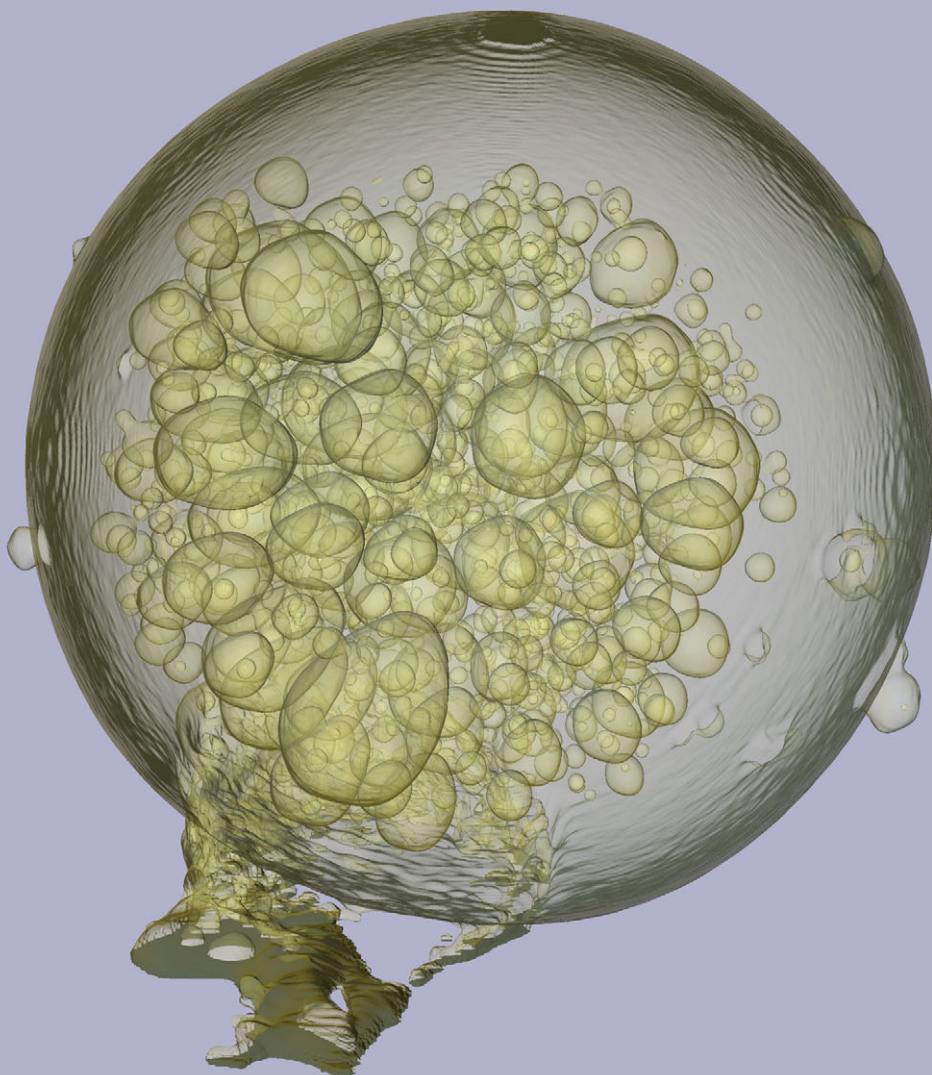


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Limonene: a versatile chemical of the bioeconomy

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(+)-Limonene is a renewable chemical with numerous and growing applications. Its traditional uses such as flavor, fragrance and green solvent are rapidly expanding to include its utilization as a platform chemical, extraction solvent for natural products and an active agent for functionalized products. We anticipate that the expansion in uses for limonene will translate into increasing production and use of this relevant natural product, especially for advanced applications.

1. Introduction

Often mistakenly denoted as “D-limonene”,¹ the dextrorotatory isomer (+)-limonene (or d-limonene, Fig. 1) is a monocyclic terpene comprising two isoprene units abundantly produced in nature as a secondary plant metabolite.² This isomer is the principal component of the essential oils present in the rind of citrus fruits, such as orange, lemon, mandarin, grapefruit and lime. The other optical isomer, (–)-limonene or l-limonene, has a turpentine smell and is also found in plants as the major component of volatiles emitted by oaks and pines.³

d-Limonene is a colourless oil sparingly soluble in water (13.8 mg L⁻¹ at 25 °C) with a sweet orange smell, widely used in food and cosmetic industries. Commercially, the terpene is

mostly obtained from waste orange peel (dry orange peel waste contains 3.8 wt% of d-limonene on a dry weight basis).⁴

The molecule, whose correct formula was first proposed by Wagner in 1894, has 76 electrons, with six stable conformational isomers (conformers).⁵ The electronic configuration of the ground state contains 38 doubly occupied molecular orbitals, with the highest occupied MO (HOMO, 2 π) corresponding to the π bond in the carbon ring, and the second highest occupied orbital (SHOMO, 1 π) corresponding to the π bond of the isopropenyl group (Fig. 2).⁶

