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Review

Applications of non-conventional "green" extraction technologies in process industries: challenges, limitations and perspectives

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Received: date; Accepted: date; Published: date

Abstract: In the present study, we review five different non-conventional technologies which are aligned with the "green" concepts for product recovery from raw materials in industrial scale with the minimal energy consumption and chemicals use. This paper provides an overview of relevant works done in innovative processing industries to different plant matrices for functional added-value compounds and by-products production. A comparison of the five extraction methods showed a supercritical CO_2 process to be more reliable despite some limitations and challenges in term of extraction yield and solubility of some bioactive compounds when applied in processing industries. However, these challenges can be solved by using ionic liquids as a trainer or co-solvent to supercritical CO_2 during the extraction process. The choice of ionic liquid over organic solvents used to enhance extraction yield and solubility is based on properties such as hydrophobicity, polarity and selectivity in addition to a safe environment.

Keywords: green extraction technology; value-added compounds; process industries; ionic liquids

1. Introduction

Recently, considerable emphasis is placed on the reduction of "carbon footprint" for the development of "smart city" worldwide. Chemical process industries would play an important role in achieving this objective by adopting technology which is environmental using green solvent in separation and extraction processes referred to "green" technology. Green solvents and sustainable technologies are integrated into the extraction and separation of a wide range of bioactive products from biomass conversion. The new pyridyme shift in the usage of bioactive compounds in different industries such as pharmaceutical, food, refinery, textile suggests on one hand the acceptance towards healthy life style and on the other hand, the need for chemical industries to use safe and most appropriate techniques for extraction from biomass or fermentation broths [**1-3**]. In view of the foregoing, many methods, "non-conventional" as well as conventional methods have been reported. [**4-6**].

Non-conventional methods including supercritical fluid extraction (SCFE), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), ultrasound extraction (UAE), pulsed electric fields extraction (PEFE) have been reported in different process industries [**1, 7-8**]. The above mentioned extraction is advantageous compared to conventional techniques [**9**]. Indeed, these techniques can be carried out in the absence of light and oxygen, at elevated temperature or pressure, cope with reduction in organic solvent consumption and extraction time. The longer extraction time, high cost solvent, low selectivity and thermal decomposition of thermos-labile compounds are major challenges of conventional extraction [**10**]. These limitations can be removed using non-conventional extraction techniques.

The process industries are regarded as one of the fastest growing sectors today with an estimated compound annual growth rate of 8.6% [**11**]. The advancement in process has been instrumental in the growth of pharmaceuticals, chemicals, food, textiles and refinery industries [**12**]. These industries are network of equipment covering a wide range of combined technologies lead to a sustainable transformation of biomass for the concomitant production of biofuels, chemicals, natural products, food supplements, or active compounds preferably of added value [**13**]. In this review, some of the non-conventional extraction techniques employed in processing industries were discussed and compared with the view to highlight their merits and demerit especially with respect to their application to a typical scale up process and as well as their economics. The application of high pressure technology with respect to SCF was extensively discussed to highlight its comparative advantage especially with the use of ionic liquid as additional solvents to achieve relatively more efficient extraction and fractionation.

2. Process industries

Typical process industry raw materials feedstocks are processed in a production plant which may consist of different unit operations operated in a continuous and/or batch mode. This definition was schematized as presented in Figure 1 which explains the complex production chain that characterizes significant feature importance with regard to product and process development in process industry. The greener nature and high efficiency of non-conventional technologies have been shown to make them superior to the conventional, especially with respect to product quality and integrity. While some industries still really solely on the conventional technologies, the following section will discuss some selected non-conventional techniques used in process industry that are of relevance to refinery, food, health and textile. Details on these conventional technologies have been reviewed elsewhere [**14**]. Table 1 describes products that can be obtained from various feedstocks (raw materials) using non-conventional techniques reviewed in this paper in process industries with a zoom into food and pharmaceutical industries. This then shows that more interest had been given to food and pharmaceutical industries as compare to refinery, textile and chemical industries using non-conventional technique.

