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The Case for a Lemon Bioeconomy

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Dedicated to Prof. Tatiana Budtova, Centre de Mise en Forme des Materiaux, MINES ParisTech, for all she has done for the development of bio-based aerogels

Today's green chemistry technologies open the route to a broader and richer economy for lemons, well beyond the fresh fruit and fruit juice markets. This has important social, environmental, and economic consequences for all lemon-growing countries and for many industries. Which are the new bioproducts obtainable from lemon and its by-products? And what are the unforeseen new applications of old bioproducts such as pectin? Following an updated outlook on the global lemon economy, it is shown through selected examples how the lemon bioeconomy might unfold in the course of the next few years (2021–2025).

1. Introduction

The use of fruit processing by-products as a source of valued chemicals and bioproducts, well beyond biogas production, is now a common industrial practice in many countries of the world.[1] From apple to strawberry, for example, a recent book on the valorization of fruit by-products lists twelve fruits whose co-products such as peel, seed, leaf, shell, and flowers are routinely used a source of essential oils, phytochemicals, organic acids, pectin, enzymes, dietary fiber, and even protein.[1]

Amid them, citrus fruits grown chiefly as orange, lemon, grapefruit, mandarin, lime, and tangerine varieties in over 146 million tons in 2016 are the largest and richest potential source of valued bioproducts.[2]

In the course of the last decade, successful research efforts have established several new and cleaner production routes to all valued products contained, for instance, in the citrus peel. Microwave-assisted extraction in water,[3] solar energy driven hydrodistillation,[4] microwave-assisted hydrodiffusion and gravity,[5] and hydrodynamic cavitation in water,[6] are eminent examples of the said new routes.

Plentiful work has been dedicated to the orange bioeconomy. The concept of the waste orange peel biorefinery was extensively discussed as early as of 2010.[7] Less research has been dedicated to the lemon biorefinery, even though lemon (and not orange) peel is the industry's preferred source of pectin since almost a century,[8] and lemon was the source of citric acid until the introduction, in 1923, of sugar fermentation over *Aspergillus niger*.[9]

The fruits of lemon (*Citrus limon* L.) contain numerous phytochemicals, including biophenols, terpenes, citric acid, and tannins.[10]

Today's green chemistry technologies, we argue in this account, open the route to a broader and richer economy for lemon based on valorization of the so important biological resources so far unused and either disposed of as waste or given away for low valued added uses such as cattle feeding.

This outcome has important social, environmental, and economic consequences for all lemon-growing countries as well as for many industries. Driven by powerful megatrend demand for healthy "naturals" in food, beverage, cosmetic, personal care, and nutraceutical products, the demand of lemons has been growing steadily. Main producing countries are expected to report significant increase in productions by over 1.2 million tons in the next five years (>700 000 t in the northern hemisphere and >550 000 t in the southern hemisphere).[11]

For example, in 2017 the surprisingly high amount of free biophenols extracted (with methanol at 30 °C) from freeze dried lemon fruit was found to show high angiotensin I-converting enzyme and α-glucosidase inhibitory activity;[12] whereas powerful lipase inhibition makes lemon a suitable agent for antilipolytic purpose.[13]

Following an updated outlook on the global lemon economy, we show through selected examples how the aforementioned bioeconomy might unfold in the course of the next few years (2021–2025).

2. The Global Lemon Economy

Between 1980 and 2016, the lemon share of the citrus market increased from 5% to 13%, going from 5.2 to 17.5 million tons.[11]

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Table 1. Leading lemon exporting countries in 2017.

