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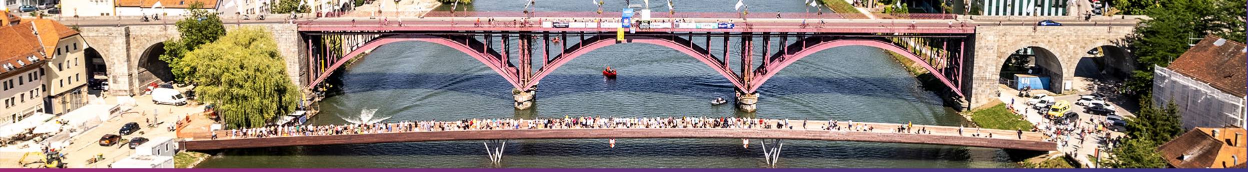
20th European Meeting on Supercritical Fluids

Book of Abstracts

University of Maribor Press



University of Maribor

Faculty of Chemistry and
Chemical Engineering

20th European Meeting on Supercritical Fluids

Book of Abstracts

Editors

Željko Knez

Milica Pantić

Darija Cör Andrejč

July 2024

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Foreword

ŽELJKO KNEZ

Dear attendees.

On behalf of all organizers, I am pleased to welcome you to the **20th European Meeting on Supercritical Fluids** (EMSF 2024). This year, **EMSF 2024** is a joint meeting of the International Society for the Advancement of Supercritical Fluids (**ISASF**) and the European Federation of Chemical Engineering (**EFCE**) Working Party on High Pressure Technology (**WP HPT**) Event No. 807.

The conference will encompass various subjects, from **fundamental studies** to **practical applications**, offering insight into the state-of-the-art work being carried out by researchers from around the world.

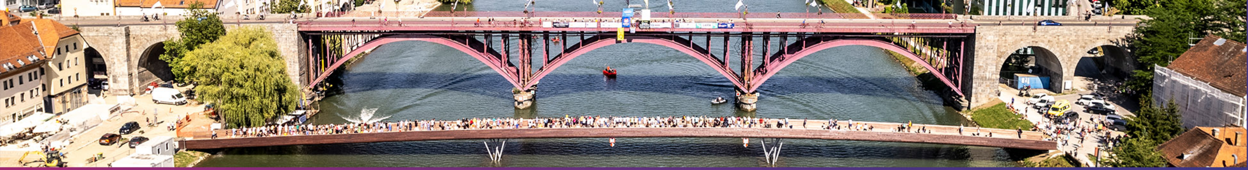
The conference program pages present a selected collection of topics highlighting the latest research and advances in supercritical fluids and high-pressure engineering. We invite you to explore the diverse topics covered in this conference program and the exciting possibilities offered by supercritical fluids. Whether you are an experienced practitioner or a newcomer to the field, we hope that both the lectures and the posters will inspire you and stimulate new ideas for future research and collaboration.

I would like to thank all the participants for sharing their insights with us, the Organizing and Scientific Committees members, the reviewers, the donors and sponsors, and the volunteers whose work made EMSF 2024 possible.

Sincerely,

ORAL
ABSTRACTS

20th European Meeting on
Supercritical Fluids
Maribor, Slovenia, May 26 - 29, 2024



Industrial applications of supercritical fluid technologies

C. LÜTGE

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Our living environment displays a severe impact of our human activity and the industrialization over the last 200 years. This industrial development made huge progress in the world possible, and improved the living conditions in an unprecedented, though often undervalued way [1]. Nevertheless, we also see our natural habitat under stress, and realize the need to reflect and correct our style of living. The United Nations have defined "*17 Sustainable Development Goals*" to emphasize the urgent need for a turning point in this very age.

Process technologies applying high pressures contributed in an extraordinary way to the development in the world and made prosperity in many aspects possible. The paper will therefore highlight achievements through applications of high pressure and supercritical fluids in the context of the UN sustainability goals.

Firstly, examples of long established processes will be presented which might be considered the historical cradle of supercritical fluid technologies. These processes still enjoy a broad and growing industrial use and continue to be a ray of hope for future wealth, and form part of the solution for current environmental problems.
Secondly, more recent innovations will be summarized, to demonstrate the broadness and versatility of supercritical fluid applications. Due to their particular physical and chemical properties, supercritical fluids must be considered an

extraordinary tool in a sustainable world of process technologies. However, the timeline from the first laboratory experiments through final industrial use must not be underestimated. [2]

Finally, an outlook shall be presented to encourage scientists, industry, as well as funding institutions and financing bodies, to invest time, effort and money into the very promising field of supercritical fluid technologies to help in transforming our world toward a new era.

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Trends in the development of high-pressure processes

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Nowadays, there is a trend to develop alternative technologies with minimal environmental impact for products with special custom-designed properties. Reduced energy consumption, less toxic residues, efficient conversion of reactants to products, less by-products and higher quality and safety of final products, are crucial requirements for the future processes. Recent trends in the developments of these technologies will be presented in our lecture.

An important advantage of the use of supercritical fluids (SCFs) as **extraction** solvents is the selective isolation of components or fractionation of total extracts, by changing the process parameters – pressure and temperature in the extraction process, or stepwise separation. The legal limitations of solvent residues and isolation/fractionation of special components from total extracts in combination with different formulation may propel future applications as the requirements of sustainability, and also demand for new technologies. The trend about the pressure of extraction units installed in the world – one direction is towards ultra-high pressure – the most common, and the other is still in the direction of lower pressure units.

High pressure technologies have also found extensive application for the production of **nanostructured materials** (aerogels, particles, foams) especially in the pharmaceutical, food and fine chemicals industries.

Supercritical drying is used to remove liquids from solids without altering the structure of the solid. It is based on the liquid-like properties of supercritical fluids and their capacity of dissolving organic solvents, and is used in the production of aerogels of micro electro mechanical systems.

Conventional **textile dyeing** processes are environmentally unfriendly and economically costly. SCF technology for dyeing textile materials is a water free process with lower operational costs than conventional methods. SCF technology is applicable to both synthetic and natural textiles.

In the field of microelectronics SCFs, especially supercritical (SC) CO_2 found application as **cleaning** agents. This application relies upon the solvent properties of SC CO_2, its low surface tension, and its ability to infiltrate into microcavities with complex geometry.

Natural products sources contain potential contaminants, like bacteria, viruses, spores, toxins, etc. The low temperature **sterilization** technology using SC CO_2 or high hydrostatic pressure **pasteurization** is interesting for food and pharma products. One of the main advantages of using dense gases as solvents for **chemical** (polymerization, hydrogenation, alkylation, hydroformylation, …) and **biochemical reactions** is the tunability of solvent properties. Sub and SC water are used as reaction media for waste treatment – processing of waste polymers and biomass. For biochemical reactions the process parameters influence the activity, stability and selectivity of several enzymes. SC CO_2 has been studied as a refrigerant in mobile air-conditioners and heat pump systems, being considered a possible next-generation, environmentally benign **heat transfer** fluid. The excellent heat transfer properties of supercritical fluids have also found application in the field of energy production, as they were proposed for use in power cycles.

Our lecture will illustrate the trends in high-pressure technologies that are opening up new "avenues" for materials and products obtained through cost-effective and environmentally friendly processes.

Assessment of a flow pattern heat transfer model in the design of evaporators and condensers in SFE industrial plants

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In SFE industrial plants two of the equipment that are most critical for the good design of the plant are the evaporator and the condenser. It is common practice to use a double tube heat exchanger for the evaporator, because it is easy to clean from extract carried by CO_2, and provides enough heat exchange area for the evaporation of the CO_2. For the condenser, since the CO_2 is clean, the choice falls on a shell and a tube heat exchanger.

In this work, two computational models are developed and implemented in Python for the design of evaporators and condensers.

The models are applied to the heat transfer in macrotubes with dimensions ranging from DN25 PN100 to DN40-65 PN100: condenser and evaporator cases, respectively.

The heat transfer is modeled through an overall heat transfer coefficient obtained from the combination of the inside CO_2 heat transfer coefficient and those outside (water or brine).

In common, the computational models have the mathematical treatment of the heat transfer for the flow of CO_2 inside horizontal tubes, with phase change supported in a flow pattern map [1-4]. Using the expressions given by the authors for the boundaries of the flow regimes in the flow pattern map, our model builds a computational flow pattern map. The computation of the local heat transfer coefficients proceeds according to the existing flow pattern. In the evaporator the evaporation and the subsequent heating of the CO_2 is considered, while, in the condenser, is considered the cooling of the gaseous CO_2 and its subsequent condensation.

The complementary heat transfer coefficients (water side - annulus) for the evaporator are calculated using the correlation of E.S. Davis [5].

For the condenser, the brine side heat transfer coefficient was calculated using the method given in VDI-Wärmeatlas [6].

The models were used to design industrial-size evaporators and condensers, and the results were compared to existing equipment in industrial plants built by Natex Prozesstechnologie GesmbH. It was verified that the designs produced by the models agreed with those already realized. This demonstrates the good performance of the models in describing the heat transfer in these two different types of heat exchangers.

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20th European Meeting on Supercritical Fluids
Maribor, Slovenia, May 26 - 29, 2024

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Reduction of energy consumption in supercritical CO_2 processes using a commercial membrane for CO_2 regeneration

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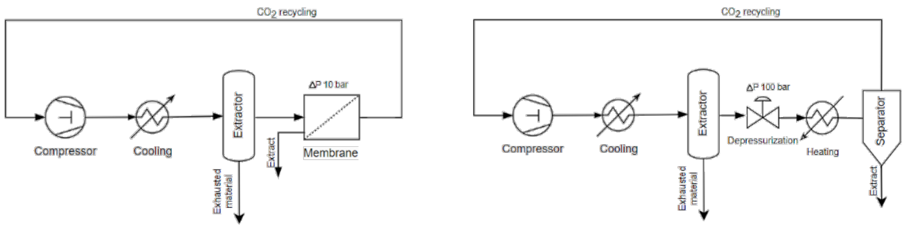
Regeneration of the CO_2 in supercritical processes is usually done by expansion to recover the extract, followed by recompression, which yields a high-energy consumption which represents the major operating cost of these processes. Using membranes for solute recovery with very limited pressure reduction (a few bars compared to hundreds in the conventional process), can reduce energy consumption drastically (see Fig.1). Indeed, this hybrid process can make sc-CO_2 extraction economically feasible, even for low and medium value-added products. However, this requires a membrane with adequate selectivity and permeance in respect to sc-CO_2, and a sufficient lifetime.



a) b)

Figure 1: a) CO_2 recycling by means of membrane b) CO_2 conventional recyclage

The first part of this study has assessed a commercial polyamide reverse osmosis membrane (type AG – Veolia) in respect to sc-CO_2 permeation [1] and to the retention of sunflower oil, as edible oils are an attractive target for this clean extraction technology. Subsequently, the operational cost of this coupled process was estimated, and compared to the conventional one. The experiments of sc-CO_2 permeation with the AG membrane were performed on a specifically designed membrane cell, at 40.1±0.5°C. This membrane exhibited moderate permeance values (3.6±0.5 kg/(h.m^2.bar)). Retention rate R in respect to sunflower oil, at a constant inlet pressure of 150 bar, was found at around 90%, and this retention rate value was checked to persist throughout a filtration time of about 15 hours. The second part of the study refers to economic evaluation of the process in respect to operating cost. The operating cost equation for this coupled process, C_{ope}, in €/kg of oil, is indeed the sum of the cost of the consumable membrane (depending on its lifetime and area needed, inversely proportional to ΔP) and energy costs of recompression (proportional to ΔP):

$$C_{ope} = \frac{P_m}{Perm\, C_S\, R\, t_{life}} \, \frac{1}{\Delta P} + \frac{\alpha}{C_S\, R} \, \Delta P \tag{1}$$

where *Perm* is the permeance referred to as pressure difference, in kg.(h.m^2.bar)$^{-1}$, P_m is the price per square meter of the membrane, in €/m^2, R is the retention rate of the oil on the membrane, t_{life} is the membrane lifetime, C_s is the saturation solubility of the oil in sc-CO_2, in kg of solute/kg of CO_2, □ is the proportionality factor for the cost of recompression in € (kg of CO_2)$^{-1}$ bar^{-1} (recompression costs were shown to be quasi-linear in the considered ΔP range). Minimizing this operational cost with respect to ΔP yielded defining a performance index I_p for the membrane, whose optimal value was found at around 150 kg. €$^{-1}$.bar^{-1}, a value allowing very significant reduction of the operating cost of the CO_2 recycling (around 90% compared to the conventional process). This performance index is defined by

$$I_p = R^2 \frac{Perm\ t_{life}}{P_m} \tag{2}$$

In conclusion, this study underscores the potential of these hybrid supercritical processes, which enhance the economic feasibility of sc-CO_2 extraction processes in the case of low to medium added-value extracts. Especially, criteria are given for the choice of the best-suited membrane.

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Plastics recycling by scCO$_2$: evaluation of OPEX

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In 2018, a new EU Directive of the European Parliament was published, to amend the old Directive (94/62/EC) on packaging and packaging waste. The document states that waste management in the Union should be improved, to "protect, preserve, and improve the quality of the environment and human health" [1]. By the end of 2025, at least 65% of all packaging waste by weight should be recycled. The amendment refers to every type of packaging material, including plastic, wood, aluminum, glass, paper, and cardboard. During summer breaks in Europe, especially in the Mediterranean Sea, it is becoming more and more difficult to find beaches without plastic contamination. The plastic content in the sea is growing yearly, due to the rapid growth of plastic production in the last decades with annexed landfilling or waste mismanagement. Indeed, the production of plastic has grown from 370.5 million tons in 2018 to 400.3 million tons in 2022, an increase of 8% in only four years. Circular plastic, which is not produced newly from fossil-based sources, constitutes only 9.5%, i.e., mechanically recycled, chemically recycled, bio-based plastic, and carbon-capture plastic. Most plastic introduced into the market each year is made of PP, with 18.9%, followed by 14.1% of PE [2]. Therefore, it is no coincidence that most microplastics found in the western Mediterranean Sea were constituted by low-density polymers such as PE and PP [3]. Nowadays, only PET bottles are recycled successfully. Other plastics, such as PP and PE, used mainly in packaging, are not recycled, but dispersed in the environment by landfill, or incinerated for energy production in the best scenarios. So far, there are no established recycling processes for the most produced plastic in the world (PE and PP). PET derived from garments is still challenging to recycle, due to dyes, impregnation agents and blends with natural fibers. Moreover, plasticizers used in PVC production, often phthalate esters, found to be endocrine disruptors, were banned in the EU from 2015 in plastic products destined for children or pregnant women [4]. In addition, PVC must not be burnt, due to chloride, which forms dioxin compounds [5]. Therefore, we must find solutions to comply with plastic circularity and public health goals. Supercritical fluids, especially supercritical carbon dioxide ($scCO_2$), which is not flammable and toxic, could offer a technological solution. Indeed, the low critical parameters of $scCO_2$ make it a perfect solvent for the removal of residual fats, oils, and printed inks from packaging films, without damaging the structure of the polyolefins, which are prone to thermomechanical and thermos-oxidative chain scission [6]. Different molecules are absorbed by the plastic (PP, PET) when in contact with beverages or foods, such as phenyl ethyl alcohol from beer and β-myrcene from Coca-Cola. These contaminants and other molecules used as surrogates were reduced in concentration up to 80% in PP by $scCO_2$ treatment at 200 bar and 80°C for 1 hour [6]. NATEX can upscale and industrialize decontamination processes of different kinds of plastics, thanks to two installed in-house extraction units equipped with co-solvent pumps: a 5L/1000 bar unit and an 80L/550 bar as a pilot scale. OPEX were estimated for the decontamination of PE and PP, discoloration of PET garments, and removal of plasticizers from PVC regarding S/F ratios, pressures, and temperatures used in the $scCO_2$ extraction processes. According to our first calculations, to decontaminate 10,000 tons of plastic per year, OPEX are in the range of 0,20-0,50 €/kg of raw material for an S/F ratio of 25 to 50. It remains to be seen whether these prices are economically attractive for European recycling companies, which must compete with the prices of virgin polymers imported outside Europe. Considering that EU member states pay a levy of 0,80 €/kg of non-recycled plastic packaging waste and countries start to introduce taxes, this might become of interest to more companies.

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Keynote Lecture

Modeling the solubility of β-carotene by a modified Peng-Robinson or Redlich-Kwong equations of state

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The solubility of carotenoid compounds in supercritical carbon dioxide ($scCO_2$) is modeled using the modification of the Peng-Robinson or Redlich-Kwong equations of state (EoS) proposed by Estévez *et al.* [1]. The main advantage of this approach is that no critical properties of the solutes are needed. In the classical equation-of-state approach, *fictitious* critical properties must be “estimated”. In a nutshell, the approach is to embed the critical-property dependence into two adjustable parameters, α and β, defined as:

$$\alpha = \sqrt{\frac{a_2}{a_1}} \quad \text{and} \quad \beta = \sqrt{\frac{b_2}{b_1}}$$

where a_1 and b_1 are the EoS parameter of the solvent, while a_2 and b_2 are those of the solute. (No k_{ij} is needed in this approach.) Then, α and β are found by minimizing *AARD,* or maximizing R^2.

Several sources were found of experimental solubility data of β-carotene in $scCO_2$[2-9]. The EoS approach proposed by Estévez *et al.* [1] was then used to correlate the data. The solute sublimation pressure is needed when using any EoS method, and the data presented in Table III of Lazzús and Rivera [10] were used. The data were correlated using a two-constant Antoine equation, which resulted in the following expression:

$$\ln\left(p^{sub}\right)=23.93-\frac{15140}{T}$$

Then, the α and β values that minimize *AARD* were sought. Using the data at 40°C resulted in the values of 16.03 and 21.59 for α and β, respectively. Figure 1 shows the results graphically. In summary, this model gives good results, that do not depend on the fictitious values of solute critical properties that are normally used when EoS methods are used.

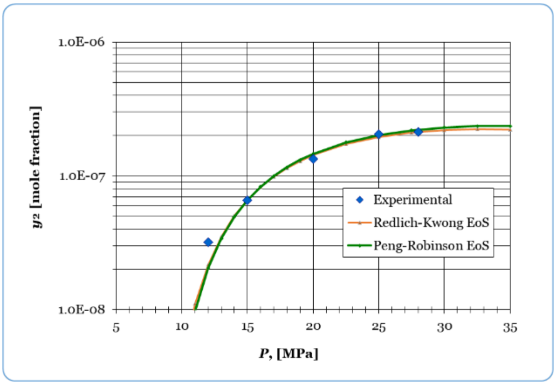

Figure 1: Model results at 40°C.

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In situ microfluidic investigations of APIs crystallization dynamics in $scCO_2$: from thermodynamic equilibrium to growth kinetics

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In the intricate landscape of pharmaceutical manufacturing, crystallization stands as a fundamental unit operation, constituting approximately 90% of the isolation of active pharmaceutical ingredients (API) [1]. Supercritical fluids, notably CO_2, are gaining prominence as environmentally sustainable alternatives, due to their unique properties. Furthermore, in an era of miniaturization, microfluidic technology enhances heat and mass transfer, reduces preparation volumes and waste, improves reproducibility, and, crucially, provides optical accessibility for *in situ* analyses such as optical microscopy, UV, IR, and Raman spectroscopy. This study focuses on utilizing a specialized microfluidic platform under supercritical CO_2 ($scCO_2$) conditions to crystallize APIs, enabling an in-depth understanding and real-time observation of crystallization under elevated pressures.

The development of the microfluidic platform presented a significant technical challenge, requiring the design of tailored micro-reactors. The validated design ensures precise CO_2 diffusion within a micro-well system, presenting a pioneering approach for observing and studying. Prior to crystallization, the study addresses the rapid attainment of phase equilibrium through the microfluidic system, focusing particularly on the CO_2-acetone mixture. The experimental setup and protocol detail the reliability of the microfluidic device in examining phase equilibria in binary and ternary systems under pressure. Raman spectroscopy emerges as a key *in situ* characterization tool, facilitating the quantification of CO_2 composition over time, with values validated through numerical simulations.

Experimental efforts concentrate on the crystallization of naproxen, our model pharmaceutical compound. Parameters are explored, such as initial concentration, pressure, and stereoisomerism. The results indicate that near-saturation concentrations reduce crystallization time, regardless of pressure, aligning with classical crystallization theories. The presence or absence of a counter-enantiomer influences crystallization times significantly, suggesting potential avenues for enantiomeric separation. In the context of crystal growth kinetics, the analysis of 2D images acquired via optical microscopy facilitates the estimation of growth kinetics through an inline model [2]. Unexpectedly, observations at 8 MPa demonstrated higher growth values than those at 10 MPa. The occurrence of liquid-liquid phase separation, a rare phenomenon, was observed, accompanied by theoretical thermodynamic propositions.

The microfluidic platform is also repurposed as a mini-GAS (Gaseous Anti-Solvent) reactor for the rapid characterization of the $S\text{-}NPX_2{:}BiPY_1$ co-crystal under high pressure [3], thanks to Raman spectroscopy, showcasing its versatility.

In brief, this in-depth study not only broadens our understanding of pharmaceutical crystallization, but also offers a unique perspective on the process under supercritical CO_2 conditions. The fusion of $scCO_2$ and microfluidic technology suggests a potential shift in how we produce pharmaceutical compounds, especially those with low solubility, to increase it. Overall, this study stands out by highlighting the synergy between advanced technology and scientific exploration, providing profound insights into the complex dynamics of crystallization under $scCO_2$ [4].

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Generation of liquid CO_2 jets under atmospheric conditions for cutting applications

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In the field of Industrial Manufacturing, water jet cutting is a well-established process for cutting various materials. In the jet cutting process, water is compressed to some thousand bar before expanding through a nozzle to atmospheric pressure to form a jet. Instead of water, liquid carbon dioxide (CO_2) or other fluids can be used as the cutting medium. This enables residue-free and dry processing of water-sensitive materials, as CO_2 evaporates completely after the process. Cutting with liquid CO_2 is also promising for the treatment of toxic or harmful materials, as no contaminated wastewater is produced.

In the cutting process, liquid CO_2 is first pressurized from about 60 bar up to 3,000 bar. Afterward, it is cooled to the desired pre-expansion temperature, down to minus 25 °C, and directed to the cutting nozzle, where it is expanded to atmospheric pressure. Due to a triple point pressure of 5.18 bar, CO_2 should here only exist in a solid or gaseous state in thermodynamic equilibrium. However, under some conditions, a liquid CO_2 jet can be observed of some centimeters` length. This is especially the case for very small nozzles with diameters below 0.1 mm. After a few centimeters of a coherent liquid jet phase transition occurs, and the jet disintegrates into a spray. So far it has been possible to generate stable liquid CO_2 jets suitable for cutting soft materials such as polymers, metal foils, or natural materials.

In the last few years, CO_2 jet cutting has been subject to intensive research. It has been shown that the generation of liquid jets is only possible under certain conditions. Factors such as pre-expansion temperature and pressure affect cutting properties such as jet stability and length significantly. It is further observed that the same pre-expansion conditions sometimes lead to a stable liquid jet, and sometimes to an immediate jet break-up. However, post-expansion conditions, such as the density of the surrounding atmosphere, also influence the jet break-up. This indicates that there is still a lack of comprehensive understanding for the formation of liquid CO_2 jets.

In our contribution, we aim to identify and narrow down the parameters that enable the generation of liquid CO_2 jets under atmospheric conditions.

Thermodynamic assessment of two-step crystallization occurrence in supercritical fluid

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A consensus is emerging to rule that the classical nucleation theory is not the only pathway of crystallization: recent works [1] proposed the demonstration of two-stage nucleation for different media, liquid-solid, solid-solid and vapor-solid, with possible spinodal decompositions.

In the case of the crystallization of an Active Pharmaceutical Ingredient (API) in supercritical CO_2, a possible way to describe a two-step crystallization mechanism involves the apparition of transient metastable liquid droplets in the vapor phase of the API dissolved in the $scCO_2$, before crystallization. In order to find out under which pressure and temperature conditions such a two-step mechanism could be observed in supercritical conditions, we proposed a thermodynamical modeling of the stability / metastability / instability for {(S)-Naproxen + CO_2} and {(RS)-Ibuprofen + CO_2} vapor binary mixtures at 313K, based on the well-known Peng – Robinson equation of state.

The binary interaction parameters of the PREOS describing the fluid phases have been fitted using solid solubility experimental data from the literature [2,3]. We have compared two different fugacity models for the solid phase: the first one is based on a classical subcooled liquid like approximation, whereas the second one is based on the Lee – Kesler equation. to estimate the sublimation pressure of (S)-Naproxen or (RS)-Ibuprofen in $scCO_2$.

A classical fugacity approach then shows that the binary vapor can condense in a liquid phase, metastable relatively to the solid phase, on the condition for which moderate supersaturation levels are reached. We have shown that the compositions of the predicted metastable liquid phases depend slightly on the pressure.

A study of the curvature of the Helmholtz free energy was then performed, based on Hessian matrices, in order to find the limits of intrinsic stability of the mixtures (the spinodal limits): it shows that the vapor mixtures can become intrinsically unstable at higher supersaturation.

Phase diagrams have been presented with stable, metastable and unstable domains (Figure 1). Finally, we rationalized the probability of occurrence of two-step crystallization by estimating the supersaturation ratio required to reach the metastability and instability limits.

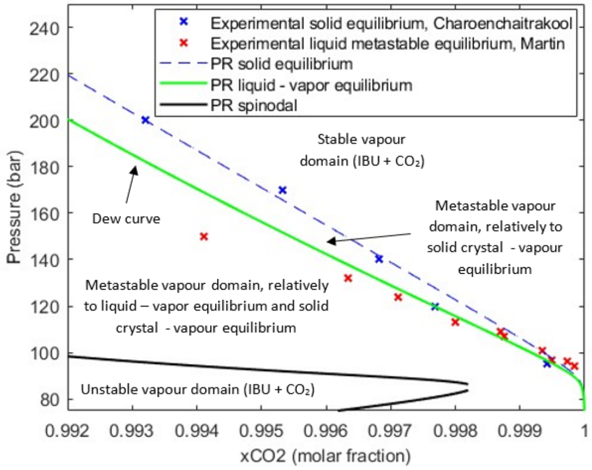

Figure 1: {(RS)-IBU + CO2} mixtures at 313.1K

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Keynote Lecture

Supercritical extraction of *Scenedesmus obliquus* BGP and *Porphyridium cruentum*: assessment of the potential for the algal oils utilization

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The main aim of our work was to evaluate the valorization potential of algal oils recovered from two different algal species. The first was *Scenedesmus obliquus* BGP, a recently isolated Bulgarian strain representative of the freshwater green algae of the genus *Scenedesmus,* while the second one was *Porphyridium cruentum* - a deep-sea red algae [1]. A Soxhlet extraction and an advanced sustainable extraction with supercritical CO_2 ($scCO_2$), either neat or with a co-solvent, were applied to obtain the algal oils.

The effectiveness and efficiency were compared of the techniques and the impact of their specificity (operational parameters, nature of solvents, etc.) on the yield, oils` composition (fatty acid composition from FAME GC-FID analysis and polyphenols from LC-MS/MS analyses), total phenolic content, antioxidant activity. The oils` oxidation stability index (OSI), the Σ hypocholesterolemic fatty acids/Σ hyperechoic polemic fatty acids` ratio (h/H), and the index of atherogenicity (IA) were also calculated additionally.

The study revealed ways to convert the two strains of oils into energy-relevant substances and bioactive metabolites for potential use in various industries.

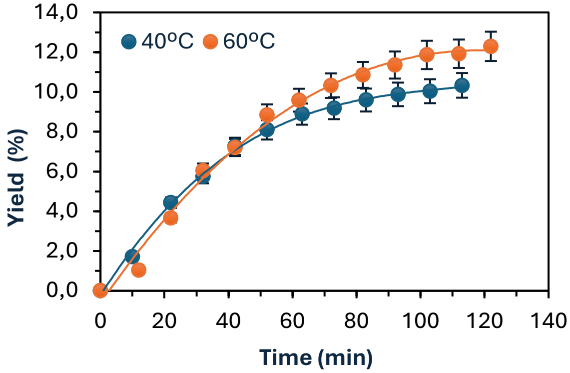

Figure 1: Cumulative extraction yield curves representing the influence of temperature at 400 bars, with $scCO_2$ + 10% cosolvent ethanol on the *S. obliquus BGP* yield, as a function of time.

Thus, both *S. obliquus* BGP and *P. cruentum* oils, regardless of the technique employed to obtain them, can be used to produce biodiesel without the addition of any antioxidants, since they belong to the group of "best oils" with OSI values in the range of 3.89-3.9.

P. cruentum oils can be used as prospective substitutes for fish oils, because they are rich in the nutritionally very important PUFAs—eicosapentaenoic and arachidonic acids, the latter in particularly high amounts. Regardless of the technique used, the PUFA:SFA ratios calculated for P. cruentum oils were higher than 0.4, which defines them as excellent additives for realizing a "balanced diet."

One additional important perspective for the oils of both strains is to use them as additives to human nutrition as potent alternatives to shellfish and fish oils. Such an application is supported by the fact that, in all the examined cases, the h/H indices of both microalgal species oils were higher than, or commensurable (in the worst case), with the range of h/H indices calculated for the shellfish/fish oils, and, hence, more beneficial for human health. Furthermore, *S. obliquus* BGP oils obtained by scCO2+10% ethanol showed the lowest IA = 0.25, making them appropriate for enriching foods or products that could inhibit plaque accumulation and lower the levels of "bad" cholesterol in particular.

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Pressurized Gas eXpanded (PGX) liquid technology as a separation, concentration and drying technique for acid and sweet whey streams

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The Pressurized Gas eXpanded (PGX) liquid technology utilizes CO_2-expanded ethanol (EtOH) to micronize, purify and dry high molecular weight biopolymers simultaneously, producing micro-sized powders and fibrils with low bulk densities and high surface areas [1]. In our previous study, bench-scale (5 L) PGX processing of sweet whey (SW) liquid resulted in powders with protein levels up to 55% wt. and containing micronized amorphous lactose [2]. Changing the flow rate ratios of the PGX fluid (CO_2+EtOH) to the aqueous solution had variable effects on the whey protein secondary structure, affecting the overall physicochemical properties of the obtained whey powders. The objective of this study was to compare the PGX technology to conventional whey processing (ultrafiltration (UF) and spray drying (SD)) using acid and sweet whey feedstocks.

PGX processing involves the co-injection of the PGX fluid with acid (AW) or SW liquid into a pressurized chamber at 100 bar and 40 °C. After injecting the whey, water removal proceeds using CO_2 and EtOH, and, finally, with SC-CO_2, to remove EtOH. All the PGX experiments were performed in duplicate using a 5 L bench-scale system. The concentrated whey powders were characterized in terms of their physicochemical attributes (bulk density, particle size distribution, surface area, and pore size), surface morphology, as well as the compositional analysis, and protein composition and structure (soluble protein content, protein secondary structure, intrinsic protein fluorescence and protein hydrophobicity).

Compared to conventional processing using UF and SD, PGX processing was an effective single-unit operation for concentrating whey proteins and reducing lactose levels. PGX processing of AW and SW concentrated the protein levels by 2.7× and 4.4× to 17% and 57%, respectively. The lactose content was reduced by 25% and 50% in the AW and SW matrices, respectively. The PGX whey powders had 10× lower bulk densities (~20 g/L) compared to the SD powders, with average particle sizes of 11-17 μm, featuring micropores and a larger specific surface area up to 28 m^2/g. The major whey proteins β-lactoglobulin and α-lactalbumin were recovered in both types of whey powders, but bovine serum albumin, immunoglobulins and lactoferrin were only recovered in the SW powders. Milk minerals (Ca, K, Mg, Na, and P) were concentrated together with the whey proteins in both the AW and SW matrices. The AW proteins had similar protein solubilities in water (>70%), regardless of the drying technique (SD or PGX-AW). In low ionic media (0.1 M NaCl), the small amounts of proteins in the PGX-AW had reduced protein solubility, due to a salting-out effect. The micronization of the concentrated proteins, together with the precipitation of amorphous lactose, improved the solubility of SW to > 90% in water and 0.1 M media. The AW and SW protein hydrophobicity values were affected differently by PGX processing. In the AW powders, larger quantities of lactose and ash content increased the hydrophilicity of the proteins. The SW proteins displayed higher hydrophobicity, due to the increased protein-solvent interactions during the precipitation and drying using PGX.

The PGX liquid technology was an effective single unit operation for fractionating, concentrating and drying whey proteins directly from sweet- and acid-type whey, to produce concentrated whey protein powders with unique physicochemical properties, which would not be possible with conventional whey processing techniques.

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Increasing food preservation with supercritical CO_2 drying technology

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Supercritical carbon dioxide (SC-CO_2) drying presents a low-temperature, innovative technology, pivotal for enhancing food preservation and safety. This method, characterized by temperatures ≤45°C and pressures ≤14 MPa, offers a versatile drying solution across various food products, including fruits [1,2], vegetables [3], herbs [4], and meats [5]. The process parameters—temperature, pressure, flow rate, and time—can be optimized easily with an *ad hoc* design of experiments, to achieve efficient drying kinetics, characterized by significant weight loss, moisture reduction, and water activity [6]. Furthermore, SC-CO_2 drying is able to inactivate pathogenic microorganisms after a few minutes of processing [7]. The technology preserves the food's nutritional and sensorial properties, maintaining its quality compared to conventional drying methods [8]. The process has been explored recently within the project entitled "Upcycling pea waste side streams for developing future food ingredients" (UPea, PRIN2022-Prot.20222P5C3E), funded by MUR and NextGenerationEU, aiming to pioneer innovative, zero-waste transformation pathways of pea waste, to produce valuable ingredients for human consumption. The exploration of SC-CO_2 drying, especially in combination with high-power ultrasound, shows promising results in food safety and quality, suggesting a significant potential for industrial scalability in the near future.

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Keynote Lecture

Supercritical fluids in materials science: synthesis, shaping and recycling

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The specific properties of supercritical fluids have been exploited in the field of materials science since the beginning of the 90's [1]. Many solvents have already been used as water, carbon dioxide, alcohols, ammonia, hexane, *etc.*, depending the nature of the targeted phase(s) among oxides, metals, nitrides, sulfides, carbonaceous materials, *etc*. Beyond the choice of the solvent(s), the access to different processes allows playing with homogeneous and heterogeneous nucleation & growth conducting to the synthesis of powders, and to the deposition of nanostructures and continuous film at the surface of a substrate. In other words, the coupling of a rich chemistry to versatile processes is at the origin of the development of the supercritical fluid technology in materials science from basic research to industry applications.

This presentation aims to highlight the main achievements of the use of the supercritical fluids in materials science in the last 30 years. The first part will propose a focus on the correlation between the different kinds of chemical reactions (hydrothermal, sol-gel, redox, thermal decomposition, *etc.*) and the associated nature of materials which have been obtained [2]. The second part will discuss how we can control the characteristics of materials (composition, structure, size, size distribution, *etc.*) depending on the type of process (continuous flow reactor, stirred vessel reactor, cold wall reactor, *etc.*) [3]. This will be illustrated by different examples: i) the supercritical continuous hydrothermal synthesis of geominerals with the industrial development for the production of powders [4], ii) the surface engineering of materials from supported nanoparticles to continuous film, with applications for the protection of materials for positive electrodes for Li-ion batteries [5], and iii) the deposition of functional films on complex substrates as an alternative solution for hard chromium coating replacement. The benefits of the supercritical fluid technology include not only better performances for advanced applications, but also environmental issues associated with the synthesis process. This will be emphasized with the studies performed using LCA approaches coupled with risk assessment ones [6]. This presentation will also highlight the growing axis of development of the supercritical fluid technology in the field of the materials recycling with the following cases: recycling of fibers (carbon, glass and natural fibers) from fiber reinforced polymers (FRP), recycling of critical metals from the new technologies of energy (magnets, batteries), recycling of food packaging and shoes. A focus will be also proposed on the industrial development in this field. A vision of the use of AI in supercritical fluids research will be highlighted as a perspective of this presentation [7].

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Tuning cathode porosity for electrochemical reduction of CO_2 at high pressure

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The development of active and stable catalytic cathodes is critical for advancing electrochemical carbon dioxide reduction into fuels and chemicals from Lab to market. This is a technology with a high potential to contribute to combat climate changes by using captured CO_2, water, and renewable energy [1]. The use of pressures higher than atmospheric pressure to carry out the co-electrolysis of CO_2 and water has been recognized as an important process intensification parameter to increase productivities and energy efficiency [2]. Ongoing work addresses the preparation of aerogels by the sol gel method, and impregnation with zinc and copper metallic particles to be used as cathodes for the co-electrolysis of CO_2 and water to produce syngas at temperatures near room temperature and high-pressure. Ionic liquid-based electrolytes are used to increase CO_2 concentration at the surface of the electrode, and, consequently, productivities, as some ionic liquid families are known to solubilize high amounts of CO_2. Aerogels have been investigated for many different applications, including as catalyst supports, due to their high surface area, stability in gaseous or liquid phases, and efficient transport through large meso and macropores. The present work reports a strategy to tune the pore sizes of the catalytic electrodes by the use of reticulating agents and supercritical CO_2 drying. Productivities and faradaic efficiencies of the porous materials with the different reticulating agents are compared and interpreted in respect to their surface characterization, e.g., BET surface areas and morphologies determined by SEM. The potential of new aerogel-based catalytic cathodes on the efficiency of the electrochemical CO_2 reduction will be discussed, and its impact in fostering supercritical fluids technology through its use in processes for the mitigation of climate changes.

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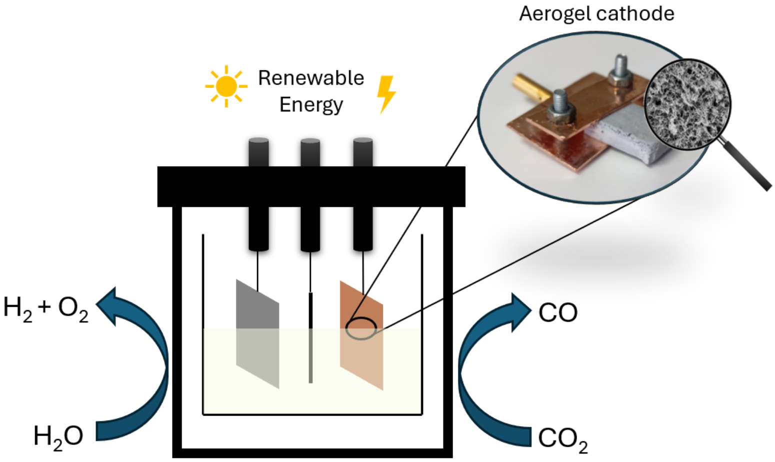

Figure 1: Electrochemical reduction of CO_2

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Foaming hydrogels: a new approach in tissue regeneration

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Tissue Engineering (TE) involves combining scaffolds, selected cells, and biologically active molecules. Many different types of hydrogels have been used for this purpose, as their high water-absorbing capacity makes them ideal for hosting cells and growth factors, and/or mimicking the extracellular matrix. [1] However, some authors report that, in many cases or tissues, a porous matrix is required to provide the physical space necessary for proliferation, differentiation, and cellular migration. [2]

Pluronic polymers are a family of triblock copolymers containing polypropylene oxide (PPO) and polyethylene oxide (PEO) arranged in the PEO-PPO-PEO manner. One of them, Pluronic F127, is studied widely in the field of Tissue Engineering. Pluronic F127 is thermo-sensitive, injectable, biodegradable, non-toxic, and biocompatible. [3]

It is well-known that supercritical CO_2 can diffuse through polymeric matrixes, dropping the Tg. When the pressure decreases and the CO_2 expands, the creation of pores is induced in the polymer, leading to the foaming process. Furthermore,

$scCO_2$ also stands out for its innocuousness, making it a great alternative for processing compounds in this type of application.

