

Applications of Supercritical Fluids in Latin America: Past, Present and Future Trends

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Abstract Latin America possesses expansive natural resources, which has attracted scientists from several areas to study means of improving the use of these resources. Supercritical fluids have been used for such purposes in many technological applications. Therefore, this paper provides an overview of Latin America scientific findings on supercritical technologies. Web of Science and Scopus were used as reference databases to search for information dated from 2004-2013. The Latin-American studies were classified into 6 main areas: extraction & mathematical modeling (57%), emerging applications (15%), thermodynamics & fundamentals (9%), reviews & perspectives (8%), reactions in supercritical media (7%) and analytical applications (4%). A compilation of scientific documents from 1994-2003 indicates that supercritical technology has progress greatly over the last 10 years in the major scientific countries in Latin America, such as Brazil, Argentina, Chile, Mexico and Colombia. These advances are associated with the development of new research subjects. Emerging applications, such as micronization and the encapsulation of nanoparticles, adsorption processes, gas sensors development, power generation and bioresidue hydrolyzation, are reported.

Keywords Latin america, Supercritical fluids, Emerging applications, Reactions, Micronization, Particle formation

1. Introduction

Latin America (LA) consists of 33 countries: Antigua and Barbuda, Argentina, Bahamas, Barbados, Belize, Bolivia, Brazil, Chile, Colombia, Commonwealth of Dominica, Costa Rica, Cuba, Dominican Republic, Ecuador, El Salvador, Granada, Guatemala, Guyana, Haiti, Honduras, Jamaica, Mexico, Nicaragua, Panama, Paraguay, Peru, Saint Kitts, Saint Vincent and The Grenadines, Santa Lucia, Suriname, Trinidad and Tobago, Uruguay, and Venezuela.

Advances in the research & development sectors of these countries have been mentioned by several scientists, such as del Valle *et al* [1] and Crespi and Zuniga [2]. Many applications are being reported for supercritical technologies from the study of fundamental thermodynamics [3] to emerging applications such as nanoparticle production and encapsulation [4]. Supercritical fluids are of interest to the global scientific community because of their special properties (e.g., low viscosity, high diffusivity and large solubilization capacity), which makes these fluids preferable to organic solvents. Furthermore, products obtained using supercritical technologies are free of toxic residues and possess high quality.

The rich biodiversity of some countries in LA provides numerous natural pigments (found in roots, aromatic herbs, leaves, seeds and tropical fruits for instance). The food, cosmetic, pharmaceutical and chemical industries are all interested in these pigments.

In this context, the use of supercritical fluids in several processes has increased over the last few years. Nonetheless, in LA, these processes are still being developed on the laboratory or pilot scales. The challenge is transferring knowledge acquired via scientific investigations to the industrial scale to show potential for supercritical technologies to overcome their implementation costs.

In 2005, Rosa and Meireles [5] presented the historical insertion/evolution of supercritical technologies in Brazil and summarized the South America contribution to this field from 1994-2003. Therefore, the present article was written to update this contribution and expand it to all LA countries. The objective is to emphasize the emergence of novel research programs focusing on processes integration, such as micronization of functional pigments, hydrolyzation of supercritical fluid extraction co-products, performance of reactions in supercritical media and application of supercritical fluids to energy.

2. Supercritical Technology in Latin America

This section details supercritical fluid applications in LA

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Published online at <http://journal.sapub.org/fph>

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from 2004 to 2013. Web of Science and Scopus (two large, global databases) were used to find and index published patents and Journal papers. A search was done using the term ‘supercritical fluid*’ and requiring the presence of one of the 33 countries listed above in the address field.

The Web of Science search returned 10,164 scientific documents for the period defined above with as many as 500 addressed to LA countries. To filter the responses, the word ‘extraction’ was combined with other terms as follows: ‘supercritical fluid* extraction’ or ‘compressed carbon dioxide extraction’ or ‘pressurized carbon dioxide extraction’ or ‘pressurized CO₂’ or ‘supercritical CO₂’. These searches returned 3,598 documents with as many as 286 linked to researchers associated with research centers and institutions from LA. These 286 documents were divided as follows: 254 papers published in Journals, 29 papers from conference proceedings, 2 patents and 1 book chapter.

The low contribution of patents in this search is related to their indexing in local (national) databases. The same justification is valid for papers published in conference proceedings. Furthermore, few book chapters are indexed by Web of Science.

The Scopus search returned 12,668 documents during 2004-2013 with as many as 534 addressed to LA. The same terms used with Web of Science were used for the filtered Scopus search. A total of 3,291 documents were found with as many as 195 linked to Latin-American scientists. The documents were divided as follows: 177 Journal papers and 18 conference proceeding papers.

Of the supercritical technology areas, extractions had the largest representation with approximately 55% of the published documents. However, supercritical fluid extraction (SFE) is still poorly diffused throughout the global scientific community, even with its significant growth after the 1990s. Based on the Web of Science search, before 1993 a total of 32,778 scientific documents were published for all extraction methods with only 211 correspond to SFE (0.6% of the total). Over the last 20 years, 227,809 scientific documents were published for all extraction methods with 6,221 corresponding to SFE (2.7% of the total). These findings mean the contribution of SFE around the world increased 4.5 times since 1993 relative to other methods.

Research in LA has been responsible for 2.5% of the worldwide publications on supercritical technology before 2010. In the past three years (2010-2013), the effort of Latin

American scientists and new supercritical fluid applications expanded the LA contribution to 4.8% of the worldwide publications.

