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In this review, we describe the use of supercritical CO_2 (scCO$_2$) in several cellulose applications. The focus is on different technologies that either exist or are expected to emerge in the near future. The applications are wide from the extraction of hazardous wastes to the cleaning and reuse of paper or production of glucose. To put this topic in context, cellulose chemistry and its interactions with scCO$_2$ are described. The aim of this study was to discuss the new emerging technologies and trends concerning cellulosic materials processed in scCO$_2$ such as cellulose drying to obtain aerogels, foams and other microporous materials, impregnation of cellulose, extraction of highly valuable compounds from plants and metallic residues from treated wood. Especially, in the bio-fuel production field, we address the pre-treatment of cellulose in scCO$_2$ to improve fermentation to ethanol by cellulase enzymes. Other reactions of cellulosic materials such as organic inorganic composites fabrication and de-polymerisation have been considered. Cellulose treatment by scCO$_2$ has been discussed as well. Finally, other applications like deacidification of paper and cellulosic membranes fabrication in scCO$_2$ have been reviewed. Examples of the discussed technologies are included as well.

Keywords: cellulosic materials; supercritical carbon dioxide; biomass materials; green engineering; product design and manufacture; sustainability

1. Introduction and state of the art

Cellulose constitutes the most abundant renewable biopolymer available today. It is widely used in industry and in daily life. Approximately 3.2 million tons of cellulose were used in 2003 for cellulose esters and ether synthesis, and fibres and film fabrication. These materials are used in coatings, laminates and optical films. But the potentialities of this material have not been extensively exploited yet and a bright future for this biopolymer can be predicted due to the exhaustion of fossil resources. New applications of cellulose take advantage of its biocompatibility and the inherent chiral structure in each cellulose sugar unit, giving rise to an enormous pool of possibilities in materials science (Klemm *et al.* 2005).

The combination of biopolymers such as cellulosic materials and the use of supercritical CO_2 (scCO$_2$) as a processing method, are still a relatively new research field. Although there is growing publication activity combining these two topics as shown in Figure 1, the number of reports is still modest. However, the number of publications and patents is expected to grow as biopolymers and green processing methods are gaining an important place in research and development. The unique physical properties associated with scCO$_2$ allow a number of research and application possibilities for chemists, engineers and physicists in fields as vast as polymers science, catalysis, coordination chemistry, and fundamental research. There exist environmental and chemical challenges that can be addressed with this technology that has been a subject of study for at least 20 years.

In this review we describe the use of scCO$_2$ in several cellulose applications. The focus is on the different technologies that either exist, or are expected to emerge in the near future. The applications are wide, from the extraction of hazardous wastes to the cleaning and reuse of paper or production of glucose. To put this topic in context, cellulose chemistry and its interactions with scCO$_2$ are described in particular sections of the text. The main text is dedicated to presenting and discussing new emerging technologies and trends concerning cellulosic materials processed in scCO$_2$, such as cellulose drying to obtain aerogels, foams and other microporous materials, impregnation of cellulose, extraction of highly valuable compounds from plants and metallic residues from treated wood. Especially, in the field of bio-fuel production, we will address the pre-treatment of cellulose in scCO$_2$ to improve fermentation to ethanol by cellulase enzymes. Other reactions of cellulosic materials such as organic–inorganic composites fabrication and de-polymerisation have been considered. Cellulose treatment by scCO$_2$ has been discussed as well. Finally, other applications such as deacidification of paper and cellulosic membrane

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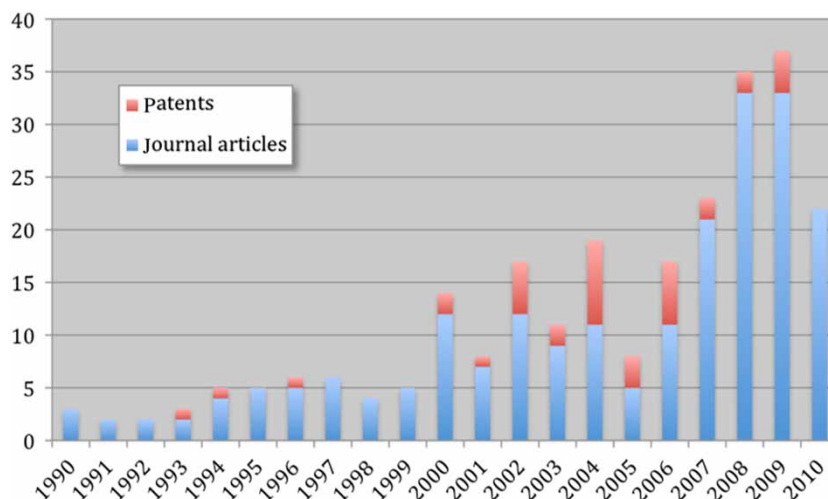
Figure 1. Illustration of the annual number of scientific publications and patents since 1990. Data analysis completed using the SciFinder Scholar search system on 29 September 2010 using the search terms 'cellulose' and 'scCO$_2$' and its synonyms such as 'supercritical carbon dioxide' and 'wood'.

fabrication in scCO$_2$ have been reviewed. Examples of the discussed technologies are included as well.

2. Structure and morphology of celluloses

Cellulose is the most abundant biopolymer on Earth (Siró and Plackett 2010), its regeneration occurs rapidly, and cellulose does not represent a direct food resource for humans (Argyropoulos and Xie 2008). Cellulose naturally occurs in wood, hemp and other plant-based materials and serves as the dominant reinforcing material in plant structures. This biopolymer is also synthesised by algae, tunicates, some fungi, invertebrates and certain bacteria belonging to the genera *Acetobacter*, *Agrobacterium*, *Alcaligenes*, *Pseudomonas*, *Rhizobium* or *Sarcina*. Even some amoeba (protozoa, for example, *Dictyostelium discoideum*) can synthesise cellulose. Cellulose production is estimated to be over 7.5×10^{10} tonnes per year (Klemm *et al.* 2006, Henriksson and Berglund 2007, Iwamoto *et al.* 2007).

Cellulose was discovered and isolated for the first time in 1838 by Payen. Since its discovery, the chemical and physical properties of cellulose have been extensively investigated. A number of efforts of scientists from very different fields have been dedicated to understanding and controlling its biosynthesis, assembly and structural features. Several reviews about research advances and applications for cellulose have already been written, showing increasing interest in this biopolymer (O'Sullivan 1997, Salmon and Hudson 1997, Eichhorn *et al.* 2001).

Native cellulose (cellulose I) is a high molecular homopolymer of β-1,4-linked anhydro-D-glucose units in which every unit is corkscrewed at 180° with respect to its neighbours, and the repeated segment is frequently treated as a dimer of glucose, known as cellobiose. Each cellulose chain possesses a directional chemical asymmetry with respect to the terminus of its molecular axis: one end is a chemical reducing functionality (hemiacetal unit) and the other is a hydroxyl group, known as the non-reducing end (Figure 2; Habibi *et al.* 2010). The number of glucose units or the degree of polymerisation (DP) is up to 20,000, but cellulose types with shorter chains can occur and are mainly found in the primary cell walls. Cellulose chains present a highly ordered structure in crystallites resulting from a 3D intramolecular and intermolecular hydrogen
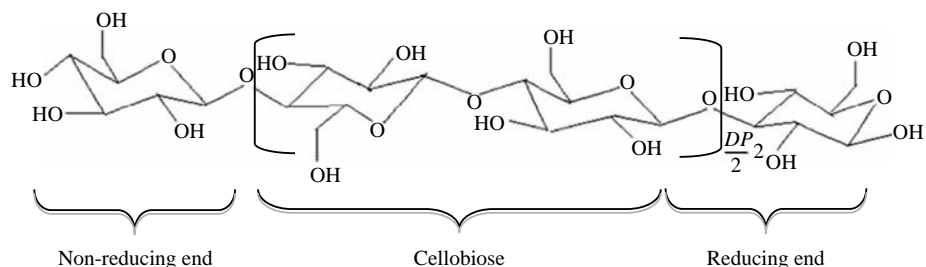

Figure 2. Chemical structure of cellulose.

bond (H-bond) network between the hydroxyl groups attached to each polymer chain. Cellulose presents six polymorphs: I, II, III_I, III_{II}, IV_I and IV_{II}. Native cellulose (cellulose I) has two sub-allomorphs known as Iα and Iβ. Both cellulose I structures adopt parallel configurations but differ in their H-bonding patterns, giving rise to different crystalline structures.

Hemicelluloses are the second most common polysaccharides in nature; they represent about 20–35% of lignocellulosic biomass (Saha 2003). Hemicelluloses are heterogeneous polymers of pentoses (xylose and arabinose), hexoses (mannose, glucose and galactose), and sugar acids. Unlike cellulose, hemicelluloses are not chemically homogeneous. Hardwood hemicelluloses mostly contain xylans, whereas softwood hemicelluloses mostly contain glucomannans (McMillan 1993). Lignocellulosic biomass includes various agricultural residues (straws, hulls, stems, stalks), deciduous and coniferous woods, municipal solid wastes, waste from the pulp and paper industry, and herbaceous energy crops. The composition of these materials varies. The major component is cellulose (35–50%), followed by hemicellulose (20–35%) and lignin (10–25%; Saha 2003).

Chemically modified forms of cellulose include cellulose acetate, obtained by the acetylation of cellulose with acetic anhydride using a catalyst (Malm and Tanghe 1955). This material can then be modified to obtain cellulose acetate butyrate, and cellulose diacetate. Their applications are in textiles, fibres, filtering media, thin-coating films and so on. Ethyl cellulose is a thermoplastic polymer, currently used as thin-film coating material and as a food additive. It is fabricated by treating about two-thirds of the hydroxyl groups of the cellulose molecule with sodium hydroxide and then etherifying with ethyl chloride (Davis *et al.* 1951). Hydroxyalkylcelluloses are water-soluble cellulose derivatives, with a delicate balance between hydrophobic and hydrophilic interactions inside the molecule, which provide an associative behaviour of these molecules in water (Porsch *et al.* 1997). Hydroxypropyl cellulose and hydroxypropyl methylcellulose are natural cellulose ether macromolecules widely used as food additives and as excipients in oral medicaments (Lu *et al.* 2000). Carboxymethyl celluloses are cellulose derivatives that are used as additives in papermaking, in pharmaceuticals and cosmetics, and in food products. They have good solubility, high chemical stability and are toxicologically innocuous. They have recently been used to produce nanocomposites for biological applications (Nadagouda and Varma 2007).

3. Supercritical CO$_2$

The supercritical domain of a fluid was first identified by Tour (1822). He defined it as a domain in which the liquid
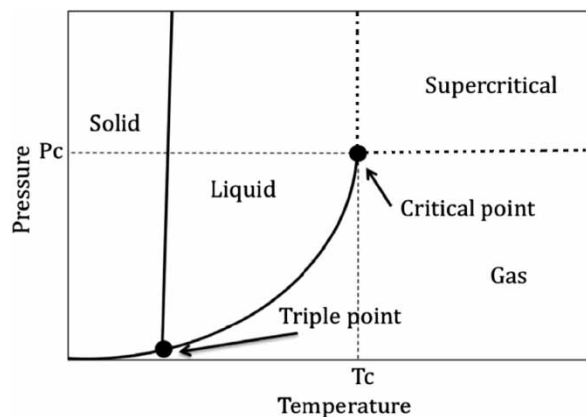

Figure 3. P–T phase diagram of a typical compressible fluid. T_c, critical temperature; P_c, critical pressure.

and the vapour phases no longer seemed distinguishable. Despite this early discovery, the first technological application of a supercritical fluid arrived 150 years later when Zosel (1978) used scCO$_2$ to extract caffeine from coffee beans. Note that the residuum oil supercritical extraction de-asphalting process in the 1970s was not identified as a supercritical process as propane, the solvent, was actually used in the subcritical state (Gearhart and Garwin 1976). In such processes, once the supercritical domain is reached, an increase in pressure and temperature will not produce any phase change (Figure 3). Critical temperature (T_c) and pressure (P_c) of CO$_2$ (30.95°C and 72.8 atm) can be easily reached in industrial reactors. The critical values depend crucially on intermolecular forces such as dipole–dipole interactions, hydrogen bonding and London dispersion forces (polarisability). T_c is in general more affected by these forces than P_c. The abnormally high critical pressure of CO$_2$ is a result of its strong quadrupole moment (Beckman 2004).

The physical properties of scCO$_2$, such as low viscosity, high diffusivity and the absence of surface tension effects impart high penetrating capability to scCO$_2$ together with good mass and heat transport properties. However, density is the parameter that reveals the properties of scCO$_2$. At densities around those of conventional organic solvents, scCO$_2$ exhibits similar solvent power than typical non-polar solvents such as hexane, benzene or toluene. Diffusivity in scCO$_2$ has been measured and compared with toluene (Niessen and Woelk 2007) showing that scCO$_2$ exhibits diffusivities about five or more times higher than those measured in toluene even if the dissolution capabilities of both solvents are similar. The low viscosity exhibited by scCO$_2$ is the result of the reduced solvent–solvent molecular interactions in CO$_2$. CO$_2$ is non-flammable and is the result of the complete oxidation of organic material, rendering it useful as a safe inert solvent in oxidation and in reactions such as

hydrogen peroxide production, where hydrogen and oxygen need to react. $ScCO_2$ presents rather low dielectric constant values, between 1.1 and 1.5 depending on its density. Indeed, this relatively low value can be disadvantageous when dissolving polar compounds is the target. Despite its inertness, CO_2 is a Lewis acid, reacting readily with strong bases such as amines, alkyl anions and phosphines (West *et al.* 2001); other compounds reacting with CO_2 are metal alkoxides, metal alkyls and meta hydrides; carbanions readily react with CO_2 to form carboxylates.