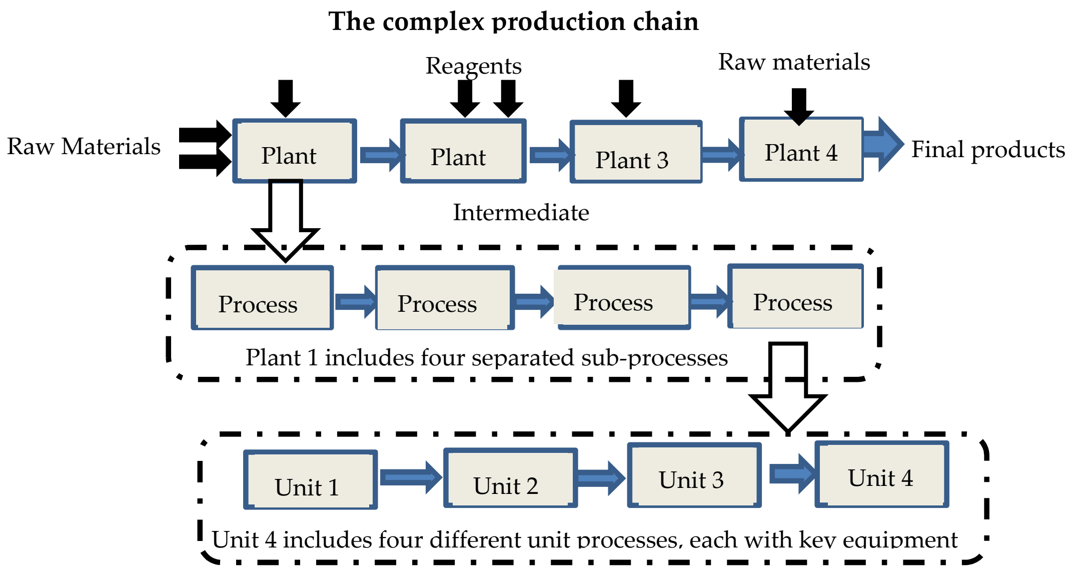

Figure 1. A schematic production process in industry

Table 1. Some processing target ingredients and their sources in different industrial sectors reviewed in this work

Industrial sectors	Sources	Target ingredients	Refs.
Refinery	-Oil sands, oil shale rock, lignite, tire, rubber	- Crude oil, diesel fuel, kerogen, hydrogen, methane	[15-17]
	- Tar sands	- Bituminous	[18]
	- Cannabis seeds	- Oil	[19]
	- Palm kernels	- Palm kernel oil	[20-22]
	-Heavy petroleum feedstocks	- Vanadium, nickel and iron	[23]
pharmaceutical	- Tinctures of sage, valerian	- Cineole, borneol, mixture of α- and β-thujones	[24]
	-Penggan (Citrus reticulata) peel	- Hesperidin	[25]
	- Grapes	- Tartaric acid	[26]
	- Vegetal sources	- Flavonoids	[27]
	-Bovine meat, Porcine meat, Poultry meat, Sea bream fish, Truite Fish	-Antibiotic (Erythromycin A, Josamycin, Roxithromycin, Spiramycin, Tilmicosin, Troleandomycin, Tylosin)	[28]
	- Meat	-Tetracyclines (tetracycline, chlorotetracycline, oxytetracycline and doxycycline), sulfonamides	[29,30]
	-Sewage sludge	- Macrolides	[31]
	-Fish	- Paroxetine and fluoxetine	[32]
	- Chlorella vulgaris	- Carotenoid and chlorophylls	[33]
	- Soil	- Estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2), estriol (E3)	[34-36]
	- Red pepper	- Vitamin E and provitamin A	[37]
Food	- olive leaves/fruit	-Sugars (polysaccharides), protein, fatty acids, pigments, and polyphenols, polyalcohols, lipids and pectins, tyrosol, hydroxybenzoic	[38-41]

