

Review

Heterogeneous Catalytic Conversion of Terpenes into Biofuels: An Open Pathway to Sustainable Fuels

Magín Lapuerta ¹, Indira Tobío-Pérez ², Marianela Ortiz-Alvarez ³, David Donoso ¹, Laureano Canoira ⁴ and Ramón Piloto-Rodríguez ^{2,*}

¹ Escuela Técnica Superior de Ingenieros Industriales, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain

² Center for the Study of Renewable Energies, Universidad Tecnológica de La Habana “José A. Echeverría”, La Habana 19390, Cuba

³ Institute of Basic Sciences, Universidad Tecnológica de La Habana “José A. Echeverría”, La Habana 19390, Cuba

⁴ Tecminergy, Escuela Técnica Superior de Ingenieros de Minas y Energía, Universidad Politécnica de Madrid, 28031 Madrid, Spain

* Correspondence: rpiloto.rodriguez@gmail.com; Tel.: +53-52430232

Abstract: The production and use of terpene-based fuels represents a renewable source of energy in the transportation sector, especially in the aviation sector. The literature on the conversion of terpenes into valuable compounds is not new but has been based on the production of products for cosmetics and pharmaceuticals. Several established chemical routes are also a way to develop drop-in fuels. The present work explores all the main chemical processes that can transform terpenes into more valuable fuels or additives, focusing on the use of heterogeneous catalysis, catalyst type, operating conditions, and reaction performance. α -pinene is the most studied catalyst, since it is the main component of turpentine. Isomerization is the most frequently applied chemical pathway used to enhance fuel properties, and a wide group of heterogeneous catalysts have been reported, with sulphonic acid resin catalysts, transition metals, alumina, and silicates being the most used. This work also explores the current production and commercialization of terpenes, as well as the challenges for their use as fuels at a commercial scale. The future challenge is to discover new catalysts or to improve the performance of the current products and reduce production costs. The feasibility of the production and commercialization of terpene-derived fuels is also linked to oil prices.

Keywords: terpenes; terpenoids; biofuels; heterogeneous catalysis; drop-in fuels



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1. Introduction

The transportation sector worldwide is mainly based on the use of fossil fuels. Even though a turn to e-mobility is on the agenda for the world's main economies, the transition will take a long time, and it will be difficult to complete. Related to this, the search for alternative fuels or smart mobility is driven by strict regulations in the transport sector. The search for biofuels that meet international standards and regulations is a big issue for their use in internal combustion engines. In contrast to terrestrial transportation, where electric, hybrid, and other clean-energy vehicles are fully suitable and complementary, in aviation, this substitution is almost impossible, and, therefore, much effort has been devoted to the development of alternative jet fuels. Additionally, heavy industrial transport is also in need of the next generation of liquid biofuels with similar properties to conventional fuels [1]. The aviation sector needs to integrate biofuels into its activities. In reality, conventional jet fuel prices, the high demand for less pollution and renewable fuels, and the difficulty of electrifying this transport sector are some of the reasons for the inclusion of biofuels [2].

Advancements in process technology are providing alternatives for producing new fuels or processes focused on renewable energy sources. The processing technologies for the

production of liquid hydrocarbons may provide fuels that have similar properties to Jet A-1, thus increasing the number of potential drop-in alternative fuels. Jet A-1 is a kerosene-type fuel well suited to most airplanes (both civil and military), turbine engines, turboprops, and compression ignition engines [3]. Among other physical and chemical properties, it has a boiling point between 150 and 250 °C and a freezing point lower than that of Jet A-1 fuel. Jet A-1 fuel meets the ASTM D1655 specifications for aviation. Nevertheless, for its production, several issues must be taken into account, such as availability, renewability, sustainability, and Life Cycle Assessment (LCA) of the technology.

“Drop-in” fuels, which can be blended with standard jet fuels without any modification to the current technology in any aspect and also extended to the automotive sector, would ensure a fast implementation into the fuel market [4]. Until today, only six alternative fuels for aircraft have been accepted for blending with jet fuel and mainly biodiesel, bioethanol, and Hydrogenated Vegetable Oils for automotive fuel. In the case of aircraft fuel, some examples of incorporation of Fatty Acid Methyl Esters (FAME) blended with jet fuel are known, but over 5 mg/kg [5] of FAME cannot be used for specific technical reasons. The decarboxylation of fatty acids has produced potential aircraft biofuels, but these have poor cold flow behavior [6]. For fuels derived from the petrochemical industry, aromatic and other cyclic hydrocarbons efficiently increase the fuel density with little loss of gravimetric energy density. However, most alternative fuels have to be blended with their respective standard fuel in order to meet the density requirements. In addition to jet fuels, specialty military fuels have even more demanding density requirements [7], including the gravimetric net heating value, freezing and flash point, and storage stability, among others [8].

It is essential to evaluate the feedstock sources, extraction, conversion, quality, and final use of biofuels in order to achieve new sustainable and industrially feasible biofuels. One of the most promising feedstocks is terpenic waste [9]. However, there is a need to understand how to produce terpene-based fuels compatible with existing engine technologies, and in particular, it is important to understand their basic fuel properties. In a zero-waste context, using environmentally friendly technologies, their transformation using heterogeneous catalysis is a relevant issue [10].

The required fuel standards cannot be met by current renewables, and therefore specified fuel blends must be used. To address this need, terpenes have been investigated as precursors to become renewable high-density fuels [3].

Among the possibilities to replace conventional aviation fuels, terpenes, and their derivatives, including blends, are promising alternatives [11]. Nevertheless, terpenes' waste should be transformed before fueling engines, and direct use must be avoided. In this respect, terpenes can be enhanced by adding hydroxyl groups, carbonyls, ether bridges, etc. Knuutila [12] points out that the direct use of Crude Sulfate Turpentine (CST), a waste product from the paper industry, as engine fuel leads to fast contamination of engine oil with metal sulfides and deep corrosion of engine parts. To be used in engines, CST must be purified, eliminating all sulfur compounds and the excessive chemical unsaturation due to resin formation on the inlet valve. Nevertheless, the use of blends of turpentine with diesel and a cetane booster has been reported, pointing out its potential to be used in engines [13]. Yumrutas et al. [14] studied the use of purified sulfate turpentine on an engine, blending gasoline with turpentine at 5 and 10%. The results showed that through blending, the engine's performance is adequate but also increases NO_x, HC emissions, and exhaust temperature.

In some applications, particularly aircraft, oxygen and double bonds in fuel content are not desired because they negatively impact energy density and storage stability. Consequently, terpenes must be hydrogenated to saturated hydrocarbons prior to being used as fuels. On the other hand, poplar and switch grass can be modified to increase terpene production. A key factor to reaching commercialization is the increase in the metabolic efficiency of terpene production levels in microbes to the requested scale.

The suggestion of terpenoids as a potential feedstock for synthesizing advanced biofuels is not a new issue [15]. The rings in their structure are an advantage for synthesizing cycloalkanes. The most favorable examples include monoterpenes such as α -pinene [16,17], β -pinene [18,19], and limonene, the sesquiterpenes farnesene, and bisabolene, which can be used as fuel additives or directly as replacements for gasoline, jet fuel, and diesel [20–23].

Ninety percent of all commercially produced chemical products request the use of catalysts at some step in the production at any scale. Nowadays, the chemical industry is encouraged to develop cleaner processes, technologies, and products. Some of the advantages of using heterogeneous catalysts are easier catalyst separation and recovery, catalyst regeneration and reuse extended to several cycles, less use of chemicals, and lower prices compared to homogeneous catalysts depending on the catalyst technologies, materials, and precursors [24,25]. A main issue today is the development of heterogeneous catalysis, as well as its application at industrial scale processes in order to reduce production cost and environmental impact [26].

Terpenes are organic compounds derived from isoprene units (C_5H_8), whereas terpenoids are terpenes with additional functional groups, such as hydroxyl, epoxy, and carbonyl. Several terpenoid compounds used in the chemical industry are produced by the oxidation or acid-catalyzed transformations of more abundant terpene precursors. Most of these processes are still based on the use of oxidants or mineral acids, generating huge levels of industrial wastes [27].

The growing interest on this source for biofuel production can be represented through the number of publications in the last nine years on the field of synthesis of biofuels from terpenes. The yearly production of papers is represented in Figure 1. Data were gathered by the use of the artificial intelligence web app dimensions.ai. In addition to journal publications, 3160 patents and 52,540 policy documents were quantified in the same time period.

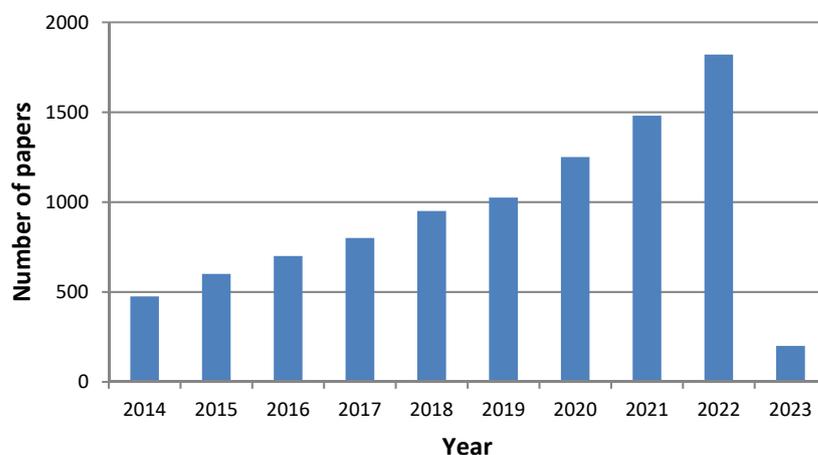


Figure 1. Publications on synthesis of biofuels from terpenes.