Rank	Country	Tons exported
1	Mexico	733 918
2	Spain	688 256
3	Turkey	451 911
4	South Africa	299 020
5	Argentina	237 653
6	USA	132 616
7	Brazil	92 393
8	Chile	76 806
9	Italy	47 470
10	Egypt	25 051

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Argentina is the largest lemon producer in the world, followed by Spain (1.15 million tons in 2018/19).[14] Italy (424 000 tons in 2018/19) is the second largest lemon producer in Europe, with 88% of the overall production located in Sicily, followed by Greece (88 258 tons), and Portugal (16 000 tons).[14]

Mexico is the largest exporter, followed by Spain and Turkey (**Table 1**). The overall amount of lemons traded in 2016 amounted to 3.1 million tons, namely 19% of the overall citrus trade.[11]

Following banana (148 million tons in 2016), citrus (146.5 million tons in the same year) is the second leading fruit globally. Its production between 1980 and 2016 has increased by 140% (lower than the 155% average fruit). Also due to decline of consumption of fresh citrus produce in many countries, the share of citrus in total fruit production has gone from 18% to 17%.[11]

Within the citrus family, the market demand of lemons is growing at the fastest rate, leading to rapid increases in lemons planted area. For example, in western Europe the overall planted area has gone from 68 000 ha in 2013, to 78 000 ha in 2019.[14]

Beyond costly lemon essential oil, currently lemon juice is the most valued product obtained from lemon. The juice is mostly exported as fresh or concentrate juice. In the latter case, after transport, concentrated juice is reconstituted with water. In general, the industry chiefly produces lemon juice concentrate which is stored and delivered to customers at low temperature (–22 °C) to preserve its organoleptic properties.

The global demand for lemon juice is between 110 000–130 000 t per year, with Argentina's companies supplying between 65 000–75 000 t in normal harvesting seasons.[15]

Being an agricultural product subject to weather, the market is intrinsically volatile. Annual volatility has been 23% for European lemon juice 400 gpl, and 21% for Argentinian lemon juice concentrate of the same titer.[15] The acronym "gpl" stands for grams per liter of citric acid since the latter acid content is the most important parameter in end beverage applications. Lemon juice concentrate is also traded at 500 gpl level.

In late 2018 the "free on board" Buenos Aires price of 400 gpl lemon juice concentrate was between \$3000 per t and \$3100 per t. Six months later, the price was significantly lower, quoting around \$2600–2700 per t.[16]

Lemon essential oil is a much valued product. The price for the Italian product by mid-2018 was €35 000 per t (\$41 000 per t), similar to the Argentinian product.[17] The global market for the oil is expected to grow at 7% annual growth rate during the period 2019–2023, adding \$260 million to the 2018 revenues.[18]

On late 2019 in Madrid sector representatives from Argentina, Chile, Italy, Morocco, Peru, Spain, and South Africa agreed to establish a new global association (the World Citrus Organization, WCO) as a "global platform for dialogue and action between the citrus producing countries worldwide" and "to increase coordination in the industry." In a few months, the association was joined by sector representatives of seven more countries (Australia, Bolivia, Brazil, Egypt, Greece, Portugal, and the United States of America).[19]

Perhaps not surprisingly, "to identify and promote research and innovation projects specific to the citrus sector" was third amid the six points specifying the WCO mission. New research on lemon, we summarize in the following, is opening the route to several new uses and applications of this key citrus fruit.

3. New Research on Lemon

New research undertaken in the last decade (2010–2019) has shown both new biological and nutraceutical properties of lemon and new ways to extract and valorize the fruit by-product components, some of which were previously not known.

For instance, in 2019 scholars in the USA reported the discovery of a water soluble yellow dye isolated from the ethanol extract of the zest of *C. limon* (**Figure 1**).[20]

Called by Hamann and co-workers as "Yellow 15," the dye limocitrol 3-*O*-6"-[3-hydroxyl-3-methylglutaryl)]-glucopyranoside is not only more soluble in water than curcumin and crocin natural yellows, but it is significantly more stable than the latter dyes. For example, when exposed to sunlight at room temperature for one month the color of a Yellow 15 solution barely changes, whereas the color of the crocin and curcumin solutions is significantly altered.[20]

We briefly remind that besides flavonoid glycosides, the lemon color is due to chlorophylls and carotenoids.[21] Flavone glycosides such as naringin, hesperidin, narirutin, and neohesperidin also add color and are also powerful antioxidants which, preventing for example the oxidation of lipids, might replace

Figure 1. From left to right: ethyl acetate, ethanol, and water extracts of *Citrus limon* outer peel (zest). Image courtesy Prof. Mark Hamann, The Medical University of South Carolina.

