
Review

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

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Abstract: A renewable cyclic monoterpene obtained from citrus peel, limonene is widely used as a fragrance, nutraceutical ingredient, antibacterial, biopesticide, and green extraction solvent. Industrial demand largely exceeds supply. After reviewing recent advances in the recovery of limonene from citrus peel and residues with a particular attention to benign-by-design extractive processes, we focus on the latest results in its dehydrogenation to p-cymene via heterogeneous catalysis.

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 and products [6,7].

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 [8]. 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) [9-12], limonene is widely used as a flavor and fragrance additive in the cosmetic and perfume industries due to its pleasant citrus smell, and in the food industry as flavor and preservative 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 [13] 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 [14-16]. For example, it was recently proved its unique ability in the recovery marine oils rich in omega-3 lipids, vitamin D and carotenoids from shrimp and anchovy leftovers [17-19]. These uses are particularly

important in light of its anticancer, anti-tumoral and anti-diabetic properties [20,21]. 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 revenues for the orange juice industry [10,22].

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 [10,23,24]. 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 [25-27]. Likewise, limonene can be used as a substrate for the production of p-cymene, a fine chemical intermediate widely used in a wide range of industrial chemical processes [28,29]. The latter aromatic terpene is involved in the synthesis of fragrances, perfumes, fungicides, pesticides, and antioxidants such as butylated hydroxytoluene [30-32].

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 by-products. Moreover, the use of large quantities of hazardous acid catalysts gives rise to safety, corrosion, handling, and waste disposal problems considering. 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 catalysis, 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 [33-35]. Alternative methodologies for the production of p-cymene have been widely investigated including the use of renewable limonene also in consideration that a relatively low amount of p-cymene (4000 tonnes) is manufactured yearly [36-40].

In this account, we highlight recent advances in the extraction of limonene from citrus processing waste with a 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 on the final result and can be performed with different technologies [41]. 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) [42], 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) [43] and solvent extraction, are still considered reference methods [41].

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 [44, 45] while lower values were obtained for clementine and grapefruit. A lower extraction efficiency resulted also from the lemon, with a yield of limonene that does not exceed 70% [46].

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	[43]
	MAHD	80.0	Water, 60 min, 100 °C	[63]
Orange peel fresh (after juicing)	HD	96.8	Water, 240 min, 100 °C	[45]
	MAHD	97.4	Water, 240 min, 100 °C	[45]
	MAHD	80.0	Water, 80 min, 100 °C	[63]
Orange peel thawed	HD	94.4	Water, 155 min	[44]
	MAHD	94.7	Water, 76 min	[44]
	SFME	95.2	Solvent-free, 5 min	[44]
	US-MWHD	95.0	Water, 60 min	[44]
Orange flavedo peel fresh	HD	95.5	Water, 180 min	[43]
	MAHD	55.0	Water, 75 min, 100 °C	[63]
Orange whole fresh	CP	96.0	Water, 90 min	[43]
Lemon peel fresh	SFME	74.0	Solvent-free, 30 min	[43]
	MAHD	50.0	Water, 80 min, 100 °C	[63]
Lemon peel fresh (after juicing)	MAHD	68.4	Water, 240 min, 100 °C	[45]
	MAHD	65.0	Water, 70 min, 100 °C	[63]
Lemon flavedo peel fresh	HD	72.9	Water, 180 min	[57]
	HD	93.0	Water, 180 min	[43]
	MAHD	30.0	Water, 60 min, 100 °C	[63]
Lemon whole fresh	CP	73.8	Water, 90 min	[43]
Grapefruit peel fresh	SFME	91.6	Solvent-free, 30 min	[43]
	MAHD	45.0	Water, 70 min, 100 °C	[63]
Grapefruit peel fresh (after juicing)	MAHD	89.2	Water, 240 min, 100 °C	[45]
Grapefruit flavedo peel fresh	HD	92.6	Water, 180 min	[43]
Grapefruit whole fresh	CP	94.5	Water, 90 min	[43]

The limonene recovery from citrus has been widely achieved by using the 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 [47, 48]. 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), that allows to reach the higher OEO yields of 1.31% with a limonene content of about 90% [49]. 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 [50, 51].