In this context, we propose the fabrication of thermo-stable hydrogels based on Pluronic F127 diacrylate, that are photocurable with UV radiation-induced crosslinking. When the hydrogels were formed, they were freeze-dried, and then contact took place with $scCO_2$. The working conditions that were studied were pressure and temperature, which ranged from 100 to 200 bar and 33 to 60 ºC. The characterization of the foamed hydrogels was physical, morphological, and mechanical. SEM, compression testing, 3D scanning, and other techniques were used for this purpose.

The formation of porous polymeric matrices with high water content could be useful in the study of soft tissue regeneration.

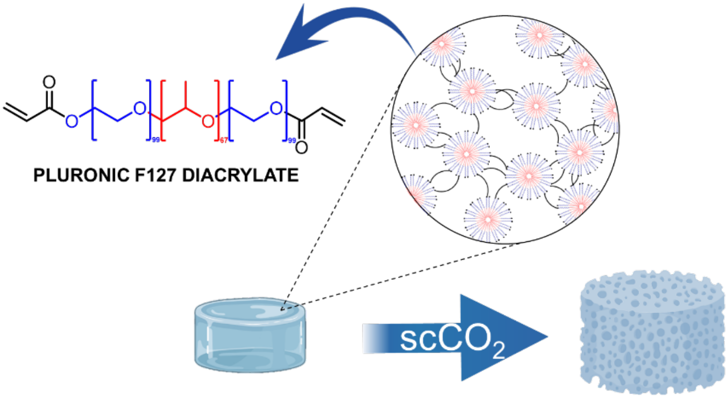

Figure 1: Graphical abstract

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Innovative and flexible synthesis of strontium titanate nanoparticles with new composition in supercritical water/ethanol mixture

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Strontium titanate (SrTiO3) has emerged as a material of significant interest, due to its exceptional properties and versatile applications across various scientific and technological domains. Its unique combination of electrical, optical, and catalytic properties, along with its high chemical stability, has positioned SrTiO3 as a promising material for a wide range of applications [1]. One of its main features is the possibility of having its physical properties tuned by the doping of elements, which can lead to the enhancement or decline of its electronic properties. As an example, it is used frequently as a component for multilayer ceramic capacitors [2], but it can also be used in thermistors, gas sensors, and catalysts.

Currently, extensive research is conducted on perovskite (ABO3) catalysts as the preferred material for oxidative coupling of methane (OCM) [3]. In order to meet the requirements for an application of advanced high-temperature electrolysis

(HTE) based on the electrolysis of water and CO2 and their combined conversion into hydrocarbons, it is essential to have a material presenting mixed ionic and electronic conductivity (MIEC).

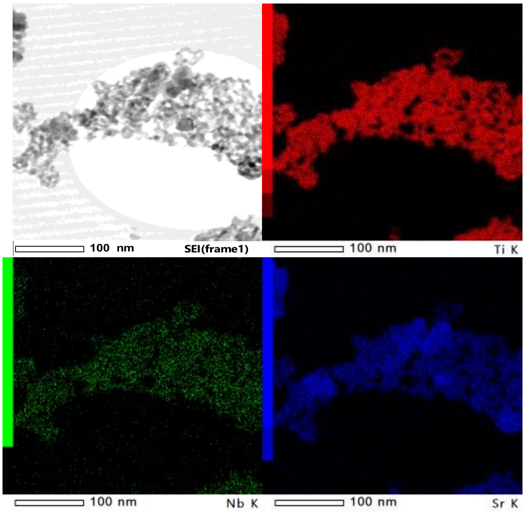

Figure 1: EDS picture of $SrTiO_3$ doped with Niobium with the Sr element in red, Ti element in blue, and Nb element in green.

ICMCB mastered the combination of multi-cationic oxide synthesis and supercritical continuous solvothermal synthesis, leading to compounds never synthesized before using the technique. Deep studies of the accessible substitutions in solid solutions - on the: i) A site, in this case, barium with strontium (BST), and ii) B site, in this case, titanium with zirconium (BTZ)

have been conducted since the first synthesis of BaTiO3 (BT) using this approach with alkoxide precursors [4,5]. Recently, a new synthesis route based on the use of acetylacetonate has been developed, leading to the successful synthesis of undoped and doped Strontium Titanate.

This communication focuses on the synthesis of high-quality SrTiO3 nanocrystals, doped and co-doped on A and B sites with various atomic percents (5% and 10%) and elements (Nb, Y, and Fe), showing the flexibility of supercritical continuous flow conditions. We will detail the physicochemical characterizations of the produced particles and the influence of the doping on their electronic properties.

These observations will be discussed using numerous characterization techniques, such as X-ray diffraction, Raman spectroscopy, ICP-OES, and HRTEM. To summarize, an optimization of the synthesis using the never-before-used precursors, allowed us to synthesize new multi-cationic compounds, which is a first in supercritical continuous solvothermal synthesis.

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Keynote Lecture

High-pressures phase equilibria in carbon dioxide + branched alkanes binary systems

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In recent years, we focused on examining the phase behavior of carbon dioxide (CO_2) and organic substances belonging to different classes that could be applied as physical solvents for carbon capture, CO_2 enhanced oil recovery and oil upstream treatment, or as substrates for clathrate hydrates, motivated by the increased interest in reducing the amount of CO_2 in the environment of the Earth [1-5]. Moreover, the investigation of the phase behavior, thermodynamic or transport properties of carbon dioxide containing mixtures, is essential in many other industries, as well as from a fundamental point of view.

Among the organic compounds studied as second components in carbon dioxide binary systems, despite their potential applications, some classes received less attention, particularly the carbon dioxide + branched n- alkane binary systems [6]. Our careful literature study revealed that, for instance, only for two, i.e., 3-

methylhexane and 3, 3-dimethylpentane, of the eight position (chain) isomers of n-heptane + carbon dioxide binary systems, few equilibrium data are reported [6].

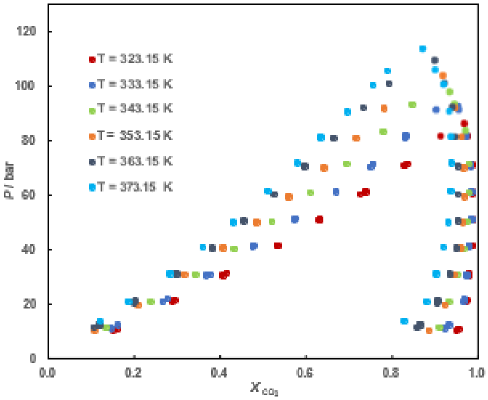

Figure 1: Pressure-composition data for CO2 (1) + 2,3-dimethylbutane (2) at different temperatures

This study presents the experimental results for carbon dioxide + branched alkanes (e.g., Figure 1). Critical curves, isothermal vapor-liquid equilibria, and liquid phase densities were determined experimentally using a high-pressure visual cell with variable volume coupled with an analyzing system. The new experimental data and literature ones, when available, are modelled with several thermodynamic models.

Acknowledgement

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20th European Meeting on
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Phase behavior of Therapeutic Deep Eutectic Solvents (THEDES) in presence of supercritical carbon dioxide

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Deep Eutectic Solvents (DES) are a new type of green solvents formed by mixing two solid substances. Due to strong intermolecular interactions, the melting point of the mixture is low enough so that the mixture is liquid at room temperature. These solvents are finding novel applications in different fields related to Green Chemistry, due to their low vapor pressure, tunability, low cost, and versatility.

Therapeutic DES (THEDES) are a type of DES in which one of the components is a drug with a therapeutic function. THEDES can be combined with supercritical CO_2 ($scCO_2$) to open new possibilities in drug formulation, like its impregnation using $scCO_2$ [1] However, the lack of knowledge of the phase behavior of CO_2 + THEDES systems hinders the development of new technologies. Although there are some examples of CO_2 solubility in DES, only one study of the solubility of the DES, menthol:thymol in CO_2, determined by our group, is available in the literature. [2]

In recent years, we have been devoted to studying the phase equilibria of systems formed by THEDES + CO_2 at high pressure. We intend to understand these systems, and solve many of the unknowns about them, such as: a) How is the solubility of the DES in CO_2 related to that of the single components? b) Does the composition of a DES remain stable under CO_2 pressure? c) How is the phase diagram affected under CO_2 pressure? Our recent findings are summarized in this communication.

We have investigated the binary THEDES formed by L-menthol, thymol and ibuprofen at different compositions. The behavior of these DES with $scCO_2$ at temperatures between 35 and 60 ºC and pressures up to 220 bar was studied using a high-pressure variable volume view cell. Both dew and bubble points were measured. The vapor phase was sampled with a 6-way valve, and analyzed by ^1H NMR. Furthermore, the melting points of the solid mixtures were also determined under CO_2 pressure. Low and high-pressure FTIR was also performed, to obtain information about the interactions between the DES.

We observed that the solubility of DES in $scCO_2$ can be related to the interactions of the components in the binary DES. The stronger they are, the less soluble is the DES. Another interesting finding is that the vapor phase is enriched in the most volatile component, meaning that DES do not behave as pseudocomponents. This behavior is very sensitive to temperature. Some simple excess Gibbs Energy models are proposed, to understand this behavior qualitatively.

The FTIR spectra showed that intermolecular interactions are present between different molecules in the vapor phase, but at much lower extent than in the liquid. The spectra for the liquid fractions at different compositions were also taken, and the maxima can be estimated in associated molecules.

In the same way that single solids do, the melting point of DES is lowered by CO_2 partial pressure. Our results showed that the temperature and position of the eutectic is affected greatly, even by relatively low pressures. This is relevant in the sense that the liquid window of a DES can be enhanced if combined with CO_2.

Acknowledgements

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Liquid or supercritical CO_2 as cooling fluid for cryogenic minimum quantity lubrication

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New innovative technologies require high precision machining of difficult-to-cut materials, such as Inconel or titanium, where standard manufacturing processes show limited productivity. Especially, deep hole drilling is challenging, since the cooling and lubrication fluid needs to be transported to the effective zone at the drill tip. This is done commonly by Minimum Quantity Lubrication (MQL), where compressed air carries a small amount of lubrication oil through thin capillaries inside the drill (sometimes only 0.33 mm in diameter). A disadvantage of this process however is an insufficient heat removal due to the low heat capacity of air. [1] Further, a separation of air and oil due to centrifugal forces in high-speed spindles has been reported, which may lead to process instability. [2] Nevertheless, without MQL, machining of many materials would not be possible at all.

Cryogenic Minimum Quantity Lubrication (cMQL) with liquid or supercritical carbon dioxide instead of air is a promising approach to overcome these limitations. A small amount of lubrication oil is injected into a stream of compressed CO_2, that is conducted internally through the drill, where the pressure drops to atmospheric conditions. The phase transition of the expanding CO_2 provides sufficient cooling of the cutting edge, and the oil precipitates from the gas and lubricates. [1] To ensure stable process conditions and a continuous delivery of lubricant, both components, oil and CO_2, need to be in a single-phase state before being fed into the rotating spindle. Then, the process-interfering separation due to centrifugal forces is no longer possible. [2]

In our studies, we examined the entire cMQL process with compressed carbon dioxide. This includes phase equilibria measurements, solution kinetics during the preparation of the mixture, and, finally, the expansion. We present the p-x behavior of different oils used typically for minimum quantity lubrication and CO_2. Measurements were taken in a range of 65 - 250 bar and at 25 °C, 40 °C and 60 °C using the static analytical method.

The dissolutions kinetics of the oils in CO_2 under application conditions have been investigated optically in the range of 65 - 80 bar and at 25 °C and 40 °C. For the observations, a mixing pipe has been designed, of variable length with transparent sections on both ends, the geometry of which resembles the conditions in a real drilling machine. Pictures taken with a high-speed camera revealed an insight into the flow pattern of the oil and CO_2, before and after the mixing section. It can be observed that, despite sufficient solubility in CO_2, the oils showed different flow behavior and dissolution times. We related the types of mixing behavior to polarity, molar mass and viscosity of the oils, and comment on the consequences for the cMQL-process.

The expansion at the non-rotating drill was analyzed with a high-speed camera regarding the spray behavior. With two cooling ducts of 0.33 mm in diameter at 80 bar, a CO_2 flow rate of 3 g/s was measured, which is already considered high. Since the flow rate of the CO_2 at the given pressure depends on the flow resistance of the cooling ducts, larger channels (in larger drills) would lead quickly to unreasonably high flow rates. This indicates the need for improvement in the drill design.

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Melting point depression of a eutectic mixture under carbon dioxide pressure

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High-pressure phase-equilibrium data may be highly relevant in the design of separation processes, particle formation techniques, or even polymer processing. A measurement device has recently been developed to provide a quick and automated solution for the determination of the solid – liquid transition temperature (melting temperature) in a pressurized atmosphere. During the gradual heating of the vessel containing the sample, its pressure was compared to another, identical cell, which only contained carbon dioxide. The dissolution of the high-pressure medium in the melt, together with the change in the molar volume during the phase-transition induce the differential-pressure signal. The beginning and end of the melting procedure may be determined using the automatically logged data in a similar fashion to high-pressure differential scanning calorimetry. The applicability of the device has been shown in the case of single, crystalline materials. [1]

The investigation of – for example – potential drug delivery systems may contribute to the fields of phase-equilibria and high-pressure particle formation. To assess the applicability of the device for the melting temperature measurements of mixed solids, ibuprofen and myristic acid (C14 aliphatic fatty-acid) were chosen as model molecules. The high-pressure melting behavior has been studied of the two pure compounds and their mixtures at various compositions.

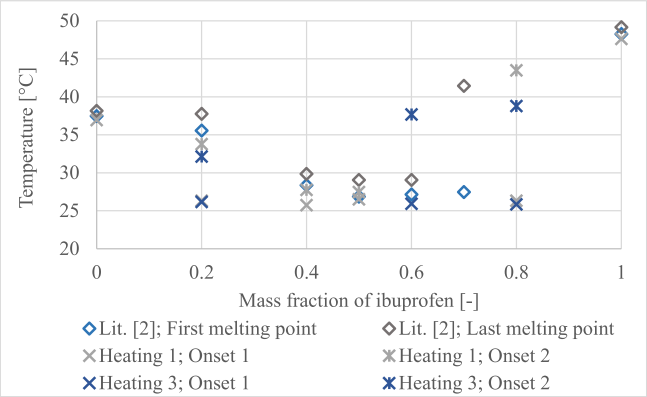

Figure 1: Composition-dependent melting phase diagram of the ibuprofen – myristic acid system under 10 MPa CO_2 pressure

The mixtures of racemic ibuprofen and myristic acid, when molten under carbon dioxide pressure, often showed two different signals, matching the behavior of a eutectic mixture. Literature data were available for comparison [2], but the obtained results showed differences. Despite the experienced melting point depression when starting the measurements at 10 MPa pressure, the eutectic character is still carried by the phase-diagram.

Acknowledgement

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Keynote Lecture

Electrochemical activation of supercritical carbon dioxide

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The transformation of our industrialized society into a sustainable society will be one of the main challenges in the near future. As a defossilized society means the loss of today's most important source of carbon, new sources of carbon must be tapped, in order to continue operating our process engineering and chemical production facilities. One possibility is the direct electrochemical activation of carbon dioxide.

In recent years, the electrochemically catalyzed activation of carbon dioxide under supercritical conditions has been investigated at the Chair of Particle Technology and Fraunhofer UMSICHT. Under supercritical conditions, the formation of hydrogen is suppressed compared to many studies under atmospheric pressure, and the reduction of carbon dioxide becomes the dominant reaction. This leads to high Faraday efficiencies in the formation of low-molecular compounds, such as ethanol, CO, formic acid, etc. In order to achieve high current densities, and, thus, high production rates, high conductivities must be present in the reaction media during electrolysis. These conductivities are particularly difficult to achieve in supercritical carbon dioxide.

This contribution summarizes the results of three doctoral projects. Firstly, the results of the electrochemical conversion of carbon dioxide in a view cell electrolyzer are presented, in which low current densities are achieved. Primarily formic acid is formed, with good Faraday efficiencies but low production rates [1, 2]. In further work, the phase equilibria, and the conductivity of different salts in organic solvents with and without carbon dioxide were investigated, in order to identify systems that can lead to better current densities, and, thus, higher production rates. The experimental results and an initial modeling of the phase behavior and the conductivity of the binary and ternary systems are presented here [3]. Figure 1 shows the results for the system NaI-methanol-CO_2. In a further study, a new reactor design was used, that dispenses with electrolytes completely. With the so-called zero-gap reactor, good Faraday efficiencies can be achieved with significantly increased current densities [4, 5].

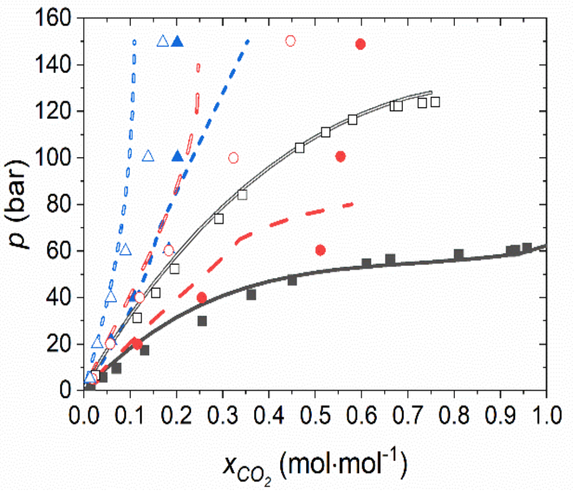

Figure 1: CO_2 solubility in the NaI-methanol electrolyte. Symbols: experimental data. Lines: ePC-SAFT. Solid symbols and fat lines: 298.15 K. Empty symbols and doubled lines: 343.15 K. Black: CO_2 solubility in pure methanol from literature (298.15 K & 343.15 K). Red: CO_2 solubility in NaI-methanol at $\tilde{m}_{NaI}$ = 1 mol kg^{-1}. Blue: CO_2 solubility in NaI-methanol at $\tilde{m}_{NaI} = \tilde{m}_{kmax,NaI}$ = 4.83 mol kg^{-1}

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Cellulose-based packaging material made of wheat straw by combining pressurized water + ethanol and high-intensity ultrasound

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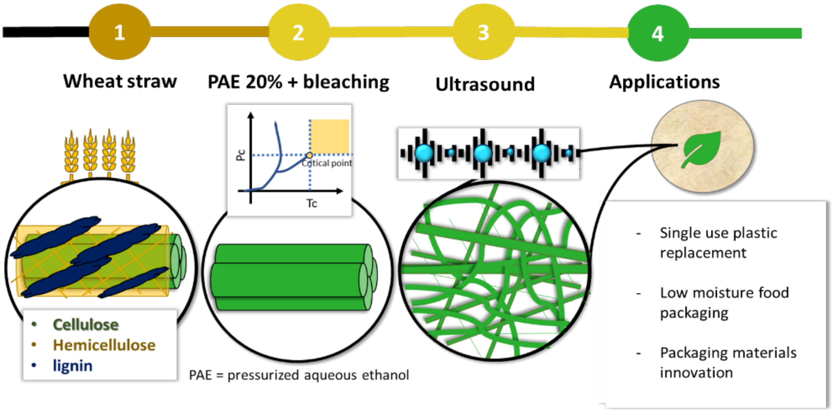

Figure 2: Processing of wheat straw.

Petroplastics are among the most employed materials for food packaging development [1]. However, in recent decades, concerns on the welfare of both society and the environment have increased, requiring a sustainable replacement for petroplastics [2]. Paper-based materials, made primarily of cellulose, represent an appealing alternative to petroplastics [1].

Nevertheless, the conventional treatments for cellulose isolation involve the use of corrosive and toxic solvents [3]. Pressurized fluid (water + ethanol) hydrolysis is a potential sustainable treatment for cellulose isolation. The main objective of this study was to develop a cellulose-based material with potential food packaging applications. Such material consisted of wheat straw hydrolyzed with pressured water + ethanol (EtOH), bleached with alkaline hydrogen peroxide (AHP), and fibrillated with high-intensity ultrasound (HIUS) (Fig. 1). The effects were analyzed of pressurized EtOH-treated wheat straw (180°C, 50 bar, 20% EtOH, 5 mL/min) and bleaching treatment with AHP (1:1.7 v/v, solid-to-solvent ratio of 1:10 w/w for 1, 2, 2.5 h) on the cellulose and lignin contents. Additionally, the cellulosic fibrils` diameter size distribution were also studied after the HIUS treatment (dispersion concentrations at 1 and 2% w/v using nominal powers of 720 W (20 min) and 1200 W (6, 13, and 20 min)) and the water retention value (WRV) of the dried treated samples (treated dispersions were casted on a petri dish and dried at ~35°C overnight). The pressurized fluid hydrolysis treatment increased the cellulose content from 35.62±0.14% to 68.79±4.14%, while decreasing the lignin content from 20.52±0.44% to 14.01±0.19%. Hydrolyzed wheat straw bleached with AHP for 1, 2, and 2.5 h showed no significant difference in the cellulose content. However, the AHP treatment for 2.5 h achieved the lowest lignin content. Thus, the AHP treatment for 2.5 h, which achieved a cellulose content of 85.48±0.65% and a lignin content of 3.71±0.25%, was used for the packaging development. Fibers with a wide range of diameter sizes, both in the nano (<1 μm) and micro (>1 μm) ranges, were obtained after the HIUS treatment at 1200 W for 6, 13, and 20 min. The average diameter size of the former ranged from 21 nm to 30 nm, whereas the latter was 2 μm to 23 μm. In addition, the WRV analysis showed no significant difference among dispersions treated at 1200 W for 6, 13, and 20 min at concentrations of 1 and 2%. This research contributed to the understanding of cellulose isolation from wheat straw employing pressurized water + EtOH hydrolysis and AHP bleaching, along with the fibrillation using the HIUS technology to develop new packaging materials.

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The chemistry of microalgae conversion under HTL conditions

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This communication concerns the conversion of micro-algal biomass under hydrothermal liquefaction (HTL) conditions for biofuel production. Micro-algae are an interesting and diverse biomass. This resource is studied widely for biofuel applications, as well as for the production of biomolecules. The unicellular organisms can grow in various aqueous media in heterotrophic or autotrophic mode. This last mode is based on the photosynthesis conversion of CO_2 with light and some nutrients, in opposition to the heterotrophic mode based on the conversion of carbon from small organic molecules like sugars. The biochemical composition of the micro-algal biomass can be modulated by the available nutrients. Their metabolisms change from species to species, but also, considering only one species, with the cultivation conditions: light, nutrients available, duration, etc., so that a conversion process of this biomass must be able to take into account this variability in the initial biomass composition and the difference in reactivity of the biomolecules. Understanding of the chemical conversion of the biomolecules could be helpful to adapt the process conditions, in order to maximize the conversion yields and the quality of the products. This work is a contribution to this understanding.

The biochemical composition of microalgae can be classified under lipids, proteins and carbohydrates categories. Lipids also includes pigments like chlorophyll. Proteins are giving the wider diversity, with amino-acids of different chemical reactivity. Based on a literature survey [1] and our previous work [2], some conversion routes for each type of biochemical component were stated after a first hydrolysis step. Interactions were also considered between intermediates products. This mechanism allows the establishment of a list of potentially formed molecules. This list was compared with identified molecules in the different HTL products: in the biooil and in the organics of the aqueous phase. HTL experiments were performed with different batches of *Chlorella sorokiniana* and *Chlorella vulgaris* cultivated in different conditions. The biochemical composition analyses of the different microalgae were performed with amino-acids, fatty acids, and carbohydrates profiles. The HTL experiments were performed in a batch autoclave at different temperatures between 300 and 350°C, under the corresponding vapor pressure, for residence times between 0 and 30 min. Analytical tools like 2D gas chromatography coupled with a mass detector was used, as well as liquid chromatography coupled with a QTOF mass detector. Some quantifications were also performed by an FID detector for different residence times. The identification of molecules allowed to validate or invalidate postulated conversion routes from the initial biomass composition to the final products. This work resulted in the proposition of a comprehensive conversion mechanism for micro-algae biomass based on its biochemical composition, and giving a description of compounds recovered into the different HTL products: biooil, organics in the aqueous phase, biochar and gas.

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The *Hohenheim* hydrothermal biorefinery: production of a platform chemical and phosphate fertilizer

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Crops build-up chemical structures, which can be used as substitutes for fossil-based products. Nutrients and the amount of carbon required for humus formation are returned to the field, or remain there. This approach, known as the circular or bio-economy, is implemented in biorefineries connected closely with agriculture [1].

Cellulose, inulin and other carbohydrates made up of C6 sugars can be converted to 5-hydroxymethylfurfural (HMF) (Fig. 1). HMF is regarded as one of the most important platform chemicals of the bioeconomy. It can be used to produce beverage bottles (PEF), food packaging, fibers for car seats, nylon for stockings, sportswear, car parts, etc. [1]

Various biomasses can be converted into carbon materials by carbonization processes. In the case of dry biomass, this is done by using the so-called "slow pyrolysis". Hydrothermal carbonization is preferred for wet substrates. In both cases, the chars obtained can be activated subsequently by different methods [2].

Especially interesting is the hydrothermal carbonization (HTC) with separation of phosphate known as Struvite. The *Hohenheim* process is one of the few that is able to extract phosphate from the solid phase of sewage sludge or digestate to approx. 80 %, as Struvite [3].

HMF formation and HTC are conducted in liquid water at increased pressures, above the vapor pressure. The ionic product is increased compared to liquid water at ambient conditions. As a consequence, reactions catalyzed by acids and bases have increased reaction rates. This means here that carbohydrates in biomass are hydrolyzed fast in sugars, mainly glucose and fructose. The fructose reacts to HMF easily. This is an intermediate compound, and a very important platform chemical. Secondary char by hydrothermal carbonization is formed by further polycondensation. The chars formed by this process are called hydrochar.

Lignin and partly crystalline cellulose are reacting via the elimination of small compounds (CO_2, H_2O), and not via solved intermediates like HMF. This reaction is similar to dry pyrolysis.

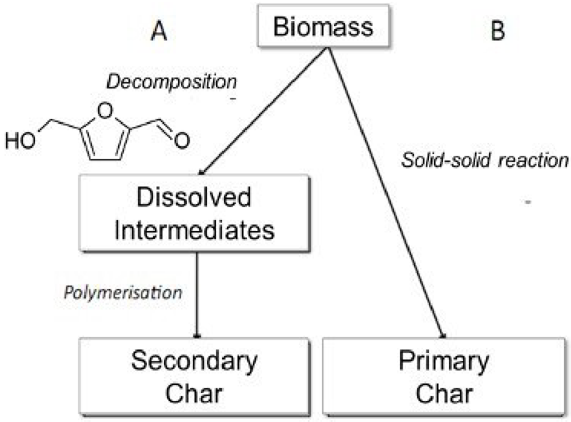

Figure 1: Hydrothermal reaction of biomass to HMF and consecutively to hydrochar. [4]

Like the carbohydrates, all kind of phosphates can be hydrolyzed and solved. The phosphates are precipitating again, but as acid-soluble ortho-phosphates. By leaching, pH-change and the addition of Magnesium salts, the phosphates can be precipitated as Struvite ($MgNH_4PO_4$). The NH_4-ion also comes from the biomass. Struvite is a well-known slow-release fertilizer.

The production of HMF (including separation and cleaning) is conducted on the bench-scale as part of a small pilot plant. Also, a small pilot exists for the HTC with phosphate recovery. The hydrochar can be converted further to activated coal or advanced carbon materials, for example, for electricity storage devices.

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Keynote Lecture

Flow modelling and high pressure systems design

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Understanding non-Newtonian mixing is a key challenge, particularly when attempting to synthesise nanomaterial in continuous flow hydrothermal or solvothermal systems. Poor mixing can lead to uncontrolled particle formation and/or blockages, or the formation of poor-quality materials. We have been working for a number of years on how standard high-pressure fittings can be assembled to create efficient systems, from initial design stages (e.g., the equivalent of paper-based design) through to 3D rendering of actual systems. This can aid the ordering of the correct parts, as well as the assembling of safe and optimised systems.

However, regardless of how these fittings are used, they can create unexpected flow dynamics, particularly with multiphase systems where there are solids (particulates) flowing in sub-, near- or supercritical fluids. In order to model how mixing is impacted, and how blockages can arise, a novel set of techniques have been used to simulate fluid flow through high pressure fittings. This approach used a Perspex model of a Swagelok® reducer, clamped vertically in front of a photographic light panel, and the camera was mounted to a clamp stand in front of the model. 75% isopropanol, 0.5% wt SDBS and 0.2g of 106-150μm carbon particulates was set atop a hotplate stirrer, and stirring was started at a speed sufficient to prevent any settling,

Figure 1 illustrates the equipment and flow of fluid through the reducer model. Slow motion video capture allowed the movement of particles to be tracked.

Figure 1: A Perspex based flow visualisation approach

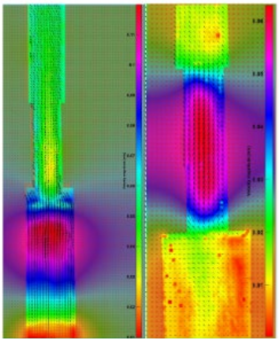

Figure 2: Heat map of velocity profiles across a reducer fitting

Figure 2 shows a heat map of velocity magnitude across the simulated reducer with overlaid vector arrows. There is a hotspot of high velocity magnitude near the centre of the lower chamber, with lower velocities being exhibited in the narrow channel and outlet area towards the top of the reducer. Figure 2 (Right) shows a heat map of velocity magnitude across the reducer with overlaid vector arrows. The largest velocity magnitude is exhibited in the centre of the narrow reducing section. There is evidence of vortex formation and stagnation in the lower section of the reducer, along with possible channelling due to a bias in vector direction to the left. This has implications on the potential for blocking around the entrance into the reducer pipework. This approach has been used for a number of fittings, to understand the impact on residence time and mixing dynamics. This approach can be 'additive', where multiple fittings are compounded to create a whole reactor system, to assess the combined potential for blocking, as a result of particulate recirculation and back mixing.

This paper will present how the design, from initial ideas through to final build, can be visualised, as well as how fittings can be modelled to understand why particle quality is impacted by the cascade of high pressure fittings from initial pumps through to the back pressure regulator.

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Melting and crystallization temperatures and foaming of poly(ɛ-caprolactone) in CO_2 and N_2, and fluid-induced crystallization during foaming

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Melting and crystallization temperatures of Poly(ɛ-caprolactone) (PCL) in carbon dioxide and in nitrogen have been determined using High-Pressure Torsional Braid Analysis (HP-TBA). The technique involves an inertial mass suspended from a polymer-impregnated glass braid in a high-pressure chamber that is subjected to an initial oscillation [1]. The resulting oscillations, which are represented as decaying sine or cosine functions, are analyzed for changes in the frequency, and the period of the oscillations that accompany changes in the rigidity and the damping of the polymer as a function of temperature or pressure. As the transition temperatures are approached, mechanical damping goes through a maximum, which is accompanied with a significant change in relative rigidity.

Experiments are typically carried out in a temperature-scan mode while the polymer is exposed to carbon dioxide or nitrogen at selected pressures. The system is heated at a controlled rate up to a target temperature while recording the oscillations, from which the melting transition temperature (Tm) is determined. Then the system is cooled, while again monitoring the oscillations, from which the crystallization transition temperature (Tc) is identified. The pressure is maintained constant during both the heating and cooling stages with the aid of a programmable syringe pump.

Even though PCL melting temperature and its depression in carbon dioxide have been reported previously [2], no published information could be found on how the melting point is altered in nitrogen. Similarly, data on the crystallization temperature of PCL in either carbon dioxide or nitrogen are not well documented. The present results show that, in contrast to carbon dioxide, exposure to high pressure nitrogen does not lead to a depression of Tm or Tc. Instead, these transition temperatures tend to increase, which is indicative of a greater influence of hydrostatic pressure as opposed to the diluent effects in nitrogen. Hydrostatic effects also become observable in carbon dioxide, but only at high pressures, in this case, above 100 bar, as reflected by a slight upward turn in the lowered Tm values. The present study indicates that, along with the hydrostatic effect, another factor may play a role in the trends observed in the melting temperatures, which is the solvent-induced crystallization that tends to increase the melting temperature.

Knowing the melting and crystallization temperatures of a polymer exposed to compressed carbon dioxide or nitrogen provides a rational approach to their foaming in these physical blowing agents. In this presentation, we will report on the Tm and Tc of PCL in CO_2 or N_2 at pressures up to 125 bar. We will also present the results of foaming of PCL at selected pressures and temperatures in the interval between the Tc and Tm of the polymer in the presence of CO_2 or N_2. DSC analyses of the foams will also be presented, to provide insights on the fluid-induced crystallization that PCL undergoes in these compressed fluids.

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Experimental determination and modeling of the diffusion coefficient as a function of the composition of binary mixtures of CO_2 and ethanol

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Compressed carbon dioxide (CO_2) is often used in high-pressure process engineering as a solvent, precipitant, extraction-, reaction-, or drying agent. The mass transfer in such processes can be governed by diffusion. For binary mixtures consisting of CO_2 and organic solvents such as ethanol, experimentally measured diffusion coefficients can be taken from the literature for conditions of "infinite dilution", both for high pressures and for various organic solvents. For mixture compositions between the limits of infinite dilution $0 < x_{CO2} < 1$ the dependence of the diffusion coefficient on the mixture composition is taken into account by using simplified correlations, which are often based on experiences from incompressible mixtures. For compressible mixtures under pressure, these correlations are not supported by experimental data. An experimental method for the determination of composition-dependent diffusion coefficients and the calculation of them using a thermodynamic model will be presented in this paper.

The determination of the diffusion coefficients in binary mixtures consisting of CO_2 and ethanol at temperatures between 308 K and 333 K and pressures between 8 MPa and 12 MPa is carried out as follows: *In situ* Raman spectroscopy is utilized for the spatially and time-resolved determination of compositions in transparent, highly porous materials during mass transfer of the pore fluid [1]. Using a region-of-interest approach, the diffusion coefficients of a mass transfer model, which takes into account not only diffusion, but also the composition-dependent excess volume of the binary mixture by means of a coordinate transformation, are fitted to the experimentally measured compositions.

These experimentally determined binary diffusion coefficients are compared with modeled diffusion coefficients: Unsaturated densities of the non-ideal mixture were measured as a function of pressure and temperature [2]. The nonrandom hydrogen bonding (NRHB) theory introduces a compressible lattice model, which is occupied by molecules of each compound, as well as holes, in order to describe density changes arising from temperature and pressure variations [3]. Self-association of ethanol is accounted for by the hydrogen bonding contribution. The single, temperature-independent binary interaction parameter of the NRHB model was fitted to the densities. The thermodynamic model is applied to determine the composition-dependent activity coefficient. A thermodynamic correction factor is calculated on the basis of the activity coefficient. This factor determines the deviation between the ideal and the real diffusion coefficient as a function of composition. The ideal diffusion coefficient is determined on the basis of the simplified Vignes correlation, using known measurement data of the diffusion coefficient at infinite dilution.

Both the experimentally determined diffusion coefficients and those determined by thermodynamic modeling showed large differences to the simplified correlation for the description of composition-dependent diffusion coefficients.

Acknowledgement

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Interfacial properties of ethanol, water and their mixtures in contact with stainless steel under dense CO_2 atmosphere

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The necessity to characterize interfacial properties under dense CO_2 atmosphere has been identified for discussing their influence on numerous processes involving supercritical CO_2, such as on the hydrodynamics in counter-current packed columns [1]. Moreover, the interfacial tension and the contact angle measurements enable the use of both the Young-Dupré equation and the Zisman plot method, which remain applied scarcely for systems under dense CO_2 atmospheres. Hence, interfacial tension and contact angle measurements of various liquids (water, ethanol and three of their mixtures containing 25, 50, and 75%w/w of ethanol) were realized under CO_2 atmospheres up to 15.1 MPa at 313 K and 333 K on two types of stainless steel. This system has been identified as a good model system, and also of industrial interest [2,3]. The experimental set-up and the measurement procedures of interfacial tension and contact angle are described in published articles [2,3]. In a first step, the results obtained allowed to discuss the evolution of the interfacial tension and the contact angle through the studied parameters (pressure, temperature, ethanol composition and type of stainless steel). In a second step, these

measurements constituted the database used in the following parts of this work. Since the solid-liquid interfacial tension is not directly measurable, the work of adhesion between the liquid and the solid within a dense CO_2 atmosphere allows a characterization of this interface. The work of adhesion was calculated using the Young-Dupré equation:

$$WSLF = \gamma LF \cdot (1 + Cos\theta)$$

where $WSFL$ is the work of adhesion, γLF is the liquid-fluid interfacial tension, and θ is the contact angle. Hence, evolution of the work of adhesion through pressure, temperature, type of stainless steel and ethanol composition is presented in accordance with the studied domain for interfacial tensions and contact angles. Finally, the work of adhesion was used in the calculation of a new dimensionless number called factor of adhesion, which compares the gravitation and the adhesion forces. In addition, the solid-fluid interfacial tension is not directly measurable, and the critical surface tension of the solid is often used as a substitute. The critical surface tension of the solid is determined graphically using the Zisman plot method. This method was used rarely for systems under dense CO_2. Nonetheless, the Zisman plot method appears to be applicable to the series of ethanol-water mixtures on stainless steels under CO_2 atmospheres up to 7.5 MPa, while no determination was reliable for higher pressures. The critical surface tension of both stainless steels was then estimated at 313 K and 333 K, and up to 7.5 MPa. These results show good consistency with the available literature, despite measurement uncertainties.

This work is the synthesis of the characterization work of interfacial properties of the system CO_2/ethanol- water/stainless-steel. On the one hand, this work brings new experimental data, and allows to discuss the application and the limitation of the well-known methods used in interfacial science for systems involving a dense CO_2 phase such as the Young-Dupré equation and the Zisman plot method. On the other hand, such experimental data are useful in the development of numerous processes involving a supercritical fluid phase.

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Keynote Lecture

SuperSomes process used for the production of antioxidant nanoniosomes

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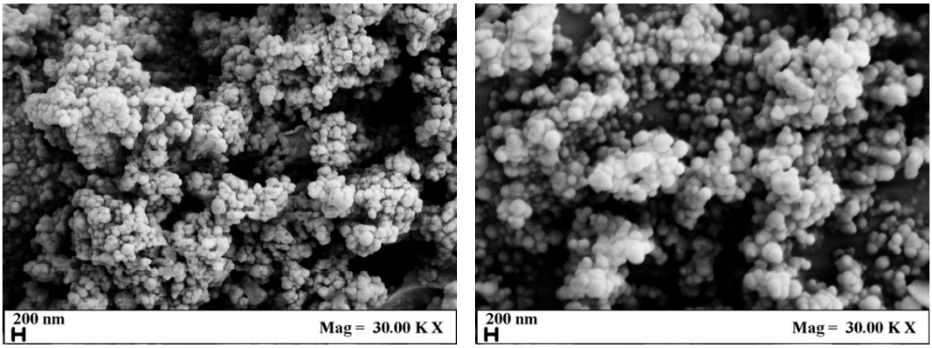
The SuperSomes process was used for the production of nanometric niosomes loaded with ascorbic acid, a model antioxidant compound. The aim of the work was to test this innovative and continuous process, assisted by supercritical CO_2 [1,2] for the production of controlled size vesicles, characterized by a high drug encapsulation efficiency and the ability to protect it from thermal and environmental degradation. The SuperSomes operating conditions were fixed at [1,2]: 100 bar pressure, 40 °C temperature, 6.5 g/min CO_2 flow rate, and 7 mL/min water flow rate. The non-ionic compounds selected for the formulation of niosomes were Span® 80 (HLB= 4.3) and Tween® 80 (HLB= 15), in a volume ratio equal to 90:10 (total surfactant concentration in ethanol equal to 20 mg/mL). Ascorbic acid was dissolved in the aqueous phase using a 5% w/w concentration with respect to the total surfactant concentration.