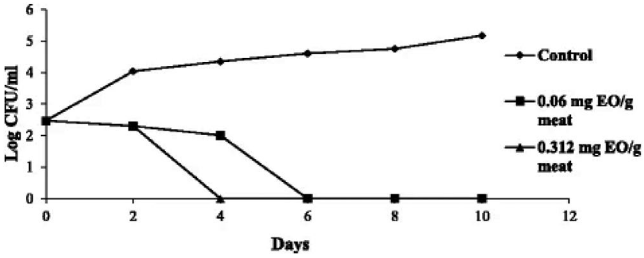

Figure 2. Time-related survival of *L. monocytogenes* at 4 °C following treatment with increasing concentrations of ClEO. Bacteria were supplemented in minced beef meat samples at 106 CFU g^{-1} of meat. Values are the average of three individual replicates. Reproduced under the terms of the Creative Commons Attribution 4.0 International License.[25] Copyright 2017, The Authors.

synthetic food antioxidants such as butylated hydroxyanisole and butylated hydroxytoluene.[22]

In 2011, a randomized, double-blinded, placebo-controlled study in subjects with joint discomfort revealed that supplementation with a nutritional supplement containing standardized lemon verbena extract (14% verbascoside, w/w) and fish oil omega-3 lipids significantly reduced symptoms of pain and stiffness.[23] Improved physical function was clearly shown after 9 weeks of treatment, with onset of the effect observed at the third and fourth weeks.

In 2012, scholars in Italy reported that lemon essential oil (EO), particularly EOs from fresh Sicily's lemons rich in oxygenated monoterpenes such as 4-terpineol, α-terpineol, cis-geraniol, β-citral, nerol, and α-citral are able to inhibit several strains of *Listeria monocytogenes*, *Staphylococcus aureus*, and also Gram-negative *Salmonella enterica* at very low microbial inhibitory concentration (between 0.019 and 0.156 µg mL^{-1}).[24] The latter pathogenic bacteria are often associated with serious foodborne diseases.

Applying and expanding the latter in vitro findings, in 2017 a team in Tunisia reported that lemon EO added to minced beef meat successfully inhibits development of *L. monocytogenes* in meat treated with EO at a concentration between 0.06 and 0.312 mg of EO per g of meat (**Figure 2**), reducing the growth of the bacteria by 2.5 log cycles after 4 and 6 days of storage at 4 °C, respectively, thereby opening "new promising opportunities for the prevention of contamination from and growth of pathogenic bacteria… during minced beef meat storage at 4 °C."[25]

In the same year, Tsuji and co-workers in Japan found that daily intake of citrus fruits, such as oranges, grapefruits, lemons, or limes, can reduce the risk of dementia developing among older adults by almost 15%.[26]

Analyzing 13 373 pensioners living in Ohsaki City, aged 65 years and older on December 1, 2006, to see how many developed dementia in the seven years following 2012, the team found that rates of dementia among those eating citrus fruit at least once a day were 23% lower than in those who ate them less than twice a week.

Having characterized the baseline of other factors that may be related to dementia, such as psychological distress, motor functions, and cognitive functions, the team made the hypothesis that this outcome is due to citrus flavonoids, known to be able to cross the blood–brain barrier, playing antioxidant and anti-inflammatory action in the brain.

