Development of Multiple Unit-Fluid Processes Using Critical Fluids

Jerry W. King
Chemical Engineering Department

Keerthi Srinivas
Chemical Engineering Department

I. Introduction

Supercritical fluids and their liquefied analogues have been traditionally used in single unit operations, i.e. extraction, fractionation, using neat SC-CO_2 or with appropriate modifiers [1]. Since the 1980s, almost 38% of the supercritical fluid extraction processes have been devoted to extraction of food and natural products [2]. Beginning in the mid-1980s, columnar and chromatographic techniques followed by reactions in supercritical fluids were developed to facilitate supercritical fluid derived extracts or products [3], thereby extending the application of a critical fluids processing platform beyond SFE. These newer developments were investigated in part due to the complexity of many natural product matrices and the desire to concentrate specific target components for food and other industrial uses, as illustrated in Figure 1.

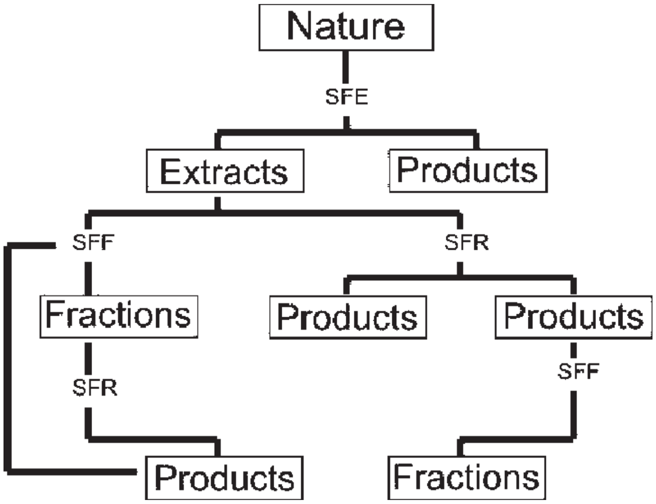


Fig. 1 : Integration of Multiple Unit Critical Fluid Processing for Processing Natural Products.

We have found that the generic solvation properties of the two principal critical fluids, CO_2 and water, to be explained by an extended solubility parameter approach [4,5]. Hence by adjustment of pressure and temperature for CO_2, or temperature in the case of water, one can optimize the solubility of solutes or reactants in these media, or predict their miscibility, by comparing their relative solubility parameters as a function of temperature and pressure. Such an approach has a practical value considering the molecular complexity of many solute types processed in critical fluids. Their solubility parameters or solute-fluid interactions can be explained by using the Hansen three-dimensional solubility concept which allows the application of functional group contribution methods for calculating requisite physical property data as well as solute or solvent solubility parameters as recently reported by Srinivas et. al. [6]. As indicated by Figure 2, the reduction in water's total solubility parameter with increasing temperature is largely due to a reduction in the hydrogen-bonding propensity as reflected by its hydrogen-bonding solubility parameter component, δ_H [7]. Water does not attain the solvation properties of solvents like ethanol or methanol until quite elevated temperatures which is in contrast to the often cited dielectric constant concept which is invoked to explain the solvent properties of subcritical water [8].

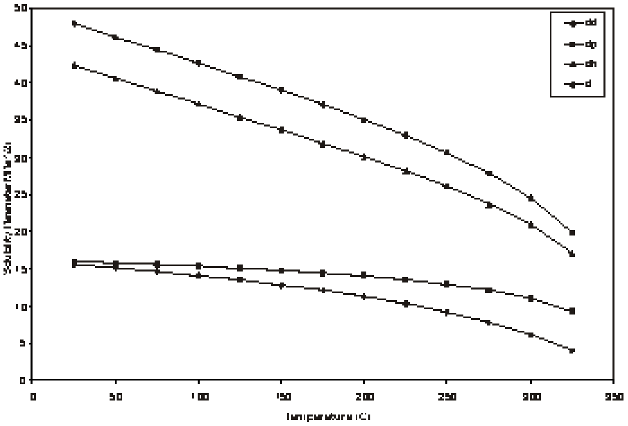


Fig. 2 : Three Dimensional Solubility Parameters of Water as a Function of Temperature.

The above solvent properties of water as described by the solubility parameter concept has some implications with regard to its use as a "green" solvent and a substitute for ethanol in hydroethanolic-based extractions which are GRAS (Generally Regarded as Safe) -approved food processing solvents. Its substitution for ethanol as a processing medium is highly desired to save on processing costs, its separation from water in solvent recycle schemes, and oversight by revenue authorities. These are some of the factors which accelerate research in the use of subcritical water for the extraction of natural products and nutraceutical food components. This is part of the overall critical fluid technology platform using only water and carbon dioxide which result in widespread utilization [9].

