Review

The Limonene Biorefinery: From Extractive Technologies to Its Catalytic Upgrading into p-Cymene

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Abstract: Limonene is a renewable cyclic monoterpene that is easily obtainable from citrus peel and it is commonly used as a nutraceutical ingredient, antibacterial, biopesticide and green extraction solvent as well as additive in healthcare, fragrance and food and beverage industries for its characteristic lemon-like smell. Indeed, the lack of toxicity makes limonene a promising bio-alternative for the development of a wide range of effective products in modern biorefineries. As a consequence, industrial demand largely exceeds supply by now. Limonene can be also used as starting substrate for the preparation of building block chemicals, including p-cymene that is an important intermediate in several industrial catalytic processes. In this contribution, after reviewing recent advances in the recovery of limonene from citrus peel and residues with particular attention to benign-by-design extractive processes, we focus on the latest results in its dehydrogenation to p-cymene via heterogeneous catalysis. Indeed, the latest reports evidence that the selective production of p-cymene still remains a scientific and technological challenge since, in order to drive the isomerization and dehydrogenation of limonene, an optimal balance between the catalyst nature/content and the reaction conditions is needed.

Keywords: limonene; green extraction; essential oil; citrus processing waste; p-cymene

1. Introduction

The chemical conversion (upgrade) of lignocellulosic biomasses and wastes for the production of fuels and chemical building blocks, the so-called "biorefinery", has been widely explored in the last two decades [1,2]. Modern biorefineries already use cellulose, hemicellulose and lignin (the three-key components of lignocellulose) as starting feedstocks for the preparation of furans, polyols, acids and aromatics [3–5]. However, other important platform chemicals can be easily extracted from biomass-derived wastes and residues and used as biobased building blocks for the preparation of value-added intermediates, products, renewable energy and biofuels, supporting and slowly replacing the well-assessed technologies that gave a great contribution to these fields [6–10].

In this context, limonene (1-methyl-4-(1-methyl phenyl) cyclohexene), the main constituent of citrus essential oil (around 68–98% *w/w*) is industrially derived from the citrus industry from orange processing waste [11]. An optically active cyclic monoterpene that exists in two enantiomeric forms, *R*-limonene (the predominant isomeric form in citrus varieties, also known as *d*-limonene) and *S*-limonene (the less common isomer found in

mint oils) [12–15], limonene is generally adopted as a flavor and fragrance additive in the cosmetic and perfume industries due to its pleasant citrus smell, and in the food industry as a flavor and preservant, avoiding alterations of the organoleptic properties. Moreover, it is also extensively adopted as an ingredient in household cleaning products, as wetting and dispersing agent in manufacturing resins, in the production of varnishes, in germicide treatments for wastewaters [16] and as insect control. In this regard, limonene represents an efficient alternative to halogenated carbon hydrates or conventional degreasing agents. Likewise, due to its elevated apolar solvent properties, limonene is a versatile compound used as a green solvent for the extraction of natural products, replacing toxic oil-based solvents such as *n*-hexane [17–19]. For example, it was recently proven to have a unique ability to recover marine oils rich in omega-3 lipids, vitamin D and carotenoids from shrimp and anchovy leftovers [20–22]. These uses are particularly important in light of its anticancer, anti-tumoral and anti-diabetic properties [23,24]. The industrial demand of limonene largely exceeds its supply, limited by the yearly global production of orange crops. As a result, the price of orange essential oil (EO) has increased to such an extent that it is now a primary source of revenue for the orange juice industry [13,25].

Due to its versatile chemistry, when the supply of the terpene obtained via bacterial fermentation will replace limited supply from citrus processing waste, limonene will replace a number of aromatic intermediates currently produced from oil [13,26,27]. For example, 1,2-limonene oxide obtained via catalytic selective oxidation readily reacts with carbon dioxide to form biobased polycarbonates of exceptional optical and mechanical properties, with some important reviews published in recent years on this subject [28–30]. Likewise, limonene can be used as a substrate for the production of p-cymene, a fine chemical intermediate in several industrial chemical processes [31,32]. In fact, p-cymene is involved in the synthesis of fragrances, perfumes, flavors, fungicides, pesticides and pharmaceutical products [23]. At the same time, in the perfume industry, it is used as a raw material for the production of key intermediates including p-cresol that is used, for example, in the production of antioxidants such as butylated hydroxytoluene (BHT) [33–35]. Moreover, p-cymene can be added to inks, adhesives, paints and pigments and is widely used for the manufacture of some products that are normally obtained from petroleum-based compounds. Finally, p-cymene can be transformed into aromatic monomers, including terephthalic acid and dimethyl styrene, or used as starting substrate for the synthesis of non-nitrate mosses (i.e., tonalide).

The current industrial route to p-cymene using the Friedel-Crafts alkylation of benzene with methyl and isopropyl halides or of toluene with 2-propanol generates a large amount of byproducts. Moreover, the use of large quantities of hazardous acid catalysts gives rise to safety, corrosion, handling and waste disposal problems. In further detail, the FC alkylation is performed at high temperatures (200–450 °C) in the presence of $AlCl_3$, BF_3 or H_2SO_4 as catalysts, producing significant amounts of by-products (especially o- and m-cymene along with other multiple alkylation products) with an overall yield of p-cymene that usually does not exceed 50%. Finally, since the conventional p-cymene production occurs in a liquid phase, the separation of the reactants from the catalyst is an energy-intensive process [36–38]. Alternative methodologies for the production of p-cymene have been widely investigated, including the use of renewable limonene, also considering that a relatively low amount of p-cymene (4000 tonnes) is manufactured yearly [39–43].

In this account, we highlight recent advances in the extraction of limonene from citrus processing waste with particular attention to benign-by-design extractive processes, and its catalytic dehydrogenation for the production of p-cymene.