To evaluate the importance of supercritical fluid processes to obtaining value-added products, Table 1 shows the evolution of publications addressed to LA over the last 10 years. The scientific investigations of the major scientific countries were classified into 6 groups: extraction & mathematical modeling, emerging applications, thermodynamics & fundamentals, reviews & perspectives, reactions in supercritical media and analyses.

From 2004 to 2013, 15% of scientific production comprised “emerging applications”. Micronization, encapsulation, both precipitation and impregnation of nanomaterials, sensors development, biomass conversion into value-added products and energy are applications included in this area.

Many of these emerging applications have been studied with increasing intensity since 2008. For example, the research of Santos et al [6] studied the production of stabilized sub-micrometric carotenoid particles via supercritical CO₂ extraction of an emulsion. This emerging and promising area combines supercritical CO₂ with nano-emulsions to form and encapsulate nanoscale substances within the emulsions. The goal is to stabilize the target components to reduce their degradation rate in aqueous media. An illustrative flowchart of this process is shown in Scheme 1.

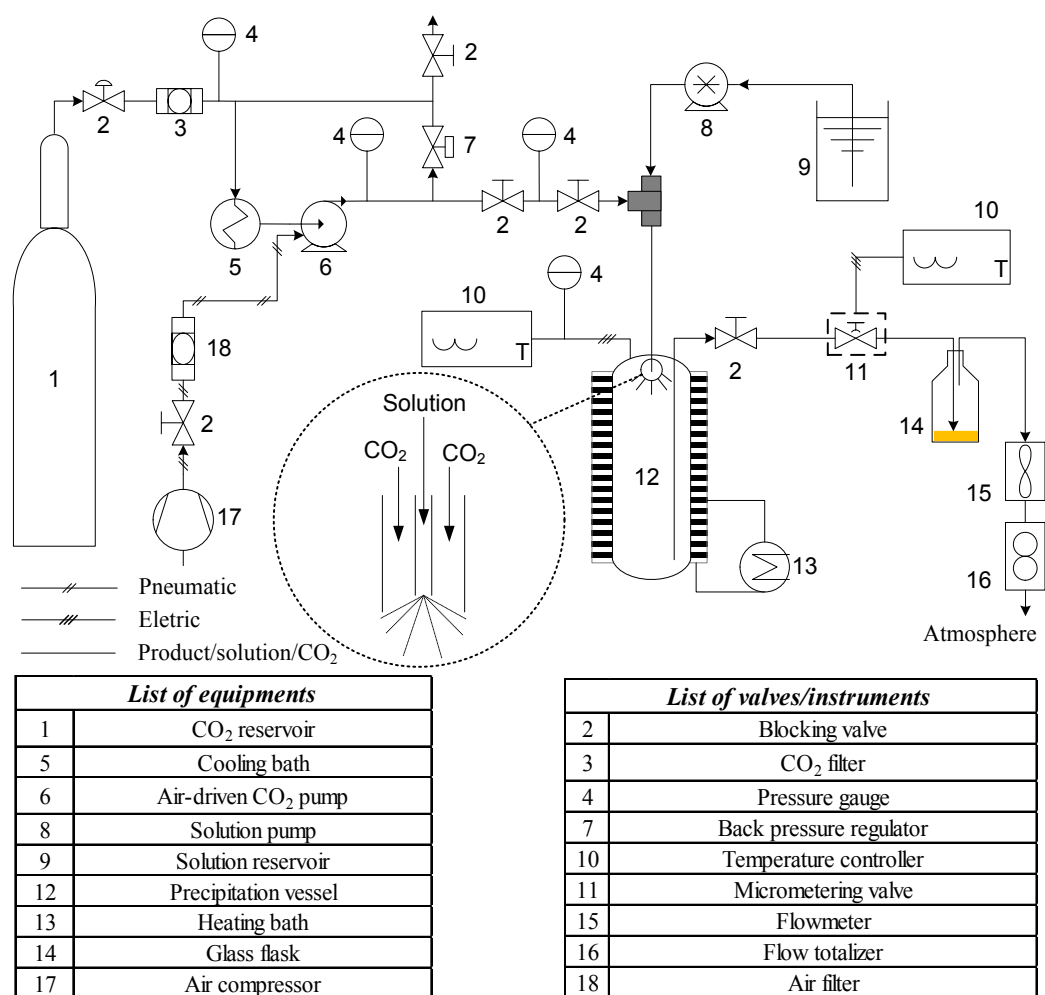
The first work in this area from LA and published by a Journal indexed in these two databases appeared in 2006 by Corazza et al [7]. Afterwards, in 2008, Franceschi et al [8] and Franceschi et al [9] studied the encapsulation of β -carotene and precipitation of theophylline, respectively. By July 2013, 8 other scientific documents had been published on this issue in LA [4], [6], [10-15], which indicates significant growth in this line of research.

In mid-2009, low-cost sensors were developed on paper by line patterning a graphite and polyaniline coating using supercritical CO₂ [16], [17]. Under supercritical conditions, CO₂ possesses low viscosity and low surface tension, which increases the uniformity of the polymer particles deposited on the surface. Furthermore, the properties of CO₂ have made it a very promising fluid for improving the sensor performance and sensitivity [18]. One application indicated for these gas sensors is the detection of fruit ripeness as demonstrated for bananas [19].