Traditional oleochemical processing operations such as fat splitting or hydrogenation are often conducted under either subcritical or supercritical processes. Fat-splitting processes such as Twitchell process [10] or Colgate-Emery synthesis [11] utilize temperatures and pressures in excess of the boiling point of water under the appropriate pressure, but below the critical point of water to facilitate the hydrolysis of triglycerides to fatty acids. However, it should be noted that these processes were frequently interpreted as steambased hydrolysis rather than hydrolysis using sub-critical water. Hydrogenations using binary mixtures of CO_2-H_2 or propane-H_2 are supercritical with respect to the pure component critical constants, but reaction conditions are conducted under less dense conditions due to the high temperatures involved, hence the cited rapid kinetics associated with hydrogenations conducted under these conditions [12] are due to accelerated mass transfer effects as opposed to reactant solubility enhancement.

The advantages of coupling processing options using critical fluids are illustrated in Figure 3. Hence by combining different unit processes and sequencing them with the use of multiple fluids held at operational densities by the application of different temperatures and pressures, one can obtain multiple products and optimize the extraction or reaction process. Several specific options are illustrated for the case of processing essential oils as noted previously [13] in Table 1 for the processing of citrus oils using pressurized fluids. Here six discrete unit processes are listed which include standard SFE with SC-CO_2, SFF employing stage-wise pressure reduction, SFF as practiced using column-based deterpenation [14], supercritical fluid chromatography (SFC), another variant of SFF called subcritical water deterpenation [15], and utilization of a SC-CO_2 or LCO_2 with a permselective membrane described by Towsley et al. [16].

2. Multiple Critical Fluid Processing Platforms

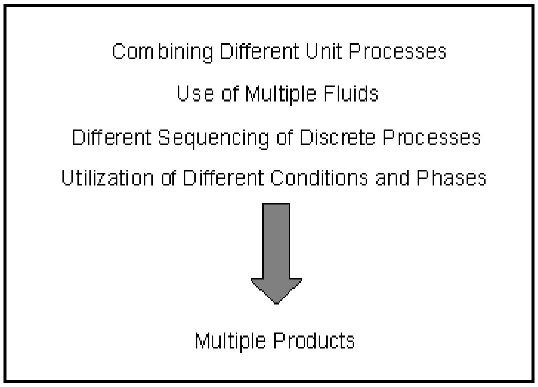
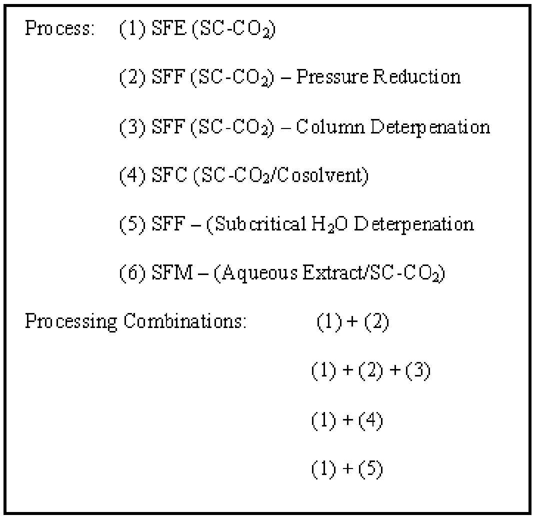


Fig. 3 : Coupled Processing Options for Critical Fluids.



Process: (1) SFE (SC-CO_2)

(2) SFF (SC-CO_2) – Pressure Reduction

(3) SFF (SC-CO_2) – Column Deterpenation

(4) SFC (SC-CO_2/Cosolvent)

(5) SFF – (Subcritical H_2O Deterpenation

(6) SFM – (Aqueous Extract/SC-CO_2)

Processing Combinations: (1) + (2)

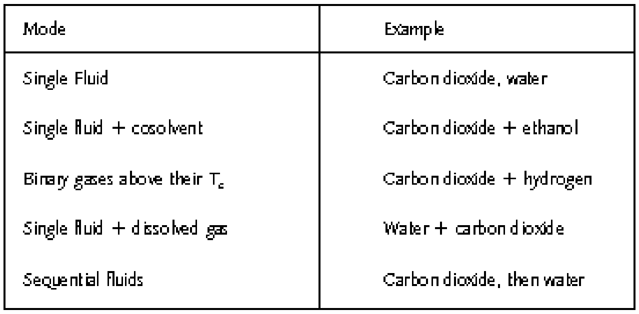
(1) + (2) + (3)

(1) + (4)

(1) + (5)

Table 1. Coupled Processing Options for Essential Oils Processing using Pressurized Fluids.