As shown in Fig. 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 4h at 68 °C and 1 bar pressure with a matrix/solvent ratio 1:25 [50].

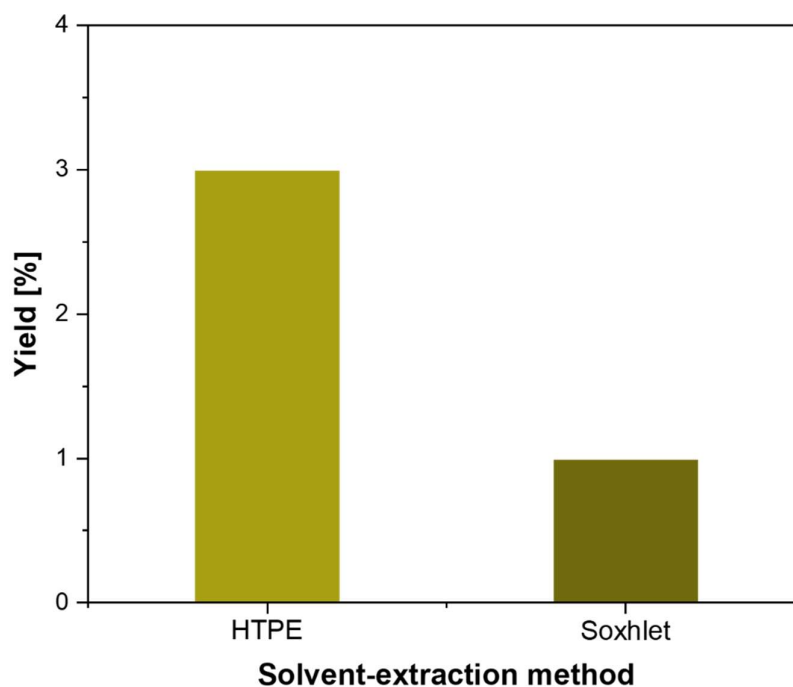


Fig 1. Comparison between non-conventional HPTE and conventional Soxhlet extraction. Adapted with permission from Lopresto et al. [50]. Copyright (2014) Elsevier Ltd.

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 [52]. 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 $T=70\text{ }^{\circ}\text{C}$, $t=150\text{ min}$ and substrate/liquid ratio equal to 1:10, allows 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 [8].

The cold press, one of the ancient essential oil extraction methods and already integrated in most of the modern juice production systems, is based on the use of needles to tear the oil glands in the peels [20, 53] and the use of a mechanical pressure to release the oils [46], has the major advantage of minimizing the degradation of the essential oil constituents [54], being 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 [55]. Although the cold press extraction provides an inexpensive opportunity compared to conventional methods, being the equipment very simple and not requiring heat supply, usually it has the lowest yield of essential oil extraction with respect to the 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 Lemon whole fresh (*Villa Franca, Citrus limon* (L.) *Burm cultivar*), while, starting from Grapefruit whole fresh (*Marsh Seedless, Citrus deliciosa* Ten C. *tangerine cultivar*) and Orange whole fresh (*Valencia cultivar Citrus sinensis* (L.) *Osbeck; Bouquetier de Nice (Citrus paradisi) cultivar*) a yield of ca. 95-96% has been 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, both in terms of 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) [43].

As above mentioned, hydrodistillation (HD) is a classic method for the extraction of aroma producing compounds, not involving 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 [11, 41, 56]. 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 [56, 57]. 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) [58], according to the results previously obtained by Cannon et al. [59]. 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% [28], while on using the same technique Uwida et al. reached limonene yields above 95% [12]. In any case, the limonene extraction efficiency, obtained in the above studies, cannot be directly compared owing to the different operating conditions.

The 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 [60]. 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 [61]. 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 to obtain a better extraction efficiency of oxygenated compounds 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 [42]. In recent years, coupling MAE with other technologies, such as microwave-assisted hydro distillation (MADH) [20], and microwave Steam Distillation (MSD) [11], a particular interest, due to reducing the time of the extraction process and to allowing the recovery of essential oil without causing any change in the composition of the oil gas has aroused. On this account, Bustamante et al. studied the up-scaling 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 an intermittent power, during the extraction time obtaining a substantial saving in energy costs and a significant increase in the extraction efficiency. Indeed, as it can be observed in Fig. 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 significative extraction efficiency [45].