The obtained niosomes were analyzed by DLS and SEM to determine their mean diameter, Z-potential and morphology; whereas, the drug encapsulation efficiency and antioxidant activity were measured by UV-Vis spectrophotometry and DPPH assay, respectively.

The results demonstrated that spherical nano-niosomes were produced successfully by SuperSomes, as shown in Figure 1. In particular, empty niosomes were characterized by a mean diameter of 171 ± 65 nm (PDI= 0.261; Z-potential= -25.9 ± 3.0 mV); whereas, niosomes loaded with ascorbic acid showed a mean diameter of 180 ± 72 nm (PDI= 0.367; Z-potential= -20.3 ± 2.5 mV).



(a) (b)

Figure 1: SEM images of empty niosomes (a) and niosomes loaded with ascorbic acid (b).

The drug encapsulation efficiency was equal to 95%; a DPPH assay demonstrated that the bioactive compound preserved up to 93% of its antioxidant activity after processing.

Therefore, this work proved further the capacity of the SuperSomes process to produce in a continuous and sustainable way nano-vesicles that can be used for high added-value industrial applications. Future studies will be focused on the investigation of other surfactant formulations and process operating conditions, to assess the effect on the mean size and morphology of the produced niosomes.

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Sterilisation of alginate-gelatine aerogels through an integrated high-pressure and supercritical CO_2-based process

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The application of biopolymers in tissue engineering has witnessed a decline assigned to the physicochemical degradation occurring during conventional processing/sterilisation methods [1]. Conventional sterilisation methods (steam heat; γ-radiation), compromise the physicochemical/mechanical functional properties of various natural polymers, but may also leave undesirable residues, as is the case with ethylene oxide sterilisation (EtO). This study explores the use of supercritical carbon dioxide ($scCO_2$) as an alternative method for sterilisation/disinfection of biopolymer-based materials. Despite its effectiveness in microbial inactivation, $scCO_2$ has not yet been approved by European regulatory bodies as a sterilisation method [2].

Additionally, $scCO_2$ can be used as a drying method for aerogels [3]. Yet, it requires a lengthy processing step, the solvent exchange, to convert a hydrogel into an alcogel. High-pressure solvent exchange (HPSE) can be used to reduce the duration of this step significantly by improving mass transfer between the phases [4]. The integration of HPSE, $scCO_2$ drying, and $scCO_2$ sterilisation in a single process enables optimised and faster preparation and sterilisation of biopolymer-based aerogels, with lower associated costs. The integrated method was used in this study to produce alginate-gelatine sterilised aerogels (Figure 1). FTIR and DSC analysis demonstrated that the sterilisation process did not affect the chemical and thermal properties of the aerogels adversely. However, the mechanical properties and BET surface area were impacted. Despite these changes, the sterilisation efficiency was confirmed by a significant reduction in contamination, achieving a SAL-10^{-4}. The sterilised alginate-gelatine aerogels demonstrated no *in vitro* cytotoxicity, and showed improved wound-healing properties, as evidenced by the fibroblast Scratch-Wound assay. In conclusion, the integrated process generates sterile biopolymer-based aerogels successfully, suitable for biomedical and tissue engineering applications.

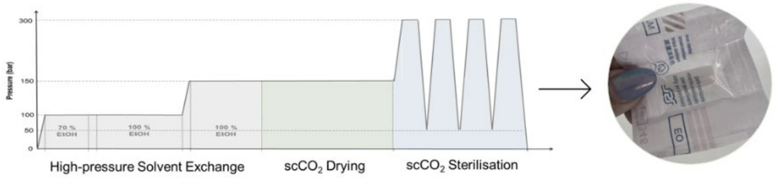

Figure 1: Integrated high-pressure and $scCO_2$ process for the preparation of alginate-gelatine sterilised aerogels.

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Enhancing sterilization efficacy: evaluating bacterial resistance to supercritical CO_2 for sterilization of implantable medical devices

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Hospital-associated infections pose a significant challenge in healthcare, with prevalence ranging from 5-10% in developed regions to 40% in some developing countries [1, 2]. A substantial portion of these infections arises from contaminated implantable medical devices [3, 4]. While conventional sterilization methods work for many devices, they are inadequate for thermosensitive products like polymeric implants. Ethylene oxide gas sterilization, used for about 50% of global implants, has drawbacks due to the gas residues' carcinogenic nature [5]. Hence, there is a pressing need to explore alternative sterilization methods, especially for implants, to minimize infection risks.

Supercritical fluid technology, especially with supercritical CO_2, offers a solvent-free processing advantage for medical devices, distinguishing it from conventional methods. To assess sterilization efficiency, the resistance was evaluated of endospore-forming bacilli and nosocomial pathogens such as *Klebsiella, Escherichia coli,* and *Staphylococcus*. Glass slides simulated device surfaces for contamination experiments; bacterial or spore aliquots were deposited onto sterile glass slides, and dried in a desiccator for 45 minutes at room temperature. Sterilization was conducted under specific conditions (Figure 1): 110 bar, 20 minutes hold time at 40°C, with H_2O_2 (hydrogen peroxide) as an additive.

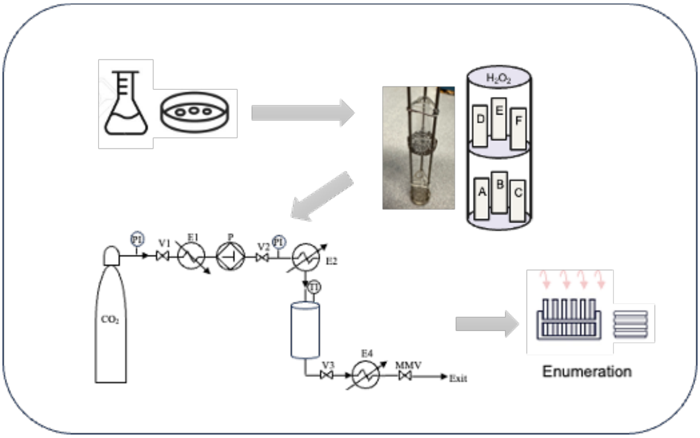

Figure 1: Experimental process.

Under these conditions, the spore counts of *Bacillus subtilis* 168 and *Bacillus amyloliquefaciens* was reduced by more than 9 log (CFU (colony forming units)/mL). These two strains differ substantially in their heat and pressure resistance, owing to the presence of *spoVA*^{2mob} in *B. amyloliquefaciens,* suggesting that *spoVA*^{2mob} does not impact resistance to supercritical CO_2 with H_2O_2 under these conditions. Dry vegetative cells of *E. coli* AW1.7, *E. coli* MG1655 and *Staphylococcus aureus* ST70 were also eliminated effectively, irrespective of the presence of the transmissible locus of stress tolerance, which mediates resistance to heat and pressure. Conversely, cells counts of dried *Salmonella enterica* Heidelberg and six *Klebsiella pneumoniae* isolates from chlorinated wastewater, decreased only by 2 to 3 log (CFU/mL) after treatment. The wastewater isolates of *S. enterica* were previously shown to resist oxidative stress and several pathogen intervention technologies after drying [6]. Even an increase of the H_2O_2 concentration to 1000 ppm did not enhance the reduction of cell counts. This study thus did not identify supercritical CO_2 conditions that eliminate all relevant target organisms, but allowed the identification of resistant organisms as targets for future studies on the sterilization efficacy of supercritical CO_2.

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Thermal investigations of supercritical CO_2 jet impingement and its cooling applicability in a machining context

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In the context of safer, more cost-effective, and environmentally friendly machining methods, supercritical carbon dioxide (sCO_2) emerges as a promising solution [1], particularly in drilling operations involving hard material with low thermal conductivity like titanium alloys (TA6V). The dual role of the sCO_2 jet needed in this type of machining assistance has been the focus of interest, where enhancing chip removal through lubrication and improving cooling efficiency underscores its potential to extend tool life and reduce cutting forces [2]. However, a consolidated understanding of the optimal sCO_2 jet parameters for drilling remains unavailable and difficult to determine. This study focuses on the thermal transfer properties of sCO_2 jet impingement, exploring various parameters in order to optimize machining processes.

This study proposes an experimental methodology to explore the thermal dynamics of supercritical CO_2 (sCO_2) jet impingement on a heated thin titanium plate. The cooling ability of the jet is determined through the space distribution of the heat transfer coefficient (HTC). The cooling process and the behavior of the sCO_2 jet, including the observation of snow formation were documented utilizing infrared thermography and high-speed imaging. In-process parameters, such as nozzle-to-plate distance, jet angle of incidence, and sCO_2 initial temperature and pressure were varied systematically, in order to quantify their impact on the cooling efficiency. This comprehensive analysis intends to highlight the critical parameters for optimizing sCO_2 jet impingement in machining processes, and helps understanding the phase transitions phenomena inherent to the sCO_2's cooling mechanism.

The outcomes of the study provide a clear path for improving machining cooling operations. It is shown that the sCO_2 jet exhibits a similar order of magnitude of the HTC to water-based coolant. However, it is also shown that the affected area is smaller than surfaces involved in liquid coolant, and therefore the optimization of the cooling process needs to be studied further, due to the complex structure and nature of this jet. A critical aspect of the results lies in the significant influence of nozzle-to-plate distance on cooling efficiency, with closer proximities improving HTC values markedly, but also decreasing the affected area. Additionally, the angle of jet impingement and the initial temperature and pressure of the sCO_2 dictate the cooling performance of the jet critically, suggesting that a precise control over these parameters can lead to optimized cooling effects. Surprisingly, increasing the mass flow rate did not show a linear and continuous correlation with the heat transferred between the jet and the plate. The production of solid carbon dioxide particles seemed to alter the cooling ability of the jet. However, the exact influence on heat transport and snow nature requires additional investigations.

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Keynote Lecture

Lignin conversion in fuels and chemicals: role of sub- and supercritical fluids

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Because of current global warming, the production of carbon-neutral fuels and chemicals from renewable and sustainable resources has received considerable attention recently. Lignin, which is an aromatic polymer that is present abundantly in lignocellulosic biomass, is considered a highly promising resource for producing renewable fuels and chemicals. However, the intrinsic recalcitrant of technical lignin and complex lignin structures, which are dependent on lignin isolation methods and types of lignocellulosic biomass, make it difficult to develop a generalized conversion technique. This talk consists of three parts; traditional hydrothermal and solvothermal liquefaction of lignin will be discussed first [1–7]. Almost complete conversion of biomass into liquids and gases could be achieved under supercritical ethanol conditions. The second part of this talk will cover catalytic lignocellulosic biomass fractionation to produce aromatic monomer-enriched lignin oil and solid cellulose [8–10]. An almost theoretical maximum of lignin-derived monomers could be produced during the catalytic lignocellulosic biomass fractionation. The lignin-derived oil containing monomers, dimers, and oligomers could be used as a feedstock for producing sustainable aviation fuels. Lastly, the possibility will be covered of using lignin as a carbon source to produce renewable electrodes for next-generation sodium-ion batteries [ref].

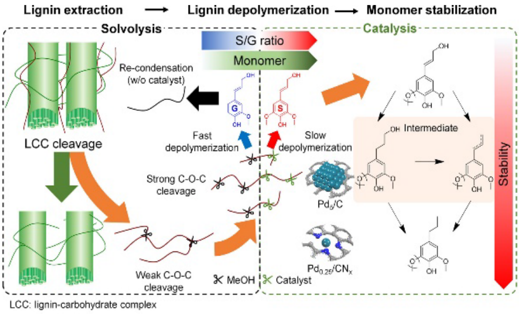

Figure 1: Catalytic fractionation of native lignin

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Mechanism and kinetic study of hydrothermal recycling of PET/PE multi-layer film using a semi-batch system

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The overuse and improper disposal of plastics have led to a severe environmental problem with a global concern [1]. Plastic wastes not only clog landfills and oceans, but also harm wildlife and pose a threat to human health. Most plastic wastes are disposed of by incineration and landfilling. In contrast, recycling is a more environmentally friendly approach to managing plastic waste and mitigating its negative impact [2]. Among current plastic recycling methods, the processes of material and chemical recycling, with products of regenerated polymers and depolymerized monomers, respectively, can shorten the route from plastic waste to plastic products, in line with the needs for a green circular economy and closed-loop recycling of plastics [3].

Multi-layer plastic films, made by laminating different types of plastics into a single film, have a wide application in various fields. PET/PE (PET: Polyethylene terephthalate; PE: Polyethylene) films possess a market share of more than 50% in multi-layer plastic films. The recycling of PET/PE films could make a substantial contribution to carbon recycling, and is vital in mitigating the environmental impact of plastic waste and achieving the global goal of reducing plastic packaging. However, it is challenging to recycle PET/PE films through traditional methods, such as material recycling via melting extrusion, reformation, and pelletization, because the recycled products are usually a complex blend [4], thereby limiting further utilization.

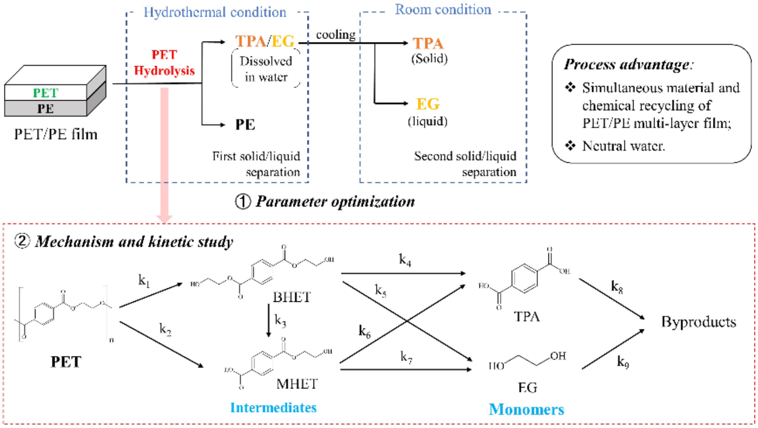

Figure 1: Diagram of hydrothermal recycling of PET/PE film and the research targets in this work.

In this study, we proposed a hydrothermal process for recycling PET/PE films. PET can be hydrolyzed to monomers of terephthalic acid (TPA) and ethylene glycol (EG). Using a hydrothermal semi-batch system equipped with two filters, PE, TPA, and EG were collected separately, indicating the simultaneous material and chemical recycling of PET/PE films was achieved firstly. At 300 °C and 10 MPa for 60 min, PET conversion reached around 100%, and a TPA yield of 83.0% was obtained with a high TPA purity of 96.1%. The effects were investigated of reaction temperature, pressure, holding time, water flow rate, and residence time on PET conversion, TPA yield, EG yield, and TPA purity. Furthermore, an in-depth mechanism and kinetic study was conducted, as shown in Figure 1. This research opened up a new and sustainable pathway to recycle multi-layer plastic films in both labs and industry.

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Syngas production from organic fraction of municipal solid waste by supercritical water gasification

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Rapid population growth increases waste generation and energy consumption. According to the World Bank Report, global waste generation is estimated at 2,200 million tons annually by 2025, and energy demand is expected to increase sixfold following the current trend [1]. Nowadays, the Organic Fraction of Municipal Solid Waste (OFMSW) are either disposed in landfills or, at most, used for anaerobic digestion or composting, although, considering that food wastes consist mainly of carbohydrates, lignin, proteins, lipids, and organic acids, there is potential to valorize their organic content within a circular economy framework. In this context, sustainable waste management becomes crucial for generating revenue through the conversion of waste into energy, material recovery, valuable substances, and recycling methods. Various technologies have been devised to transform biomass and other waste into environmentally friendly energy sources, encompassing fuel, heat, electricity, and organic fertilizer [2,3].

The supercritical water gasification (SCWG) process involves the conversion of organic compounds to gaseous products in an aqueous system, under conditions above its critical point (i.e., 374 °C and 22.1 MPa) [4]. Beyond the critical point, both the density and viscosity decrease, enhancing the diffusivity and reducing transport limitations. Moreover, the reaction kinetics increase, because of the high temperatures, favoring cracking of heavy organic compounds to light ones [5]. A high-quality syngas is obtained as a result of the gasification of OFMSW. To minimize the cost-effectiveness of SCWG, diverse heat sources can be employed, including renewable sources. Among them, solar thermal energy appears the most suitable. In the context of this study, the heat necessary for promoting SCWG is supplied by Fresnell solar thermal collectors modified and adapted for high-pressure fluids and stored in an innovative heat-storing system. In this way, the exploitation of two different renewable sources, as the solar thermal energy and the solid wastes, can reduce the operational costs significantly, encouraging the application of this technology at an industrial scale.

In the present study, a 500 mL lab-scale reactor was used to investigate the gasification of OFMSW with supercritical water. A real organic waste was preliminarily minced, homogenized, and, finally, diluted with water. The gasification tests were carried out at 400°C and 25 MPa. At the end of the test, the products were analyzed, to determine the composition of the produced syngas and liquid/solid residues. The effects were investigated of the reaction time and of the water/waste weight ratio on the final product. The results showeed the production of a good-quality syngas with a high hydrogen percentage (up to 30% mol/mol) and with an H_2/CO ratio around 4, demonstrating that the SCWG of OFMSW could represent a feasible method for syngas production.

The present work was carried out within the framework of the "SUNGAS" project, Action 1.1.5 of the P.O. F.E.S.R. Sicily 2014-2020.

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Process development for catalytic cyclohexene oxide copolymerization with scCO$_2$

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Polycarbonates, a crucial and commercially successful class of polymers, have gained significant attention in studying their synthesis using supercritical CO2 (scCO2). This work highlights the use of scCO2 as a comonomer and solvent for the copolymerization reaction with cyclohexene oxide (CHO), employing an Fe- based catalyst [1] alongside PPNCl as a co-catalyst (Figure 1). Previous research has proven that the initial physical state of the system affects the efficiency of the copolymerization profoundly [2]. The scope of this work is to optimize and gain a deeper understanding of the reaction performances. Central to this endeavor is the analysis of how initial conditions, guided by the CO2/CHO phase diagram, affect the reaction. Additionally, the study assesses the evolving alterations in the mixture's physical properties during polymer formation. Kinetic studies of the reaction have been run on the conditions of Table 1, leading to significant and non-trivial variation in the conversion rate with changing pressure.

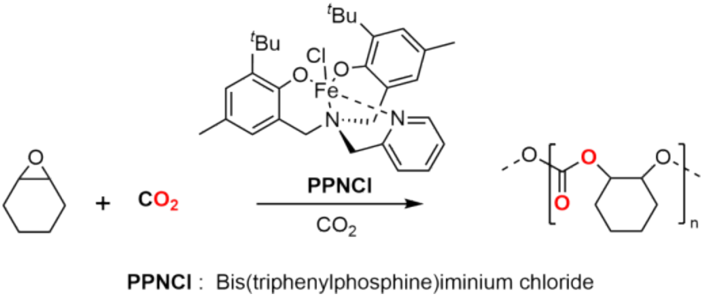

Figure 1: CHO/CO2 Fe-catalyzed copolymerization reaction

Table 1: Influence of operating conditions on reaction performances (CHO:0.11 mol, CHO:cat:cocat=100:1:1), T=73°C. a determined by 1H NMR Spectroscopy

Entry	P [MPa]	t [min]	CHO Conv % a
1	4.0	240	76%
2	8.0	240	98%
3	12.3	240	97%
4	16.0	360	37%

Kinetic studies were performed in a 90 ml batch reactor with a high-pressure sampler. The evolution of the mixture was monitored visually with a camera in a variable volume view cell, equipped with a sapphire window. The reactor and cell are shown in figure 3. The estimated initial composition of the CO_2/CHO system at the conditions of Table 1 are reported in Figure 2.

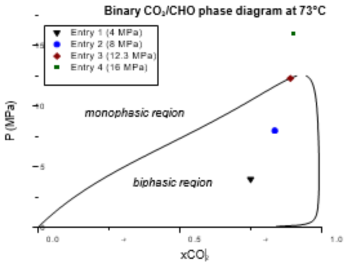

Figure 2: Starting conditions on the phase diagram

The reaction performances and evolution of the copolymerization reaction were monitored at different P. In conclusion, the results emphasized the advantage of working with a starting mixture in the biphasic region. Particularly, the conversion rate proved to be favorable at higher pressure in the biphasic regime. Hence, they provided tools for educated process optimization, advancing the production of these plastics toward sustainability.

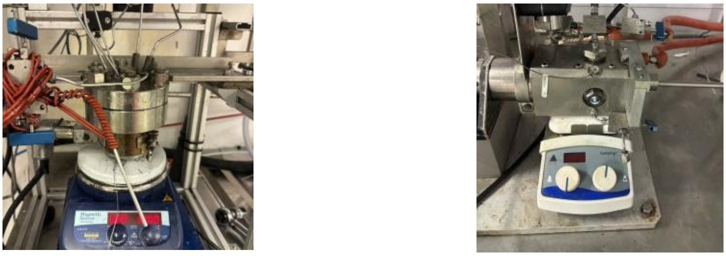

Figure 3: Reactor and variable volume view cell for CHO/CO_2 copolymerization

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Plenary Lecture

Industrially relevant high pressure polymer research based on fundamentals

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We have been conducting high pressure research on polymers exposed to compressed fluids for more than three decades, covering a wide range of concentrations, pressure, and temperature conditions, that involve homogeneous solutions at one end, and fluid swollen polymers at the other. In the process, a number of unique experimental systems and techniques for characterizations have been developed, to address a host of fundamental and applied questions. While pursuing the fundamentals, the goal has always been to make the research industrially relevant. In this presentation I will provide perspectives from our ongoing industrial application-oriented fundamental research on (a) thermophysical transitions of polymers toward rational selection of conditions for effective foaming of polymers with physical blowing agents; (b) miscibility and phase separation of polymers in compressed fluids toward the development of strategies for polymer purifications and recycling, and (c) volumetric and rheological properties of polymer solutions toward improved understanding of packing density on viscosity for applications in lubricant systems.

Supercritical fluids – a family story

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Beginning with the first industrial applications of the unique properties of supercritical fluids from the 1950´s on in Europe and in the US in the field of the Extraction of natural products, a worldwide scientific and technical community has developed in the last 7 decades. The Journal of Supercritical Fluids, initialized and founded by Erdogan Kiran, is a unique basis of exchanging knowledge, ideas and results between academia and industry. Some success stories will be highlighted from the history of the journal and values, shared by the supercritical family.

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Speech

Some remarks on 55 years working with supercritical fluids

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Speech

Reviving forgotten wisdom about the fundamentals of supercritical fluids

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Fundamental data for rational selection of foaming conditions in supercritical fluids

Lessons learned under pressure from 7 years in Kiran lab

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The study of physical blowing agents for the foaming of polymer systems at high-pressure has been an active area of research and development for decades. Numerous studies present on the phenomenological results of saturation and subsequent depressurization to form microcellular structures, but a common gap in both fundamental research and industrial practice is the knowledge of the given polymers thermophysical and rheological properties at high-pressure.

While developing a fundamental understanding of the foaming behavior of these copolymer systems three different novel high-pressure characterization techniques were developed, including (1) high-pressure torsional braid analysis (HP-TBA), (2) view-cell modified magnetic suspension balance, and (3) several custom high-pressure foaming techniques. The findings will be presented on the high-pressure characterization and foaming of EVACO-0010, EVACO-1010, and EVACO-2010 in carbon dioxide. The number designations refer to the vinyl acetate (0, 10, and 20 %) and carbon monoxide content (10 %) with the remainder by ethylene.

High-Pressure Torsional Braid Analysis (HP-TBA) characterizations have been performed at 50, 100, 150, 200, and 250 bar in carbon dioxide. The HP-TBA allowed for the determination and mapping of the depression of both the melting and crystallization temperatures of these polymers in the presence of carbon dioxide. A saturation pressure of 200 bar in carbon dioxide was found to lead to the greatest reduction in Tm and Tc for each of these polymers. Assessments of the sorption of carbon dioxide with MSB showed that increasing the vinyl acetate content leads to an increase in the level of carbon dioxide sorption. The foams were characterized for their average pore size and pore distribution, along with assessments of the bulk foam density, and the outcomes are linked to the depressed thermal transitions in carbon dioxide.

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Keynote Lecture

SC-CO_2 assisted manufacturing of membrane materials for separation of high-pressure gas mixtures

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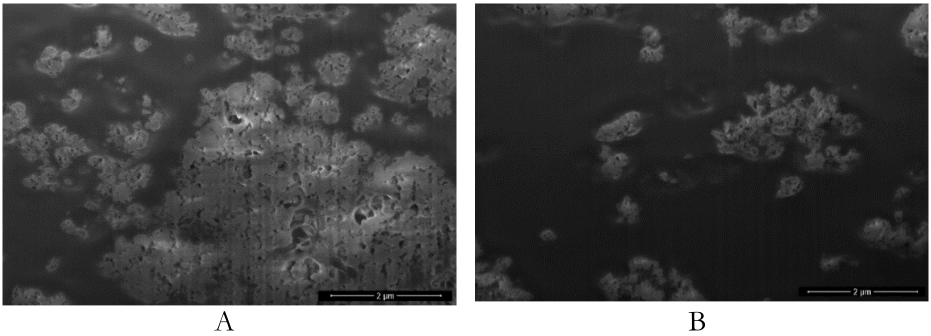
The development and application of so-called mixed matrix membranes (MMMs) are presented in this contribution. The membranes under investigation are based on cellulose acetate as an organic matrix containing different inorganic fillers, such as molecular sieves (zeolites) and nanosilica. The major issue in MMM design is void formation at the interface between the organic phase and inorganic filler [1]. In this study, grafting reactions in supercritical carbon dioxide were applied to overcome this problem. The surfaces of the fillers were functionalized by silanization, to ensure better contact between the phases and to avoid the formation of interfacial voids. Two techniques were employed, namely, supercritical solvent impregnation (SSI) and supercritical assisted impregnation (SAI). Depending on the technique and process parameters, grafting degrees of several percent and up to 18 % were observed for zeolites and nanosilica, respectively. Subsequently, the composite membranes were manufactured via the solvent casting method by dispersing the filler nanoparticles within a polymer-solvent solution. The production and drying methods were optimized for each filler. In the case of pristine fillers with unmodified surfaces, microvoids were visible through SEM-FIB imaging. A strongly improved filler dispersion in the cellulose acetate matrix and less agglomeration in MMMs with nanosilica modified by 3-aminopropyl(diethoxy)methylsilane (APDEMS) were also visible in the SEM images (Fig. 1). To verify the effect of silanization on the quality of the bonding between the polymer matrix and fillers further, the constant volume variable pressure technique was employed, to test the permeability of pure gases at elevated pressures [2]. Tests conducted with pure hydrogen at 2 MPa and 18.5 °C demonstrated a 14-fold permeability reduction of membranes with silanized nanosilica compared to membranes prepared with pristine nanosilica, confirming the role of silanization in interfacial void elimination. The application of the proposed membranes in the separation of hydrogen-carbon dioxide gas mixtures under elevated pressures is discussed from the point of view of solution-diffusion and molecular sieving mechanisms occurring in the membrane matrix based on the observed permeation data of pure gases.



A B

Figure 1: The cross-section of cellulose acetate MMM with pristine (A) and silanized nanosilica (B).

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Structural changes in gels by imaging tracer particles using X-ray microtomography

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Mass transfer and structural changes in the polymer matrix need to be understood for a rational optimization of the aerogels` production. Herein, the uniformity is studied of changes that occur in the gel structure during the aerogel production by a newly developed method which is based on the imaging of metal tracer particles using X-ray microtomography (X-ray micro-CT) alongside the application of point pattern techniques such as the K-nearest-neighbor (KNN) distances. Agar was used initially as a system of validation for the developed method, after which other polysaccharide and protein-based gels were studied, such as alginate, whey protein isolate (WPI), and gelatin. The KNN distance was seen to reduce from hydrogel to aerogel. Furthermore, by means of the KNN distances, the biopolymers were observed to experience a nonuniform distribution of tracer particles correlating to nonuniform shrinkage. Densification at specific sites of the gel, represented by lower KNN distance values, could be distinguished for each biopolymer. Finally, the spatially resolved polymer network density profile was estimated from the KNN distance by correlating it to an experimentally determined polymer network density [1].

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20th European Meeting on
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Biopolymer based carbon aerogels: influence of crosslinking strategy and pyrolysis conditions on textural properties

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Mesoporous carbon aerogels (CAs) show distinctive properties, which make them promising materials in different areas: beside application as adsorbents or as supercapacitors, CAs show potential as advanced catalyst carriers, since they exhibit a multiscale porosity, which has the potential to enhance the catalytic efficiency in comparison to commercial solutions (e.g. activated carbons). In particular, they provide electrical conductivity, a high microporous specific surface area (for the anchoring and dispersion of, e.g., metal nanoparticles) and meso- to macroporosity for the efficient transport of products and reactants [1]. The production of CAs involves commonly the pyrolysis of organic aerogels, which is performed under an inert atmosphere (e.g., N_2). An additional activation step in the presence of reactive gases (e.g., CO_2, NH_3) might be used for further modification, e.g., for enhancement of the microporosity. Due to the outstanding textural properties of the products, tailorability and comparably high pyrolysis yield, polycondensated resorcinolformaldehyde (RF) gels have been the most common starting materials in the polymer-to-carbon aerogel route since the 1990s.[2,3] A green alternative to RF as a starting material is the use of biopolymer aerogels, which can be derived from abundant resources, e.g., from alginate, cellulose or chitosan, the latter showing the advantage of having naturally incorporated nitrogen containing functions. Due to changes of the pore network during pyrolysis (e.g., shrinkage, collapse), the challenge arises to preserve the textural properties during pyrolysis. Our main findings focus on the role of different crosslinking strategies and chemical stabilization during chitosan and cellulose aerogel synthesis, as well as on the heating rates during aerogel-pyrolysis. A screening of the heating rates (1 °C min^{-1} – 10 °C min^{-1}) in the pyrolysis of chitosan and cellulose aerogels was carried out in a thermogravimetric analysis setup (final temperature = 800 °C, N_2 atmosphere). Hereby, the final mass loss could be reduced to 55% via the chemical modification of chitosan.

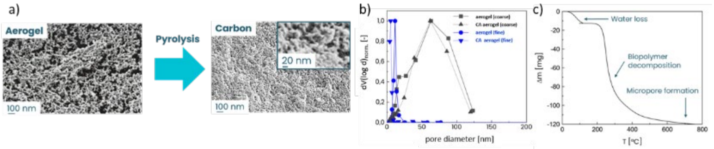

Figure 3: SEM images of a purely mesoporous chitosan-based aerogel and the resulting carbon aerogel after pyrolysis (a). Normalized BJH pore size distributions of two different aerogels and resulting carbon CAs after pyrolysis (b). Typical biopolymer aerogel to CA conversion curve obtained via thermogravimetric analysis (c).

It was found that that the textural properties of aerogels and resulting CAs can be controlled by the gelation strategy, the crosslinking agent and applied heating rate. Purely mesoporous aerogels with specific surface areas S_m of up to ~750 m^2 g^{-1} were obtained by direct crosslinking, while better preservation of the pore structure during pyrolysis was achieved at lower heating rates, as proofed by SEM, CO_2- and N_2-physisorption data (Figure 1). The resulting CAs showed a multiscale porosity and high overall S_m of up to ~ 2500 m^2 g^{-1}.

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Modifying the properties and the morphology of starch aerogels using cellulose

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Aerogels are nanostructured lightweight mesoporous/microporous materials with high specific surface areas. Starch-based aerogels showed great potential as carriers for active compounds and controlled release, templates for making novel materials, packaging materials, thermal insulators, and adsorbents. The properties of starch-based aerogels are tuned mainly by the processing parameters (source of the starch, biopolymer concentration, amylose/amylopectin ratio, and gelatinization degree). By combining other biopolymers with starch, an immense influence can be made on the properties of the final materials. [1,2]

This study aimed to investigate the effect of bacterial nanocellulose (BNC) and cellulose nanocrystals (CNC) addition on the properties and morphology of starch aerogels. The preparation of the starch and composite starch-cellulose aerogels included hydrogel preparation with different BNC and CNC content, followed by solvent exchange and supercritical drying. A comprehensive characterization was conducted through N_2 absorption-desorption analysis, thermogravimetry (TGA) and differential scanning calorimetry (DSC), scanning electron and ion microscopy (SEM-FIB), Fourier transform infrared spectroscopy (FTIR), and swelling behavior. The obtained aerogels were impregnated with xanthohumol (XH) from the ethanol solution. The polymeric structures loaded with XH were, afterward, exposed to supercritical carbon dioxide in the presence of usnic acid (UA), to perform one-step supercritical drying and impregnation.

All the prepared aerogels encompassed high specific surface areas, ranging from 180-220 m^2/g, depending on the BNC/CNC content. The higher the BNC/CNC content, the higher the surface area. Cellulose-starch aerogels were shown to be more thermally stable than neat starch aerogels. SEM imaging of surfaces and cross-sections revealed highly porous structures with interconnected networks of pores. Fig. 1 shows the cross-section of starch/CNC aerogel. The possible applicability of the prepared aerogels was investigated through the swelling behavior over seven days. It was shown that all the aerogels reached 250-550 % of the swelling ratio, depending on the BNC/CNC ratio. The higher the BNC/CNC content, the greater was the swelling.

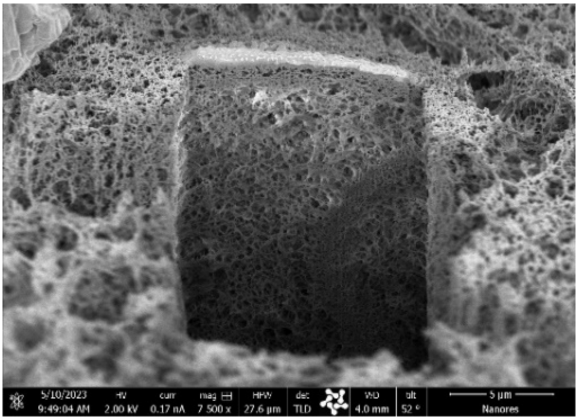

Figure 1: Cross-section of starch/CNC aerogel

The impregnation process was successful. It was shown that the addition of BNC/CNC improved the aerogel sorption capacity, and, therefore, the XH intake (12.9 – 16.6 µg/g). The higher the BNC/CNC concentration, the higher the XH intake. The UA loading acquired in the next step was less affected by cellulose. Most importantly, the post-impregnation characterization studies confirmed the preserved structure of starch and starch-cellulose aerogels loaded with active substances.

Acknowledgment

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PolyHIPEs, hydrogels, and aerogels derived from aliphatic π-conjugated polyazines

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Conjugated polymers (CPs) represent a unique class of materials that have captivated the scientific community's interest due to their remarkable electronic and optical properties. [1] These materials, characterized by alternating single and double bonds along their backbone, allow for delocalized π-electrons that endow them with conductive/semiconducting and photophysical properties not found in other types of materials. This inherent electronic versatility has led to their widespread application in organic electronics, photonics, and as active components in various sensor and catalysis technologies.

Among the numerous CPs porous conjugated polymers stand out, due to their large surface area, adjustable porosity, and structural diversity, which extend their applicability in gas storage, separation technologies and as scaffolds for catalysis. [2] Focusing on porous polyazines, a subclass of CPPs, these materials offer a unique combination of π-conjugation with high nitrogen content and increased porosity. This combination not only improves their chemical stability, but also affects the electronic properties and introduces additional features that are crucial for catalytic applications. Porous polyazines in the form of polymeric high internal phase emulsions (polyHIPEs), and hydrogels, have emerged as prime candidates for the further development of the porous CPs field.

We have developed a sustainable, in-water synthetic method for the production of porous aliphatic polyazines into structures such as polyHIPEs and hydrogels. [3] This approach is characterized by its minimal environmental impact, as demonstrated by the low E-factor and the synthetic complexity index, both key indicators of the sustainability and scalability of a process. By replacing conventional purification processes such as Soxhlet extraction with supercritical CO_2 extraction, we were also able to improve the porosity and purity of the porous polyazines. This is of crucial importance, as the photophysical properties of the final material could be affected significantly by the presence of residual impurities. Our work demonstrates that supercritical CO_2 technology in the synthesis of CPPs plays an important role in the green transition, and represents a significant step toward environmental responsibility while maintaining the integrity and functionality of the materials.

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Functional nanomaterial inks for 3D-printed electronics *via* supercritical continuous-flow synthesis

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Three-dimensional (3D) printing techniques, such as vat polymerisation and material jetting, are showing great promise for the scalable, digital manufacture of embedded electronic devices with arbitrary complexity [1]. This requires functional materials beyond those used typically in 3D-printing for rapid prototyping and the production of end-use structural parts [2]. For ink-based deposition methods, functionality is often achieved through the inclusion of electronically-active nanofillers within solvents or polymeric resins. Conductive inks have been explored widely and are commercially available, whilst complex functionalities, e.g., magnetism, can be difficult to obtain in printed features. Nanomaterial properties, including particle size, shape, and surface chemistry, may all affect the ink stability, the printability, and, ultimately, the electronic performance. Continuous hydro/solvothermal production methods are capable of generating a wide variety of functional nanomaterials [3]; the particles are suspended in a solution and delivered at scale, with a high degree of control over product characteristics, rendering this synthesis approach highly complementary to functional ink formulation work. Furthermore, nanoparticles resulting from hydrothermal syntheses typically possess an increased coverage of surface hydroxyl groups, rendering them amenable to capping agent functionalisation – a crucial step in obtaining stable, uniform dispersions of electro-active particulate fillers within printable inks. In this work, a counter-current nozzle reactor [4] within a bench-scale continuous-flow system was used to synthesise cobalt ferrite nanoparticles ($CoFe_2O_4$), with a view to formulating magnetic inks for 3D-printed devices. Generally, 0.01-0.10 M aqueous cobalt-iron precursor solutions are fed, at room temperature, upwards into the reactor, with a flow of between 5-25 mL min^{-1}, meeting 5-25 mL min^{-1} of sub/supercritical water, between 200-450 °C, leading to product formation. Pressure is maintained at 240 bar. A capping agent flow may also be fed into the system part-way through product cooling, to enable in-line particle functionalisation.

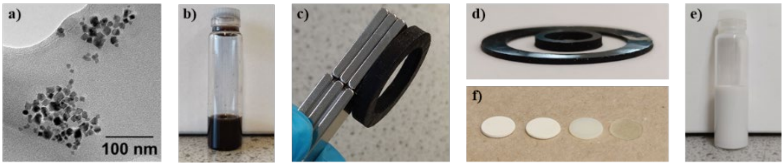

Figure 1: a) TEM image of synthesised $CoFe_2O_4$ nanoparticles. b) Stable UV-curable $CoFe_2O_4$ ink. c-d) Printed $CoFe_2O_4$ samples. e) Stable UV-curable $BaTiO_3$ ink. f) Printed samples with decreasing $BaTiO_3$ content, from left to right.