Table 1. Number of publications (Web of Science) related to supercritical fluids from research in Latin American countries

Area	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013*	Total
Analytical applications	-	1	1	1	-	1	-	1	2	2	9
Emerging applications	1	4	2	2	5	4	5	6	8	5	42
Extraction & mathematical modeling	4	13	12	14	20	20	18	22	28	12	163
Reactions in supercritical media	-	2	1	3	2	2	1	2	3	5	21
Reviews & perspectives	-	3	2	2	2	4	3	2	5	1	24
Thermodynamics & fundamentals	6	5	5	3	3	1	3	1	-	-	27
Total	11	28	23	25	32	32	30	34	46	25	286

* Search covered to July, 2013



Scheme 1. Flowchart for an experimental micronization apparatus using supercritical CO₂ (Adapted from Santos and Meireles [4])

Polymerization via the rapid expansion of supercritical solutions (RESS) is a promising technology that requires more detailed experiments. The trend is that the number of studies in LA on this subject will become more expansive and allow production of these devices on an industrial scale.

Another supercritical fluid application emerging in LA countries corresponds to the high-pressure treatment of lignocellulosic biomass called explosion with supercritical CO₂ (ESC). This treatment improves the subsequent heavy metal-removal step. Copper adsorption experiments were performed on waste banana peels submitted to extraction and ESC. Integrating these processes had a more pronounced effect on the vegetable structure and retained the adsorption capacity [20].

In contrast, the number of publications discussing the thermodynamics & fundamentals has decreased. From 1994-2003, 49 scientific documents (25% of the total) published by researchers from LA related to this topic. Since 2004, only 27 documents (9% of the total) were published on this topic. Documents classified as “thermodynamics & fundamentals” cover research on thermodynamic parameters and properties [21], the determination of solubility for compound mixtures [22], thermodynamic modeling and simulation [23], [24] and

phase equilibrium in supercritical conditions [25], [26].

The recent reduction in the percent of publications comprising this research topic in LA (25% at 1994-2003; 9% at 2004-2013) is justified for the following two reasons: (i) the emergence of new lines of research and (ii) the high availability of information from global scientific literature discussing such concepts, which hinders novel studies. Nevertheless, there is still much to explore in the food sector because the behavior of biological and nutraceutical substances in extraction systems is very complex.

Some research groups in LA, mostly located at Argentina, Brazil, Chile, Colombia and Mexico, are focusing their studies on emerging areas which involving supercritical fluids. For energy applications, the hydrolysis of sugar biomass and second generation ethanol production have been studied by several researchers [27-29].

In these fields, Pellegrini *et al* [30] simulated a cogeneration system for producing energy for sugarcane mills using supercritical steam (pressures up to 30 MPa and temperatures up to 600°C) and integrated biomass gasification cycles. The proposed system generated roughly three times the excess electricity relative to currently available condensation-extraction steam turbines (≈ 2 MPa and 300°C). This thermal integration system reduced the

steam consumption by 43%.

Some authors simulated integrated processes for power generation and reported increased efficiency [30], [31]. These findings mean integrating processes to increase their energetic yields tends to be an industrially useful thermo-economic alternative.

Microbiological inactivations and reactions in supercritical media that may or may not be catalyzed by enzymes have also been researched more intensely in LA over the last few years [32-35]. Numerical data indicate there were 21 scientific works ($\approx 7\%$ of the total) published in the Journals indexed by Web of Science and/or Scopus since 2004, whereas there were only 4 scientific works during 1994-2003 ($\approx 2\%$ of the total).

In the same way, the use of supercritical fluids for

analytical applications has progressed greatly over the world in recent years. In LA, papers discussing the development of an SFE method for determining pesticides in fruit and vegetables [36], enantioseparation of mitotane via supercritical fluid chromatography (SFC) [37], analysis of nitrosamines in sausages [38] and determination of hydrocarbons in petroleum products [39] were published.

Brazil ranks 11th in the world for publications on supercritical fluids. Approximately 3.1% of the worldwide publications in this field are from Brazil. Considering only Latin-American publications, the country has the highest contribution, with 59% of the total publications (Figure 1). The current research of the 5 major scientific countries in LA is shown in Table 2.

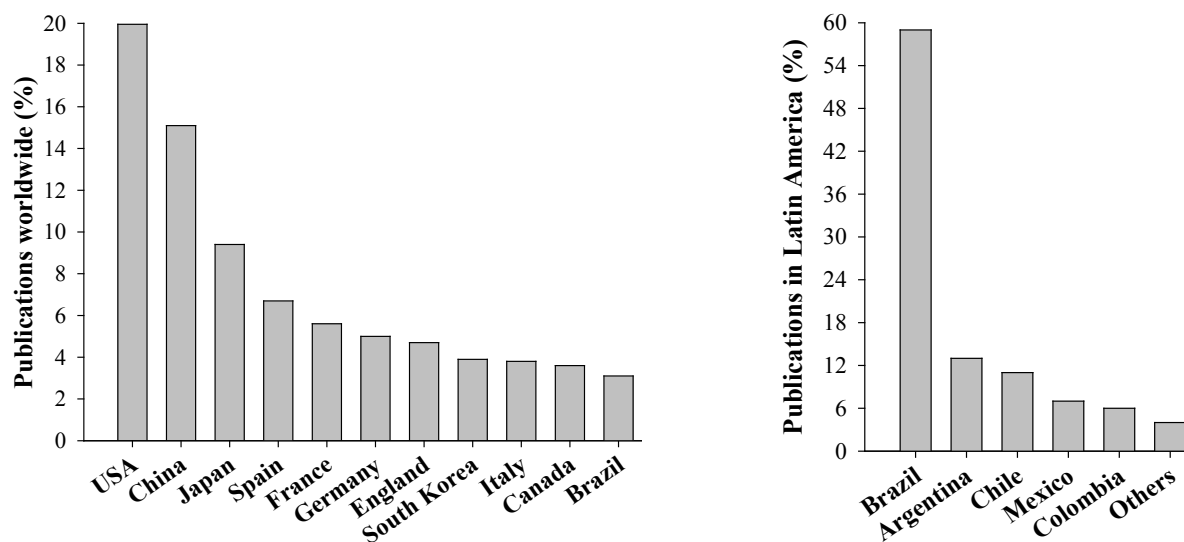


Figure 1. Contributions of the major scientific countries that have been researching supercritical fluids from 2004-2013