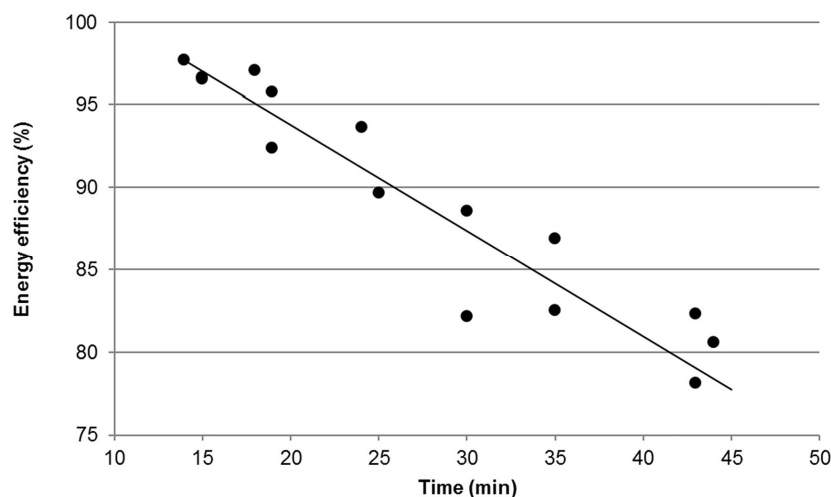


Fig. 2. MAHD energy efficiency (%) at different extraction times. Reproduced with permission from Bustamante et al. [45]. Copyright (2016) Elsevier Ltd.

One of the most innovative approaches is the 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 considerable shorter extraction time and without the post-treatment steps [62, 46]. 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 [63].

The ultrasounds (US) technology has been also applied for the recovery of essential oils [42]. The use of ultrasounds has the advantage to be fast, simple and low cost [64], is based on milder extraction operative conditions [20]. The control and optimization of process parameters (e.g. time, temperature, pressure, speed and power) makes this method useful not only for the limonene extraction but also for the selective extraction of different compounds from citrus and plants [64]. According to Aliaño-González et al. the technique exploits the energy of ultrasounds for the extraction of different raw materials deriving organic [65]. 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 Fig. 3, the ultrasound-assisted extraction (EAU) under optimized conditions, allows to achieve yields 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 [66].

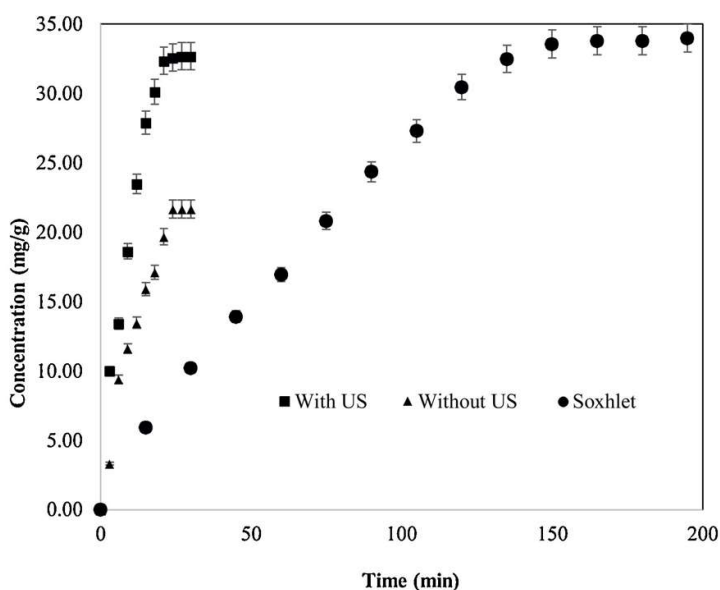


Fig. 3. Comparison of UAE with conventional extraction methods. Reproduced with permission from Khandare et al. et al. [66]. Copyright (2021) Elsevier Ltd.