With two double bonds easily functionalized, the molecule has a broad organic chemistry that was nicely summarized in 1989.⁷ During the last decade, and especially in the last three years, the utilization of d-limonene in different domains has significantly increased. The use of the terpene as a platform chemical, too, has been intensively investigated, and many new catalytic processes were reported affording valuable chemicals

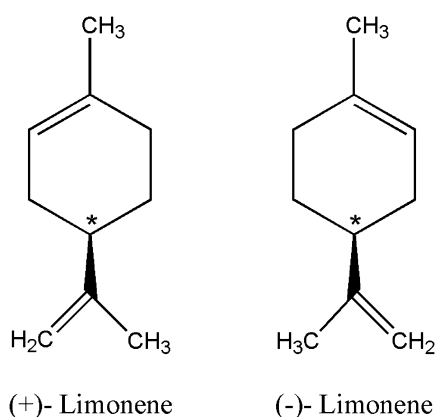


Fig. 1 Stereoisomers of limonene.

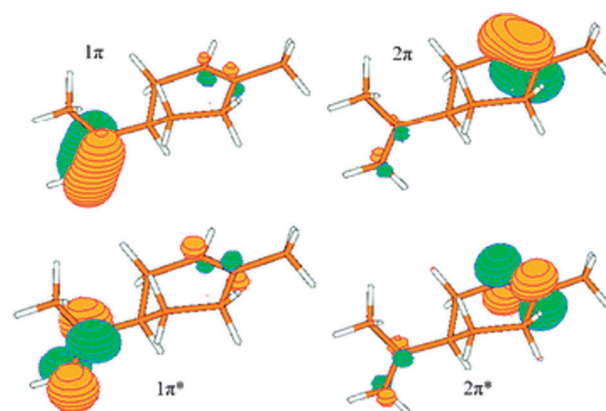


Fig. 2 Localisation of HOMO bonding and LUMO antibonding orbitals of the d-limonene molecule. The lowest unoccupied molecular orbital (LUMO) is the 1 π^* anti-bonding counterpart of the SHOMO; whereas the 2 π^* anti-bonding MO is located on the ring. [Reproduced from ref. 6, with kind permission.]

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and polymers. Indeed, terpene offers a wide range of potential products *via* chemical⁸ or biochemical⁹ catalytic conversion.

The recently developed new chemistry and uses of d-limonene, some of which are summarized in this account, show the great potential of this by-product of the citrus industry as an innovative green chemical for a wide variety of uses. In the following, we identify open opportunities for its development, and conclude by providing arguments supporting our conclusions that (+)-limonene will emerge as a valuable product and an intermediate of the 2nd generation biorefinery where high value added chemical products, and not low EROI (Energy return on energy invested) biofuels, are produced from biomass.¹⁰

2. Production

Generally recognized as a safe substance (holding the GRAS status of the US Food And Drug Administration) and included in the European Pharmacopoeia, orange oil (content of d-limonene 94–96%, depending on the crop's origin) is a widely employed flavoring agent for medicine and food found in a range of products like fruit juices, soft drinks, baked goods, ice cream and syrups. In perfumery, d-limonene is a highly volatile top note that finds use in a large number of commercial perfumes and fragrant products.¹¹

Since the late 1800s many chemical companies, mainly in Europe and later in the US, Brazil and Argentina, started to distill orange oil for the flavor and fragrance industry.¹² Along with limonene, essential orange oil contains over 140 chemical compounds in trace amount which impart color and further fragrance and healing properties.¹³

Today, (+)-limonene is obtained as a by-product of citric fruit juice processing, mainly by a cold process involving centrifugal separation or by steam distillation.

In the latter process, oranges are first squeezed for juice. The orange oil that floats on the top is food-grade d-limonene. Then, after a second pressing for further limonene extraction, the peels are transferred to a steam extractor. Upon addition of immiscible water, d-limonene is volatilized at 97 °C, rather than at the boiling point (175 °C) of the pure substance. The steam is then condensed forming a layer of orange essential oil comprising 90–95% pure d-limonene floating on condensed water.

In the low-temperature process the essential oil is obtained before the juice. A water jet hits the citrus fruits and the resulting emulsion is purified in a finisher before a centrifugation step produces high quality orange oil (Fig. 3) due to the low temperature minimizing oxidation.

Aiming to extract all the valuable components of waste orange peel (WOP) Clark's and Luque's teams have recently introduced a hydrothermal microwave process capable of extracting d-limonene, pectin and a form of mesoporous cellulose in a single step at 180 °C without drying or any other pre-treatment (Fig. 4).¹⁴

Beyond limonene, indeed, waste orange peel mainly contains pectin (23 wt%) and flavonoid (4.5 wt%) along with the structural polysaccharides (cellulose at 37 wt% and hemicellulose at 11 wt%).¹⁵ Investigation of the reaction conditions on a larger



Fig. 3 Orange essential oil from orange peel obtained at room temperature after centrifugation of the water oil emulsion. [Image courtesy of Fratelli Indelicato Srl.]