## 2. Extraction Methods for an Efficient Recovery of Limonene

Extraction techniques are the first step in any treatment of citrus fruits and medicinal plants. The extraction has a significant and crucial role in the final result and can be performed with different technologies [44]. Recently, eco-friendly unconventional extraction methods, such as microwave-assisted extraction (MAE), ultrasonic-assisted extraction

(UAE), supercritical fluid extraction (SFE) and enzyme-assisted extraction (EAE) [45], which reduce time and the use of chemical solvents improving the yield and quality of the extracted essential oil, have been developed. At the same time, conventional extraction methods, such as hydrodistillation (HD), cold press (CP) [46] and solvent extraction, are still considered reference methods [44].

Table 1 summarizes the recovery of limonene from different species of citrus by means of conventional and novel extraction technologies. The amount of limonene recovered strongly depends on the extraction technique and on the type of citrus fruit used. Indeed, as shown in Table 1, the maximum yield of about 94–96% has been reached for the orange peel [47,48], while lower values were obtained for clementine and grapefruit. A lower extraction efficiency resulted also from the lemon, with a yield of limonene that did not exceed 70% [49].

The limonene recovery from citrus has been widely achieved by using conventional solvent extraction with different types of various solvents such as n-hexane, dichloromethane, diethyl ether and ethyl acetate. Among the several solvents used, n-hexane, due to its low boiling point, highly hydrophobic character and excellent solubilizing ability, was found to be the most efficient extracting agent [50,51]. Besides the type of the starting citrus fruit, the solvent extraction efficiency depends also on the operating parameters, such as extraction temperature, cycle number and substrate–solvent ratios. Battista et al. recently reported the recovery of limonene from the orange essential oil (OEO), extracted from orange peels (Ops) by means of a Soxhlet n-hexane extraction under optimized reaction parameters (85 °C; solvent/OPs ratio equal to 2:1) allowed higher OEO yields of 1.31% to be reached with a limonene content of about 90% [52]. At the same time, the high-pressure–high-temperature extraction (HPTE) process, using hexane, in an agitated reactor, has been successfully used by Lopresto et al. to recover d-limonene from lemon fruits, highlighting that the high temperature excites the analyte solubilisation by increasing both solubility and mass transfer rate, thus enhancing the extraction efficiency [53,54].

As shown in Figure 1, the non-conventional HTPE processes, carried out at 150 °C and 6 bar pressure with a matrix/solvent ratio equal to 1:4 during an extraction time of only 30 min, led to a yield in d-limonene three times higher (2.97% vs. 0.95%) compared to that of the classic Soxhlet extraction performed for 4 h at 68 °C and 1 bar pressure with a matrix/solvent ratio 1:25 [53].
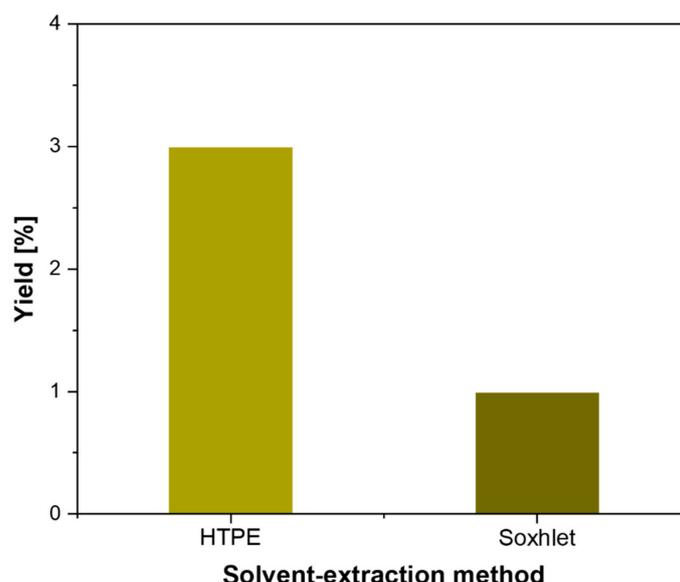
Figure 1. Comparison between non-conventional high-pressure–high-temperature extraction (HPTE) and conventional Soxhlet extraction. Adapted with permission from Lopresto et al. [53]. Copyright (2014) Elsevier Ltd.

However, due to its high toxicity, the use of hexane has been severely limited by various regulations, such as the REACH (EC 1907/2006) and the IPPC (96/61/EC), pushing the scientific research towards the use of green solvents, as an alternative to n-hexane, without compromising the yield of oil [55]. On this account, the use of green solvents obtained from the biomass (i.e., bio-based solvents) or nontoxic and biodegradable environmentally friendly petrochemical solvents could represent a valid alternative to replace hazardous volatile organic solvents, not only in terms of environmental and healthy impact, but also in terms of extraction efficiency. Ozturk et al., evaluated the performance of several bio-solvents, demonstrating how the use of cyclopentyl-methyl and 2-methyl-tetrahydrofuran, operating at T = 70 °C, t = 150 min and substrate/liquid ratio equal to 1:10, allows us to obtain a better performance of recovery and reuse in consecutive extraction cycles, and limonene extraction yields up to 80% and 40% respectively, in comparison with the conventional hexane extraction methodology [11].

The cold press, one of the ancient essential oil extraction methods and already integrated into most of the modern juice production systems, is based on the use of needles to tear the oil glands in the peels [23,56] and the use of a mechanical pressure to release the oils [49]. It has the major advantage of minimizing the degradation of the essential oil constituents [57], with the oil expeller pressed at low temperature and pressure. Additionally, the resulting oil is 100% pure and retains most of the volatile compounds and waxes, which are important for their aromatic properties [58]. Although the cold press extraction provides an inexpensive opportunity compared to conventional methods, as the equipment is very simple and does not requiring heat supply, usually it has the lowest yield of essential oil extraction compared most recent extraction techniques, such as hydro (HD) and steam (SD) distillation. Therefore, in recent years, the number of reports based on the cold press extraction of limonene was very limited.