4. scCO$_2$ as a green process and its place in sustainable engineering

In the last 20 years, the number of scientific publications relating $scCO_2$ to the development of green processes has been increasing faster than for the publications about $scCO_2$ fundamental research. Indeed, this number has increased proportionally to the increase in environmentally motivated research and technology (Niessen and Woelk 2007).

CO_2 is considered a greenhouse gas; however, most of the CO_2 used in processes today is obtained from naturally occurring deposits or from man-made sources such as effluents from ammonia plants. Indeed, when CO_2 is used confined in a process, it can be considered as sequestered (Beckman 2004) and this statement is even more sound when CO_2 is used as a reactant. However, the sources of the CO_2 used need to be considered when analyzing the global 'greenness' of a $scCO_2$-based process and using CO_2 from a natural deposit is obviously counter productive. The 12 principles of Green Chemistry can be used to assess the sustainability of a process (Anastas and Warner 1998). From these principles, the substitution of common solvents by safer solvents, safer chemicals, and use of renewable raw materials are fulfilled when $scCO_2$ is employed. However, the use of $scCO_2$ has some drawbacks because these processes have always operated under pressure (above 50 bar) and designing, building and operating a high-pressure process include higher costs than low-pressure processes because special equipment needs to be used. Also, one must also admit that CO_2 is a relatively weak solvent and this leads to increased quantities of solvent used in the process.

Finally, the economic viability of processes employing $scCO_2$ must be assessed, as their environmental benefits will never be realised if economic reliability is not demonstrated. However, good designs can become real industrial successes: two examples are coffee decaffeination (Zosel 1978, Prasad *et al.* 1981) and the $scCO_2$-based thermoplastic foaming process commercialised by Trexel and developed by the Massachusetts Institute of Technology (Park *et al.* 2000).

5. ScCO$_2$–cellulose interactions

Literature on the behaviour of cellulosic materials in contact with $scCO_2$ has not been very extensive in these last 20 years. However, because of the potential applications in this domain, the need to study both the fundamental and applied aspects of interactions of $scCO_2$ with cellulosic materials has become crucial, in particular with regard to wood and its components. Understanding the behaviour of compounds, carrying complexity from relatively simple model compounds to complex polymers or multi-component polymeric networks or solutions, is valuable for applications in industries of pulping, paper, and natural, pharmaceutical and cosmetic products (Li and Kiran 1988).

Especially, with regard to material production, it is important to dissolve and process cellulose without degradation (Li *et al.* 2009a, Pinkert *et al.* 2009). Cellulose resistance towards dissolution arises from its high crystallinity given by its highly ordered structure (Pinkert *et al.* 2009). Successful cellulose solvents must possess the ability to compete for the existing intermolecular H-bond interactions in order to separate the polymer chains, resulting in the dissolution of the biopolymer (Feng and Chen 2008). In addition, other requirements for a good cellulose solvent are low viscosity and toxicity, ease of recycling and high thermal stability. Solvent efficiency at low temperatures is required, as cellulose becomes degraded at high temperatures (Pinkert *et al.* 2010). An extensive study of dissolution and the ease of precipitation of the dissolved fragments of cellulose in supercritical fluids, including $scCO_2$, has been published by Li and Kiran (1988), analysing the interactions between $scCO_2$ and cellulosic compounds and wood species. From their extraction results and thermogravimetric analyses, they have shown that no specific interactions occur with $scCO_2$ alone, but they found that the mixture $scCO_2$–water exhibits high reactivity towards carbohydrate fractions of wood.

6. Cellulose drying by scCO$_2$

Cellulose gels have attracted more attention recently as environmentally friendly, biodegradable and biocompatible products from a nearly inexhaustible raw polymeric material such as cellulose. They are particularly useful in the domain of foods, pharmaceuticals, cosmetics, textiles and biomedical sectors due to their wide applications as texture modifiers for controlling rheological properties, gelling agents, thickeners, emulsifiers, stabilisers, coating and packaging films (Klemm *et al.* 2005).

6.1 Porous materials

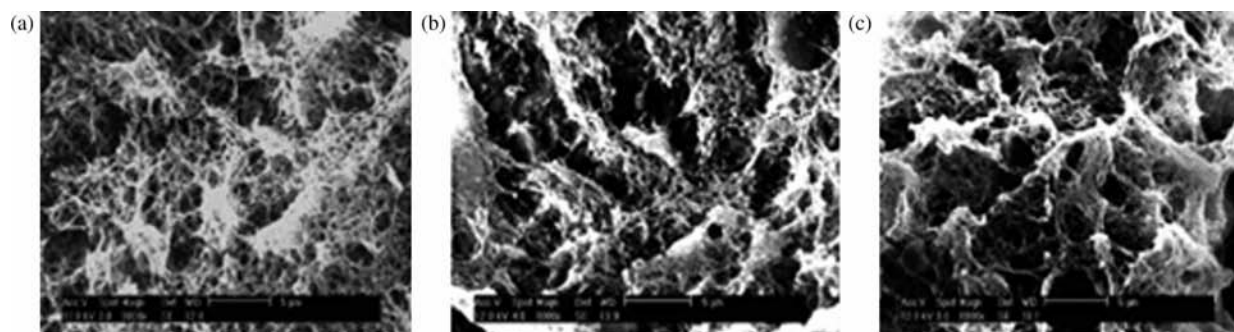Preparation and properties of porous materials from cellulosic materials have recently attracted attention. Most

Figure 4. SEM micrographs of aerocellulose from five Avicel/NaOH/water gelled solutions (a) without Simusol (b) with 0.5% Simusol and (c) with 1% Simusol. Reprinted with permission from Gavillon and Budtova (2008). Copyright 2008 American Chemical Society.

of these materials have been prepared through freeze-drying of solutions or gels. An alternative way to prepare highly porous solid materials is drying of gels in supercritical conditions. Briefly, a gel of cellulose or cellulose derivative is realised by dissolution in a suitable solvent, then a solvent exchange is formed and the gel is efficiently dried thanks to supercritical carbon dioxide. The supercritical drying technique is particularly advantageous because it allows production of high specific surface area aerogels without any shrinking due to the lack of surface tension of $scCO_2$, which prevents the structure from collapsing as is the case when a liquid–vapour interface is present when the solvent is conventionally evaporated. The first cellulose aerogels made using $scCO_2$ were reported by Kistler (1932); however, it is 40 years later that these materials have started to draw attention. Recently, cellulose acetate aerogels prepared from chemically cross-linked cellulose acetate gels dried in $scCO_2$ have been reported (Tan *et al.* 2001, Fischer *et al.* 2006). Fabrication of other cellulose acetate porous materials by drying cellulose acetate gels with $scCO_2$ is described in a patent by Thies *et al.* (1996).

Pure cellulose aerogels obtained by drying aqueous solutions of cellulose in NaOH with $scCO_2$ have also been studied recently (Gavillon and Budtova 2008). The influence of the addition of a surfactant (Simulsol) on

the porosity has been studied showing that the higher the concentration of the surfactant, the larger the pore size and the lower the density of the aerogels obtained (Figure 4). Regeneration of these materials using acetic acid and $scCO_2$ drying has been reported by the same authors (Sescousse and Budtova 2009). In these studies, a solvent exchange of water with acetone or ethanol prior to $scCO_2$ drying was used to avoid water/$scCO_2$ immiscibility. By this method, materials of $0.06\,g/cm^3$ have been obtained. Liebner *et al.* (2007, 2008) have reported the cellulose aerogels produced by $scCO_2$ drying of regenerated cellulose obtained by solvent exchange of a solution of cellulose in *N*-methylmorpholine-*N*-oxide; these materials showed surface areas of $172-284\,m^2/g$. In another study, cellulose aerogels have been prepared by $scCO_2$ drying of the bacterial cellulose produced by the gram-negative bacterium *Gluconacetobacter xylinum*, resulting in highly porous dry cellulose aerogels showing a density of $8\,mg/cm^3$ (Figures 5 and 6; Haimer *et al.* 2010, Liebner *et al.* 2010). Cellulose gels have been dried in $scCO_2$ followed by calcination and subsequent doping by platinum nanoparticles, yielding nanostructured highly porous electrocatalysts used for oxygen reduction (Guilminot *et al.* 2008). Heath and Thielemans (2010) successfully prepared cellulose nanowhiskers, which are rigid rods with a rectangular cross-section with dimensions

Figure 5. Different gel states of bacterial cellulose obtained from *G. xylinum*: aquagel vs. aerogel (left). Due to the extremely low density of the material, electrostatic charge is sufficient to make the aerogel stick to a finger (right). Reproduced with permission from Liebner *et al.* (2010), Copyright Wiley-VCH Verlag GmbH & Co. KGaA.
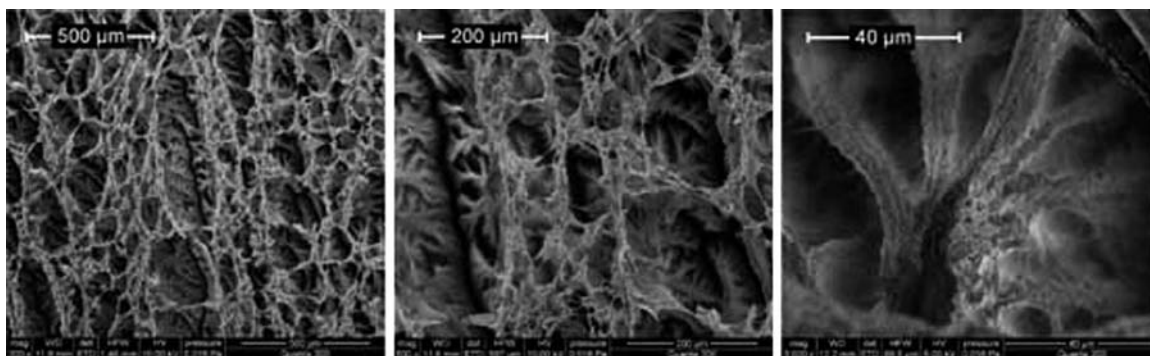
Figure 6. Scanning electron microscopy (SEM) pictures at various magnifications (200×, 500× and 3000×; from left to right) of a scCO$_2$-dried aerogel from bacterial cellulose. Reproduced with permission from Liebner *et al.* (2010), Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

between 3 and 20 nm and lengths ranging between 100 nm and several microns. These materials have been dispersed in water under sonication and then solvent exchanged with anhydrous ethanol to obtain alcogels followed by scCO$_2$ drying to obtain aerogels with densities lower than 0.078 g/cm^3 and surface areas of up to 605 m^2/g.

6.1.1 Cellulosic membranes

ScCO$_2$ has been used to fabricate cellulose-based membranes obtaining continuous structures characterised by interconnected cells. These materials can be used in applications such as filtration processes and medical applications. Cellulose acetate microporous membranes have been prepared by phase inversion using scCO$_2$ as an anti-solvent and a solution of cellulose acetate in solvents such as acetone, methyl acetate, 1,3-dioxolane and 2-butanone. The use of scCO$_2$ allowed the preparation of highly porous membranes without macro-voids despite the observed instantaneous demixing. These studies have shown that the properties of membranes such as porosity can be controlled by temperature and pressure variations. The membranes obtained by this method presented solute rejection coefficients in the microfiltration domain (Matsuyama *et al.* 2002, Reverchon and Cardea 2004). In all the studies, the anti-solvent precipitation of scCO$_2$ allowed a control of membrane pore size distributions as parameters such as pressure, temperature and polymer content effect have been studied. Figure 7 shows examples of cellulose acetate membranes obtained with polymer concentrations of 20% and 5% (w/w) in the initial solutions (Reverchon and Cardea 2004).

6.1.2 Cellulose-based foams by scCO$_2$

Foams are porous structures which present cavities or cells that are not interconnected. These cavities enhance lightness, softness, impact strength and thermal insulating

properties. For these reasons, they are widely used in aircraft, automotive, building and packaging industries. The most common foaming technique uses a chemical blowing agent added into the polymer formulation which produces a gas during polymer processing. ScCO$_2$ has become very attractive for circumventing the use of
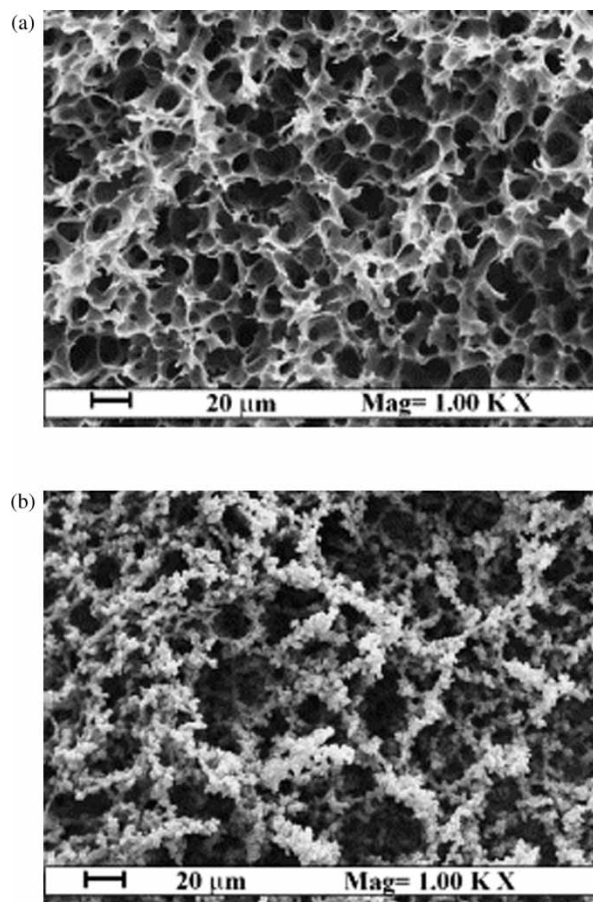

Figure 7. Membrane section $T = 65°C$, $P = 100$ bar: (a) 20% (w/w); (b) 5% (w/w). Reprinted from Reverchon and Cardea (2004). Copyright 2004 with permission from Elsevier.