The magnetometry data indicated that the synthesised $CoFe_2O_4$ was magnetically semi-soft. Functionalisation of the nanoparticles with silane coupling agents improved their stability in UV-curable inks vastly, with printability demonstrated *via* vat photopolymerisation; as-synthesised powders and printed structures demonstrated a good response to an external magnetic field. The continuous-flow synthesis and *in-situ* functionalisation was extended to produce printable inks with hard magnetic barium ferrite and dielectric barium titanate (Figure 1).

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20th European Meeting on
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Keynote Lecture

Supercritical fluid technologies for the incorporation of synthetic and natural active compounds into materials for drug formulation and delivery

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The pharmaceutical industry is interested in obtaining the successful formulation of poorly soluble active compounds, in order to increase their bioavailability and dissolution rate. The current delivery options for improving the dissolution properties of drugs are particle size reduction, crystal modification, pH modification, self-emulsification, amorphization, and the formulation of drugs with surfactant carriers and amorphous polymers. Particle size reduction and drug formulation with polymeric carriers incorporate the most promising options in this regard. A number of conventional methods have been developed to improve the dissolution properties of drugs. Many of these methods possess drawbacks, such as thermal and chemical degradation of drugs, large quantity organic solvent use, broad particle size distribution, and low drug load. To overcome these limitations, supercritical fluid technology promises to be an excellent option. The reasons for the widespread use of supercritical fluids lie mainly in the simplicity of the processes, high purity of products, no organic solvents in the process, no communication steps in drug preparation, mildness of the operating conditions, and the possibility of obtaining non-contaminated fine particles with narrow size distributions [1]. The production of fine particles with improved characteristics using supercritical fluids has been obtained with rapid expansion of supercritical solutions (RESS), the gas antisolvent process (GAS), supercritical antisolvents (SAS), solution enhanced supercritical dispersion processes (SEDS), aerosol solvent extraction systems (ASES), supercritical fluid extraction of emulsions (SFEE), and particles from gas-saturated solution (PGSS™). In particular, the PGSS™ used in our study is an organic solvent-free process, in which polymeric carriers with the target pharmaceutical drug to be micronized and encapsulated are loaded into a high-pressure autoclave together with supercritical CO_2.

Keywords: supercritical fluid technologies; active compounds; drug formulation; drug delivery

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Supercritical millifluidic process for the production of lipid-based formulations of anti-cancer drugs

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Supercritical fluid technology applied to the elaboration of lipid-based formulations, especially liposomes, has been described quite widely in the literature over the last three decades. Many advantages of using supercritical carbon dioxide for liposome formation are often highlighted, such as size control, stability enhancement, and mitigation of organic solvent use. The main recent challenges in this field are the size reduction, since vesicles smaller than 100 nm allow for a higher rate of cell internalization. Another point of attention, whatever the application field, is the development of less energy intensive processes, consuming less raw materials and solvents. The present study addresses all the different challenges mentioned above. A millifluidic process enabling fluid, equipment and energy savings, has been applied to the formation of nanoliposomes. This process, previously applied to the encapsulation of small interfering RNA for gene therapy applications [1], has been used in this work for the elaboration of pegylated nanoliposomes encapsulating docetaxel, an anti-cancer drug used for the treatment of different types of cancer.

Phosphatidylcholine (PC) (CAS: 97281-44-2, purity >99%), supplied by Sigma-Aldrich (Saint-Quentin-Fallavier, France), was used as the main source of lipids. Cholesterol (CAS: 57-88-5) and polyethelene glycol (PEG) (CAS: 474922-22-0, Mw = 2941.605 g/mol) were supplied by Sigma-Aldrich (Saint-Quentin-Fallavier, France). Docetaxel (CAS: 114977-28-3, purity: 98%) was supplied by Sigma-Aldrich, Saint-Quentin-Fallavier, France. Carbon dioxide (purity > 99.7%) was supplied by Air Liquide (Marseille, France).

The main feature of the studied process is the use of a millifluidic device for mixing supercritical carbon dioxide with the aqueous ethanolic solution containing the drug, the lipids and polyethylene glycol (when used). The process was conducted in a continuous mode, enabling the continuous production of a liposomal solution.

Nanoliposomes have been formed at 150 bar and 35 °C, starting from an aqueous ethanolic solution (79/21 wt%) containing PC (0.1 wt%), docetaxel with a concentration of 34 $mg.L^{-1}$, cholesterol and PEG. The vesicle size is understood between 90 and 120 nm, with a drug encapsulation rate of 95 %. Drug-free liposomes have been formed with a similar size range.

This work has highlighted that nanolipomes encapsulating an anti-cancer drug can be produced in a continuous and repeatable way. A unimodal population can be isolated, enabling then the recovery of more stable formulations. Since the presence of the drug in the liposome did not impact the vesicle size, nanoliposomes encapsulating different types of drugs may be formed successfully using a millifluidic device.

Acknowledgements

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Polymorphic control of pharmaceutical cocrystals using conventional bench-top and continuous particle production techniques

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Poor solubility effects approx. 90% of new chemical entities [1]. Unlike common strategies like salt formation and amorphization, cocrystallization provides an avenue to tackle this challenge of improving drug bioavailability, while avoiding losses in stability. In addition, recent regulatory changes make this a more attractive strategy [2]. This study aims to investigate the ability to control cocrystal polymorphism by several cocrystallization methods further.

Liquid assisted grinding (LAG) and solvent evaporation (SE) were employed to investigate the effect of solvent choice. Two atomization-based methods were also used; electrospraying, which applies a high voltage to atomize a feed solution, and supercritical CO_2-assisted spray drying (SASD), which employs a heated, high-pressure coaxial nozzle to atomize a methanolic feed solution into a heated drying chamber held at atmospheric pressure. Three pharmaceutical cocrystals were investigated in this work. One cocrystal was isonicotinamide-citric acid (IsoCa), which is reported to exhibit 2 stable cocrystalline forms (α and β), a metastable γ form, and a metastable salt form. LAG and SE led primarily to the stable α form, however, the metastable γ form was produced when employing methanol in the solvent evaporation, while the electrospraying process produced either pure α, or a mixture of α and γ, depending on the conditions employed. The SASD process, however, produced either pure α or pure β polymorphs, depending on the solution flow rate used, which effects the droplet sizes directly.

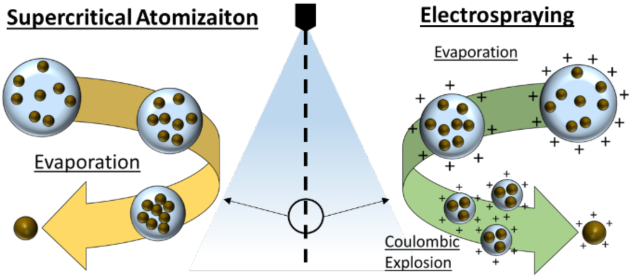

Figure 1: Diagrammatic representation of atomization methods

The cocrystal of ethenzamide and saccharin (EthSac) was also investigated, which exhibits two polymorphic forms, a stable form I and metastable form II. Regardless of the solvent choice, LAG led to metastable form II, while SE led to the stable form I. While the electrospraying process only produced the stable form II, the SASD method produced form II at lower solution flow rates, and mixtures of forms I and II at higher solution flow rates, owing to the larger droplets and longer drying time, promoting polymorphic conversion.

The final cocrystal investigated was that of ethenzamide and gentisic acid (EthGa). This cocrystal exhibits three known polymorphs, a stable form I and metastable forms II and III. The LAG process produced primarily form II, with form I resulting from the use of solvents IPA or tetrahydrofuran. SE produced primarily from I, with form III produced when evaporated from ethanol. A similar observation is made here as to the EthSac cocrystal, in that electrospraying led to form I production, while SASD processing led to form II production.

In conclusion, while distinct differences in polymorphic outcome were observed depending on the method employed, variation of the critical process parameters also led to changes in the polymorphic outcome, with metastable forms being favored when the feed flow rate was decreased, and/or solution concentration was increased.

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Recovery of valuable cosmetic ingredients from berry seeds and pomace using sub/supercritical extraction methods, and their application for cream

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Berries, rich in biologically active compounds, can be consumed fresh, or processed into various products. Juice production typically yields 70-80% target product and 20-30% by-product (pomace), containing valuable dietary fiber, vitamins, and bioactive compounds. Despite its potential, pomace is often underutilized or discarded. Bioactive compounds in berries, including tocopherols, phytosterols, and polyphenols, offer health benefits such as reducing cardiovascular risk, and possessing anti-cancer, anti-inflammatory, and antioxidant properties. The efficient processing of berry seeds or pomace requires diverse extraction methods, such as cascade biorefining technology. Extracts or oils from strawberries, raspberries, blueberries, blackberries, and elderberries, are used widely in cosmetics for skin hydration, protection against UV damage, and as antioxidants.

This study focused on developing a separation technology for extracting nutrients (extracts rich in bioactive components) from strawberry, blackberry, elderberry seeds, and rowanberry pomace, utilizing biorefining and green extraction concepts. The obtained extracts were characterized and applied in a cream formulation. Supercritical fluid extraction with CO_2 (SFE-CO_2) was performed at 35 MPa pressure and 50 °C temperature. The lipophilic extracts were analyzed by different methods. Sterols and tocopherol content were analyzed by UPLC, while the fatty acid composition was determined by GC. The total carotenoid content was measured by the spectrophotometric method. Defatted pomace was further extracted by pressurized liquid extraction (PLE) with a mixture of ethanol and water (70:30). The antioxidant activity of polar extracts was evaluated by using ABTS, ORAC, and CUPRAC assays. The total phenol content (TPC) was measured by the *Folin-Ciocalteu* method. Creams were prepared with 2% of strawberry seed lipophilic and hydrophilic extracts, and evaluated for their antioxidant capacity, SPF, and stability.

The total yield of the extracted lipophilic substances was in the range of 4.56 (rowanberry pomace) – 14.28% (elderberry seeds). Linoleic, oleic, and palmitic acids were the major fatty acids in the extracted oils. Palmitic (3.66–7.33%), stearic (1.12–3.76%), oleic (10.76–23.25%), linoleic (39.11– 59.74%), and linolenic (1.32-43.83%) acids were the major fatty acids in the extracted oils. Polyunsaturated fatty acids accounted for between 61.06% (sea buckthorn pomace) and 82.94% (elderberry seeds) of total fatty acids, and were remarkably greater than that of monounsaturated. Significant differences in the concentration of the determined bioactive constituents were observed in the extracts obtained from different berry seeds and pomace. The content of α and $\beta+\gamma$ in the CO_2 extracts of different fractions was 29.93 – 254.55 and 114.23 – 505.71, respectively. Four phytosterols, namely, campesterol, stigmasterol, ergosterol, and β-sitosterol, were identified and quantified in different extracts obtained by SFE-CO_2. β-Sitosterol was dominating in all the extracts. The PLE with ethanol and water mixture (70:30) yielded 20.61–47.29% of polar extracts. The total phenolic content (TPC) by the *Folin-Ciocalteu* method and antioxidant activity by ABTS•+ scavenging and cupric reducing antioxidant capacity (CUPRAC) assays were investigated of the obtained polar fractions. The highest TPC was determined in the strawberry seed PLE extract (92.18 ± 3.90 mg GAE/g), while the blackberry seed PLE extract exhibited the best radical scavenging and CUPRAC values. The addition of 2% lipophilic or hydroethanolic strawberry seed extract to the cream did not have any effect on the pH values compared with the control. All the creams were stable during the freezing and heating tests. The addition of extracts to the cream did not have a huge impact on the total phenolic content and antioxidant activity, but the values with the PLE extract were slightly higher. The SPF factor of all the creams was between 0.45 – 0.85. According to the US Food and Drug Administration (FDA), a product must have an SPF of at least 2 to be approved as a sunscreen. Thus, to have photo-protective properties, a higher concentration of hydroethanolic extract should be used in the cream`s formulation. In conclusion, the proposed biorefining scheme of berry seeds and pomace utilizing green and modern extraction techniques may serve as a platform for producing various functional ingredients for foods, nutraceuticals and cosmetics.

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Supercritical CO_2 impregnation: a novel approach in the elaboration of active stents

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In Cardiology, stenosis is the narrowing of an artery due to fatty deposits on its wall. Angioplasty, using stents to restore blood flow (Figure 1), is a dominant treatment to avoid fatal complications. Recently, this medical device has been improved considerably, especially with the emergence of active stents. This medical device has the particularity of releasing an anti-proliferative agent (Sirolimus) via a polymeric layer, to prevent re-stenosis post-implantation. The traditional stent elaboration process involves organic solvents, and, hence, can result in residues within the medical device. Supercritical carbon dioxide ($scCO_2$) impregnation of Sirolimus within the stents offers an alternative solution to conventional methods. Initially, a classical batch mode impregnation process has been carried out on stents, resulting in low drug loading, polymer swelling and detachment observed after treatment. To overcome these challenges, a modified version of the process has been developed, improving drug loading considerably, while preserving the integrity of the polymer layer after treatment.

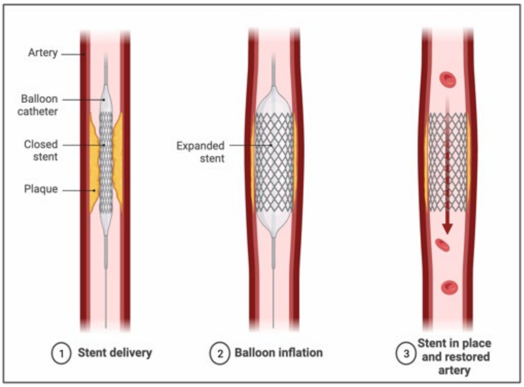

Figure 1: Angioplasty using stent

$ScCO_2$ impregnations were carried out on stents supplied by AlchiMedics (France). The stents were made of stainless steel with a poly (lactic-co-glycolic acid) (PLGA) layer. The Sirolimus was supplied by Curia Global (Italy). Carbon dioxide (purity > 99.7%) was supplied by Air Liquide (France).

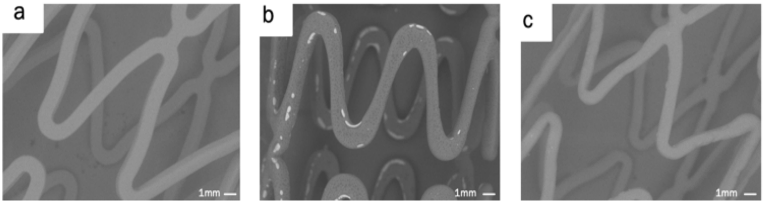

Figure 5: SEM observation of the stents a) before impregnation, and after sc impregnation through b) conventional process and c) innovative process

The $scCO_2$ impregnations were carried out in a batch mode. The stents were placed in a heated cell with sirolimus, under magnetic stirring. This cell was then filled with CO_2 until reaching the desired temperature and pressure conditions (ranging from 308.15 to 328.15 K, and 8 to 20 MPa, respectively). The cell was then isolated, respecting a set contact time (varying between 30 min and 4 hours), before proceeding to depressurization. A modified version of the process was developed and allowed to optimize impregnation.

After $scCO_2$ impregnation, the drug loading was quantified by UV spectrometer, and the stents were observed under a scanning electron microscope.

The nitial impregnation set-up yielded a maximum drug loading of 0.1 µg.mm-2, lower than the 1.2 µg.mm-2 target. Polymer swelling and detachment were also encountered, even at the mildest conditions. Repeatable high drug loading of 7.3 µg.mm-2 was achieved without altering the polymer when applying the innovative impregnation process (Figure 2). The key parameter highlighted was the contact time.

The innovative impregnation process has demonstrated the potential to achieve a high drug loading within active stents without altering the polymer coating successfully. Further studies are still required, to explore the drug release capabilities of the treated stents and their in-vivo performance in animal models.

Supercritical solution impregnation (SSI) of orthopedic prosthesis to prevent infections

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The most notable complication in orthopedic surgery is infection. Most bacterial infections in prosthesis are caused by microorganisms which are resistant to antibiotics and to the host immune system. The usual treatment requires a surgical approach and systemic and local antibiotic treatment [1]. Thus, it is urgent to find new strategies to eradicate microorganisms' growth on the prosthesis fully and avoid infections. Loading an Active Pharmaceutical Ingredient (API) into the prosthesis may prevent the development of infections.

A project is underway in our laboratory to explore the use of $scCO_2$ as an impregnation and sterilization medium to treat an orthopedic prosthesis to prevent infections. In this communication we present our results on the incorporation of antibiotics into the prosthesis using supercritical CO_2 ($scCO_2$). The Supercritical Solution Impregnation (SSI) technique involves the dissolution of the API in $scCO_2$ and its sorption/precipitation into the support. In porous materials, the low surface tension of supercritical CO_2 favors the wetting of narrow structures, and enhances its adsorption on the pore surface. In polymers, $scCO_2$ diffuses through the polymer chains, leading to the polymer's swelling/plasticization and the absorption of the drug. In both cases, the use of $scCO_2$ leads to a good dispersion of the drug in the different substrates without leaving any toxic residue.

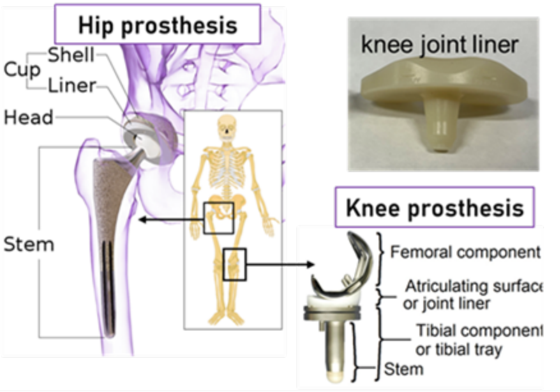

Figure 1: shows hip and knee prosthesis and their different parts. The interpositional materials (acetabular cup and knee joint liners) are composed by Ultra High Molecular Weight polyethylene (UHMWPE), whilst the rest are metallic parts covered with different coatings to improve adhesion and biocompatibility.

Experiments were performed using pieces of knee joint liners of UHMWPE, cut into small pieces. For the metallic parts, we used pieces of Mg-Ca alloys coated by plasma electrolytic oxidation (PEO) with bioactive coatings containing Mg, Ca, P, Si and F. These materials have been proposed for bone reconstruction and cardiovascular stents [2].

Materials were loaded with the antibiotic clindamycin dissolved in CO_2 at 35-55 °C and 100-200 bar. The mole fraction solubility of clindamycin in $scCO_2$ at these conditions is between $(1.95\text{-}3.75)\cdot 10^{-4}$ [3]. The experiments were performed under saturation conditions. Slow and fast depressurization rates were assayed of the reactor. The drug was loaded successfully into the polymeric parts at 0.3-5.0% mass. The highest drug loading was obtained at the highest CO_2 density. Loadings at the low depressurization rate were moderate, due to the weak interaction between the drug and the support. Higher loadings were obtained at the fast depressurization rate. In the metallic parts, loadings up to 4% mass of the PEO coating were obtained at similar conditions. Antimicrobial plate assays showed the formation of inhibition halos in *S. Epidermidis,* confirming the antibacterial activity of the drug impregnated pieces. As an additional advantage, impregnation and sterilization of the materials can be carried out in one step.

Acknowledgements

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20th European Meeting on Supercritical Fluids
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Keynote Lecture

Solvent dissolution based purification and recycling of polypropylene: fundamental data for industrial applications

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The recovery and recycling of polymeric waste is a global problem of growing concern. More than 150 million tons of plastics are reported as ending up in landfills. Only about 9 % of plastics are recycled in the United States, and about 30 % are recycled in Europe [1]. In the US, the current problem is labeled as the "Plastics crisis" [2]. A major difficulty is the ability to generate recycled plastics that are comparable to virgin resin in odor, mechanical properties, and color. To address the problem, a variety of approaches are being explored which have been the subject matter of a workshop of the National Academies [3]. Notable among these are (1) mechanical recycling, where the polymer is typically sorted and extruded and pelletized, (2) chemical recycling, which involves catalysts and/or high temperatures to break down plastics to lower molecular weight products, and ideally convert them to the constituent monomers, and (3) solvent dissolution physical recycling methods, to purify or clean plastic waste. Mechanical recycling is limited in its ability to remove colorants and odor, and typically leads to a reduction in mechanical properties.

Chemical recycling has its challenges, in that complete depolymerization to monomer is difficult and energy intensive. Solution-based separations have their challenges as well, in that the mixtures are complex, and the process requires designing solvent-nonsolvent combinations with selectivity.

In this talk we will present a novel solution-based polymer purification and recycling technology that is targeted toward the recycling of polypropylene. The process is a patented process developed by The Proctor and Gamble Company (P&G). The technology has been proven at the pilot scale; and the first large capacity (107 million lbs/year) commercial plant has been built in Ironton, Ohio (USA) by PureCycle, and is currently being optimized for process efficiencies and more continuous operations. The technology is based on the high pressure phase behavior of polymers in hydrocarbon solvent systems.

In this Industry-University collaborative talk we will discuss the path PureCycle has taken in transforming fundamental high-pressure polymer solution science to industrial practice, and how the sophisticated high-pressure research capabilities at Virginia Tech address important questions and generate the critical data needed in industry.

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Design of integrated polymeric sandwiches through physical foaming

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Numerous hybrids have been developed to optimize properties, incorporating base materials reinforced with fibers, particles, or lamellae of different natures [1]. An evolution of those composite matrices is represented by sandwiches. Typically, a sandwich comprises two external skins to ensure material rigidity, and an internal core that is used to distribute shear and compressive stresses over a large area [2]. Thermal or mechanical joining techniques are used commonly to produce sandwiches. However, the drawbacks of these processes are thermal instability while joining the core to skins, plastic deformation, use of glue and polymer mass loss. Moreover, the production of sandwiches using thermosetting polymers is less sustainable, since these materials cannot be re-used at the end of life.

An alternative way to produce sandwiches has been proposed in this work, involving thermoplastic materials, with a focus on sustainability. Despite requiring higher process temperatures than thermosetting polymers, these materials can be melted and reused multiple times without losing their original structural properties. To address the challenges associated with the use of bonding agents, the idea of this work is to provide mono-material integrated sandwiches using a physical foaming process [3], creating structurally and functionally optimized products for aerospace applications.

In this study, integrated sandwiches were designed using polypropylene (PP). Specifically, skins of PP and glass fiber composite (60% w/w fiber) were bonded to a core of PP slab, expanded with a carbon dioxide physical foaming agent. Pre-treatment conditions for PP, as well as those for the subsequent sandwich production, were designed, to prevent expansion of the skins while maximizing the expansion of the core. Core densities as low as 0.10 g/cm^3 were obtained. To achieve this goal, it was necessary to design an isotropic expansion by modifying the geometry of the initial polymer slab (Figure 1).

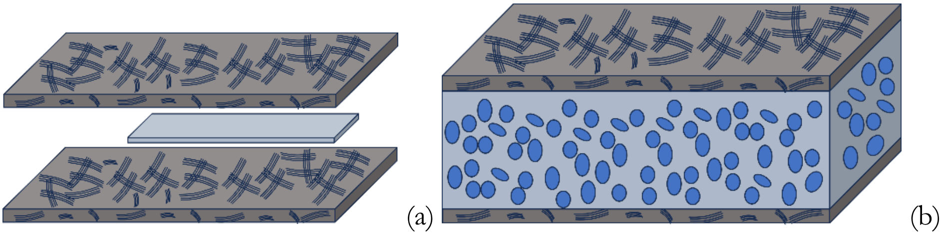

Figure 1: A sketch of the not assembled (a) and foamed (b) PP core + PP/glass fibers skin sandwich

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Polymer self-assembly and high resolution structural control in sub-critical fluids

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Organic electronic materials are pi-conjugated polymers and small molecules that have electronic functionality and have found uses in devices like organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). Although polymeric materials frequently have superior properties, the main commercial applications of organic electronic materials use vapor deposited molecular films. It would seem that the ability to deposit structures and control the thin-film morphology reproducibly is both fundamental to successful technologies, and achieved more easily by physical vapor deposition.

In order to develop a deposition technique for polymers that is analogous to physical vapor deposition in small molecule organic semiconductors, we are developing a technique we call physical supercritical fluid deposition (p-SFD)[1-5]. The technique relies on a maximum in the isobaric saturation solubility with respect to temperature to deposit thin polymer films onto a heated substrate. Importantly, the location of the material deposition can be controlled by controlling the local temperature of the substrate. Importantly, this technique can also be applied to curved and flexible surfaces. In addition, it is not a line-of-sight deposition technique, allowing the patterned deposition of functional materials on virtually any surface for any geometry that is in contact with the fluid.

The technique has been demonstrated for two polymer semiconductors, referred to commonly as PBTTT, and the ubiquitous P3HT. Moreover, the technique has been demonstrated in the deposition of isotactic polypropylene films. We hypothesize that any material with sufficient thermal stability can be deposited using this technique, so long as a suitable solvent can be identified. Progress has been made in identifying the relationship between the solvatochromic shift of polymers in solution, the critical temperature of the solvent, and the position of the maximum in the isobaric saturation solubility with respect to temperature.

The deposition conditions also have a strong influence on the morphology of the deposited thin films. The pressure and the presence of a co-solvent has been demonstrated to exert a particularly strong influence. This behavior has been rationalized in terms of the Rayliegh number of the solvent, which controls an aggregation step prior to polymer precipitation onto the surface. Once on the surface, the polymer aggregates can take advantage of a solvent shell comprised of a solvent with higher T_c to move parallel to the surface, forming larger aggregates.

In conclusion, we are developing a novel material deposition technique which is amenable to a wide range of materials and substrate geometries. The development of deposition conditions and solvents is a key consideration in process design and control over polymer nanomorphology.

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Green extraction of marine phospholipids from conger eel byproducts: lipidomic profiles and biological activities

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The objective of this study was to extract phospholipids (PLs) from conger eel (*Conger myriaster*) byproducts (CEB) using a green extraction system—supercritical carbon dioxide (SC-CO_2)—in conjunction with ethanol and conventional organic solvents. Additionally, the study aimed to characterize the lipidomic profile and biological activities of the extracted PLs.

Analyses were conducted of the PLs` purity, PLs` composition using ^{31}P nuclear magnetic resonance (NMR), and fatty acid (FA) composition using GC-FID for the lipidomic profile. Regarding biological activities, the study verified antioxidant activities through assays such as ABTS, DPPH, FRAP, and ORAC. The antimicrobial, antihypertensive, anti-inflammatory, and anticancer activities were also confirmed additionally.

The yield of organic solvent-extracted CEB PLs (OSCP) was 9.02±0.21% and the purity was 18.29±0.04%, while the yield of SC-CO_2-extracted CMH PLs (SCCP) was 3.26±0.20% and the purity was 76.18±0.09%. The primary PLs composition of SCCP was 88.88% phosphatidylcholine, followed by 11.05% phosphatidylethanolamine and 0.07% phosphatidylserine. Conversely, the OSCP exhibited a diverse composition of various PLs, with PC accounting for 54.23%, PE for 27.62%, and LPC for 7.78%. In terms of ω-3 PUFAs, the OSCP was determined to be 19.12%, while the SCCP exhibited a higher content at 29.45%.

In relation to antioxidant activities, the SCCP demonstrated superior antioxidant efficacy compared to the OSCP, with IC_{50} values of 16.23 mg/mL and 38.71 mg/mL for ABTS and DPPH, respectively. Additionally, the SCCP exhibited higher FRAP and ORAC values, measuring 3.32±0.05 mg Trolox equivalent (TE)/g and 133.12±1.19 μm TE, respectively. In terms of antimicrobial activity, the SCCP demonstrated a MIC of 3.125 mg/mL and MBC of 6.25 mg/mL against *Salmonella enterica*, and a MIC of 0.391 mg/mL and MBC of 0.781 mg/mL against *Escherichia coli*, indicating superior antimicrobial efficacy compared to the OSCP. Concerning antihypertensive effects, the OSCP exhibited an inhibition rate of 89.18±0.78%, while the SCCP demonstrated a higher inhibition rate of 96.57±0.21%. Above a certain concentration, both the OSCP and SCCP exhibited inhibition of nitric oxide (NO) production in LPS-induced RAW264.7 cells. Notably, high toxicity was observed in the SK-N-SH cells, a human neuroblastoma cell line; however, no cytotoxicity was observed in the RAW264.7 cells and HaCaT cells. These findings suggest that both the OSCP and SCCP may possess specific anti-cancer effects on certain cancer cells.

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Carbonation kinetics of calcium silicate minerals synthesized by supercritical flow synthesis considering its use for CO_2 sequestration application

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Anthropogenic greenhouse gas emissions have increased since the growth of the urbanization. The main component of greenhouse gases is CO_2. Globally, the CO_2 emissions are accounting for about 36 billion tonnes each year. In this regard, the cement industry is one of the main producers of carbon dioxide. In fact, the production of cement accounts for about 10% of the total CO_2 anthropogenic emissions. Therefore, reducing the carbon footprint is essential to prevent the progression of climate change. One promising option is employing CO_2 sequestration and utilization technologies [1]. Mineral CO_2 sequestration is a chemical storage way in which CO_2 is captured by materials that are rich in calcium silicates, such as Wollastonite ($CaSiO_3$), converting into a stable carbonate such as Calcite. The general carbonation reaction is shown as follows [2]:

$$Ca_xSi_yO_{x+2y} + xCO_2 \longrightarrow xCaCO_3 + ySiO_2$$

In this work, Xonotlite $Ca_6Si_6O_{17}(OH)_2$ is synthesized in a supercritical flow reactor using supercritical water as a solvent at 400 °C and 25 MPa. This innovative advanced methodology provides ultra-fast reaction kinetics, which allows the synthesis of Xonotlite in only 7 seconds with a high crystallinity and purity [3]. The as-prepared Xonotlite is further transformed into Wollastonite upon a dehydration process at a lower temperature than found in the literature [4]. These synthesized calcium silicate minerals (CS) were tested as a CO_2 sequester, which could be a binder in Cement production; the key ingredients of clinker cement production are usually $CaCO_3$ mixed with a clay as a source of silicates. This study highlights the carbonation kinetics of Xonotlite and Wollastonite using CO_2 in a range of reaction conditions of temperature, pressure, and reaction time.

The structural and morphology properties of Xonotlite, Wollastonite, and their carbonation products were analyzed by X-ray diffraction (XRD), and scanning electron microscopy (SEM). In addition, the carbonation process was evaluated, to quantify the CO_2 capture efficiency by thermogravimetric analysis (TGA). Our results have shown that the use of Wollastonite as a CO_2 sorbent compared to Xonotlite has the advantage of a much faster reaction rate of carbonation with a larger conversion degree to $CaCO_3$ with a pure single phase of only calcite, not mixed with other phases such as Aragonite or Vaterite, as shown in Figure 1.

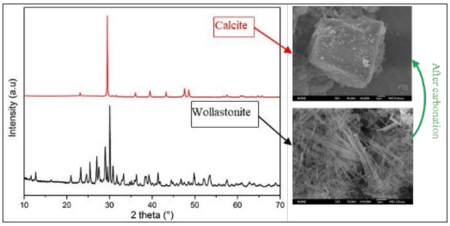

Figure 1: XRD patterns and SEM pictures of Wollastonite before and after the carbonation process.

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20th European Meeting on Supercritical Fluids
Maribor, Slovenia, May 26 - 29, 2024

Keynote Lecture

Sequential extraction of high-value added molecules from grape pomaces using supercritical fluids with water as a co-solvent

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Food waste management is an urgent global issue; therefore, the valorization of organic waste, with a particular focus on food, is essential for guiding us toward a more sustainable economy. To achieve this goal, a green chemistry extraction technique utilizing supercritical carbon dioxide (SC-CO_2) in combination with water as a co-solvent has been employed for the primary by-product of wineries and grape pomaces. The primary objective of this study was to extract high-value molecules selectively, particularly phenolic compounds and polysaccharides.

The experimental design involved the application of three distinct temperature conditions (40, 60, and 80 °C) while maintaining a constant pressure of 400 bar. The SC-CO_2 extracts, in combination with water as a co- solvent, revealed the presence of phenolic compounds and high-molecular-weight isolates (449–478 kDa) containing low methoxyl (% DE = 23) pectic substances. Among these, phenolic acids such as gallic (GA), protocatechuic (PCA), coumaric (CouA), and caftaric (CTA), as well as flavonoids including procyanidin B1 (PRC B1), procyanidin B2 (+) (PRC B2), (+) catechin (CT), and (−) epicatechin (ECT), were found in all the extracts under the tested experimental conditions.

This study underscores the potential of the pressurized CO_2/H_2O medium as an effective solvent with minimal environmental impact for the comprehensive valorization of the primary winery by-product, with a specific focus on polysaccharides and phenolic compounds. The sustainable extraction technique presented here contributes to the development of a greener and more environmentally friendly approach to organic waste management and resource utilization.

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Subcritical water extraction of *Vincetoxicum spp*. leaves: a promising approach for isolation of antiviral compounds targeting Zika virus

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Vincetoxicum is a genus of flowering plants in the family Apocynaceae, which is native to Europe and Asia [1]. Some *Vincetoxicum* spp. are well-known for their alkaloids, while the studies on other phytochemicals, such as phenolic acids and flavonoids, are rather scarce. Considering the widely documented health benefits (antioxidant, anticancer, anti-inflammatory, antiviral and other bioactivities), there is an interest in a more systematic evaluation of *Vincetoxicum* spp. (poly)phenolic and other bioactive compounds, as well as their properties. For instance, quercetin, luteolin, and rutin were reported as the strongest antiviral flavonoids, which may have antiviral activity against numerous enveloped RNA viruses, including *Flavivirus*. The aim of this study was to isolate bioactive compounds from *Vincetoxicum* species with antiviral activity using subcritical water extraction (SWE) (Figure 1). The SWE operating conditions were 110 °C, 10.3 MPa, and 60 minutes extraction time. Also, to perform a preliminary screening of the phytochemical composition of the obtained extracts by the HPLC method. In addition, considering the possible antiviral activity of phenolic compounds against different viruses, the extract antiviral activity was evaluated against the Zika virus *in vitro* on human lung epithelial (A549) cells.

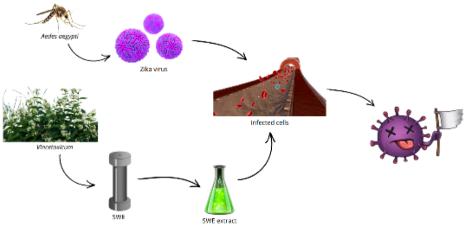

Figure 1: Subcritical water extracts of Vincetoxicum suppress Zika virus infection.

Firstly, an MTT assay was performed, to determine the non-cytotoxic doses of the extract to the human lung epithelial cells. Then, the extracts` effectiveness against ZIKV-MR766 (ZIKV_{GFP}) was performed by a flow cytometry assay. Initially a concentration-dependent toxicity was determined, where the cytotoxic concentration to inhibit 50% of mitochondrial activity (CC_{50}) was found to be from 200 to 500 μg/mL. A549 cells were infected with ZIKV in the presence of non-toxic concentrations of the extracts. The flow cytometry assay showed that the extracts had a dose-dependent anti-ZIKV activity. The HPLC analyses revealed the presence of many compounds in the extracts, such as quercetin, isoquercetin and rutin, according to the ion intensity being the major flavonoids. Several other compounds have also been identified tentatively: chlorogenic acid, quercetin-3,7-diglucoside, malic acid, kaempferol, antofine, septicine. In summary, the subcritical water extraction of *Vincetoxicum* spp. leaves offers a promising methodology for isolating bioactive compounds with demonstrated antiviral efficacy against the Zika virus, suggesting potential broad-spectrum activity against other viral pathogens.

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Simulation of SC-CO_2 extraction kinetics: a novel methodology considering the broken and intact cell mathematical model and experimental design

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The main adopted approach to simulate the SC-CO_2 extraction kinetics consists of considering the neural network tool (NNT) [1]. It is well known that NNT is a very specific tool, not accessible to everyone needing a huge amount of experimental data to be reliable. In the literature, response surface methodology (RSM) is also presented as a predictive tool. but only for predicting the extraction yields or the solute solubilities with the variation of operating conditions. To our knowledge, no "friendly" methodology was proposed to simulate the SC-CO_2 extraction kinetics from a biomass. The simulation of the SC-CO_2 extraction kinetics can be crucial to simplify scale-up studies. The subject dealing with the simulation of the SC-CO_2 extraction kinetics is then very challenging. Furthermore, it is well-known that, whatever the methodology, experimental data are needed at least to have access to the extraction yield depending on the operating conditions. Hence, a novel

methodology was developed, based on the association of the response surface methodology tool and the mathematical model of broken and intact cell (BIC). The BIC model was selected because it a very reliable model, which enables to describe very well the SC-CO_2 extraction kinetics whatever the biomass. Furthermore, it was possible to use this powerful model to simulate the end of incomplete extraction kinetics [2]. RSM is a powerful tool enabling reliable variation predictions of parameters. The methodology consists in considering extraction kinetics established by an experimental design, modeling the extraction kinetics using the BIC model, and considering the model parameters as answers in the experimental design to be able to predict their values whatever the operating conditions. The simulated extraction kinetics can then be plotted by using the predicted model parameters in the BIC model. The proof of concept was established on argan kernels considering different experimental designs, and the results are promising: the absolute average relative (AARD) deviations were found to be very good (ranging between 2.28 and 9.17 %) between the experimental and the predicted curves. Only one experiment was not found to be reliable (AARD = 50 %). The methodology was also applied to various types of biomasses: *Nannochloropsis maritima* (2.86 < AARD (%) < 15.76), *Evening primrose* (3.38 < AARD (%) < 25.73), *Punica granatum* (1.86 < AARD (%) < 5.99) and *Camellia sinensis*. The main advantage of this methodology is that it is very easy to use, as it does not require the knowledge of specific tools such as NNT, and it requires only 9 extraction kinetics.