Table 1. Continue……………

Food		acid, cinnamic acid, hydroxytyrosol, caffeic acid, syringic acid, elenolic acid, chlorogenic acid, ligstroside, oleuropein, verbacoside, tocopherols, p-coumaric acid, vanillic acid, verbascoside, elenolic acid, catechol, and rutin	
	- Carrrot, grapes, black tea, apple ginger	- Beta-caroten, polyphenol, tartaric acid, phenol, antioxidants, anthocyyanines, Polyphenol, Aroma components, Polyphenols, gingerol	[42-44]
	- Ginseng roots,	- Ginseng saponins,	[45]
	-Caraway	- Caryone and limonene	[46]
	-Amaranthus caudatus seeds	- Vitamin E	[47]
	- Adlay seed	-(Coix lachrymal-jobi L. var. Adlay) oil and coixenolide	[48]
	- Egg yolk	- lutein	[49]
	- Garlic	- Essential oil: organo-sulfur compounds, Aroma,	[50,51]
	- Citrus Flowers and honey	- Linalool	[52]
	- Peppermint leaves	- Menthol	[53]
	- Tomatoes	-Carotenoids (all-trans-lycopene,b-carotene)	[54,55]
	-Vegetal sources	-Phenolic acide, tannins, stilbenes	[56]
	- Crude palm oil and soybean oil	-Tocotrienols and tocopherols	[57]
	-Olive mill wastewater, sea buckborn, berries pomace, mango peel, white grape pomace	-Phenols	[58]
	-Soybean	- Isoflavones	[59]
	-Artichoke, blueberry, grapes and grape seeds, flaxseed hulls, orange peel, and tomato	- Phenolic compounds, flavonoids, anthocyanins, carotenoids	[60]
	-Orange juice and pasteurized juices	- Vitamin C	[61]
	-Fed cabbage	-Anthocyanin	[62]
	-Crude palm and soybean oil	-Tocotrienols and tocopherols	[63]

Table 1. continue……………

Textile	-Dye (turmeric, henna)	- Turmeric and henna extracts	[65]
	-Mordants(harda, Tamarind seed coat)	-Harda and tamarind extracts	[65]
	- Red Beetroot (Beta vulgaris)	-Cyanins and betanin (red) and Betaxanthins. (Yellow)	[56]
	- Lac (Kerria lacca)	- Lacciac acid	[66]
	-Dastylopius coccus, kermes licis, kerria lacca,	- Cochineal (red), Kermes (red), Lac	[67-69]
	-Artichoke, red cabbage, blueberry, grape seeds, flaxseed hulls, orange peel, tomato	-Phenolic compounds, flavonoids, anthocyanins, carotenoids	[71]
	- Ricinus communis leaves	-Natural dye	[72]
Chemical	- Grapes	-Tartaric acid	[36]
	- Corn starch or corn pericarp	-Carbohydrates (glucose, xylose and arabinose)	[73]

3. Non-conventional extraction methods in process industries

3.1. Ultrasound-assisted extraction (UAE)

Many reports on extraction of medicinal plants using ultrasound have been published and the main improvements for such extractions have been found to be in efficiency and shortening of extraction time [**74**]. Valachovic et al. extracted tinctures of sage (Salvia officinalis L.) and valerian (Valeriana officinalis L.) with high antimicrobial activities using UAE at 20 kHz (600 W) for 6h with ethanol/water [**24**]. On the other hand, Yaqin Ma et al. extracted hesperidin from Penggan (Citrus reticulata) peel at 60 kHz frequency, 40 °C temperature for 60 min in methanol [**25**]. In pharmaceutical industry, the active zone and distribution of ultrasonic power are challenges that should be considered. The application of UAE technology in food processing technology is of interest to increase the extraction yield of compound such as polyphenolics, anthocyanins, aromatic compounds, polysaccharides, oils and functional compounds from plant and animal materials. Wu et al. in 2001 and Chemat et al. in 2004 used the UAE at lower temperatures to extract ginseng saponins from ginseng roots, and caryone and limonene from caraway, respectively [**46, 47**]. As Egg yolk is one of an important source of lutein in our foods [75], Kjartansson et al. attempted the extraction of chitin from fresh water prawn shells [**76**] and Xiaohua et al. extracted lutein from egg yolk [**77**] by using sonication. From this study, it was found that depolymerization can lead to the decrease of the degree of acetylation which can limits this technique in food processing. Recently, Xiaohua, et al. have reported higher extraction yield of luetin when ultrasonic used in combination of saponificated organic solvent. Essential oil have been extracted from aromatic plants such as peppermint leaves [**54**], artemisia [**78**] and lavender [**79**], or from other vegetal matrix such as garlic [**80**] and citrus flowers [**53**] using UAE. Extraction of natural dyes using conventional method but, the extraction using ultrasound is explored to a limited extent in textile industry sector. Sheikh et al. extracted natural dyes (turmeric, henna) and mordants (harda, Tamarind seed coat) for textile materials using UAE in water in comparison with conventional method [**81**]. Moreover, Kamel et al. 2004 studied the effects pH, salt concentration, ultrasonic power, dyeing time and on the extraction of lactic acid dye form Lac in distilled water for dyeing wool fabric [**82**]. Due to various mechanochemical effects associated with cavitation induced in liquid, ultrasound has been beneficially applied in chemical processes. Presently, UAE is mainly limited due to inefficient ultrasound generation and high operating costs, although it is a promising technology for high added-value pharmaceuticals, food and chemical ingredients in industrial scale [**83-85**]. One of the challenges of UAE in chemical industry is to obtain effective mass transfer by providing suitable mixing in order to facilitate strong contact between the two immiscible phases.

