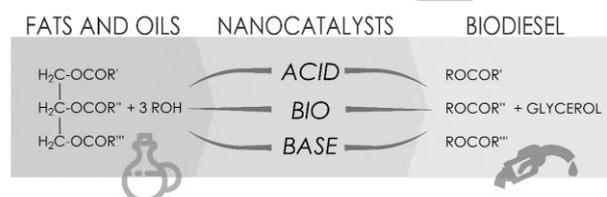


Figure 2. Classification of nanocatalysts for the transesterification of triglycerides.

On the other hand, the research on enzyme biocatalysts, supported on nanomaterials, have opened the doors to new technologies for biofuel productions, especially characterized by milder reaction conditions, avoiding saponification, and with simpler product purification.^[26] In the last years, also enzymes have been proposed in the form of magnetically recoverable nanocatalysts.^[27, 46] Anyway, cost and reaction rates using enzymes have still to be improved.^[47]

The main drawback to avoid in nanocatalysts is the nanoparticles sintering. At high temperatures in the reactive environments of many catalytic processes, metal atoms are mobile to the point that, induce important changes in size and shape of metal nanoparticles. Those structural alterations lead to undesirable effects such as inhomogeneity, lose or reversion in selectivity and catalytic deactivation. Therefore, sintering in nano-catalysts, unless prevented, may limit their application to low temperature ranges and short term uses. Utilization of ligands or coating materials; such as carbon, inorganic components like silica, zeolites, polymers and proper metals; has been proved to be the best solution to hinder nanoparticle agglomeration.^[48] For instance, by coating metal nanoparticles with a mesoporous silica shell, temperatures approaching 1,000 K without evidence of sintering and preserving the shape and morphology of nanoparticles has been reached.^[49] The catalytic activity is not inhibited for reactions not limited by transport of catalytic reactants and products through the silica mesoporous. This porous coating approach can even enhance selectivity providing additional size and shape selectivity of products depending on how they fit or are inhibited by constrains imposed by the pores. The same effect applies to zeolites, which also play an important multifunctional role on the design of nanocatalysts (i.e. increasing the thermal and mechanical stability of supported nanoparticles) affecting shape and size product selectivity through their pores, as well as providing tuneable acid-base properties and additional cooperative active sites for multi-step reactions.^[50] However, in the case of zeolites, their characteristic microporosity, which offer higher diffusional constrains than mesoporous materials, limits their use to catalyze reactions for biodiesel production, involving large molecules like triglycerides. Moreover, zeolites are usually synthesized in crystal sizes within the micrometer range leading to negligible external area surface.

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In order to overcome the accessibility limitations of zeolites, different approaches have been devised such as the synthesis of nanosized zeolite crystals, zeolites with a secondary mesopores network, or zeolite composites.^[50] Those creative approaches, singly or combined, have allowed the development of new zeolitic materials, so-called hierarchical zeolites, with the enhanced accessibility suitable for biomass conversion. As a case in point, nanocrystalline hierarchical zeolites would contain bimodal micro- and meso-porosity, and high external surface area where either internal or external active sites can catalyze reactions involving molecules used for biodiesel synthesis, as triglycerides.^[50, 51]

All the achievements above mentioned, in the development of advanced nanocatalysts, have been possible by combination of deep understanding of surface chemistry and creative use of modern methods for the synthesis of nanostructured materials. This interdisciplinary approach has resulted in well-defined nanocatalysts; with an impressive control over their particle size, shape, morphology and thermal stability; that could not have been created decades ago. In order to overcome the current challenges for energy- and cost-efficient biomass conversion into biofuels, efforts should focus on the detailed understanding of the mechanisms governing the surface catalytic reactions, which is key to establish rational strategies for new generations of catalysts with predefined enhanced catalytic performance for the reactions of interest.

2.2. Base nanocatalysts

Base-nanocatalysts refer mainly to solids with Brønsted basic and Lewis basic activity centers that can accept protons from reactants or supply electrons to them. Among the numerous alkali nanocatalysts for biodiesel production, calcium oxides, hydrotalcites and zeolites have received more attention. Above all, calcium oxides have been intensively studied for its higher basicity and activity, long catalyst lifetimes, low cost and mild reaction conditions.^[52-55] Aiming to increase CaO activity, during the last years the research has focused on the doping of calcium oxide with different compounds such as lithium^[56, 57], potassium fluoride^[58-60] and zinc^[61].

Recently, a highly active catalyst has been prepared by dropping a solution of potassium carbonate into a solution of commercial CaO.^[62] The resulting precipitate was dried and calcined to obtain an activate K-doped calcium oxide with a strongly enhanced activity in the transesterification of Canola oil, compared with the pure CaO based catalyst. Thus, a maximum yield of 97.76% was reached at the low temperature of 338 K with 3%wt catalyst and a methanol/oil molar ratio of 9:1.