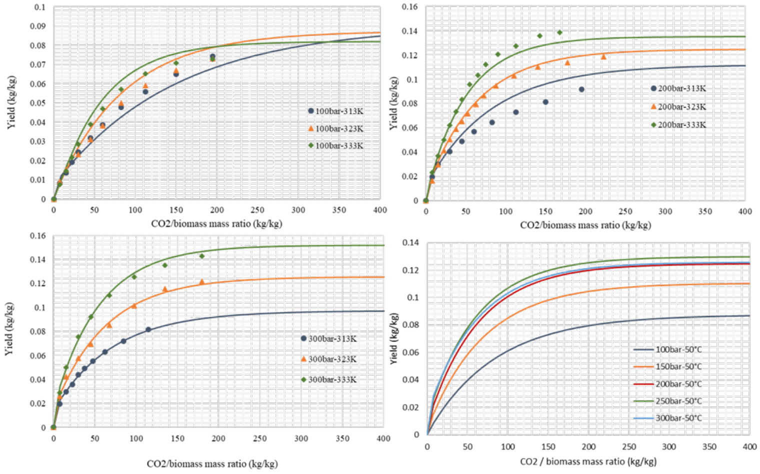

Figure 1: Experimental and predicted SC-CO_2 extraction kinetics from *Nannochloropsis maritima*

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A systematic supercritical CO_2 extraction study to produce terpene-rich and terpene-depleted cannabidiol fractions from hemp flowers

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Despite their high added value, terpenes currently have limited exploitation in the hemp industry, often ending up in the side streams of cannabidiol extraction and/or purification [1]. Nevertheless, over 90 terpenes have been documented as aroma-active ingredients in hemp flowers. In addition to their unique fragrance properties, terpenes were also shown to have beneficial health effects (e.g., antioxidant, antimicrobial, neuroprotective), or enhance the bioactivity of the cannabinoids (the so-called 'entourage effect') [2]

In this study, the influence of different combinations of pressures and temperatures on the recovery of three representative terpenes (caryophyllene, humulene, caryophyllene oxide) and, secondarily, cannabidiol from hemp flowers by supercritical fluid extraction with carbon dioxide (SC-CO_2) was investigated systematically. The influence of the particle size (450-1000 μm) and storage time of the starting materials (0-30 days) on the SC-CO_2 process was evaluated first. Then, the extraction kinetics curves of the monitored compounds were plotted for a series of experiments performed at pressures and temperatures ranging from 80-300 bar and 40-50 °C, respectively. It was noticed that low pressures (90-110 bar) can be used for a fast and efficient extraction of the three representative hemp terpenes. In contrast, higher pressures (200–300 bar) are needed for a good recovery of cannabidiol. Lastly, a step-gradient experiment was designed, to separate compounds with different SC-CO_2 solubility (i.e., terpenes from cannabidiol). In the first step (1), the extraction was carried out at 100 bar and 40 °C for 10 min; then, the pressure and temperature were increased to 110 bar and 50 °C, and maintained at these conditions (step 2) for 20 min. Steps 3 and 4 (15 min each) were performed at the same temperature (50 °C), but at 300 and 400 bar, respectively. The step-gradient SC-CO_2 experiment generated terpene-rich and terpene-depleted cannabidiol fractions. In conclusion, our study brings essential knowledge on selecting the SC-CO_2 process parameters for extracting hemp terpenes efficiently from hemp flowers. Furthermore, it was shown that the simultaneous removal of terpenes and extraction of cannabidiol from hemp flowers could be achieved using a step-gradient SC-CO_2 approach.

Acknowledgments

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Optimization of $scCO_2$ extraction of insect flour oil

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By 2050, there will be around 9 billion people on earth. Although this scenario could be advantageous for cultural variety and economic progress, it also represents a threat to the food sector, because of the increasing pressure on soils that might result in poorer food production leading eventually to malnutrition [1]. Highlighting the worsening resource shortage, insects appear as a promising source of both macronutrients and micronutrients. The second greatest component of the insect, after the protein portion, is made up of lipids, which may be used to replace other fat sources in feed or food applications. Nevertheless, its valorization has not yet developed at an industrial scale [2].

Supercritical CO_2 extraction has been attracting high interest in various industries, including food, beverage, and cosmetics, for the recovery of natural extracts for human consumption. CO_2 has the advantage of being readily available, non-flammable, non-toxic, can be recycled, and is removed easily from the final product by simple depressurization. Furthermore, the process selectivity can be tuned easily by changing the extraction conditions of pressure and temperature, or by using a co-solvent. The application of $scCO_2$ extraction in the field of Insect flour is still limited

[3]. Nevertheless, there are numerous reports on the use of supercritical CO_2 to extract oils selectively from different plant matrices [4]. Supercritical CO_2 represents a highly promising and environmentally friendly substitute for traditional solvent extraction considering the industry's desire to use safe and cost-effective separation technologies [5]. The $scCO_2$ extraction of oil from the *Tenebrio molitor* (mealworm), *Hermetia illucens* (black soldier fly) and *Acheta domesticus* (domestic cricket) larvae flour have been studied in this work, (Figure 1). The effect of operating conditions (pressure, temperature, co-solvent) have been evaluated on extraction kinetics, oil composition and acidity.

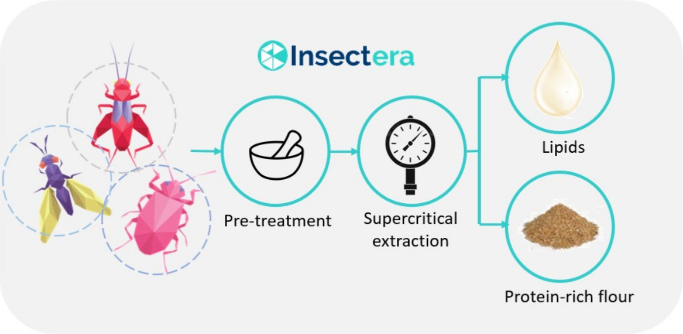

Figure 1: Supercritical CO_2 extraction of insect larvae flour.

Furthermore, the $scCO_2$ extraction results were compared with solid-liquid extraction procedures developed using solvents such as isopropanol, and the extracts were characterized by Nuclear Magnetic Resonance Spectroscopy (NMR). It is expected to obtain extraction yields close to the total oil content of the insect flour. The feasibility and advantages will be discussed, brought to the process by the utilization of the $scCO_2$ extraction method.

Acknowledgements

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Plenary Lecture

Chemical reactions in supercritical water and their applications

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This lecture will explain the supercritical water reactions and its related technologies that our group in Tohoku university has explored for more than 30 years. The research has focused on the fundamentals and applications of a flow reaction process that has enabled detailed kinetic studies of unusual reactions in supercritical fluids. The use of supercritical water in diverse applications has been studied, such as heavy oil reforming, waste polymer decomposition and chemical raw materials recovery, cellulose hydrolysis and sugar recovery, lignin decomposition and chemical raw materials recovery, relevant organic reactions, and nanoparticle synthesis, all without using any catalysts. The research and developments have been done based on the understanding of the unique feature of supercritical water to dissolve organic molecules, and the ability of water molecules to function as an acid or base catalyst in promoting hydrolysis. That fundamental research led to the commercial process for the first supercritical chemical recycling process in Japan, in which the distillation bottom residue of the toluene diisocyanate (TDI) production process (raw material for polyurethane) was hydrolyzed in supercritical water without any catalyst to recover toluene diamine, which can be re-used in the TDI production process. Also, in Korea, larger chemical recycle plants were constructed for TDI or Melamine.

Regarding inorganic materials` synthesis, the author invented "supercritical hydrothermal synthesis" for the continuous preparation of metal oxide nanoparticles, that have found worldwide industrial applications. In supercritical water, especially near the critical point, both the dielectric constant and density change significantly, which affects the reaction greatly. The two-fluids mixing type flow system, where an aqueous metal salt solution is mixed with supercritical water, enables heating the solution to the supercritical state with a very short mixing time constant, that could never be achieved by conventional reactor systems. Detailed kinetics, combined with DFT simulation studies around the critical point, have elucidated that the intrinsic reaction kinetics in SCW can be predicted by the Kirkwood theory, namely, by the dielectric constant effect. The flow supercritical hydrothermal synthesis process has been commercialized first in Korea for LIB cathodic materials` production (1000 t/year), followed by the UK. Prof. Lee combined the supercritical hydrothermal synthesis with supercritical water oxidation to recover the metal oxides nano catalysts with treating the waste sludges from the chemical industries, which has also been commercialized already. For the application of NPs, dispersibility control is the key. Based on the understanding of both inorganic nanoparticle synthesis and organic reactions in supercritical water, the simultaneous reactions of these two reactions wer studied under supercritical conditions. As a result, organic-inorganic hybrid nanoparticles could be synthesized in a supercritical state. This material represents a new class of nanomaterials that can only be prepared in the supercritical phase. This achievement led to the successful synthesis of nano inks (highly concentrated nanofluids) for 3D inkjet printing and printed electronics. New hybrid polymers with nanoparticles demanded by the industry have also been developed, including transparent high-refractive-index flexible film, and materials with high thermal conductivity, high insulation, and modality.

Recent research in catalysis revealed that high catalytic activity can be achieved by controlling the exposure of the active face of the catalyst. In the case of organic-modified nanoparticle synthesis, an unstable face exhibits higher reactivity with the organic molecules, and, thereby, the most reactive face will be modified selectively and protected during nanoparticle formation and growth. In the evaluation of the catalytic activity, extremely high oxygen mobility and oxidative catalytic activity were obtained, even at low temperatures. In general, high oxygen mobility in such materials as ceramics is only observed at high temperatures of 400 ˚C or higher. In contrast, for the nanoparticles with the most active face exposed, high oxygen mobility was observed, even at 150 ˚C, suggesting its use for low temperature solid electrolytes (oxygen carriers), or its high catalytic activity for oxidation. Indeed, it is demonstrated that steam reforming of heavy oils or biomass wastes (black liquor) in water can occur even at low temperatures (waste heat in the factory).

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Keynote Lecture

Synthesis of bio-oils by hydrothermal reaction of biomass - Toward carbon neutral society by combining pulp & paper industry, waste treatment industry and chemical industry -

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Significant efforts have been made to establish a carbon neutral society (zero total CO_2 emission by 2050) all over the world, including the introduction of renewable energies (PV, wind, biomass, geothermal energy etc.), reducing energy consumption. Regarding the production of chemical products, the raw material petroleum should be replaced with the use of waste plastics, CCU (CO_2 usage with H_2) or biomass, as renewable hydrocarbons. In Japan, around 13 M carbon t/year of naphtha are used for producing chemicals, while Japanese forests and wastes have high potential to supply such amounts of hydrocarbons (carbon basis). One of the methods to convert biomass to oil is the hydrothermal reaction process. This lecture explains the potential of these technologies, with showing our previous basic research results of cellulose conversion, lignin conversion in SCW, and with demonstrating the newly obtained results of oil recovery from sawdust. In high temperature water conditions, a homogeneous phase is formed for water and organic matters, which suggests that water can be a reaction solvent for organic reactions, including wastes and biomass conversion. Water properties vary significantly around the critical point, depending on temperature and pressure, and thus, various reactions, such as hydrolysis, dehydration, oxidation, hydrogenation, can be tuned with the supercritical water solvent. Moreover, water molecules themselves work as an acid or a base catalyst, as well as a nucleophile in supercritical water reactions. Thus, sub- and supercritical hydrothermal processes have a high potential to fractionate and transform biomass and waste into specific chemicals. Poly-condensation polymers including cellulose can be hydrolyzed in the high temperature water, and oligomers or monomers can be recovered. Glucose is decomposed into smaller aldehydes through retro-aldol condensation in water. Lignin that has a repeating unit of glyceraldehyde and phenolic compounds can be also hydrolyzed, but, since glyceraldehyde is decomposed further into smaller aldehydes and those work as binding molecules of phenolic compounds through Friedel-Crafts reactions, polymers are formed, which suppresses the chemical recovery.

Supercritical hydrothermal conditions with a flow reaction system can provide nanoparticles that show unusually high oxygen ion mobility. CeO_2 nanoparticles thus synthesized showed catalytic performance for hydrothermal reforming, even at a low temperature (300 C). The CeO_2 NPs are oxidized with water to produce H_2 gas, and the oxidized $CeO_2(O)$ oxidize the aldehydes formed in the hydrothermal treatment of lignin. This leads to suppressing the FK polymerization reactions in lignin treatment in high temperature water, and, thus, phenolic compounds and H_2 gas are recovered. Waste heat from industries is not fully recovered and large amounts of heat are emitted. The hydrothermal bio-oil synthesis process operated at low temperature may be suitable to be combined with this thermal management utilizing low-temperature waste-heat.

As above, subcritical and supercritical hydrothermal treatment is a promising method to recover bio-oils from biomass, and thus to contribute to combine the pulp & paper industries, waste treatment industries, and chemical industries.

Hydrothermal recycling of plastic waste – technology of the future?

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The amount of plastic waste generated in the EU increased by 54 % between 2010 and 2020, while the recycling rate decreased by 7.4 % (Figure 1). The problem of recycling plastic waste is, therefore, one of the biggest issues facing humanity in the 21st century. The search for new technologies and processes to reuse plastic waste in the most favorable way possible, or to convert it into useful raw materials and fuels, is therefore the goal of many researchers. One promising technology is the use of subcritical and supercritical water in the plastics recycling process. As the temperature of the water increases, the dielectric constant of the water decreases, which changes the polarity of the water from a polar solvent to a non-polar solvent. Due to this special property, supercritical water can dissolve non-polar organic compounds that do not dissolve in water at ambient conditions. Another important property that influences the reactivity of water strongly is its ionic product, which increases with increasing temperature and reaches a maximum at around 300 ^{0}C, after which it begins to decrease. Due to the higher ionic product of water at subcritical and supercritical conditions, water can catalyze a variety of reactions, and thus cause the degradation of different materials [2].

The main objective of this contribution is to present the state of research, and demonstrate the applicability of the technology for processing the most common plastic waste (polyethylene (PE), polypropylene (PP), polyethylene terephthalate

(PET) and polyvinyl chloride (PVC)) into valuable products. The influence will be presented of the quality (virgin, recycled) and the structure of the different polymers in different forms (granulate, waste, blends) on the hydrothermal decomposition process. In the decomposition of PE and PP plastics, the oil phase, which consists of various hydrocarbons (alkanes, alkenes, arenes, cycloalkanes, alcohols), is the main product. The optimum conditions for the conversion of plastic into oil and the composition of the oil obtained are different for different materials. In the degradation of PE plastics, the maximum yield of the oil phase (93 %) was achieved at 450 °C and a reaction time of 30 min [3], while, in the degradation of PP plastics, the optimum conditions were 450 °C and 30 min, with the yield of the oil phase being 97 % [4]. The calorific value of the oil obtained depends on the process conditions and the type of plastic. If the conversion is performed at optimal conditions, it is generally in the range of petroleum fuels, and thus represents an excellent alternative to fossil fuels. In the degradation of PVC, a maximum yield of oil phase (26 %) was achieved after 60 min at 425 °C, and the composition was similar to that of crude oil [5]. On the other hand, the most important product in the degradation of PET is terephthalic acid (TPA), the monomeric unit of PET. The maximum yield of TPA was 90 % at 300 °C and a reaction time of 30 min [6].

The current state of research suggests that the hydrothermal treatment of plastic waste is a promising and environmentally friendly technology for the future, capable of converting plastic waste into useful products or fuels without the addition of catalysts or other chemicals.

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Supercritical fluid assisted ionothermal relithiation of $Li_{1-x}(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ positive electrode materials for Li-on battery direct recycling

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In response to the escalating demand for Li-ion batteries, the management of their end-of-life has emerged as a critical concern. While conventional recycling methods, such as hydrometallurgy and pyrometallurgy, have traditionally been employed, they are associated with drawbacks, including high energy consumption, total destruction of valuable components with incomplete critical raw materials recovery and emission of greenhouse gases contributing to environmental concerns [1]. A growing interest is observed in an alternative approach known as direct recycling [2]. This innovative method involves the retrieval of various battery components, potential repairs, and subsequent reuse, aiming to extend the lifecycle of the batteries and complying with current Regulations [3, 4] without resorting to destructive processes.

The present work deals with $Li_{1-x}(Ni_{1-y-z}Mn_yCo_z)O_2$ positive electrode materials, in particular, with NMC622 (y=z=0.2), which are used predominantly in commercial Li-ion batteries nowadays. Once aged, these layered phases become lithium-deficient and exhibit changes in their surface and bulk structure [5]. This project proposes a novel regeneration scheme, comprising an ionothermal route [6] combined with supercritical fluid technology in mild conditions (Figure 1.). The main goal is to shed light on the structural evolution behind relithiation for further understanding and optimization. Delithiated samples were prepared chemically in a glovebox under argon using nitronium tetrafluoroborate as the oxidant, the cutoff delithiation state being set to 50% to ensure full relithiation in real-life settings. The ionothermal reaction was carried out in an unstirred custom reactor setup employing supercritical carbon dioxide, argon, and nitrogen. Lithium bromide was utilized as the lithium source and reducing agent, with EMIM TFSI serving as the ionic liquid medium. The influence was tested of several parameters on efficiency. Identifying the optimal relithiation conditions led to the production of a material whose structure is indistinguishable from that of the pristine phase, all while reducing both reaction time and temperature significantly. The versatility of the process was evaluated by regenerating successfully in a single batch NMC622 with varying degrees of delithiation (10%, 30%, 50%), an unprecedented outcome not reported previously in the literature.

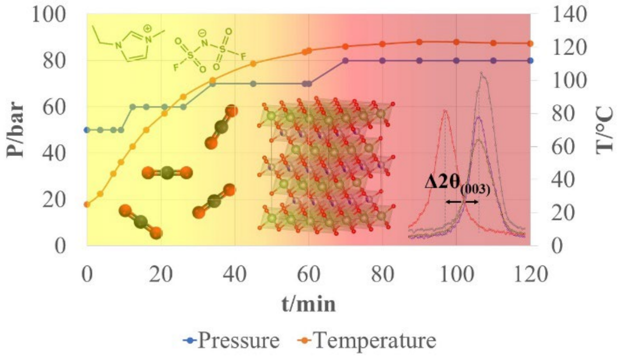

Figure 1: T/P profiles during ionothermal relithiation and evolution of the (003) peak.

This presentation outlines the ionothermal relithiation process, emphasizing the impact of optimized variables such as pressure and gas nature in achieving complete regeneration of the lithium content in NMC622. Multiple techniques are combined to characterize the structure, chemical composition, and physical properties of the regenerated active material. The proposed procedure can be considered an effective and convenient approach to the direct recycling of layered oxide positive electrode materials.

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Life cycle assessment of an innovative process assisted by pressurized CO_2 for the direct recycling of lithium-ion battery positive electrode production scraps

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The battery market continues to expand, due to the electrification of mobility, resulting in a rising need for lithium-ion batteries (LIB) and, subsequently, their recycling. As this demand rises, the amount of waste generated during the manufacturing process, including production scraps, is also expected to increase. These scraps can account for up to 30 wt.%, and represent an initial and accessible target for recycling within a closed loop [1]. In addition, the European Commission has signed a Regulation for battery recycling and e-waste management, to improve recycling efficiency, material recovery rates and to ensure a minimum recycled content in new batteries [2]. Currently, the two main recycling processes operating at the industrial scale are pyro and hydro-metallurgy. Despite their capabilities in recovering components, these processes have limitations, as they require high-energy inputs or excessive use of high concentrated acid solvents, respectively. In the context of recycling electrode production scraps, the current technology seems inappropriate, as the materials are in a pristine state and only partially assembled. To answer this challenge, direct recycling – a promising alternative process that aims to separate the different components of a battery and recycle them independently – seems suitable for retaining the positive electrode material's morphology and functionality. While this method is still at the laboratory scale, it has the potential to be environmentally friendlier than other recycling methods.

This presentation aims to assess an innovative LIB direct recycling process using pressurized CO_2 mixed with organic solvents in batch conditions under optimized experimental parameters. The feasibility of this recycling process is demonstrated using $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) battery electrode production scraps. To develop the direct recycling of LIB further, there is a need for tools to quantify, compare, and analyse the potential environmental impacts of these processes. In this context, Life Cycle Assessment (LCA), a standardised method used in the literature to evaluate the potential impacts and benefits of existing LIB recycling methods, [3,4] is employed in our study. Environmental hotspots are identified with LCA, and, subsequently, an eco-design approach is applied to propose experimental solutions aimed at reducing the targeted environmental impacts. A best-case scenario after upscaling can also be modelled, to assess the potential benefits of this innovative recycling process in comparison with primary production and other recycling processes. Preliminary results show that this innovative direct recycling process at the lab scale saves mineral resources, reducing their consumption by up to 70% compared to primary production. Nonetheless, there is an observed increase in the carbon footprint, due primarily to differences in scale modelling. Additionally, two main hotspots are identified: electricity consumption and the use of solvents. To address these hotspots, laboratory-scale optimisation can be employed initially. Subsequently, an upscaling methodology can be implemented, with a particular focus on achieving the best-case scenario by increasing the solid/liquid ratio and minimising electricity consumption.

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Recycling of $LiFePO_4$ cathode material by hydrothermal leaching with glycine, oxalic acid or citric acid and precipitation isolation

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The lithium iron phosphate ($LiFePO_4$ or LFPO) battery finds diverse applications because of its advantages in cyclability, thermal stability, costs, and toxicity over other LIB cathode materials. With an increase in demand and consumption, the number of spent LFPOs is also rising year by year. Efficient disposal or recycling of spent LFPO cathode materials is beneficial to conserve natural resources, reduce environmental pollution, keep resource stability and security, and have economic benefits. Our laboratory has achieved high leaching efficiency and element recovery of the LIB cathode materials successfully, including $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$ under hydrothermal conditions[1]. Here, **the purpose of this research focuses on achieving the metal element recycling of LFPO cathode materials by applying the method of hydrothermal leaching and precipitation isolation. Furthermore, parameter optimization, a mechanism study, and a kinetic study were conducted.** As shown in **Figure 1**, the whole research contained four steps, including pretreatment, hydrothermal leaching, precipitation isolation, and hydrothermal re-synthesis.

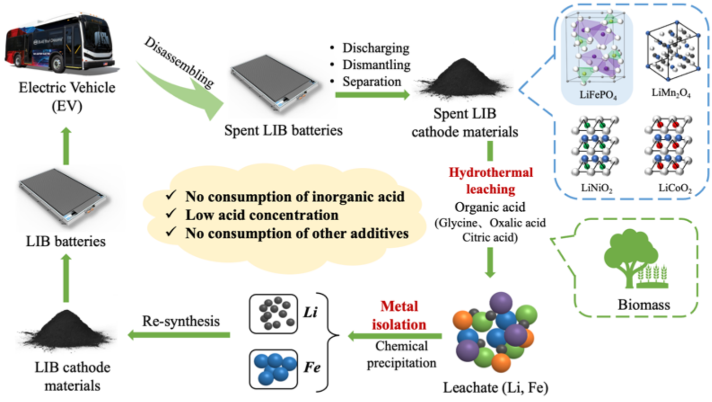

Figure 1: The diagram of overall project work.

It was the first time the hydrothermal leaching of LFPO cathode materials was performed with organic acids, which resolved many problems during the leaching process of LFPO cathode materials, such as acid corrosion, high costs, or severe environmental pollution. Citric acid was found to be the most efficient for leaching all the components of Li, Fe and P under hydrothermal conditions. Under hydrothermal conditions of 90 °C, 10 min, 10 g/L of pulp density, and 0.8 mol/L of citric acid concentration, the leaching efficiencies of Li, Fe, and P reached 96%, 100%, and 88%, respectively [2]. Oxalic acid achieved high leaching efficiencies for Li and P at 100% and 97%, respectively, and separated 98.5% of Fe from the LFPO as FeC_2O_4 precipitate, under the conditions of 200 °C, 10 min, 30 g/L of pulp density, and 0.8 mol/L of oxalic acid concentration. The purity of the FeC_2O_4 reached up to 99.7%. Additionally, it was the first attempt to realize the total-element recycling of commercial or LFPO cathode materials by hydrothermal leaching and precipitation isolation. 99.6% of Fe could be recovered from the citric acid leachate, while the Li^+ could be separated in the form of Li_3PO_4/Li_2CO_3. As for the oxalic acid leachate, due to 99% of Fe having been precipitated in the form of FeC_2O_4 with purity of 99.7% during the leaching process, the only element recovered from the leachate was Li. After the isolation process, the purity of the Li_3PO_4 recovered from the oxalic acid leachate could reach 99.4%. In the future, the leachate obtained from spent LFPO cathode materials by hydrothermal leaching, or elements recovered after precipitation isolation, will be used firstly as the raw materials for the hydrothermal re-synthesis of LFPO cathode materials.

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Keynote Lecture

Plant barrier biopolyesters from cuticle wastes via ultrafast supercritical hydrolysis

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A plant-barrier biopolyester is a polymer formed from hydroxy or epoxy fatty acids joined by ester linkages, which are produced by plants in their external tissues (i.e., cuticles, stems and roots). The plant cuticle is the outermost membrane that covers and protects the epidermis of the aerial parts of almost all land plants. Cuticles are essential, to prevent desiccation due to massive water loss from internal issues to the environment, and provide a resistant, yet flexible, insoluble, infusible, and chemically inert barrier at the interface between the plant surface and the atmosphere. The cuticle is composed by a macromolecular scaffold of cutin (*i.e.,* biopolyesters formed mainly by condensed polyhydroxy fatty acids), polysaccharides (cellulose, pectin, and hemicelluloses) from the cell wall, and a variety of aliphatic hydrocarbons collectively named waxes. In the aerial parts of plants, the biopolyester scaffold is generally formed by cutin**,** whereas the roots and stems of wood contain suberin instead. Biopolyesters can be separated from the cuticle by a long multi-step procedure, that comprises a previous dewaxing with chloroform and methanol, and the use of hydrolysis to remove the polysaccharides [1].

The aim of this contribution is to present a continuous process for obtaining these polyesters based on the use of supercritical fluids, the characterization of the polyesters obtained, and their applications.

The process is a two-stage process: 1) Pretreatment by supercritical carbon dioxide extraction to separate the extractives fraction, mainly waxes. 2) A supercritical water ultrafast hydrolysis stage to hydrolyse the carbohydrates. The use of SCW as a solvent and reaction media, allowing the change ofproperties of the SCW, such as the ionic products and dielectric constant [2], The kinetic of the hydrolysis of carbohydrates is faster than the kinetic of the hydrolysis of the ester bond, that allow getting to the polyesters without hydrolysis, to ester bond to the acids monomers. As an example,.

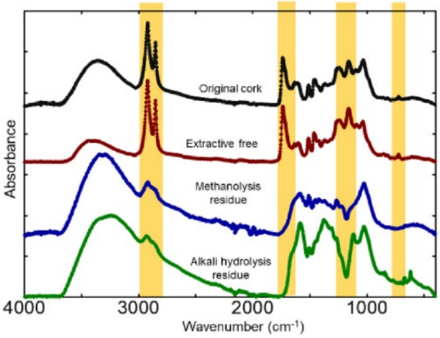

Figure 1: presents evidence as the ester-links are not hydrolyzed during the suberin fractionation process [3]

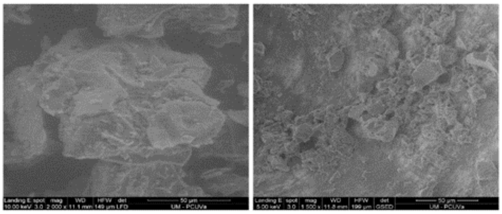

Figure 2: SEM particles tomato peel (left) and 3 D cutin product (right).

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Tuning the polymorphism of ZrO_2 nanocrystals from purely monoclinic to purely tetragonal playing with supercritical hydro-solvothermal conditions

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Tuning the polymorphism of ZrO_2 nanocrystals has gained significant interest in the fields of Materials Science and Nanotechnology. ZrO_2 exists in multiple polymorphic crystal structures, including monoclinic (up to 1170°C), tetragonal (up to 2370°C), and cubic (above 2370°C) structures, each exhibiting distinct physical and chemical properties. The ability to control and manipulate the polymorphic composition of ZrO_2 nanocrystals opens up new avenues for tailoring their mechanical, electrical, and catalytic properties. This interest is driven by the potential applications of ZrO_2 nanocrystals in fields such as catalysis, fuel cells, sensors and biomedical devices, where precise control over polymorphism (pure or a mixture of them) can lead to improved functionality and efficiency. The quest to understand

and optimize the polymorphic behavior of ZrO_2 nanocrystals is, thus, of major interest, especially when going at the nanoscale, where the well-defined temperature boundaries between each polymorph become less evident.

In recent years, we were able to develop in our lab an original continuous supercritical based sol gel like synthesis route enabling the synthesis of either pure monoclinic ZrO_2 nanocrystals, pure tetragonal ones, or a controlled mixture of them. This was achieved only by playing with the quantity of water in the system for nanocrystals sizes below 7 nm, thus questioning the existence of any critical size limit below which the stabilization of pure t-ZrO_2 is attainable at low temperatures (Figure 1) [1].

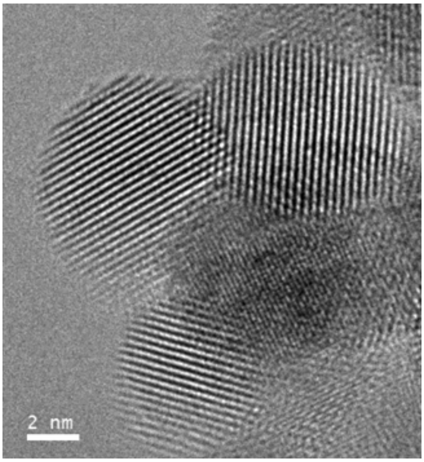

Figure 1. High resolution TEM picture of tetragonal ZrO_2 nanocrystals.

This water effect was studied further by means of *in situ* total X-ray scattering studies, in which we were able to confirm that the variation of tetragonal/monoclinic phase ratios within the produced powders was correlated directly to the amount of water available in the system. This was demonstrated by controlling the dehydration kinetics, either choosing primary alcohols with varying thermal stability, or by changing the synthesis temperatures [2]. The main limitation of this original approach is the amount of powder produced, correlated directly to the quantity of available water (sol-gel based synthesis), which can be limited, depending on the targeted polymorph mixture. We thus explored the possibility to balance this effect by adding yttrium to the system and making Y_2O_3-ZrO_2 solid solutions, where the capability of Y_2O_3 to stabilize the tetragonal structure is well established and documented in the literature [3].

In this presentation, we will first describe this original continuous supercritical based sol gel like approach, then, combining *ex situ* physicochemical characterizations (DRX, FTIR, Raman, TEM, etc.) with *in situ* total scattering ones (PDF data treatment), we will highlight the importance of the water quantity within the system on the tunability of the produced polymorph mixtures. Finally, we will demonstrate the interest of adding yttrium within our system, to balance the yield limitations encountered in some cases.

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Production of biomass nanofibers self-sustaining hydrogels by hydrothermal gelation

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The ultimate biomaterial will be able to be prepared using only a biomass resource and water, without additional chemical modification. Although chemical modification is a useful way to control the shape and strength of biomaterials, there are concerns that chemical additives harmful to the human body may remain. If chemical modification is not performed, and no chemical additives are used, the production of biomaterials requires the use of simple attractive forces.

In this work, we propose a new method of preparing self-sustaining hydrogels using only water, called "hydrothermal gelation", which is achieved by placing cellulose nanofiber (CNF) dispersions under hydrothermal conditions at 160 °C [1, 2]. At first, the CNF dispersions were prepared by the wet pulverization process with a water jet at 25 °C from raw cellulose powder. Next, the CNF dispersion can be converted by hydrothermal gelation (160 °C, 10–120 min) to a mechanically strong hydrogel that can maintain its shape. The gelation mechanism and physicochemical properties of the hydrogels were elucidated in addition.

The CNF dispersions were prepared by the wet pulverization process at 25 °C [3]. Cellulose powder (0.1–3 wt.%) was suspended in distilled water, and then the slurry was subjected to mechanical disintegration to form CNFs. In the disintegration process, the slurry was pressurized at approximately 245 MPa and 25 °C, and ejected into the device chamber through a 100-µm aperture nozzle, then pulverized with a ceramic ball for 5–100 collisions with a Star Burst Mini, a wet pulverization machine, and dispersing device equipped with a ceramic ball-collision chamber. The physicochemical properties of CNF dispersions, such as transmittance and viscosity, can be controlled through the disintegration time; however, CNF dispersions prepared in this manner cannot maintain a constant shape due to their flowability.

To prepare the hydrogels, approximately 3 mL of CNF dispersion was loaded into a 6 cm^3 316-grade stainless steel tube reactor, which was subsequently immersed in a 160 °C molten salt bath. At this temperature, the saturated vapor pressure in the reactor was calculated to be 0.6 MPa. After the hydrothermal treatment, the reactor was taken out of the molten salt bath and cooled rapidly to 25 °C by submerging it in a water bath, after which the obtained hydrogel was taken out of the reactor.

From the analysis of the CNF hydrogels, we concluded that the CNF hydrogels formed via hydrothermal treatment were physical gels, and that the network structure may have formed through simple attractive forces, such as van der Waals forces.

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Preparation of liposomes by SFEE. Application to encapsulate Amphotericin B.

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Liposomal Amphotericin B (AmB) is the commercial treatment for visceral leishmaniasis (Ambisome). The diameter is 80 nm. The objective of this work was to obtain AmB loaded liposomes through the process of Supercritical Fluid Extraction of Emulsions (SFEE). This is the first-time liposomes have been produced by SFEE. Liposomes were also produced by the traditional evaporation method.

The SFEE technique is based on the ability of $scCO_2$ to extract the organic phase of an emulsion, in which the drug and the lipids (lecithin and cholesterol) were dissolved previously. When the organic solvent is removed, liposomes are produced. The SFEE was carried out at 40°C and 100 bar, to operate outside the two-phase region of the organic solvents, avoiding the decomposition/degradation temperature of all the components. The AmB was encapsulated successfully inside the liposomes, although the liposomes presented broad size distributions (between 100 and 1000 nm). An amplified TEM image of an isolated liposome is shown in Figure 1, distinguishing both the core and the lipid bilayer surrounding it. Several parameters were varied to narrow the diameter. First, the type (Span 80, APG, Tween 80), and then the amount of surfactant (0.3-7.0 % of Tween 80), but it was concluded that the liposome size was independent of the surfactant concentration. Then, all the parameters were investigated that, according to the emulsions` theory, were likely to cause changes, especially in the droplet size of the starting double ($W_1/O/W_2$) emulsion, as it acted as the frame for the liposomes. These were the organic solvent, the viscosity of the phases, and the agitation speed. The organic solvent is important, as it solubilizes the drug and lipids. Amphotericin B is practically insoluble in water, and very poorly soluble in most organic solvents. It is slightly soluble in methanol, although the best solvent is dimethyl sulfoxide (DMSO). [1] However, due to the high boiling point of DMSO (190ºC), it is difficult to remove all traces in the final product. So, other green, low toxicity solvent mixtures were tested, that were more easily extractable with $scCO_2$: a) Methanol/Chloroform (1:1); b) Chloroform/Diethyl ether (3:7), and c) Methanol/Ethyl acetate (1:1). Also, the increase of the viscosity of the organic phase was studied by adding Vit E, and of the external aqueous phase by adding glycerol. However, none of these changes were influential. On the contrary, by adding anionic lipids (DSPG and DPPG) and by optimizing the way the two emulsions were stirred to form the double emulsion, it was possible to center the emulsion droplets at 200 nm. However, liposomes` size dispersion occurred after subjecting this emulsion to the SFEE process. It also happened when we used the traditional evaporation method. Consequently, the SFEE produced liposomes have to be homogenized afterward to achieve a sharp size distribution.

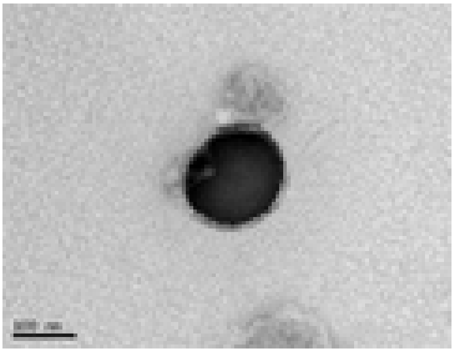

Figure 1: TEM image of one of the liposomes obtained from the chloroform/diethyl ether solvent mixture with 0.7% Tween 80.

Fortunately, when studying the encapsulation efficiency, it was found that, regardless of the method and emulsion used, it was around 100% with a 15 % drug loading. This is also a very promising result for the encapsulation of other drugs. Moreover, in a commercial-scale process, the process could have a very high-capacity production, as the SFEE allows continuous operation. [2]

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New supercritical flow synthesis of $Ba_{1-x}Sr_xTiO_3$ nanocrystals using acetylacetonate precursors for the development of dielectric composites

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In order to meet the miniaturization needs of electronic systems, the industry has moved gradually toward thin-film embedded capacitors positioned as internal layers in printed circuit boards (PCB). This technology of components allows a reduction in weight, volume and cost, in addition to an increase of the integration density, reliability, and radiofrequency performances [1]. These components are in the form of laminated strips made of a dielectric composite (a few tens of microns thick), usually a polymer loaded with inorganic particles, inserted between two copper electrodes [1]. The goal of this architecture is to combine: (i) the dielectric properties of the particles (including high permittivity and low losses), and (ii) the electrical properties of the polymer (including high dielectric strength) associated with its processability (thin and/or thick film deposition).

$BaTiO_3$-based nanoparticles are one of the most widely used fillers thanks to their well-known dielectric properties [1,2]. However, when decreasing their sizes down to a few tens of nanometers, the apparition of structural defects (vacancies, amorphization, etc.) tends to alter their performances. It is thus necessary to develop synthesis processes enabling to maintain, as much as possible, the bulk properties of these materials while being at the nanoscale, and the supercritical fluid technology has shown this capability. During the last 20 years, the ICMCB has been developing the sol-gel like supercritical flow synthesis of high quality $BaTiO_3$ nanoparticles and the solid solutions $Ba_{1-x}Sr_xTiO_3$ (with $0 \leq x \leq 1$) and $BaTi_{1-y}Zr_yO_3$ (with $0 \leq y \leq 1$), based on the use of alkoxides. In the specific case of $Ba_{0,6}Sr_{0,4}TiO_3$, they showed nanoparticles with properties never observed before: a *high k* behavior ($\varepsilon_r = 260$ @ 1 kHz and 300 K), a size of about 20 nm, and a wide transition from a ferroelectric to a paraelectric state [3,4].

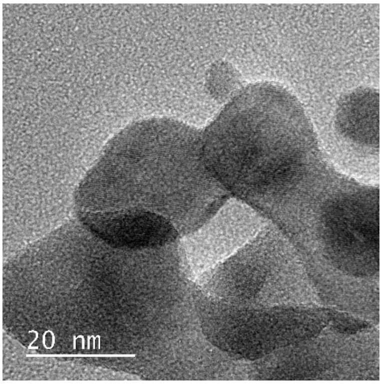

Figure 1: **TEM picture of barium- titanate based nanoparticle synthesized by supercritical fluid technology.**

Recently, $SrTiO_3$ nanoparticles were synthesized successfully using acetylacetonates based precursors for barium and strontium, which are less sensitive to air and thus easier to handle. Now the strategy is to explore this new synthesis route, extending it to other compositions while assessing their physicochemical properties, together with their relative permittivity.

During this presentation will be exposed: (i) the continuous supercritical fluid synthesis of $BaTiO_3$ and $Ba_{0,6}Sr_{0,4}TiO_3$ nanoparticles, starting with these new precursors, and (ii) their physicochemical characterizations, including numerous techniques, such as X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectrometry, inductively coupled plasma spectroscopy and high resolution transmission electron microscopy.