(a)

30μm   Mag = 1.00 KX
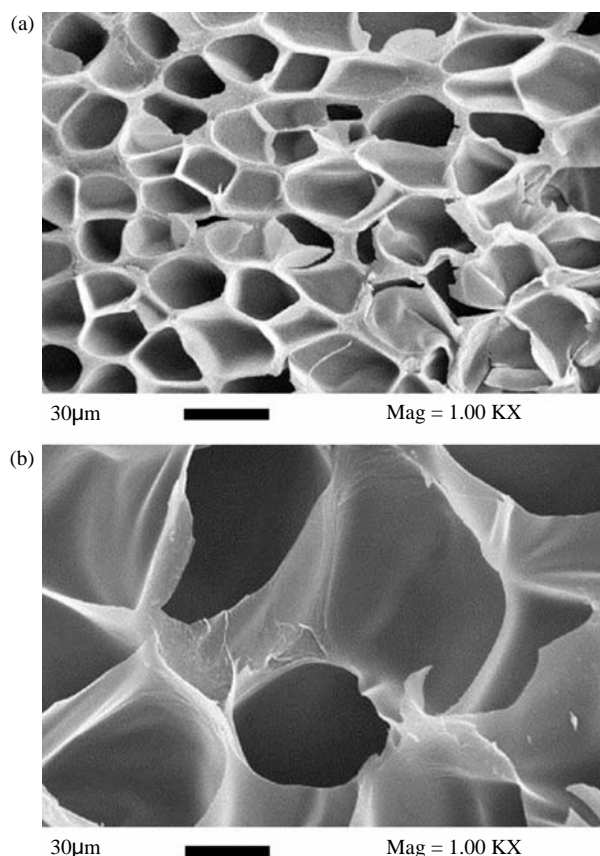
(b)

30μm   Mag = 1.00 KX

Figure 8. Effect of pressure on the foam structure of cellulose acetate (temperature = 230°C, contact time = 480 min) (a) 250 bar; (b) 100 bar. Reprinted from Reverchon and Cardea (2007). Copyright 2007 with permission from Elsevier.

chemical blowing products to produce foams. One of the most interesting applications of scCO$_2$ foaming is in medical applications as scCO$_2$ can be completely separated from the polymer. Cellulose acetate butyrate foams with a bimodal cell distribution have been produced by using scCO$_2$ as the blowing agent. Depending on the depressurisation rate, the resulting morphology of the foams has been homogeneous or bimodal with an open cellular structure (Jacobs *et al.* 2008). Reverchon and Cardea (2007) have reported an increase in cell sizes as pressure decreases during the formation of cellulose acetate foams (Figure 8) explaining this behaviour by the decrease of scCO$_2$ diffusivity inside the substrate at higher pressures, limiting the contribution of scCO$_2$ to cell growth.

6.2 Particle design

Particle design is at present a major development of scCO$_2$ applications (Jung and Perrut 2001). As we have

mentioned above, because scCO$_2$ lacks surface tension effects, no cohesion along the evaporation process occurs, avoiding aggregation of the particles. Ethyl cellulose microparticles have been prepared by Li *et al.* (2008a) using scCO$_2$ as the drying medium showing that pressure had a great influence on the size of microparticles. Biocompatible microparticles of ethyl cellulose/methyl cellulose blends have been prepared by scCO$_2$ anti-solvent precipitation from solutions in dicloromethane, acetone, and dimethylsulphoxide. ScCO$_2$ density seemed to have high influence on particle diameter (Duarte *et al.* 2006b). In a study published by Haimer *et al.* (2008), precipitation and drying of hemicelluloses (xylans and mannans) from solutions in dimethylsulphoxide/water with scCO$_2$ have allowed the preparation of spherical particles with a narrow size distribution. The addition of small quantities of water allowed controlling of the particle size and morphology, given that hemicellulose is insoluble in water. On the other hand, batch precipitation yielded large xylan aggregates or sponge-like mannan structures. The semi-continuous mode was revealed to be useful for obtaining small particles.

Wood has been used as a template to produce porous SiO$_2$ and TiO$_2$ materials in scCO$_2$ by impregnating wood with the precursors (tetraethylorthosilicate or titanium butoxide) by using scCO$_2$ and subsequent hydrolysis. After calcination in air flow, organic components were removed and the porous materials that were obtained have shown the framework of wood templates. It has been shown that porous material properties such as pore size and structure can be adjusted by changing the wood species and operation conditions (Li *et al.* 2008b).

7. Impregnation of cellulose using scCO$_2$

The impregnation process can be described by the same thermodynamic and mass principles as used for scCO$_2$ extraction of compounds from the matrix such as polymers or vegetal matter, since these two processes are the inverse of one another (Shen *et al.* 2008).

During the polymer impregnation process, it is important to consider the possible evolution of the polymer glass transition temperature (T_g). In fact, scCO$_2$ may act as a plasticiser for polymers and this has been also observed for cellulose-derived polymers used in pharmaceutical applications such as cellulose esters and hydroxyalkylcelluloses (Laksman 2007, Verreck *et al.* 2007). This plasticisation or swelling reduces the glass transition temperature, impacting many polymer processing steps through phenomena such as viscosity reduction during polymer extrusion and polymer blending or foaming, and changes in morphology due to induced crystallisation (Chow 1980). Also, in processes where high temperature is needed, like hot stage extrusion, the high

level of temperature may be a drawback for the preservation of the quality of the processed polymer and adding a plasticiser may reduce the viscosity of the mixture and thus lower the process temperature settings. Conventional plasticisers, however, usually remain in the product, affecting its properties and performance and require purifying steps whenever the polymer is used in pharmaceutical and food industries. In these cases, the use of a reversible plasticiser, which lowers the processing temperature without being present in the final formulation, is highly beneficial. $scCO_2$ may serve this role since it is gaseous upon expansion to atmospheric conditions, and as such, escapes from the processed material at the end of the process by a pressure release. Plasticisation by $scCO_2$ results from a reduction of chain–chain interactions and increase in the interchain distance by swelling the polymer (Verreck *et al.* 2006, 2007). The low temperature at which these phenomena occur with $scCO_2$ is interesting for thermally sensitive drugs, biomaterial or biomatter (e.g. enzymes) formulations, where the incipient may degrade when exposed to high temperatures. A near-critical CO_2-assisted impregnation process has been proposed (Shen *et al.* 2008) to load vanillin and L-menthol into cellulose acetate fibres without disruption of the fibre morphology, taking advantage of the polarity of these two compounds and of their hydroxyl groups that are suitable hydrogen bonding sites. Another example is the impregnation of D-panthenol into cellulosic fibres by $scCO_2$ drying (Kraft *et al.* 2004). A drug release system of indomethacin, which is a poorly water-soluble non-steroidal anti-inflammatory drug, inside hydroxypropyl methylcellulose fabricated by $scCO_2$-assisted impregnation, has been studied by Gong *et al.* (2008). Naproxen-loaded ethylcellulose/methylcellulose microspheres have been prepared in $scCO_2$ by Duarte *et al.* (2006a) for controlled delivery of this non-steroidal, anti-inflammatory drug. Release profiles of the systems were studied and showed that almost all the drug was released during what is considered to be the gastrointestinal transit time. York and Hanna (1994) described in their patent the use of $scCO_2$ in the impregnation of salmeterol xinafoate in hydroxypropyl-cellulose from a solution of these two compounds in acetone obtaining the inclusion of particles of the active compound inside the polymeric matrix by gas anti-solvent recrystallisation.

Yin *et al.* (2007) and Yin and Shen (2007) have impregnated urea into cellulose pulp by $scCO_2$, followed by the esterification of the cellulose to obtain cellulose carbamate, an environmentally friendly material, considered as an interesting alternative to petroleum-based polymers because of its renewable, biocompatible, biodegradable nature and its solubility in conventional solvents.

The use of $scCO_2$ as a solvent for synthetic and natural textile dying came from the need to decrease the large water consumption of the traditional textile dying industry.

$ScCO_2$ can facilitate dye penetration into the fibres and decrease dying times compared to traditional water-based processes (Bach *et al.* 2002). Textile dying using $scCO_2$ is usually operated at around $100°C$ and 300 bar. Cellulosic textile materials have been dyed employing dispersed dyes in $scCO_2$ by treating the cellulosic materials with an auxiliary that promotes dye uptake. The tested auxiliary molecules were polyethylene glycol (PEG), alkanolamines, aromatic compounds (Schlenker *et al.* 1994) and acids (Fernandez Cid *et al.* 2010). Ramie is a hard perennial plant whose fibres have high tensile strength and excellent thermal conductivity when used as textile materials. This cellulosic material has been dyed in $scCO_2$ with the colourant disperse red 74 after pre-treatment with alkali and benzoyl chloride. Colour yields increased with temperature, pressure and dying time (Liu *et al.* 2006). $ScCO_2$ with synthetic and natural dyes obtained by $scCO_2$ extraction has been employed by Beltrame *et al.* (1998) to dye cotton. PEG was used as a plasticizing agent of cellulose and benzamide as a synergistic agent as it is a good solvent for disperse dyes given its ability to form hydrogen bonds with cellulose and PEG, thus favouring dye entrapment (Beltrame *et al.* 1998). Good yields for cotton dying (99% of dye fixation) were obtained by Fernandez Cid *et al.* (2005) by employing monofluorotriazine reactive dyes and by adding a little amount of acids. The role of water in the mechanism of dying of natural fibres was revealed by (van der Kraan *et al.* 2007) and, according to the authors, water is necessary for swelling the fibres and participates in the chemical fixation of the dye. They showed that the best dying yields were obtained when both the textile and $scCO_2$ were saturated with water.

Preservation of wood-based composites has received considerable attention, since their utilisation as building and structural components under conditions of possible biological attack is gaining increasing importance. Conventional treatments with waterborne preservatives swell the composites reducing their mechanical resistance. An alternative recently explored consists in using $scCO_2$ as a carrier solvent for the impregnation of preservative compounds as proposed in the Supertrae process (Henriksen 2003), in which wood is treated with $scCO_2$ as a carrier for preservative compounds, and temperature is not allowed to exceed the plasticisation temperature of the wood during pressurisation and depressurisation avoiding damage to wood during the process. Different types of biocides and termiticides have been impregnated in wood-based composites without any negative effect on their physical or mechanical properties after the impregnation. It has been shown in these studies that the optimum pressure level would depend on the permeability of the composite (Morrell *et al.* 1993, Acda *et al.* 1996, Acda *et al.* 1997a, 1997b, Morrell *et al.* 1997, Tsunoda 1998, Acda *et al.* 2001, Muin *et al.* 2003, Muin and Tsunoda 2003a, 2003b, Yong Feng Li 2010).

Cellulose/TiO$_2$ hybrid materials have been prepared by scCO$_2$-assisted adsorption and impregnation onto cellulose fibres with a titania sol which was prepared through a non-hydrolytic sol–gel route (Yu *et al.* 2008).

8. Extraction

Extraction of natural compounds from cellulosic vegetal matrices has been the most widely studied application of supercritical fluids, in particular using scCO$_2$. Mcdonald *et al.* (1983) have successfully applied scCO$_2$ extraction to obtain resin and fatty acids from southern pine and wax from Douglas fir bark. Extraction of pine wood with scCO$_2$ was reported to cause no significant change in microscopic morphology of wood (Ritter and Campbell 1986, 1991). Another study has shown that scCO$_2$ extraction enhances the permeability of Douglas fir (Demessie *et al.* 1995).

Lignocellulosic materials can be used to obtain ethanol by fermentation. Two main processes are involved in the conversion: hydrolysis of the cellulose present in the lignocellulosic materials to produce reducing sugars and fermentation of these sugars into ethanol. The main drawbacks of this process are the low yields and high costs, which do not allow obtaining ethanol from lignocellulosic biomass at a competitive cost with current technologies. Feedstock pre-treatment has been recognised as a necessary step to eliminate biomass recalcitrance for microbial and enzymatic hydrolysis. Pre-treatment includes reduction in size and extraction of hemicelluloses and lignine, which interfere with biomass cellulose saccharification. Zhu and Pan (2010) have published a review of conventional pre-treatment technologies (not employing scCO$_2$), which estimates the energy consumption of different techniques, showing that issues associated with cellulosic material conversion are still to be addressed.

ScCO$_2$ extraction has been used as a pre-treatment of lignocellulose prior to cellulose enzymatic hydrolysis. It has been reported that Aspen (hardwood) and southern yellow pine (softwood) pre-treatment with scCO$_2$ resulted in a significant increase of final sugar yields from the enzymatic hydrolysis of the pre-treated cellulose when moisture was present in the initial material (Kim and Hong 2001). Kiran and Balkan (1994) have reported extractions and delignification of red spruce with mixtures of acetic acid–water–scCO$_2$. Sugar cane bagasses and *Pinus taeda* wood chips had been processed in mixtures of alcohol/scCO$_2$ showing a delignification extent of 88.4% and 93.1%, respectively, for these two cellulosic materials. It has been shown that temperature had a more important influence than pressure on the delignification yield (Pasquini *et al.* 2005a, 2005b).