Table 2. Current research performed in LA countries

Raw material	Methods	Experimental determinations	Extracts/Products characterization	Theoretical studies	Ref.
Annatto (<i>Bixa orellana</i> L.)	SFE; SAS; RESS	PY; EE	SEM	-	[4]
Grape (<i>Vitis vinifera</i>)	SFE	X0	HPLC; AA; MIC	-	[40]
Nut (<i>Anacardium occidentale</i>)	SFE	OEC	TLC	MM; COM	[41]
Sage (<i>Salvia officinalis</i>)	SFF	OEC	GC-MS	PS	[42]
Mushroom (<i>Agaricus brasiliensis</i>)	SFE	X0; IE; OEC	AA; MIC; AAac	-	[43]
Boldo (<i>Peumus boldus</i> M.)	SFE	OEC	SEM	MM	[44]
Jaboticaba (<i>Myrciaria cauliflora</i>)	PLE	X0; OEC	TMA; TPC	PS; COM; SU	[45]
Guava (<i>Psidium guajava</i>)	SFE	X0; IE; OEC	TLC; GC-MS	MM	[46]
Ginger (<i>Zingiber officinale</i>)	SFE	OEC	GC-FID; AAac	-	[47]
Garlic (<i>Allium sativum</i>)	SFE	IE; OEC	Spectrophotometer	MM	[48]
Mint (<i>Mentha spicata</i> L.)	SFE	X0; IE	AAac; GC-MS	-	[49]
Buriti (<i>Mauritia flexuosa</i> M.)	SA	AK	SEM; GC-FID	MM	[50]
Banana (<i>Musa spp.</i>)	ESC; SFE	AK; AE	SEM; DSC	MM	[20]

SFE: Supercritical fluid Extraction; SAS: Supercritical CO₂ as Antisolvent; RESS: Rapid Expansion of Supercritical Solutions; PY: Precipitation Yield; EE: Encapsulation Efficiency; SEM: Scanning Electron Microscopy; X0: Global Extraction Yield; HPLC: High Performance Liquid Chromatography; AA: Antimicrobial Activity; MIC: Minimum Inhibition Concentration; OEC: Overall Extraction Curves; TLC: Thin Layer Chromatography; MM: Mathematical Modeling; COM: Cost of Manufacturing; SFF: Supercritical Fluid Fractionation; GC-MS: Gas Chromatograph – Mass Spectrometer; PS: Process Simulation; IE: Isotherms of Extraction; AAac: Antioxidant Activity; PLE: Pressurized Liquid Extraction; TMA: Total Monomeric Anthocyanin Content; TPC: Total Phenolic Compounds Content; SU: Scale up; GC-FID: Gas Chromatograph – Flame Ionization Detector; SA: Supercritical Adsorption; ESC: Explosion with Supercritical CO₂; DSC: Differential Scanning Calorimetry; AK: Adsorption Kinetics; AE: Adsorption Equilibrium

3. Patent Survey

A search of patents containing the term ‘supercritical fluid*’ in the Derwent Innovations Index (Web of Science database) returned 5,632 patents by inventors around the world. However, only 2 patents were addressed from one of the 33 countries in LA. Indeed, most patents are registered in local databases, as is the case in Brazil where patents are deposited at INPI (Brazilian National Institute of Industrial Property).

The 2 patents found in Web of Science were invented in Colombia. Invention WO2012066389 [51] is a novel process for producing aqueous suspensions of calcium salt micro- and nanoparticles smaller than 10 μm using critical, subcritical and supercritical carbon dioxide. This property of the fluid increases the solubility of the calcium salt, which allows enriching nutritional, nutraceutical and pharmaceutical beverages with calcium salts.