Ferhat et al., in a comparative study of essential oil extraction from fresh citrus peels by conventional hydrodistillation (HD), cold pressing (CP) and innovative microwave-accelerated distillation (MAD), obtained via cold press extraction a yield of 73.75% from whole fresh lemon (*Villa Franca*, *Citrus limon* (*L.*) *Burm cultivar*), while, starting from whole fresh grapefruit (*Marsh Seedless*, *Citrus deliciosa Ten C. tangerine cultivar*) and whole fresh orange (*Valencia cultivar Citrus sinensis* (*L.*) *Osbeck*; *Bouquetier de Nice* (*Citrus paradisi*) *cultivar*), a yield of ca. 95–96% was reached. Such results further highlight the fundamental role played by the type of starting fruit on limonene yields, since a higher amount from oranges (around 95%) is obtained, while it is significantly less from lime and lemon fruit (around 70%). In any case, Ferhat et al., in the same study, showed that the innovative microwave process offers substantial advantages over conventional processes, in terms of both shorter distillation time (30 min vs. 3 h for hydrodistillation and 1 h for cold pressing), and improved yields (0.24% vs. 0.21% for hydrodistillation and 0.054% for cold pressing) [46].

As mentioned above, hydrodistillation (HD) is a classic method for the extraction of aroma-producing compounds that does not involve the use of organic solvents. It is performed before the dehydration of citrus materials, and it is generally widely used. Three main types of HD processes can be listed: (i) water distillation, (ii) steam distillation and (iii) water–steam distillation. HD requires long extraction times and cannot be widely used for thermolabile compounds extraction, such as terpenic compounds, due to the volatility of some components, possibly lost at high extraction temperatures [14,44,59]. The technique shows a simple apparatus based on the evaporation of a solution containing immiscible liquid compounds at a boiling temperature lower than the one of each component [59,60]. Starting from fresh orange peels, Ruiz et al. achieved a maximum extraction efficiency of limonene, above 44%, for the treatment at the higher steam flowrate (16 mL min^{-1}) and the longest contact time (180 min) [61], according to the results previously obtained by Cannon et al. [62]. The extraction efficiency of limonene, obtained by Martin et al. by steam distillation at lab scale, with a distillation time ranging from 0 to 6 h, was above 70% [31], while, using the same technique, Uwida et al. reached limonene yields above 95% [15].

In any case, the limonene extraction efficiency obtained in the above studies cannot be directly compared owing to the different operating conditions.

Microwave-assisted extraction (MAE) is a green and versatile extraction technology usable starting from several raw materials and providing both faster extraction and lesser solvent consumption [63]. Recently, MAE has been largely used also for the extraction of pectin and betanin from the peel of red and green *Opuntia ficus*-indica fruits with high efficiency [64]. MAE shows many advantages, such as a less solvent volume, faster extraction, mass transfer intensification and protection of thermo-labile compounds from high temperatures. The temperature is the main control parameter. Moreover, MAE allows a better extraction efficiency of oxygenated compounds to be obtained compared to the classical hydrodistillation (HD), since the absence of solvent reduces the thermal and hydrolysis reactions, thus hindering the degradation of the oxygenated compounds [45]. In recent years, coupling MAE with other technologies, such as microwave-assisted hydro distillation (MADH) [23] and microwave Steam Distillation (MSD) [14], is of particular interest due to the reduced time of the extraction process and its allowing the recovery of essential oil without causing any change in the composition of the oil gas. On this account, Bustamante et al. studied the upscaling of the MAHD process for the extraction of the essential oil from citrus peel, developing a two-step process, where the microwave energy was supplied, with intermittent power, during the extraction time, obtaining a substantial saving in energy costs and a significant increase in the extraction efficiency. Indeed, as can be observed in Figure 2, the energy efficiency of the applied microwave energy decreases as the extraction time increases, confirming that short irradiation times are required to reach a significant extraction efficiency [48].
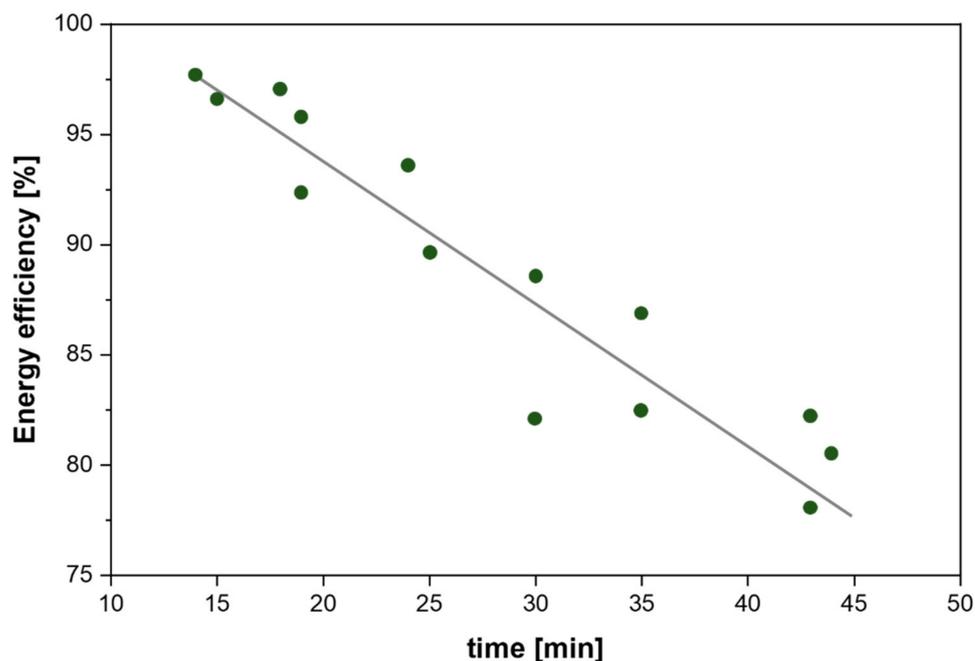
Figure 2. MAHD energy efficiency (%) at different extraction times. Adapted with permission from Bustamante et al. [48]. Copyright (2016) Elsevier Ltd.