3.2. Microwave-assisted extraction (MAE)

MAE is as a green technology commonly use for the extraction of organic and organometallic compounds that are more intact, it utilises water or alcohols as solvent at elevated temperature and controlled pressure conditions [**86**]. However, numbers of reports have succefully investigated on the extraction and separation of oil sands or oil shale. Indeed, Renouf et al. in 2003 irradiated for 10 min at 6400±100 MHz the Lloydminster oil sands as stubborn to separate and were tested with exposure to variable frequency microwaves [**87**]. Moreover, Bosisio et al. used MAE to extract oil sands under inert atmosphere in a quartz reactor with an incident microwave power of 100 W at 2450 MHz frequency [**88**]. In addition, Balint et al. describes describing how oil sand, oil shale rock and lignite samples can be irradiated in a pressure vessel with gaseous or liquefied carbon dioxide and other gaseous or vapour hydrocarbon solvent [**89**]. Pharmaceutical industry deals with many analytical procedures for preparation of samples and literature present some reports involving the use of MAE [**90**]. Food processing industry uses MAE to process vitamins in foodstuffs [**91**]. Ergosterol was extorted from hyphae and spores using SCFE and the process resulting in yield lower than that of MAE [**92**]. MAE has been effectively employed to produce muticlasse of antibiotics like levofloxacin, norfloxacin, ciprofloxacin, enfloxacin, fluoroquinolones, tetracyclines from soil [**93**] sewage and wastewater sludge [**94,95**], compost [**96**] and aquifer sediments [**97**]. Sinha et al. evaluated the effect of extraction time, pH of solution and the amount of pomegranate rind extracted dye from brown dry rind of the pomegranate using MAE for textiles [**98**]. On the other hand, the effect of water and ethanol solvent at different temperature with different material to solvent ratio and microwave power was studied for the extraction of natural tannins and flavonoids dyes from coleus atropurpureus leaves [**65**]. Raza et al. extracted natural colorant for textile industry form munj sweet cane by optimazing the temperature, time, fabrics to extract ratio, salt type and salt concentrations [**99**]. In chemical industry, few works have been done on extraction using MAE. In 2010, Yoshida et al. optimized the heating temperature, come-up time, heating time and solid to liquid ratio for the extraction of carbohydrates compounds from corn pericarp with water as a solvent [**100**]. As challenges, polar or volatile compounds and solvent make the efficiency of the microwave to be weak, and it is applied at high temperatures which requires additional treatment as compared to supercritical fluid extraction. In addition, the extraction of micobial oils using microwave could still prove industrially difficult scale up.