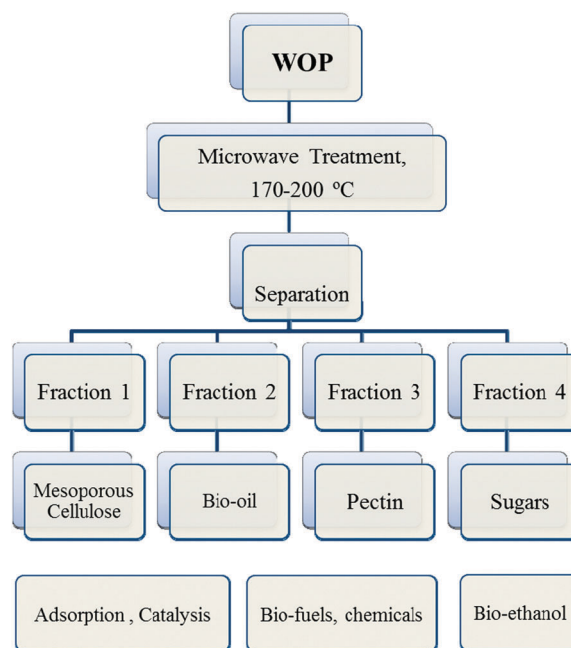


Fig. 4 Scheme of microwave hydrothermal pyrolysis of waste orange peel. WOP stands for waste orange peel. [Adapted from ref. 14, with kind permission.]

scale demonstrates the industrial potential of this approach for the production and the separation technology of d-limonene, pectin and also minor amounts of highly valuable flavonoids.

3. Market insight

The worldwide production of d-limonene in 2013 was estimated to exceed 70 000 tons (see below). On the other hand, the global orange production for 2013–2014 is projected to rise by 5% from the previous 2012–2013 season, to reach 51.8 million metric tons as a result of increased production in Brazil, China, and the European Union (EU, Table 1).¹⁶

Brazil is by far the largest producer, with an output approaching 40% of the world's orange production. To grow oranges and citrus fruits in general, hot, humid weather are required conditions because oranges and citrus are susceptible to cold.

Table 1 Orange production in selected countries in 2013–2014. Data are in 1000 metric tons

Country	Production	Country	Production
1 Brazil	17 750	9 Morocco	1000
2 China	7600	10 Vietnam	675
3 United states	6707	11 Argentina	550
4 European union	6600	12 Australia	465
5 Mexico	3900	13 Costa rica	315
6 Egypt	2570	14 Guatemala	150
7 Turkey	1700	15 Israel	100
8 South africa	1500	16 Other	191

Source: US Department of Agriculture, 2014. Adapted from ref. 16, with kind permission.

Manufacturers of d-limonene are ubiquitous across the globe.¹⁷ Some 300 orange oil distillation plants are installed worldwide, generally supplying customers with technical grade (95% in d-limonene) or food grade (96%) orange oil. A short list of selected suppliers showing such ubiquity includes Cutrale (Brazil), Hangzhou Dayangchem (China), Merck Schuchardt OHG (Germany), Capua 1880 (Italy), Finetech Industry Limited (UK), Tokyo Chemical Industry (Japan), Acros Organics (USA), Frutarom (Israel) and LemonConcentrate (Spain).

Like with any other agricultural product, the price of d-limonene is intrinsically volatile. For example, in 2011 the price first reached \$11 per kg, and then, within months, it fell to \$3.3 per kg, before resuming its ascent.¹⁷ Demand, in any case, has been constantly rising, and so have supply and price. As of mid 2014, the price in the US has exceeded \$10 per kg. A decade ago, manufacturers of industrial cleaning products were paying as low as \$0.4 per kg.

4. Alternative biosolvent

In the early 1950s Henry Schulz created in Florida the first large volume markets for d-limonene commercializing the isomer as a versatile solvent alternative to toxic solvents generally obtained from fossil fuel sources.¹⁸ Cleaning products for industrial and household purposes originally represented the largest market for d-limonene.

Toxic solvents such as toluene, *n*-hexane and chlorinated organic solvents can be effectively replaced by environmentally friendly d-limonene in many industrial contexts (Table 2).¹⁹

With a high Kauri-Butanol (KB) value of 67, (+)-limonene holds up to 2.5 times its own weight before becoming ineffective

Table 2 Relevant properties of d-limonene and commonly employed organic solvents^a

Properties	<i>n</i> -Hexane	Toluene	Dichloro- methane	d-Limonene
Boiling point (°C)	68.7	110.6	40	175.5
KB	29	105	136	67
Density	0.66	0.87	1.32	0.84
Toxicity	High	High	High	Absent
Environmental impact	High	High	High	Absent

^a Source: *Paint and Coating Testing Manual*, ed. J. V. Koleske, American Society for Testing and Materials, Ann Arbor, MI, 14th edn, 1995, ch. 18.

as a cleaning agent (the KB value is the outcome of a test method that demonstrates how much dirt a compound can hold relative to its own weight). Moreover, d-limonene is much more versatile and can clean widely different substrates (for example, a manufacturer of recreational vehicles in the US replaced 25 different products with a single d-limonene cleaner)¹⁹ than most oil-derived solvents allowing manufacturers to use d-limonene in place of many different solvent products.