One of the most innovative approaches is solvent-free microwave extraction (SFME), a combination of microwave heating and dry distillation, performed at atmospheric pressure without using solvents or water. This technique affords similar yields as the traditional steam distillation with a considerably shorter extraction time and without the post-treatment steps [49,65]. The SFME extraction process was performed by Ciriminna et al. for the isolation of essential oils from different parts of the fruit: outer skin (exocarp), peel (exo- and mesocarp) and waste (exo-, meso- and endocarp), starting from three types

of citrus fruits, orange, lemon and grapefruit, grown in Sicily. Numerous compounds have been identified in EOs with very high yields compared to other industrial methods (0.4% vs. 0.05–0.25%), with limonene as the main constituent (50–80%) in most cases [66].

Table 1. Comparison of different extraction methods for the recovery of limonene.

Citrus Peel Waste	Extractive Method	Limonene (% in EO)	Extraction Conditions	Ref.
Orange peel fresh	SFME	94.6	Solvent-free, 30 min	[46]
	MAHD	80.0	Water, 60 min, 100 °C	[66]
Orange peel fresh (after juicing)	HD	96.8	Water, 240 min, 100 °C	[48]
	MAHD	97.4	Water, 240 min, 100 °C	[48]
	MAHD	80.0	Water, 80 min, 100 °C	[66]
Orange peel thawed	HD	94.4	Water, 155 min	[47]
	MAHD	94.7	Water, 76 min	[47]
	SFME	95.2	Solvent-free, 5 min	[47]
	US-MWHD	95.0	Water, 60 min	[47]
Orange flavedo peel fresh	HD	95.5	Water, 180 min	[46]
	MAHD	55.0	Water, 75 min, 100 °C	[66]
Orange whole fresh	CP	96.0	Water, 90 min	[46]
Lemon peel fresh	SFME	74.0	Solvent-free, 30 min	[46]
	MAHD	50.0	Water, 80 min, 100 °C	[66]
Lemon peel fresh (after juicing)	MAHD	68.4	Water, 240 min, 100 °C	[48]
	MAHD	65.0	Water, 70 min, 100 °C	[66]
Lemon flavedo peel fresh	HD	72.9	Water, 180 min	[60]
	HD	93.0	Water, 180 min	[46]
	MAHD	30.0	Water, 60 min, 100 °C	[66]
Lemon whole fresh	CP	73.8	Water, 90 min	[46]
Grapefruit peel fresh	SFME	91.6	Solvent-free, 30 min	[46]
	MAHD	45.0	Water, 70 min, 100 °C	[66]
Grapefruit peel fresh (after juicing)	MAHD	89.2	Water, 240 min, 100 °C	[48]
Grapefruit flavedo peel fresh	HD	92.6	Water, 180 min	[46]
Grapefruit whole fresh	CP	94.5	Water, 90 min	[46]

Ultrasound (US) technology has been also applied for the recovery of essential oils [45]. The use of ultrasound has the advantage of being fast, simple and low cost [67] and is based on milder extraction operative conditions [23]. The control and optimization of process parameters (e.g., time, temperature, pressure, speed and power) make this method useful not only for the limonene extraction but also for the selective extraction of different compounds from citrus and plants [67]. According to Aliaño-González et al., the technique exploits the energy of ultrasounds for the extraction of different organically derived raw materials [68]. US was successfully used to intensify the extraction of d-limonene from the *Citrus limetta* (sweet lime) peel by Khandare et al. As evidenced in Figure 3, the ultrasound-assisted extraction (EAU) under optimized conditions allows yields to be achieved similar to those obtained by using Soxhlet, close to 100%, in very short extraction times, due to the physical and structural changes on the substrate surface and the consequent improvement of extraction efficiency [69].

On this account, Pingret et al. designed and developed the sono-Clevenger process, a new procedure employing the US technology for the extraction of essential oils from orange peels. Compared to the conventional Clevenger technique, this advantageous alternative provides a substantial reduction of the extraction time without interfering with the composition of target compounds [70].
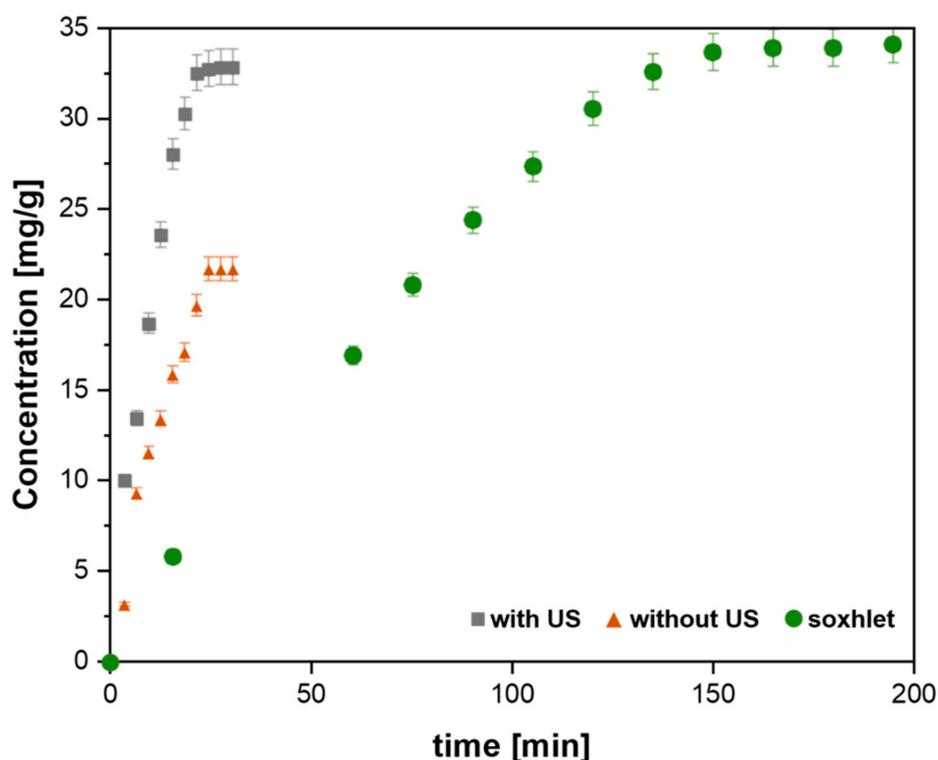
Figure 3. Comparison of ultrasonic-assisted extraction (UAE) with conventional extraction methods. Adapted with permission from Khandare et al. [69]. Copyright (2021) Elsevier Ltd.