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DELOS-SUSP for the production of highly homogeneous non-liposomal nanovesicles

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Nanovesicles are one of the most promising supramolecular assemblies in nanomedicine, due to their ability to encapsulate and deliver bioactive molecules. Some of their pharmacological properties, such as stability or loading capacity, are determined by their structural characteristics [1, 2]. However, conventional methods for vesicle formation result in vesicles with low structural homogeneity and large heterogeneity in terms of size and lamellarity. For this reason, further post-formation steps are required for size reduction and homogenization, which have a high risk of damaging the functionality of the bioactive and oxidizing vesicle membrane components. In this regard, compressed fluid (CF)-based methodologies are attracting increasing interest for the direct preparation of nanovesicles and other micro/nanoparticulate materials with structural characteristics not reachable by already existing particle production procedures using liquid solvents [3]. In addition, one of the most extended CFs in materials processing is CO_2, which is non-toxic, non-flammable, and can be brought to a compressed state at mild conditions, allowing for the preparation of colloidal bioconjugates with expensive and/or fragile active biomolecules, such as proteins, peptides, enzymes, or hormones. In this context, we developed the DELOS-SUSP *(Depressurization of an Expanded Liquid Organic Solution into aqueous solution*) process, a one-step, compressed-fluid based method that enables the reproducible and scalable production of nanovesicles with remarkable homogeneity in terms of composition, lamellarity and particle size [4, 5]. Here, we present the advantages of the DELOS-SUSP method for the preparation of non-liposomal, cholesterol-rich nanovesicles, and we compare it with other conventional, non-compressed fluids-based methods, based on thin film hydration, ultrasounds, and microfluidics. We demonstrate that nanovesicles produced by compressed fluid methods are smaller and have a narrower size distribution (Fig.1 *left*) [5], likely due to a more homogeneous distribution of membrane components and the absence of cholesterol-rich regions in the vesicular membrane. Furthermore, we demonstrate that the CO_2-assisted method produces vesicular systems with greater intrasample homogeneity when compared to standard techniques such as thin-film hydration [5, 6]. This is due to the solvent-free stage in the thin-film hydration technique, which promotes heterogeneous membrane domains during film formation (Fig. 1 *right*). Finally, we show that DELOS-SUSP enables the production of cholesterol-rich nanovesicles at high concentration, which are challenging to prepare by microfluidics, due to cholesterol precipitation in the microfluidic channels.

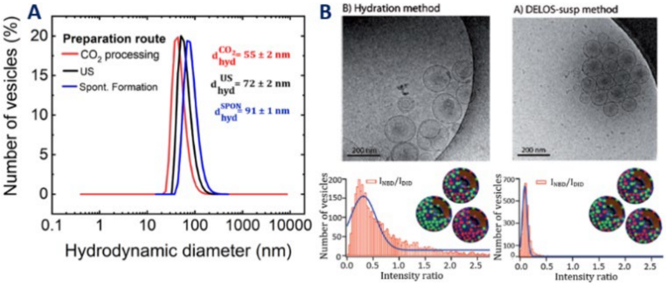

Figure 1: A: Size and size distribution analysis by DLS of nanovesicles produced with ultrasounds (US) (Black), CO_2-processing (Red) and spontaneous formation (Blue); B: Cryo-TEM images and intensity histogram obtained by fluorescence confocal microscopy depicting the heterogeneity of two different dyes in the membrane of nanovesicles prepared by thin film hydration and DELOS-SUSP.

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20th European Meeting on
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Keynote Lecture

Integrated sub-/supercritical fluids to produce highly stable encapsulated astaxanthin/*β*-cyclodextrin microparticles from wet *Haematococcus pluvialis*

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An increasing awareness of the multifunctional health benefits and safety of natural astaxanthin has led to growing demand for this high-value-added bioactive compound in the nutraceutical, pharmaceutical, cosmeceutical, and food industries [1]. However, the utilization of astaxanthin in medicines and functional foods is currently limited by its instability, low oral bioavailability, and poor water solubility [2]. The molecular structure of astaxanthin, which consists of a chain of conjugated double bonds with a *β*-ionone ring at each end, is highly sensitive to oxidation and degradation by light or heat during processing, which can decrease the antioxidant activity of the final products. Moreover, the robust, highly chemical resistance cell wall structure of *Haematococcus pluvialis* (*H. pluvialis*) makes the efficient recovery of astaxanthin and other biomolecules from the red cysts of *H. pluvialis* challenging. Recently, the encapsulation of astaxanthin molecules has received attention as a promising approach for improving stability and shelf life [3].

To overcome these issues, in this study, subcritical dimethyl ether (sub-DME) was applied as a green extraction solvent for the recovery of intracellular astaxanthin directly from wet *H. pluvialis* red cysts, without involving high-cost, energy-intensive pretreatment processes, such as drying and cell wall disruption. Herein, astaxanthin was encapsulated in *β*-cyclodextrin (βCD) using CO_2 as a supercritical antisolvent (SAS). A green solvent, dimethyl sulfoxide (DMSO) was used to prepare astaxanthin and βCD solution mixtures prior to the SAS process.

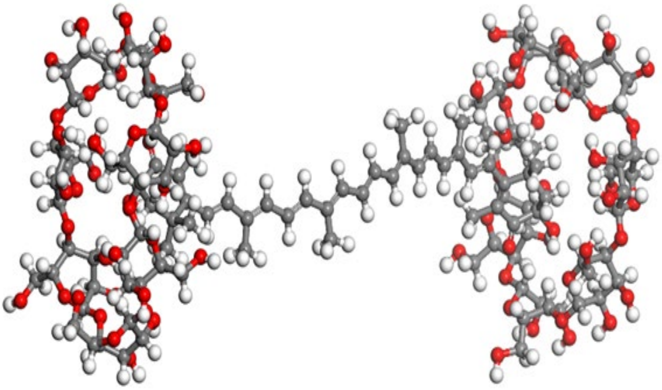

Figure 1: A possible encapsulation configuration of astaxanthin and βCD (1:2 configuration).

We demonstrated that astaxanthin can be almost completely encapsulated in βCD using the SAS process (99.6% encapsulation efficiency), **Figure 1**, and the produced astaxanthin-βCD inclusion complex contained a negligible residual solvent of DMSO (0.22 ppm), although no additional separation or purification steps were employed. Furthermore, the encapsulated astaxanthin-βCD complex microparticles exhibited enhanced thermal stability and antioxidant activity compared to free astaxanthin. This highly sustainable, energy-efficient, eco-friendly, and scalable approach of integrated sub-DME and SAS processes can recover high-purity and bioactive astaxanthin and produce high thermal stability of encapsulated astaxanthin microparticles with potential utility for food and pharmaceutical applications. These insights can aid in advancing the development of functionalized astaxanthin-rich drug and food supplement formulations.

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Continuous manufacturing in pharma: a benchmarking between supercritical fluids and electrospraying in drug crystallization

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Continuous manufacturing (CM) has been used successfully by several industries, although it has only started to gain traction in the pharmaceutical industry over the last 10 years, and is still far from being fully implemented in this sector. CM of both drug substances and formulated drug products also provides a more rational approach for drug manufacturers to reduce the development time and costs while increasing quality, process throughput, robustness, and yields [1]. Furthermore, in recent years, regulatory agencies have encouraged pharmaceutical companies highly to shift from batch to continuous processes. In this work, we highlight the high versatility of CM in the pharmaceutical industry in the processing of drug nanoparticles, aiming to improve the oral bioavailability of drugs belonging to the biopharmaceutics classification system (BCS) classes II and IV. Every year, approximately 75% of new active pharmaceutical ingredients (APIs) fail to reach the market due to their poor solubility in water and bioavailability. This results in a total waste of 65 billion US dollars for pharma companies. To enhance the bioavailability of APIs, R&D centers have been working on producing more soluble solid-state forms (*e.g.,* amorphous solid dispersions, cocrystals), inclusion complexes and solid nanoparticles/nanosuspensions with a typical particle size below 500 nm [2]. Therefore, in this work, we provide a benchmarking between two continuous production techniques - – electrospraying and supercritical enhanced atomization (SEA) [3] to produce celecoxib (CEL) drug nanoparticles with controlled polymorphism. All the particles were characterized in terms of powder x-ray powder diffraction (PXRD), Differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The benchmarking followed a quality-by-design (QbD) approach using the DoE (Design of Experiments) tool and statistical analyses. In electrospraying, with a constant solution flow rate and distance between the needle and collector, CEL solutions at different concentrations (15 – 60 mg/mL) were processed at different voltages (25 – 40 kV), producing particles with mean particle sizes (PS) ranging from 289 nm to 758 nm. In parallel, CEL solutions were processed using SEA, generating CEL nanoparticles with a mean PS ranging from 253 nm to 1229 nm.

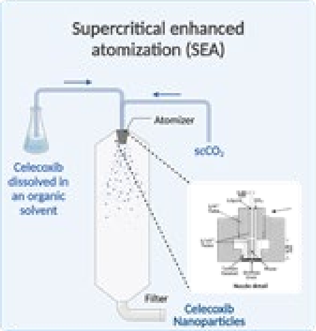

Figure 1: **Schematic representation of the production of CEL nanoparticles using SEA.**

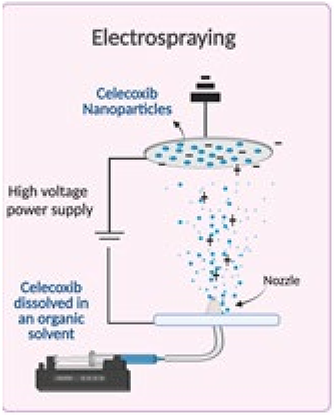

Figure 2: **Schematic representation of the production of CEL nanoparticles using electrospraying.**

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Solubility of chlordiazepoxide in supercritical carbon dioxide: modeling investigation

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Chlordiazepoxide, a member of the 1,4-benzodiazepine group, has a poor aqueous solubility and dissolution rate in water. Therefore, a supercritical fluid-suitable strategy may be adopted, depending on the drug properties (such as those in BCS classes II and IV) and the type of delivery required. The solubility of medicines in SCF is also critical for the development and design of various pharmaceutical processes. To use supercritical technologies in the medication production effectively, the availability of precise solubility data in $scCO_2$ is imperative. Solubility experiments can be categorized either as static or dynamic ones (i.e., in a closed-cell or in flow systems). Gravimetric, spectrometric, and chromatographic tests are ways to measure solubilities, although other methods are also available. To use supercritical technologies in medication production effectively, the availability of precise solubility data in $scCO_2$ is imperative.

This study aims to enhance our comprehension of the chlordiazepoxide solubility in $scCO_2$. To this end, the solubility of chlordiazepoxide in supercritical carbon dioxide was measured at temperatures from 308.15 K to 338.15 K and pressures from 12

MPa to 30 MPa. The solubilities of the drug (expressed as the mole fraction) were in the range of 2×10^{-5} to 5.76×10^{-4}. A detailed explanation of how the solubility in $scCO_2$ is measured is documented elsewhere [1-3]. Figure 1 summarizes the results.

The data were correlated with six density-based models (K-J, MST, Chrastil, Garlapati and Madras, Bartle et al., and Sparks et al.) and four equations of state (Peng-Robinson, Soave, and Estévez *et al.* EoS models). The mean relative deviation (*AARD*) and corrected correlation coefficient (R_{adj}) were used to assess the goodness of the models.

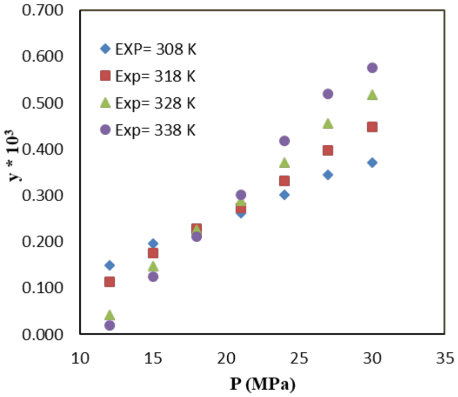

Figure 1: Experimental chlordiazepoxide solubility in the binary system.

In conclusion, this study delves into the solubility in SCF in this binary system. As mentioned above, the experimental solubility data obtained were in the range from 2×10^{-5} to 5.67×10^{-4} (20 ppm to 567 ppm, molar basis).

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CFD modelling of supercritical CO_2-assisted spray drying for drug particle production

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The importance of Computational Fluid Dynamics (CFD) modeling in pharmaceutical manufacturing is driven by the increasing demand for producing drug particles with stringently defined critical quality attributes (CQAs) [1]. The operating parameters of atomization-based particle production processes can alter these CQAs, leading to undesirable outcomes in poorly designed setups, while experimental design optimization may entail extensive costs, especially when dealing with expensive pharmaceutical materials [2]. Among these parameters are the nozzle geometry, injection pressure, drying chamber pressure, and solution flow rate. CFD analysis can reduce the size of the required experimental matrices by examining the operating parameters through simulations, underpinning the efforts of shifting pharmaceutical manufacturing toward a quality-by-design (QbD) approach [3]. In this context, our work is oriented towards advancing atomization-based drug nanoparticle manufacturing technologies through detailed analysis of the $scCO_2$-assisted spray drying (SASD) process. Due to the limited research efforts reported on modeling the high pressure trans-critical operation of atomization nozzles, we aim to characterize its key features while attempting to link those features to the CQAs of SASD-produced particles. To this end, we have developed a finite volume

CFD model using Ansys Fluent (2023R1) to describe the SASD atomization process, starting from pure CO_2 trans-critical expansion, and proceeding to simulating the expansion process of the $scCO_2$-solvent mixture, and, ultimately, the $scCO_2$-assisted atomization of a model drug solution. The simulation domain was a 100 mm (L) x 50 mm (W) 2D axisymmetric domain, discretized into a grid of 3.17M cells refined near the orifice area. The inlet pressure ranged from 70-140 bar, while the outlet pressure was set to an ambient pressure (0 bar-g). A realizable $k - \epsilon$ model was used to capture the turbulence effects. Simulations were run on the national high-performance computer in Ireland (ICHEC), using 40 cores of processing. A user-defined function was developed and integrated into the model, where the Peng-Robinson real gas equation was used to capture the thermodynamic gas properties throughout the process. Pure CO_2 model predictions were validated against experimentally measured temperature distribution induced by the supercritical CO_2 jet on an impingement surface, and against experimentally measured mass flow rates (Figure 1). For supercritical pre-expansion conditions and a nozzle orifice size of 80 μm, the experimental results of the pure CO_2 jet matched the predictions with a maximum error of 10%. The predicted jet morphology demonstrated the occurrence of shock waves, a prerequisite for fine droplets` formation. A discrete particle model (DPM) was used to simulate the $scCO_2$-solvent mixture using Methanol as the model solvent. The Kelvin-Helmholtz Rayleigh-Taylor (KHRT) breakup model was used to simulate droplet breakup upon expansion. For a pressure range of 80-120 bar and Methanol flow rate of 1 ml/min, the simulations of the CFD-DPM model revealed initial Methanol droplet sizes in the order of 3 μm. Future work involves validating the CFD-DPM model results by means of Phase Doppler Anemometry (PDA) measurements for the droplet size and velocity distributions. The same technique will be employed to validate the $scCO_2$-assisted atomization of the model drug solution.

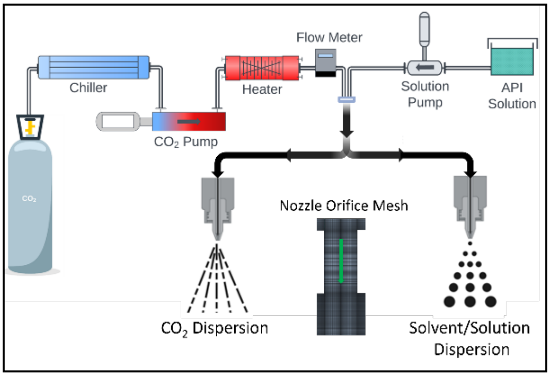

Figure 7: $scCO_2$-assisted atomization setup.

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20th European Meeting on Supercritical Fluids
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Keynote Lecture

Antimicrobial activity of the supercritical CO_2 in the healthcare field

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This is a summary of our work on the use of supercritical ($scCO_2$) in pathogens` inactivation in the Healthcare field. We investigated its virucidal activity in SARS-CoV-2 and its bactericidal activity in *Staphylococcus epidermidis*. To ensure sterilization, research must be carried out on spores. We used the ones that are normalized as bioindicators: *Geobacillus stearotermophilus* and *Bacillus atrophaeous*. As supports we explored several materials as gauzes made of cotton, implants made of polymers or metals, and different fabrics of sanitary wear. In the past, we also checked the sterilization of electronic devices. The interest arises from the low availability of sterilization techniques for thermosensitive materials.

The CO_2 alone at 100 bar, 35 ºC and 5 min, could inactivate the virus SARS-CoV-2 that was atomized on top of all the components of the bio-sanitary personal protection equipment (PPE), at the highest virus contamination of 10^7 Plaque-Forming Units per g (PFU/g). The appearance of a cytopathic effect and cell death (indicative of an active viral infection) and the increase in viral load with successive cell passages (indicative of viral replication) were evaluated. Based on these analyses, it was concluded that the application of $scCO_2$ also prevented virus amplification.

The bacterium *S. epidermidis* is the main cause of most infections related to the skin, catheters, and prostheses. However, the inactivation achieved with CO_2 at 40 ºC at 100 bar and 15 min contact was only two orders of magnitude. the use of additives was required to achieve the total inactivation. Three different "conventional" ones (isopropanol 70% at 1000 ppm, acidic water at 1000 ppm, and H_2O_2 6% at 200 ppm) were explored in a PVA hip coating. The most efficient was the H_2O_2. SEM revealed superficial de-laminations and voids, while thermograms showed *Tg* dip, but these micro-imperfections could be helpful for the adhesion to the prosthesis.

Less aggressive and natural additives to the $scCO_2$ were investigated on the inactivation of *S. epidermidis* sprayed on a cotton gauze. These were essential oils (EOs) from lemon, cinnamon, origanum, clove, and peppermint, at concentrations of 200 to1000 ppm. These compounds, which have antimicrobial power by themselves, improved the action of CO_2, with the peppermint EO being the most effective. Thus, 500 ppm of mint EO, or its combination with water (200 + 200 ppm), was the best solution to provide total inactivation (5 logs). The gauze maintained its macro-structure, and its fibers were not modified significantly. This could be an option for hydrolyzable/oxidable materials. Mint oil scent is also very compatible in the sanitary area.

The PPE were subjected to sterilization using $scCO_2$ at 40 ˚C and 100 bar pressure, with treatments of 30, 45, 60 and 90 min, using the sporulated bioindicators. As their inactivation was not achieved, many additives were used: acids (anhydrous acetic/peracetic acid); oxidants (H_2O_2, 6%); alcohols (ethanol, 70%); peppermint essential oil and their mixtures thereof, in a wide range of concentrations from 0.1% (1,000 ppm) to 3.3% (33,000 ppm). The assays were repeated in the presence and absence of water, to study the impact of the moisture. The sterilization of both bioindicators was only achieved using mixtures of water + hydrogen peroxide + acetic anhydride or peracetic acid, in minimum concentrations of 500 ppm + 250 ppm + 1000 ppm or 50 ppm, respectively. Seeding on PCA plates confirmed the non-viability of the spores. The masks, gowns, overalls, caps, and shoe covers of the PPE were not affected significantly, but the NBR gloves and protective glasses suffered visible alterations. The IR spectra of the polypropylene (PP)/polyethylene (PE) based materials showed slight modifications. These could be related to changes in the mobility of the polymer chains that resulted in weak modifications of the thermograms (by DSC).The $scCO_2$ sterilization is effective for the inactivation every kind of pathogens, and it is applicable to many types of sensitive materials. It could be established as a new low temperature sterilization technique. Market studies give a very good growth prediction, especially in the hospital sector.

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PVDF removal from shredded spent Li-ion battery via supercritical CO_2

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The amount of Li-ion battery (LIB) production has increased tremendously in the last decade. LIBs are in used in mobile devices, such as smart phones, digital cameras, electrical vehicles (EV), and laptops. Among all the applications, the total battery weight in EVs is more than 50% of the total weight of the batteries. In addition, the average life span of an LIB in an EV is 9 years [1]. Thus, after production, there is a time for the batteries to reach their end-of-life. Besides, the collection rates of spent batteries need to be improved.

The recycling of spent Li-ion batteries has been investigated intensively for the last decade. The main recycling methods are hydro- and/or pyro- metallurgy based. Fluorine based materials in LIBs, such as $LiPF_6$ salt and polyvinylidene fluorine (PVDF), are emitting fluorinated toxic gases when pyrometallurgical methods are applied. In terms of hydrometallurgy, the existence of polymeric materials, such as PVDF binder and polypropylene/polyethylene separator, decrease the efficiency of the method [2]. Therefore, recycling of those polymeric materials forehand is beneficial.

The removal of organic matter before the recycling of valuable metals from the spent LIB is enhancing the yield of the recycling process, while it is also preventing toxic gas emission. However, the other concern is that the global number of spent LIBs will be two million metric tons per year by 2030 [3]. Therefore, in that scenario, the PVDF amount in spent batteries will be around fifty thousand metric tons per year. Waste management of this amount will be problematic.

In our research group, Fu et al. showed previously that dimethyl sulfoxide (DMSO) can dissolve PVDF from cut pieces from spent pouch cell batteriesusing supercritical CO_2 [5]. In this study, shredded black mass (SBM) was used to study PVDF removal from black mass using supercritical carbon dioxide (sc-CO_2). For this purpose, DMSO was added in different liquid/solid ratios to recover the PVDF. ScCO_2 was used as the carrying agent for the co-solvent, and, thus, for those dissolved PVDF in the co-solvent. The collected DMSO were investigated via FT-IR analysis, and the remaining black mass in the reactor was investigated via thermogravimetric analysis (TGA). The FT-IR analysis showed that the PVDF from the SBM was able to dissolve in the co-solvent and transferred successfully to the collection chamber. The TGA suggested that the highest percentage of the polymeric materials were separated from the SBM when the L/S ratio was 4 ml/g. The preliminary results suggest that the volume of the sc-CO_2 also has an important role for the dissolution mechanism. Further increasing the co-solvent ratio yielded lower polymeric material transfer. This might be due to the decreasing portion of sc-CO_2 in the reactor.

Acknowledgement

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Hydrolysis of cutin from tomato peels in subcritical and supercritical water: new polyester building blocks and products

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The majority of epidermal cells found in the aerial parts of higher plants, including leaves, fruits, and nonwoody stems, are shielded from the environment by a continuous extracellular membrane known as the cuticle or cuticular membrane. Plants, organs, and growth phases, all have different cuticle structures and compositions; but, in general, the cuticle is made of thebiopolyester cutin with waxes embedded in (intracuticular) and deposited on the matrix's surface (epicuticular). Tomato peels represent a highly promising biomass residue, due to their substantial content of cutin, which ranges between 40% to 85% [1].

Cutin has been obtained from the by-product of tomato processing by a methodology that required several time-consuming steps and the use of organic solvents. Their depolymerization has been carried out by total hydrolysis to acid monomers. Partial hydrolysis using LIs is advancing our knowledge of the polyester structure of cutin, which remains unknown [2].

Our group has developed a new process to obtain cutin with a structure close by natural cutin. The use of supercritical water (SCW) allows the hydrolysis of the carbohydrates present in the cuticle of the tomato skin, and the control of the residence time avoids the hydrolysis of the polyester bonds of the cutin. It is a continuous process, operating in a pilot plant with a TRL of 5. The availability of abundant natural cutin allows us to tackle its depolymerization, and to obtain new building blocks and products.

This study aims to explore the properties of sub/SCW as solvents and reaction media in cutin depolymerization. The variation of density with pressure and temperature allows us to vary the dielectric constant, increasing the solubility of the hydrolysis products. Varying the ionic product allows us to avoid ionic reactions that take place under subcritical conditions, and to improve hydrolysis selectivity. The strict control of the reaction time avoids degradation of the hydrolysis products [3]. The investigation encompasses a comprehensive analysis of reaction parameters, including temperature (250 – 400C), pressure (22.0 – 25.0 MPa), and residence time (0.7 – 30 s), to achieve different polyester products. The study delves into the breakdown of cutin polymers, elucidating the role of water in cleaving ester linkages and generating useful polyesters monomers. The preliminary results indicate that new building blocks could be obtained with polyester linkages. Overall, this presentation is going to give valuable insights into the hydrolysis of cutin from tomato peels in subcritical and supercritical water, paving the way for innovative products.

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POSTER
ABSTRACTS

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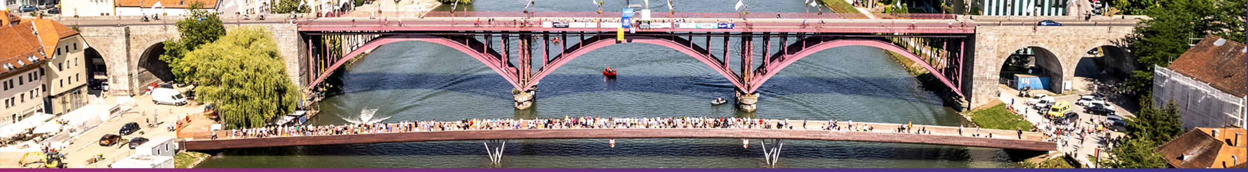

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Numerical modelling of thermoplastic CO_2 assisted extrusion foaming: exploring the process-microstructure relationship

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Sandwich structures are used largely in lightweight applications thanks to their enhanced strength-to weight-ratio. Nomex® and aluminum honeycombs are used widely as core materials, due to their mechanical properties, ease of processing, along with fire, smoke and toxicity compliancy with Standard Transportation Regulations. However, their lack in sound insulation, damping capabilities and recyclability for Nomex® honeycombs, represent a major concern. A promising and emerging solution consists in the use of multifunctional thermoplastic foams developed by supercritical CO_2 assisted extrusion foaming technology. This green, non-inflammable solvent/solute can be used as a physical blowing agent during an extrusion process, allowing a fine control of the foaming process, and, thus, of the final foam microstructure. Several functional properties can be associated to the material: enhanced sound insulation can be obtained for fine open cells, while closed fine cells provide an enhanced thermal insulation capability [1], the nature of the functionality of the foam clearly resides in the structures of the porosity. Starting from this assumption, it is important to establish a clear processing-microstructure relation, in order to tune the foam for a desired functional property. To follow this, we decided to develop a numerical model of the CO_2-assisted extrusion foaming process. To do so, experimental analyses are associated with numerical modeling, as shown in **Figure 1**. The experimental approach, based on Chauvet and Dimos previous work [2,3], consists of three different phases, spanning from the foam manufacturing by CO_2-assisted extrusion foaming, foam assembly, and final vibro-acoustic characterization using a Kundt tube. These experimental phases will then be simulated using the existing literature models. The first step, describing bubble nucleation, growth and coalescence, will be implemented in Matlab® using a microscopic approach based on Shafi and Taki models [4,5]. A macroscopic approach will then be implemented in a finite element software, in order to simulate foam assembly and vibro-acoustic response. The first experimental results have shown that processing temperature and CO_2 mass fraction influence density, the inner cell's structure and material crystallinity strongly. By dropping the extrusion temperature (90 °C), a crystalline foam (crystallinity rate Xc = 24 %) with reduced cells` size and diameter was obtained, while, at higher extrusion temperature (110°C), the results indicate a more expanded and amorphous foam (Xc = 7 %) with a higher cell diameter. The first simulations, based on the Shafi and Taki models, are currently under development, and will be used to correlate the processing-microstructure relation during extrusion. The final goal of this work is to establish a clear link between the extrusion parameters, foam microstructure after assembly, and the vibro-acoustic response of the structure.

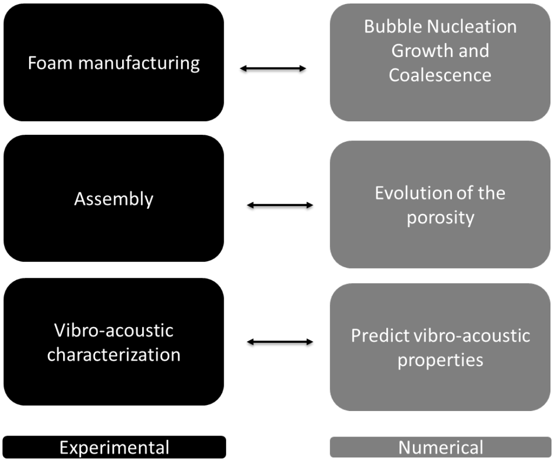

Figure 1: Representation of the main step of the current work.

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Melting point depression of tetrabutylammonium halides in supercritical carbon dioxide

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High-pressure carbon dioxide is capable of dissolving in ionic liquids, reducing their viscosity and also the melting temperature. The combined use of carbon dioxide and ionic liquids has been shown beneficial in many applications, including extraction processes and two-phase catalytic reactions. [1] Optimal operation of these processes requires knowledge of the thermodynamic properties of the system as a function of pressure and temperature.

The aim of this publication is to present new solid – liquid – gas phase equilibrium data of ionic liquids and carbon dioxide. Measurements were taken in parallel, using a variable-volume high-pressure view-cell and an automated device, which was developed in our research group. [2] The results of the measurements taken in the view-cell are based on visual observation of the solid-liquid transition. During the measurements with a new device, the pressure difference between a sample holder and a reference cell is detected as a function of temperature. The melting is indicated by a sudden change in pressure difference, which is caused by the dissolution of the media into the sample.

First, both devices were validated with a previously investigated compound. The melting temperature of tetrabutylammonium bromide was measured under 15 MPa carbon dioxide pressure. The melting point depression, formerly described in the literature, was reproducible. [3] After confirming the correct operation of the device, the pressure dependence of the melting behaviour of tetrabutylammonium halides was investigated in a pressure range between 0.1 and 40 MPa. The maximum melting point depression (33.7 °C) was observed at ~15 MPa in the case of tetrabutylammonium iodide (*Figure 1.*). The melting point depression was lower in the case of the bromide and chloride salts.

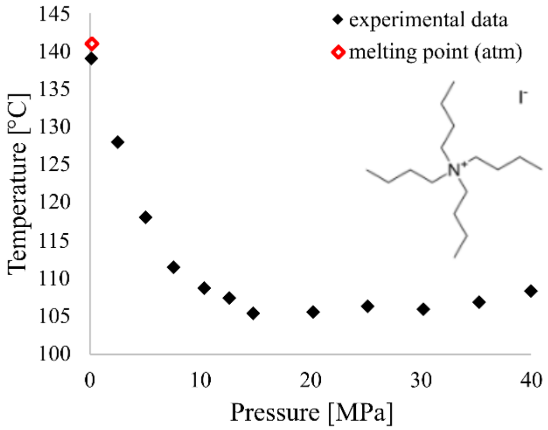

Figure 1: Melting temperature of tetrabutylammonium iodide as a function of pressure.

A decrease in the melting temperature caused by the dissolution of the high-pressure medium into a solid or molten sample can be observed at a lower pressure. After reaching a maximum in melting point depression, the melting temperature increases with the pressure, due to hydrostatic or mechanical pressure.

Acknowledgement

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Formulation, characterization, and properties of agar-based aerogels

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Agar is a hydrophilic biopolymer obtained from red seaweed. Chemically, it consists of repeating units of two polysaccharides, agarose and agaropectin, of which agarose is a gel-forming component. Its ability to form strong and robust gels, even at low concentrations, facilitates the formation of stable and consistent structures with strong 3D-like networks [1]. These properties, combined with its great stability, which does not require reagents to preserve it indefinitely, and its high water absorption capacity, make it a prime candidate for applications where moisture retention and controlled release are required, such as wound care [2] and tissue engineering [3]. In addition, this marine polysaccharide is biocompatible, biodegradable, and non-toxic, meeting the growing demand for environmentally friendly materials in modern research and Materials Science [1]. Due to its versatile properties, agar is suitable for the development of innovative aerogel materials that offer promising prospects for advances in biomedical applications and environmental remediation. In our study, two different methods were used to formulate agar aerogels, resulting in materials with different properties, reflected mainly in the specific surface area (BET) and structural properties. The aerogels produced by both methods showed high BET values, high porosity, and prolonged stability when immersed in distilled water. On the other hand, we noticed differences in the mechanical characteristics. The mesoporous structure was observed consistently in all obtained aerogels. However, the number and size of the macropores also increased with a proportional increase in the concentration of the starting material. Additionally, we investigated the effect of ethanol aging duration on the eventual properties of the material. Our results showed that agar-based aerogels stored in ethanol for a longer period before supercritical drying exhibited higher specific surface area compared to those aged for only 24 hours. It was also noteworthy that all the materials synthesized in our study exhibited barely perceptible volumetric shrinkage, and maintained their structural integrity after drying with CO_2. The results of our research emphasize the potential utility of agar aerogels in various applications, ranging from biomedical to environmental, and have implications for the development of sustainable materials from low-cost and naturally occurring polysaccharides.

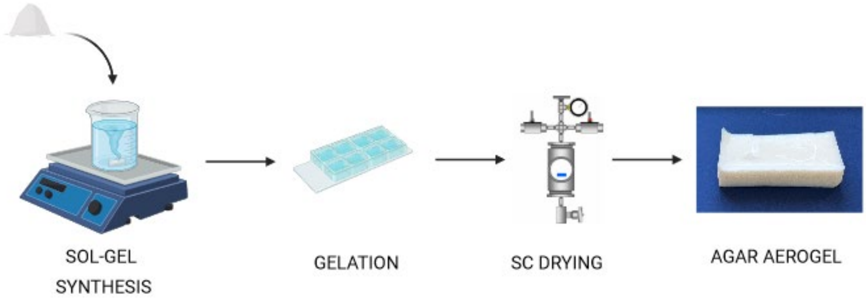

Figure 1: Preparation of the agar aerogel (Created with BioRender.com).

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Free-volume and density scaling-based modeling of the high-pressure viscosity of lubricant oils modified with polymethacrylates

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Lubricant oils reduce friction and wear, and are critical to fuel economy in cars. These oils are base oils modified with a variety of additives to improve their performance. This study examines the effects of polymethacrylate additives, which are viscosity index modifiers, on the viscosity of a mineral based oil at high pressures (10-45 MPa) and high temperatures (298-373K), and the modeling of viscosity with free-volume and density-scaling approaches. Viscosity index modifiers are polymeric additives that aim to reduce the change in the lubricant's viscosity with temperature, preventing, for example, a lubricant from becoming too "thin" at high temperatures.

The density of these lubricant oils systems were determined in a high-pressure variable-volume view-cell equipped with sapphire windows and a motorized pressure generator at the temperatures and pressures of interest. The density data were then correlated with the Sanchez-Lacombe Equation of State.

The viscosity determinations were carried out in a high-pressure rotational viscometer consisting of a rotating cylindrical shaft with jewel bearings to reduce the friction. A magnet embedded in the upper part of the rotating inner shaft allowed for magnetic coupling of the shaft to an outside torque transducer. Magnetic coupling allows the rotational speed to be controlled without compromising the sealing arrangement of the system.

The viscosity data were generated as a function of pressure at selected temperatures. The data were then correlated with the free-volume and density scaling models, using the density values from the Sanchez-Lacombe EOS correlations.

The free volume-based correlations of viscosity describe the variation of viscosity with pressure at each temperature. In the density scaling approach, viscosity is expressed as a mixed function of density (ϱ) and temperature (T), given by ($\varrho\gamma$ /T), where the exponent γ is the density scaling parameter. This approach unifies all the viscosity data at different temperatures and pressures into a single curve. This provides a rational approach for comparative assessment of different oils with respect to their sensitivity, and the relative importance of packing density versus temperature.

In this poster, we will present recent results on the high-pressure viscosity of a mineral base oil modified with viscosity index modifiers, specifically polymethacrylates with different functionality. The effect of the additives will be discussed in terms of the change in the dissipation length and overlap concentration (based on the free-volume description of viscosity), and the scaling parameter (based on the density scaling description of viscosity).

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Reactor configuration for subcritical water extraction of pectin-derived compounds from onion peel wastes: a comparative study

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The increasing interest of pectin derived compounds as functional additives in the pharmaceutical and food industries demands new sources and eco-friendly extraction approaches. In this regard, onion peel wastes (OPW) hold great potential, with over 450,000 tons of OPW being discarded annually [1], despite their remarkable pectin content. Pectins are commonly extracted acid hydrolysis (pH 2, >85 °C), that yield mainly the HG domain, due to complete hydrolysis of the branched domains [2] or enzymatic hydrolysis, which is time consuming, but yields branched pectin rich in RG-I and RG-II domains [1]. As an alternative to the conventional process for producing pectin derived compounds (PDC), hydrothermal hydrolysis based on subcritical water (SubW) is emerging as an eco-friendly technique. SubW refers to water at temperatures ranging from 100 °C (boiling temperature) to 374 °C (critical temperature), which remains in a liquid state due to the application of pressure. SubW can facilitate the extraction of pectin from natural matrices, and by controlling the operational parameters, pectin can be tailored into smaller units with varying degrees of polymerization to produce PDC. However, in practice, accurate control of experimental conditions has emerged as the primary challenge of the SubW extraction process, which can lead to the formation of undesired degradation products [3], and uncontrolled molecular weight reduction of the pectin [4].

In this regard, the extraction of PDC has been carried out using three different reactor configurations: batch, semi-continuous and continuous (ultra-fast reactor). It has been demonstrated that there is a narrow window of experimental conditions that maximize the extraction of PDC; going beyond these conditions led to the depolymerization of PDC (modeled by the Panchev's equation) and the formation of degradation products, mainly formic acid and furfural. As a tool for comparison between the three-reactor configuration, the severity factor was used, demonstrating that continuous configuration provided similar conversion than those achieved with the batch configuration (30% at 125 ºC for 150 min), but working at 200 ºC with an ultrafast reactor with a residence time of around 5 s. Under these experimental conditions, the average molecular weight for the PDC was 108 kDa for the continuous reactor and 78 kDa for the batch configuration, reducing the presence of degradation products dramatically. This fact will simplify the downstream processing required to obtain high purity PDC.

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One-phase semi-batch hydrothermal depolymerization of poly(ethylene terephthalate): pressure and temperature effect on TPA yield

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Back-to-monomer chemical recycling of waste polymers is of increasing interest [1]. Hydrothermal systems offer abundant solvent sources, while providing a greener approach than most organic solvent-based solutions. Poly(ethylene terephthalate) (PET) is an extensively studied example of chemical recycling (studies are available regarding alcoholysis, glycolysis, aminolysis/ammonolysis and neutral/acidic/alkaline hydrolysis) [1]. Each approach provides different products suitable for merging into different production phases of PET. However, the most all-encompassing products are neat terephthalic acid (TPA) and ethylene glycol, which is provided by controlled hydrolysis — in the case of an alkaline product mixture, liberation is needed from the salt of TPA and enolate of glycol.

In this work, a semi-batch equipment, with a 1 ml/min ambient water flow, was used to depolymerize virgin PET granules, to gain insight into the TPA formation and subsequent migration into the water phase. Since TPA has low atmospheric solubility, a 0.08 w/w NaOH(aq) quench side stream was applied with a 1 ml/min ambient flowrate to avoid precipitation. The water was kept to above saturation pressure to maintain a liquid (water) – polymer melt system. A 3^3 (523-548-573 K and 10-20-30 MPa) type experimental design- based study was conducted, and complemented with 528-538-558 K measurements at 10 MPa. Samples collected fractionally at the end-of-pipe were measured by HPLC, and TPA recovery curves were calculated.

The resulting final-recovery were above 0.8 $w/w_{\text{terephthalic acid}}$ at all pressures and temperatures. The curves followed the literature observation that the reaction accelerates with temperature. On the other hand, sigmoid recovery curves were observed consistently, not common in the literature's batch experiments. This is presumably connected to the flow system phenomenologically. The continuous removal of products simultaneously gave insight into the course of reaction and the solubility properties of hydrothermal water. Most likely the oligomer formation observed previously in batch systems [2] was hindered by the low solubility in the hydrothermal water, and, mostly, TPA can migrate into the mobile phase, thus oligomers are not extracted. Therefore, higher final-recovery can be achieved in flow-systems.

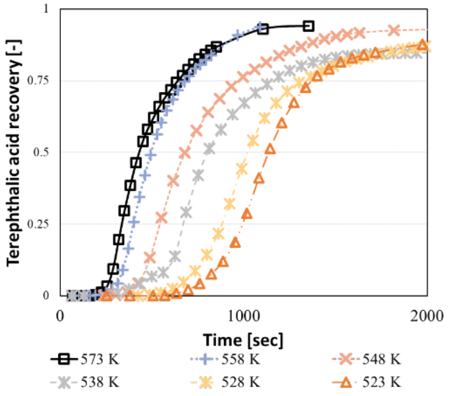

Figure 1: TPA recovery curves at 10 MPa; lines only guide the eye.