An increasing interest in the extraction of high added value substances, such as antioxidants, pharmaceuticals, essential oils and colouring matters has shown in the last 20 years. Useful compounds have been extracted from cellulosic matrices by scCO$_2$ such as humulones and lupulones from hop resins; oil from sheatnut kernels and *Canarium* pulp, piperine from ground black pepper, essential oils from ground nutmeg, capsaicine from ground chillies, nicotine, tobacco aroma, caffeine, limonene, menthol and tryglycerides from tobacco, raw coffee, caraway fruits, peppermint leaves and sunflower seeds (Williams 1981, Nkouam *et al.* 2007). The extraction of tall oil and turpentine from coniferous woods has been developed as well in a patent by Frement (1981). The extraction of natural compounds with scCO$_2$ has been the subject of several reviews in the past (Moyler 1993, Kerrola 1995, Reverchon 1997, Lang and Wai 2001, Reverchon and De Marco 2006).

For successful extraction, not only has the solubility of the compounds to be extracted and/or of the undesired compounds to be taken into account but mass transfer resistances due to the structure of the raw material and the specific location of the compounds to be extracted can also play a prominent role. The complex interplay between thermodynamics (solubility) and kinetics (mass transfer) has to be understood to properly perform supercritical fluid extraction and propose adequate extrapolation on an industrial scale. Supercritical fluid extraction has been applied to fractionation of the extracts also. Indeed, in many cases, it is not possible to avoid the co-extraction of some compound families. In these cases, it is possible to perform an extraction in successive steps by increasing pressures to obtain the fractional extraction of the soluble compounds contained in the organic matrix, selected by decreasing the solubilities in the supercritical solvent. The aim of this process is to induce the selective precipitation of different compound families as a function of their different solubility in the supercritical fluid. This procedure has been applied in the extraction of essential oils (Reverchon 1992, Reverchon *et al.* 1994, 1995a, 1995b, 1995c, Reverchon and Porta 1996). Due to the complexity of the materials to be treated and the large variety of compounds that can be extracted, supercritical fluid extraction is far from being exhaustively studied. However, some industrial applications have been already developed such as recycling cellulose esters from the waste from cigarette manufacture (Schiraldi 1994); removing adhesives from cellulose (Hossain and Blaney 1991); extracting terpenes and oils from wood (Fremont 1981); removing lignin from Kraft streams (Avedesian 1985), removal of natural oils from plant matter (Sevenants 1987) and removal of dioxins and dibenzofurans from cellulosic materials from waste paper, newsprint, ledger stock, packaging materials, cartons, boxes, computer printouts, telephone directories, corrugated boards and the like (Hossain and Blaney 1993).

9. Extraction of metals

Wood containing preservatives has been used for a long time for telegraph poles, railway ties and street lighting poles among other applications. Treatment of this wood has become a major concern given that many of the preservatives used are agents containing heavy metals such as copper, chromium, arsenic and so on. Most of the time, treated wood is incinerated causing air, soil and groundwater pollution. Even more, if this wood is recycled, heavy metals content becomes highly dangerous for human health. No effective techniques exist to treat this wood as traditional extraction processes require large quantities of toxic and volatile solvents. $ScCO_2$ has been proposed as an environmentally friendly solvent to extract metals from treated wood (Takeshita *et al.* 2000, Takeshita and Sato 2002, Abd El-Fatah *et al.* 2004, Wang and Chiu 2008). Direct extraction of metal ions by $scCO_2$ is highly inefficient because of the charge neutralisation requirement and the weak solute–solvent interactions. One suggested approach of extracting metal ions by $scCO_2$ is to convert the charged species into metal chelates using a chelating agent in the fluid phase (Laintz *et al.* 1992). In particular, extraction of Hg^{2+} and Au^{3+} from cellulose-based matrices has been achieved using bistriazolo-crown ethers as chelating compounds in $scCO_2$. In this study, extraction efficiencies appeared to be determined by the formation of metal chelates with the ligand at the pH defined by the CO_2—H_2O system (Wang *et al.* 1995, Wai and Wang 1997). Au^{3+} ions have been extracted from cellulosic materials by using fluorinated calixarenes as chelating compounds as well (Glennon *et al.* 1999), the dynamics of chelation of metals with lithium *bis*(trifluoroethyl) dithiocarbamate from wood fibres in $scCO_2$ has been studied by Al-Jabari obtaining a high extraction yield (Al-Jabari 2004). Hg^{2+} and CH_3Hg^+ (methyl mercury ion) have been extracted from cellulosic materials using methanol-modified $scCO_2$ coupled with an *in situ* derivatisation (Sun *et al.* 2001). In both studies, extraction of almost 100% has been achieved by varying the operating conditions. On the other hand, $scCO_2$ extraction of lanthanides and actinides (La^{3+}, Eu^{3+} and Lu^{3+}) from cellulosic matrices by complexation with a fluorinated β-diketones and tributyl phosphate has been studied as a potential application to nuclear waste analysis and management. Efficiencies of extraction have been found to be up to 90%. The same complexing agent was used to extract uranyl ions obtaining 95% when $scCO_2$ was modified with 5% of methanol (Lin *et al.* 1993, Lin and Wai 1994).

10. Bio-fuel production

The supplementary and eventual replacement of petroleum fuels with renewable biologically produced fuels has been recognised as a critical goal by both the US Department of Energy and the Biofuels Research Advisory Council of the European Union (Gowen and Fong 2010).

Biomass consists of cellulose, hemicellulose and lignine. Lignocellulose biomass represents a renewable source of raw feedstock for conversion into bio-fuels and chemicals (Rout *et al.* 2009). According to the World Energy Council, the availability of biomass in the world is 220 billion tonnes per year or 4500 EJ (10^{18} J) and its utilisation would lead to considerable reduction in fossil fuel consumption (Council 2004, Ragauskas *et al.* 2006).

The different types of biomass differ in their composition. Inorganic compounds (commonly known as ash), are associated with oxygen-, nitrogen- and sulphur-containing functional groups. The hemicellulose, cellulose and lignin content in the biomass determines the theoretical yield of biochemical reactions in bio-fuels production and greatly impacts the economic aspect of the entire process (Rout *et al.* 2009).

Different methods are currently being used to obtain bio-oil from different types of biomass. Pyrolysis is one of the methods most used and can be applied as slow, normal or fast pyrolysis, depending on the conditions that are used. Many researchers have noted that bio-oil produced by the pyrolysis method contained 25–40% water, which forms an azeotrope with bio-oil. The moisture present in the bio-oil finally affects many of the physicochemical properties. Therefore, the separation of water from bio-oil is one of the objectives for increasing fuel efficiency. Among the different processes, $scCO_2$ is one of the most advanced processes for the separation of water from bio-oil (Rout *et al.* 2009).

One of the most specific and versatile routes to produce fuels or other bio-products is to obtain monosaccharides from biomass. These monosaccharides can be converted to fuels or bio-products through fermentation as well as through catalytic processes (Luterbacher *et al.* 2010). Selectively producing sugars from the lignocellulosic biomass is challenging and typically involves several stages. The 'pre-treatment' stage consists of partially extracting the cellulose, hemicellulose and lignin while avoiding the production of unwanted degradation products as they have an inhibitory effect on microorganisms during fermentation leading to decreased yields and thus higher production costs (Persson *et al.* 2002). On the other hand, efficient enzymatic saccharification of cellulose at low cellulose loadings continues to be a challenge for commercialisation of a process for bioconversion of lignocellulose to ethanol. Currently, effective pre-treatment followed by high enzyme loading is needed to overcome the limitations of complete hydrolysis (Arantes and Saddler 2010). $ScCO_2$ extraction has been successfully employed to treat a hydrolysate of spruce prior to ethanolic fermentation with *Saccharomyces cerevisiae*. The extraction provides a clean and concentrated hydrolysate with increased fermentability as well as lowered

concentrations of inhibitors such as phenolics and furan derivatives (Persson *et al.* 2002).

11. Cellulose reactions and chemical modifications in scCO$_2$

During the last few years, increasing interest has been shown in the reactions in supercritical solvents. Supercritical solvents can constitute the reactant medium and the same properties that make scCO$_2$ interesting in the separation and extraction processes and can be used advantageously in reactive systems. Thermodynamic equilibrium can be adjusted by P and T manipulation, which allows control of the yields and reaction rates. Reactions can be performed in combination with separation processes, giving products of high purity. Transport properties are more favourable in the supercritical region as diffusivities are higher and viscosities are lower than in liquids. Solvent effects can be studied by perturbations of the system by small changes in pressure (Munshi and Bhaduri 2009, Skouta 2009).

Over the past 40–50 years, many groups have assessed the ability of carbohydrate-degrading enzymes. Cellulase enzymes process cellulose under certain conditions, cleave glucoside bonds, reduce the degree of cellulose polymerisation and eventually cleave it to soluble, fermentable sugars such as glucose. However, the efficient, rapid and complete enzymatic hydrolysis of lignocellulosic materials using low protein loadings has proven to be one of the major technical and economical bottlenecks in the overall bioconversion process of lignocellulose to biofuels (Arantes and Saddler 2010). Recent studies have shown that the use of scCO$_2$ in the enzymatic hydrolysis processing of various cellulose-containing substrates increases substantially the yields of reducing sugars and glucose (Zheng and Tsao 1996, Park *et al.* 2001). Several methods to obtain glucose and fructose by contacting cellulose with scCO$_2$ and supercritical water have been disclosed in a patent by Kilambi (2010). Indeed, it has been shown that pressure has an effect on the enzymatic hydrolysis of cotton fibre by using enzymes from *Trichoderma viride* in scCO$_2$, increasing the reaction rate by 1.4 times when pressure was increased from 1 to 120 atm (Muratov 2007). Mixtures of dioxane–scCO$_2$ have been used by Reis Machado *et al.* (1994, 1996, 1997) in the reactive extraction and characterisation of lignins from *Eucalyptus globulus* wood.

Other reactions of cellulose in scCO$_2$ reported in the literature include acetylation, oxidation and linkage to other organic/inorganic materials.

Acetylation of wood has proved to be a chemical modification suitable for improving dimensional stability, decreasing hygroscopicity and, in general, improving the stability of wood against the effects of water and humidity (Rowell *et al.* 1987, Minato *et al.* 2003). Acetylation of wood has been performed in scCO$_2$ with acetic anhydride at 120–130°C and 10–12 MPa (Matsunaga *et al.* 2010). Anti-swelling efficiency has been calculated from a comparison of swelling coefficients of treated and untreated wood. After 3–4 h of acetylation, wood with 75–80% of anti-swelling efficiency is obtained. Treatment of starch, maltodextrines, cellulose acetate and paper with mixtures of scCO$_2$ and oxygen (19:1 v/v) have led to corresponding oxidised materials (Yalpani 1993). Camy *et al.* (2009) used scCO$_2$ at 40°C and pressures of up to 200 bar as a solvent to dissolve nitrogen oxide (NO$_2$), an efficient oxidant to oxidise primary hydroxyl groups of cellulose, producing oxidised cellulose. Oxidised cellulose is a bioresorbable and haemostatic material that can be used as a biomedical implant. ScCO$_2$ was advantageously used as a replacement of perfluoro-solvents traditionally used in cellulose oxidation. ScCO$_2$ allowed soft and homogeneous oxidation of cellulose; however, a slight inhibitory effect of NO$_2$ reactivity has been evidenced.

Surfaces of cellulose fibres obtained from sugar cane bagasse by an organosolv/scCO$_2$pulping process have been modified by esterification and used in the fabrication of a low-density polyethylene/cellulose composite (Pasquini *et al.* 2006, 2008).

In some cases scCO$_2$ may serve as a reactant. For instance, cellulosic materials such as carboxymethyl cellulose and its sodium salt have been used as crystal growth modifiers in CaCO$_3$ synthesis employing calcium salts and scCO$_2$ as reactants. Control of the morphology of the calcite particles has been achieved by adjusting the concentration and chain length of the polymer. These studies represent a step forward to understand the mechanism of biomimetic mineralisation (Li and Wu 2009, Li *et al.* 2009b).

Multifunctional inorganic–organic composites CaCO$_3$–biopolymer have been developed using scCO$_2$ and calcium acetate as reactants to facilitate the deposition of CaCO$_3$ onto cellulose and chitosan matrices (Wakayama *et al.* 2005a, 2005b). In this study, polyacrylic acid has been used as a crystal growth additive to fine-tune the structure and composition of mineralised biopolymer films to produce carbonate-containing materials with tailored optical, mechanical and chemical properties. Composites silicone–wood and silicone–bamboo have been prepared by the incorporation of polymer precursors into the cellulosic matrix using scCO$_2$ as the transport medium and subsequent polymerisation. These composites have shown improved fire resistance and retention of their mechanical properties after exposure to thermo-oxidative conditions (Eastman *et al.* 2008, 2009).

The efficiency of biomass conversion depends on hydrolysing agents gaining access to plant monosaccharides, such as glucose and polysaccharides. Once hydrolysed, these compounds are available to microorganisms

allowing fermentation to ethanol. In this context, the depolymerisation process has gained increased attention as a method to increase saccharification yield; however, efficiency and cost-effectiveness remain key challenges in its use. One important tool for reducing the cost of this depolymerisation is pre-treatment of lignocellulosic to make the biomass matrix more accessible to microorganisms (Ragauskas *et al.* 2006). Recently, it has been shown that scCO$_2$ alone can depolymerise cellulose. After 4 h at 120°C in scCO$_2$, the DP of cellulose fibres starts to decrease (Schmidt *et al.* 2002). Indeed, the scCO$_2$ phase offers high diffusivities and has proven to have a swelling effect on the plant material. Recently, Stamenic *et al.* (2010) have shown that the extent to which swelling of plant material occurs depends on the structure of the material and on the operating conditions: pressure, temperature and time. They have tested several plants from the Lamiaceae family (mint, wild thyme, hyssop, sage and rosemary), valerian root, ginger rhizome and hop cones and found that while the Lamiaceae family plants swelled during exposure to scCO$_2$ (at 40°C and 10 MPa; increase in leaf thickness up to 30% after 1 h of exposure), valerian root and ginger rhizome swelled during the depressurisation step (up to 45% increase in thickness). This behaviour was explained by the fact that the Lamiaceae family exhibits peltate glands (seats of the essential oil) that are located at the very surface of the leafs that crack when exposed to supercritical fluids. On the contrary, valerian root and ginger rhizome are characterised by small secretory cells located within the plant tissue.