González-Rivera et al. studied the solvent-free, microwave-assisted extraction (SMWAE) and the simultaneous ultrasonic and microwave irradiation hydrodistillation (US–MWHD). The cavitation effect of US favors the breakage of the internal cell membranes rushing the extraction of limonene and promoting the volatilization of compounds with higher boiling point, such as valencene. Indeed, the amount of limonene and myrcene, the two main compounds of the orange peel EOs, increases over time and reaches a limit value at the end of the process (Figure 4), resulting in a limonene content above 95% and a higher amount of valencene. Since the valencene amount in the orange EOs, due to its aromatic and flavoring characteristics, contributes to an increase in its quality and commercial value, it is evident that the US-MWHD cavity-less configuration can be considered not only a faster method, compared with the microwave coaxial hydrodistillation (MWHD) and conventional hydrodistillation (CH), but also the best way to obtain the highest quality of EO (Figure 4) [47].

The extraction by supercritical fluid (SFE) has been extensively studied and is generally considered a non-traditional eco-friendly extraction technique [71], using CO_2 as green and renewable solvent. Although many other solvents can be used for plant extraction (such as propane), CO_2 is considered an ideal solvent for SFE. The critical temperature of CO_2 is slightly higher than room temperature, and the low critical pressure allows it to operate at moderate pressures, generally between 100 and 450 bar [44,45]. Therefore, limonene's extraction by the traditional hydrodistillation technique may be replaced by the supercritical fluid extraction (15 MPa, 40 °C), which offers the possibility to save time and represents an eco-friendly alternative method [72]. Several researchers, by using supercritical CO_2 to investigate the extraction of volatile components from the orange peel, showed that the concentrations of limonene and linalool depend significantly on the applied process parameters [73]. The optimization of process conditions for supercritical CO_2 extraction plays a key role for the selectivity of the extracted components and their subsequent application in the food industry [55]. Finally, it is worth mentioning that, in recent years, the use of the supercritical CO_2 (SC-CO_2) as a solvent and hydrotropic

extraction tool has been evaluated to extract limonoids from the citrus waste, allowing yields up to 13 times higher to be obtained than the traditional cold-pressing technique, recovering the 100% limonene yield. However, it is impossible to compare the efficiency of this technique with others, as the yield depends on the amount of CO_2 used [49,74].
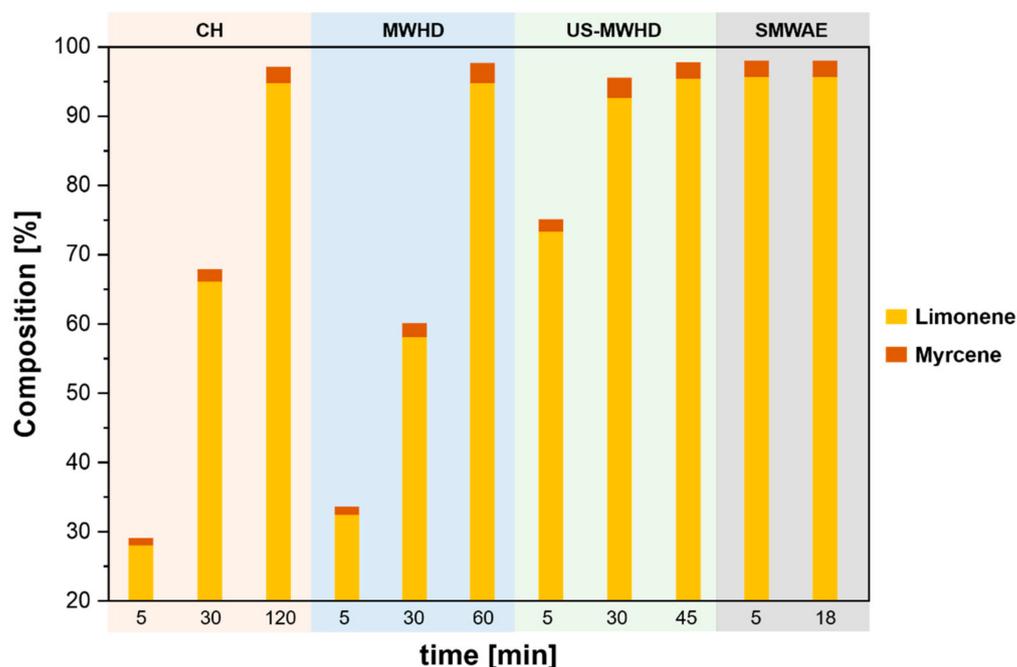
Figure 4. Chemical composition of the orange peel essential oils (Eos) obtained by conventional hydrodistillation (CH), solvent-free, microwave-assisted extraction (SMWAE), ultrasonic and microwave irradiation hydrodistillation (US–MWHD) and MWHD at different extraction times with a composition higher than 2%. Adapted with permission from González-Rivera et al. [47]. Copyright (2016) Royal Society of Chemistry.

A recent study employed the enzymatic pre-treatment of cellulose for the extraction of essential oils from three different citrus peels [75]. Compared to conventional methods, the use of assisted enzymes allows an increase in essential oil yield by 2- and 6-fold for orange peel and grapefruit, respectively. The enzymatic treatment has the advantage of reducing the overall viscosity, which facilitates the breaking of an emulsion for the recovery of the oil from the aqueous phase [76]. The preliminary steps play an important role during the extraction of compounds from the biomass. Among these, drying and grinding are two factors that predominantly affect the final yield. Generally, dehydration involves the removal of the bound water from the peel by increasing the porosity of the cellular matrix, thereby facilitating diffusion rate and promoting the contact with enzymes, consequently enhancing the overall process [77]. Most important, the enzyme-assisted extraction can be coupled with other techniques (e.g., microwave-assisted, ultrasound-assisted, supercritical fluid and high-pressure) to increase the overall yield of the limonene.