In the broadest sense, multiple critical fluid processing involves the integration of two or more fluids held under pressure applied as either mixtures or in a sequential manner for one or more unit processes. Listed in Table 2 are the most prevalent combinations that have been utilized or have potential application in process development. Solubility of solutes and reactants in SC-CO_2 has been extensively studied and a recent tome has assembled much of the available data [17]. Likewise there is a fair understanding as to the choice of a suitable cosolvent to pair with SC-CO_2 to enhance the solubility of more polar solutes in the compressed CO_2 medium, although binary phase equilibria data is not always available over the desired range of pressure – temperature for such systems. This is critical if one is concerned with operating in the one phase supercritical fluid region with respect to both components, however as noted by several investigators [18-20], there are several examples where processing can be done with SC-CO_2 - cosolvent systems in the two phase region. This situation becomes of interest particularly when large amounts of an organic cosolvent are used in conjunction with SC-CO_2 to enhance the solubilization of a solute which exhibits limited solubility in neat SC-CO_2. The critical question then becomes whether another compressed fluid might better be integrated into the design of the process. As remarked previously, compressed water at high temperatures and pressures, i.e., supercritical water has been extensively investigated for many years. In the 1990s a similar but somewhat more diffuse focus on using water in its subcritical state with respect to it T_c. received attention due to its application as a reaction medium to transform organic chemicals and biomass into targeted products [21, 22]. Concurrently, particularly in the field of analytical chemistry, subcritical water and other subcritical fluids were explored as alternative extraction solvents under external compression above their boiling points [23-25]. Analytical methods developed with the use of pressurized solvents essentially use subcritical fluids above their boiling point – the pressure applied frequently is far in excess of what is required by inspection of the V-L curves for these fluids [26]. Unfortunately researchers in these disparate areas despite using a common compressed fluid, water, have not always recognized the generic utility of water as a universal compressed fluid medium as well as "green" complimentary solvent to compressed CO_2 [4].



Mode	Example
Single Fluid	Carbon dioxide, water
Single fluid + cosolvent	Carbon dioxide + ethanol
Binary gases above their T_c	Carbon dioxide + hydrogen
Single fluid + dissolved gas	Water + carbon dioxide
Sequential fluids	Carbon dioxide, then water

Table 2. Multiple Critical Fluid Processing Options.

Recently we have attempted to explain the solvent characteristics of water using an extension of the solubility parameter concept, i.e., a 3-dimensional solubility parameter approach, by applying it to sub- and supercritical water [5, 6]. Using the Hansen 3-dimensional solubility parameter approach coupled with SPHERE and Hsp3D [27] software programs, we have studied the interaction between subcritical water and complex organic solutes, including biopolymers, as a function of temperature. Water under compression has the ability by adjustment of the applied temperature and pressure to serve as an extraction solvent as well as a reaction medium depending on what is desired. Residence time of the solute (reactant) in the aqueous medium thus becomes a critical parameter in conducting extractions above the boiling point of water and for optimizing reaction conditions "higher up" the V-L curve for water. There appears in our opinion the lack of rationale design for choosing reaction conditions in sub-critical water, although the semi-empirical "severity" parameter often-cited in biomass conversion studies is one attempt to quantify the required hydrolytic conditions [28]. Using a simple solubility parameter approach, as depicted in Figure 4, in which the solubility parameter for water as a function of temperature is plotted along with the solubility parameters for cellulose oligomers (n = 1-10), it can be seen that the intercept between the solvent and the cellulose oligomers corresponds to the chosen conditions for depolymerizing the carbohydrate polymers [4]. This confirms that conditions are commensurate with those in which the biopolymer is dissolved or miscible in the subcritical water medium. We have also used this approach for other biopolymers treated in subcritical water such as hemicellulose and chitin and rationalized the difficulty in dissolving lignin-type polymers in subcritical water [4]. A similar approach also has utility in understanding the subcritical water extraction of target solutes from natural product matrices, such as silymarins from milk thistle, B-vitamins from brewers yeast, and anthocyanins from grape pomace.

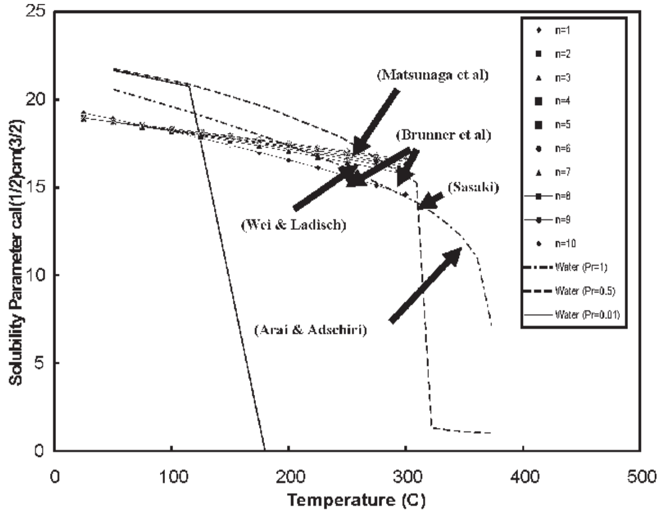
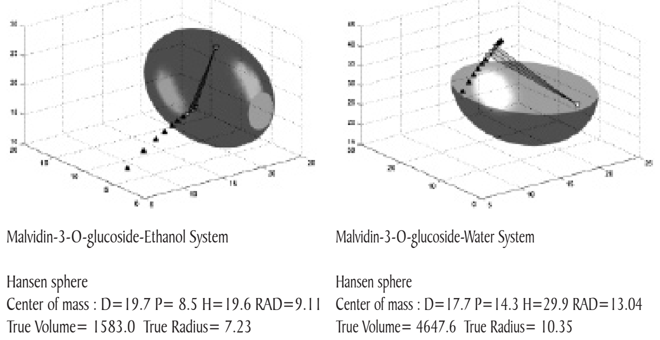