The scope of this work is to develop a comprehensive review of the different potential terpene-type biofuels, emphasizing the heterogeneous catalysis route for conversion of terpenes into fuels. The present work describes the main terpenes; biomass sources, such as their extraction, synthesis, and most used solid catalysts; and, finally, a survey of the actual scenario concerning their use at the industrial scale.

2. Terpenes and Turpentine

Terpenes are formed in the natural metabolism of plants, being present in leaves, flowers, and fruits. They constitute the essential oils of plants and traditionally have been used as fragrances and flavors, but have the potential to be used as cutting-edge biofuel precursors [9,23]. Terpenes (C_5H_8)_n have n isoprene units [28], and are hydrocarbons classified by the number of isoprene units (C_5), the most common being the monoterpenes (C_{10}),

sesqui-terpenes (C_{15}), diterpenes (C_{20}), sester-terpenes (C_{25}), and triterpenes (C_{30}) [28,29]. Table 1 shows a summary of some terpenes identified and some of their fuel properties for combustion in internal combustion engines. Terpenes are in both cyclic and acyclic forms.

Table 1. Terpenes suitable to replace or blend with standard liquid fuels.

Compound	Chemical Formula	Density (g/mL)	Kinematic Viscosity (mm ² /s at 40 °C)	Cetane Number
camphene	$C_{10}H_{16}$	0.842 [30]	34.96 [30]	29 [31]
β -caryophyllene	$C_{15}H_{24}$	0.900 (15 °C) [28]		29 [31]
1,8-cineole	$C_{10}H_{18}O$	0.920 (25 °C) [32]		
(-)- β -citronellene	$C_{10}H_{18}O$	0.760 (20 °C) [32]		
α/β -farnesene	$C_{15}H_{24}$	0.841 (20 °C) [32]		32 [28]
Geranial	$C_{10}H_{16}O$	0.887 (20 °C) [33]		
Geraniol	$C_{10}H_{18}O$	0.874 (25 °C) [34]	7.652 (25 °C) [34]	19.25 [31]
D-limonene	$C_{10}H_{16}$	0.841 (25 °C) [34]	1.089 (25 °C) [34]	18.9 [34]
Linalool	$C_{10}H_{18}O$	0.857 (25 °C) [34]	5.324 (25 °C) [34]	16.45 [34]
α -pinene	$C_{10}H_{16}$	0.855 (25 °C) [34]	1.502 (25 °C) [34]	23.13 [34]
β -pinene	$C_{10}H_{16}$	0.867 (25 °C) [34]	1.766 (25 °C) [34]	21.25 [31]
Sabinene	$C_{10}H_{16}$	0.844 (20 °C)		
Squalene	$C_{30}H_{50}$	0.858 (20 °C) [33]		
β -bisabolene	$C_{15}H_{30}$	0.809 (25 °C) [34]		32.2 [31]
γ -terpinene	$C_{10}H_{16}$	0.845 (25 °C) [34]	1.008 (25 °C) [34]	20.3 [31]
Nerol	$C_{10}H_{18}O$	0.876 (20 °C) [33]		
2-carene	$C_{10}H_{16}$	0.862 (25 °C)		
3-carene	$C_{10}H_{16}$	0.857 [8]		27 [31]
α -terpineol	$C_{10}H_{18}O$	0.931 (25 °C) [34]	40.08 (25 °C) [34]	

The qualitative and quantitative position of terpenes in lignocellulosic biomass composition is shown in Figure 2, demonstrating the relatively low yield limits for obtaining terpenes using a biomass route. Nevertheless, turpentine global production is estimated to be 330,000 t/year mainly obtained as a by-product of the pulp industry [35–37] in the manufacture of paper, and this is recognized as the most important source of terpenes [38,39]. The distributed worldwide production of turpentine in 2019 was 60% from the paper industry and 40% from the pine resin industry [40].

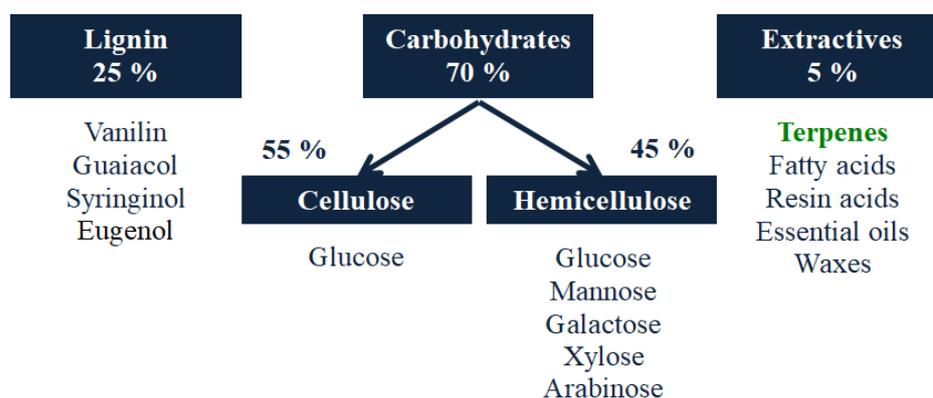


Figure 2. Presence of terpenes in lignocellulosic biomass.

An overview of the organic compounds associated with terpenes is shown in Figure 3. Due to its chemical–structural range (linear, cyclic, or polycyclic) and to the existence of double bonds with different reactivity, terpenes are very versatile [35].

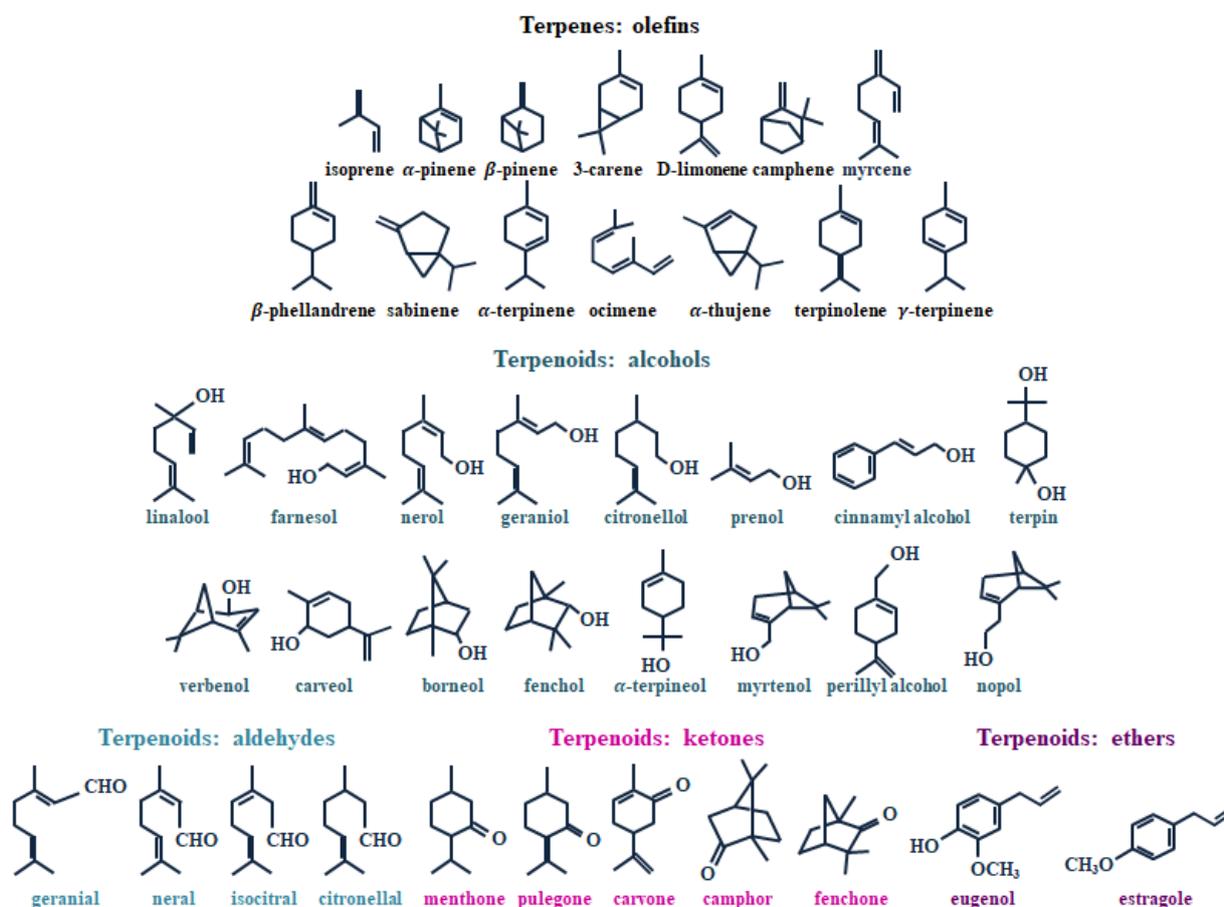


Figure 3. Main terpenes and terpenoids.

Turpentine is a collective name representing a natural product that can be obtained from different processes. It is mainly obtained via the distillation of resin harvested from living trees, mainly pines. It is mainly composed of monoterpenes but also of small quantities of sesqui-terpenes. The main compounds found in turpentine are α -pinene and β -pinene with very low amounts of D-limonene, camphene, and myrcene. Turpentine has a higher olefinic nature, as compared to hydrogenated and oxidized turpentine. Using vacuum distillation of pine resin, barely 20% of turpentine can be obtained. The bottom of vacuum distillation is rosin, representing 80% *w/w* of the resin, and represented by diterpenes with carboxylic acid functionality [7,29]. Turpentine has been formerly used as a solvent in paints, but it was banished by much cheaper petroleum derivatives. For this reason, currently, it can be considered as a secondary product or by-product of industry [4,7].