Even as solvent the uses and field of applications of d-limonene are rapidly expanding. For example, the Gulf of Mexico's Deepwater Horizon oil spill²⁰ in 2011 contributed to absorbing a significant amount of d-limonene supplies, as a formulation of d-limonene with a surfactant was used to degrease and clean vessels and equipment with encrusted heavy oil (Fig. 5).²¹ Similarly, d-limonene is used to improve yields in the petroleum extraction (separation) from oil sands in Canada, Utah and other countries as it affords 96% recovery of bitumen.²²

Limonene can be conveniently formulated with surfactants to form environmentally friendly water-based cleaning formulations of lower flammability, lower odor and VOC suitable for treating contaminated surfaces in many industrial environments (cleaners for concrete, marine vessel, print inks and for adhesive removal).

For example, Rhodia has developed a microemulsion formulation comprising a dibasic ester solvent and nonionic surfactant, that lowers the amount of d-limonene required by 50–80%, without reducing its effectiveness.²³ Blends of dibasic ester compositions (such as dialkyl glutarate, dialkyl adipate and dialkyl succinate) are used as a vehicle ("solvent extender") to deliver d-limonene at reduced concentrations while maintaining or improving cleaning performance.

Another rapidly emerging application of d-limonene as a bio-based solvent is found in organic chemistry, as a green alternative to petroleum-based solvents in counter-current



Fig. 5 Workers in Louisiana using limonene-based cleaning agent PES-51 to decontaminate equipment used to clean large vessels following the Macondo well blowout and Deepwater Horizon explosion on April 20, 2011. [Image reproduced from ref. 20, with kind permission.]

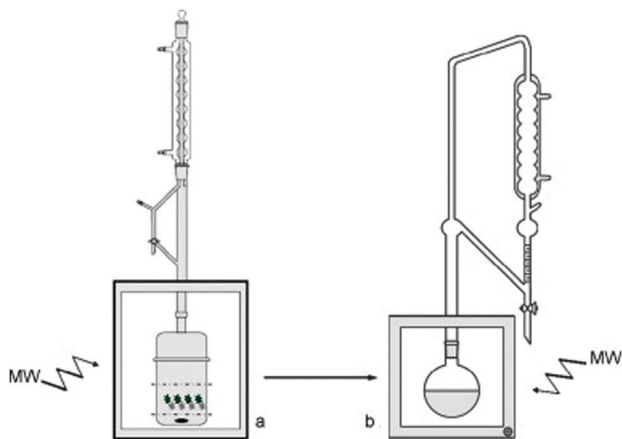


Fig. 6 Proposed extraction procedure using limonene: microwave-integrated Soxhlet extraction (a) followed by microwave Clevenger distillation (b). [Image reproduced from ref. 27, with kind permission.]

chromatography,²⁴ or in the extraction of natural products.²⁵ In 2008, the team of Chemat in France first described the use of d-limonene instead of *n*-hexane in the extraction of fats and oils in food *via* an efficient combination of microwave-integrated Soxhlet extraction and solvent removal through microwave Clevenger distillation (Fig. 6).²⁶

Analysis of the oils obtained from olive seeds *via* conventional heating (with *n*-hexane) and microwave Soxhlet extraction with d-limonene showed no significant difference between each extract.²⁷ Now, however, natural products are extracted thanks to another natural product in a materials cycle involving only renewable substances.

The microwave integrated extraction and solvent removal apparatus has been patented,²⁸ and is currently manufactured by an Italian company (Milestone) to be ideally utilized with d-limonene as extraction solvent.

5. Pest control agent and medical uses

First registered as an insecticide in the US in 1958 (and later as an antibacterial in 1971), d-limonene has been amongst the first natural pesticide ingredient used in environmentally-friendly pest control (Table 3). The terpene has indeed has low oral and dermal toxicity to mammals, birds and fish. Furthermore, it does not harm or repel honey bees. Today pesticide products containing limonene are used for flea and tick control on pets, insecticide sprays, mosquito larvicides, and insect repellents.²⁹

Table 3 Effect of spray treatments using 1% limonene, 2% insecticidal soap, or 2% horticultural oil on scales and mealybugs infesting gardenia in the greenhouse^a

Formulation sprayed	Mortality of green scales on potted gardenia plants (%)
1% limonene	95
2% insecticidal soap	89
2% horticultural oil	88

^a Adapted from ref. 29, with kind permission.