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 on composition of target compounds [67].

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 higher boiling point compounds, 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 (Fig. 4a), 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 increase 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 (Fig. 4b) [44].

The extraction by supercritical fluid (SFE) has been extensively studied and it is generally considered a non-traditional eco-friendly extraction technique [68], using CO₂ as green and renewable solvent. Although many other solvents can be used for plant extraction (such as propane), CO₂ is considered an ideal solvent for SFE. The critical temperature of CO₂ is slightly higher than the room one, and the low critical pressure allows to operate at moderate pressures, generally between 100 and 450 bar [41, 42]. Therefore, limonene's extraction by the traditional hydrodistillation technique may be replaced by the supercritical fluid extraction (15 MPa, 40 °C), that offers the possibility to save time and represents an eco-friendly alternative method [69]. Several researchers, by using supercritical CO₂ to investigate the extraction of volatile components from the orange peel, showed that the concentration of limonene and linalool depend significantly on the applied process parameters [70]. The optimization of process conditions for supercritical CO₂ extraction plays a key role for the selectivity of the extracted components and their subsequent application in the food industry [52]. Finally, it is worth mentioning that, in

recent years, the use of the supercritical CO₂ (SC-CO₂) as solvent and hydrotropic extraction tool has been evaluated to extract limonoids from the citrus waste allowing to obtain yields up to 13 times higher 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 the CO₂ used [46, 71].

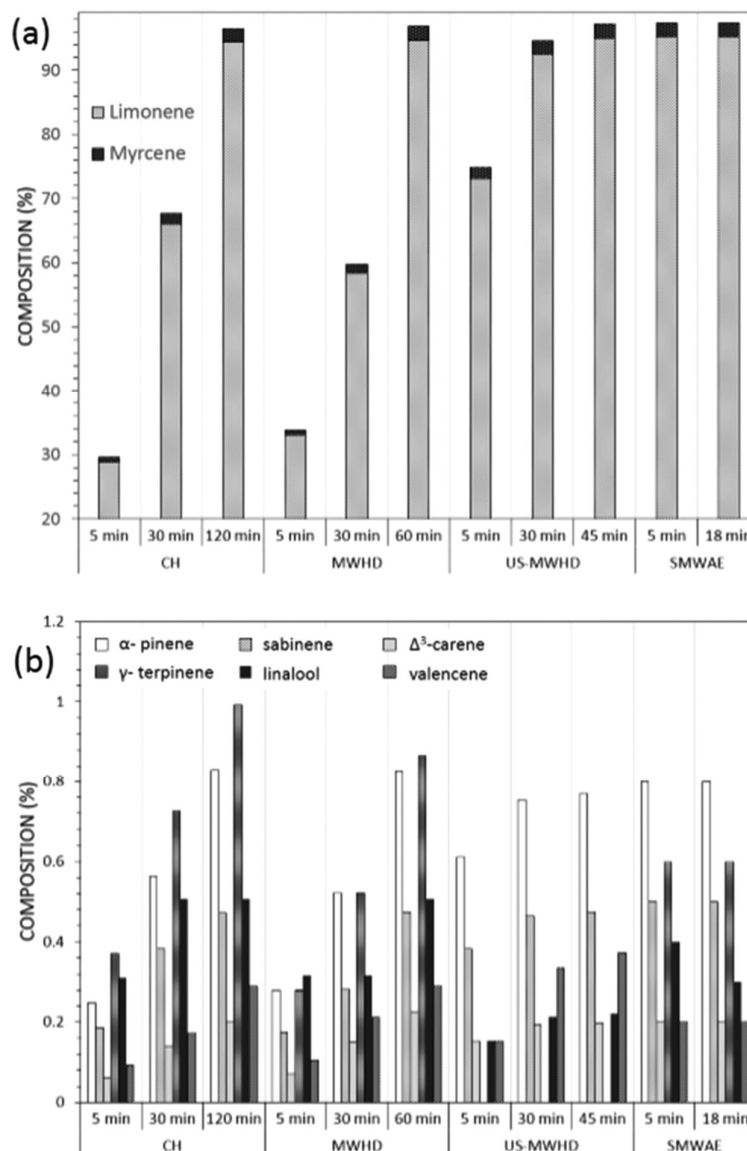


Fig. 4. Chemical composition of the orange peel EOs obtained by CH, SMWAE, US-MWHD and MWHD at different extraction times, (a) composition higher than 2%, (b) composition lower than 2%. Reproduced with permission from González-Rivera et al. [44]. Copyright (2016) Royal Society of Chemistry.