3. Upgrading of Limonene into p-Cymene over Heterogeneous Catalysts

Limonene tends to turn into monocyclic terpenes (terpinenes and terpinolenes) that can dissociate into menthenes and cymenes as final products [42]. Indeed, in an alternative process, p-cymene can be produced via isomerization or hydrogenation, as well as by the direct dehydrogenation of limonene [78].

Reports on the transformation of limonene into p-cymene by homogeneous catalysts are quite limited since low yields and separation drawbacks generally occur, thus driving the interest towards heterogeneous systems (Table 2), able to ensure good performances and, at the same time, an easy separation from the post-reaction mixture [38,79].

Table 2. Conversion of Limonene into p-cymene promoted by heterogeneous catalysts.

Catalyst	Limonene	p-Cymene	Reaction Conditions	Ref.
	Conversion (%)	Yield (%)		
Ni-SD	96	17	Batch, n-dodecane, 150 °C, 15 min	[80]
H-FER (T)	38	n.d.	Batch, 65 °C, 60 min	[81]
SIRAL 20	100	100	Batch, microwave, 175 °C, 10 min	[26]
SepNi	100	100	Batch, microwave, 210 °C, 20 min	[31]
Pd/HZSM-5 (258)	100	82	Batch, n-dodecane, 260 °C, 2 h, 8 bar N_2	[82]
Ti-SBA-15	99	56	Batch, 160 °C, 23 h	[43]
TECHNOSA-H2	98	65	Batch, tetraethylene glycol dimethyl ether, 140 °C, 7 h, N_2	[83]
TiO_2	100	90	Continuous flow, 300 °C, 6 h, H_2	[37]
Pd/Al_2O_3	100	80	Continuous flow, SC-ethanol, 300 °C, 30 s, 6.5 MPa	[78]

In an interesting approach, Catrinescu et al. used several metal-modified bentonites as catalysts at 150 °C for 15 min in the presence of n-dodecane as solvent. The results show that the nickel-modified bentonites are the most active with respect to analogous Al- and Cr-based catalysts [80].

The catalytic conversion of limonene to p-cymene was also performed by Martin-Luengo et al., using sepiolite, a clay (hydrated magnesium silicate) of natural and economic origin, as a catalyst by microwave irradiation. High conversion of limonene to p-cymene, under solvent-free conditions, was achieved using a modified catalyst with Na, Ni, Fe or Mn oxides. Modification of the catalyst with nickel allows the complete conversion of limonene with a selectivity of 100% to p-cymene, after 20 min of reaction [31]. The same research group as before used mesoporous silica-alumina supports as catalysts with a SiO_2 content ranging from 1% (SIRAL 1) to 40% (SIRAL 40) [26]. Both the limonene conversion and the p-cymene selectivity linearly increase with the silica content with SIRAL 20 and SIRAL 40 catalysts, leading to complete conversion of limonene into p-cymene.

In another approach, limonene was previously isomerized into α-terpinene, γ-terpinene and terpinolene and then converted into p-cymene over the H-FER (T) (ferrierite from Tosoh in which the Si/Al ratio amounts to 8.9) catalyst at 65 °C. At this temperature, after a reaction time of 60 min, a 38% limonene conversion was gained. Interestingly, limonene transformation was not observed over H-FER (Z) ferrierite catalysts characterized by Brønsted sites with higher acid strength [81].

The dehydrogenation of limonene to p-cymene was explored by Cui et al. using a Pd/HZSM-5 catalyst under both inert (N_2) and reductive (H_2) reaction conditions. Due to the endothermic nature of dehydroaromatization reactions, an increase in the reaction temperature is beneficial to the shift of the equilibrium toward p-cymene production both in the presence and in the absence of added hydrogen (Figure 5).
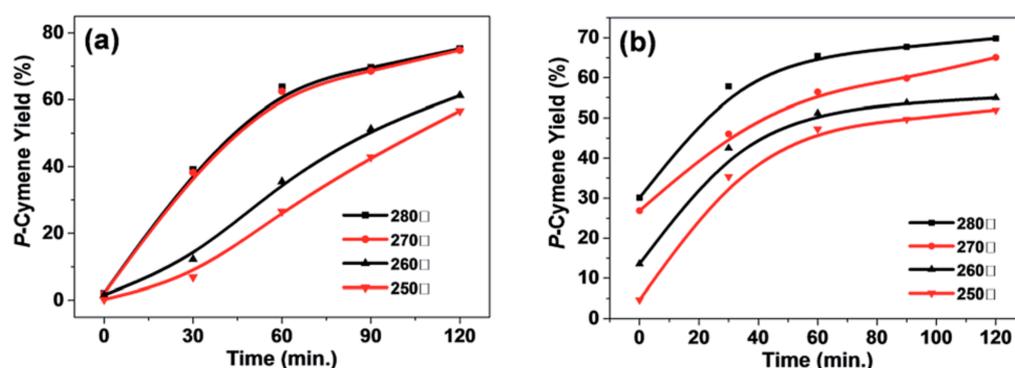
Figure 5. Conversion of limonene into p-cymene over the Pd/HZSM-5 catalyst as a function of time at 240, 260, 280, 300 °C (**a**) in absence of added hydrogen and (**b**) under inert atmosphere. Reproduced with permission from Cui et al. [82]. Copyright (2016) Royal Chemical Society.

The addition of hydrogen leads to a lower selectivity to p-cymene, since it increases the hydrogenation rate on the double bonds, facilitating the isomerization reaction of limonene and preventing its reverse reaction [82]. Most important, it was proved that the first step in the conversion of limonene into p-cymene is the isomerization, followed by a sequential dehydrogenation process.