Several water-based formulations using d-limonene as an active agent are commercialized in the US such as, for instance, the *Orange Guard* product line manufactured in California.³⁰ Recently, the European Food Safety Authority published a review of orange oil risk assessment,³¹ which was used by the European Commission to approve a formulation containing orange oil as an insecticide active ingredient.³²

Finally, d-limonene has numerous (and growing) nutritional and medical uses, even though d-limonene is a moderate dermal, eye, and upper respiratory tract irritant. The molecule indeed is sensitive to oxygen in air, forming hydroperoxides that rapidly degrade forming numerous potent allergens including perillyl alcohol, carveol acetate, and carvone.³³

Aptly formulated in numerous commercial products, d-limonene is used as a metabolism aid and dietary supplement for detoxifying purposes. Its effective anticancer and cancer prevention properties were identified in the late 1980s.³⁴ Later on, it was discovered that d-limonene promotes the GST (Glutathione *S*-transferase) system in the liver and small bowel, which eliminates carcinogens.³⁵ Miller and co-workers have recently discussed in depth the use of limonene for chemotherapeutic and chemopreventive treatments.³⁶

A decade ago, Keinan's team in Israel identified the anti asthmatic properties of d-limonene in animals.³⁷ According to the proposed hypothesis, the increasing levels of asthma in urban centers that lack vegetation are due to the lack of limonene as well as of other terpenes in the troposphere which leads to increased levels of ozone. Indeed, radical reactions with OH radicals and O₃ molecules at 298 K (affording calculated tropospheric lifetimes of limonene for gas-phase reaction values of less than 2 h) are responsible for the tropospheric removal of monoterpenes.³⁸ On the other hand, Limão-Vieira and co-workers have shown that the UV photolysis of d-limonene requires several days.⁶

6. An emerging platform chemical?

Since structurally d-limonene possesses two double bonds, a chiral centre, and a 6-member hydrocarbon ring, the terpene can be readily converted into useful chiral intermediates or benzene-like structures *via* isomerization, addition, epoxidation, or hydration–dehydration reactions.⁶ Hence, at least in principle, d-limonene might be used as a platform chemical to produce valued added products.

In detail, the potential application of d-limonene as a platform chemical for making polymers arises from the ease with which the six membered hydrocarbon ring of d-limonene is either converted into that of aromatic *p*-cymene *via* dehydrogenation;^{39,40} or with which the two distinct unconjugated electron-rich C=C double-bonds are radically polymerized.

In the first approach, *p*-cymene is oxidised to terephthalic acid, and the acid is easily polymerized by polycondensation to afford polyesters such as PET.⁴¹ Alternatively, a cleaner route to these polyesters is the metal complex-catalyzed ring-opening copolymerization of cyclic anhydrides and limonene epoxide.^{42,43}

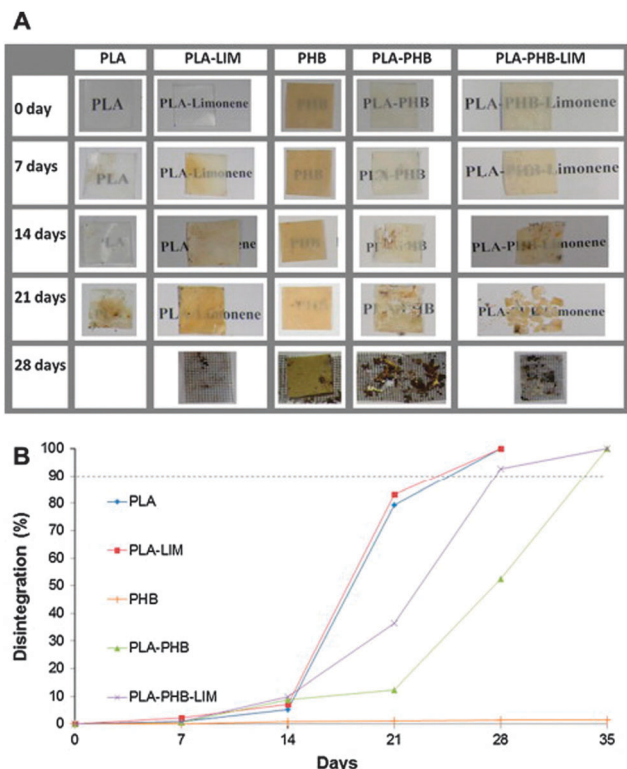


Fig. 7 Appearance of film samples before and after different days of disintegration under composting conditions (A). Film samples with d-limonene (PLA-LIM and PLA-PHB-LIM, B) disintegrate much faster than their counterparts without d-limonene (PLA and PLA-PHB). [Image reproduced from ref. 45, with kind permission.]

The intrinsic high value of d-limonene and the current and foreseeable production levels, even at 100 000 tonnes per year, suggest that d-limonene will not be used as a platform chemical for polymers or chemicals produced in massive amount ($>10^6$ t per y) such as PET to make plastic bottles, nor to replace polystyrene.

Valued (and expensive) d-limonene will be rather conveniently used to produce advanced polymers for specialized applications such as, for example, bio-based polyesters derived from limonene and 5-hydroxymethylfurfural (HMF) to make patented bioaxially oriented window films and laminates that exhibit excellent clarity and light stability higher than the oil-derived counterparts;⁴⁴ or the transparent, flexible films (Fig. 7) with an enhanced oxygen barrier, water resistance and biodegradability properties for biodegradable food packaging applications obtained by simply blending poly(lactic acid) and poly(hydroxybutyrate) with d-limonene.⁴⁵

7. Limonene-based advanced polymers

A decade ago, the first biodegradable polylimonene carbonate was formed by Coates and co-workers through the copolymerization of carbon dioxide with limonene oxide catalyzed by

zinc complexes.⁴⁶ The thermoplastic polymer has properties similar to those of polystyrene.