Mixtures of scCO$_2$–solvent have been tested in cellulose depolymerisation. Among some of the systems studied, such as CO$_2$–H$_2$O, CO$_2$–acetone, CO$_2$–methanol and ternary mixtures of these solvents, CO$_2$–H$_2$O has been found to be the best mixture to depolymerise the cellulose at 127°C and 34 MPa. However, impregnation of cellulose with ethylene glycol, improved the action of CO$_2$–H$_2$O, decreasing even more the polymerisation degree of cellulose (Boumghar 1996). In another study, biphasic H$_2$O–scCO$_2$ depolymerisation produced glucose yields of 73% for wood using 160–170°C and 60 min of residence time (Luterbacher *et al.* 2010). Cotton fibres have been hydrolysed by cellulase enzymes from *T. viride*, *T. reesei* and *Aspergillius niger* at 160 atm for 48 h; the glucose yield showed a maximum value at 50°C, which was 1.2 times higher than the yield obtained at atmospheric pressure, the highest activity was obtained with *T. viride* with a conversion yield of 92% (Muratov and Kim 2002, Muratov *et al.* 2005).

12. Cellulose treatment by scCO$_2$ explosion

The difficulty in cellulose hydrolysis arises due to two main reasons: (1) its strong crystalline structure formed by the H-bond network and (2) tight packing of the crystalline structure, which strongly reduces accessibility to hydrolytic enzymes. We already mentioned that efficient, rapid and complete enzymatic hydrolysis of cellulosic materials is one of the major technical and economic problems in the conversion of lignocellulose to bio-fuels. To increase the efficiency of the hydrolysis of cellulose, many physical and chemical techniques have been developed. These treatments are intended either to disrupt the crystalline structure of cellulose or to increase the exposure of the substrate to the hydrolytic enzymes increasing the yield. Among these treatments, 'steam explosion' and 'ammonia explosion' have been proposed as pre-treatments prior to cellulose hydrolysis (Holtzapple *et al.* 1991, Dottori and Benech 2010, Lee *et al.* 2010, Zhenyu Du 2010). During steam explosion, lignocellulosic feed is exposed to high-pressure steam to let water molecules penetrate the substrate structure. The pressure is then suddenly released to let the water molecules escape in an explosive way (Zheng *et al.* 1998). During this process, lignocellulosic structures are disrupted to increase the accessibility of cellulose to the enzymes. Steam explosion has been observed to enhance the rate of cellulose hydrolysis and increase glucose yield from about 40% to 80%. Nevertheless, because of the high temperature needed, this technique causes extensive damage to xylose, incomplete disruption of the lignin–carbohydrate matrix and generation of compounds, which may be inhibitory to microorganisms used in the downstream processes (Mackie *et al.* 1985, Sun and Cheng 2002). In the ammonia explosion technique, biomass is treated with high-pressure liquid ammonia at a temperature ranging from 90 to 100°C for a 5 min residence time and then the pressure is explosively released. However, ammonia explosion is a more expensive process than steam explosion (Lee *et al.* 2010).

The scCO$_2$ explosion technique has been recently developed in an attempt to improve cellulose treatment given the low temperature of scCO$_2$ compared with steam explosion and low price compared to ammonia explosion. In this technique, the explosive release of carbon dioxide pressure disrupts the cellulosic structure increasing the accessible surface area of the substrate to enzymatic hydrolysis. This process takes advantage of the properties of scCO$_2$: 'gas-like' mass transfer and 'liquid-like' solvating power. It has been hypothesised that CO$_2$ would form carbonic acid and increase the rate of hydrolysis. Dale and Moreira (1982) used this method to pre-treat alfalfa (4 kg CO$_2$/kg fibre at 5.62 MPa) and obtained 75% of the theoretical glucose released during 24 h of enzymatic hydrolysis. The yields were relatively lower than steam or ammonia explosion pre-treatment, but high compared to enzymatic hydrolysis without pre-treatment. Zheng *et al.* (1995, 1998) compared to scCO$_2$ explosion with steam and ammonia explosion for

pre-treatment of recycled paper mix, sugarcane bagasse and repulping waste of recycled paper, and found that $scCO_2$ explosion was more cost-effective than ammonia explosion and did not induce the formation of inhibitory compounds as may occur in steam explosion. This study also showed that $scCO_2$ explosion pre-treatment enhanced the rate of cellulosic material hydrolysis and increased glucose yields by 50%. Puri and Mamers (1983) tested high-pressure $scCO_2$ explosion in the pre-treatment of lignocellulosic materials from wheat straw, bagasse and *Eucalyptus regnans*, successfully removing and solubilising the hemicellulose fraction, giving an autohydrolysed liquor rich in xylose and a fibrous residue readily hydrolysable by cellulases, and saccharification could be completed within 48 h. The treatment times required to obtain substrates of maximum digestibility were 5 min for wheat straw and bagasse and 15 min for *E. regnans*. Hohlberg *et al.* (1989) have shown an increase in the *in vitro* digestibility of pine sawdust after steam explosion in the presence of CO_2 attributed to the acid character of this gas, obtaining 32.5 g of reducing sugar/100 g of the substrate after hydrolysis of pre-treated samples.

13. Other applications

Other applications of $scCO_2$ together with cellulose concern treatment of paper and organic–inorganic composites fabrication. Paper treatment has drawn attention in the last 20 years as it has been observed that books and paper documents suffer degradation with time due to their acidic content. This is particularly important when historical documents need to be preserved and paper aging and destruction in prolonged storage need to be decelerated. Current treatments employ aqueous and organic solutions which present serious drawbacks such as consumption of toxic and volatile solvents. Use of $scCO_2$ has been proposed to treat paper documents in a mixture with 1% to 20% of ethanol in a patent by Perrut (SEPAREX, Champigneulles, France) together with the equipment adapted to this application (Perrut *et al.* 1997). On the other hand, $CaCO_3$ and catechol, both in $scCO_2$ have shown improvement in the mechanical properties of aged papers as catechol has great affinity with cellulose (Selli *et al.* 2000). Dobrodskaya *et al.* (2004) have developed a treatment for paper with basic agents in $scCO_2$ (magnesium methoxide or magnesium methoxycarbonate); the use of $scCO_2$ has shown a decrease in the consumption of toxic and volatile solvents by almost two orders of magnitude and decrease in the cost of paper conservation. These applications would be useful in numerous libraries all over the world. Besides the advantage of decreasing the consumption of solvents, an important advantage of $scCO_2$ use for these applications is that this solvent does not cause any deterioration of inks, photos, adhesives or leather bindings of books, which is not the case when aqueous or organic solutions are used.

Cellulose diacetate–polypyrrole composites have been produced in $scCO_2$ taking advantage of the swelling properties of $scCO_2$. *In situ* polymerisation was performed and it has been observed that composites with higher conductivities were obtained using higher pressures as a result of the increase of solubility of pyrrole (Li *et al.* 2006).

14. Conclusions and Outlook

Research in new technologies continues to progress towards developing sustainable processes that use renewable feedstock. $ScCO_2$ as a process and cellulosic materials as raw materials have received increasing interest all over the world in the last 20 years. In this context, it has been necessary to establish research facilities, pilot plants and employ scientists from many fields like engineering, chemistry, physicists and wood technologists. This development has made possible a deeper understanding of the fundamental science and application possibilities under the new insight of more ecological processes.

Work on $scCO_2$ and cellulosic materials, in the period of time considered (1990 to present time), has evolved in three major fields: extraction of high-value compounds, obtaining bio-fuels (ethanol) and modification of the properties of cellulose. Very high interest was found in bio-fuels (ethanol) production due to major concern about oil price, worldwide consumption of liquid petroleum and global climate stability. More prospective but very promising is the potential replacement of polymeric materials issued from fossil resources by cellulose-based materials. In many cases, some unsuitable properties of cellulose, for instance, its sensitivity to water, must be alleviated by an adapted process, where $scCO_2$ based-processes would be the best tools to respect the environmental-friendly character of the cellulose as a multi-functionalised material. In the future, a steady focus on environmental research in $scCO_2$ is expected, with more and more developments in CO_2-philic materials and catalysts, design of more adapted equipment, exploration and design of co-solvents and additives and last, but not least, the development of prediction and modelling tools. Other enhancements will come from genetically modified cellulases and microorganisms to improve the cellulose-to-ethanol conversion yield. The aim of this review is to show the current state of development in the field of $scCO_2$ as a green process and cellulose as a raw material and its applications.

All the improvements expected in environmentally friendly processes will be certainly influenced by economic factors and applied research and ecological policies.

References

Acda, M.N., Morrell, J.J., and Levien, K.L., 1996. Decay resistance of composites following supercritical fluid impregnation with tebuconazole. *Material und Organismen*, 30, 293–300.

Acda, M., Morrell, J., and Levien, K., 1997a. Effect of process variables on supercritical fluid impregnation of composites with tebuconazole. *Wood and Fiber Science*, 29 (3), 282–290. Available from: http://swst.metapress.com/content/X3691343719LQ47R.

Acda, M., Morrell, J., and Levien, K., 1997b. Effects of supercritical fluid treatments on physical properties of wood-based composites. *Wood and Fiber Science*, 29 (2), 121–130. Available from: http://swst.metapress.com/content/B3082H0T5VL84716.

Acda, M.N., Morrell, J.J., and Levien, K.L., 2001. Supercritical fluid impregnation of selected wood species with tebuconazole. *Wood Science and Technology*, 35 (1), 127–136. Available from: http://dx.doi.org/10.1007/s002260100086.

Al-Jabari, M., 2004. Dynamics of chelation-supercritical fluid extraction from wood fibers. *Journal of Separation Science*, 27 (9), 686–690. Available from: http://dx.doi.org/10.1002/jssc.200401751.

Anastas, P.T., and Warner, J.C., 1998. *Green chemistry, theory and practice*. New York: Oxford University Press.

Arantes, V., and Saddler, J.N., 2010. Acces to cellulose limits the efficiency of enzymatic hydrolysis: the role of amorphogenesis. *Biotechnology for Biofuels*, 3, 4.

Argyropoulos, D.S., and Xie, H., 2008. Polymer derivatives and composites from the dissolution of lignocellulosics in ionic liquids. Patent WO/2008/098037.

Avedesian, M.M., 1985. Apparatus and method involving supercritical fluid extraction. Patent 4493797. Available from: http://www.freepatentsonline.com/4493797.html.

Bach, E., Cleve, E., and Schollmeyer, E., 2002. Past, present and future of supercritical fluid dyeing technology – an overview. *Review of Progress in Coloration and Related Topics*, 32 (1), 88–102. Available from: http://dx.doi.org/Â10.1111/j.1478-4408.2002.tb00253.x.

Beckman, E.J., 2004. Supercritical and near-critical CO_2 in green chemical synthesis and processing. *The Journal of Supercritical Fluids*, 28 (2–3), 121–191. Available from: http://www.sciencedirect.com/science/article/B6VMF-48FKBX3-2/2/f941ced1b40d4313047ece8c70257889.

Beltrame, P.L., *et al.*, 1998. Dyeing of cotton in supercritical carbon dioxide. *Dyes and Pigments*, 39 (4), 335–340. Available from: http://www.sciencedirect.com/science/article/B6TFY-3VWP0S2-D/2/b867cd42652b5c573c86aee751a23232.

Boumghar, M.Y., 1996. *Dépolymérisation de la cellulose dans des mélanges fluides binaires et ternaires riches en CO_2 à hautes pressions*. Université de Sherbrooke.

Camy, S., *et al.*, 2009. Oxidation of cellulose in pressurized carbon dioxide. *The Journal of Supercritical Fluids*, 51 (2), 188–196. Available from: http://www.sciencedirect.com/science/article/B6VMF-4X66S5B-2/2/5226054ae5e9be50d9146033501d4d62.

Chow, T.S., 1980. Molecular interpretation of the glass transition temperature of polymer-diluent systems. *Macromolecules*, 13 (2), 362–364. Available from: http://dx.doi.org/10.1021/ma60074a029.

Dale, B.E., and Moreira, M.J., 1982. A freeze-explosion technique for increasing cellulose hydrolysis. *Biotechnology and Bioengineering Symposium*, 12, 31–43.

Davis, R.E., Biby, J.E., and Brantley, L.R., 1951. Lecture demonstrations with the newer types of plastics. *Journal of Chemical Education*, 28 (12), 654. Available from: http://dx.doi.org/10.1021/ed028p654.

Demessie, E., *et al.*, 1995. Supercritical carbon dioxide treatment: effect on permeability of douglas-fir heartwood. *Wood and Fiber Science*, 27 (3), 296–300. Available from: http://swst.metapress.com/content/BG25QK0780343206.

Dobrodskaya, T.V., *et al.*, 2004. Treatment of paper with basic agents in alcohols and supercritical carbon dioxide to neutralize acid and prolong storage time. *Russian Journal of Applied Chemistry*, 77 (12), 2017–2021. Available from: http://dx.doi.org/10.1007/s11167-005-0211-5.

Dottori, F.A., Benson, R.A.C., and Benech, R.O., 2010. Pretreatment of lignocellulosic biomass through removal of inhibitory compounds. Patent WO2010CA00483 20100407 (20100263814).