Retajczyk et al. carried out studies on the limonene isomerization process using Ti-SBA-15 and Ti-MCM-41 as catalysts, performing the limonene isomerization without any organic solvents [43]. The conversion of limonene increases by increasing both the reaction temperatures as well as the reaction time (Figure 6).
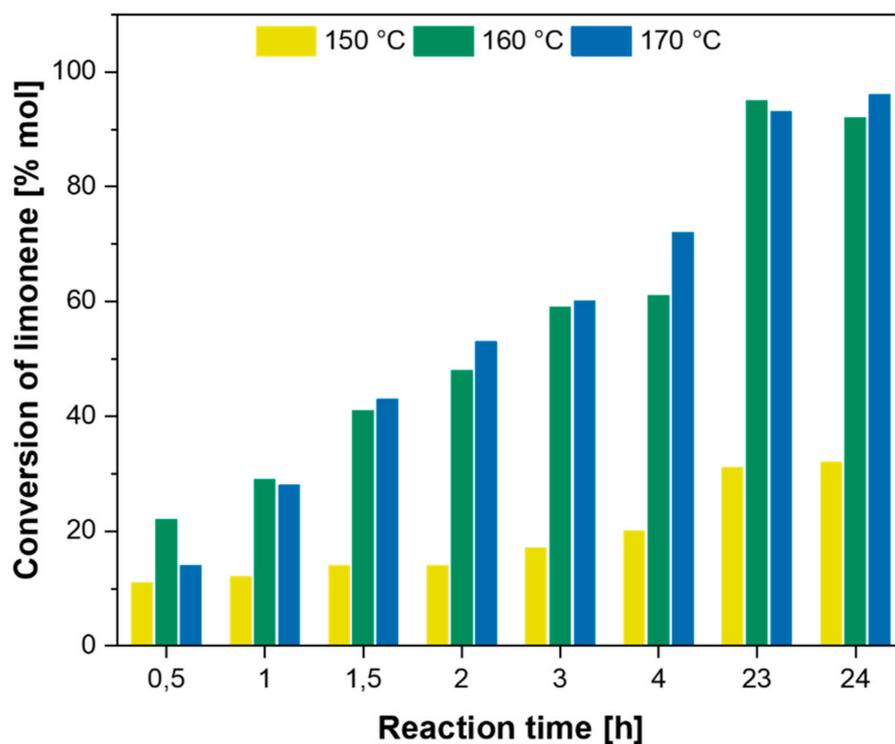

Figure 6. Temperature effect on the isomerization of R-limonene. Adapted with permission from Retajczyk et al. [43]. Copyright (2019) MDPI.

Results clearly show that, under the same processing conditions (temperature 160 °C, catalyst content 15% wt, for 23 h), the different mesoporous silica structures of MCM and SBA give rise to different yields of p-cymene (29% with a limonene conversion of 92% for Ti-MCM-41 and 56% with a limonene conversion of 99% for Ti-SBA-15).

A 2-step mechanism was proposed by Makarouni et al., starting from the limonene isomerization over activated natural mordenites and then its isomerization into p-cymene in a non-catalytic process, using atmospheric oxygen as a green oxidant (Figure 7).

The acid treatment with sulfuric acid aqueous solutions of natural mordenite causes the removal of sodium oxide from its micropores, which drastically increases the specific surface and acidity, making natural mordenite very active in the catalytic transformation of limonene into p-cymene and causing a significant enhancement in both the limonene conversion and in the amount of p-cymene obtained in the reaction mixture. A rather high p-cymene yield (63%) at 140 °C, with a limonene/catalyst ratio of 15 and a reaction time of 7 h, was obtained [35]. Another achievement of the same group was the use of aqueous solutions of various acids (CH_3COOH, HCl, H_2SO_4, HNO_3) to further improve the surface area and the acidity of natural mordenite with a significant increase in the conversion of limonene to p-cymene up to 65% [83].
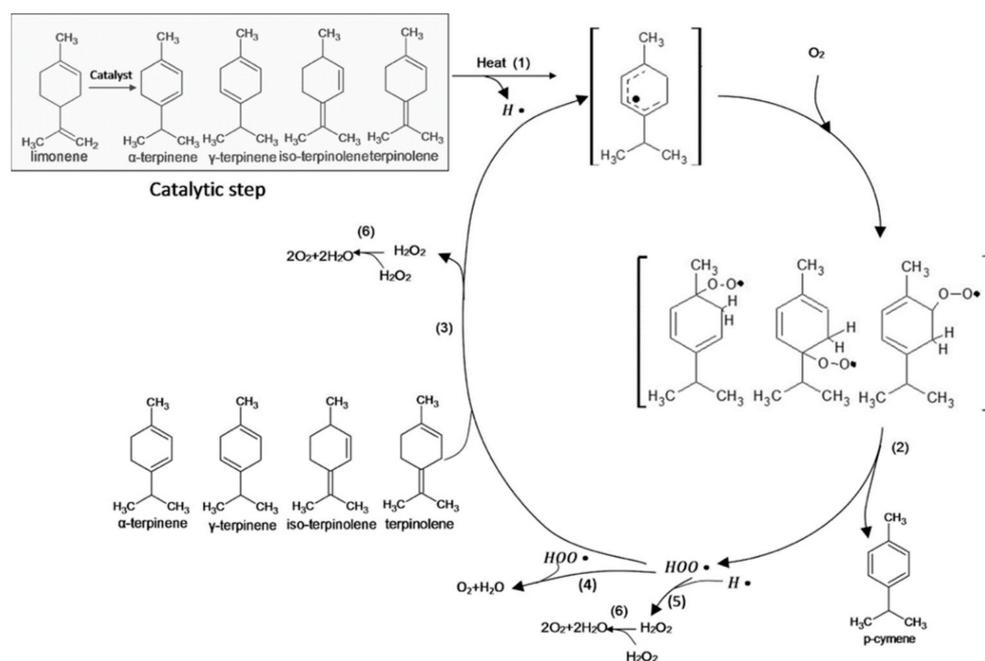
Figure 7. The reaction mechanism of the two-step conversion of limonene into p-cymene. Reproduced with permission from Makarouni et al. [38]. Copyright (2018) Elsevier Ltd.