Despite its advantages, the utilization of CaO shows some limitations in the recovery step. In fact, during the transesterification process, lattice oxygen species form hydrogen bonds with methanol and glycerin, increasing the viscosity of glycerin and forming solids in suspension with CaO, which is therefore hardly recovered.^[63]

The magnetic functionalization of calcium-oxide overcome these limits. Thus, Zhang et al.^[64] combined a magnetic material with calcium oxide and a strontium oxide to prepare a magnetic

CaO@(Sr₂Fe₂O₅-Fe₂O₃) catalyst. The catalyst was synthesized by a simple co-precipitation method. The catalyst was applied to the transesterification of soybean oil into biodiesel, reaching, after 2h reaction, a maximum yield of 94.9% at 343 K, with methanol/oil molar ratio of 12:1, and 0.5%wt catalyst. Due to the magnetic properties, the catalyst was easily recovered after every cycle, showing high efficiency and high stability upon five repeated runs.

Some hydrotalcites were also successfully employed as catalyst for environmentally benign transesterification processes of vegetable oils. Deng et al.^[65] prepared a hydrotalcite Mg/Al (3:1) nanocatalyst by a co precipitation method, using urea as precipitating agent, followed by a microwave-hydrothermal treatment. With a charge of 1%wt catalyst, the transesterification of Jatropha oil reached a yield of 95% after 1.5 h at 318 K with a methanol/oil molar ratio of 4:1. From a commercial point of view, the properties of the biodiesel were close to those of the German standard (DIN V 51606).

Xie et al.^[66] prepared a functionalized zeolite catalyst, coupling SBA-15 with a guanidine derivative. The hydroxyl group on the SBA allowed the grafting of the guanidine derivate (DCOG), where the tertiary amine groups acted as active site for the transesterification of soybean oil. Despite reaching a transesterification yield of 92.6%, a rather long reaction time (16 h), high catalysts loading (8 wt%), and high methanol:oil ratio (15:1) was required. In any case, DCOG-functionalized SBA-15 showed advantages in terms of easy separation and recovery and high stability in the reutilization.

Another magnetic basic nanocatalyst based on Na₂O-SiO₂/Fe₃O₄ has been recently reported.^[45] The catalyst was prepared by loading Na₂SiO₃ on commercially available Fe₃O₄ nanoparticles, using Na₂O·3SiO₂ and NaOH as precipitant agents. The catalyst with a Si/Fe molar ratio of 2:5 showed the best catalytic activity in the transesterification of cottonseed oil. The biodiesel yield was strictly related to the methanol/oil molar ratio, with the optimum for a 7:1 ratio providing 99.6% yield to biodiesel, obtained at 333 K after 100 min. reaction time with a 5%wt catalyst.

2.3. Acid nanocatalysts

Acid-nanocatalysts usually show less activity, but, due to the hydrophobic surface, they have much higher tolerance to polar impurities such as FFAs and water, being more suitable for low-quality oil feedstocks with high FFAs content. Acid catalysts can simultaneously catalyze both esterification of free fatty acids and transesterification of triglycerides simultaneously, allowing the use of waste cooking oil as feedstock for biodiesel production.^[67, 68] Most attractive acid nanocatalysts recently produced include functionalized magnetic particles, zeolites and zirconia.

Wang et al.^[69] prepared a magnetic acid catalyst in the form of sulfamic acid and sulfonic acid functionalized silica-coated crystalline Fe/Fe₃O₄ core/shell magnetic nanoparticles (MNPs). These MNPs have demonstrated to be efficient recoverable catalysts for the biodiesel production from waste cooking oil. As

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illustrated in Figure 3, the synthesis of the catalysts consisted of three steps: preparation of magnetic nanoparticles, coating with silica and functionalization. The catalysts were tested in the transesterification of glyceryl trioleate and in the esterification of oleic acid in methanol. In 20 hours at 373 K, 88% and 100% conversion were obtained with MNPs functionalized with sulfonic acid or sulfuric acid, respectively. The esterification of oleic acid was completed within 4 hours with 100% of conversion for both catalysts at 343 K in methanol. While the sulfonic acid functionalized MNPs showed low reusability, with a conversion drop to 62% at the fifth run, sulfamic acid functionalized MNPs maintained 95% conversion throughout five reaction cycles.