3.3. Pressurized Liquid Extraction (PLE)

Several bioactive compounds are extracted from different plants using PLE which is an attractive alternative technique uses due to its short time operation extraction (<30 min), inert environment under high-pressures (<20 MPa) and temperatures (25-200 oC), and low solvent consumption [**101**]. In 2009, Blasco et al. evaluated the temperature, pressure, treatment of sand, static time, cell size, number of extraction cycles and flush volume for the extraction of four tetracyclines (tetracycline, chlorotetracycline, oxytetracycline and doxycycline) from different types of meat in water [**102**]. Estrogens are the most widely used pharmaceutical product in the world because of his contraceptive activity. Therefore, a number of work have been reported on the extraction of estrogens produced such as estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2), estriol (E3) from soil using PLE [**103**]. Recently, Göbel et al. extracted macrolides using PLE procedures in water/methanol as the extracting solvent in sewage sludge [**104**]. Kwang H. Cha et al. in 2010 optimized temperature and time to extract carotenoids and chlorophylls from the green microalga Chlorella vulgaris using PLE [**105**]. On the other hand, reference [**106**] explores the extraction of polyphenols from the needles of Pinus taiwanensis and Pinus morrisonicola by involving enzymatic hydrolysis using mixed enzyme of cellulase, hemicellulase, pectinase and protease. Essential oils from herbal plants been with great importance in food, pharmaceutical and cosmetic industries due to their antimicrobial, antioxidant and antifungal activities, aroma-active constituents and flavor properties, many researchers have found interest on them [**56, 107-109**]

3.4. Pulsed electric fields extraction (PEFE)

PEFE is mostly applies in food preservation and recovery of intracellular from plant food materials, food wastes, and by-products. The extraction of intracellular compounds is the most interesting feature of PEF treatment in biorefinery industries. For example, the extraction of sucrose from sugar beet, colorants from grapes and red beet, polyphenols from green biomass, and lipids from microalgae using PEFE [**110**]. Haji-Moradkhani et al. studied the influence of PEF intensity and the speed of oil extraction screw press on the physicochemical properties of cannabis oil from cannabis seeds by reference [**111**]. Leong et al. produced anthocyanins from grape juices after pulsed electric field treatment at a pulse of 20 mS, a frequency of 50 Hz and an electric field strength of 1.5 kV/cm. C [**112**]. The technique was shown to be efficient in providing pure extracts as well as the ability to protect cells from oxidative stress. Moubarik et al. reported that Fennel (Foeniculum vulgare) extracts with valuable antioxidants and medicinal properties have also been obtained using PEFE and the extraction yield was enhanced [**111**]. The PEF treatment subject to artichoke, blueberry, grapes and grape seeds, flaxseed hulls, orange peel, and tomato enhance the extraction yield of phenolic compounds, flavonoids, anthocyanins, carotenoids [**113**]. The extraction of polyphenols and flavonoids from orange peel using PEFE has been reported [**114**]. Moreover, Segovia et al.

investigated on the extraction of polyphenols from Borago officinalis leaves using PEF treatment [**115**]. The polyphenol and Oxygen Radical Absorption Capacity (ORAC) values were increased between 1.3 and 6.6% and from 2.0 to 13.7%, respectively. Jaeger et al. on the other hand used the PEF technique for extraction of apple juice [**116**]. Elez-Martinez and Martín-Belloso extracted vitamin C from orange juice and the content of vitamin C was compared with that in conventionally pasteurized juices which showed higher in orange juice than in pasteurized juice [**62**].