The cheapest commercial source of terpenes currently available is Crude Sulfate Turpentine (CST), a by-product of the pulp and paper industry [41]. Erman et al. [42] reported the extraction of α - and β -pinene from CST found in waste streams of paper and pulp mills. The authors found that the ratio of α - and β -pinene in CST depends on factors such as tree species and regional and seasonal conditions.

3. Processes for Valorization of Terpenic Feedstock as Fuels

Terpenes and terpenoids have an extensive use in industry as sources of fine chemicals, flavors, polymers, fragrances, etc. According to their chemical structure, they are suitable for catalytic conversion into fuels or fuel additives.

The chemical transformation of most of the terpene feedstocks is possible, versatile, and not new. This is an advantage to find cheap, effective, and efficient routes to upgrade or to transform basic terpenes into fine chemicals, especially to convert them into potentially useful biofuels. The use of a heterogeneous solid catalyst for this purpose has also been

well reported for several decades. An extensive review on the main transformation and upgrade of basic terpenes is reported by Swift [43]. A wide range and nature of solid catalysts can be used to transform basic terpenes using hydrogenation, isomerization, or other organic synthesis paths. An overview of the main solid catalysts reported for the conversion of terpenes is presented in Table 2, which is based on information collected, structured, and organized from a comprehensive report on this subject. As can be observed, most of the reports included in Table 2 show that researchers have used raw material for the synthesis based on commercial products and not the natural source, and many works do not include the assessment of catalyst reuse, meaning that the subject of study is not the catalyst performance and that the studies are not focused on reducing the cost of the process.

Table 2. Transformation of terpenes using solid catalysts.

Process	Terpenes	Source	Solid Catalysts	Yield (%)	Reuse Cycles	References	
Hydrogenation	Myrcene	Pine resin	Pd-charcoal/Ni-Raney	nr	nr	[4,43]	
	Limonene	Millipore	Ni-Raney/Pd/PtO ₂	89.4	nr	[4,44]	
	Terpinolene	nr	Ni-Raney	nr	nr	[43]	
	α -pinene	Millipore	Amberlyst-15/Ni-Raney/molecular sieve	85.8	nr	[44,45]	
	β -pinene	Pine resin	Ni-Raney	nr	nr	[4,43]	
	Camphene	Pine resin	Ni-Raney	nr	nr	[4,43]	
	Verbenone	nr	NiO-MgO/Sn-Pt/PtSiO ₂	nr	nr	[43,46]	
	Geraniol	Aldrich	Pt/PtO ₂ /Ni/MoS ₃ /Rh-based/Ru-based	98	nr	[43,47]	
	Citral	nr	Pd/MoS ₃ /Ni/Cr-based/Pt-SiO ₂	80–92	nr	[43,48]	
	Nerol	Fluka	SiO ₂ /Pt/SiO ₂ /Pt/H-Y	22–66	nr	[49]	
	Linalool	nr	Amberlyst 15/Pd-C	81	nr	[50]	
	Isomerization	α -pinene	nr	Ankalite KT-3/TiO ₂ /kaolin/natural zeolite/HCl-activated Montmorillonite/Al ₂ O ₃ /cation-exchanged bentonite/Ag-NiY zeolite/H ₃ PW ₁₂ O ₄₀ -SiO ₂ ;TiO ₂ ;ZrO ₂ ·nH ₂ O/Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ -Nb ₂ O ₅ ;ZrO ₂ ;TiO ₂	35.9–80	nr	[27,43,51,52]
		β -pinene	nr	HCl-activated Montmorillonite/TA-4/MA-4	35.9–83	nr	[43]
Dipentene		nr	MoS ₃ / γ -Al ₂ O ₃	nr	nr	[43]	
Limonene		nr	Ti-SBA-15	0–33	nr	[53]	
α -pinene		nr	Al-MCM-41	43–87	4	[54]	
Dimerization	β -pinene	Sigma	H ₃ PW ₁₂ O ₄₀ ·12-H ₂ O	nr	3	[55]	
Addition of alcohols	β -caryophyllene	copaiba oil	PW/PW-SiO ₂	70	nr	[27]	
	dihydromyrcene	nr	PW/PW-SiO ₂	nr	nr	[27]	
Hydration	α -pinene	Sigma Turpentine	HPW ₁₂ O ₄₀ /trichloroacetic acid-SiO ₂ ;TiO ₂ ;SiO ₂ ;Al ₂ O ₃ /Amberlyst 15/Y-Zeolite	10.2–35.5	3–8	[44,56–59]	
	β -pinene	GMP	Amberlyst 15	nr	nr	[36]	
Oxyfunctionalization	β -caryophyllene	copaiba oil	PW/SiO ₂	70	nr	[27,60]	
	α -terpineol	terpenic alcohols	AIPW ₁₂ O ₄₀	92–95	nr	[27]	
Acetoxylation	Limonene	nr	Amberlite IR120	nr	nr	[43]	
	Camphene	nr	PW/SiW-TiO ₂ /SiW-ZrO ₂	nr	nr	[27]	

nr: no reported.

Among different chemical process, hydrogenation, isomerization, dimerization, alkylation, oxyfunctionalization, hydration, addition of alcohols, and acetoxylation are the most attractive. Part of the life cycle of the production and use of biofuels from terpenes is shown in Figure 4.

Hydrogenation is a well-known chemical process in which double bonds react with Hydrogen to reduce or eliminate the unsaturation in an organic compound. For several applications, particularly actual aircraft engines, double bonds and oxygen are not acceptable since they significantly affect energy density and fuel stability, and in this respect, hydrogenation of terpenes plays an important role. The hydrogenation process of α -pinene to *cis*-pinane is shown in Figure 5 beside other chemical conversion processes. Terpenes must be hydrogenated to saturated hydrocarbons before they can be used as fuels [8]. On the other hand, its high sooting tendency makes turpentine inadequate as a

diesel fuel. Hydrogenation and oxyfunctionalization are the main processes used to tackle this drawback.

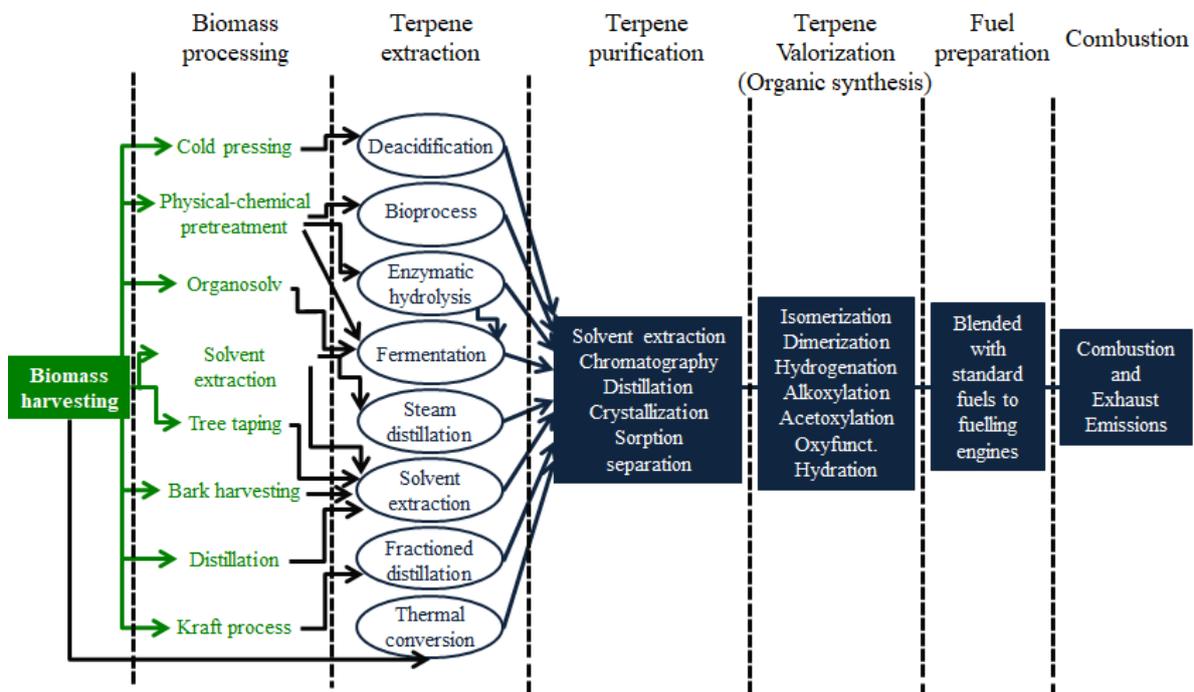


Figure 4. From well-to-wheel terpene processes, technologies, and pathways.