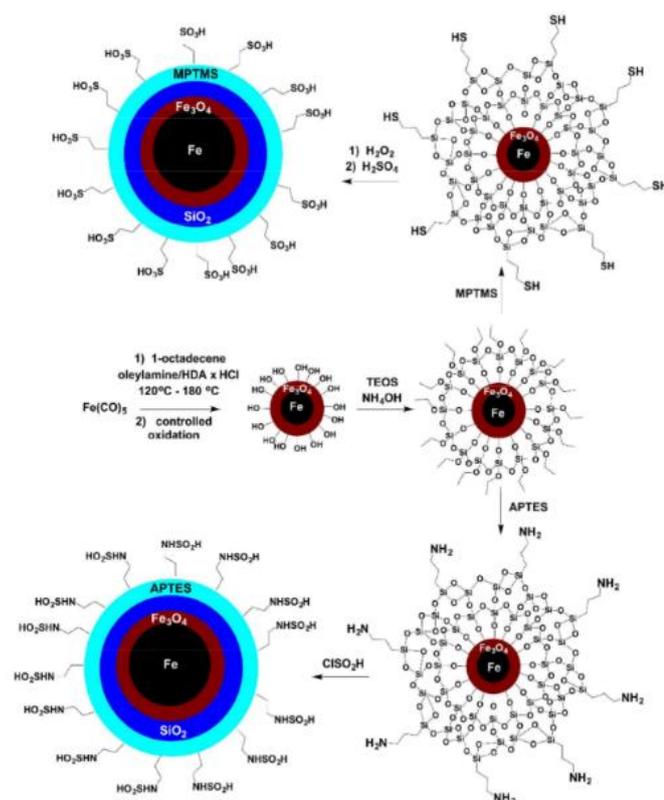


Figure 3. Preparation of sulfonic acid functionalized magnetic nanoparticles and sulfamic acid functionalized magnetic nanoparticles. Taken from Ref.^[69] Copyright (2015), American Chemical Society.

HUSY zeolite acid catalysts have been studied as highly active catalysts for the transesterification process.^[39] However, the high content of acid sites decreases the reusability of the catalysts, increasing the production costs. The incorporation of Cerium on HUSY zeolite has been proposed as a solution to reduce the acid site on both external and micropore surface area of the zeolite, increasing the reusability.^[70] Ce/HUSY was prepared by calcination of NH_4HUSY followed by impregnation with cerium nitrate solution. Before utilization, the catalyst was activated through calcination at 573 K for 4 h. The transesterification

reaction was carried out at 473 K with an ethanol/soybean oil molar ratio of 30:1. Ce/HUSY showed 99.5% of conversion after the third cycle, compared to 96.4% conversion of HUSY.

Zirconia nanocatalysts produced by sonochemistry have been recently proposed as catalysts for biodiesel production.^[71] The catalysts were synthesized by an ultrasound-assisted impregnation/hydrothermal hybrid method, producing nanoparticles of 1-30 nm supported on MCM-41. The performance of the catalyst was investigated in the biodiesel production from sunflower oil, showing a significantly higher activity compared to the same catalyst produced by traditional method. Biodiesel yield reached the amount of 96.9% at 333 K with 5% catalysts concentration with a methanol/oil molar ratio of 9:1.

2.4. Bi-functional nanocatalysts

Base catalysts are well known to accelerate the alcoholysis reaction, while acid catalysts are tolerant toward the purity (FFA content) of the feedstocks. The utilization of nanocatalysts for a two-steps biodiesel production could gain relevance for a fast production of biodiesel from low-grade oils (containing high percentage of FFA). For example, biodiesel has been produced from cooking oil using 25%wt TPA/ Nb_2O_5 for the esterification of FFA, while 20%wt ZnO/ NaY zeolite catalyst was used for the transesterification of the remaining feedstock.^[72]

In that sense, bi-functional nanocatalysts have been recently proposed as advanced solutions for biodiesel production from low-grade oils in a one-step reaction. These catalysts, comprising both acid and basic sites, could promote the esterification and transesterification at the same time. This technology could reduce the costs of biodiesel production not only by replacing a two-step reaction with a one-step, but also by avoiding the utilization of high cost equipment.^[73] A bi-functional Quintinite-3T nanocatalysts has been reported as transesterification and esterification promoter from soy, canola, coffee and waste vegetable oils with variable amounts of FFAs (0–30%wt).^[74] The catalysts were easily prepared by a sol-gel method, at 393 K for 24h, followed by calcination at 773 K. This easy synthesis, combined with the natural availability of the reagent, made the catalysts economically cheap. The Quintinite-3T catalyst showed high activity even after five cycles, keeping a yield of 96% in 2h at 75 °C with 10%wt catalyst amount and a methanol/oil molar ratio of 12:1.

Also Mo-Mn/ $\gamma\text{-Al}_2\text{O}_3$ -15 wt.% MgO has been reported as efficient catalyst for the biodiesel production from waste cooking oil and methanol.^[75] The catalyst was prepared by an impregnation method, using $\gamma\text{-Al}_2\text{O}_3$ -MgO with small pore diameter (~ 60 Å) as support material. The maximum yield of 91.4% was reached in 4h at 100°C using a methanol/oil molar ration of 27:1 and 5 wt.% catalyst.