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Design, scale-up and process flow diagram approach for supercritical fluid extraction of high-value compounds from aquaculture biomass

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Supercritical CO_2 fluid extraction (SFE) has shown significant benefits for the extraction of high-value compounds from natural biomass, as it allows a mild processing of thermo-sensitive compounds [1]. Moreover, the SFE technique can be developed at different scales: from the laboratory to a large industrial scale. However, the scientific literature has not yet provided an effective approach for this process. Studies based on scale-up are inconclusive [2, 3] because of the interaction between several parameters. Due to the restrictions and difficulties that revolve around the process, there is a need to study scale-up criteria meticulously.

The purpose of this work was to design a supercritical extraction system, taking into account factors such as materials, wall thickness, valves, number and types of separators, pumps, as shown in Figure 1. The properties of the biomass source, as well as the importance of avoiding the Joule-Thompson phenomena, were key factors in the selection of the design parameters. The scale-up was carried out based on this proposed design. The scaling up process was focused on the geometric relationships of the main elements, the addition of auxiliary elements and operability. This scale up design has allowed estimating a yearly output of 0.5 Tons of carotenoid extracts from microalgae biomass. Finally, and due to the diversity of the biomass, the extraction process was focused on a biotechnology application, targeting specifically the extraction of compounds from aquaculture. A process flow diagram was designed, encompassing both the processing and post-processing stages. Various factors, including sample moisture, particle size, matrix effects, etc., were taken into consideration to achieve the objective.

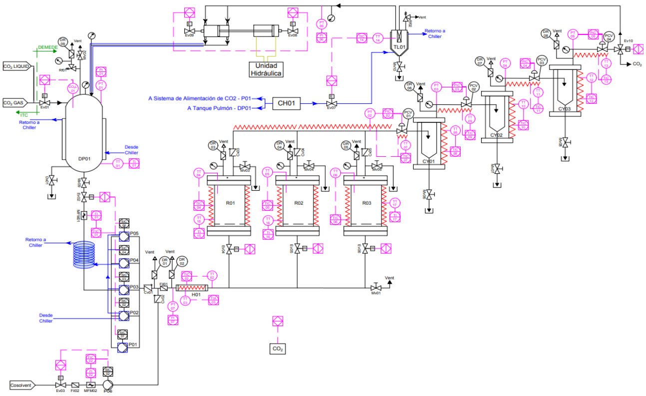

Figure 1: Process diagram of the industrial scale equipment.

This study provides an overview from equipment design, through scale-up, to its final integration into a whole process design for the extraction of bioactive compounds.

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Optimizing the surface area and morphology of TiO$_2$ aerogels by supercritical drying

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Titania (TiO2) aerogels made with the sol-gel method are mostly preferred, due to their high stability, low cost and low toxicity, large specific surface area and high porosity [1]. On the basis of these superior features, they have a wide range of uses, such as wastewater treatment, gas sensing, photocatalyst, semiconductor [2]. Typically, these aerogels are produced by supercritical drying of wet gels. Supercritical drying of aerogels is done typically by heating up the solvent to a supercritical regime in a pressurized vessel, followed by depressurizing and venting. In the literature, either a fast or slow heating regime is generally used to reach the supercritical points of the used solvents during the supercritical drying of the aerogels [3, 4]. Therefore, it is difficult to determine the role of the heating regime on specific surface area, surface morphology, pore size and volume, as well as the skeletal density of the aerogels. The objective of this study is to explore how varying heating rates impact the properties of titania aerogels, all of which were synthesized using the sol-gel method. Specifically, titania aerogels were subjected to increasingly slower heating rates, with specific attention given to separating the time spent on both the subcritical and supercritical regimes. The results indicated that the heating rate affects specific surface area, pore diameter, pore volume, as well as skeletal density. These findings can assist researchers in optimizing their processes according to specific application areas. Figure 1 shows the SEM images of two samples with fast and slow heating rates. It can be inferred that the fast heating rate causes smaller and more agglomerated particles.

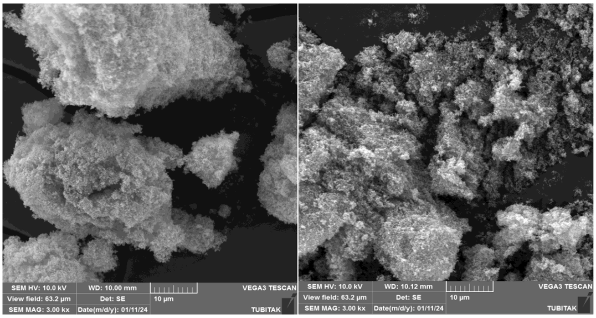

Figure 1: **SEM image of a) Fast heating rate sample, and b) Slow heating rate sample at 3kx magnification**

Table 1: Effects of heating rate on BET surface area and pore volume of the samples.
*** SC-1 to 4 represents fast to slow heating rates.**

Sample Name	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
SC-1	119	0.567
SC-2	165	0.953
SC-3	149	0.638
SC-4	125	0.511

The preliminary findings showed the BET surface area and pore volume given in Table 1, where heating too fast (SC-1) or too slowly (SC-4) reduces the surface area and porosity. The results showed that the heating rate effects the BET surface area and pore volume significantly.

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Modelled mixture temperatures vs. experimentally measured temperatures across a spray cone cross section during the transcritical injection

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In previous experiments we investigated the mixture formation between the biofuel ethanol and nitrogen, which we used as a substitute for air, at relevant engine conditions [1]. While the ethanol was injected in a high pressure and high temperature chamber as a liquid with an injection pressure of 120 MPa and a temperature of 363 K, the nitrogen ambient atmosphere within the spray chamber covered pressures of 3-8 MPa and temperatures of 573-923 K. We chose this range of pressures and temperatures, as we hoped to observe supercritical single-phasic (fluid fluid), as well as two-phasic (vapor liquid) mixing processes, to get a glimpse into the transcritical mixing processes, which is the case when the phase boundaries disappear due to a change of the ambient atmosphere. Therefore, we used, especially on the spray chamber, an adapted configured one-dimensional Raman measurement technique, to measure simultaneously the temporally and spatially resolved composition of the mixture, the fraction of the liquid phase within the mixture, and the temperature of the liquid phase.

Within the planned EMSF contribution we are going to compare the experimentally measured temperatures with the modeled temperatures for spatial positions along the spray cone cross-section. The modeled temperatures were computed via the cubic Volume-Translated Peng-Robinson equation of state (VTPR-EOS) using an excess-Gibbs energy based mixing rule according to Wong and Sandler [2] under the assumptions of either adiabatic-isobaric (model 1) or isothermal-isobaric (model 2) mixing. The comparison of the experimentally obtained temperatures and the computed modeled temperatures provided insights about the eligibility of the adiabatic and isothermal mixing assumption at these conditions across a spray cone.

Most of the experimental data showed a significant deviation from the here applied two models toward a higher mixture temperature, which proves that the spray processes cannot be described by the two in practice widely applied models based on thermodynamic equilibrium. These findings give the opportunity for further investigations in this field in the future to understand these processes better.

Acknowledgment

The project leading to this result has received funding from the Deutsche Forschungsgemeinschaft under Project number 530178493 (Transkritische Gemischbildung).

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Extraction of ß-carotene and cellular lipids from the oleaginous yeast *R. toruloides* with supercritical CO_2

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Organic solvents find widespread use in laboratories and industry. However, their inherent health and environmental risks necessitate exploring solutions to minimize their usage. Seeking greener alternatives is crucial to address these concerns [1,2].

In this work, we explored the application of supercritical CO_2 for the extraction of biotechnologically produced ß-carotene and cellular lipids by oleaginous microorganisms like *Rhodosporidium toruloides*.

Supercritical CO_2 extraction is usually performed with dried samples, which would require an energy-intensive drying step before the extraction from the aqueous biomass [3]. Therefore, in this study, the supercritical CO_2 extraction was investigated with wet biomass (moisture content >80%). First, the extractions were conducted at different pressures and temperatures, varying from 200 – 350 bar and 40 – 70 °C, to determine suitable process parameters, and the extraction kinetics were measured.

Additionally, the influence was studied of the water content of the biomass on the extraction kinetics. Therefore, the water content was adjusted to different percentages, and extractions were performed with the same conditions. Furthermore, a possible increase of extraction yield was examined by the usage of ethanol as a co-solvent [4].

Acknowledgement

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Preparation of wound dressings containing the ibuprofen: thymol Therapeutic Deep Eutectic Solvent (THEDES)

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Biomolecules such as chitosan (Ch) and gelatin (G) are materials currently used in the preparation of wound dressing, as they can be polymerized easily in water to produce biocompatible hydrogels that can hold large quantities of water or biological fluids in their structure. Furthermore, they can be loaded with a considerable amount of active pharmaceutical ingredients (API), keeping the wound hydrated, allowing the permeation of air and water, and protecting the wound from infection or further injury. Hydrogels formed by mixtures of chitosan and gelatin (Ch/G) present improved mechanical and barrier properties beyond those present in pure gelatin or chitosan.

Therapeutic Deep Eutectic Solvents (THEDES) are mixtures of two or more solid APIs, which form a liquid mixture at room temperature at a particular composition. The decrease in the melting point of the mixture is due to strong interactions between the different species, leading to a more disordered structure that remains liquid at room temperature. The THEDES formed by ibuprofen + thymol in a 1:3 ratio have a melting point of 34.5 ºC very close to the body temperature, so it would melt in a wound dressing. Mixing ibuprofen with thymol can help to overcome the low solubility of the drug, and improve its permeability through the upper layers of the skin, improving its transdermal delivery.

In this communication we have prepared gelatin/chitosan wound dressings incorporating the 1:3 ibuprofen: thymol THEDES. Ch/G hydrogel films were prepared following an approach described previously [1]. The introduction of the API into the films was carried out following two different procedures: (1) Adding the THEDES during the gel preparation, and (2) Impregnating the THEDES dissolved in $scCO_2$ into the gel films by the Supercritical Solution Impregnation (SSI) technique. For comparative purposes, gels containing only one of the APIs were also prepared by both techniques. To define the impregnation conditions, the phase diagram of the THEDES and CO_2 mixtures at high pressure was determined previously [2]. The impregnation experiments were performed at 40ºC and 120 and 200 bar at compositions of complete solubility of the THEDES. For both APIs, drug loading decreased as the pressure increased, and was highly dependent on the humidity of the hydrogel. The materials prepared by SSI did not keep the composition of the THEDES, due to the much higher volatility and solubility in CO_2 of thymol in comparison to ibuprofen. Strategies are discussed to increase the concentration of thymol into the Ch/G films to reach the THEDES composition.

Acknowledgements

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Extraction of cherry leftovers and encapsulation of the extracts in ethyl cellulose by SFEE

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Various neurodegenerative diseases, such as Alzheimer and Parkinson, are associated with a lack of antioxidants; therefore, they have been treated with good results with plants rich in bioactive compounds. [1] Anthocyanins are a group within polyphenols with high antioxidant activity depending on their structure; the simpler, the more antioxidant capacity. Cherries are the main food source of these compounds, but up to 10% of the cherry cultivation is discarded due to excessive ripening or defects. The main objective of this project was, firstly, the obtention of an extract rich n anthocyanins from cherry wastes. The second objective was to protect this extract with a coating, as anthocyanins are very sensitive to light and high temperatures. The graphical abstract is shown in Figure 1. The extractions were carried out by maceration to choose the most adequate solvent, between methanol and ethanol. Although the methanol produced higher values of anthocyanins, polyphenols and extraction yield (57 %), it is a solvent with greater limitations in its use due to its toxicity and higher price. An extraction yield of 42% was achieved with ethanol in maceration at 37ºC and 90 minutes, with a ratio of 10 mL of solvent per g of cherries. The extract contained 0,15 mg anthocyanins/g and 0,92 mg polyphenols/g. The maceration was then compared with the ultrasound assisted extraction at two energy levels (20 J/mL;1.1 Wh and 40 J/mL, 2.2 Wh) provided in 1.5 and 3 min, respectively. During the procedure, the suspension temperature was raised from room (22 °C) to 28 °C and 32 °C, correspondingly. The extraction yield at 1.1Wh was 16%, and that obtained at 2.2 Wh was 18%. In comparison, maceration provided a much higher yield with higher antioxidant fraction, due to the prolonged contact time and the higher temperature. In this latter procedure, the power required was estimated to be 1.1 Wh. The advantage of the US-extraction *vs.* maceration is its much lower operation time and the possibility of continuous operation. This could be critical if high production capacity is required. Following the extraction, the extracts were encapsulated in ethylcellulose (EC) using the Supercritical Fluid Extraction of Emulsions (SFEE) method, to preserve the properties of the anthocyanins. Ethyl acetate was used as the organic solvent for the inner phase, while water with Tween 80 was the outer phase. The cherry extract and the EC were incorporated into the organic phase. The emulsion was brought into contact with supercritical CO_2 in a bubbling column. The CO_2 dragged the solvent, precipitating the EC with the extract. The experiments were done for different ratios of EC and the cherry extract (1:1 to 1:4), the latter being enough to trap the red liquid extract to obtain a transparent suspension of the particles with 100 % encapsulation efficiency. The particles were sterile, spherical in shape (based on TEM) and submicron in size, ranging from 170 nm (at the 1:1 EC:extract ratio) to 380 nm (at the 1:4 EC:extract ratio). Possible applications could be as ingredients in nutraceutical foods (novel food). Nevertheless, cytotoxicity and release tests would be necessary, as the effects for nanoparticles on the body are still unclear. Other possible applications could be the formulation of skin care products, or even drugs.

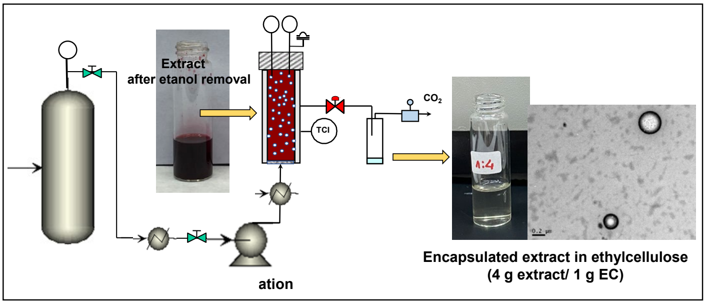

Figure 1: The ethanolic extract after evaporation of the solvent is incorporated in an emulsion together with ethyl cellulose. Then, it is subjected to supercritical CO_2 extraction to obtain a suspension of submicron-sized capsules.

Acknowledgements

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Subcritical water-assisted biorefinery of fucoidan - laminarin from bull kelp (*Durvilllaea potatorum*) and brown seaweed (*Ecklonia radiata*)

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Recently, modern extraction techniques using supercritical CO_2 (SC-CO_2) and subcritical water (SCW) as solvents have been receiving more and more interest. These techniques are superior compared to conventional processes due to their significant advantages, such as being solvents-free products and environmentally-friendly processes. While SC-CO_2 has been used widely in different fields, including food, cosmetics, and pharmaceuticals, SCW has been approved as a safe solvent as compared with conventional ones. SCW is an adjustable solvent by varying its temperatures and pressures. Therefore, it can extract high to low-polarity bioactive compounds such as polysaccharides, proteins, and phenolics effectively from various resources. The extracts obtained from this process can be purified further to acquire a high-purity product that contains a high portion of the targeted compounds. Therefore, in the present study, SCW was used to assist the biorefinery of fucoidan-laminarin (FL) from two species of seaweeds obtained from Australia, namely, bull kelp and brown seaweed. The temperatures of the SCW varied from 120 °C to 180 °C with an interval of 20 °C, whereas, the solid/liquid ratio, extraction time, and pressure were fixed at 1/35, 5 min, and 50 bar, respectively and were kept constant. Then, the freeze-dried extracts were treated with ethanol (20%, v/v) to precipitate a mixture of alginate, fucoidan, and laminarin. In the next step, the alginate was precipitated after mixing with $CaCl_2$ overnight at 4 °C. The refined FL was achieved after washing with ethanol, and characterized carefully for its physicochemical and bifunctional properties. The experimental results showed that the SCW treatment contributed significantly to the biorefinery process, by enhancing the recovery yield and reducing the processing time. The maximum refined FL from bull kelp and brown seaweed (13.4% and 9.0%, respectively) was obtained from the extracts treated at 160 °C in SCW. Fourier-transform infrared spectroscopy (FTIR), 1H NMR, and thermalgravimetric analysis (TGA) of the refined FL demonstrated the success of the process. The refined FL exhibited good emulsifying properties, whereas its bio-functionalities in terms of antioxidant and anti-inflammatory activities were the highest when being treated at 160 °C in SCW. The findings of the present study demonstrate the potential use of SCW in assisting the biorefinery of FL from bull kelp and brown seaweed [1].

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Pressurized liquid extraction of polyphenols from *Porphyra spp.* (“*nori*”)

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Seaweeds have been used in Chinese medicine for more than two thousand years, and are applied for several medical purposes [1]. The old-fashioned extraction method of their bioactive compounds consisted of the use of high temperatures under atmospheric pressure conditions, and that could affect their bioactivity strongly, especially for those from the class of the polyphenols. For that reason, novel and more sustainable extraction methods are under investigation (e.g. pressurized liquid extraction, ultrasound-assisted extraction, supercritical fluid extraction, etc.).

Porphyra spp. is popularly known as “nori” in Japan, and is characterized as a red macroalgae with a high content of polyphenols [2]. The current work reported in the literature exploring this class of compounds in *Porphyra spp.* is limited to conventional solid-liquid extractions [3], [4] or ultrasound-assisted extractions (UAE) [2]. In this context, pressurized liquid extraction (PLE) presents a good alternative to obtain polyphenols, as reported previously for other seaweeds [5]. If using green alternative solvents (e.g., water, ethanol, natural deep eutectic solvents, etc.), PLE represents a more sustainable alternative to those conventional extraction methods that are still applied widely at the industrial scale. However, to the best of our knowledge, the results of phenolic content or composition in *Porphyra spp.* extracts obtained under high pressure conditions were not found in the open literature. Therefore, the aim of this work was to apply PLE performed in ASE 200 (Dionex, Sunnyvale, CA, USA), to maximize the total phenolic content and antioxidant capacity of the extracts of *Porphyra spp.* The dried seaweed was kindly donated by Porto-muiños S.L. (A Coruña, Spain). As a first step, UAE (US bath, Sonica®, 260 W, 40 KHz) was applied to the dried seaweed using different solvent compositions (ethanol: water 40:60 and 70:30 v/v) at 70 ºC, for 10 min. The best solvent was chosen, based on the total phenolic content (TPC) determined by a Folin-Ciocalteu assay [5]. Then, PLE was performed at 10.3 MPa for 20 min, using the solvent determined in the first step at different temperatures (50, 70, 90, 110 and 130 ºC), and the best extraction condition was defined as the high TPC and antioxidant capacities to a given extract, assessed by the ABTS and DPPH assays described in Keramane et al. [5]. Finally, in order to characterize the phenolic composition of *Porphyra spp.*, a tentative identification was performed by UHPLC-q-TOF-MS/MS, according to the method described in dos Santos et al. [6].

In conclusion, this work facilitates valuable information regarding the use of an alternative extraction method (PLE) to recover enriched polyphenols extracts from *Porphyra spp.* Such composition could be very useful in assessing the potential future application of their extracts in medical-related purposes.

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Determination of the solubility of resveratrol and formulation of resveratrol composites in supercritical argon

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A large proportion of active pharmaceutical substances are poorly soluble in water. The solubility of the active substance in water or in a biological fluid is an essential factor in achieving the desired pharmacological effect of the drug, especially in the oral administration of solid dosage forms, which are the preferred form in modern medicine. The development of formulations with improved solubility and bioavailability is crucial for the commercial success of new drug candidates, and represents a major challenge for the pharmaceutical industry [1].

One of the most interesting bioactive compounds is resveratrol. Due to its many potential benefits for human health, resveratrol is highly sought after in pharmaceutical, food and cosmetic products, but its use is very limited, due to its poor water solubility, low bioavailability and chemical instability. To exploit its medicinal effects, research into new approaches to improve its solubility and oral bioavailability is crucial [2].

The thermodynamic and transport properties of the active ingredient resveratrol were investigated in a supercritical argon system. The aim of the research was to obtain data relevant for the design and optimization of high-pressure processes for the production of particles and composites with supercritical fluids.

The solubilities of resveratrol were determined using the static-analytical method [3] in a high-pressure cell with variable volume at pressures between 50 bar and 400 bar and temperatures between 40°C and 60°C. The proportion of dissolved resveratrol in supercritical argon was determined spectrophotometrically. The results were presented graphically in the form of solubility isotherms.

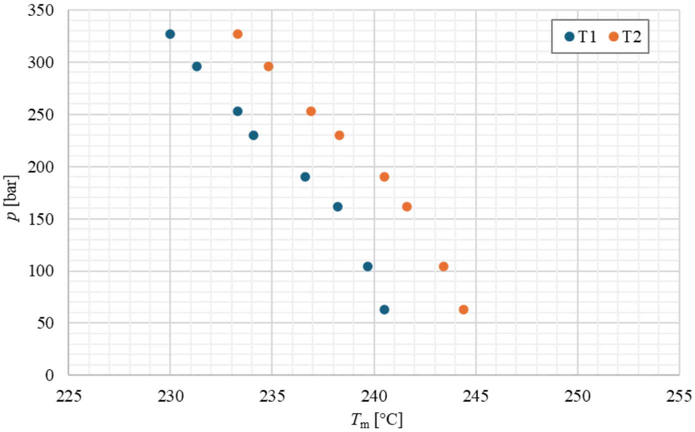

Figure 1: **Melting point curve for the resveratrol/argon binary system determined with the modified capillary method in the high-pressure optical view cell.**

In the following, the melting points of resveratrol in supercritical argon were determined in the range from 50 bar to 350 bar. The capillary method was used to determine the melting point. The melting temperature decreases with pressure. The melting curve shows a negative dp/dT deviation (Figure 1). Finally, we performed batch micronization of resveratrol with a Brij S100 polymer carrier using the high-pressure PGSS^{TM} method in the presence of supercritical argon. The influence of pressure and mass ratio of resveratrol/Brij S100 was investigated on the yield and efficiency of the process. Micronization was carried out at a temperature of 60°C and pressures of 100 bar and 200 bar for two mass ratios (2g/20g and 4g/20g). Lastly, the LC-MS method was used for the quantitative analysis of the resveratrol content in the formulated composite particles.

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Supercritical CO_2 extraction of lipids from larvae of *Galleria mellonella*: kinetic modelling and characterization

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Edible insects are currently considered the main feed for the future, due mainly to the high amount of protein. Adults and larvae stage insects have been part of human diets mainly in Asian countries, but have beeb expanding to European and American countries in recent years. However, after exploring the benefits of the quality of the protein content from these foods, fats and oils (up to 60 % of the insect) remain unexplored. Recent studies have been focusing on the use of insects as a lipid source [1]. In this context, species with a low protein-to-fat ratio (P/F) and novel lipid extraction methods represent an excellent alternative to explore the recovery of bioactive lipid soluble compounds from insects. *Galleria mellonella* (also known as "waxmoth") are a rich source of lipid (with $P/F < 1.0$), but are reared mainly to feed reptiles and birds [2]. Nonetheless, in the near future, this specie is ranked as a potential insect to be used as food and feed in the European Union [3]. Therefore, the aim of this work was to apply supercritical CO_2 extraction (SFE) to recover lipid soluble compounds from *Galleria mellonella*. The larvae were purchased in a Madrid local market in their growth larvae stage, washed, and dried carefully with towel paper. Then, after 24 h at room temperature, the larvae were submerged in $N_{2(l)}$, followed by freeze-drying, vacuum sealing, and kept at -20 °C until the milling step requested prior to the SFE and proximate composition analysis. The SFE was applied using a homemade high-pressure extractor comprised of a CO_2 pump from Jasco (PU-2080 CO_2 Plus), a 20 mL cell placed inside a Finnigan MAT oven from GCQ™. For the extraction, 1 g of milled and dried insects was added into the stainless-steel cell filled with glass beads and glass wool in the ends. The extraction condition was set to 400 bar, 60 °C and a $CO_{2\,(g)}$ flow of 1.5 L/min. The extracts were collected at stipulated times from 3 to 150 min to build the kinetics. The results were given as mean accumulated yield (%, g extract/ g dried larvae) and the two-site model was fitted to the experimental data. In addition, the lipid soluble profile was identified tentatively by an Agilent GC-qTOF-MS/MS using the Fiehn method [4].

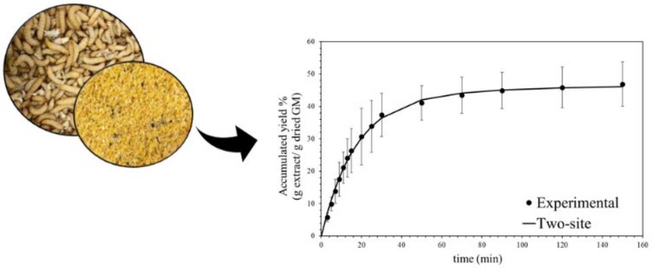

Figure 1: ***G. mellonella*** **mass transfer SFE kinetics.**

The results indicated an extraction yield of 48 ± 5 % after 150 min, and the two-site model was well-fitted to the experimental data ($R^2 = 1.0$ and ARD % = 4.1), as shown in Figure 1. According to the model, the fraction of easily accessible extract was only 11 %. The extract composition indicated the possible presence of glutamic acid, sterols and fatty acids such as palmitic, 13-octadecenoic, and stearic acid. In conclusion, the lipid extract of *G. mellonella* represents a valuable source of bioactive compounds, and the extraction variables should be investigated to obtain a faster and selective mass transfer kinetics.

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Supercritical CO_2 extraction of bioactive molecules from tomato plant residues

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Present agricultural methods, such as greenhouse substrate cultivation, yield substantial amounts of underutilized or untreated by-products, resulting in large quantities of downgraded goods or environmental problems from mishandling biomass, such as uncontrolled emissions of CO_2 and CH4 [1]. Fruits and their plant residues contain valuable essential oils and bioactive compounds with highly potential applications in agriculture and healthcare [2,3]. Examination of the tomato plant residues via maceration and soxhlet extraction revealed the presence of bioactive elements, such as tetracontane or neophytadiene. In this study the potential of extracting bioactive molecules from tomato plant residues using supercritical CO_2 extraction (scCO2) was explored, to get a comprehensive understanding of the extraction methods.

The plant residues were air-dried, ground to 3-5 mm, blended with sunflower oil as a molecule carrier, and extracted at temperatures of 40 – 80 °C and pressures of 10 – 30 MPa within a SPEED-SFE extraction plant. To enhance oil dispersion within the solid matrix, the reactor was filled with supercritical CO2 and sealed for 30 minutes before the extraction started. Thr extract analysis utilized gravimetric analysis, gas chromatography-mass spectrometry (GC-MS) and a Folin-Ciocalteu assay.

Depending on the used temperature and pressure parameters, the equilibrium attainment ranged from 3 – 14 hours, with CO_2 consumption ranging from 1.21 – 4.93 kg for 6 g of raw material, resulting in a solvent to feed ration of 201.6 – 821.6 kg/kg. Higher pressure correlated with decreasing extraction time and CO_2 usage. The energy expenditure to reach equilibrium at 60°C and 20 MPa was calculated with 274.72 Wh. The compounds identified in the $scCO_2$ extracts through GCMS analysis included tetracontane, tetratetracontane, squalene, nonacosane, cannabidiol, neophytadiene, and (Z)-9,17-octadecadienal, classified into alkanes, terpenes/terpenoids, fatty acids/esters, and phenolic compounds. These natural compounds are currently being investigated highly for their antimicrobial, antibacterial, antioxidant, or insecticidal properties. Predominantly, bioactive hydrocarbons accompanied with a high amount of waxes, were extracted, followed by terpenes/terpenoids and fatty acids/esters. The data aid in modeling optimal extraction conditions for various bioactive molecules within the temperature and pressure parameters. The study underscores the potential of enhancing the value of tomato plant residues by supercritical CO_2 extraction.

Detailed results will be given at the poster presentation.

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Unveiling novel phases: CO_2 -assisted cocrystallization of proxyphylline with 4 hydroxybenzoic acid

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In the field of Pharmaceuticals, characterized by the dual challenges of low water solubility and inherent chirality, this study pioneers an innovative approach in crystal engineering. Employing supercritical fluid techniques, specifically Gaseous Anti-Solvent (GAS) methodology, we delve into the nuanced dynamics of cocrystallization between racemic proxyphylline (PXL) and hydroxybenzoic acid isomers.

Cocrystallization of PXL with 4-HBA through GAS technology and Liquid-Assisted Grinding (LAG) methods unveileds two previously unreported 1:1 stoechiometric cocrystalline phases – Phase **I** and Phase **II**. Phase **I**, synthesized via LAG, exhibited thermodynamic stability in the orthorhombic space group $Pna2_1$. Phase **II**, formed during supercritical CO_2-assisted cocrystallization, adopted a monoclinic structure (C2/c) characterized by layered formations housing intriguing vacant spaces [1].

This work accentuates the distinctive feature of the cocrystalline phases, particularly emphasizing the unique structure of Phase **II** obtained with CO_2. Thermogravimetric analyses, coupled with mass spectrometry, unraveled solvent inclusions, revealing compositional variations of CO_2 and H_2O based on the initial solvent. The operational conditions, including solvent choice and temperature, dictate the purity of the kinetic phase. Indeed, the production of pure PXL:4-HBA cocrystals of Phase **II** demands specific in supercritical conditions, either in isobutanol with a temperature superior at 40°C, or in acetone, with a temperature exceeding 51°C (supposed). Various supercritical technologies – GAS, Solution Enhanced Dispersion of Solids (SEDS), and Cocrystallization from aSupercritical Solvent (CSS) – highlight the exclusive susceptibility of Phase **II** to be formed with CO_2 as an anti-solvent or solvent, emphasizing its pivotal role in the cocrystallization process. Moreover, the natural evolution of phases over time, coupled with kinetic transitions influenced by the initial proportion of the stable phase, imparts valuable insights into the dynamic nature of these cocrystals.

In conclusion, this investigation offers a multifaceted perspective on the exploration of $scCO_2$ assisted cocrystallization, revealing novel phases of proxyphylline cocrystals with potential implication in crystal engineering and pharmaceutical sciences. The findings presented here hold promise for addressing key challenges in the pharmaceutical landscape, especially in enhancing the solubility and resolving the chirality of essential drug compounds.

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Phase behavior of supercritical carbon dioxide and polyhedral oligomeric silsesquioxanes (POSSs)

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The phase behavior was investigated of supercritical carbon dioxide (scCO_2) and a polyhedral oligomeric silsesquioxane (POSS). The cubic structures of POSSs have eight silica ends, which can be bonded with various functional groups, making the POSS compounds suitable for many different applications. The effect of different mono-functionalities on the POSS-CO_2 phase behavior was investigated in previous studies [1,2]. Here, a bifunctional POSS molecule, trifluoropropylisobutyl (TFIB) POSS (Figure 1), was selected, to observe how the addition of one trifluoropropyl group to an octa-isobutyl POSS contributes to its CO_2 solubility.

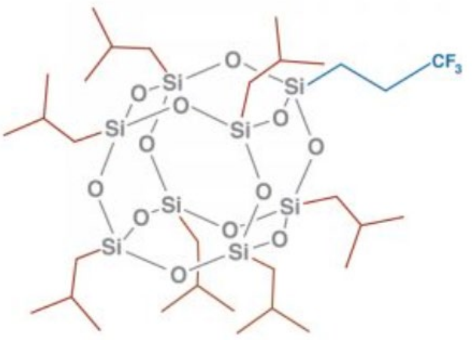

Figure 1: Chemical structure of TFIB POSS.

Cloud-point measurements (Figure 2) at the temperature and pressure ranges of 308 - 323 K and 8.8 - 14.5 MPa, respectively, show that TFIB POSS solubilities (up to $1.0\text{x}10^{-3}$ by mole fr.) in $scCO_2$ are between those of its monofunctional POSSs; however, the solubility difference between TFIB and octa-trifluoropropyl POSS diminishes at high temperatures. The results show that TFIB POSS, which has a melting temperature of around 270 °C, exhibits relatively high solubilities in $scCO_2$, promoting it as a suitable additive to heat-sensitive materials, to improve their thermal stability and applicability in environmentally benign supercritical CO_2 processes. In addition to the measurements, this study includes different theoretical models to predict solubilities. Like in previous studies with POSSs [3], six CO_2 density-based semi-empirical equations were used to predict the solubilities. This study also includes solubility modeling with the Peng-Robinson (PR)+COSMOSAC Equation of State (EOS), a modified PR-EOS [4]. The application is composed of density functional theory (DFT) investigations and fugacity calculations through the COSMO segment activity coefficient model [5]. Moreover, this study covers the investigation of possible improvements in the EOS (by introducing different electrostatic & dispersion contributions and mixing rule applications) to improve its prediction capabilities. New contributions are found, to improve the prediction accuracies of the EOS to estimate the phase equilibria of some compounds, such as TFIB POSS, anthracene, and naphthalene. While the density-based relations still provide better fits to the experimental data and are easier to apply, the main advantage of the EOS is its applicability in the absence of experimental solubility data and critical properties. Therefore, improving its estimation accuracy, it may provide a tool for the phase equilibria predictions of the novel materials and solvents including supercritical fluids.

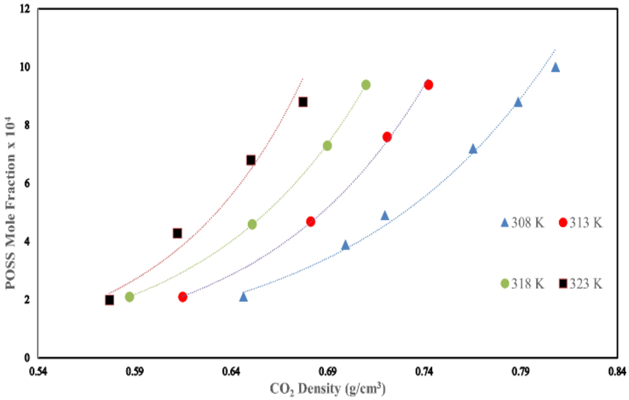

Figure 2: TFIB POSS solubility isotherms with scCO$_2$ density.

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Beyond the hype: delving into the environmental impacts of supercritical fluids' applications

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The application of supercritical fluids (SCFs) in diverse industrial and R&D processes has gained significant attention in recent years for their unique properties and potential environmental benefits [1]. SCFs are usually presented in the literature as "*green solvents*", since their processes allow for the reduction or suppression of the use of conventional organic solvents (e.g., acetone, ethanol, toluene…) that can be toxic or require waste treatment [2-3]. However, supercritical processes can be associated with higher energy and more complex equipment than conventional methods, because they are characterized by higher pressure and varying temperature ranges (above the critical pressure and critical temperature, depending on the fluid chosen). It is, therefore, crucial to scrutinize the overall environmental impacts of such processes, in order to verify their relevance depending on the application, and to understand the influence of the key design parameters (such as temperature, pressure, time, and type of reactor).

In this context, this work aims to review Life Cycle Assessment (LCA) case studies that analyze the environmental implications of SCFs processes, focusing particularly on the interplay between energy consumption, solvent use, concentration, and process type. The primary objectives of the review are to compile all papers related to LCA studies on supercritical fluids processes, and to analyze them through an analysis grid derived from the four phases of the LCA ISO Standards.

Based on the review analysis grid, it is possible to compile key information related to:

(i) Goal and scope, that includes the industrial sector, the type of SCF application,
(ii) Life cycle inventory, that compiles energy use, solvent use, and equipment per unit of product,
(iii) Life cycle impact assessment, that aims to show the impacts of SCFs processes (such as the carbon footprint) depending on the type of application, and key parameters (scale, concentration, etc.),
(iv) Interpretation, that sums up key findings for the reviewed case studies.

Overall, this review provides valuable insights into the environmental performance of SCF technologies across diverse applications, emphasizing the importance of integrating LCA methodology to guide informed decision-making and foster sustainable practices in SCF-based industries. Identifying key areas for improvement and optimization, this analysis serves as a foundation for future research and development efforts aimed at advancing the eco-efficiency of SCF processes.

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High-pressure extraction of five marigold (*Calendula officinalis*) fractions: evaluation of chemical composition and natural pigments potential

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As marigold (*Calendula officinalis*) flowers and leaves represent a familiar source of bioactive compounds well known due to their positive impact on human health, such as antioxidant, hepatoprotective, and wound healing [1], the present study aimed to elucidate the natural pigments` potential and the chemical composition of other underestimated parts of this plant. The five marigold fractions, including petals (MP), calyxes (MC), stems (MS), then a binary mixture of calyxes and petals (MCP), and a ternary mixture of stems, calyxes and petals (MSCP), were subjected to the supercritical CO_2 extraction (SC-CO_2). The main parameter, the CO_2 pressure, was varied (10 MPa, 20 MPa, and 30 MPa), while the extraction time (4 h), temperature (40 °C), and CO_2 flow rate were constant. The extraction time was determined empirically based on numerous performed supercritical extractions. According to the GC-MS profile, the most dominant compounds in the obtained extracts were found to be sesquiterpenes including ledene (1.24-8.87%), α-muurolene (9.62-12.92%), δ-cadinene (19.13-26.96%), α-cadinol (1.42-5.81%), and τ-muurolol (2.08-10.07%) and monoterpenes including thymol (1.85-2.87%), camphor (1.77-2.07%), carvacrol (0.58-1.25%) and β-thujone (0.93-1.13%).

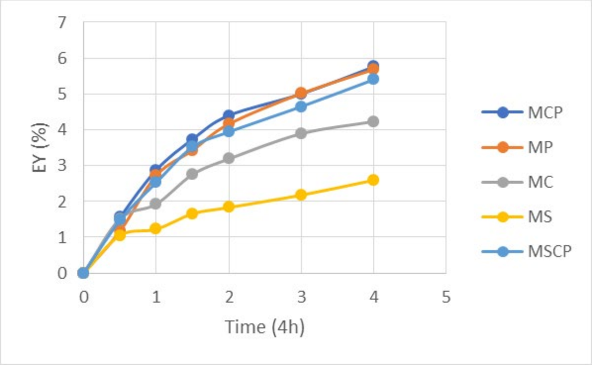

Figure 1: SC-CO_2 kinetics in marigold fractions at 30 Mpa.

To observe the kinetics of the process, the extraction yield (EY) was measured after 0.5, 1, 1.5, 2, 3, and 4 h at 30 MPa (Fig.1). In all five marigold supercritical extracts, the EY was increased by increasing the extraction pressure. In general, the lowest EY (1.71%) was achieved under the pressure of 10 MPa in the MS extract, while the highest EY (5.76%) was achieved under the pressure of 30 MPa in the MCP extract. The typical orange color of marigold flowers is present because of the content of different carotenoids, including β-carotene, ζ-carotene, lycopene, lutein, and citroxanthin [2]. Therefore, HPLC analysis of carotenoids will be performed, in order to evaluate the natural pigments potential of marigold supercritical extracts containing calyxes.