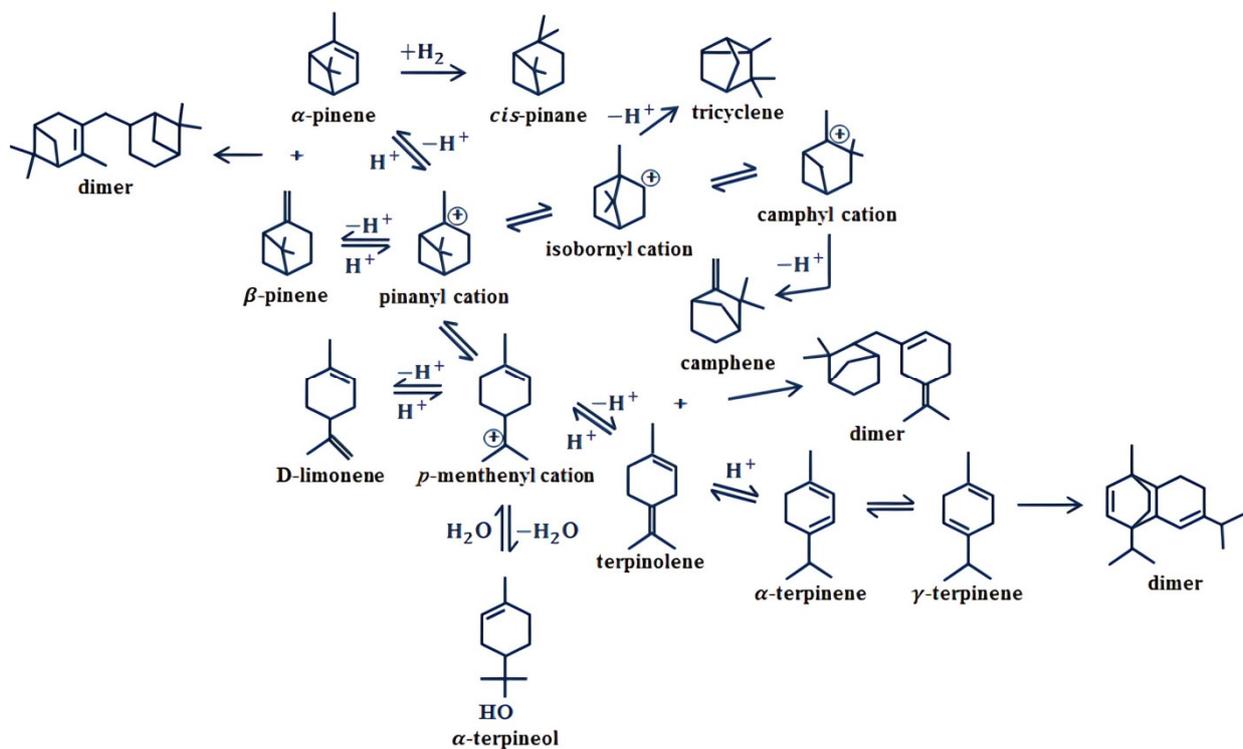


Figure 5. Reaction pathway scheme for the transformation of α -pinene and β -pinene based on acid catalysis.

Oxyfunctionalization is a type of chemical process in which Hydrogen is retired from a double bond structure and an oxygen group is introduced, changing the functional group of the terpene to ketones, aldehydes, esters, and ethers. This process is effective in changing characteristics of the terpene for its use as fuel or for other applications. For instance, oxyfunctionalized turpentine decreases particulate matter emissions, despite reducing its energy density [36], and low flash point can also be tackled using terpene oxyfunctionalization [40]. The chemical process for oxyfunctionalization of α -pinene to terpineol is shown in Figure 5.

The dimerization process with an acid catalyst is effective in synthesizing high-energy density fuels from turpentine [16]. The acid-catalyzed dimerization of α -pinene is accompanied by isomerization, which is followed by cross-dimerization, making the reaction mixture consistent in isomers of α -pinene and dimers. To develop saturated hydrocarbon fuels from terpenes, the biosynthetic route is an attractive way, wherein organisms may convert cellulose- and/or hemicellulose-derived sugar solutions into neat terpene products [30]. According to several authors [23,61,62], the biosynthetic way is the closest approach to a sustainable production of terpenes. On the other hand, the chemical approach based on the use of heterogeneous solid catalysts from natural sources or industrial wastes is another approach to find sustainable routes for the production of drop-in fuels.

Isomerization of terpenes improves their cold flow properties for their use as fuel components. On the other hand, alkoxylation is an effective process for enhancing low-temperature properties, such as cloud and pour points. Oxyfunctionalization helps to reduce the sooting tendency of turpentine by converting unsaturated hydrocarbons and cyclic compounds. Hydration is a chemical route to obtain α -terpineol from α -pinene, leading to a higher octane number, leading to potential improvements in brake thermal efficiency and reduction of HC and CO exhaust emissions. Some examples of isomerization and hydration processes are shown in Figure 4.

4. Heterogeneous Catalysis for Terpene Conversion

Heterogeneous catalysis implies that the solid catalyst can be easily separated from the reaction mixture, and this is an important advantage alongside the reality of catalyst reuse and the lower use of chemicals such as solvents in the process [25]. Many solid catalysts have been reported as being effective in heterogeneous catalysis for the conversion of terpenes into desirable liquid fuels, as is shown in Table 2. Sulfonic acid-type catalysts have sulfonated cross-linking polystyrene and are usually less corrosive, with lower environmental impact and more efficiency for conversion. Among several catalysts of this type, nonporous Nafion resins and porous Amberlyst are the most used.

Catalyst preparation strongly influences the reaction yield and the product mixture composition. Catalysts are often chemically treated with acids in order to activate their surfaces, improving the catalysts' performance.

Depending on the product target, availability of the solid catalyst or precursor, yield, selectivity, and conversion, several catalytic routes and processes can be established for the transformation of terpenes into valuable potential fuels.

4.1. Isomerization and Dimerization

Isomerization of α -pinene has been reported over many heterogeneous catalysts such as: TiO_2 , clays, halloysite, natural or synthetic zeolite, and active carbon. This process enhances the cold flow properties that are essential for fuels. The acid-catalyzed isomerization of α -pinene can be conducted in two parallel ways: one of them conducts to bi- and tricyclic products, as camphene, β -pinene, tricyclene and bornylene via ring expansion, whereas the other leads to limonene, terpinolene, p-cymene, and α - or β -terpinenes. Catalyst acidity has a significant influence on the ratio of the bicyclic and tricyclic molecules to monocyclic products [63]. Since α -pinene is the main component of turpentine, it is reasonable that the majority of reports are focused on its conversion via heterogeneous catalysis into valuable chemicals and fuels compared to other turpentine components. The main chemical routes

for the transformation of α - and β -pinene and its products based on acid catalysis are shown in Figure 5. The solid acid catalyst introduces the possibility of obtaining phenyl carbocation, leading to several transformation possibilities and products, determined by reaction conditions and the solid catalyst nature and characteristics.

Although terpenes and terpenoids have excellent cold flow properties, isomerization would be necessary in case of previous dimerization, since dimerization tends to worsen cold flow properties.

Montmorillonite clays are typically the most popular catalyst for pinene isomerization, although kaolin-based ones are also effective [26]. These clays containing the ferric ion exhibit the highest activity. The isomerization of α -pinene in the presence of acid-treated polycation-exchanged Montmorillonite clay leads to a higher yield of camphene compared to the alternative obtained by using non-polycation-exchanged equivalents [26]. The aluminum exchange cations used in combination with tetramethyl ammonium have lower effectiveness concerning isomerization of α -pinene than aluminum exchange clays due to a significant conversion decrease with the increase in tetramethyl ammonium amounts [64]. Alumina clays have demonstrated good activity and high selectivity with respect to camphene. The selectivity of the best catalysts based on clays in isomerization of α -pinene is 40–65% with respect to camphene, 15–40% with respect to limonene, and 70–90% for conversion of α -pinene [26].

There are several drawbacks related to the use of heterogeneous catalysis in the conversion of this family of compounds: (a) a main issue related to α -pinene isomerization is to attain high selectivity for the targeted products, because there is a group of reaction products that can be obtained; (b) industrial production of camphene with acidic TiO_2 has one important disadvantage, which is that the activated TiO_2 catalyst must be in situ activated by H_2SO_4 [24].

The isomerization of turpentine based on the utilization of different heterogeneous and homogeneous acid catalysts is reported by Handojo et al. [65] wherein they compared three different solid catalysts such as TiO_2 , SiO_2 , and zeolite. Each catalyst was prepared by saturating the solid precursor 50 wt.% of hydrochloric acid while heated up to 110 °C for 24 h. Then, the catalyst was activated and used for isomerization. Homogeneous catalysts consisting of sulfuric acid and formic acid were used for comparison with heterogeneous catalysis. For comparison purposes, homogeneous acid catalysts such as H_2SO_4 and formic acid were used. The results showed that for isomerization using a heterogeneous catalyst, the highest limonene yield was barely 24%, corresponding to the use of zeolites with 0.08 g/mL of turpentine blended with 1 M hydrochloric acid at 85 °C and 6 h of stirring. Through the use of homogeneous catalysis, the highest limonene yield was 48.2% achieved by combining H_2SO_4 and formic acid at the same temperature and reaction time, showing that the homogeneous acid catalyst achieves better isomerization and higher limonene yield compared to the solid catalyst.

Camphene and di-pentene are mostly produced by the isomerization of α -pinene. It is assumed that this process is catalyzed by Brønsted acid sites, which provide a proton that can freely be involved in the reaction. These active sites occur in acid catalysts (solid acids insoluble in α -pinene). The main paths of the reaction are the formation of camphene and a mixture of monocyclic terpenes (dipentene, terpinolene, α and γ terpinenes, and p-cymene) [66].

Yamamoto et al. [67] investigated the formation of active acid sites on silica-based rare earth oxide catalysts with the aim of determining the active site for α -pinene isomerization. Silica-based oxides reveal solid acidity for α -pinene isomerization, and the efficiency is dependent on the selected supported element (Pr, La, Tb, Sm, Eu, and Yb were tested).