To the best of our knowledge the process was not improved further, until 2012 when Mülhaupt and co-workers reported a carbonation synthesis with CO₂ catalysed either by tetrabutylammonium bromide or, better, by silica supported 4-pyrrolidino-pyridinium iodide to afford 34.4 wt% CO₂ incorporation in the form of limonene dicarbonate (LC).⁴⁷

Organic carbonates are excellent organic solvents with great potential to replace many toxic volatile solvents.⁴⁸ Further to find a renewable source for the organic carbonate utilising biomass waste, the utilisation of CO₂ in the synthesis of polycarbonates is clearly desirable for environmental and economic reasons.⁴⁹

The mono- or di-limonene epoxides formed by d-limonene oxidation are copolymerized with carbon dioxide or with succinic anhydride affording valued thermoplastic polycarbonates or polyesters (Fig. 8); whereas thermoset polyurethanes with excellent properties are obtained *via* copolymerization of limonene dicarbonate with polyfunctional amines.

After the curing process with di-, tri- and polyfunctional amines, limonene carbonate could be converted into a variety of crosslinked terpene-based non-isocyanate polyurethane resins (NIPUs) with good and tuneable polymer properties. For example, the mechanical and thermal properties of these resins, such as stiffness and glass transition temperatures (with values of Young's modulus of 4100 MPa and 62 °C) increase proportionally as a function of the amine groups present in the curing agent.

Another advanced route to limonene-based polyamides and NIPUs has been developed by Meier and co-workers who utilized the ene-thiol "click" reaction for the synthesis of the precursor monomers (cysteamine hydrochloride added to d-limonene).⁵⁰ The aforementioned compounds allow a range of varied arrangements, ending up with copolymers of amides, fatty acids and limonene whose properties are tuneable for several applications.

Similarly, Johansson and co-workers in Sweden have lately shown⁵¹ how the thermoset polymers synthesized *via* the free-radical mediated thiol-ene reaction applied to d-limonene are potentially useful as sealants and adhesives in a wide variety of applications including organic coatings. The versatility of UV-irradiation over thermal initiation makes the method particularly suitable for green industrial syntheses using d-limonene and multifunctional thiols.

8. Microencapsulation

Microencapsulation is eminently suited to provide limonene-functionalized products with several potential uses. Rodrigues and co-workers have shown how perfumed polyurethane-urea microcapsules using d-limonene can be used to make scented fabrics that lose the microencapsulated terpene after five dry cleaning cycles.⁵²

Improving on these results with the aim to afford an anti-microbial and fragrant finishing, Sundrarajan in India recently

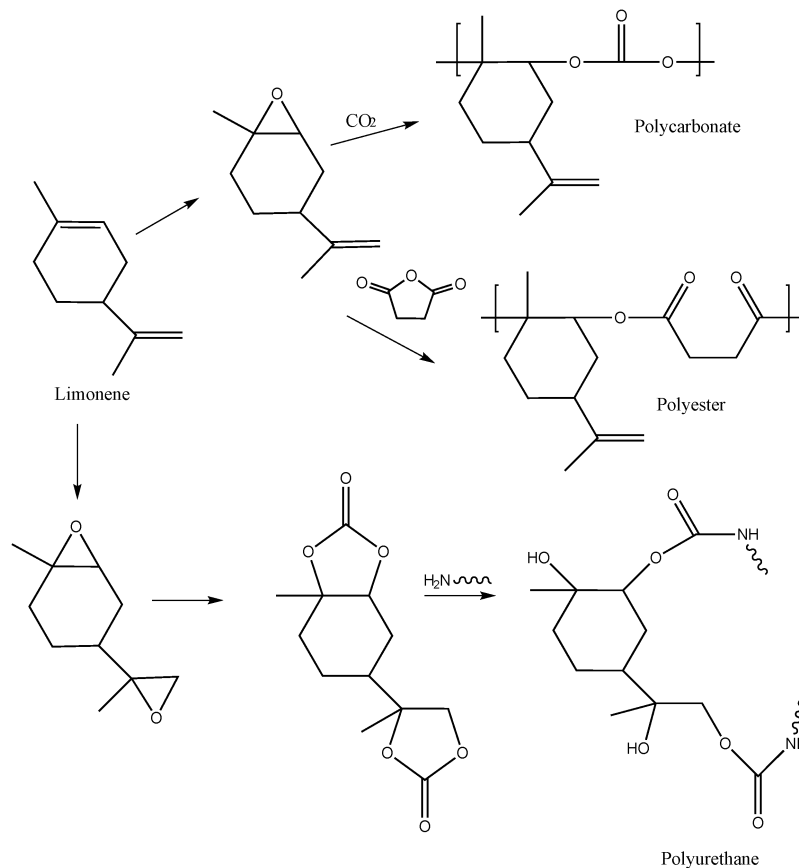


Fig. 8 A general strategy to bio-plastics from d-limonene according to Mülhaupt and co-workers. [Adapted from ref. 47, with permission.]

used biodegradable gum acacia to encapsulate limonene *via* coacervation.⁵³ The resulting cotton fabrics are capable of retaining antibacterial properties even after 5 washing cycles due to covalent bonding of terpene to the gum acacia microcapsule through the citric acid cross linker.