Two years later, indeed, another team based in South Korea reported that nobiletin (2-(3,4-dimethoxyphenyl)-5,6,7,8-tetramethoxychromen-4-one), one of the major polymethoxyflavones in the peel of citrus fruits abundant in lemon peels,[27] is a potent inhibitor of β-amyloid peptide, the hallmark of Alzheimer's disease ultimately causing the death of neurons.[28]

Nobiletin significantly ameliorated Aβ_{25-35}-mediated cell death by restoring abnormal changes in intracellular oxidative stress (**Figure 3**), cell cycle, nuclear morphology, and activity of apoptotic caspase; showed excellent anti-inflammatory activity in response to Aβ stimulation; and inhibited Aβ-stimulated inducible NO synthase and cyclooxygenase-2 expression. These data, the team concluded, "implicate nobiletin as a potential candidate for the prevention of Alzheimer's disease through the inhibition of oxidative stress, apoptosis, and inflammation."[28]

Given these extraordinary properties, it is perhaps not surprising to learn that a supplement derived from Spain's lemon "verbena" taken in 1.2 g per day amount over a three-week trial was found in 2015 to help university athlete participants in a placebo-controlled study to sleep better (a 44% improvement in sleep, compared to those taking a placebo), reduce muscle pain and improve recovery time.[29] Hematic analyses clearly showed reduced levels of protein carbonyls, malondialdehyde,

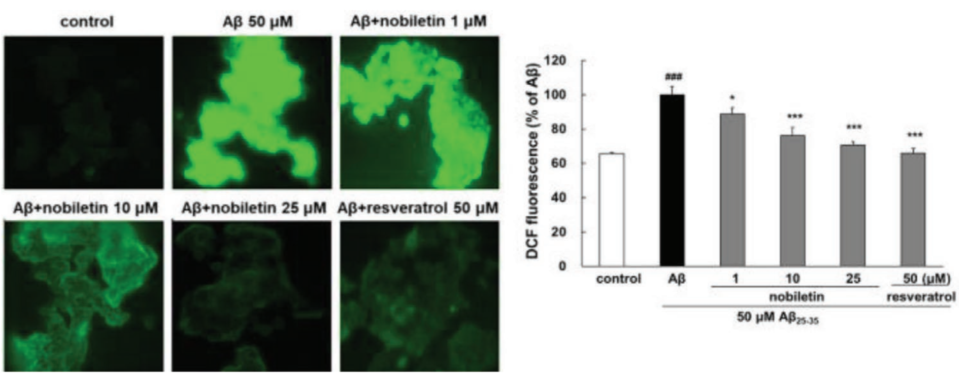

Figure 3. Intracellular radical oxygen species (ROS) production was observed by CM-H_2DCFDA fluorescent dye. ###$p < 0.001$, ##$p < 0.01$, and #$p < 0.05$ versus control. ***$p < 0.001$, **$p < 0.01$, and *$p < 0.05$ versus Aβ_{25-35}. Reproduced under the terms of the Creative Commons Attribution 4.0 International License.[27] Copyright 2018, The Authors.