Relevant experimental data collected from reports concerning the isomerization of terpenes by using heterogeneous catalysts are shown in Table 3. The most reported is the isomerization of α -pinene, since it is the main component in turpentine. According to Table 3, there is a wide group of heterogeneous catalysts effective for the isomerization of terpenes. Particularly in the case of α -pinene, many tests have been conducted. Nevertheless, several issues can be enhanced such as yield, which in many cases is relatively low, and attention must be paid to the selectivity to the isomerization products.

Table 3. Catalytic isomerization of terpenes (1 bar).

Reactant	Catalyst	Load (wt.%)	Temp. (°C)	Time (h)	X (%)	Y (%)	S (%)	Ref.
α -pinene	TiO ₂ -SO ₄₂	nr	nr	nr	91	61 ¹	67	[24]
	Fe-Mn-SZrO ₂	1	130	3	95	57 ¹	60	[68]
	MoO ₃ /ZrO ₂	nr	120	nr	93.5	56.8	60.7	[69]
	SO ₄₂ /ZrO ₂ -TiO ₂	nr	130	nr	96.6	55.4	57.4	[70]
	Al ³⁺ /TMA ⁺ /MMT	nr	120	1	83	55.6 ¹	67	[64]
	NH ₄ ⁺ /exchanged HY	3	150	1–4 min.	99	50.5 ¹	51	[24]
	SO ₄₂ ⁻ /ZrO ₂	nr	130	nr	88.8	49.2	55.4	[71]
	Kaolin	5.8	150	2	86	45.6 ¹	53	[72]
	Clinoptilolite-BaO	2.7	155	3	100	39.5 ^{1*}	39.5	[73]
	Clinoptilolite	2.5	155	2	92	43.73 ¹	48	[24]
	Raw clay	1	155	3	87	43.5 ¹	50	[63]
	Silica-alumina	3	30	0.5	99.8	42.9 ¹	43	[24]
	Y-zeolite	5.8	200	1	84	41.2 ¹	49	[24]
	Mordenite	5.8	120	1	92	35 ¹	38	[24]
	Ce ³⁺ /MMT	5.8	150	2	99	48.5 ¹	49	[72]
	Ag/NiY	nr	156		94.5	46.1	48.7	[74]
	natural zeolite	nr	155	3.25	100	37.8 ¹	37.8	[75]
	Yb/Al ₂ O ₃	3	50	3	63.2	32 ¹	49	[67]
	ion exchange resin	1	120	2	80	29.6 ¹	37	[76]
	Sulphated zirconia	9	60	4.03	66	21 ¹	32	[77]
	Yb/SiO ₂	3	50	3	26.5	6 ¹	23	[24]
	Y/SiO ₂	3	50	3	28.3	5 ¹	17	[24]
	HPWZr	1	130	20 min	8	3.6 ^{1*}	45	[52]
	HPWZr	1	130	2	14	7.14 ^{1*}	51	[52]
	HPWTi	1	130	20 min	12	6.12 ^{1*}	51	[52]
	HPWTi	1	130	2	55	25.85 ^{1*}	47	[52]
	HPWSi	1	130	20 min	96	8.64 ^{1*}	9	[52]
	HPWSi	1	80	20 min	42	21.84 ^{1*}	52	[52]
	HPWSi	1	80	2	93	34.41 ^{1*}	37	[52]
	HPWSi	1	45	20 min	8	4.16 ^{1*}	52	[52]
	HPWSi	1	45	2	20	10.40 ^{1*}	52	[52]
	Al-Si RB	3	130	6	85	46 ¹	54.12 [*]	[61]
	Al-Si RB (50 mL of 10% HCl)	0.5	130	5.5	85	48 ¹	56.47 [*]	[66]
Al-Si RB (50 mL of 10% H ₃ PO ₄)	1	130	1.7	85	49.1 ¹	57.76 [*]	[66]	
Al-Si RB	3	140	5.5	85	51.5 ¹	60.59 [*]	[66]	
Al/Diatomite	1	140	4	85	43 ¹	50	[66]	
ZSM-5/Bentonite	1	140	7	85	43.5 ¹	51.18 [*]	[66]	
β -pinene	γ -Al ₂ O ₃ -Na	nr	nr	nr	100	99.5 ²	99.5	[24]
	Cs _x O/ γ -Al ₂ O ₃	3	25	2	98	98 ²	100	[24]
	MgO	3	80	3	83.5	81.8 ¹	98	[24]
3-carene	0.1 wt.% Sn	2.7	120	4	48	37 ³	77	[24]
	2.6 wt.% Ni/SiO ₂	2.7	120	1	61	30.5 ³	50	[24]
α -pinene oxide	Sulphated Al ₂ O ₃	nr	0	1	100	76 ³	76 [*]	[78]
	B ₂ O ₃ /SiO ₂	15	25	4	84	58 ³	69	[79]

nr: no reported; ¹ camphene; ² α -pinene; ³ campholenic aldehyde; * calculated by authors. Where: Conversion; X (%) = $\frac{R_0 - R_t}{R_0} \cdot 100$; Selectivity; S (%) = $\frac{P_t}{R_0 - R_t} \cdot 100$; Yield; Y (%) = $\frac{P_t}{R_0} \cdot 100$. R₀ is initial reactant amount; R_t is reactant amount at instant t; P_t is product amount at instant t.

Via the synthesis of complex, high density, and less volatile fuel blends obtained by the heterogeneous, acid-catalyzed dimerization of β -pinene, jet fuel meeting the standards can be obtained [7]. In this case, a starting point based on β -pinene is caused by the simplicity of dimerization thanks to its exocyclic double bond. Nevertheless, dimerization affects volatility more than other fuel properties.

The dimerization of α -pinene is not new. In recent years, heterogeneous catalysts have been tested in this chemical process. Mesoporous materials, such as Al-MCM-41, dealuminated ferrierite-type zeolites, SO_3^{2-} , functionalized MCM-41, Ga-SBA-15, MSU-S, and HPW/MCM-41 have been used for α -pinene isomerization [54].

Meylemans et al. [30] used Nafion powder, Nafion NAC-13 (Nafion-silica nanocomposite), and Montmorillonite K10 (MMT-K10) in different experiments to convert α -pinene, (-)- β -pinene, (R)-(+)-limonene, camphene, and turpentine using dimerization reaction. For dimerization, heptane 40–100 mL was used as a solvent, and the reaction took place with stirring and heating at 100 °C and 2 to 12 h of reaction time. The authors removed all the solid catalyst by filtering; PtO_2 (100 mg/100 mL dimer) was added, and the blend was hydrogenated at room temperature under a Hydrogen pressure of 2.1–2.8 bar.

Meylemans et al. [80] produced high density fuel through solid-acid catalyzed dimerization of α -pinene, camphene, limonene, and crude turpentine. In this respect, several heterogeneous catalysts were tested such as Nafion, Montmorillonite K10 (MMT-K10) and Nafion SAC-13; in all cases, testing occurred under specific pretreatment and conditioning techniques. Concerning the use of Nafion SAC-13, it was not effective for the dimerization of neat α -pinene or camphene, meaning that the silica support reduces the catalyst acidity. Both catalysts, Nafion SAC-13 and MMT-K10, were effective for the dimerization of crude turpentine and blends of α -pinene and camphene.

MMT clay has been used more than other types of clay minerals. Cations present in the interlayer parent clay can be exchanged with high charge density cations such Al^{3+} and Fe^{3+} and, thus, acidity can be imparted in the clay. This property makes MMT a suitable heterogeneous catalyst [81]. On the other hand, the commercial polymer Nafion encloses active acidic sulfonic groups ($-\text{SO}_3\text{H}$) and is well reported as a heterogeneous catalyst in many synthesis processes [82].

A biphasic tandem catalytic process, efficient for the conversion of 1,8-cineole to the cycloalkane p-menthane, is reported by Yang et al. [15]. Almost 100% conversion of 1,8-cineole and 100% selectivity to p-menthane was achieved at 120 °C in 1 h.

The patent US9266792B2 [83] reports a highly efficient process for the dimerization of terpenes using a cost-effective solid-acid catalyst and low-cost equipment to produce jet/turbine and diesel-like biofuels with a high flash point and outstanding cold flow properties. The invention includes transition metals serving as catalysts chosen from the group Pd, Pt, Ni, and combinations, supported on a high surface substrate consisting of silicate, aluminate, zeolite, and other mesoporous inorganics.

Valorization of terpenes is in most cases based on the reaction of α -pinene in the presence of Heteropoly Acids (HPAs) to produce camphene and limonene using $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (0.15–5 wt.%) catalysts at 30–100 °C. The use of HPA catalysts typically reaches near 80% yield of camphene and limonene [60], which is high compared to other catalysts. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ catalyst brings a camphene yield of 51% after 15 h of reaction on stream [46]. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on mesoporous silica is also reported for the aromatization of α -pinene with a yield of p-cymene of 70% [84]. HPAs have attracted considerable interest as catalysts due to their multifunctionality and their well-defined structures, being strong acids more active than conventional acid catalysts, zeolites, or ion-exchange resins [32,85]. They are less corrosive compared to mineral acids and do not lead to unwanted side reactions, such as sulfonation and chlorination.

Besides isomerization and dimerization, other reactions for the valorization of terpenes are reported. Among them, hydrogenation, hydration, dehydration, alkoxylation, oxyfunctionalization, acetoxylation, etherification, and esterification are possible pathways.