A recent study employed the enzymatic pre-treatment of cellulose for the extraction of essential oils from three different citrus peels [72]. 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, that facilitates the breaking of an emulsion for the recovery of the oil from the aqueous phase [73]. The preliminary steps play an important role during the extraction of compounds from the biomass. Among these, drying and grind-

ing 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. [74]. Most important, the enzyme-assisted extraction can be coupled with other technique (eg. 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 [39]. Indeed, in an alternative process, p-cymene can be produced via isomerization or hydrogenation, as well as by the direct dehydrogenation of limonene [75].

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

Catalyst	Limonene Conversion (%)	p-Cymene Yield (%)	Reaction Conditions	Ref.
Ni-SD	96	17	Batch, n-dodecane, 150 °C, 15 min	[77]
SIRAL 20	100	100	Batch, microwave, 175 °C, 10 min	[23]
SepNi	100	100	Batch, microwave, 210 °C, 20 min	[28]
Pd/HZSM-5 (258)	100	82	Batch, n-dodecane, 260 °C, 2 h, 8 bar N ₂	[79]
Ti-SBA-15	99	56	Batch, 160 °C, 23 h	[40]
TECHNOSA-H2	98	65	Batch, tetraethylene glycol dimethyl ether, 140 °C, 7 h, N ₂	[80]
TiO ₂	100	90	Continuous flow, 300 °C, 6 h, H ₂	[34]
Pd/Al ₂ O ₃	100	80	Continuous flow, SC-ethanol, 300 °C, 30 s, 6.5 MPa.	[75]

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 [35, 76].

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 [77].

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 catalyst by microwave irradiation. High conversion of limonene to p-cymene, under solvent-free conditions, was achieved using a modified with Na, Ni, Fe or Mn oxides. Modification of the catalyst with nickel allows to gain the complete conversion of limonene with a selectivity of 100% to p-cymene, after 20 minutes of reaction [28]. The same research group of before used mesoporous silica-alumina supports as catalysts with a SiO₂ content ranging from 1% (SIRAL 1) to 40% (SIRAL 40) [23]. Both the limonene conversion and the p-cymene selectivity linearly increase with the silica content with SIRAL 20 and SIRAL 40 catalysts leading to a complete conversion of limonene into p-cymene.

In another approach, limonene was previously isomerized into α-terpinene, γ-terpinene, 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 [78].

The dehydrogenation of limonene to p-cymene was explored by Cui et al. using a Pd/HZSM-5 catalyst under both inert (N₂) or reductive (H₂) reaction conditions. Due to

the endothermic nature of dehydroaromatization reactions, an increase of the reaction temperature is beneficial to the shift of the equilibrium toward p-cymene production both in presence and in absence of added hydrogen (Fig. 5).

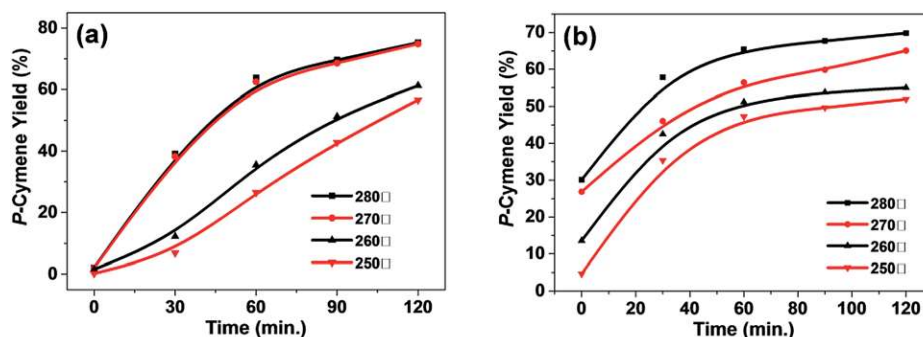


Fig. 5. Conversion of limonene into p-cymene over the Pd/HZSM-5 catalyst as function of time at 240, 260, 280, 300 °C (a) in absence of added hydrogen and (b) under inert atmosphere. Reproduced with permission from Cui et al. [79]. Copyright (2016) Royal Chemical Society