Fig. 4 : Solubility Parameter Variation for Subcritical Water at Different Reduced Pressures p_r and Cellulose Oligomers (n = 1-10) with Temperature.

Similarly in Figure 5 are the Hansen spheres for the anthocyanin, malvidin-3-O-glucoside, in water and ethanol, respectively. The sphere plots indicate a greater miscibility of malvidin-3-O-glucoside in ethanol since the Hansen sphere has the lowest radius of 7.23 $MPa^{1/2}$ in the temperature range of 25-75°C. For the water-malvidin-3-O-glucoside system, the corresponding solubility sphere occurs over a different temperature range and a RED radius of 10.35 $MPa^{1/2}$., higher than that for ethanol [5]. While both subcritical solvents dissolve the target anthocyanin at different conditions, clearly ethanol would be the preferred subcritical solvent with respect to anthocyanin miscibility and solubility.

The 3-dimensional solubility parameter- sphere approach can also be used to explain experimental results we have obtained for the solubility and extraction of malvidin-3-O-glucoside in compressed - hydroethanolic solvent medium. As shown in Figure 6, Hansen solubility spheres were plotted for water-ethanol mixtures, and their corresponding interaction radii versus the composition of subcritical water-ethanol mixture. Figure 6 shows a initially a substantial decrease in the interaction radius between the anthocyanin and hydroethanolic mixture upon addition of 10% ethanol to water (this is due to the substantial decrease in the hydrogen bonding solubility parameter with the addition of ethanol to water). This is consistent with the enhanced extraction recorded for the flavonoid upon addition of ethanol to the extraction medium. Note that although in Figure 6 the minimum interaction radius occurs at 80% ethanol concentration, there is not a significant difference with that recorded at 10% ethanol content. This has important implications for designing the best extraction conditions and minimizing the amount of co solvent (ethanol) required in extracting the target flavonoid.


Malvidin-3-O-glucoside-Ethanol System

Hansen sphere
Center of mass : D=19.7 P= 8.5 H=19.6 RAD=9.11
True Volume= 1583.0 True Radius= 7.23

Malvidin-3-O-glucoside-Water System

Hansen sphere
Center of mass : D=17.7 P=14.3 H=29.9 RAD=13.04
True Volume= 4647.6 True Radius= 10.35

Fig. 5 : Variation of Hansen 3-dimensional solubility parameter sphere of malvidin-3-O-glucoside with subcritical water and ethanol at different temperatures.

Recently, compressed gases in their supercritical fluid state; particularly SC-CO_2, dissolved in liquids and subcritical liquids have become of interest as in-situ catalysts or modifiers for reaction and extraction unit processing. The use of SC-CO_2 as a replacement for metallic catalysts in glycerolysis reactions was reported by Temelli and King [29] and a review of its use in synthetic organic reaction chemistry has been published by Rayner [30]. Dissolving SC-CO_2 under pressure in pressurized water creates a versatile medium with

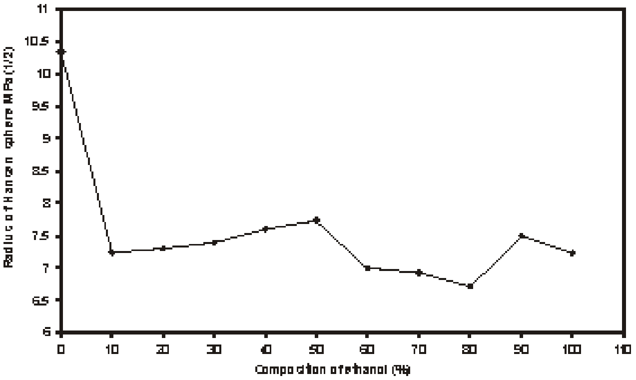


Fig. 6 : Variation in the Hansen Sphere Radius ($MPa^{1/2}$) versus % Ethanol in Compressed Water-ethanol Extraction Solvent.