4.2. Hydrogenation

Menthol hydrogenation on Nb₂O₅-supported catalysts effectively led to high yields of p-menthane with fuel properties under the specifications of aircraft fuels [86]. Among the studied metals, Palladium and Platinum showed higher effectiveness, with around 90% of yield, while the lower hydrogenation activity of Ruthenium led to p-menthane. The reaction proceeded as a cascade reaction, wherein acid-catalyzed menthol dehydration and metal-catalyzed cycloalkane hydrogenation conducted to the formation of cycloalkane. The reaction temperature and the balance between acid and metal sites were the most influencing factors on catalyst performance.

Hydrogenation of α -pinene over Platinum nanoparticles reduced and stabilized by sodium lignosulfonate is reported by Chen et al. [87]. A catalyst based on stable Platinum nanoparticles was prepared using sodium lignosulfonate acting as a stabilizing and reducing agent. The nanoparticle system showed high efficiency for α -pinene hydrogenation in obtaining cis-pinane.

A series of commercially available heterogeneous catalysts based on different active metals (Pd, Pt, Ru, and Rh) supported on charcoal and alumina were studied by Moutombi et al. [88] for the hydrogenation of pinenes to assess the influence of the active metals, supports, and reaction conditions on catalytic activity and selectivity. Among the catalysts, Ruthenium was the most selective and Palladium, the least. In general, the supports showed a high influence on the catalytic properties, but the effect was strongly linked to the metal tested. Activation by sonication had a slight effect on the hydrogenation of pinenes except when Ruthenium was used. In the case of sonication to Ru/C, a complete and selective solvent-free hydrogenation of pinenes in favor of cis-pinane was reached. On the other hand, sonication of Ru/Al₂O₃ fully deactivated the catalyst, which was able to efficiently hydrogenate favoring the obtaining of cis-pinane without sonication.

4.3. Alkoxylation

Castinheiro et al. [85] tested different variants of solid catalysts with a base of PW-SBA impregnated with HPA at loads of HPA between 1.8 and 19.3%. The performance of the catalysts was based on the conversion of α -pinene, β -pinene, and limonene through alkoxylation. PW4-SBA-15 with 10.8% showed the highest catalytic activity for the alkoxylation of α -pinene with ethanol. This catalyst was used for the alkoxylation of other terpenes, including β -pinene and limonene. PW4-SBA-15 showed high catalytic stability for the alkoxylation of α -pinene with ethanol. The highest yield obtained was 51.2% and the main drawback associated with the processes studied was the long time spent (85 h) to reach relatively low yields.

The Ce salt of tungstophosphoric heteropoly acid, Cs_{2.5}H_{0.5}PW₁₂O₄₀, is an active and environmentally friendly solid-acid catalyst for the liquid-phase alkoxylation of a wide range of monoterpenes, such as camphene, limonene, α -pinene, and β -pinene. Through this process, isobornyl or α -terpenyl ethers can be obtained. The reaction occurs under equilibrium conditions and no catalyst leaching takes place. Heteropoly acid H₃PW₁₂O₄₀ also efficiently catalyzes the alkoxylation of these monoterpenes under homogeneous conditions [89]. Some experiments on α -pinene alkoxylation are described in Table 4.

4.4. Acetoxylation

Sutijan et al. [90] evaluated the direct acetoxylation of turpentine using macropore and strong acidic cation exchange resin Amberlyst 36 wet as a catalyst. Acetoxylation of α -pinene produces several compounds including isomers (camphene, limonene, terpinenes, and terpinolene), which have high potential for their use as biofuels. The experiments were developed in a reactor with stirring. Equal volumes of turpentine and glacial acetic acid were added to the batch reactor. The mixture was then stirred and heated up, 5 wt.% catalyst was added, and the reaction time was 8 h. The reaction temperature was varied between 45–90 °C among experiments. The yield of isomers over reaction time at various temperatures was 50% at 45 °C at 8 h, near 85% at 60 °C, 80% at 75 °C, and at 90 °C in less than 1 h the maximum yield was obtained, but it was significantly decreased when the reaction was settled for longer times, being around 60% at 8 h due to the development of parallel reactions.

Acetoxylation of limonene and α -pinene into terpineol and terpinyl acetate was studied using a transition metal and a rare earth ion-exchanged beta zeolite [91]. The tested catalysts under optimized operating parameters showed higher activity and selectivity compared to conventional acid catalysts such as H₂SO₄ and Amberlyst-15. Conversions of 9 to 26% using glacial acid and 58 to 82% with acetic acid were obtained, and the selectivity for the main products α -terpinyl acetate and terpineol were 54% and 65%, respectively. Conversions of 62 to 100% and 72 to 100% were obtained for α -pinene for glacial and aqueous acetic acid, respectively. No undesired oligomerization of monoterpenes took place under the selected experimental conditions.

4.5. Oxyfunctionalization

One way for the valorization of turpentine is the oxyfunctionalization of its components obtaining a range of alcohols such as α -terpineol (from α -pinene or limonene via hydration), nopol, borneol, myrtenol, verbenol, and pinocarveol [36]. The reaction mechanism suggested for obtaining α -terpineol from α -pinene and limonene involves the formation of an intermediate with a carbenium ion, which is subjected to nucleophilic attack by water molecules to form α -terpineol [92].

Garcia et al. [36] studied the production of nopol via a β -pinene and paraformaldehyde reaction over a solid catalyst. The Prins reaction was performed with turpentine as the β -pinene source, in order to avoid the use of solvents, leading to full conversion of β -pinene and a high selectivity toward nopol, which was higher than 99%. According to the authors, α -pinene may act as solvent. The reaction was scaled up to produce up to 3.5 L of oxyturpentine with favorable results. The Sn-MCM-41 catalyst was obtained through hydrothermal treatment at room temperature, bringing an easy scale-up of the process.

Aguas et al. [93] explored the oxyfunctionalization of turpentine. The selective condensation of β -pinene presented in turpentine over the catalyst Sn-MCM-41 was effectively developed. According to the authors, turpentine oil can be oxyfunctionalized to the nopol molecule with 81% yield and 92% selectivity after 24 h of reaction. According to their findings, oxyfunctionalization might be scaled without substantial modifications.

4.6. Hydration

The hydration of α -pinene can be performed in aqueous acetone solutions by using H₃PMo₁₂O₄₀ acid immobilized on various solid materials as the catalyst. H₃PMo₁₂O₄₀ acts as a polymeric membrane allowing α -terpineol to be obtained from α -pinene with 65 to 75% selectivity and 80 to 90% conversion. An increase in membrane hydrophobicity increases the selectivity for α -terpineol [27].

The hydration of α -pinene by acid catalysis leads to a complex mixture of monoterpenes (alcohols and hydrocarbons). α -pinene reacts in acid medium, leading to terpenic hydrocarbons via organic ring expansion, obtaining products such as camphene and bornylene, or via the opening of the four-carbon ring, obtaining p-menthanes such limonene, terpinolene and γ -terpinene. Through the hydration reaction with acid catalyst, in addition

to the products mentioned above, α -terpineol and borneol are also obtained [56]. Mochida et al. [57] reported the use of zeolites for α -pinene hydration reaching 100% conversion, with around 57% of selectivity towards alcohols.

Avila et al. [56] tested a solid catalyst TCA/ZrO₂·nH₂O for hydration of α -pinene. The conversion to alcohols had a conversion of 27–96%, depending on reaction time. The highest percentage was achieved for 5 h at 80 °C and a selectivity of 91%. Further, two catalyst runs were considered, showing an increase in selectivity but a decrease in conversion. The carboxylate group of trichloroacetic acid incorporated Zirconium, forming a ring, which enabled the increase in the carboxylate group loaded onto the support, improving acidity.

Xie et al. [94] used kraft lignin to prepare biomass carbon-based catalysts via an incomplete carbonization at 400 °C with loaded phosphoric acid and -SO₃H groups at 180 °C. The conversion of α -pinene and the selectivity of α -terpineol reached 95.3% and 55.3%, respectively. The authors noticed that the pore structure of the catalysts could be controlled by adjusting the phosphoric acid dosage during lignin carbonization. The catalyst had a strong catalytic activity on the synthesis of α -terpineol from hydration of α -pinene, showing a conversion of 97.8% and yield of 52.2%, higher than that obtained using H₂SO₄ or Amberlyst-15 based on the same experimental conditions. Furthermore, it was observed that oxygen-containing groups such as carboxyl, hydroxyl, and carbonyl functioning as binding sites in the catalyst were considerably enriched after sulfonation, playing an important role on the increase in selectivity.

Wei et al. [95] developed and tested a Carbon-Based Solid Acid Catalyst using rice straw for the hydration of α -pinene to α -terpineol. The solid catalyst precursor was prepared via the calcination of raw straw at different temperatures. The performance of the catalyst based on the selectivity and conversion percentage showed that the conversion of α -pinene and the selectivity of α -terpineol reached 67.6% and 57.07% at 80 °C and atmospheric pressure in 24 h, respectively. The main results for any experimental condition are shown in Table 4 beside other selected conversion pathways and reaction conditions. Since the calcination temperature reached 350 °C, the biomass surface was irregular and cracked, which was associated with the increase in carbonization temperature that might lead to extreme breakdown of the macromolecules and cracking of glycosidic bonds. At 240 °C, massive tearing structures were observed, which might be associated with rice straw-retained, partially bound water and the structure of original cellulose at low-temperature carbonization in concentrated H₂SO₄. The biomass precursor activation included chemical activation by sulfonation. With the increase in carbonization temperature, the pore structure of the catalyst was enhanced and became more abundant, and the overall structure of the catalyst looked split and damaged. The first phenomenon is associated with the soft structure of precursor under low carbonization temperature, which is changed by concentrated H₂SO₄ during sulfonation, including dehydration, hydrolysis, and -SO₃H groups loading.