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 [79]. Most important, it was proved that the first step in the conversion of limonene into p-cymene is the isomerization then 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 [40]. The conversion of limonene increases by increasing both the reaction temperatures as well as the reaction time (Fig. 6).

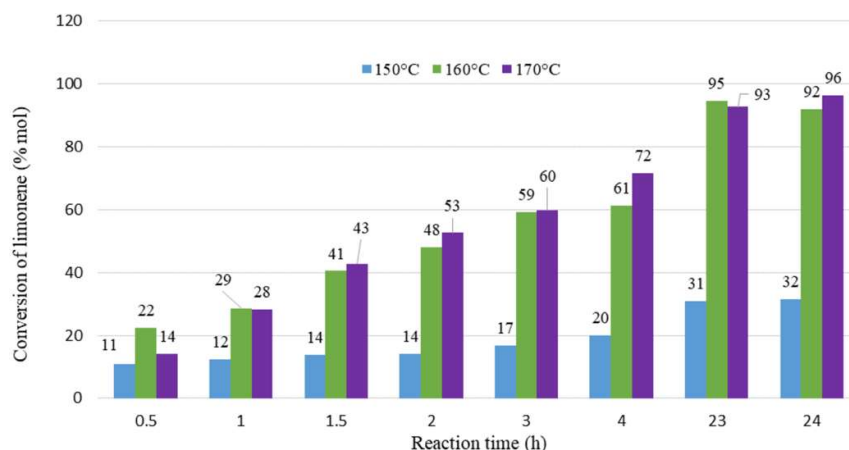


Fig. 6. Temperature effect on the isomerization of R-limonene. Reproduced with permission from Retajczyk et al. [40]. Copyright (2019) MDPI.

Results clearly show that, under the same process conditions (temperature 160 °C, catalyst content 15% wt, for 23 hours), 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 (Fig 7).

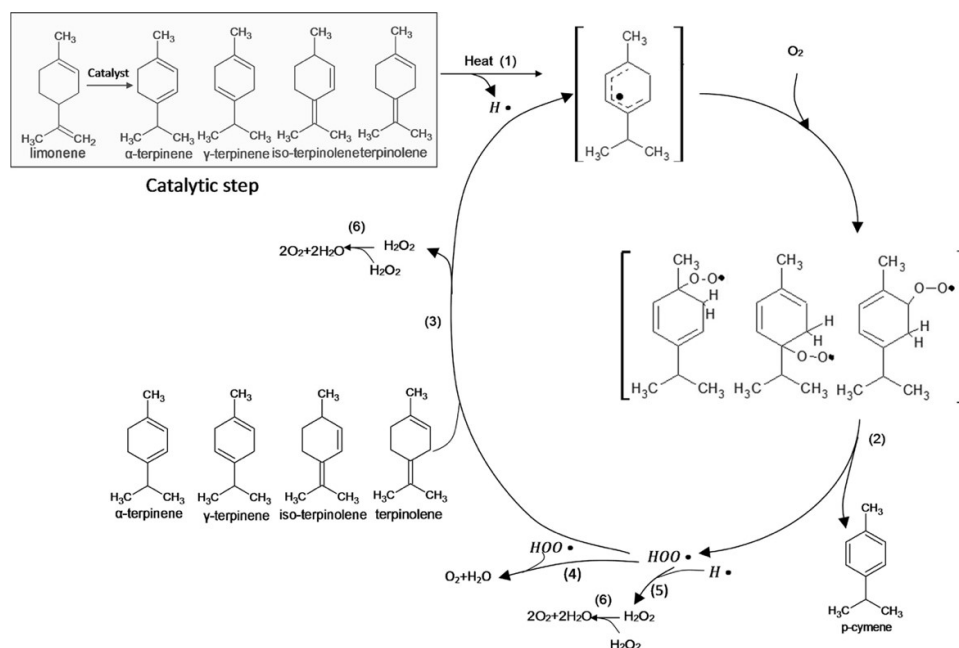


Fig.7. The reaction mechanism of the two-step conversion of limonene into p-cymene. Reproduced with permission from Makarouni et al. [35]. Copyright (2018) Elsevier Ltd.