respect to acidic-based extraction chemistry and reactions due to the inherent carbonic acid equilibrium that is pressure dependent as studied by Toews et al [31]. We and others have found that if sufficient CO_2 under pressure is applied to aqueous solutions, that pH's between 2.0-2.5 can be achieved. The basis of this enhanced dissolution can be seen from the literature data that we have plotted in Figure 7 [32, 33, 34 and 35]. Intuitively, increasing the temperature of water should decrease the amount of gas dissolved in water as borne out by the data taken at lower pressures and temperatures shown in Figure 7, however as more pressure is applied to SC-CO_2, the amount of dissolved gas in water increases lowering the solution pH (Figure 7). Our research group and others have recently exploiting this trend to assist in the conversion of various types of carbohydrate-laden biomass by converting the constituent carbohydrate polymers to lower oligomers for eventual conversion to biofuels. Similarly control of solution pH by dissolution of SC-CO_2 can also affect the equilibrium-based species that is extracted when using subcritical water as is the case for anthocyanins and similar flavonoid-based solutes [36]. This technique offers definite advantages with respect to avoiding the use of mineral acids in extraction and reaction chemistry since the dissolved SC-CO_2 can be jettisoned to the atmosphere or recycled by a reduction in pressure. Studies using supercritical carbon dioxide as reaction solvent especially in catalytic hydrolysis as described above have also shown good product separation characteristics by increasing the pressure from 20 bar to as high as 120 bar. Approximately 90% of the hexanes were successfully separated from the hydrolytic mixture dissolved in supercritical carbon dioxide [37].

It was remarked previously (Table 2) that it should be possible to use one critical fluid at different temperatures and pressures to perform multiple unit operations. For SC-CO_2, it is well documented that changes in the fluid density can be used as a basis for the supercritical fluid-based fractionation (SFF) of a number of complex mixtures. This is also possible in the case of subcritical water, but usually through the adjustment of temperature. As the authors have previously noted, hot compressed water is a versatile medium in both its sub- and super-critical regions by using it over a range of reduced temperatures (T_r) and pressures (P_r) depending on the unit processing result that is desired. High values of T_r (1.02 – 2.5) and P_r (1.2 – 1.8) are used for destructive schemes, such as supercritical water oxidation, while a lower range of T_r's and P_r's are employed for selective molecular transformations such as biomass conversion via specific reaction pathways. Biomass conversion in hot compressed aqueous media embrace operational parameters (T_r = 0.65-1.05, P_r = 0.35 – 2.0) in both the sub- and super-critical phases for water The use of sub-critical water for extractions depends on the physical properties of the dissolved solutes and their tendency to degrade under the chosen extraction condition. For example, T_r's and P_r's are typically in the range of 0.50 – 0.80 and 0.02 – 0.35, respectively, for the extraction of natural products.

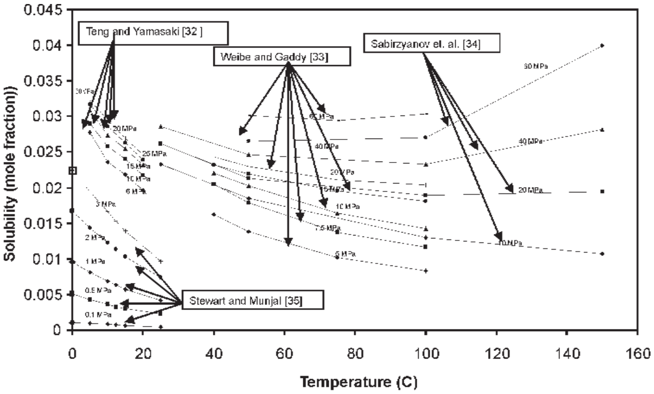


Fig. 7 : Mole Fraction Solubility of CO_2 in Water as a Function of Temperature and Pressure.

Figure 8 shows a hypothetical multi-unit processing scheme based entirely on subcritical water for the treatment of a potential biomass substrate [4]. Here the target substrate is pretreated with pressurized water to prepare it for eventual extraction or reaction using subcritical water. The pretreatment with pressurized water can be used to swell the substrate or comminute it for more effective extraction or reaction. Using the above criterion, an extraction can be performed using pressurized water above its boiling point to recover high value botanical extracts from the substrate prior to using subcritical water as a reaction solvent. Post-extraction treatment is then performed over a higher temperature range (150 – 300°C) to hydrolyze the remaining biomass for further conversion to a lower molecular weight hydrolyzate suitable for fermentation to a liquid fuel. The advantage of the described process is that it can be potentially conducted in one reactor of integrated processing plant therefore saving on capitalization costs.