Table 3. Summary of studies developed in Latin America from 2010-2012

Country	Study group	Article title	Year	Ref.
ARGENTINA	Analytical applications	Sorption and diffusion of compressed carbon dioxide in polycaprolactone for the development of porous scaffolds	2012	[60]
		Proton transfer from 2-naphthol to aliphatic amines in supercritical CO ₂	2011	[61]
	Energy applications	Ketalization of glycerol to solketal in supercritical acetone	2011	[62]
	Fundamental & thermodynamic studies	Fractionation of essential oils with biocidal activity using supercritical CO ₂ -experiments and modeling	2011	[63]
		Critical effects on attractive solutes in binary liquid mixtures close to their consolute point: a new experimental strategy	2011	[64]
		AVA seismic reflectivity analysis in carbon dioxide accumulations: sensitivity to CO ₂ phase and saturation	2011	[65]
		Computation of solid-fluid-fluid equilibria for binary asymmetric mixtures in wide ranges of conditions	2011	[66]
		Equation of state modeling of the phase equilibria of asymmetric CO ₂ + n-alkane binary systems using mixing rules cubic with respect to mole fraction	2010	[67]
		Near-critical and supercritical dilute solutions viewed from macroscopic and molecular-scale perspectives	2010	[68]
		Experimental cloud points for polybutadiene plus light solvent and polyethylene plus light solvent systems at high pressure	2010	[69]
		Isochoric lines and determination of phase transitions in supercritical reactors	2010	[70]
	Material and micronization applications	Precipitation and encapsulation of rosemary antioxidants by supercritical antisolvent process	2012	[71]
		Supercritical CO ₂ fractionation of rosemary ethanolic oleoresins as a method to improve carnosic acid recovery	2011	[72]
	Reactions in supercritical fluids	Grafting of styrene onto polyethylene in near critical media	2012	[73]
	Reviews and perspectives	Optimizing design in open channel	2010	[74]
BRAZIL	Analytical applications	Single laboratory validation of a SPE method for the determination of PAHs in edible oils by GC-MS	2012	[75]
		Supercritical adsorption of buriti oil (<i>Mauritia flexuosa</i> Mart.) in gamma-alumina: A methodology for the enriching of anti-oxidants	2012	[76]
		Effects of supercritical carbon dioxide on waste banana peels for heavy metal removal	2011	[20]
		SFE from <i>Bidens pilosa</i> Linne to obtain extracts rich in cytotoxic polyacetylenes with antitumor activity	2011	[77]
		Biological activities of <i>Solanum paludosum</i> Moric. extracts obtained by maceration and supercritical fluid extraction	2011	[78]
	Economic applications	Supercritical carbon dioxide selectivity to fractionate phenolic compounds from the dry ethanolic extract of propolis	2010	[79]
		Supercritical anti-solvent precipitation of carotenoid fraction from pink shrimp residue: Effect of operational conditions on encapsulation efficiency	2012	[80]
		Manufacturing cost of supercritical-extracted oils and carotenoids from amazonian plants	2010	[81]
	Energy applications	Preliminary studies on advanced power generation based on combined cycle using a single high-pressure fluidized bed boiler and consuming sugar-cane bagasse	2012	[31]
		Sustainable energy: A review of gasification technologies	2012	[82]
	Extraction applications	Radical-scavenging activity of extracts from <i>Cordia verbenacea</i> DC obtained by different methods	2011	[83]
		Supercritical extraction from vinification residues: Fatty acids, alpha-tocopherol, and phenolic compounds in the oil seeds from different varieties of grape	2012	[84]
		Supercritical extraction of linseed oil: economical viability and modeling extraction curves	2013	[85]

Table 3. (Continued)

Country	Study group	Article title	Year	Ref.
BRAZIL	Extraction applications	Radical-scavenging activity of extracts from <i>Cordia verbenacea</i> DC obtained by different methods	2011	[83]
		Supercritical extraction from vinification residues: Fatty acids, alpha-tocopherol, and phenolic compounds in the oil seeds from different varieties of grape	2012	[84]
		Supercritical extraction of linseed oil: economical viability and modeling extraction curves	2013	[85]
		Extracts from the leaves of <i>Piper piscatorium</i> (Trel. Yunc.) obtained by supercritical extraction of with CO ₂ , employing ethanol and methanol as cosolvents	2013	[86]
		Extraction from striped weakfish (<i>Cynoscion striatus</i>) wastes with pressurized CO ₂ : global yield, composition, kinetics and cost estimation	2012	[87]
		Defatting of annatto seeds using supercritical carbon dioxide as a pretreatment for the production of bixin: experimental, modeling and economic evaluation of the process	2012	[88]
		Extraction of <i>Mentha spicata</i> L. Volatile compounds: Evaluation of process parameters and extract composition	2012	[49]
		Supercritical fluid extraction from spent coffee grounds and coffee husks: Antioxidant activity and effect of operational variables on extract composition	2012	[89]
		HPLC analysis of supercritical carbon dioxide and compressed propane extracts from <i>Piper amalago</i> L. with antileishmanial activity	2012	[90]
		Extraction, fatty acid profile and antioxidant activity of sesame extract (<i>Sesamum Indicum</i> L.)	2012	[91]
		Characteristics of the extract of <i>Litopenaeus vannamei</i> shrimp obtained from the cephalothorax using pressurized CO ₂	2012	[92]
		HPLC analysis and antileishmanial activity of supercritical fluids extracts from <i>Piper amalago</i> L.	2012	[93]
		Supercritical fluid extraction of hernandulcin from <i>Lippia dulcis</i> Trev	2012	[94]
		Extraction of Mucuna seed oil using supercritical carbon dioxide to increase the concentration of L-Dopa in the defatted meal	2012	[95]
		Supercritical fluid extraction of <i>Agaricus brasiliensis</i> : Antioxidant and antimicrobial activities	2012	[96]
		Supercritical fluid extraction from guava (<i>Psidium guajava</i>) leaves: global yield, composition and kinetic data	2012	[46]
		Effect of storage time and conditions on the diene valepotriates content of the extract of valeriana glechomifolia obtained by supercritical carbon dioxide	2012	[97]
		The antitumor activity of extracts from <i>Cordia verbenacea</i> DC obtained by supercritical fluid extraction	2012	[98]
		Supercritical fluid extraction of grape seed: Process scale-up, extract chemical composition and economic evaluation	2012	[99]
		Extraction of omega-3 fatty acids and astaxanthin from Brazilian redspotted shrimp waste using supercritical CO ₂ + ethanol mixtures	2012	[100]
		Modeling oil extraction from green and roasted coffee by means of supercritical CO ₂	2012	[101]
		Supercritical extraction of neolignans from <i>Piper regnelli</i> var. <i>pallenscens</i>	2012	[102]
		Supercritical extraction of phloroglucinol and benzophenone derivatives from <i>Hypericum carinatum</i> : Quantification and mathematical modeling	2011	[103]
		Supercritical fluid extraction of volatile and non-volatile compounds from <i>Schinus molle</i> L.	2011	[104]
		Antifungal activity of supercritical fluid extract obtained from <i>Calophyllum brasiliense</i> Cambess	2011	[105]
		Identification of organic sulfur compounds in coal bitumen obtained by different extraction techniques using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometric detection	2011	[106]
		Supercritical fluid extracts from the Brazilian cherry (<i>Eugenia uniflora</i> L.): Relationship between the extracted compounds and the characteristic flavour intensity of the fruit	2011	[107]
		Pink shrimp (<i>P. brasiliensis</i> and <i>P. paulensis</i>) residue: Influence of extraction method on carotenoid concentration	2011	[108]
		Extraction of sunflower (<i>Heliantus annuus</i> L.) oil with supercritical CO ₂ and subcritical propane: Experimental and modeling	2011	[109]