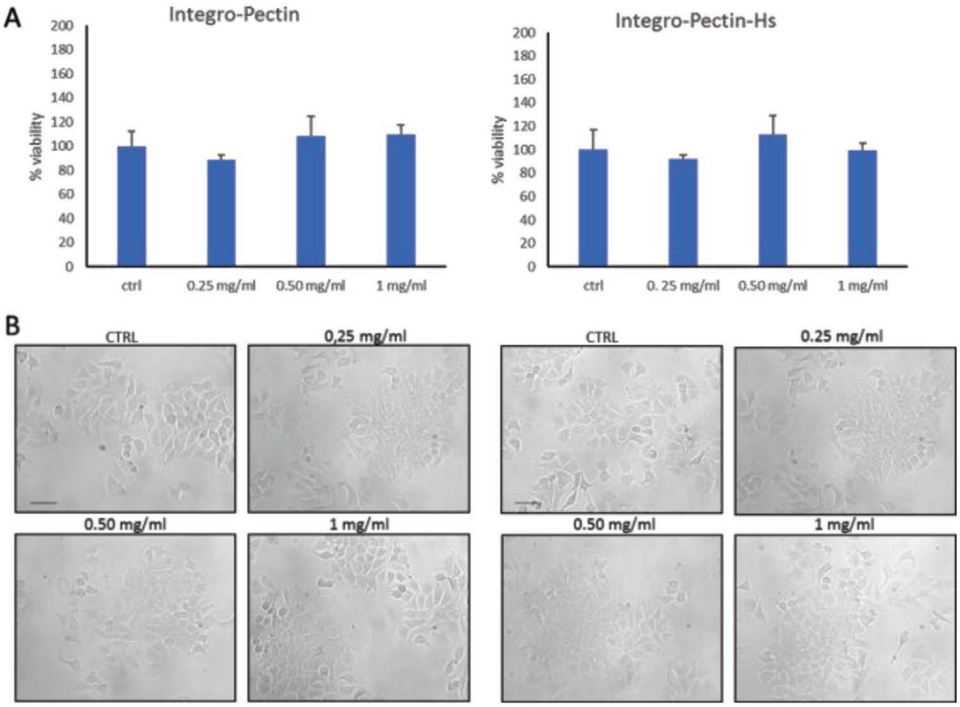

Figure 4. A) Epithelial human cell viability at different integral lemon pectin (IntegroPectin) and heat-stressed pectin concentrations compared with control and B) cellular morphology at different pectin concentrations compared with control. Bar = 100 µm, Control = CTRL. Reproduced under the terms of the Creative Commons Attribution 4.0 International License.[33] Copyright 2019, The Authors.

and myeloperoxide, markers associated with oxidative stress and inflammation.

Lemon pectin is also a source of valued pectin oligosaccharides showing potent prebiotic activity, for example, by increasing the population of healthy bacterial species like the lactobacilli.[30] The latter fermentative lactic acid bacteria today are widely used as probiotics, namely as microbes which transiting the gastrointestine benefit the health of the user.[31] Non-digestible prebiotic lemon pectin oligosaccharides pass the small intestine and access the lower gut where they become accessible to probiotic bacteria.

In light of these results and of the emerging nutraceutical and pharmaceutical applications of lemon pectin, it is therefore remarkable that pectin integrally extracted with all water-soluble phytochemicals from waste lemon peel via hydrodynamic cavitation in water (directly at pre-industrial scale) shows exceptionally high antioxidant and non-cytotoxic activity (**Figure 4**).[32]

Getting to advanced functional materials surprisingly obtainable from lemon pectin, in 2014 Budtova and co-workers reported the discovery that pectin aerogels obtained from medium and highly methylated citrus pectins are mechanically strong and thermal superinsulating materials (conductivity below 0.025 W m^{-1} K^{-1}) with conductivity increasing from 0.018 to 0.03 W m^{-1} K^{-1} for "aeropectins" having densities from 0.05 to 0.15 g cm^{-3}.[33]

Four years later, Groult and Budtova optimized the aeropectin morphology and density obtaining from a solution of commercial lemon pectin having a degree of esterification (DE) of 35% at pH 2 (pectin concentration of 2 wt%) a bio-based aerogel having thermal conductivity as low as 0.0147 W m^{-1} K^{-1} (**Figure 5**).[34]

The latter is the lowest value ever reported for bio-aerogels, very close to silica aerogels (0.013–0.014 W m^{-1} K^{-1}) but with the key advantage that pectin-based aerogels do not break under compression.[33]

At the aforementioned pH value the galacturonic acid moieties in the pectin structure are highly deprotonated resulting in molecular chain extension and repulsion. Solvent exchange takes place directly within the cavity of the alcogel (the pectin chains do not form continuous junction zones) resulting in a mesoporous material with high specific surface area. Mesopores minimize the conduction of the gaseous phase, thanks to the Knudsen effect.