Many other microencapsulation routes and microencapsulants have been reported in the last few years, including sol-gel silica microspheres⁵⁴ (Fig. 9) and beta-cyclodextrins.⁵⁵ In general, microencapsulation, protection and controlled release of valued d-limonene, especially through GRAS approved substances such as silica⁵⁶ or carbohydrates is a chemical technology for the valorization of terpene that will find widespread application.

9. Perspectives and conclusions

In the 2013–2014 season, about 40% of the 51.8 million tons global orange production¹⁶ will be used for orange juice production. This will lead to about 13 million tonnes of waste orange peel, from which 520 000 tons of d-limonene could be obtained (assuming a d-limonene content of 3.8 wt%).⁴ Yet, market estimates⁵⁷ suggest that only 70 000 tonnes of d-limonene will be extracted and commercialized from such waste in the said season. In other words, most of the limonene, cellulose, pectin and other valued products comprising the orange peels will end in landfill where they will slowly biodegrade, in one of the most eminent examples of waste in modern industrial societies.

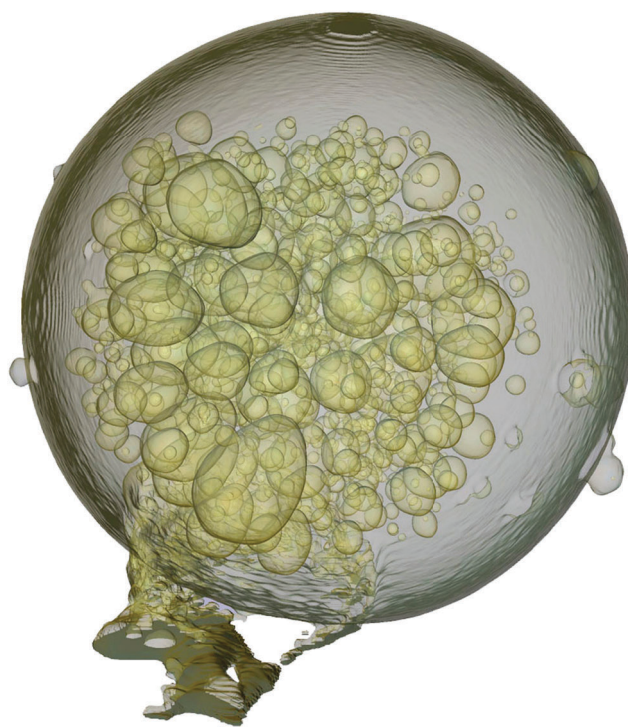


Fig. 9 X-ray micro-tomography image of a Ceramisphere (a trademark of Ceramisphere Pty Ltd) containing encapsulated limonene. [Photo courtesy of Dr Sherry Mayo, ANSTO, reproduced with kind permission of Ceramisphere.]

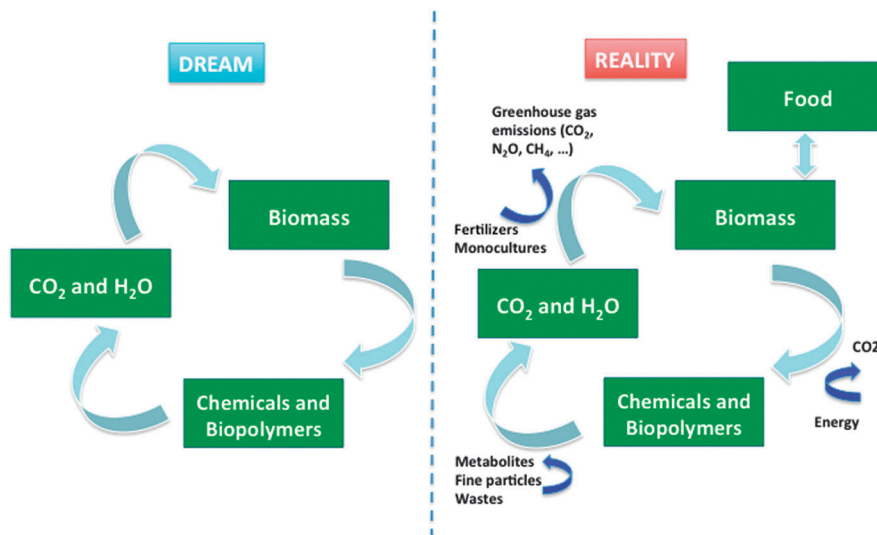


Fig. 10 The reality of the bioeconomy (right) strides with the illusion of closed carbon cycle chemical and polymer manufacturing based on biomass (left). [Adapted from ref. 58, with kind permission.]