The invention US2011237857 [52] is a process for the destruction of toxic residues via oxidation in the presence of water and oxygen developed in homogeneous supercritical condition of 374°C and 22 MPa. The proposed mobile processing unit is composed of a reactor, which includes pressurization, reaction, cooling, depressurization, and sampling zones for the destruction of toxic residues, such as

polychloride biphenyls and pyridines.

4. Cost of Manufacturing of Processes Involving Supercritical Fluids

Mostly, supercritical technology processes present technical feasibility. Nonetheless, detailed studies about

economic aspects are needed to transfer the knowledge acquired at laboratory/pilot scales to industrial scale. These studies are necessary to indicate (or not) the economic feasibility of the proposed system.

Based on the lack of detailed information, some LA studies have simulated the cost of manufacturing (COM) of extracts, mostly of SFE from vegetal raw materials. Cavalcanti *et al* [53] simulated the COM of jabuticaba extract obtained in extractors of several sizes. The lowest COM was about US\$ 10.00/kg in a system containing two 300-liter extractors.

Veggi *et al* [54] compared the COM of jabuticaba extract obtained via PLE (Pressurized Liquid Extraction) to that of conventional extraction techniques for a system with two 300 liter extractors. The COM values differed as follows: US\$ 15.53/kg for PLE, US\$ 410.21/kg for ultrasound assisted extraction and US\$ 778.42/kg for a conventional Soxhlet extraction. Likewise, some scientists simulated the COM values for extracts from Amazonian plants obtained via SFE, such as buriti, pupunha, pressed palm fiber [55], annatto [56], pomegranate [57], grape [58] and sugarcane residues [59].

Table 3. (Continued)

Country	Study group	Article title	Year	Ref.
BRAZIL	Extraction applications	Acute toxicity and anti-inflammatory effects of supercritical extracts of <i>Ilex paraguariensis</i>	2011	[110]
		Extraction of canola seed (<i>Brassica napus</i>) oil using compressed propane and supercritical carbon dioxide	2011	[111]
		Scale-up study of supercritical fluid extraction process for clove and sugarcane residue	2011	[59]
		Chamomile extraction with supercritical carbon dioxide: Mathematical modeling and optimization	2011	[112]
		Supercritical CO ₂ extraction of lipids and astaxanthin from Brazilian redspotted shrimp waste (<i>Farfantepenaeus paulensis</i>)	2011	[113]
		Proximate composition and extraction of carotenoids and lipids from Brazilian redspotted shrimp waste (<i>Farfantepenaeus paulensis</i>)	2011	[114]
		Extraction with supercritical fluid and comparison of chemical composition from adults and young leaves of <i>Zanthoxylum tingoassuiba</i>	2011	[115]
		Bioactive extracts of orange (<i>Citrus sinensis</i> L. Osbeck) pomace obtained by SFE and low pressure techniques: Mathematical modeling and extract composition	2010	[116]
		Supercritical fluid extraction and high performance liquid chromatographic determination of benzopyrans and phloroglucinol derivative in <i>Hypericum polyanthemum</i>	2010	[117]
		Supercritical fluid extraction of alkaloids from <i>Ilex paraguariensis</i> St. Hil	2010	[118]
		Extraction of sesame seed (<i>Sesamum indicum</i> L.) oil using compressed propane and supercritical carbon dioxide	2010	[119]
		Supercritical fluid extraction of lycopene from tomato juice and characterization of its antioxidation activity	2010	[120]
		Recovery of gamma-oryzanol from rice bran oil byproduct using supercritical fluid extraction	2010	[121]
		Supercritical fluid extraction of peach (<i>Prunus persica</i>) almond oil: Process yield and extract composition	2010	[122]
		A study of the methods of carotenoid extraction in carrots using supercritical fluid extraction (SFE) and conventional methods	2010	[123]
		Supercritical fluid extraction from dried banana peel (<i>Musa spp.</i> , genomic group AAB): Extraction yield, mathematical modeling, economic analysis and phase equilibria	2010	[124]
		Characterization and functional properties of macela (<i>Achyrocline satureioides</i>) extracts obtained by supercritical fluid extraction using mixtures of CO ₂ plus ethanol	2010	[125]
		Extraction of the essential oil of abajeru (<i>Chrysobalanus icaco</i>) using supercritical CO ₂	2010	[126]
	Fundamental & thermodynamic studies	Thermodynamic study of enantioseparation of mitotane by supercritical fluid chromatography	2012	[37]
		High-pressure phase behaviour of the system (CO ₂ + CI Disperse Orange 30 dye)	2012	[127]
		Selectivity of supercritical carbon dioxide in the fractionation of fish oil with a lower content of EPA plus DHA	2012	[128]
		Safety study of an experimental apparatus for extraction with supercritical CO ₂	2012	[129]
		Phase equilibrium data for the ternary system (propane plus chloroform plus oryzanol)	2011	[130]
		Supercritical technology as an alternative for biotechnological xylitol purification	2011	[131]
		Phase behavior of (CO ₂ + methanol plus lauric acid) system	2011	[132]
		High-pressure experimental data of CO ₂ + mitotane and CO ₂ + ethanol plus mitotane mixtures	2011	[133]
		Thermodynamic modeling of liquid-fluid phase equilibrium in supercritical ethylene plus copolymer plus co-solvent systems using the PC-SAFT equation of state	2010	[134]
		Phase behavior of binary systems of lactones in carbon dioxide	2010	[135]
		Phase behavior of the ternary system poly(epsilon-caprolactone) plus carbon dioxide plus dichloromethane	2010	[136]
		Phase equilibrium data and thermodynamic modeling of the system propane plus NMP plus methanol at high pressures	2010	[137]