3.5. Supercritical CO_2 (SC-CO_2) extraction

Supercritical extraction is characterized by changes in temperature and pressure which transform the gas in supercritical fluid [**117**]. Supercritical CO_2 (SC-CO_2) extraction has being applied in several sectors such as food, chemical and pharmaceutical industries [118]. The main drawbacks remain its high cost and difficulties to perform continuous extractions [**119**]. The SC-CO_2 process in oil refinery industry is used for deasphalting of oil and heavy residues by reducing the solvent ratio when removing raw materials and improving the efficiency of the process. Magomedov et al. investigated on the demetallization of heavy petroleum feedstocks (HPF) using SFE for the extraction of vanadium, nickel and iron [**23**]. Many important food ingredients in the health point of view have been extracted using SC-CO_2 process by many researchers [**120**]. Some products produced by SCF technology such as flavour orange juice, vitamin additives, de-alcoholized wine/beer, defatted meat, defatted potato chips, spice extracts may be found on our everyday's table [**121**]. Supercritical fluid process is also used in refinery industry for food ingredients production such as colorants, antioxidant preservatives, texture agents and low-fat products. To use supercritical systems in dyeing, some properties must be known and the phase behavior of a system consisting of solids and gas has been well described by reference [**122**]. Saus et al. reported laboratory results on the dyeing of poly(ethylene terephthalate) and other synthetic materials and on factors influencing dye uptake and levelness [**123**]. In addition, Sanchez-Sanchez et al. impregnated a polyester textile with a mango leaf extract (MLE) in the mixture of CO_2/methanol (50%) at 120 bar and 100 °C and the extract presented antioxidant, bacteriostatic and bactericidal activities [**124**]. The use of supercritical fluids in chemical and biochemical reactions arises mainly from a desire to replace volatile organic solvents. Some chemical reactions (ammonolysis, alkylation, polymerization, field Crafts, hydroformylation, hydrogenation, inorganic catalytic processes, metathesis and oxidation) performed in SCFs media ave already been implemented at industrial scale to obtain value-added products [**125**]. The ammonolysis reaction of ester to amides and of mesylates to amines in supercritical ammonia, asymmetric hydrogenation in SC-CO_2 and also the synthesis of D, L-α Toccopherol in SC-CO_2 and in SC-N_2O have been reported by Wang and Kienzle [**131**]. In addition, the hydrogenation reaction of organic compounds in SCFs has been introduced into practice at industrial scale [**126**] by Thomas Swan and Co Ltd Company in 2000.

4. Comparison of SCFE with other extraction methods

Table 2 compares the green extraction methods considered in this review in terms of their operational conditions. Unlike SCFE (that use SC-CO_2), all these techniques in addition to water, ethanol and methanol, use more other organic solvents which compromise the greener nature of the technique. When comparing the energy consumption, SCFE process requires lesser energy than other techniques. These make the SCFE to be more economically suitable for research and industrial applications. Even though UAE, MAE, PLE, PEFE methods are widely used in extraction techniques, they present many drawbacks such as high energy costs, low selectivity and the generation of large quantities of solvent waste [**127**] which is not the case with SCFE. Besides that, MAE and PLE techniques are not suitable for thermos labile compounds due to high temperature applied, that gives benefice to SCF CO_2 process which does not destroy thermo labile compounds at critical temperature and pressure. With all the advantages of SCFE, this technique also has some limitation when extracting/separating polar compounds due to the non-polar character of CO_2. But many researcher have shown that the use of polar solvent as modifier or co-solvent overcome the challenge [**128**].

Table 2: Summary of non-conventional (green) extraction methods considered in this review

Conditions	UAE	MAE	PLE	PEFE	SCFE	Comments
Extration solvent	Hexane, water, Dichloro-methane, Acetone, Ethanol	Hexane, water, Dichloro-methane, Acetone, Ethanol	H_2O/EtOH, Ethanol	EtOAc/MeOH/ H_2O, CO_2/MeOH, olive oil	SC-CO_2, SC-CO_2/MeOH SC-CO_2/EtOH	• CO_2 suitable solvent for extraction of bioactive compounds • density of CO_2 can be controlled for selectivity • CO_2 has low viscosity and high diffusivity • MAE requires large solvent volume • In SCFE, CO_2 has limited ability to dissolve high molecular weight compounds such as carotenoids, triacyl-glycerides….
Extraction Temperature	10-70 °C	80–350 °C	50-190 °C	< 100 °C	30-100 °C	• MAE is applied at high temperatures • PLE and MAE are not suitable for thermos labile compounds • With SCFE, low critical temperature and low reactivity of CO_2. • SFE is performed at low temperatures, ideal technique for thermally labile compounds
Extraction time	10–90 min	3–30 min	< 1h	< 1h	10–60 min	• with SCFE, few tens of minutes for extraction time • MAE has the limitations of requiring longer extraction time
Power Amount	48-600 W	180-1200 W	Moderate	30 kW	Moderate	• in SFE, the solvation power can be manipulated by changing pressure and/or temperature leading to high selectivity • the active zone and reasonable distribution of ultrasonic power are challenges, ideal for potentially industrial production
Cost effective	High cost	Low cost	Low cost	Low cost	Relatively low	• For SCFE, operating cost including cleaning and maintenance can be underestimated • For the PEFE, the electricity cost is about $0.33 per metric ton • For PLE, high low manufacturing cost US$29.2/kg extract as compared to PEFE • For MAE, low product cost