Duarte, A.R.C., *et al.*, 2006a. Preparation of controlled release microspheres using supercritical fluid technology for delivery of anti-inflammatory drugs. *International Journal of Pharmaceutics*, 308 (1–2), 168–174. Available from: http://www.sciencedirect.com/science/article/B6T7W-4HVDJFN-1/2/f5b25e8411ab3307322c1f6c5a738517.

Duarte, A.R.C., *et al.*, 2006b. Preparation of ethyl cellulose-/methyl cellulose blends by supercritical antisolvent precipitation. *International Journal of Pharmaceutics*, 311 (1–2), 50–54. Available from: http://www.sciencedirect.com/science/article/B6T7W-4J2TSK0-3/2/21d1cb64204cd40343c16d3d60bbae6c.

Eastman, S.A., Lesser, A.J., and Mccarthy, T.J., 2008. Bamboo is a suitable template for polymerizations. *Journal of Applied Polymer Science*, 109 (6), 3961–3967. Available from: http://dx.doi.org/10.1002/app.28476.

Eastman, S., Lesser, A., and Mccarthy, T., 2009. Supercritical CO_2-assisted, silicone-modified wood for enhanced fire resistance. *Journal of Materials Science*, 44 (5), 1275–1282. Available from: http://dx.doi.org/10.1007/s10853-008-3224-7.

Eichhorn, S.J., *et al.*, 2001. Review: current international research into cellulosic fibres and composites. *Journal of Materials Science*, 36 (9), 2107–2131. Available from: http://dx.doi.org/10.1023/A:1017512029696.

El-Fatah, S.A., *et al.*, 2004. Supercritical fluid extraction of hazardous metals from CCA wood. *The Journal of Supercritical Fluids*, 28 (1), 21–27. Available from: http://www.sciencedirect.com/science/article/B6VMF-483SXVW-2/2/94c4813b109d220874b4d64a3656f63c.

Feng, L., and Chen, Z.L., 2008. Research progress on dissolution and functional modification of cellulose in ionic liquids. *Journal of Molecular Liquids*, 142 (1–3), 1–5. Available from: http://www.sciencedirect.com/science/article/B6TGR-4SR710Y-5/2/13677785fcf857f9655a3213d14454a4.

Fernandez Cid, M.V., *et al.*, 2005. Excellent dye fixation on cotton dyed in supercritical carbon dioxide using fluorotriazine reactive dyes. *Green Chemistry*, 7 (8), 609–616. Available from: http://dx.doi.org/10.1039/B503801D.

Fernandez Cid, M.V., *et al.*, 2010. Method of dyeing a substrate with a reactive dyestuff in supercritical or near supercritical carbon dioxide. Patent application number 7731763. Available from: http://www.freepatentsonline.com/7731763.html.

Fischer, F., *et al.*, 2006. Cellulose-based aerogels. *Polymer*, 47 (22), 7636–7645. Available from: http://www.sciencedirect.com/science/article/B6TXW-4KYXHXV-4/2/a7ed7ee249e1ed545415aa3e6adce8aa.

Fremont, H.A., 1981. Extraction of coniferous woods with fluid carbon dioxide and other supercritical fluids. Patent

application number US 4308200. Available from: http://www.freepatentsonline.com/4308200.html.

Gavillon, R., and Budtova, T., 2008. Aerocellulose: new highly porous cellulose prepared from cellulose-NaOH aqueous solutions. *Biomacromolecules*, 9 (1), 269–277. Available from: http://dx.doi.org/10.1021/bm700972k.

Gearhart, J.A., and Garwin, L., 1976. Rose process improves resid feed. *Hydrocarbon Process*, 55 (5), 125.

Glennon, J.D., *et al.*, 1999. Carrying gold in supercritical CO_2. *Gold Bulletin*, 32 (2), 52–58.

Gong, K., Rehman, I.U., and Darr, J.A., 2008. Characterization and drug release investigation of amorphous drug-hydroxypropyl methylcellulose composites made via supercritical carbon dioxide assisted impregnation. *Journal of Pharmaceutical and Biomedical Analysis*, 48 (4), 1112–1119. Available from: http://www.sciencedirect.com/science/article/B6TGX-4TCYCFX-1/2/6c2a8a488c6e603cbb84-be5cf67f17c1.

Gowen, C., and Fong, S., 2010. Exploring biodiversity for cellulosic biofuel production. *Chemistry and Biodiversity*, 7 (5), 1086–1097. Available from: http://dx.doi.org/10.1002/cbdv.200900314.

Guilminot, E., *et al.*, 2008. New nanostructured carbons based on porous cellulose: elaboration, pyrolysis and use as platinum nanoparticles substrate for oxygen reduction electrocatalysis. *Journal of Power Sources*, 185 (2), 717–726. Available from: http://www.sciencedirect.com/science/article/B6TH1-4T8HHF2-2/2/0ed9ea9abc5826d56b1fceff1e430ac3.

Habibi, Y., Lucia, L.A., and Rojas, O.J., 2010. Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chemical Reviews*, 110 (6), 3479–3500. Available from: http://dx.doi.org/10.1021/cr900339w.

Haimer, E., *et al.*, 2008. Precipitation of hemicelluloses from DMSO/water mixtures using carbon dioxide as an antisolvent. *Journal of Nanomaterials*, 2008, Article 10 826974.

Haimer, E., *et al.*, 2010. Loading of bacterial cellulose aerogels with bioactive compounds by antisolvent precipitation with supercritical carbon dioxide. *Macromolecular Symposia*, 294 (2), 64–74. Available from: http://dx.doi.org/10.1002/masy.201000008.

Heath, L., and Thielemans, W., 2010. Cellulose nanowhisker aerogels. *Green Chemistry*, 12 (8), 1448–1453. Available from: http://dx.doi.org/10.1039/C0GC00035C.

Henriksen, O., 2003. Method of performing an impregnating or extracting treatment on a resin-containing wood substrate. Patent application number 6623600. Available from: http://www.freepatentsonline.com/6623600.html.

Henriksson, M., and Berglund, L.A., 2007. Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. *Journal of Applied Polymer Science*, 106 (4), 2817–2824. Available from: http://dx.doi.org/10.1002/app.26946.

Hohlberg, A.I., *et al.*, 1989. Catalyzed flash pretreatments improve saccharification of pine (*Pinus radiata*) sawdust. *Biomass*, 18 (2), 81–93. Available from: http://www.sciencedirect.com/science/article/B75CD-48XK62Y-BM/2/3f855973cc0e6cafd8d71e4560a4ec7b.

Holtzapple, M., *et al.*, 1991. The ammonia freeze explosion (afex) process. *Applied Biochemistry and Biotechnology*, 28–29 (1), 59–74. Available from: http://dx.doi.org/10.1007/BF02922589.

Hossain, S.U.M., and Blaney, C.A., 1991. Method for removing stickies from secondary fibers using supercritical CO_2 solvent extraction. Patent application number 5009746. Available from: http://www.freepatentsonline.com/5009746.html.

Hossain, S.U.M., and Blaney, C.A., 1993. Secondary fiber cellulose product with reduced levels of polychlorinated dibenzodioxins and polychlorinated dibenzofurans. Patent application number 5213660. Available from: http://www.freepatentsonline.com/5213660.html.

Iwamoto, S., Nakagaito, A.N., and Yano, H., 2007. Nanofibrillation of pulp fibers for the processing of transparent nanocomposites. *Applied Physics A: Materials Science and Processing*, 89 (2), 461–466. Available from: http://dx.doi.org/10.1007/s00339-007-4175-6.

Jacobs, L.J.M., *et al.*, 2008. Porous cellulose acetate butyrate foams with a tunable bimodality in foam morphology produced with supercritical carbon dioxide. *Macromolecular Materials and Engineering*, 293 (4), 298–302. Available from: http://dx.doi.org/10.1002/mame.200700353.

Jung, J., and Perrut, M., 2001. Particle design using supercritical fluids: literature and patent survey. *The Journal of Supercritical Fluids*, 20 (3), 179–219. Available from: http://www.sciencedirect.com/science/article/B6VMF-438TWFH-1/2/3b4e053a45f1ca80fb18f089e2b2ef4f.

Kerrola, K., 1995. Literature review: isolation of essential oils and flavor compounds by dense carbon dioxide. *Food Reviews International*, 11 (4), 547–573. Available from: http://www.informaworld.com/10.1080/87559129509541061.

Kilambi, S., 2010. Solvo-thermal hydrolysis of cellulose. Patent application number 20100048884. Available from: http://www.freepatentsonline.com/y2010/0048884.html.

Kim, K.H., and Hong, J., 2001. Supercritical CO_2 pretreatment of lignocellulose enhances enzymatic cellulose hydrolysis. *Bioresource Technology*, 77 (2), 139–144. Available from: http://www.sciencedirect.com/science/article/B6V24-4227GWM-6/2/883b60440f13f65a39ac2807d5098224.

Kiran, E., and Balkan, H., 1994. High-pressure extraction and delignification of red spruce with binary and ternary mixtures of acetic acid, water, and supercritical carbon dioxide. *The Journal of Supercritical Fluids*, 7 (2), 75–86. Available from: http://www.sciencedirect.com/science/article/B6VMF-4DVN8DS-3/2/005e1cda03b633d8824ed4e38-dad01e7.

Kistler, S.S., 1932. Coherent expanded-aerogels. *The Journal of Physical Chemistry*, 36 (1), 52–64. Available from: http://dx.doi.org/10.1021/j150331a003.

Klemm, D., *et al.*, 2005. Cellulose: fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, 44, 3358–3393.

Klemm, D., *et al.*, 2006. Nanocelluloses as innovative polymers in research and application. *In*: D. Klemm, ed. *Polysaccharides ii*. Berlin/Heidelberg: Springer, 49–96.

Kraft, G., *et al.*, 2004. Treatment of cellulosic fibers with supercritical carbon dioxide. *Lenzinger Berichte*, 83, 117–121.

Laintz, K.E., Yu, J.J., and Wai, C.M., 1992. Separation of metal ions with sodium bis(trifluoroethyl)dithiocarbamate chelation and supercritical fluid chromatography. *Analytical Chemistry*, 64 (3), 311–315. Available from: http://dx.doi.org/10.1021/ac00027a012.

Laksman, J.P., 2007. Process for making pharmaceutical compositions with a transient plasticizer. Patent WO2007106182 (A2).

Lang, Q., and Wai, C.M., 2001. Supercritical fluid extraction in herbal and natural product studies – a practical review. *Talanta*, 53 (4), 771–782. Available from: http://www.

sciencedirect.com/science/article/B6THP-426XW3F-17/2/9106f8eff7df8896a76c8505ce6b74f7.

Lee, J.M., Jameel, H., and Venditti, R.A., 2010. A comparison of the autohydrolysis and ammonia fiber explosion (afex) pretreatments on the subsequent enzymatic hydrolysis of coastal bermuda grass. *Bioresource Technology*, 101 (14), 5449–5458. Available from: http://www.sciencedirect.com/science/article/B6V24-4YKF6V8-6/2/4ddbee0ff505e48b023244f1a8c83118.

Li, G., *et al.*, 2006. Supercritical carbon dioxide assisted preparation of conductive polypyrrole/cellulose diacetate composites. *Journal of Applied Polymer Science*, 100 (6), 4575–4580. Available from: http://dx.doi.org/10.1002/app.22569.

Li, B.G., *et al.*, 2008a. Supercritical CO_2 spray drying of ethyl cellulose (ec) for preparing microparticles. *Drying Technology: An International Journal*, 26 (4), 464–469. Available from: http://www.informaworld.com/10.1080/07373930801929441.

Li, J., *et al.*, 2008b. Controlled synthesis of monolithic hierarchical porous materials using wood as a template with assistance of supercritical carbon dioxide. *Industrialand Engineering Chemistry Research*, 47 (20), 7680–7685. Available from: http://dx.doi.org/10.1021/ie071269.

Li, Q., *et al.*, 2009a. Improving enzymatic hydrolysis of wheat straw using ionic liquid 1-ethyl-3-methyl imidazolium diethyl phosphate pretreatment. *Bioresource Technology*, 100 (14), 3570–3575. Available from: http://www.sciencedirect.com/science/article/B6V24-4VY168M-3/2/5e283f61455696ca19370c55f33e1dfa.

Li, W., Yu, Q., and Wu, P., 2009b. Submicronic calcite particles with controlled morphology tailored by polymer skeletons via carbonation route with compressed or supercritical CO_2. *Green Chemistry*, 11 (10), 1541–1549. Available from: http://dx.doi.org/10.1039/B914787J.

Li, L., and Kiran, E., 1988. Interaction of supercritical fluids with lignocellulosic materials. *Industrialand Engineering Chemistry Research*, 27 (7), 1301–1312. Available from: http://dx.doi.org/10.1021/ie00079a035.

Li, W., and Wu, P., 2009. Biomimetic synthesis of monodisperse rosette-like calcite mesocrystals regulated by carboxymethyl cellulose and the proposed mechanism: an unconventional rhombohedra-stacking route. *Cryst Eng Comm*, 11 (11), 2466–2474. Available from: http://dx.doi.org/10.1039/B901580A.

Liebner, F., *et al.*, 2007. Ultralight-weight cellulose aerogels from nbnmo-stabilized lyocell dopes. *Research Letters in Materials Science*, 2007, 73724.

Liebner, F., *et al.*, 2008. Cellulose aerogels: highly porous, ultra-lightweight materials. *Holzforschung*, 62 (2), 129–135. Available from: http://dx.doi.org/10.1515/HF.2008.051.

Liebner, F., *et al.*, 2010. Aerogels from unaltered bacterial cellulose: application of scCO$_2$ drying for the preparation of shaped, ultra-lightweight cellulosic aerogels. *Macromolecular Bioscience*, 10 (4), 349–352. Available from: http://dx.doi.org/10.1002/mabi.200900371.