Table 3. (Continued)

Country	Study group	Article title	Year	Ref.
BRAZIL	Fundamental & thermodynamic studies	Phase equilibrium measurements and modelling of ternary system (carbon dioxide plus ethanol plus palmitic acid)	2010	[138]
		Chemical characterization and phase behavior of grape seed oil in compressed carbon dioxide and ethanol as co-solvent	2010	[26]
		High-pressure phase diagram of the drug mitotane in compressed and/or supercritical CO ₂	2010	[139]
		A first-principles simulation model for the thermo-hydraulic performance of fan supplied tube-fin heat exchangers	2010	[140]
	Material and micronization applications	Development of gas sensors coatings by polyaniline using pressurized fluid	2012	[141]
		Purification of single-wall carbon nanotubes by heat treatment and supercritical extraction	2011	[142]
		CO ₂ geological storage in saline aquifers: Parana basin caprock and reservoir chemical reactivity	2011	[143]
		Synthesis and characterization of ZnO/PET composite using supercritical carbon dioxide impregnation technology	2011	[144]
		Economic viability of SFE from peach almond, spearmint and marigold	2011	[145]
		In vitro release profiles of beta-carotene encapsulated in PHBV by means of supercritical carbon dioxide micronization technique	2011	[13]
		Impregnation of composite from polycarbonate (PC) and silica gel (Si) films with photochromic dye in supercritical fluid	2010	[146]
		Precipitation and encapsulation of beta-carotene in PHBV using carbon dioxide as anti-solvent	2010	[12]
		Gas sensors development using supercritical fluid technology to detect the ripeness of bananas	2010	[19]
	Petroleum applications	Mesophase evolution in heat-treated solid petroleum pitches	2012	[147]
		Comparison of residual oil saturation for water and supercritical CO ₂ flooding in a long core, with live oil at reservoir conditions	2011	[148]
		Methods for the determination of conjugated dienes in petroleum products: a review	2010	[149]
	Reactions in supercritical fluids	Biocomposites based on cellulose acetate and short curaua fibers treated with supercritical CO ₂	2012	[150]
		Enzymatic synthesis of galactooligosaccharides using pressurized fluids as reaction medium	2012	[34]
		Assessment of carotenoids recovery through cell rupture of <i>Sporidiobolus salmonicolor</i> CBS 2636 using compressed fluids	2012	[151]
		Effect of compressed fluids treatment on the activity of inulinase from <i>Kluyveromyces marxianus</i> NRRL Y-7571 immobilized in montmorillonite	2011	[152]
		Effect of compressed fluids treatment on the activity, stability and enzymatic reaction performance of beta-galactosidase	2011	[153]
		Optimization of laccase catalyzed degradation of reactive textile dyes in supercritical carbon dioxide medium by response surface methodology	2010	[154]
		Compressed propane as a new and fast method of pre-purification of radish (<i>Raphanus sativus</i> L.) peroxidase	2010	[155]
		Effect of treatment with compressed propane on lipases hydrolytic activity	2010	[156]
		Branched polyethylenes fractionated in supercritical propane	2010	[157]
		Lipase from <i>Rhizomucor miehei</i> as a biocatalyst in fats and oils modification	2010	[158]
		Lipase from <i>Rhizomucor miehei</i> as an industrial biocatalyst in chemical process	2010	[159]
	Reviews and perspectives	Technological aspects of beta-carotene production	2011	[160]
		Occurrence and chemical speciation analysis of organotin compounds in the environment: A review	2010	[161]
		Supercritical fluid extraction of bioactive compounds: Fundamentals, applications and economic perspectives	2010	[162]

Table 3. (Continued)