Recently Mülhaupt has criticized the “illusion” of the solar-driven closed carbon cycle chemical and polymer manufacturing based on biomass, calling for a realistic approach (Fig. 10).⁵⁸ Intensive crop monocultures will threaten biodiversity. Competition for land with food production will start, whereas plenty of energy is required to convert biomass into chemicals and polymers. Finally, degradation does not take place in the absence of water or oxygen, and even in that case formation of hazardous metabolites, waste and fine nanoparticles must be taken into consideration.

Along these lines, we critically emphasize here that progress in the chemical valorization of d-limonene from waste orange peel will actually boost, rather than undermine, the efficiency of the citrus

and food industries. No intensification of agriculture is required to make use of d-limonene, currently largely wasted in landfills; nor the production of limonene interferes with food production.

Indeed, the results of a recent life cycle analysis (LCA)⁵⁹ carried out in the US on behalf of the Renewable Citrus Products Association suggest that d-limonene has the most sustainable environmental profile (lowest contribution to global warming, acidification, smog formation and natural resource depletion) when compared to petroleum-based counterparts. For example, the contribution to global warming from the production and transportation of d-limonene is the lowest (321 kg CO₂-eq. per 1000 kg of product) when compared to petroleum-derived solvents (Fig. 11).

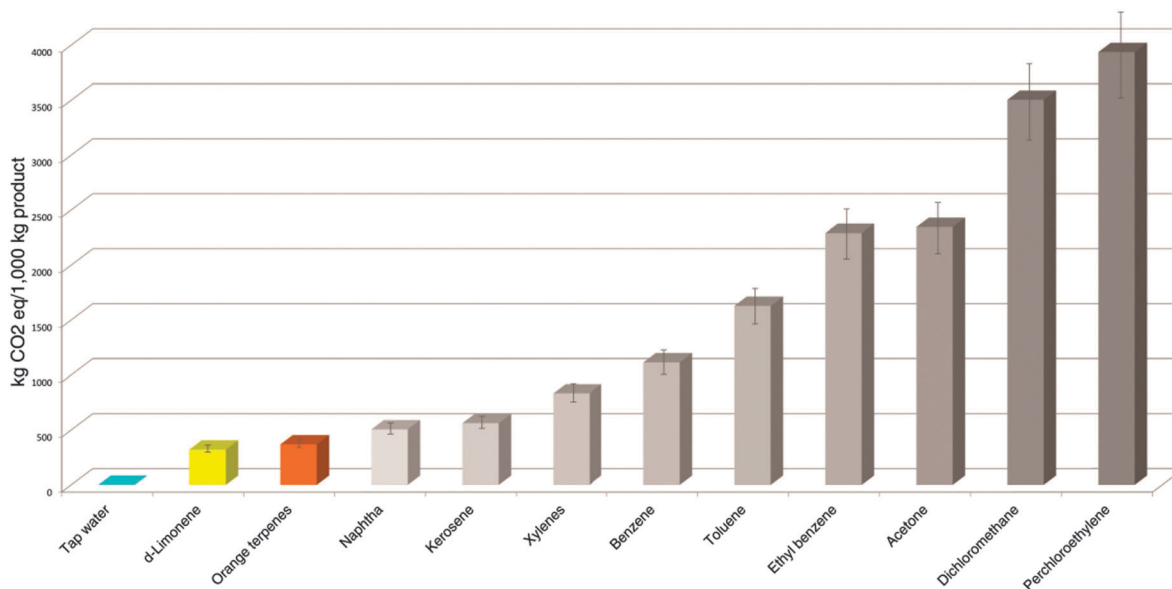


Fig. 11 Global warming potential for d-limonene and petroleum-based solvents based on life cycle analysis. [Reproduced from ref. 59, with kind permission.]

The use of (+)-limonene in the emerging bioeconomy, we argue in conclusion, will be twofold. First, the natural product will be increasingly used formulations allowing more effective use (*i.e.* to further exploit its remarkable chemical and biological properties) for example in new home and personal care products, nutraceuticals, pesticides, cleaning formulations as well as organic solvents for natural products extraction. New direct uses of limonene will also rely on effective microencapsulation to fabricate valued antimicrobial and fragrant products.

Second, (+)-limonene will be used as chemical raw material to manufacture valued fine chemicals and advanced polymers for special applications, especially using as co-monomer CO₂ retrieved from the atmosphere⁶⁰ to form easily polymerized limonene carbonate. The examples selected in this study demonstrate how these uses are actually emerging.

The rapidly growing direct and indirect industrial uses of d-limonene are indeed already translating into rising production of orange oil, without generating more waste. Eventually, the citrus industry will stop to landfill waste orange peel altogether to become a supplier of citrus-based biorefineries, closing an important manufacturing cycle of the new bioeconomy in which waste is correctly seen as a valued resource.⁶¹

Supporting this argument, a recent economic analysis⁶² of the hydrothermal microwave process developed by Clark and Luque based on processing of 50 000 tonnes of waste orange peel showed excellent profitability with revenues 2.5 higher than costs; but this only assuming that the citrus biorefinery products (pectin and d-limonene) were sold at the actual market price. In other words, the sustainable citrus-based biorefinery will require integration between orange producers and waste orange peel biorefiners, with elimination of intermediaries.

Acknowledgements

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