3. Multiple Unit Processing: Concepts and Possibilities

The concept of continuous processing of oils from seeds and meals goes back to the mid-1980s with the description of the operation of an Auger-type screw press by Eggers [38]. Here a supercritical fluid such as SC-CO_2 is used to assist in the removal of oil from crushed seeds or meals which may have been partially pre-extracted. The physicochemical basis of the process is still not well understood, but involves the addition of liquefied CO_2 to the seeds or meal inside an expeller barrel to aid in the oil extraction process. The hydraulic compression on the seed meal creates considerable pressure and heat on seed matrix resulting in the conversion of the added CO_2 to its supercritical state. The hot compressed carbon dioxide partially solvates the seed oil akin to what occurs when SFE is performed with SC-CO_2, but more importantly dilutes or expands the expressed oil enhancing its removal from the seed or meal bed. Methods to achieve this goal have been described in the patent literature most notably by Foidl [39] whose process has been partially commercialized and applied to the processing of soybeans. This CO_2 – assisted expression process has been commercialized by Crown Iron Works in Minneapolis, Minnesota under the trademark of HIPLEX process and CO_2 expression demonstrated on a Harburg Freudenberger expeller having a 25 ton per day capacity. The process is in commercial operation at SafeSoy Technologies in Ellsworth, Iowa. The ratio of oil to CO_2 is 3:1 which reduces the vegetable oil viscosity by 1/10 resulting in between 80-90% vegetable oil recovery for soybeans and over 90% recovery of canola oil. Such solvent-free oils and meals are superior in quality to solvent extracted products. A similar device would be welcomed for subcritical water extraction of natural and food-related products as well as for the conversion of biomass substrates on a continuous basis in which the substrate to be extracted or treated with pressurized water would be contacting as a slurry with the pressurized water. This could be principle then be applied to such diverse matrices as grape pomace, cocoa beans, and herbal substances provided the residence times above the boiling point of water are minimized. Current systems for affecting such pressurized water extractions are staged as semi-continuous batch systems or by combining the substrate to be processed as aqueous slurry with water before passage through a heated extraction vessel. It should be noted that critical fluid-based expeller processes compete with similar unit processing done with the aid of extruders [40]. Although extruders have shown promise in the processing of finished food products [41] their attendant expense and lower throughputs make them less attractive than the expeller-based processes described above.

Integrating critical fluid technology with membranes has permitted the separation of low and high molecular weight compounds obtained from the SC-CO_2 extraction of lipids from foodstuffs such as butter or fish oil using nanofiltration membranes [42]. Similarly, it has been reported that is possible to extract polyphenols from cocoa seeds using neat SC-CO_2 and with ethanol as a co solvent, and then concentrate the extract using polymeric nanofiltration or reverse osmosis membranes. This system operated at a pilot scale between 8-15 MPa and at 40°C resulted in a maximum yield of polyphenols of 43 % when the pressure was optimized at 8 MPa using ethanol. The study also indicated a high performance of all the membranes when the trans-membrane pressure was maintained in excess of 1 MPa [43]. The ability to concentrate extracted polyphenols using SC-CO_2 extraction paired with membranes suggest that a similar tandem involving subcritical water – membrane coupling would be advantageous since extraction with subcritical water results in a diluted extract. This concept was first advanced by King [44] and noted in a US patent issued to Wai and Lang [45]. They suggested that SFE could be implemented on a natural product matrix followed by subcritical water extraction sequentially on the same matrix and then followed by a membrane separator to yield a concentrate of the aqueous extract.

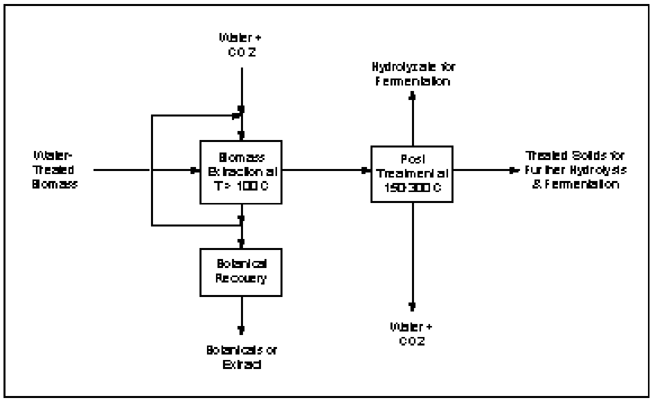


Fig. 8 : Tandem Subcritical Water Processing of Biomass.

We have on a lab scale also demonstrated the feasibility of a SFR-SFR sequential set of reactions to make fatty alcohol mixtures. The generation of fatty acid methyl esters (FAMES) in this case was based on studies involving the enzymatic synthesis of FAMES directly from vegetable oils dissolved in SC-CO_2 [46, 47]. Combining this transesterification reaction with a hydrogenation reaction using consecutively coupled packed bed reactors allowed the production of FAMES in either a SC-CO_2 or SC-C_3H_8 stream followed by exhaustive hydrogenation of the FAMES to fatty alcohols as shown in the figure. In this process a non-Cr catalyst was used to successfully convert the FAMES to the C_{16} + C_{18} saturated alcohols at 250°C and 25 mole % H_2 in SC-CO_2. This is an excellent example of how a two-step synthesis process can be conducted in supercritical fluid media that is environmentally-benign by permitting reuse of the critical fluid media as well as the reaction by-product from the hydrogenation step, methanol (Figure 9).