2.5. Epoxidation nanocatalysts

In addition to these, a recent overview by Danov et al.^[76] summarises recent progress (past 15 years) in the selective

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epoxidation of vegetable oils and their derivatives, in particular unsaturated fatty acids (UFAs) and fatty acid methyl esters (FAMES). Epoxidized vegetable oils (EVOs) have drawn much attention in recent years in the chemical industry due to their environmentally friendly, biodegradable, renewable, high availability and non-toxic nature.^[76] Four major types of catalysts have been extensively employed to produce epoxidized fatty acid compounds: homogeneous, heterogeneous, polyoxometalates and lipases. EVOs are currently produced in industry by a homogeneous catalytic conventional epoxidation process, in which unsaturated oils are converted using percarboxylic acids, such as peracetic or performic acid. However, this method suffers from several drawbacks such as (1) relatively low selectivity for epoxides due to oxirane ring opening, (2) corrosion problems caused by the strong acids in an oxidizing environment, etc. Thus, in view of the principles of green chemistry, the development of new catalytic systems for the selective epoxidation of vegetable oils and their derivatives remains a significant challenge that was partially addressed using heterogeneous catalysts.^[76] Epoxidized fatty acids and epoxidized fatty acid methyl esters can be a promising substitute for EVOs because the starting materials for their production have a lower viscosity and higher reactivity, which will significantly increase the productivity of the epoxidation process.^[76]

3. Catalytic production of high density fuels

Despite the abundance of gasoline and diesel-powered motor cars, high consumption vehicles such as jets, rockets, heavy trucks and ships, require high-density diesel with high volumetric net heat of combustion (NHOC).^[77] Commercially available high-density fuels are derived from petroleum and contain a large amount of naphthalene (~35%) which is the main responsible of the high density.^[78] Most of the recent research on renewable jet fuels has focused on synthetic paraffinic kerosenes (SPKs), which are mainly composed of purely paraffinic or isoparaffinic hydrocarbons in the C₁₀₋₁₄ range, resulting in low densities.^[79] For example, the commercial JP-8 jet fuel has densities from 0.825 to 0.850 g/mL, with a NHOC of ~120 kBTu/gal.^[80] In contrast, a normal renewable biodiesel has a density range from 0.73 to 0.76 g/mL.^[81] A possible solution to the low density of these fuels is to produce high density compounds, such as polycycloalkanes, from biomass or plastic waste, to be blended with the SPKs or directly used as biofuel.

3.1. Biomass high density biofuels

The conversion of biomass to high density fuels normally consists of sequential steps of different processes, such as alkylations, oligomerizations, condensations and hydrogenations. In all the processes, the employment of catalysts plays a crucial role in terms of efficiency, selectivity and yield.^[82-84] Figure 4 schematically summarizes latest progresses, discussed below, in the utilization of nanocatalysts to produce high density biofuels.

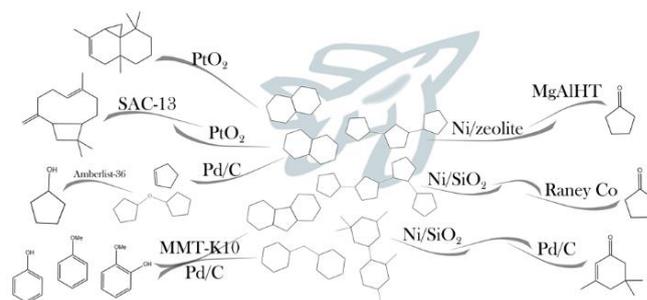


Figure 4. Illustration of recently developed nanocatalysts for the production of high density biofuels.

Terpenoids are renewable source of naphthalenes as they can be extracted from pine resins or generated through biosynthesis.^[85] Specifically, naphthalenes have been bioderived from monoterpenes, sesquiterpenes and diterpenes. Harrison et al. prepared three new advanced biofuels from sesquiterpenes feedstocks.^[86] The high-density biofuel was prepared by catalytic hydrogenation using a PtO₂ catalyst, starting from cedarwood oil as feedstock, primarily consisting of sesquiterpenes thujopsene, α -cedrene and β -cedrane. The hydrogenated cedarwood oil (HCWO) showed a density of 0.917 g/mL, with a NHOC above 12% higher than JP-8 commercial fuel.

As demonstrated by Harvey and co-workers, the blending of multicyclic sesquiterpanes with synthesis paraffin kerosene is a valid way to produce high-density renewable diesel.^[87] Sesquiterpanes were obtained from commercially available caryophyllane and limonene. Specifically, caryophyllane was heated with Nafion SAC-13 and sequentially hydrogenated over PtO₂, while limonene was directly hydrogenated with PtO₂. The synthetic paraffin kerosene, 5-methylundecane, was prepared by catalytic (Zr/MAO) oligomerization of 1-hexene and by sequential hydrogenation over a Pd/C based catalyst. The resulting biofuel, composed by 65% sesquiterpanes and 35% 5-methylundecane, had a cetane number of 45.7, a density of 0.853 g/mL and volumetric NHOC comparable to that of F-76 commercial fuel.