Lin, Y., *et al.*, 1993. Supercritical fluid extraction of lanthanides and actinides from solid materials with a fluorinated beta-diketone. *Analytical Chemistry*, 65 (18), 2549–2551. Available from: http://dx.doi.org/10.1021/ac00066a027.

Lin, Y., and Wai, C.M., 1994. Supercritical fluid extraction of lanthanides with fluorinated beta-diketones and tributyl phosphate. *Analytical Chemistry*, 66 (13), 1971–1975. Available from: http://dx.doi.org/10.1021/ac00085a008.

Liu, Z.-T., *et al.*, 2006. Supercritical CO_2 dyeing of ramie fiber with disperse dye. *Industrialand Engineering Chemistry Research*, 45 (26), 8932–8938. Available from: http://dx.doi.org/10.1021/ie061093h.

Lu, X., Hu, Z., and Gao, J., 2000. Synthesis and light scattering study of hydroxypropyl cellulose microgels. *Macromolecules*, 33 (23), 8698–8702. Available from: http://dx.doi.org/10.1021/ma000776k.

Luterbacher, J.S., Tester, J.W., and Walker, L.P., 2010. High-solids biphasic CO_2–H_2O pretreatment of lignocellulosic biomass. *Biotechnology and Bioengineering*, 107 (3), 451–460. Available from: http://dx.doi.org/10.1002/bit.22823.

Mackie, K.L., *et al.*, 1985. Effect of sulphur dioxide and sulphuric acid on steam explosion of aspenwood. *Journal of Wood Chemistry and Technology*, 5 (3), 405–425. Available from: http://www.informaworld.com/10.1080/02773818508085202 [Accessed October 05, 2010].

Malm, C.J., and Tanghe, L.J., 1955. Chemical reactions in the making of cellulose acetate. *Industrialand Engineering Chemistry*, 47 (5), 995–999. Available from: http://dx.doi.org/10.1021/ie50545a034.

Matsunaga, M., *et al.*, 2010. A novel method of acetylation of wood using supercritical carbon dioxide. *Journal of Wood Science*, 56 (4), 293–298. Available from: http://dx.doi.org/10.1007/s10086-009-1098-1.

Matsuyama, H., *et al.*, 2002. Effect of organic solvents on membrane formation by phase separation with supercritical CO_2. *Journal of Membrane Science*, 204 (1–2), 81–87. Available from: http://www.sciencedirect.com/science/article/B6TGK-451S990-2/2/78bf51fdf05897e16f2ea763f606f2e7.

Mcdonald, E.C., Howard, J., and Bennett, B., 1983. Chemicals from forest products by supercritical fluid extraction. *Fluid Phase Equilibria*, 10 (2–3), 337–344. Available from: http://www.sciencedirect.com/science/article/B6TG2-43RDB8T-7F/2/b7ea7647b7c9848b2d8bafb05ce3388f.

McMillan, J.D., 1993. Pretreatment of lignocellulosic biomass. *In*: M.E. Himmel, J.O. Baker and R.P. Overend, eds. *Enzymatic conversion of biomass for fuel production*. Washington DC: American Chemical Society, 292–323.

Minato, K., Takazawa, R., and Ogura, K., 2003. Dependence of reaction kinetics and physical and mechanical properties on the reaction systems of acetylation II: physical and mechanical properties. *Journal of Wood Science*, 49 (6), 519–524. Available from: http://dx.doi.org/10.1007/s10086-002-0499-1.

Morrell, J.J., *et al.*, 1993. Treatment of wood using supercritical fluid processes. *Proceedings of the Canadian Wood Preservation Association*, 14, 6–25.

Morrell, J.J., *et al.*, 1997. Impregnating wood with biocides using supercritical carbon dioxide: process parameters, performance and effects on wood properties. *Proceedings of the Canadian Wood Preservation Association*, 93, 367–384.

Moyler, D.A., 1993. *Extraction of flavours and fragrances with compressed CO_2, extraction of natural products using near-critical solvents*. Glasgow: Blackie.

Muin, M., *et al.*, 2003. Feasibility of supercritical carbon dioxide as a carrier solvent for preservative treatment of wood-based composites. *Journal of Wood Science*, 49 (1), 0065–0072. Available from: http://dx.doi.org/10.1007/s100860300011.

Muin, M., and Tsunoda, K., 2003a. Preservative treatment of wood-based composites with 3-iodo-2-propynyl butylcarbamate using supercritical carbon dioxide impregnation.

Journal of Wood Science, 49 (5), 430–436. Available from: http://dx.doi.org/10.1007/s10086-002-0490-x.

Muin, M., and Tsunoda, K., 2003b. Termiticidal performance of wood-based composites treated with silafluofen using supercritical carbon dioxide. *Holzforschung*, 57 (6), 585–592. Available from: http://dx.doi.org/10.1515/HF.2003.088 Accessed 17 November 2010.

Munshi, P., and Bhaduri, S., 2009. Supercritical CO_2: a twenty-first century solvent for the chemical industry. *Current Science*, 97 (1), 63–72.

Muratov, G., 2007. Bioconversion of cotton cellulose to glucose by supercritical CO_2. *Chemistry of Natural Compounds*, 43 (5), 641–642. Available from: http://dx.doi.org/10.1007/s10600-007-0217-8.

Muratov, G., and Kim, C., 2002. Enzymatic hydrolysis of cotton fibers in supercritical CO_2. *Biotechnology and Bioprocess Engineering*, 7 (2), 85–88.

Muratov, G., Seo, K.W., and Kim, C., 2005. Application of supercritical carbon dioxide to the bioconversion of cotton fibers. *Journal of Industrial and Engineering Chemistry*, 11 (1), 42–46. Available from: http://www.cheric.org/article/458824.

Nadagouda, M.N., and Varma, R.S., 2007. Synthesis of thermally stable carboxymethyl cellulose/metal biodegradable nanocomposites for potential biological applications. *Biomacromolecules*, 8 (9), 2762–2767. Available from: http://dx.doi.org/10.1021/bm700446p.

Niessen, H., and Woelk, K., 2007. Investigations in supercritical fluids. *In*: J. Bargon and L. Kuhn, eds. *In situ NMR methods in catalysis*. Berlin/Heidelberg: Springer, 69–110.

Nkouam, G.B., *et al.*, 2007. Oil extraction from sheanut kernel (vitellaria paradoxa gaertn) and canarium pulp (canarium schweinfurthii engl.) using supercritical CO_2 and hexane: a comparative study. *Research Journal of Applied Sciences*, 2 (5), 646–652.

O'Sullivan, A., 1997. Cellulose: the structure slowly unravels. *Cellulose*, 4 (3), 173–207. Available from: http://dx.doi.org/10.1023/A:1018431705579.

Park, C., Ryu, Y., and Kim, C., 2001. Kinetics and rate of enzymatic hydrolysis of cellulose in supercritical carbon dioxide. *Korean Journal of Chemical Engineering*, 18 (4), 475–478. Available from: http://dx.doi.org/10.1007/BF02698293.

Park, C.B., Suh, N.P., and Baldwin, D.F., 2000. Method for providing continuous processing of microcellular and supermicrocellular foamed materials. Patent application number 56051174. Available from: http://www.freepatentsonline.com/6051174.html.

Pasquini, D., *et al.*, 2005a. Extraction of lignin from sugar cane bagasse and pinus taeda wood chips using ethanol-water mixtures and carbon dioxide at high pressures. *The Journal of Supercritical Fluids*, 36 (1), 31–39. Available from: http://www.sciencedirect.com/science/article/B6VMF-4G7NF94-1/2/0c8788cca3022df5f9f53485bfd2bac2.

Pasquini, D., *et al.*, 2005b. Sugar cane bagasse pulping using supercritical CO_2 associated with co-solvent 1-butanol/water. *The Journal of Supercritical Fluids*, 34 (2), 125–131. Available from: http://www.sciencedirect.com/science/article/B6VMF-4F6F6J5-1/2/3ff42384f55ba89054c5dfc-f2e3ed4b2.

Pasquini, D., *et al.*, 2006. Surface esterification of cellulose fibers: characterization by drift and contact angle measurements. *Journal of Colloid and Interface Science*, 295 (1), 79–83. Available from: http://www.sciencedirect.com/

science/article/B6WHR-4GYH7SD-7/2/4503d44cd638478daa0d6f9385458642.

Pasquini, D., *et al.*, 2008. Surface esterification of cellulose fibres: processing and characterisation of low-density polyethylene/cellulose fibres composites. *Composites Science and Technology*, 68 (1), 193–201. Available from: http://www.sciencedirect.com/science/article/B6TWT-4NS0KXV-8/2/02d95607ff15c01305acf9426aab2693.

Payen, A., 1838. Mémoire sur la composition du tissu propre des plantes et du ligneux. *Comptes Rendus*, 7, 1052–1056.

Perrut, M., Francais, E., and Theobald, J., 1997. Procedure and equipment for processing paper documents using supercritical pressure fluid. Patent WO/1997/039190. Available from: http://www.sumobrain.com/patents/WO1997039190.html.

Persson, P., *et al.*, 2002. Supercritical fluid extraction of a lignocellulosic hydrolysate of spruce for detoxification and to facilitate analysis of inhibitors. *Biotechnology and Bioengineering*, 79 (6), 694–700. Available from: http://dx.doi.org/10.1002/bit.10324.

Pinkert, A., *et al.*, 2009. Ionic liquids and their interaction with cellulose. *Chemical Reviews*, 109 (12), 6712–6728. Available from: http://dx.doi.org/10.1021/cr9001947.

Pinkert, A., Marsh, K.N., and Pang, S., 2010. Reflections on the solubility of cellulose. *Industrialand Engineering Chemistry Research*, 49, 11121–11130. Available from: http://dx.doi.org/10.1021/ie1006596.

Porsch, B., Nilsson, S., and Sundelof, L.O., 1997. Association of ethyl(hydroxyethyl)cellulose solutions. *Macromolecules*, 30 (16), 4626–4632. Available from: http://dx.doi.org/10.1021/ma970171x.

Prasad, R., Gottesman, M., and Scarella, R.A., 1981. Decaffeination of aqueous extracts. Patent application number 4246291. Available from: http://www.freepatentsonline.com/4246291.html.

Puri, V.P., and Mamers, H., 1983. Explosive pretreatment of lignocellulosic residues with high-pressure carbon dioxide for the production of fermentation substrates. *Biotechnology and Bioengineering*, 25 (12), 3149–3161. Available from: http://dx.doi.org/10.1002/bit.260251226.

Ragauskas, A.J., *et al.*, 2006. The path forward for biofuels and biomaterials. *Science*, 311 (5760), 484–489. Available from: http://www.sciencemag.org/cgi/content/abstract/311/5760/484.

Reis Machado, A.S., *et al.*, 1994. High-pressure delignification of eucalyptus wood by 1,4-dioxane-CO_2 mixtures. *The Journal of Supercritical Fluids*, 7 (2), 87–92. Available from: http://www.sciencedirect.com/science/article/B6VMF-4DVN8DS-4/2/dae9fc323acbababc34863c3de55330d.

Reis Machado, A.S., *et al.*, 1996. Characterisation of residues and extracts of high-pressure extraction of eucalyptus wood by 1,4-dioxane-CO_2 mixtures. Part i. Characterisation by FT-IR, UV and HPLC. *Holzforschung*, 50 (6), 531–540. Available from: http://dx.doi.org/10.1515/hfsg.1996.50.6.531.

Reis Machado, A.S., *et al.*, 1997. Characterisation of residues and extracts of high-pressure extraction of eucalyptus wood with 1,4-dioxane-CO_2 mixtures. Part II. Determination of macromolecular parameters of lignins extracted with high-pressure 1,4-dioxane. *Holzforschung*, 51 (1), 57–61. Available from: http://dx.doi.org/10.1515/hfsg.1997.51.1.57.

Reverchon, E., 1992. Fractional separation of scf extracts from marjoram leaves: mass transfer and optimization. *The Journal of Supercritical Fluids*, 5 (4), 256–261. Available from: http://www.sciencedirect.com/science/article/B6VMF-4BT8X3Y-1J/2/645204d2d8ef4c264241635a1944ab74.

Reverchon, E., 1997. Supercritical fluid extraction and fractionation of essential oils and related products. *The Journal of Supercritical Fluids*, 10 (1), 1–37. Available from: http://www.sciencedirect.com/science/article/B6VMF-3WP2JC8-9/2/51745986e1d84f02301517162cfbf345.

Reverchon, E., Ambruosi, A., and Senatore, F., 1994. Isolation of peppermint oil using supercritical CO_2 extraction. *Flavour and Fragrance Journal*, 9 (1), 19–23. Available from: http://dx.doi.org/10.1002/ffj.2730090105.

Reverchon, E., and Cardea, S., 2004. Formation of cellulose acetate membranes using a supercritical fluid assisted process. *Journal of Membrane Science*, 240 (1,2), 187–195. Available from: http://www.sciencedirect.com/science/article/B6TGK-4CRY6WD-1/2/805f8e28ddec64771901d1a5fab8eaaa.

Reverchon, E., and Cardea, S., 2007. Production of controlled polymeric foams by supercritical CO_2. *The Journal of Supercritical Fluids*, 40 (1), 144–152. Available from: http://www.sciencedirect.com/science/article/B6VMF-4K7169T-1/2/2ce617d97f165f06495f14fff8c9287e.

Reverchon, E., and De Marco, I., 2006. Supercritical fluid extraction and fractionation of natural matter. *The Journal of Supercritical Fluids*, 38 (2), 146–166. Available from: http://www.sciencedirect.com/science/article/B6VMF-4JTR966-7/2/07c5440bb7754ad380b910a03b197ed0.