Vital et al. [96,97] studied the acid-catalyzed hydration of α -pinene yielding a complex mixture of monoterpenes, alcohols, and hydrocarbons. By controlling the reaction parameters, it was possible to develop a selective process to α -terpineol. With this purpose, the authors conducted the hydration reaction of α -pinene catalyzed by polydimethylsiloxane membranes filled with zeolite USY, β -zeolite, or a surface-modified activated carbon. Seven membrane formulations were tested with catalyst loads between 21.9 and 52.8%. Near 70% of selectivity and 100% conversion was achieved in certain cases. Nevertheless, the highest selectivity was only achieved between 100 and 200 h of reaction.

Wijayati et al. [58] tested a TCA/Y-zeolite catalyst to convert α -pinene into hydrocarbons, reaching 66% of conversion and 55% selectivity for α -terpineol at 10 min: a remarkable reaction time compared to other reports. The achieved results were due to the catalyst's strong acidity.

Table 4. Catalytic conversion of terpenes and terpene oxides (1 bar).

Process	Reactant	Catalyst	Load (wt.%)	Temp. (°C)	Time (h)	X (%)	Y (%)	S (%)	Ref.
Hydration	α -pinene	Sulphonated carbon	21.9–46.5	50	nr	95	55.1 ⁷	58	[96]
		TCA/ZrO ₂ ·nH ₂ O	15	80	2	57	32.49 ^{7*}	57	[56]
		Kraft lignin	15	80	24	97.8	52.2 ^{7*}	53.4	[94]
		Amberlyst 15	20	70	nr	93.12	35.2 ^{7*}	39.21	[59]
		Rice straw ^{ct} 240 °C	11.6	80	24	57.23	20.18 ^{7*}	35.27	[95]
		Rice straw ^{ct} 300 °C	11.6	80	24	67.60	38.58 ^{7*}	57.07	[95]
		Rice straw ^{ct} 350 °C	11.6	80	24	84.16	11.10 ^{7*}	13.20	[95]
		Rice straw ^{ct} 300 °C	11.6	50	24	55.33	20.39 ^{7*}	36.85	[95]
		Rice straw ^{ct} 300 °C	11.6	120	24	74.05	25.19 ^{7*}	34.02	[95]
Oxyfunctionalization		Cr-APO ₅	nr	80	nr	85	65.6 ²	77	[24]
		Pt-Nb ₂ O ₅	nr	170	360	99	nr	95	[86]
Alkoxylation		PW1-SBA15	1.8	80	85	62	32.9 ⁶	53	[85]
		PW2-SBA15	6.5	80	85	73	38 ⁶	52	[85]
		PW3-SBA15	7.7	80	85	84	45.4 ⁶	54	[85]
		PW4-SBA15	10.2	80	85	93	51.2 ⁶	55	[85]
		PW5-SBA15	19.3	80	85	79	41.9 ⁶	53	[85]
		PW4-SBA15	10.2	80	85	99	48.5 ⁶	49	[85]
Hydrogenation	β -pinene limonene pinane-2-hydroperoxide	PW4-SBA15	10.2	80	85	99	48.5 ⁶	49	[85]
		PW4-SBA15	10.2	80	85	55	35.8 ⁶	65	[85]
		Pd/C	4	20–80 (1–11 bar)	nr	100	90.5 ³	90.5	[98]
		Pd-Charcoal	10	25	240	100	68 ⁹	nr	[88]
		Pd-Charcoal	10	25	240	100	72 ⁹	nr	[88]
		Pt-Alumina	5	25	2880	95	93	nr	[88]
		Pt-Alumina	5	25	2880	96	88	nr	[88]
Hydrodeoxygenation	Menthol	Pd/C	4	20 (11 bar)	nr	nr	83 ⁴	nr	[98]
		Nb ₂ O ₅	0.5 ^{c/m}	190 (20 bar)	4	100	3 ⁵	3	[86]
		Ru/Nb ₂ O ₅	0.5 ^{c/m}	190 (20 bar)	4	71	38 ⁵	54	[86]
		Ru/SiO ₂	0.5 ^{c/m}	190 (20 bar)	4	12	2 ⁵	17	[86]
		Pd/Nb ₂ O ₅	0.5 ^{c/m}	190 (20 bar)	4	100	88 ⁵	88	[86]
		Pd/SiO ₂	0.5 ^{c/m}	190 (20 bar)	4	18	11 ⁵	59	[86]
		Pt/Nb ₂ O ₅	0.5 ^{c/m}	190 (20 bar)	4	100	86 ⁵	86	[86]
		Low dispersion Pt/Nb ₂ O ₅	0.5 ^{c/m}	190 (20 bar)	4	99	94 ⁵	95	[86]
		Low dispersion Pt/Nb ₂ O ₅	0.5 ^{c/m}	170 (20 bar)	4	99	94 ⁵	95	[86]
		Low dispersion Pt/Nb ₂ O ₅	0.5 ^{c/m}	150 (20 bar)	4	18	10 ⁵	57	[86]
conversion to methyl cyclopentadiene	linalool	Ru-based organic	0.1–5 mol.%	25–60	15 min–16 h	nr	0–100 ⁸	nr	[80]

nr: no reported; ^{ct} calcination temperature; ² verbenone; ³ pinane-2-ol; ⁴ pinane-hydroperoxide; ⁵ *p*-menthane; ⁶ α -terpinyl ethyl ether; ⁷ α -terpineol; ⁸ methyl cyclopentadiene dimer; ⁹ *cis*-pinane; ^{c/m} catalyst:menthol ratio; * calculated by authors.

The information gathered and included in Tables 3 and 4 show no information concerning the recycling of catalysts and their efficiencies after reuse. This could be related to the fact that the majority of works are not focused on the catalyst itself, but on the chemical process. A compilation of published information regarding this catalyst parameter is shown in Table 5. The efficiency of the catalyst reuse can be analyzed by the conversion loss. In general, it is not usual to find reports of reuse exceeding four times. Nevertheless, three cases are over this value without a significant decrease in conversion. It is important to point out that the conversion loss with the number of reuse cycles in a process is dependent not only on the catalyst type, but on its amount and reaction operating conditions. On the other hand, the conversion loss values in Table 5 represent the maximum value reported in a particular research project, but fewer values can be found in experiments within the same experimental work. Neither reuse nor catalyst regeneration are generally included on studies about terpene conversion. Regeneration can extend the reuse of the catalyst for considerable additional cycles. According to the research works included in this review but also in the vast number

of papers revised, there is a gap between those works including the catalyst reuse and its impact on process cost or sustainability of the conversion process. Nevertheless, those works focused on biofuels production deal with this since the reuse of catalysts is an environmentally friendly practice and may directly impact the biofuels' production costs. According to the information gathered in Table 5, the solid catalysts based on Titanium are more effective in reuse. There are other catalysts showing variable performance, depending on the process, but also on operating parameters not described in Table 5.

Table 5. Catalyst reuse and conversion loss in terpene conversion processes.

Process	Catalyst	Reuse Cycles	Conversion Loss (%)	Ref.
α -pinene isomerization	Pd colloidal	10	5	[99]
	Titanates	4	1	[100]
	Clinoptilolite with Fe and Cr	4	3	[101]
	TiO ₂	8	5	[102]
	Pd-Zn supported on Al-SBA15	3	36	[103]
	H ₄ SiW ₁₂ O ₄₀	3	36	[104]
	TiO ₂	8	6	[105]
	H ₃ PW ₁₂ O ₄₀	3	4	[106]
	Titanates	7	0	[100]
	SPION-Nb30	5	18	[107]
β -pinene isomerization	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	2	1.5	[89]
Terpenes isomerization	Pd/C and Pd/alumina	13	1	[108]
Caryophyllene isomerization	Pd/glass	3	4	[109]
α -pinene hydrogenation	Pd-Al-MCM-41	5	8	[110]
β -pinene hydrogenation	SiO ₂ /Al ₂ O ₃ /Al-MCM-41	4	3	[54]
β -pinene dimerization	[Fe(L) ₂ (H ₂ O) ₂]-Y	4	3	[111]
α -pinene oxyfunctionalization	zeolite-Y immobilized binuclear complexes	2	2	[112]
α -pinene oxyfunctionalization	zeolite-Y immobilized binuclear complexes	2	3	[112]
Limonene oxyfunctionalization	H ₃ PW ₁₂ O ₄₀	2	0	[60]
β -caryophyllene acetoxylation	Amberlyst 70	3	60	[113]
α -pinene acetoxylation	Sn-MCM-41	4	0	[93]
Turpentine oxyfunctionalization				

One recurrent fact mentioned in every paper, in spite of whether the work checks it or not, is the ease of catalyst recovery, reuse, and regeneration. One main problem to deal with is the leaching of catalyst active sites during reaction and catalyst reuse. The main cause of deactivation of heterogeneous catalysts is the leaching of either the metal and/or the supporting materials during the chemical process, causing a loss of catalytic activity and an amount of catalyst. In this respect, the selection of the catalyst, amount, and the impregnation method and supported materials are essential. Costa et al. [114] showed that silica-supported H₃PW₁₂O₄₀ and Cs_{0.5}H_{0.5}PW₁₂O₄₀ can be used without HPA leaching under mild conditions for the conversion of limonene, α -pinene, and β -pinene.