Interestingly, it should be mentioned that caryophyllane can be also produced in a biosynthetic way. In fact, engineered *Escherichia coli* has been successfully employed as biocatalyst for the production of β -caryophyllane.^[88] Sesquiterpenes were obtained by assembling a biosynthetic pathway in an engineered *E. coli* strain. The modified strain, named YJM59, was capable to produce 220 mg/L of β -caryophyllene in flask culture. In fed-batch fermentation, after 60h, the YJM59 strain produced β -caryophyllene at a concentration of 1520 mg/L.

Even though terpenes and sesquiterpenes fuels are interesting for their high density, in terms of the source issue, lignin is far richer than terpenoids, and therefore more economically available.^[89-92] Chen and co-workers developed a three-steps route to convert cyclopentanol, a platform lignocellulose compound, into jet fuel range polycycloalkanes under solvent-free

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mild conditions.^[93] As illustrated in Figure 5, cyclopentanol was firstly dehydrated to cyclopentene over solid acids. In the second step, cyclopentene is converted to a mixture of polycycloalkenes by oligomerization/rearrangement catalysed by Amberlyst-36 resin. The high activity and stability of the catalyst lead to the overall carbon yield of 62.2%. In the last step, the mixture of polycycloalkenes was further hydrogenated with Pd/C catalyst to a C₁₀ and C₁₅ polycycloalkanes mixture. The so-produced biofuel showed a high density (0.896 g/mL) and high content of decaline comparable to those of commercial JP-900.

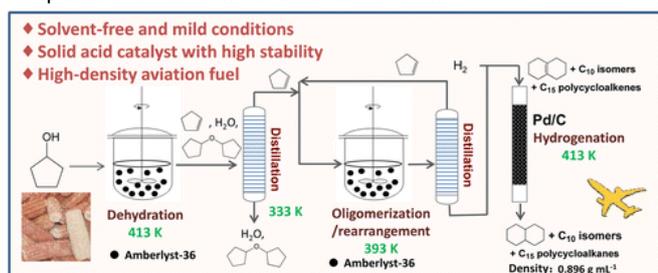


Figure 5. Schematic illustration of the reaction route for the production of decaline from cyclopentanol. Taken from Ref.^[93] Copyright (2016), American Chemical Society.

Another important lignocellulosic platform compound is cyclopentanone. In the literature, it has been reported that cyclopentanone can be produced by the aqueous-phase selective hydrogenation of furfural from hydrolysis of hemicellulose derived from forest residue and agriculture waste.^[94, 95] This compound can be used as building block in the synthesis of jet fuel range cycloalkanes. High density tri(cyclopentane), a polycycloalkane with three carbon rings, has been selectively synthesized from cyclopentanone in a dual-bed catalyst system.^[96] In the first bed, the trimerization of cyclopentanone was obtained under solvent free conditions using MgAl-HT catalysts, obtaining up to 81.2% carbon yield. The excellent performance of the catalyst was explained in terms of high surface area, combined with the strong acidity and basicity. Furthermore, the doping with noble metals, such as Pt, Pd and Ru, sensibly improved the catalytic activity. The best activity was obtained with the Pd-doping, which is highly active in the selective hydrogenation of C=C bond. In the second bed, condensation products of cyclopentanone were hydrodeoxygenated over a Ni/H β zeolite catalyst. The overall reaction produced a yield of 80% to tri(cyclopentane) with density of 0.91 g/mL, under mild reaction conditions (443 K, 0.1 MPa H₂).

1-(3-Cyclopentyl)cyclopentyl-2-cyclopentyl-cyclopentane has also been produced from cyclopentanone.^[97] The procedure consisted of three steps. In the first step, 2-cyclopentylcyclopentanone was prepared by reaction of cyclopentanone and H₂ under the catalysis of Raney metal and alkali hydroxides. With the best catalysts couple, Raney cobalt with KOH, the carbon yield of 83.3% was obtained at 353K. In the second step, solvent-free self-aldol condensation produced 2-cyclopentyl-5-(2-cyclopentylcyclopentylidene)-cyclopentanone with high carbon yield (95%). In the last step, 2-cyclopentyl-5-(2-

cyclopentylcyclopentylidene)-cyclopentanone was hydrogenated over Ni/SiO₂ under solvent-free conditions, providing a carbon yield of 88.5%. The catalyst, prepared by conventional deposition-precipitation (DP) method, was stable and no deactivation was noticed.^[98] The obtained biofuel had a density of 0.943 g/mL and a freezing point of 233 K. These characteristics indicate a possible application of the fuels as a substitute for the jet fuel blend J10.