Reverchon, E., and Della Porta, G., 1996. Rose concrete fractionation by supercritical CO_2. *The Journal of Supercritical Fluids*, 9 (3), 199–204. Available from: http://www.sciencedirect.com/science/article/B6VMF-4BRRVDH-28/2/e400a9a961fafeaabd834b79c96c4644.

Reverchon, E., Della Porta, G., and Gorgoglione, D., 1995a. Supercritical CO_2 fractionation of jasmine concrete. *The Journal of Supercritical Fluids*, 8 (1), 60–65. Available from: http://www.sciencedirect.com/science/article/B6VMF-4BRRVFS-34/2/682044ec81cc4390081216db8a25c515.

Reverchon, E., Della Porta, G., and Senatore, F., 1995b. Supercritical CO_2 extraction and fractionation of lavender essential oil and waxes. *Journal of Agricultural and Food Chemistry*, 43 (6), 1654–1658. Available from: http://dx.doi.org/10.1021/jf00054a045.

Reverchon, E., Taddeo, R., and Della Porta, G., 1995c. Extraction of sage oil by supercritical CO_2: influence of some process parameters. *The Journal of Supercritical Fluids*, 8 (4), 302–309. Available from: http://www.sciencedirect.com/science/article/B6VMF-4BRRVBB-M/2/09d9007cd1a1e65e77a7e2bf37ef0a52.

Ritter, D., and Campbell, A., 1986. *The effect of supercritical carbon dioxide extraction on pine wood structure*. New York: Wiley.

Ritter, D., and Campbell, A., 1991. Supercritical carbon dioxide extraction of southern pine and ponderosa pine. *Wood and Fiber Science*, 23 (1), 98–113. Available from: http://swst.metapress.com/content/V2840322636N7213.

Rout, P.K., *et al.*, 2009. Supercritical CO_2 fractionation of bio-oil produced from mixed biomass of wheat and wood sawdust. *Energyand Fuels*, 23 (12), 6181–6188. Available from: http://dx.doi.org/10.1021/ef900663a.

Rowell, R.M., *et al.*, 1987. Biological resistance of southern pine and aspen flakeboards made from acetylated flakes. *Journal of Wood Chemistry and Technology*, 7 (3), 427–440. Available from: http://www.informaworld.com/10.1080/02773818708085277 [Accessed 17 November 2010].

Saha, B., 2003. Hemicellulose bioconversion. *Journal of Industrial Microbiology and Biotechnology*, 30 (5), 279–291. Available from: http://dx.doi.org/10.1007/s10295-003-0049-x.

Salmon, S., and Hudson, S.M., 1997. Crystal morphology, biosynthesis, and physical assembly of cellulose, chitin, and chitosan., 37 (2), 199–276. Available from: http://www.informaworld.com/10.1080/15321799708018366.

Schiraldi, D.A., 1994. Recycling cellulose esters from the waste from cigarette manufacture. Patent application number 5328934. Available from: http://www.freepatentsonline.com/5328934.html.

Schlenker, W., *et al.*, 1994. Process for dyeing cellulosic textile material with disperse dyes. Patent US5298032.

Schmidt, A., Bach, E., and Schollmeyer, E., 2002. Damage to natural and synthetic fibers treated in supercritical carbon dioxide at 300 bar and temperatures up to 160°C. *Textile Research Journal*, 72 (11), 1023–1032. Available from: http://trj.sagepub.com/content/72/11/1023.abstract.

Selli, E., *et al.*, 2000. Preservation treatments of aged papers by supercritical carbon dioxide. *Macromolecular Materials and Engineering*, 280–281 (1), 71–75. Available from: http://dx.doi.org/10.1002/1439-2054(20000801)280:1<71:AID-MAME71>3.0.CO;2-T.

Sescousse, R., and Budtova, T., 2009. Influence of processing parameters on regeneration kinetics and morphology of porous cellulose from cellulose–NaOH–water solutions. *Cellulose*, 16 (3), 417–426. Available from: http://dx.doi.org/10.1007/s10570-009-9287-z.

Sevenants, M.R., 1987. Removal of textured vegetable product off-flavor by supercritical fluid or liquid extraction. Patent application number 4675198. Available from: http://www.freepatentsonline.com/4675198.html.

Shen, Z., *et al.*, 2008. CO_2-assisted fiber impregnation. *Polymer*, 49 (6), 1579–1586. Available from: http://www.sciencedirect.com/science/article/B6TXW-4RKTND8-4/2/376d45768eb467cecc304bbef81d4716.

Siró, I., and Plackett, D., 2010. Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose*, 17 (3), 459–494. Available from: http://dx.doi.org/10.1007/s10570-010-9405-y.

Skouta, R., 2009. Selective chemical reactions in supercritical carbon dioxide, water, and ionic liquids. *Green Chemistry Letters and Reviews*, 2 (3), 121–156. Available from: http://www.informaworld.com/10.1080/17518250903230001 [Accessed November 19, 2010].

Stamenic, M., *et al.*, 2010. Swelling of plant material in supercritical carbon dioxide. *The Journal of Supercritical Fluids*, 52 (1), 125–133. Available from: http://www.sciencedirect.com/science/article/B6VMF-4XY4GM6-1/2/08349d598fe00c3c4376b113c85511da.

Sun, Y., and Cheng, J., 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*, 83 (1), 1–11. Available from: http://www.sciencedirect.com/science/article/B6V24-44NM064-2/2/9ad340630a75e06a4b3ce8c75509660d.

Sun, Y.-C., Chung, Y.-T., and Mierzwa, J., 2001. Study of matrix influence on supercritical fluid extraction of polar mercury species from solid samples. *Analyst*, 126 (10), 1694–1699. Available from: http://dx.doi.org/10.1039/B104202P.

Takeshita, Y., Sato, Y., and Nishi, S., 2000. Study of extraction of metals from CCA-treated wood with supercritical CO_2 containing acetylacetone: extraction of Cu by continuous addition of acetylacetone. *Industrialand Engineering Chemistry Research*, 39 (12), 4496–4499. Available from: http://dx.doi.org/10.1021/ie000180l.

Takeshita, Y., and Sato, Y., 2002. Measurement of copper compound solubility in supercritical carbon dioxide and correlation using a solution model. *The Journal of Supercritical Fluids*, 24 (2), 91–101. Available from: http://www.sciencedirect.com/science/article/B6VMF-455VSF1-1/2/48d10762b7d9685d5614de0548c586ab.

Tan, C., *et al.*, 2001. Organic aerogels with very high impact strength. *Advanced Materials*, 13 (9), 644–646. Available from: http://dx.doi.org/10.1002/1521-4095(200105)13:9<644:AID-ADMA644>3.0.CO;2-#.

Thies, M.C., Aniedobe, N.E., and Serad, G.A., 1996. Processing cellulose acetate formed articles using supercritical fluid. Patent application number 5512231. Available from: http://www.freepatentsonline.com/5512231.html.

Tour, Ch., C., 1822. Exposé de quelques résultats obtenu par l'action combinée de la chaleur et de la compression sur certains liquides, tels que l'eau, l'alcool, l'éther sulfurique et l'essence de pétrole rectifiée. *Annales de Chimie et de Physique*, 21, 127–132.

Tsunoda, K., 1998. Supercritical fluid application to wood preservation: Part 1: Principle of treatment and mechanical properties of treated wood. *In*: K. Tsunoda, ed. *Super-critical fluid application to high performance treatment of wood and composite materials*. Proc. 09770184; November 2–5 1998; the 4th Pacific Rim Bio-Based Composites Symposium, Bogor, Indonesia, 24–30.

van der Kraan, M., *et al.*, 2007. Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes. *The Journal of Supercritical Fluids*, 40 (3), 470–476. Available from: http://www.sciencedirect.com/science/article/B6VMF-4KVXHPG-2/2/c838a35d28aae7b1440e64f5e592ea66.

Verreck, G., *et al.*, 2006. The effect of pressurized carbon dioxide as a plasticizer and foaming agent on the hot melt extrusion process and extrudate properties of pharmaceutical polymers. *The Journal of Supercritical Fluids*, 38 (3), 383–391. Available from: http://www.sciencedirect.com/science/article/B6VMF-4HX47HR-1/2/c62565f54f885ddb1fd22553a3d04545.

Verreck, G., *et al.*, 2007. The effect of supercritical CO_2 as a reversible plasticizer and foaming agent on the hot stage extrusion of itraconazole with EC 20 cps. *The Journal of Supercritical Fluids*, 40 (1), 153–162. Available from: http://www.sciencedirect.com/science/article/B6VMF-4K7FJGM-3/2/eba2c48d2f228ae2859eeb1f424e6dd0.

Wai, C.M., and Wang, S., 1997. Supercritical fluid extraction: metals as complexes. *Journal of Chromatography A*, 785 (1–2), 369–383. Available from: http://www.sciencedirect.com/science/article/B6TG8-3SH4951-16/2/0021b05b4bff216b764befef0b23ff4c.

Wakayama, H., *et al.*, 2005a. $CaCO_3$/biopolymer composite films prepared using supercritical CO_2. *Industrialand Engineering Chemistry Research*, 45 (10), 3332–3334. Available from: http://dx.doi.org/10.1021/ie050659j.

Wakayama, H., Hall, S.R., and Mann, S., 2005b. Fabrication of $CaCO_3$-biopolymer thin films using supercritical carbon dioxide. *Journal of Materials Chemistry*, 15 (11), 1134–1136. Available from: http://dx.doi.org/10.1039/B418569B.

Wang, J.S., and Chiu, K., 2008. Extraction of chromated copper arsenate from wood wastes using green solvent supercritical carbon dioxide. *Journal of Hazardous Materials*, 158 (2–3), 384–391. Available from: http://www.sciencedirect.com/science/article/B6TGF-4RTW3XS-1/2/66569029b8833c59dd961dd151085a67.

Wang, S., Elshani, S., and Wai, C.M., 1995. Selective extraction of mercury with ionizable crown ethers in supercritical carbon dioxide. *Analytical Chemistry*, 67 (5), 919–923. Available from: http://dx.doi.org/10.1021/ac00101a019.

West, K.N., *et al.*, 2001. *In situ* formation of alkylcarbonic acids with CO_2. *The Journal of Physical Chemistry A*, 105 (16), 3947–3948. Available from: http://dx.doi.org/10.1021/jp003846y.

Williams, D.F., 1981. Extraction with supercritical gases. *Chemical Engineering Science*, 36 (11), 1769–1788. Available from: http://www.sciencedirect.com/science/article/B6TFK-443VH1C-K7/2/f22977ca71b2001fdd42d39dc911d39c.

World Energy Council, 2004. Survey of energy resources. 20th ed. Oxford: Elsevier.

Yalpani, M., 1993. Supercritical fluids: Puissant media for the modification of polymers and biopolymers. *Polymer*, 34 (5), 1102–1105. Available from: http://www.sciencedirect.com/science/article/B6TXW-48CP4D9-23/2/4381ae44368a39367e1ec5a511d961eb.

Yin, C., *et al.*, 2007. Chemical modification of cotton cellulose in supercritical carbon dioxide: synthesis and characterization of cellulose carbamate. *Carbohydrate Polymers*, 67 (2), 147–154. Available from: http://www.sciencedirect.com/science/article/B6TFD-4K8SBXY-2/2/98657256e87769ee8854e4e2bb5278dc.

Yin, C., and Shen, X., 2007. Synthesis of cellulose carbamate by supercritical CO_2-assisted impregnation: structure and rheological properties. *European Polymer Journal*, 43 (5), 2111–2116. Available from: http://www.sciencedirect.com/science/article/B6TWW-4MYD66S-1/2/12e7cf68be7df-b0a25c66790c3d023cb.

Yong Feng, L., *et al.*, 2010. Green chemical treatment of natural wood material for decay resistance by 3-iodo-2-propynyl butyl carbamate (IPBC) with supercritical CO_2 as a carrier solvent. *Advanced Materials Research*, 113–116, 2241–2245.

York, P., and Hanna, M., 1994. Salmeterol xinafoate with controlled particle size. Patent WO/1995/001324.

Yu, Q., *et al.*, 2008. Synthesis of cellulose/titanium dioxide hybrids in supercritical carbon dioxide. *Green Chemistry*, 10 (10), 1061–1067. Available from: http://dx.doi.org/10.1039/B806094K.

Zheng, Y., and Tsao, G.T., 1996. Avicel hydrolysis by cellulase enzyme in supercritical CO_2. *Biotechnology Letters*, 18 (4), 451–454. Available from: http://dx.doi.org/10.1007/BF00143469.

Zheng, Y., *et al.*, 1995. Supercritical carbon dioxide explosion as a pretreatment for cellulose hydrolysis. *Biotechnology Letters*, 17 (8), 845–850. Available from: http://dx.doi.org/10.1007/BF00129015.

Zheng, Y., Lin, H.M., and Tsao, G.T., 1998. Pretreatment for cellulose hydrolysis by carbon dioxide explosion. *Biotechnology Progress*, 14 (6), 890–896. Available from: http://dx.doi.org/10.1021/bp980087g.

Zhenyu Du, S.X.B., 2010. Steam explosion pretreatment technique and application in biomass conversion. *Advanced Materials Research*, 113-114, 525–528.

Zhu, J.Y., and Pan, X.J., 2010. Woody biomass pretreatment for cellulosic ethanol production: technology and energy consumption evaluation. *Bioresource Technology*, 101, 4992–5002.

Zosel, K., 1978. Separation with supercritical gases: practical applications. *Angewandte Chemie International Edition in English*, 17 (10), 702–709. Available from: http://dx.doi.org/10.1002/anie.197807021.