It is impossible to separate in the multiple unit and fluid processing platform the role of fluid interchange with tandem unit processing. Toward this end the choice of solute or substrate modification and/or fluid medium can enhance the opportunity to utilize the various combinations of fluids or unit processes. Two will be cited here: (1) formation of methyl esters of lipid-type solutes such as fatty acids (FAMES), and (2) use of water primary for hydrolysis of complex naturally-occurring substrates. FAMES are an extremely versatile modification for the critical fluid processing of fats/oils and their oleochemical derivatives. Aside from the formation of FAMES for conversion to biodiesel via enzymatic synthesis [48] or in sub- and super-critical methanol [49], FAMES or similar esters can be used advantageously in SFE [50], columnar modes of SFF [51], SFC [52], and as noted above in SFR. This versatility is due to one or more of the following factors relative to the non-methylated analogs: (1) enhancement of solute volatility or solubility, (2) improvement of separation factor (α), (3) intermediate formation for downstream synthesis, and analytically-useful derivatives. Formation of FAMES before utilizing multi-unit processing can allow easier SFF of fatty acids [53], selective SFE and SFR of fatty acids from tall oil [54] for subsequent conversion to biodiesel, and to fractionate soapstsock[55] or deodorizer distillate [56]. For example, countercurrent multistage processing of edible oils using critical fluids has been shown to be capable of producing fatty acid esters, tocopherols, squalene, sterols, and triglycerides. Approximately 70% of the fatty acid methyl esters in deodorizer distillates plus tocopherols and sterols can be

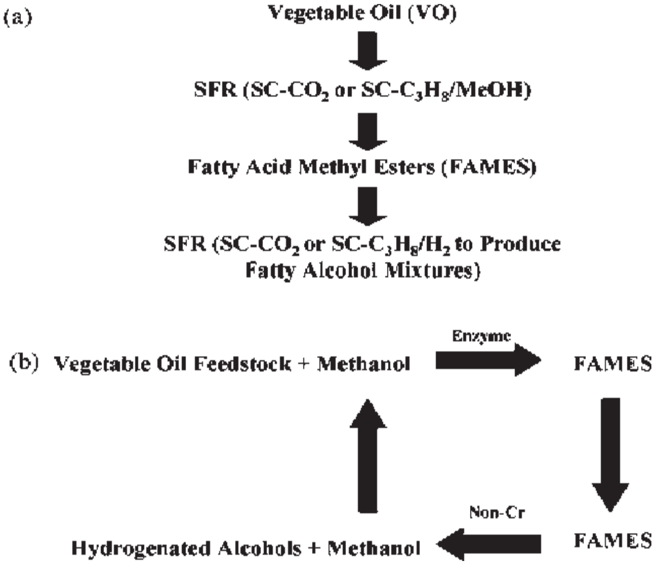


Fig. 9 : Production of fatty alcohol mixtures using a (a) SFR-SFR sequential reaction scheme, (b) feedback of methanol into the DSFR process and its inherent "greenness".

extracted with SC-CO_2 [57]. Tocopherols and sterols in the resultant extract can then be separated from the FAMES by columnar SFF by countercurrent fractionation using SC-CO_2.

4. Examples of Integrated Critical Fluid Processing

The above typical results of employing CO_2 extraction in tandem with pressurized liquid fluids suggest an interesting option and current trend in employing this mixed pressurized fluid matrix as both extraction and reaction media. As noted previously, the incorporation of pressurized CO_2 into subcritical water, i.e., a gas-expanded liquid, makes for an interesting extraction and reaction medium. The Meireles group in Brazil [58, 59] have utilized this principle in the processing of ginger bagasse both as a pre-treatment step and to degrade bagasse to sugars for potential fermentation. Pretreatment with SC-CO_2 seemed to yield somewhat ambiguous results since the authors state that non-treated bagasse was hydrolyzed more effectively then CO_2-pretreated bagasse [60]; the latter process was hypothesized to degrade the oleoresinous materials in the bagasse matrix. Their results for matrix pretreatment with SC-CO_2 are in stark contrast with other reports in the literature that indicate SC-CO_2 pretreatment is an effective procedure proceeding biomass degradation [61]. It should be noted that the above results are somewhat different then using the previously-mentioned carbonated water to hydrolyze carbohydrate polymers; also SC-CO_2 is effective in removing high value components from the biomass matrix prior to hydrolyzing the biomass matrix [60]. Since reported SC-CO_2 pretreatment methods exist and carbonated water hydrolysis has been shown by us [62] and others [63] to be an effective hydrolysis medium, the above ambiguity may be due to the varying recalcitrance of the target biomass matrix to hydrolytic degradation. The hydrolytic action patterns of carbonated water can vary quite significantly depending on the matrix being hydrolyzed although the hydrolysis temperature and residence time can be varied to produce optimal depolymerization of the carbohydrate polymers inherent in the biomass.