In the acetone-butanol-ethanol fermentation of hemicellulose, isophorone is produced as a by-product.^[99] Its cyclic chemical structure was exploited to produce high-density polycycloalkanes.^[100] In detail, 1,1,3-Trimethyl-5-(2,4,4-trimethylcyclohexyl) cyclohexane, was produced through three steps. Firstly, isophorone was selectively hydrogenated to 3,3,5-trimethylcyclohexanone using Pd/C as catalyst, achieving 99% of carbon yield at room temperature in 1h reaction with 2 MPa H₂ pressure. In the second step, the self-aldol condensation of 3,3,5-trimethylcyclohexanone catalysed with NaOH led to the production of 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene) cyclohexanone. In the last step, Ni/SiO₂ catalyst was employed in the solvent-free hydrogenation of 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene) cyclohexanone, producing high density biofuel (0.858 g/mL) with a carbon yield of 93.4%. The biofuel had the characteristic to potentially blending conventional fuels such as RP-1 and RG-1 in the rocket propulsion.

Recently, lignin-derived phenols (phenol, anisole, guaiacol) were successfully converted into a low freezing point biofuel.^[101] The simple process consisted of the sequential alkylation of the phenols, followed with hydrogenated intramolecular cyclization. The alkylation was carried out at 383 K with benzyl ether and benzyl alcohol using Montmorillonite K10 (MMT-K10) as catalyst, obtaining high conversion of anisole (32%) and high selectivity to mono-alkylated product (68%). The alkylation product was hydrogenated in the presence of Pd/C and HZSM-5, producing 68.6% of perhydrofluorene and 31.4% of dicyclohexylmethane after vacuum distillation. The biofuel had density of 0.93 g/mL and a freezing point of 233 K.

Handling the same lignin-derived phenols, Han and co-worker developed a way to produce biofuels with freezing point down to 193 K.^[102] The synthesis was carried out through an alkylation with furfural alcohols (furfuryl alcohol, 5-hydroxymethylfurfural) followed by hydrogenation. The alkylation with furfural alcohol was catalyzed with acid catalysts, as to generate furfuryl alcohol cations. While FeCl₃ showed the best activity for the alkylation of anisole and guaiacol, AlCl₃ was most active for phenol. After hydrogenation over Pd/C and HZSM-5, the biofuel had density of 0.804 g/mL, extremely close to the density of jet fuel blends J10.^[103]

Despite Pd/C catalyst is an extremely active catalyst for the hydrogenation of lignin model compounds, it is expensive.^[104, 105] Non-noble metal catalyst, based on Cu, Fe and Ni, have been proposed as valid cheaper alternatives.^[106, 107] Recently, complete arene hydrogenation of phenolic compounds was obtained over a nano-sized nickel catalyst.^[108] The catalyst was prepared through

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borohydride reduction of Ni²⁺ to Ni⁰ with application of pyridine as a ligand and using ZSM-5 as support material. Pyridine was necessary for the formation of Ni particles of controlled size around 4nm. The catalyst allowed the complete or near complete hydrogenation of the aromatic rings of phenols and its twelve derivatives at 453K in autoclave.

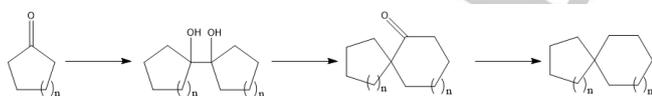
3.2. Plastic derived high density fuels

A green and captivating way to produce high density fuels could also be tracked by the recycling of plastic waste. Nowadays approximately half of plastic waste are disposed, as they cannot be recovered. This issue cause several serious environmental problems such as ocean plastic pollution.^[109] Since the direct combustion of plastics generates the release of harmful compounds, the catalytic conversion into valuable chemicals and fuels has attracted crucial interest.^[110]

Zhang and co. developed an integrated technology of a microwave-induced degradation method followed by hydrotreating process.^[111] Low density polyethylene (LDPE) was employed as a common model compound. In the first step, ZSM-5 catalyst was employed as a promoter of the microwave assisted degradation. At 650 K, the carbon yield of liquid organics achieved 66%, with a coke yield below 1%. The sequential hydrotreating process using commercially available RANEY® nickel reached up 95%wt in 2h at 523 K. The so-produced fuels showed a high content of cycloalkanes (53%), which places the fuel in the navy fuel density range.

3.3. Other recent biomass-derived fuels

Renewable high-density spiro-fuels have also been synthesized from lignocellulose-derived cyclic ketones for the first time, which show higher density, higher neat heat of combustion and lower freezing point compared with other biofuels synthesized from the same feedstock, and thus represent a new type of renewable high-density fuel attractive for practical applications (Scheme 2).^[112]



Scheme 2. Reaction route for the synthesis of spirocycloalkanes from cyclic ketones.