The addition of polar solvent such as acetone, n-heptane, toluene or mixtures of toluene and n-heptane with acetone and ethyl alcohol, methanol, ethanol, acetonitrile, ethyl acetate, toluene and o-xylene have been used to increasing the solvent power of supercritical fluids [**129**]. Even though these polar solvents enhance the extraction yield and the viscosity of the CO_2, they make the green nature of the SCF technology to be compromised. Therefore, the alternative way of increasing the polarity of the CO_2, yield of extraction and extraction time without affecting the environmental friendly nature of this SC-CO_2 technique could be the use of ionic liquid as co-solvent or modifier. A number of theoretical and experimental works have already been reported to prove the use of ionic liquids in the green extraction and separation technology (MAE, UAE, PLE, PEFE) in processing or bioprocessing industries [**130,131**]. However, the application of ionic liquids as co-solvent or entrainer or modifier for the extraction and recovering of various compounds with high concentration using SC-CO_2 technique is rare. As presented some literatures, ionic liquids are 100% soluble in SC-CO_2 so, the recovery of value-added compounds using SCFE with ionic liquids as modifier will be much easy.

5. Ionic liquids as green solvent

Ionic liquids (ILs) are molten salts at temperatures <100 °C, [**132**], composed of unsymmetrical organic cations, organic or inorganic anions and are described as design solvent with adjustable properties like thermophysical properties, biodegradation ability or toxicological features, as well as hydrophobicity properties [**133**]. Many protic and aprotic ILs has been synthesized since 1914 where the 1st IL was discovered [**134**]. Due to their ionic character, more attention has been given to aprotic ILs exhibiting excellent chemical, thermal, and electrochemical stability, broad liquid temperature range, nonflammability and negligible volatility, and high ionic conductivity [**135**]. These properties make them be potential effective solvent sources materials for organic synthesis, extraction and separation processes, catalysis, in electrochemistry, and as good stabilizing media for proteins, enzymes and nucleic acids [**136**]. The thermal stability, the solubility and the viscosity of ILs which are essential properties to their applications in the extraction and separation of bioactive compounds from biomass have been well investigated and studied in a number of works [**137-138**].

5.1. Ionic Liquid/SC-CO_2 extraction or fractionation

Much research focusing on ILs has predominantly been on their use as solvents for reaction systems especially in chemical and processing industries using SCF process which is equally essential and relatively unexplored. In the IL/SC-CO_2 extraction, organic salts in liquid form interacts selectively with polar and nonpolar compounds using π-stacking interactions, hydrogen bonding, ion exchange and hydrophobic interactions [**139**]. Due to the ionic interactions, the quality and efficiency of the extraction is very high. In metallurgical application, Mekki et al. extracted trivalent lanthanum and europium from an aqueous nitric acid solution in three-step extraction system of water/ionic liquid/supercritical CO_2 [**140**]. This work used the imidazolium-based (1-butyl-3-methylimidazolium (BMIM)) ionic liquid, with bis(trifluoromethylsulfonyl)-imide (Tf_2N^-=$(CF_3SO_2)_2N^-$) as counter anions with low complexing abilities. Shaofen Wang et al. on the other hand extracted Uranyl ions $[UO_2]^{2+}$ from aqueous nitric acid solution with imidazolium-based ionic liquid with tri-n-butyl phosphate as a complexing agent using SC-CO_2 [**141**]. The form of the uranyl complex extracted in the SC-CO_2 phase was identified to be $[UO_2(NO_3)_2$-$(TBP)_2]$. Figure 2 shows the schematic diagram of the two biphasic system for extraction process. From the literature up to date, no work has been reported using IL/SC-CO_2 mixture for extraction of bioactive products in refinery, pharmaceutical, food, textile and chemical industries. But from work done in these industrial sectors using other green techniques than SCF, with VLE data and phase behavior of IL/SC-CO_2, physical and critical properties and with IL/SC-CO_2 interaction studies [**142**], we can therefore say in this review that the extraction or fractionation of value-added products using IL/SC-CO_2 mixture in high pressure technology is possible.