It is generally accepted that the addition of a transition metal to supports like silica, alumina, silica–alumina mixed oxides, zeolites and natural clays generally improves the catalytic performance as a consequence of the dual functionality exhibited by metal-modified catalysts. In the case of the conversion of limonene into cymene, acid sites are responsible for the isomerization step, while metallic sites can promote the dehydrogenation reaction [37,84]. On this account, several Cr_2O_3, CuO, ZnO, ZrO_2, MgO, La_2O_3, TiO_2 and Pd supported on C catalytic systems have been successfully used for the dehydrogenation of terpenes [27], improving the p-cymene selectivity by up to 97% [78]. Kamitsou et al. recently reported an almost complete transformation of α-limonene into p-cymene (90% yield at 300 °C) over the TiO_2 catalyst in a helium atmosphere. Titanium oxide is a very stable catalyst, and its high catalytic performance could be attributed to a good acidity/reducibility balance, allowing the Ti (IV)/Ti (III) transformation during reaction, thus positively promoting the limonene conversion. At the same time, by using CaO catalyst, the production of p-cymene takes place directly via limonene dehydrogenation, with a conversion rate of up to 98% and a selectivity of about 100% [37].

The transformation of limonene over different heterogeneous catalysts (Pt/Al_2O_3, Ni/Al_2O_3, and Pd/Al_2O_3) and in supercritical conditions of ethanol and 2-propanol was investigated by Yılmazoğlu et al. When the Pd/Al_2O_3 catalyst was used, the limonene was completely converted with an overall p-cymene yield of 80% [78].

In a very interesting approach, Zhang and Zhao proposed d-limonene as a hydrogen-donor molecule for the deoxygenation of fatty acids into alkanes and arenes (that can be used as bio-jet fuel) in the presence of the bimetallic Pd-Ni/HZSM-5 catalyst [85,86]. Palladium promotes the conversion of limonene into p-cymene and H_2, which is the reducing agent also for the hydrodeoxygenation of stearic acid to alkanes over Ni and Pd-Ni sites (Figure 8). This kind of approach is of particular significance since catalytic transfer hydrogenation/hydrogenolysis reactions are getting increasing attention in the reductive upgrading of lignocellulosic biomasses and their relative macromolecules and derived molecules [87–93], thus opening new opportunities for the use of limonene as a green and renewable H-donor solvent.
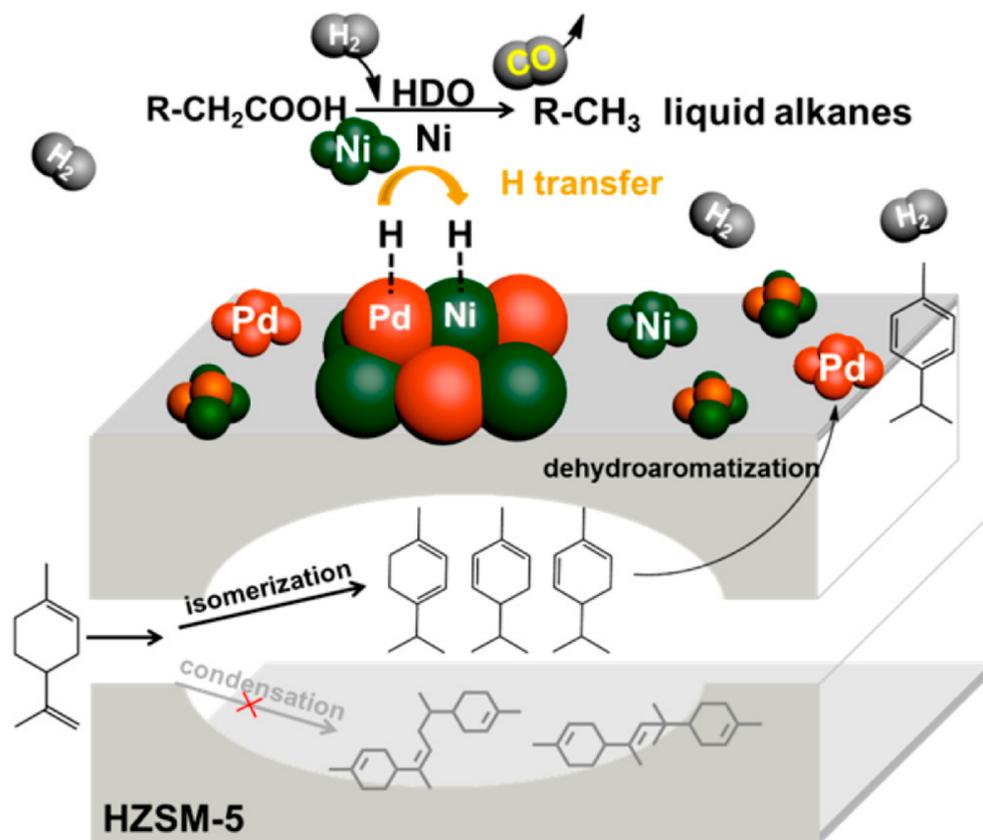
Figure 8. Brief description of individual steps for stearic acid and limonene coactivation using the bimetallic Pd-Ni/HZSM-5 catalyst. Reproduced with permission from Zhang et al. [86]. Copyright (2016) American Chemical Society.

4. Conclusions

Limonene is among the most promising renewable feedstocks for modern biorefineries. Citrus wastes are a good but intrinsically limited source of limonene. Among conventional recovery technologies, cold press extraction provides good yields and ease of applicability. Accordingly, it is the industrial state-of-the-art technology. Amid the new, solvent-free extraction technologies, the highly reproducible, versatile and simple microwave-assisted extraction is one of the more relevant alternatives. Other environmentally friendly methods include supercritical fluid and ultrasound extraction. All these methods are likely to find application when the microbial production of limonene by converting virtually unlimited raw materials such as sugars will be industrialized [94], in order to magnify its production and meet the so far largely unmet market demand for limonene.

At the same time, the development of new green pathways for p-cymene production from limonene is an excellent alternative to the traditional method of obtaining p-cymene via Friedel-Crafts alkylation of toluene with isopropene. The most recent investigations found that supercritical alcohols favoring the catalytic processes by enriching both the solubility and the diffusivity are the most interesting solvents. In almost all cases, p-cymene, γ-terpinene, α-terpinene and terpinolene are obtained. At the same time, the dehydrogenation process of limonene into p-cymene leads to hydrogen as a co-product that can be used for the reductive upgrading of other biobased molecules opening new perspectives in its use as renewable H-donor solvent.

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