The silica-occluded HPA catalysts prepared by sol-gel are stable towards leaching at moderate HPA loading [115]. Supported HPAs can be used as heterogeneous catalysts in non-polar and weakly polar media without expecting leaching problems [89]. In the isomerization of caryophyllene, HPA and HPW/SiO₂ are reported as catalysts with no significant evidence of leaching [89]. In the alkoxylation of camphene or the isomerization of α -pinene, silica-occluded tungstophosphoric acid can be recovered and reused without significant loss of selectivity [115,116]. HPA has shown no leaching effect in the isomerization of α -pinene [117]. Particularly for the hydrogenation of citral, the use of H₃PW₁₂O₄₀ implies a risk of leaching [117], which could be associated with the significant conversion loss in α -pinene isomerization [103,104].

Szücs-Balázs et al. [104] studied H₄SiW₁₂O₄₀ catalysts supported on SiO₂, TiO₂ and HZSM-5 for α -pinene isomerization. According to their findings, no leaching effect was observed at any of the experimental conditions.

For biomass conversion, Ni catalysts supported on ZrO₂, TiO₂, and ZrO₂/TiO₂ are more stable to leaching than Ni/SiO₂ due to the absence of support leaching [118], and due to this, the substitution of Ni with Ru is a common practice.

SPION-Nb30@HPW has been tested as a recyclable catalyst for the selective isomerization of terpenes. No significant loss/leaching of any component of the catalyst during the

isomerization reaction was observed [107]. On the other hand, the Ti-SBA-15 catalyst has shown higher stability and resistance to Ti leaching, and therefore it is reported for its use in the isomerization of limonene [53].

5. Production and Commercialization of Terpenes: Challenges for Their Use as Fuels

In 2019, 316,000 t of turpentine was produced around the world, of which 125,000 t was obtained from pine resin, 185,000 t from the paper industry, and only 6000 t from stump wood. China is the largest producer of turpentine in the world, being responsible for half of the global production, followed by Brazil. Other countries with important production levels are Indonesia, the United States of America, Portugal, Spain, Vietnam, Argentina, Mexico, and India [4].

There are more than one hundred countries around the world planting Eucalyptus, covering over 20 million hectares, making it the most widely planted broad-leaved tree species worldwide. More than 90% of the components of eucalyptus oil consists of 1,8-cineole [119]. As a fuel precursor, 1,8-cineole is converted to p-menthane, which is in the aircraft range of fuels. Nevertheless, the conversion process involves a series of reactions which frequently bring poor selectivity to p-menthane [15].

Commercially, terpenes have several industrial uses as agrochemicals, fragrances, nutraceuticals, and pharmaceuticals [6]. Terpenes are generally extracted using steam distillation. These extracts and steam distillates, also known as essential oils, are widely used to create perfumes, to refine flavors and aromas demanded by several industries, and for medicine. Terpenes and their derivatives represent a USD 650 million market globally [120]. They can also be manufactured from petrochemical sources and from terpene feedstocks. For instance, isoprene can be obtained through oil cracking, or as a by-product of naphtha. They are also extracted in small amounts from natural sources. The disadvantage of these processes is related to the production cost and the negative environmental impact generated by them. Due to the actual and future demand of terpenes, more economic and eco-friendly processes and related technologies are needed. Nonetheless, these methods must use inexpensive and non-toxic feedstocks. In this respect, microbial fermentation is a clear alternative for terpene production. Even so, not all bacteria can produce terpenes and/or their precursors as metabolic products. The application of biotechnology and genetic engineering to plants may considerably increase the yield of terpenes extracted, leading to a more attractive pathway and to further commercialization of products. Increases in more than 78% in monoterpene content after metabolic engineering is reported [121,122].

In recent years, biotechnology researchers have been reaching considerable advances in DNA and RNA sequencing, proteomics, and modification/editing tools such as CRISPR. According to Mewalal et al. [9], this is a favorable platform for the commercial scaling of terpenes in the near future.

In the past, commercial-scale production of specific terpenes in plants was limited by relatively low yield, but today, some commercial-scale recovery of terpenes is established in biomasses such as pine, eucalypts, mints, and citrus. During the first ten years of growth, pine trees with an average of 4% wood terpene content may produce 40 GJ/ha/year of green energy [9].

From the same feedstocks, Wu et al. [123] estimate 206 GJ/ha/year. At 500 kg/ha/year, terpene production should find industrial uses in the energy sector. 20 million ha may produce 10 million tons of high-energy jet fuel [9], which could be used as standard fuel additives.

Due to the wide range of sources of terpenes, there are important differences concerning production capabilities, cost of extraction, isolation, purification, and conversion, beside different levels of environmental impact and energy demand, especially for the distillation processes. On the other hand, sources are tackled by other feasibility constraints and concerns such as land availability. In this respect, most of the mentioned constraints are common for synthetically or biomass-produced terpenes.

Researchers have explored the production of such compounds from biomass pyrolysis, but profitability in a short or medium term must be attended to. For example, the addition of down-stream steps focused on the extraction of terpenes could lead to more sustainable and profitable activity [124].

Despite the potential economic and environmental benefits of terpenes from biomass, several challenges must be overcome. Different species show different terpene content profiles, even influenced by stress and seasonal changes for the same strains [9]. A detailed proposal roadmap presented by Mewalal et al. [11] for the commercialization of specific terpenes proposes a system–biology approach through different plant organs. Nevertheless, how to overcome the scalability of the proposed road is not fully described. According to the authors, the development of short-rotation genotypes has the potential to reach high yields in the short and medium term.

Intensive silvicultural management could also play an important role in maintaining and increasing the productivity of selected plants. Silviculture considerations may also include plantation sites, planting density, crop rotation (harvesting), fertilizer requirements, and pest management. For terpene production, in the case of Eucalyptus, shorter rotations will be advantageous, and 3000–5000 trees/ha are needed to boost productivity [125].

For commercial production, key factors include the levels of production and efficiency. In this respect, microbes may help to meet goals. For instance, bacteria would increase production of bisabolene to commercial levels, but even when it is similar to diesel fuel, the key to making it feasible economically requires production at high yields. Nevertheless, for the advance in industrial scale biofuel production from terpenes by applying biotechnology, they should be produced in microbes with a similar metabolic efficiency as ethanol, which is still not possible today.

Amyris, a publicly traded company in Brazil, has produced terpene-based diesel-fueled buses in service for more than 5 million miles, and their terpene-based aircraft fuels have also been used. Their SIP-SPK jet fuel starts off as the terpene farnesene, produced directly from a microbe, and this is an interesting example showing the potential of production and use of biofuels made from terpenes. It is estimated that bisabolene could be produced at a final cost of 1.76 USD/kg. Currently, turpentine is commercialized in the market at around 1.3 EUR/L, but a decrease in the near future is expected. For pine resin with a productivity of 4 kg/pine/y, the biofuel's cost would be 0.54 EUR/kg, and increasing the productivity to 6 kg/pine/y could reduce the production cost to 0.44 EUR/kg, which could be competitive with fossil fuels [40]. The challenge is to compete with the price of petroleum fuels and to develop new catalysts with high catalytic activity, selectivity, and operation at low temperatures in a short reaction time [126].

Plant extraction consumes large amounts of natural resources due to the low terpene content, and the downstream separation of similar terpenes in the extracts converts the separation into a complex process, limiting the extraction efficiency. In this respect, microbial conversion has the potential to tackle most of these drawbacks, but the microbial synthesis of terpenes is dependent on pathways based on microorganisms with low tolerance to toxicity. Due to this, the finding of effective microorganisms and the development of multilevel engineering strategies to increase biofuel's yield is a main developmental line. On the other hand, CRISPR technology may represent another way to reach industrial-scale production of terpenes.

Metal-based catalysts are still an insufficiently explored technology to cover the actual scale-up production of terpenes and their upgrading. Most of the solid catalysts reported and used are based on metals and zeolites. Nevertheless, zeolite's tuning and metal doping (by nanotechnologies) are a vast field of development targeted to find cheaper and more effective catalysts. In this respect, the use of self-industry waste as precursors for preparation of solid catalysts is not well studied.

6. Conclusions

The main challenge is still to develop new catalysts with high catalytic activity, selectivity, and operation at low temperatures in a short reaction time. The number of heterogeneous catalysts for the transformation of terpenes is vast, but still, improvements in selectivity and yields are issues to attend to in order to increase conversion and reduce catalyst costs. Furthermore, related to this, the reaction time is in most of the proposed techniques more than five hours or even a day, significantly influencing production cost and energy use. The feasibility of production and commercialization of terpene-derived fuels is also linked to oil prices. There are few examples of generalization of the use of terpene-based fuels, perhaps related to the above-mentioned pending issues. Nevertheless, there is a potential for boosting their production and use for energy purposes, mainly in the aviation sector. In the specific subject of this survey on the current state of the art, the production of terpene-based fuel precursors or biofuels using heterogeneous catalysis, there are many potentials or already proved catalysts, with still further optimization and enhancement possibilities. The heterogeneous acid catalysis is a well-studied pathway. From the survey, it is observed that an important number of studies concerning heterogeneous catalysis have been developed in the past two decades, wherein the focus was not always on biofuel production, but for studies and improvement of catalytic conversion to terpenes reported as suitable biofuels. Among all the chemical processes and chemical reactants converted, α -pinene is the most-studied terpene, perhaps due to it representing the main component of turpentine. In order to enhance fuel properties, isomerization is the most frequently applied chemical pathway. A wide group of heterogeneous catalysts have been reported. In this respect, Amberlyst, transition metals, alumina, and silicates are the most reported. Future work should be focused on finding new catalysts or on improving the performance of reported and used catalysts, but also on increasing the industrial production up to similar levels as currently used biofuels (bioethanol and biodiesel).

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