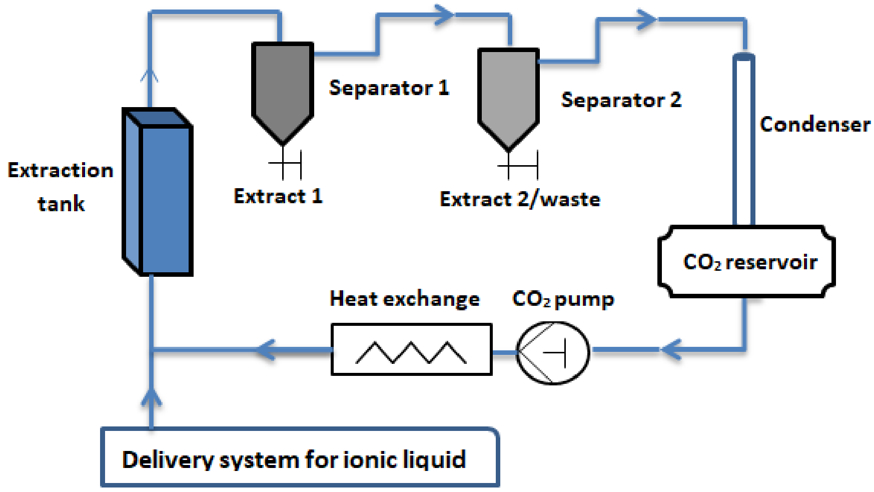

Figure 2. A simplified drawing of a process-scale IL/SC-CO_2 extractor

5.2. Extract recovery from ILs with SC-CO_2 process

The application of supercritical CO_2 for recovering of solutes from an ionic liquid relies heavily on the phase behavior of the binary IL/CO_2 system. From literatures, the behaviors of IL/CO_2 system are different from other organic liquid/CO_2 systems. As an example, Blanchard et al. studied the qualitative phase behavior of 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6])/CO_2 system over a wide pressure range. They studied the ([bmim][PF6])/CO_2 system phase behavior at pressure up to 3100 bar and found two different phases [**143**]. The two distinct phases was explained by the fact that at high-pressure density of pure CO_2, vapor phase increases but since the liquid phase does not expand, the two phases will never become identical. Blanchard et al. in 2001 showed that CO_2 dissolves in the liquid phase of ILs, while the IL remains insoluble in the CO_2 vapor phase. In addition, Kroon et al. experimentally studied the recovery of N-acetyl-(S)-phenylalanine methyl ester (APAM) from the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) using supercritical carbon dioxide as a co-solvent in extractions or as an anti-solvent in precipitation [**144**]. These authors found that solubility of this product, APAM, was lower in ionic liquid/SC-CO_2 mixture compared to the one in pure ionic liquid at atmospheric temperature and the extracted product has trace of ionic liquid.

6. Conclusions

The significant potential of non-conventional methods as extraction and separation techniques for high-added value compounds from biomass or synthetic way or fermentation broths in many process industries is increasingly being reviewed. The novel extraction technologies outlined in this paper have the potential to significantly improve the extraction efficiency. However, the maximum benefits of SCFE can be achieved only if limitation regarding low concentration of compounds with high polarity and molecular weight is overcome. This review thus presented the use of ionic liquids as co-solvent in supercritical CO_2 extraction to overcome his limitation. Another promising technology recently reported that was not reviewed in this paper consists of gas assisted mechanical expression (GAME) which has shown interesting results on oil extraction from vegetable matrices. Future research priorities in the area of high pressure processing technology should be concentrated on the use of ionic liquids as co-solvent as it has been proved to work in industrial scale for extraction/separation of high-added value compounds.

Author Contributions: Supervision, Tunde Victor Ojumu and Tafirenyika Nyamayaro Madzimbamuto. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Cape Peninsula University of Technology of the Republic of South Africa.

Conflicts of Interest: The authors declare no conflict of interest.

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