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 hours is 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% [80].

It is generally accepted that addition of a transition metal to supports like silica, alumina, silica–alumina mixed oxides, zeolites and natural clays generally improves the catalytic performance as consequence of the dual functionality exhibited by metal-modified catalysts. In the case of the conversion of limonene into cymene, acid sites are responsible of the isomerization step while metallic sites can promote the dehydrogenation reaction [81, 34]. 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 [24], improving the p-cymene selectivity by up to 97% [75]. 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 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% [34].

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 Yilmazoglu et al. When the Pd/Al_2O_3 catalyst was used, the limonene was completely converted with an overall p-cymene yield of 80% [75].

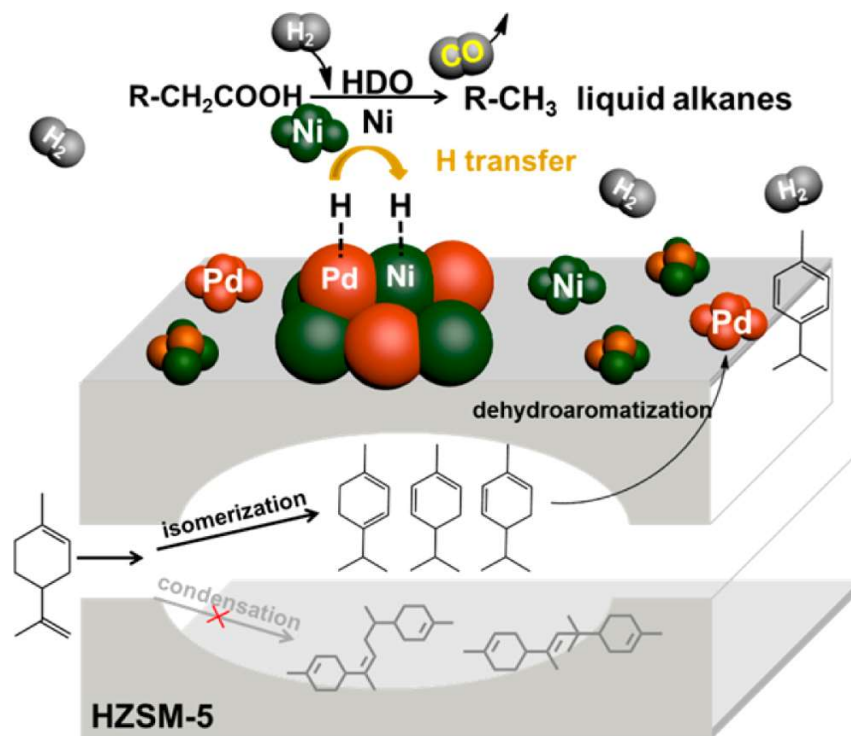


Figure 8. Brief description of individual steps for stearic acid and limonene coactivation using the bimetallic Pd-Ni/HZSM-5 catalyst. Reproduced with permission from Zhang et al. [83]. Copyright (2016) American Chemical Society.

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 biojet fuel) in the presence of the bimetallic Pd-Ni/HZSM-5 catalyst [82, 83]. Palladium promotes the conversion of limonene into to p-cymene and H_2 that is the reducing agent also for the hydrodeoxygenation of stearic acid to alkanes over Ni and Pd-Ni sites (Fig.c). Such 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 [84-88] thus opening new opportunities for the use of limonene as green and renewable H-donor solvent.

5. 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. Amide 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 converting virtually unlimited raw materials such as sugars will be industrialized [89], 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 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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