Bio-oils, produced by the destructive distillation of cheap and renewable lignocellulosic biomass, contains high energy density oligomers in the water-insoluble fraction that can be utilized for diesel and valuable fine chemicals productions. Recently, kraft lignin from black liquor was converted into bio-diesel in three steps.^[113] Firstly, a Ni catalyst promoted the reduction of ethers, carbonyls, and olefins using isopropanol as H-donor in mild

conditions at 140°C and 8.5 bar for 16 h. In the second step, the lignin residue was treated with an organocatalyst aiming to achieve an esterified lignin residue soluble in light gas oil. Finally, the esterified lignin residue was hydroprocessed with commercial NiMo to produce the biofuel. The so-produced green fuel possessed average characteristics to qualify as EN590 road diesel.^[113] More recently, an efficient hydrodeoxygenation catalyst that combines highly dispersed palladium and ultrafine molybdenum phosphate nanoparticles on silica was reported for the hydrodeoxygenation of phenol as a model substrate to cyclohexane under mild conditions in a batch reaction (100% conversion, 97.5% selectivity).^[114] The catalyst also demonstrated a remarkable regeneration ability in long-term continuous flow tests. Importantly, the synthesized catalyst could performs an efficient hydrodeoxygenation of lignin, cellulose, and hemicellulose-derived oligomers into liquid alkanes with high efficiency and yields using wood and bark-derived feedstocks. Detailed investigations into the nature of the catalyst pointed to a combination of hydrogenation activity (Pd) and high density of both Brønsted and Lewis acid sites, altogether being claimed as key features for the observed efficient catalytic hydrodeoxygenation behaviour.^[114]

A new vision of using carbon dioxide (CO₂) catalytic processing of oleic acid into C₈₋₁₅ alkanes over a nano-nickel/zeolite catalyst has been very recently reported, as shown in Figure 6.^[115] The proposed process employs an innovative catalytic reaction pathway for oleic acid transformation in a CO₂ atmosphere. C₈₋₁₅ yields could reach 73 mol% under CO₂ atmosphere, significantly larger than that obtained under hydrogen (H₂) atmosphere (ca. 50 mol%). In the absence of an external H₂ source, products in the range of aviation fuel are generated where aromatization of propene (C₃H₆), oxidative dehydrogenation (ODH) involving CO₂ and propane (C₃H₈) and hydrogen transfer reactions are found to account for hydrogen liberation in oleic acid and achieve its re-arrangement into the final alkane products.

The reaction pathway under CO₂ atmosphere is significantly different from that under H₂, as shown by the presence of 8-heptadecene, γ -stearolactone, and 3-heptadecene as reaction intermediates, as well as a CO formation pathway.^[115] Because of the highly dispersed Ni metal center on the zeolite support in the catalyst, H₂ spillover is observed under H₂ atmosphere, which inhibits the production of short-chain alkanes and reveals the inherent disadvantage of using H₂. CO₂ processing of oleic acid described in this manuscript can significantly contribute to future CO₂ utilization chemistries and provide an economic and promising approach for the production of sustainable alkane products within the range of aviation fuels.^[115]

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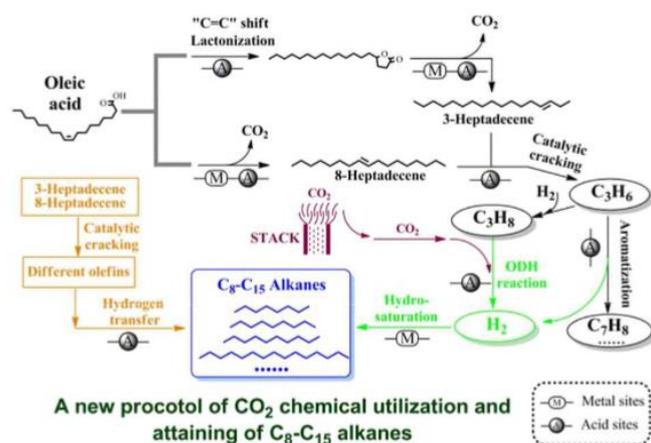


Figure 6. Schematic representation of the new protocol developed by Xing et al., taken from Ref.^[114]. Reproduced by permission of The Royal Society of Chemistry.