One aspect of our current research focuses on the application of critical fluids for processing grapes and grape by-products and similar natural antioxidant-containing matrices. These matrices and target solutes are a fruitful area in which to apply combinations of mixed critical fluid and unit processing steps. One of the seminal questions is whether SC-CO_2 and co solvent combinations or a hot pressurized fluid such as water or ethanol – or combinations thereof - are most appropriate for extracting and fractionating the targeted solutes. There is a considerable literature in the application of SC-CO_2 for extracting grapeseed oil [64, 65] as well as further fractionating the extract to enrich certain polyphenolic constituents. Recovery of solutes such as gallic acid, catechin, epicatechin, etc. via a SC-CO_2 – based method almost always require the use of methanol or ethanol as co solvents [66].

Other studies have utilized subcritical water to extract procyanidin compounds and catechins from grape processing wastes [67]. Extractions conducted at approximately 10 MPa and in the temperature range of 50 – 150°C were adequate to recover and fractionate gallic acid, procyanidin dimers, and the corresponding oligomers from the grape pomace using an analytical scale pressurized fluid extractor (ASE). Aside from water and hydroethanolic pressurized fluid extraction, sulfurized water has also proven effective for the extraction of anthocyanins and procyanidins from grape pomace [68]. This parallels similar work by the senior author in using neat and acidified water to extract anthocyanins from berry substrates using both ASE and a batch continuous subcritical water extractor. As noted in the patent issuance on this process [69], residence time of the extracted solute in the hot pressurized water must be minimized to prevent degradation of the anthocyanin moieties or their possible reaction with sugars to other products. It is unknown at this time whether such side reactions in pressurized water could be generating antioxidant moieties, but the potential ability to control the ratio of polyphenolic stereoisomers and to depolymerize or repolymerize biologically-active antioxidant oligomers in pressurized fluid media could be a significant area for future research – particularly if they come from cheap and renewable natural resources [5].

The authors have previously noted the considerable potential for applying critical fluids in biorefineries, etc. [4] but several existing examples are worth citing. Saka [70] has demonstrated a two step process for the production of biodiesel based on the Saka - supercritical methanol process for converting both fats/oils and free fatty acids to biodiesel. The Saka-Dadan process uses subcritical water in front of the Saka process for the hydrolysis of fats/oils to free fatty acids followed by a more benign supercritical methanolysis of the resultant free fatty acids to FAMES. A pilot scale unit of this process is in operation in Fuji City, Japan. This overall biodiesel production platform is an excellent example of having a critical fluid – based SFR-SFR integrated process.

Baig et al. [71] have recently reported on the combined critical fluid treatment of sunflower oil to yield value-added substances as well as a model for the "critical fluid biorefinery". This concept can be achieved by coupling two or more reaction processes into one continuous flow system; namely the subcritical water hydrolysis of sunflower oil triglycerides to free fatty acids followed by esterification of the free fatty acids to FAMES in SC-CO_2 using lipase catalysis. The subcritical water extractor conditions were maintained at 250-390°C with pressures as high as 10-20 MPa using oil: water ratios of 50:50 and 80:20 (v/v). The supercritical fluid enzymatic-based esterification process was operated at temperatures 40-60° C using a Novozyme enzyme catalyst. The subcritical water studies indicated a high rate of conversion at higher temperatures (330°C) followed by possible degradation of the free fatty acids when exposed to longer residence times. A yield of approximately 90% hydrolyzed free fatty acids was achieved in 25 mins at 330°C or for 45 mins at 310°C. The esterification process yielded between 60-70% FAMES at a pressure of 20 MPa and 60°C with low enzyme concentrations.

V. Concluding Remarks

Over the past twenty years, the author has on more than one occasion been queried on the possibility of constructing a SFE plant in close proximity to an alcoholic fermentation facility that produces high purity CO_2 as a by-product. This would seem logical since the opportunity to apply SFE for vegetable or specialty oil extraction could be facilitated with this source of CO_2 as well as any of the above mentioned CO_2 – based unit processes. The production also of ethanol at such a site facilitates a preferred co solvent for coupling with CO_2 as documented previously. Today in the renewable bioenergy field it is envisioned to build coexisting bioethanol and biodiesel production capabilities at the same site. Hence based on our discussion above, this suggests the possibility of extending the application of critical fluids platform for the production of these two renewable fuels as documented above. Similarly, it was noted above that SC-CO_2 could be mixed advantageously with pressurized water for extraction and reaction chemistry. Such a critical fluid – based processing concept supports the use of renewable resources, a sustainability platform, and does so in a "green" environmentally-benign manner.

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