Country	Study group	Article title	Year	Ref.
CHILE	Analytical applications	A protocol for evaluating the safety of herbal preparations in a rat model: the case of a supercritical fluid extract of Saw Palmetto	2010	[163]
	Extraction applications	A polyphenol extract of tara pods (<i>Caesalpinia spinosa</i>) as a potential antioxidant in oils	2012	[164]
		Extraction of oil and minor lipids from cold-press rapeseed cake with supercritical CO ₂	2012	[165]
		Effect of boldo (<i>Peumus boldus</i> M.) pretreatment on kinetics of supercritical CO ₂ extraction of essential oil	2012	[166]
		Mass transfer and equilibrium parameters on high-pressure CO ₂ extraction of plant essential oils	2011	[167]
		Oxidative stability of oils containing olive leaf extracts obtained by pressure, supercritical and solvent-extraction	2011	[168]
		Extraction of antioxidants from several berries pressing wastes using conventional and supercritical solvents	2010	[169]
	Fundamental & thermodynamic studies	A refined equation for predicting the solubility of vegetable oils in high-pressure CO ₂	2012	[170]
		Free solute content and solute-matrix interactions affect apparent solubility and apparent solute content in supercritical CO ₂ extractions. a hypothesis paper	2012	[171]
		Supercritical CO ₂ extraction of allicin from garlic flakes: Screening and kinetic studies	2012	[48]
		Molar isopycnicity in heterogeneous binary mixtures	2012	[172]
		Optimization of a cubic equation of state and van der Waals mixing rules for modeling the phase behavior of complex mixtures	2012	[173]
		Stevia rebaudiana Bertonii, source of a high-potency natural sweetener: A comprehensive review on the biochemical, nutritional and functional aspects	2012	[174]
		Solubility of beta-carotene in ethanol- and triolein-modified CO ₂	2011	[175]
		Simulation of a supercritical carbon dioxide extraction plant with three extraction vessels	2011	[176]
		Solubility of nutraceutical carotenoid compounds in pure supercritical CO ₂ and modified with triolein or ethanol	2010	[22]
		Solubilities in supercritical carbon dioxide of (2E,6E)-3,7,11-Trimethyldodeca-2,6,10-trien-1-ol (Farnesol) and (2S)-5,7-Dihydroxy-2-(4-hydroxyphenyl)chroman-4-one (Naringenin)	2010	[177]
		Data analysis, modeling and thermodynamic consistency of CO ₂ + beta-carotene high pressure mixtures	2010	[178]
	Reactions in supercritical fluids	Recent trends in biocatalysis engineering	2012	[179]
COLOMBIA	Extraction applications	Extraction of phenolic fraction from guava seeds (<i>Psidium guajava</i> L.) using supercritical carbon dioxide and co-solvents	2010	[180]
		Extraction of pesticides from soil using supercritical carbon dioxide added with methanol as co-solvent	2012	[181]
		Design and analysis of antioxidant compounds from Andes Berry fruits (<i>Rubus glaucus</i> Benth) using an enhanced-fluidity liquid extraction process with CO ₂ and ethanol	2012	[182]
		Extraction of oil from chia seeds with supercritical CO ₂	2011	[183]
		Guava (<i>Psidium guajava</i> L.) seed oil obtained with a homemade supercritical fluid extraction system using supercritical CO ₂ and co-solvent	2011	[184]
		<i>Lippia origanoides</i> chemotype differentiation based on essential oil GC-MS and principal component analysis	2011	[185]
		Integrated utilization of guava (<i>Psidium guajava</i> L.): antioxidant activity of phenolic extracts obtained from guava seeds with supercritical CO ₂ -ethanol	2011	[186]
		Extraction of phenolic fraction from guava seeds (<i>Psidium guajava</i> L.) using supercritical carbon dioxide and co-solvents	2010	[180]
		Separation of fractions from vacuum residue by supercritical extraction	2010	[187]
		Reacting flow simulations of supercritical water oxidation of PCB-contaminated transformer oil in a pilot plant reactor	2011	[188]
	Reactions in supercritical fluids	Biodiesel fuels through a continuous flow process of chicken fat supercritical transesterification	2010	[189]
		On the center of mass velocity in molecular dynamics simulations	2012	[190]

Table 3. (Continued)

Country	Study group	Article title	Year	Ref.
MEXICO	Fundamental & thermodynamic studies	Effect of a temperature gradient on ellipsometry measurements in supercritical CO ₂	2012	[191]
		Correlation and prediction of fluid-fluid equilibria of carbon dioxide-aromatics and carbon dioxide-dichlorobenzoates binary mixtures	2011	[192]
		Solubility of mesquite gum in supercritical carbon dioxide	2011	[193]
		New apparatus for solubility measurements of solids in carbon dioxide	2011	[194]
		Loci of extrema of thermodynamic response functions for the Lennard-Jones fluid	2011	[195]
		Solubility and density measurements of palmitic acid in supercritical carbon dioxide plus alcohol mixtures	2010	[196]
	Material and micronization applications	Microencapsulation of Coenzyme Q(10) in Poly(ethylene glycol) and Poly(lactic acid) with Supercritical Carbon Dioxide	2012	[197]
		Hydrothermal synthesis of monodisperse single-crystalline alpha-quartz nanospheres	2011	[198]
	Petroleum applications	Removal of polycyclic aromatic hydrocarbons from soil: A comparison between bioremoval and supercritical fluids extraction	2012	[199]
		Remediation of soils contaminated with total petroleum hydrocarbons and polycyclic aromatic hydrocarbons: extraction with supercritical ethane	2010	[200]
	Reactions in supercritical fluids	Lipase-catalyzed syntheses of linear and hyperbranched polyesters using compressed fluids as solvent media	2010	[201]

5. Current Studies Performed in Latin America

This section shows the studies that are currently being developed in LA. To facilitate visualization, Table 3 is arranged by study group for each major scientific country.

6. Concluding Remarks

The application of supercritical fluids to several processes, including emerging areas, is favorable for inclusion into technological plants in LA to obtain high value materials. Research and development of practical knowledge by universities and research centers in LA contribute to implementing supercritical technologies at the industrial scale. The large biodiversity of raw materials in these countries is a key factor for these future trends.

ACKNOWLEDGMENTS

Moyses N. Moraes thanks CAPES and Giovani L. Zabet thanks FAPESP (2011/23665-2) for their Ph.D. assistantships. M. A. A. Meireles acknowledges the productivity grant (301301/2010-7) from CNPq. The authors acknowledge the financial support of CAPES, CNPq and FAPESP.

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