Last, but not least, an interesting recent dual catalysis approach enables the selective functionalization of unconventional feedstocks composed of complex fatty acid mixtures with highly unsaturated portions like eicosapentaenoate (20:5) along with monounsaturated compounds, as shown in Figure 7.^[116] The degree of unsaturation is unified by selective heterogeneous hydrogenation on Pd/γ-Al₂O₃, complemented by effective activation to a homogeneous carbonylation catalyst [(dtbpx)PdH(L)]⁺ by addition of diprotonated diphosphine (dtbpxH₂)(OTf)₂. By this one-pot approach, neat 20:5 as a model substrate could be hydrogenated up to 80% to the monounsaturated analogue (20:1), subsequently functionalized to the desired C₂₁ α,ω-diester building block with a linear selectivity over 90%. This catalytic approach is demonstrated to be suitable for crude microalgae oil from *Phaeodactylum tricornutum* genetically engineered for this purpose, as well as tall oil, an abundant lignocellulosic waste material. Both substrates were fully converted with an overall selectivity to the linear α,ω-diester of up to 75%.^[116]

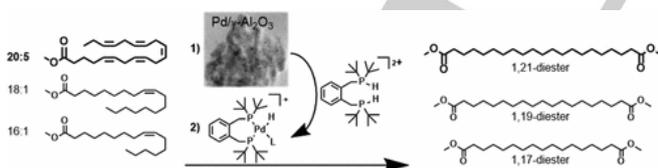


Figure 7. Selective functionalization of complex fatty. Reprinted (adapted) with permission from Ref.^[115]. Copyright (2017) American Chemical Society.

In addition to these, other interesting molecules including alkyl levulinates and gamma-valerolactone (GVL) have also interesting potential as compounds in biofuel blends and solvents. In particular, alkyl levulinates can be produced from lignocellulosic feedstocks (C₅ sugars) and have already been reported to be produced from furfuryl alcohol using alumina/SBA-15 heterogeneous catalysts.^[117]

A 20 wt% Al₂O₃/SBA-15 catalyst exhibited the best activity in the alcoholysis of furfuryl alcohol with *n*-butanol, giving 94% selectivity toward *n*-butyl levulinate in a batch process, with results also translated into a continuous flow process.

4. Conclusions and outlook

Catalysts normally employed in the synthesis of biofuels are expensive or show other disadvantages such as difficult removal from the product, low stability and low selectivity. Nanotechnology has developed nanocatalysts with intermediate characteristic between homogeneous and heterogeneous systems, combining the high activity of homogeneous catalysts, with the easy recovery of heterogeneous solid materials. Among the different possible options to produce biofuels, the alcoholysis of oils has been frequently utilized, especially for the synthesis of biodiesel. Most advanced nanocatalysts for the production of biodiesel are base nanocatalysts, acid nanocatalysts, and bi-functional nanocatalysts. Base nanocatalysts accelerate the reaction in mild reaction conditions, but need pure oils. In contrast, acid catalysts can catalyze the alcoholysis of low-grade feedstock, but in time-consuming processes. Bi-functional catalysts have been proposed as solutions for biodiesel production from low-grade oils in a one-step reaction, catalyzing at the same time the transesterification and esterification reaction of oils and fats. Nanocatalysts have been successfully employed also for the production of high density biofuels. Noteworthy, in addition to the utilization of biomass such as terpenoids or lignin as feedstock, high density biofuels have been prepared from plastic waste, offering additional possibilities to the conversion of waste-derived feedstocks into valuable products (biofuels) as part of the waste valorization concept.

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Keywords: nanocatalysis • biofuels • heterogeneous catalysis • Green Chemistry

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Rafael Luque (Departamento de Química Organica, Universidad de Córdoba) has a significant experience on biomass and waste valorisation practises to materials, fuels and chemicals as well as flow and nanoscale chemistry and green engineering. He has published over 330 peer-reviewed research articles, filed 4 patent applications and edited 10 books as well as numerous contributions to book chapters and keynote and plenary lectures in scientific events worldwide. Among recent awards, Rafael received the RSC Environment, Sustainability and Energy Early Career Award (2013) from the Royal Society of Chemistry UK, the 2015 Lu Jiayi lectureship from the College of Chemistry and Engineering in Xiamen University (China) and more recently the 2018 ACS Sustainable Chemistry & Engineering Lectureship award.



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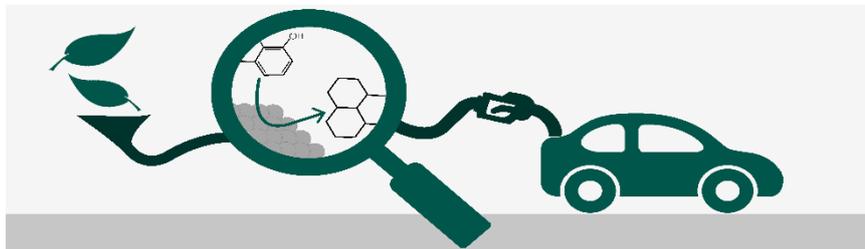
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Advances in nanocatalysts design
for biofuel production

Nanotechnology offers multiple possibilities for the sustainable conversion of biomass into biofuels. In this minireview, recent advances in nanocatalysts design for biofuels production are discussed.

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