Besides use as thermal insulating materials of far lower cost when compared to SiO_2 aerogels obtained via the sol–gel

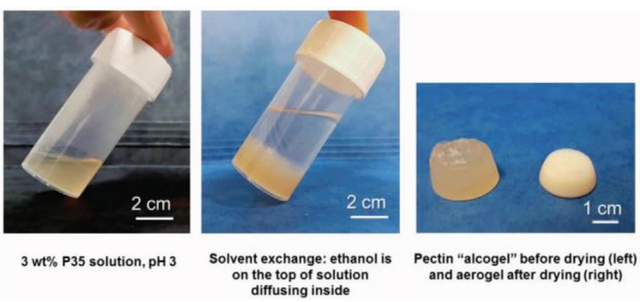

Figure 5. Illustration of solvent exchange for non-gelled solutions: pictures of non-gelled lemon pectin P35 solution (3 wt%, pH 3), solvent exchange, "alcogel" and aerogel. Reproduced with permission.[34] Copyright 2018, Elsevier.

process followed by supercritical drying, nontoxic and bio-based lemon pectin-derived aerogels hold uniquely large applicative potential in medicine and in cosmetics.[35]

4. Outlook and Perspectives

New avenues to lemon-derived bioproducts, previously unknown bio-based products, and completely new uses and applications of old products such as pectin emerged in the course last decade (2010–1019) open the route to a true bioeconomy of lemon.

In the bioeconomy, useful energy (electricity and heat) is derived from renewable energy sources (sun, wind, and water), whereas the myriad functional substances today chiefly obtained from oil in petrochemical plants are derived from biological and intrinsically renewable resources.[36]

Lemon's peel is the main source of pectin since several decades; a natural hydrocolloid in high demand from the food, beverage, pharmaceutical, and nutraceutical industries.[37] Production of pectin based on multi-step acidic hydrolysis in hot water of lemon peels previously dried at lemon-processing plants consuming large amounts of fossil fuel epitomizes the chemical industry of the 20th century.[37,8]

Today's green chemistry technologies developed in the last decade such as microwave-assisted extraction,[3,5] hydrodynamic cavitation,[6,32] and solar-energy driven extraction[4] allow to extract all the valued components from fresh citrus by-products at high energy efficiency using no acid, base, or organic solvent to eventually afford in one-pot all peel bioproducts. The latter are then easily isolated using green chemistry separation techniques.

These are the technologies that will shortly enable the full development lemon bioeconomy using waste lemon peel obtained in about 50% (in weight) yield at lemon juice processing companies. Being modular and flexibly adaptable to continuous processes, the aforementioned technologies can be easily installed at citrus processing companies making them true citrus biorefineries[3,7] able to supply high-value ingredients to nutraceutical, personal care, cosmetic, and pharmaceutical companies.

For example, nutraceutical- and pharmaceutical-grade pectins of low DE (≈25%) with high contents in galacturonic acid regions are easily extracted directly on semi-industrial scale from lemon outer skin via microwave-assisted hydrodiffusion and gravity.[38]

It is therefore relevant that entrepreneurial efforts undertaken for example in the Netherlands[39] to have waste citrus peel recognized from a regulatory viewpoint as a raw material, and no longer as waste, have been successful.

Beyond bioactive and health-beneficial molecules such as polyphenols and natural dyes, we emphasize how waste lemon peel, rich in pectin but also in cellulose microfibrils of high crystallinity and microfibril diameter affording better texturizing properties,[40] will be used to produce advanced functional materials such as bio-aerogels, but also fragrant and antibacterial fibers.

Along with fundamental economic reasons residing in the hugely expanded lemon global production (from 5.2 to 17.5 million tons between 1980 and 2016),[11] the shift to the use of waste lemon peel as a key ingredient of the emerging bioeconomy will be driven by the societal megatrends actively reshaping the global chemical industry.[41]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bioeconomies, circular economies, citrus biorefineries, *Citrus limon*, lemons

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