In conclusion, the most promising fraction turned out to be the marigold flower, namely, the binary mixture of calyxes and petals. Oxygenated sesquiterpenes were the most dominant class of compounds present. The supercritical extracts were found to contain several sesquiterpenoids as major compounds, namely, α-cadinol, δ-cadinen, γ-cadinen, τ-muurolol and α-muurolene, also present in the essential oil of marigold. The highest content of δ-cadinen (24.46-26.42%) was detected in the MC extract, regardless of the applied pressure.

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Novel aerogels from alginic acid: structural transitions in the fabrication process

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In the last few decades biopolymer aerogels have gained importance, due to their high porosity, high specific surface area, and low density. Alginates – polysaccharides obtained from the brown seaweeds – represent an important class of model system for large-scale fabrication of biopolymer-based aerogels. The conventional processing of alginate aerogels starts with the calcium-induced gelation in an aqueous media to get hydrogels. Supercritical drying using sc-CO_2 is done to remove the solvent from the hydrogel to obtain the aerogel. Since water has a large miscibility gap with CO_2, the hydrogels have to be solvent exchanged with a suitable solvent to produce lyogels. The transformation from hydrogel to lyogel results in a certain stiffening of the gel matrix. The solvent exchange and the supercritical drying steps cause gel shrinkage to a considerable level, which results in reduced porosity and a specific surface area. Although from a practical perspective the shrinkage has to be minimized [1], its origin is still understood poorly. The goal of this work is to study the evolution of both mechanical properties and shrinkage systemically on the way from hydrogel to aerogels. A plausible mechanism of shrinkage will be proposed based on both the experimental results and simulations. As a model system, we suggest employing novel acid-induced alginate hydrogels, as they are cross-linker-free, and represent a simpler system compared to calcium-alginate gels. The fabrication of this novel class of aerogels will also be discussed in this work.

Figure **1** shows the comparison of Young's Moduli (measured with a texture analyzer) of the hydrogels and the alcogels, which are gels that are solvent exchanged with an alcohol. It is clear that 5 wt% gels undergo increased structural changes, as these gels undergo more shrinkage. The result of this increases the stiffness and density of the gels, which increases the Young's Modulus. The structural changes increase with an increase in concentration of the alginate. Both direct and step-wise solvent exchange techniques are employed and compared. The Young's Moduli are measured using a texture analyzer and a dynamic mechanical analyzer.

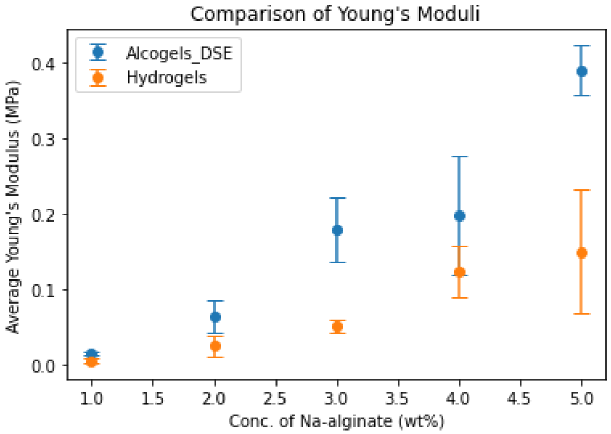

Figure 1: Young's moduli of hydrogels, and alcogels. Alcogels are solvent exchanged directly in pure alcohol.

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Process optimization for functional compounds extraction from *Sargassum thunbergii* using subcritical water: towards zero-waste biorefinery

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This study explores the application of eco-friendly technology, specifically subcritical water, for extracting functional compounds from underutilized marine biomass, with the aim of achieving complete valorization in a sustainable biorefinery process with zero waste. Using response surface methodology, we determined the optimal conditions for extracting the maximum yield of total phenolic content from *S. thunbergii* biomass to be a temperature of 195.43℃, an extraction time of 18.82 min, and a solid/liquid ratio of 0.032 g/mL. Chemical analyses were conducted, to investigate the structural characteristics of the optimized *S. thunbergii* extract (OSE), including total phenol content, total flavonoid content, total sugar, reducing sugar, monosaccharide composition, and molecular weight determination. The OSE's unknown compounds were profiled using the UPLC-QTOF-MS/MS, GC-MS, FT-IR and NMR techniques.

For OSE extracted under optimal conditions, the total phenolic content and total flavonoid content values were 29.01 ± 0.28 mg Phloroglucinol Equivalent/g and 10.33 ± 0.48 mg Quercetin Equivalent/g, respectively. Additionally, the total and reducing sugar contents of OSE were analyzed, and found to be (35.54±0.58 and 24.25±1.40) mg glucose/g, respectively. The main monosaccharides of OSE were Fucose at 35.29%, Galactose at 24.04%, Xylose at 17.71%, and Glucose at 16.65%. The average molecular weight number (Mn), weight average molecular weight (Mw), and polydispersity index (PDI, Mw/Mn) were 2190, 2499, and 1.14 at peak 1, 700, 780, and 1.11 at peak 2, and 196, 213, and 1.09 at peak 3, respectively. The main compounds identified using GC-MS were D-glucitol 39.51%, L-5-oxoproline 7.64%, and various functional components. A total of 64 phenolic compounds were identified tentatively in the OSE, including 27 phenolic acids, 16 flavonoids, and 21 other polyphenols (5 hydroxycoumarins, 3 tyrosols, 2 phlorotannins, etc.). FT-IR was also used to predict comprehensive information about the chemical structure of the OSE. An NMR analysis confirmed the presence of characteristic peaks of polysaccharides and phenolic compounds in the OSE.

This study lays theoretical foundations and provides technical guidelines for optimizing the extraction and processing of phenolic compounds from *S. thunbergii*. Our results confirmed the feasibility of employing subcritical water not only to utilize valuable substances like phenolic compounds contained in the extract, but also to convert the remaining residue into biofuel, thereby achieving a truly zero-waste biorefinery.

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Following profiles in subcritical water: the deconvolution work-around

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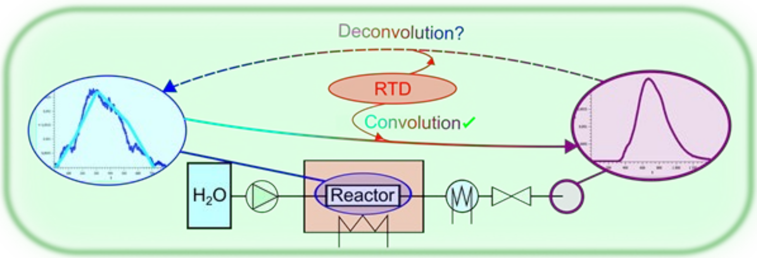

Figure 1: Prediction of a concentration profile in a subcritical reactor from end-of-pipe measurements by deconvolution.

Monitoring a process, especially a reaction's progress, is rarely an easy task in high-pressure vessels, even more so in subcritical water. The hydrothermal environment limits the range of applicable optical analytic methods, while the highly laminar nature of the flow in a micro-flow reactor renders most kinds of probe-based measurement methods unreliable, due to the high level of inhomogeneity in the reactor volume. It is an option to measure the flow at the end of piping, however, relating the results to the conditions in the reactor is not trivial. While it is relatively simple to calculate end-of-pipe profiles of concentration from known reactor profiles with convolution when the retention-time distribution (RTD) is known, reversing this operation is rather difficult. The inverse, deconvolution, does not even have a direct mathematical definition[1], much less a well-established optimal algorithm of computation, although some algorithms exist for special applications.

In our work, we propose a deconvolution algorithm based on simulated annealing, implemented in Python utilizing solely open-source packages. To test the method's predictive capabilities, we conducted measurements on a reactor system used primarily for semi-continuous hydrothermal liquefaction experiments. The reactor system is operated with subcritical water at 265-285°C at 10 MPa, to simulate typical conditions for hydrothermal processes. Multiple reaction profiles were emulated by introducing NaCl as a tracer at the inlet of the reactor, and conductivity was measured at the pipe outlet at ambient conditions. After obtaining the RTD of the system at the operating conditions by deconvolution, experiments to assess predictive capabilities were conducted, the graphical summary of which is represented in Fig. 1. New, known profiles were introduced (light blue), and the end-of-pipe conductivity profile (purple) was recorded. After sufficient data transformation (normalization, smoothing), the proposed algorithm was used to approximate the profile in the reactor using the previously determined RTD (the result represented by the dark blue graph). The evaluation of predictive power was assessed by comparison with the known reactor profile.

The results suggest that the algorithm, while computationally moderately expensive, provided a reasonable estimation of the reactor profile, even in a subcritical system, where the effect of multiple segments, mixing of flows and high temperature and density gradients complicate system dynamics, and introduce significant non-linearity. Additionally, using box-like finite-length disturbance to obtain experimental RTD improves predictive power significantly compared to calculating with RTD obtained by impulse-like disturbance. This work was supported by the ÚNKP-23-2-I-BME-256 New National Excellence Program of the Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund.

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Development of affinity polymeric particles for the selective recovery of hydroxytyrosol from aqueous solutions using supercritical CO_2 technology

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Olive polyphenols have been studied extensively on their biological activity to the benefits of the Mediterranean diet. Specifically, hydroxytyrosol, tyrosol and their derivatives have been reported for exhibiting protective effects toward cardiovascular health [1]. Based on the reported results, the European Food Safety Authority concluded to have substantial scientific evidence pointing to the ability of hydroxytyrosol (HT) and its derivatives to protect blood lipids against oxidative damage, considered the main cause of cardiovascular diseases [2].

The growing interest in HT and its derivatives led to the development of methods for extracting this substance on an industrial scale from materials derived from olives, mainly olive pomace and olive vegetation waters, using membrane technology

[3]. These natural extracts have application in several fast-growing sectors, such as food, cosmetics, pharmaceuticals and nutraceuticals.

In this work a second fractionation step based on an adsorption/desorption process was explored, in order to eliminate low molecular weight carbohydrates from the final product, recovering HT and increasing its final concentration.

In order to develop a highly-efficient solution to remove the HT selectively from crude samples, HT-affinity polymeric particles were prepared by allying the molecular imprinting technique and the supercritical carbon dioxide ($scCO_2$) technology [4,5]. The HT-molecularly imprinted polymer (HT-MIP) and its respective control, the non-molecularly imprinted polymer (NIP), were produced by free radical polymerization using acrylate-based functional monomers and V-65 as a free-radical initiator, in $scCO_2$. The materials were obtained in high yield, and were characterized chemically, physically and morphologically. Their extraction efficiency was evaluated by static and dynamic binding experiments.

Acknowledgements

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Bioaerogels for advanced dressing solutions

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The process of wound healing, which is essential for tissue repair, is complicated, and can be hindered by various factors, leading to chronic wounds with complications such as bacterial accumulation and hypoxia. Aerogels, known for their large surface area and low density, are promising candidates for facilitating wound healing by serving as oxygen and drug delivery systems. In our study, we synthesized different aerogels, combining pectin and xanthan gum with polylactic acid (PLA). While the PLA reduced the total surface area, it increased the stability. Swelling experiments showed that pure pectin aerogels degrade rapidly within hours, while xanthan aerogels are more resistant. PLA-pectin and PLA-xanthan aerogels showed longer stability and improved fluid absorption, indicating their potential as a wound dressing material.

To model drug release, diclofenac sodium, indomethacin and dexamethasone were incorporated into the samples, which showed sustained release in dissolution tests. Oxygen generation, which is important in wound healing applications [1], was facilitated by sodium percarbonate and calcium peroxide. However, their initial peroxide formation resulted in low cell viability. To mitigate toxicity, the enzyme catalase was incorporated, which improved biocompatibility with sodium percarbonate, but not with calcium peroxide, which remained toxic.

In summary, these biodegradable, oxygen-releasing materials show promise for transforming wound care, and potentially achieving better outcomes for patients with chronic wounds.

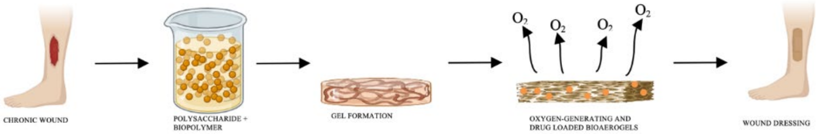

Figure 1: The process of preparing oxygen-releasing wound-healing materials.

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Controlled decomposition of an epoxy resin with subcritical water

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A significant percentage of the annual global plastic waste consists of thermosetting polymers, polymer composites and technical plastics. The degradation and recycling of waste thermosetting polymers face numerous challenges, as they cannot be melted again and they are not biodegradable. Therefore, it is not surprising that most commonly these materials are unfortunately disposed of in landfills. In addition to physical and thermal methods, the development of chemical recycling of polymers is also a subject of extensive research. The decomposition of various epoxy resins has been studied widely in the last 20 years. Successful decompositions were achieved by solvolysis with pressurized organic solvents, hydrolysis in sub- and supercritical water, acid and metal catalysis, etc. [1] Unfortunately, the majority of these studies resulted in a very heterogeneous products containing tens of compounds. [2-4] Aiming for selective product recovery, the subcritical high pressure and temperature water can be promising, due to selective bond cleavage by using catalysts or controlling the reaction time. Based on the batch experiments, the time required for complete breakdown varied significantly, depending on the temperature.[2-4]

The goal of this work is to recover thermally sensitive intermediate(s) by a flow-based, subcritical water solvolysis process of a bisphenol-A type epoxy resin (Bisphenol A diglycidyl ether, DGEBA). The crosslinker of the used epoxy was of the amine type (3-aminomethyl-3,5,5-trimethylcyclohexyl-amine). In the semi-continuous setup, we succeeded in shifting the product profile toward the formation of only four main components in the liquid phase, including Bisphenol-A, phenol and benzyl-alcohol. A Box-Behnken type experimental design-based parameter optimization was performed. The controlled parameters were the temperature (330-360 °C), the pressure (20-25 MPa), and the average residence time (2-4 min), while the response variables were the time required for decomposition and the product ratios. An in-line sampling was installed to determine the product profile and the time required for decomposition. The samples were analyzed using gas chromatography. The effect of pressure was negligible, while the temperature and average residence time had combined effects on the decomposition. There was a significant difference between the washing out profiles of the various components; while benzyl alcohol had a high concentration in the first samples, and the Bisphenol A concentration decreased at a smaller rate. In all cases benzyl alcohol gave the majority of the total yield, app. 40-50 mass%. At lower temperatures and shorter times, larger molecules also appeared. At 360 °C the full decomposition of the epoxy resin required less than 10 minutes.

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Comparison of supercritical extraction method to the cold pressing of hemp seeds

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Hemp seeds are considered a rich source of essential macronutrients, including proteins, fats and fiber, as well as a number of essential minerals such as phosphorus, potassium, magnesium, calcium, sodium, iron, manganese, zinc and copper. Hemp seeds also contain beneficial phytonutrients such as tocopherols, carotenoids, and sterols. However, it is important to note the presence of certain anti-nutritional components in hemp seeds, including phytic acid, condensed tannins, trypsin inhibitors, cyanogenic glycosides, and saponins. Hemp seed oil is characterized by a high polyunsaturated fatty acid content of more than 70%, with a significant proportion of essential fatty acids such as linoleic acid (n-6) and α-linolenic acid (n-3). The favorable ratio of n-6 to n-3 is 2.5–5.5, which contributes to its potential health benefits [1-4]. The methods used to obtain seed oil, particularly supercritical CO_2 extraction (SCE) and cold pressing, are highlighted as sustainable approaches. The supercritical CO_2 used in SCE is non-toxic, and can easily be split into a gas phase under room conditions. Cold pressing as a mechanical extraction method avoids the use of solvents and delivers high-quality oils. Both methods are suitable for isolating thermolabile components, as they operate at lower temperatures. This underlines the environmentally friendly and efficient nature of these extraction techniques [5, 6]. The cold-press extraction method and supercritical extraction were used to obtain the extracts in the study. The characterization of the fatty acids in the extracts was performed using gas chromatography-mass spectrometry (GC/MS). This analytical technique allowed the identification and quantification of the specific fatty acids present in the extracted samples, and provided valuable insights into their composition and possible differences between the two extraction methods. Slightly higher levels of linoleic and linolenic acid were obtained in the SCE extract compared to the cold-pressed oil. The compositions of the extracts from both methods are similar, with a linoleic to linolenic acid ratio of 2.73 in SCE. This ratio is somewhat closer to the desired ratio of 3:1, which is important for the human organism, than in the case of cold-pressed oil, where the ratio is 2.65.

The study shows that the supercritical CO_2 extraction (SCE) method yielded an extract with a fatty acid ratio composition similar to that of the original material. In particular, the SCE method allowed the preservation of two important fatty acids, namely, linoleic and linolenic acid. Furthermore, the study shows that SCE maintained, and, in some cases, even slightly improved, the ratio between linoleic and linolenic acid. This ratio is closer to the desired ratio of 3:1, which is considered one of the beneficial properties of hemp oil.

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Evaluation of physicochemical and biofunctional properties of makgeolli ground extracts using supercritical CO_2 and subcritical water

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The purpose of this study is to evaluate Makgeolli ground using supercritical carbon dioxide (SC-CO_2) extraction and subcritical water hydrolysis (SWH) at different conditions, and identify its potential for industrial utilization. Makgeolli is a traditional Korean wine made from rice. Makgeolli ground (MG) is a by-product generated from about 20% of raw materials during their manufacturing process and mostly discarded. Previous studies on MG have usually used hydrothermal extraction or organic solvent extraction, and suggested that there are various bioactivities such as antioxidant and phenolic compounds. In this study, new clean technologies, SC-CO_2 extraction and subcritical water hydrolysis, were utilized, instead of organic solvent. Both are safe, eco-friendly, and harmless to humans, using CO_2 and water as the solvents, respectively.

The SC-CO_2 extraction of MG was carried out under four conditions: temperatures of 45 and 55°C and pressures of 200 and 300 bar. The properties were assessed, such as yield, color, acid value, peroxide value and fatty acid composition of the oil extracts obtained from MG by SC-CO_2 extraction. Afterward, the de-oiled MG was extracted using subcritical water at different temperature conditions. The extraction temperatures were 130, 150, 170, 190, 210 and 230°C. The extracts were also evaluated for physical properties such as hydrolysis efficiency, pH, color, Maillard reaction products, chemical properties such as total phenolic content, total flavonoid content, total sugar content, total protein content, monosaccharide composition, and *in-vitro* bioactivities such as antioxidant ($ABTS^+$, DPPH, FRAP), antidiabetic (α-amylase inhibitory assay, α-glucosidase inhibitory assay) and anti-inflammatory (protein denaturation inhibitory assay).

Particularly, it was found that the extract had an increasing antioxidant activity and a high amount of phenolic compound content, as the extraction temperature increased and demonstrated the highest values 57.86, 65.00, 42.88 mg Trolox/g dried sample for $ABTS^+$, DPPH, FRAP respectively at 210°C, and 66.84 mg GA/g dried sample, 36.17 mg Rutin/g dried sample for TPC and TFC at 230°C.

Based on the results obtained, it is possible to contribute to the efficient valorization of MG for industrial purposes, such as functional, nutritional food, and cosmetics and to the zero-waste in the food industry using environmentally friendly extractions from ground Makgeolli.

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PLGA-based anti-inflammatory coating on titanium alloy for targeted drug delivery in orthopedics prepared by supercritical foaming

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The growing number of required orthopedic procedures necessitates continuous innovation in the field of Advanced Biomedical Implants. TiAl6V4 alloy has good biocompatibility and mechanical properties, and is the most widely used material for such applications, although its variable osteointegration remains a challenge. Surface modifications, especially drug-loaded bioactive coatings, are a promising way to improve the bioactivity of implants and reduce postoperative complications [1].

In this study, a novel two-step approach combining drop casting and supercritical CO_2-assisted foaming is presented, to develop a biodegradable poly(lactic-*co*-glycolic acid, PLGA) coating loaded with ketoprofen (a non-steroidal anti-inflammatory drug) on a TiAl6V4 substrate. Supercritical CO_2-assisted foaming is an environmentally friendly and cost-effective process for producing drug-loaded foamed coatings with open-pore structure, high drug loading, and minimal residual organic solvent content [2, 3].

The developed coatings were characterized using X-ray photoelectron spectroscopy, 3D profilometry, *in vitro* drug release, and cell tests. The X-ray photoelectron spectroscopy confirmed the loading of ketoprofen within the PLGA coating. 3D profilometry showed a porous surface morphology and increased surface roughness of coatings compared to the bare TiAl6V4 substrates. *In vitro* drug release studies exhibited sustained release kinetics in simulated body fluids. Cell tests with adipose-derived mesenchymal stem cells and osteoblasts confirmed the promise of the obtained coatings for use in ortohepedics with improved biocompatibilty.

In conclusion, the results of this study highlight the potential of the developed PLGA-based bioactive coating to improve the performance of orthopedic implants by offering improved surface properties, a desired biocompatibility with bone cells, and localized drug delivery capabilities. This innovative approach holds great promise in overcoming the challenges associated with implant integration and inflammation, and ultimately improving patient outcomes in orthopedic medicine.

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Machine learning for predicting solubility of cannabinoids in supercritical carbon dioxide

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Recently, machine learning (ML) techniques have been applied successfully for modeling numerous phenomena and processes involving supercritical fluids (SCFs), including estimation of SCF thermodynamical properties, solubilities of various substances in SCF, supercritical fluid extraction (SFE) yields, as well as the design and optimization of other processes involving SCFs [1].

One of the most significant applications of SCF is obtaining extracts containing cannabinoids from hemp (*Cannabis sativa* L.) inflorescences by SFE using supercritical carbon dioxide ($scCO_2$) as a solvent. However, this process is challenging to a high number of cannabinoids present in the plant raw material, as well as a pronounced impact of process conditions (especially extraction temperature and pressure) on the extraction yield and extract composition. In this work, various methods of mathematical modeling of the solubility of selected cannabinoids – cannabidiol (CBD), cannabinol (CBN), tetrahydrocannabinol (THC), and cannabigerol (CBG) – in $scCO_2$ were analyzed, using experimental data from the literature [2-4]. ML techniques, including linear regression and artificial neural networks, were compared with the thermodynamic approach and experimental data (see Fig. 1). A general ML model was proposed for cannabinoid solubility estimation. The application of the developed ML models was demonstrated for the development of a fractionation process for the separation of CBD and THC.

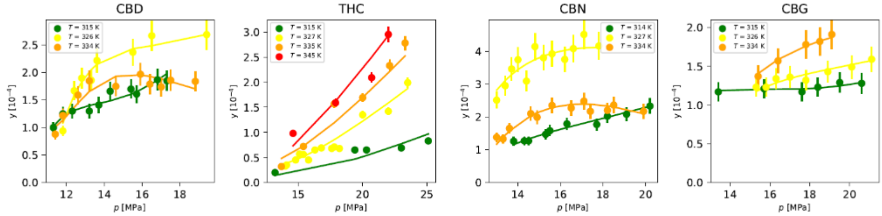

Figure 1: Solubility of CBD, THC, CBN, and CBG as a function of pressure (abscissa) and temperature (colors) – experimental values (dots) vs. values obtained using linear regression (lines) – exemplary results.

The obtained results have confirmed that machine learning techniques can be applied for modeling the solubility of cannabinoids in supercritical carbon dioxide, and that they may be useful for the development of advanced separation techniques in the hemp processing industry.

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Antimicrobial, antioxidant, and enzymatic activity of supercritical carbon dioxide extract from mango fruit waste

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In recent years, there has been increasing concern about the significant impact of organic solvents on the environment and extracts. Therefore, the use of environmentally friendly extraction methods, such as green technology with supercritical fluids (SCFs), has gained importance. Compared to conventional extraction techniques, supercritical fluid extraction (SFE) has proven to be a promising and breakthrough technology for various applications, especially for the extraction of biologically active substances with high antioxidant, antibacterial, antimalarial, and anti-inflammatory activity. Furthermore, as awareness of health and healthy diet increases, more and more fruits are being processed, resulting in enormous amounts of agro-industrial waste from fruit by-products. This can have a negative impact on the environment, due to the accumulation of organic waste [1–2]. Therefore, SFE is a suitable process to obtain valuable substances with antioxidant and antibacterial properties from fruit waste such as mango peels.

The aim of our study was to provide extracts from fruit waste with potential antibacterial properties, high antioxidant activity, and the presence of certain enzymes in a highly active form. Dried mango peels were used for our research. The extract was obtained by a supercritical extraction process using carbon dioxide and ethanol as a co-solvent at selected operating conditions of 40 °C and 200 bar. A suitable spectrophotometric analysis was carried out to determine the antioxidant potential of the obtained extract. The enzymatic activities were examined with specific enzymatic assays for each enzyme, such as α-amylase, cellulase, glucoamylase, laccase, lipase, peroxidase, polyphenol oxidase (PPO), protease, superoxide dismutase (SOD) and transglutaminase (TGM). In addition, the antibacterial potential was investigated using two different methods. The disk diffusion method was used to determine the inhibitory effect of the extract on the growth of Gram-negative and Gram-positive bacterial species qualitatively. In addition, the quantitative broth microdilution method was used to determine the microbial growth inhibition rate (MGIR) at different extract concentrations and the minimum inhibitory concentration (MIC).

Mango peel extract, obtained by an environmentally friendly extraction approach using SCFs, showed promising antioxidant and antibacterial properties against selected bacterial species. In addition, enzymes such as α-amylase, cellulase, glucoamylase, laccase, lipase, PPO, and SOD were present in a highly active form. Among the bacterial species tested, *B. cereus* was the most susceptible microorganism. In addition, it is possible to incorporate natural extracts into various nanocarriers, as this would make an important contribution to the sustainable development of new biologically active agents with antibacterial properties that are important for the pharmaceutical, medical, cosmetic, and food industries. Moreover, the negative impact on the environment can be reduced by reducing waste disposal and reducing the use of toxic extraction solvents.

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Supercritical fluid extraction of bioactive compounds from avocado seed

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Avocado (*Persea americana* L.) is a nutritious tropical fruit, the production of which has increased enormously over the last decade. Avocado seeds can account for up to 26% of the total fruit weight, therefore becoming underutilized as inedible parts, and consequently create large amounts of waste biomass. On the other hand, avocado seeds can represent an inexpensive alternative source of potential bioactive compounds [1].

As traditional and conventional methods of extractions are time-consuming, require large amounts of organic solvents, and operate at high temperatures, consequently, they can result in degradation of thermo-labile compounds, and reduce the bioactivity of the obtained compounds significantly. Supercritical fluid extraction (SFE) with carbon dioxide (scCO$_2$) as a solvent provide separation at near-ambient temperatures, therefore minimizing the degradation of the thermo-labile compounds. Due to its green process and the great characteristics of scCO$_2$ (e.g., non-toxicity, mild critical temperature, low critical pressure, non-flammability, odorless nature, prevents extract oxidation, volatilized easily, etc.), it is one of the most promising techniques in the recovery of pure and clean extracts with bioactive compounds that can be used in biomedicine and for cosmetics, pharmaceutical products, nutraceuticals, and functional food [2]. Due to the ever-increasing range of infections caused by different microorganisms and the expanding problem of antimicrobial resistance, the purpose of our study was to obtain bioactive compounds with antimicrobial properties from avocado seeds. Bioactive compounds from avocado seeds were recovered using SFE with $scCO_2$ as a solvent and ethanol as a co-solvent. Qualitative colorimetric analyses were used for the detection of various phytochemicals. Specific spectrometric assays were availed for determination of the selected enzyme activities. Moreover, the antimicrobial activity of avocado seed extracts was tested using disc diffusion and broth microdilution methods on bacteria and fungi, which often pose a problem in antimicrobial resistance, are transmitted by food, or are colonized during food packaging.

The results of our study demonstrated the presence of various phytochemicals in avocado seed extracts that inhibit the growth of many microorganisms effectively. An environmentally friendly and near-ambient temperatures SFE showed a highly active form of all the selected enzymes in the obtained avocado seed extracts. It is important to note, that the extract inhibited 11 out of 15 microorganisms, exhibiting extremely low MIC values, with 70 μg/mL being the lowest against Gram-positive bacterium *Bacillus cereus*. In addition, the results in the fields of enzymatic and antimicrobial activity of avocado seed extract, obtained by SFE, proved its extraordinary potential for further applications. The exploitation of avocado seeds for the production of value-added compounds is a huge ecological opportunity, to reduce the accumulation of food waste and for more sustainable production methods.

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Preparation of π-conjugated polyHIPE foams by Pd catalyzed C-C cross-coupling

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Π-Conjugated polymers (CP) are well known organic semiconductors distinguished by their optoelectronic features. These unique properties are utilized for the commercial production of organic electronics, such as organic-light emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs), as well as for catalysis, energy harvesting and energy storage applications [1].

In recent years, conjugated porous polymers (CPPs) have emerged as promising materials for heterogeneous photocatalysis, N2 fixation and CO2 reduction, due to adjustable pore sizes, tunable chemical structures, good stability, and large pore volumes [2]. CPPs are synthesized commonly through transition-metal mediated reactions, which can be accompanied by the use of templated polymerization techniques. High internal phase emulsion, referred to as HIPEs, allow for the preparation of macroporous materials with a characteristic 3D interconnected porous structure, known as polyHIPEs. After polymerization of the aforementioned materials, these still contain significant amounts of surfactants, catalysts, bases and solvents used during the synthesis. These compounds may leach out of the material during later applications and pollute the environment further. The more traditional method of purification is by Soxhlet extraction, which can impact the shape and morphology of polyHIPEs. Recently, a greener method of purifying polymers has emerged, by using super critical CO_2 extraction ($scCO_2$) [3], where it was also shown that this method can be used to extract certain transition metal from complex matrices [4], which may impede the photophysics of π-conjugated polymers and, hence, its performance.

In our case, the HIPEs, were prepared through Suzuki-Miyaura and Sonogashira-Hagihara cross-coupling reactions, to yield π-conjugated polyphenylene and poly(aryleneethynylene) polyHIPEs. The resulting materials were purified by Soxhlet extraction, as well as by super critical CO_2 extraction ($scCO_2$). While $scCO_2$ removed organic molecules effectively, it was unable to remove the ionic compounds. On the other hand, the Soxhlet extraction performed well at removing the aforementioned ionic compounds, but was less effective at removing organic compounds. Furthermore, while purifying polyHIPEs with the more traditional Soxhlet extraction and subsequent drying in vacuum, distorted the shape and morphology of the monoliths, whereas drying by $scCO_2$ preserved the aforementioned characteristics of the prepared polyHIPEs.

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Extraction of Chaste tree ripe fruits by near-critical liquid CO_2 and the characterization of its free fatty acids

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The chaste tree and its fruits are used in traditional herbal medicine for menstrual problems, including depression and irritability [1]. Some of the effects claimed for the plant can derive from the principal fatty acid components omega-6, well-known in the dermatology and gynecology sectors. The lipid part has to be evaluated for its value, mainly for the presence of an essential fatty acid such as linoleic acid. The recovery is evaluated of a diterpene, and casticin of chaste tree fruits by near-critical CO2 and other solvents [2].

The extraction of chaste tree ripe fruits by near critical liquid carbon dioxide at its vapor-liquid equilibrium conditions, was carried out in a high pressure autoclave, analog to the Soxhlet method (Fig. 1). The glass parts of it were placed inside an autoclave. The autoclave had an outer diameter of 80 mm, a wall thickness of 8,5 mm and a height of 430 mm. In the upper screwable cover were welded a capillary with a high- pressure valve for loading and discharging the solvent, a capillary with a pressure gauge, and a cooling finger. During extraction the bottom of the autoclave was immersed in a warm thermostatic water bath and in the cooling finger was circulated colder water. The apparatus is described in more detail in [3]. The liquid CO2 was circulated inside the autoclave by the temperature gradient inside, at a pressure 6 ± 0.2 MPa and an average temperature 297 K. The extraction was carried out for 3, 5, 7, 12 and 24 hours. The total extract was separated in four fractions by thin-layer chromatography containing mainly triglycerides (TG), diglycerides (DG), monoglycerides (MG) and free fatty acids (FFA) fraction. The FFA were present in all the four fractions, and, after their transesterification, were analyzed by GC-MS and 1HNMR in the form of fatty acid methyl esters (FAME). The FAME analysis of the extracts showed that the main fatty acid of the lipid fractions was linoleic acid (66-70%), an essential fatty acid of the omega-6 family. The second fatty acid was oleic acid (ca 10%), and saturated fatty acids were ca. 8% of the total fatty acid composition.

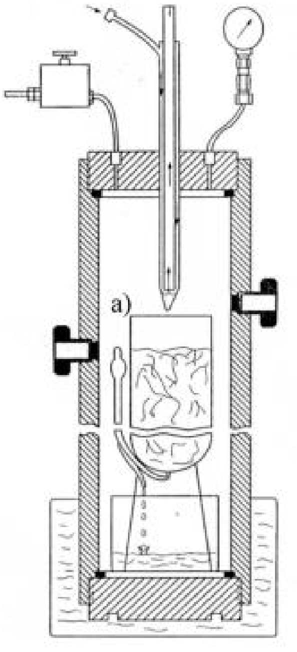

Figure 1: Apparatus for extraction in Soxhlet-like method using as solvents liquefied gases under vapor-liquid equilibrium conditions.

Combining the GC-MS and 1HNMR analysis, we identified the structure of a fatty acid with 18 carbon atoms in chain and methyl or OH groups, as substituents along the chain. No evidence on branched or hydroxylated 18:2 derivatives of chaste tree components has been reported until now.

In addition, ω-phenyl fatty acids were recognized, matching the results of GC- MS and NMR. In particular, ω -phenyl fatty acids and OH ω-phenyl fatty acids were identified, containing in total 18 and 19 carbon atoms. There are no incidences of the phenyl fatty acid in the Chaste tree, or in other plants of the verbenaceae plant genius.

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Predict: SC-CO_2 applications` modeling and prediction software

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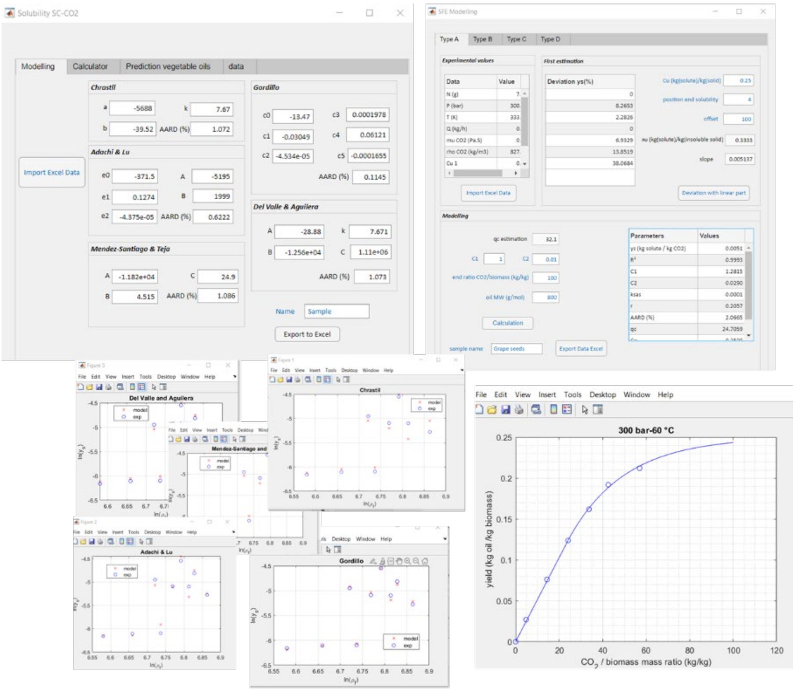
Nowadays, in the topic of SC-CO_2 applications, various studies can be found dealing with the modeling and calculations of various parameters helping the interpretation of experimental data. Nevertheless, modeling studies are still far less numerous than experimental ones. Furthermore, there is an emergence of modeling studies using experimental design and neural network (artificial intelligence). Experimental design is a very useful tool to understand the effects of operating conditions on one or several variables. Nevertheless, unlike theorical models like Sovová's broken and intact cell (BIC) model, it does not give the possibility to determine the values of physical parameters like transfer or diffusion coefficients. Artificial Intelligence is very specific method not accessible to everyone, and it does require a very large amount of experimental data.

In this context, Predict was created, a software applied to SC-CO_2 applications. This software was created with a Graphical User Interface and with the ability to communicate with Excel. It consists in several calculations' modules: the modeling of extraction kinetics using the BIC model, the modeling and prediction of solute solubility in SC-CO_2, the choice of co-solvent using the Hansen method, the calculation of SC-CO_2 thermophysical properties, the calculation of CO_2-solvent liquid-vapor equilibrium, the widom lines plot and CO_2-solvent binary mixture thermophysical properties, etc.

This software offers the possibility to perform modeling and prediction calculations to everyone using a friendly user interface. It communicates easily with Excel to read experimental data and save calculations/modeling results. The aim is to offer to researcher/engineers the ability of performing fast and accurate modeling/predictions calculations and studies.



Chrastil
a -5688
k 7.67
b -39.52
AARD (%) 1.072

Adachi & Lu
e0 -371.5
A -5195
e1 0.1274
B 1999
e2 -4.375e-05
AARD (%) 0.6222

Mendez-Santiago & Teja
A -1.182e+04
C 24.9
B 4.515
AARD (%) 1.086

Gordillo
c0 -13.47
c3 0.0001978
c1 -0.03049
c4 0.06121
c2 -4.534e-05
c5 -0.0001655
AARD (%) 0.1145

Del Valle & Aguilera
A -28.88
k 7.671
B -1.256e+04
C 1.11e+06
AARD (%) 1.073

Name Sample

Experimental values

Data	Value
N (g)	7.
P (bar)	300.
T (K)	333.
Q (kg/h)	0.
mu CO2 (Pa.S)	0.
rho CO2 (kg/m3)	827.
Cu 1	0.

First estimation

Deviation ys(%)
0
8.2653
2.2826
0
6.9329
13.8519
38.0684

Cu (kg(solute)/kg(solid)) 0.25
position end solubility 4
offset 100
xu (kg(solute)/kg(insoluble solid)) 0.3333
slope 0.005137

Modelling

qc estimation 32.1
C1 1
C2 0.01
end ratio CO2/biomass (kg/kg) 100
oil MW (g/mol) 800
sample name Grape seeds

Parameters	Values
ys (kg solute / kg CO2)	0.0051
R²	0.9993
C1	1.2815
C2	0.0290
ksas	0.0001
r	0.2057
AARD (%)	2.0665
qc	24.7059

Figure 1: Screen shots of solute solubility in SC-CO_2 and extraction kinetics modeling modules.

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Supercritical fluid extraction from cornelian cherry (*Cornus mas L.*) seeds

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Cornelian cherry (*Cornus mas L.*, CM) is a shrub from the *Cornaceae* family native to Southeast Europe and Southwestern Asia. In traditional medicine parts of CM have been used for more than 1,000 years for treatment of various conditions, including digestion problems, sore throat and measles, as well as liver and kidney diseases [1]. Findings from scientific investigations showed that CM is rich in polyphenols, specifically flavonols, anthocyanins, phenolic acids and iridoids, as well as in polysaccharides [2]. In these studies, the fruits, flowers, leaves and bark of CM have been used mostly as the source material, while the results that include seeds are scarce. The potential for the application of extracts from CM is huge, mainly for products in the category of functional foods.

In this contribution the process of supercritical fluid extraction (SFE) with carbon dioxide (CO_2) as a solvent, was used as the method for obtaining extracts from seeds of CM. The main advantages of using SFE with CO_2, in comparison with conventional methods, are the possibility of working on mild temperatures, targeting the extraction toward specific compounds or groups by the choice of operating conditions, and the absence of the solvent in the obtained extract. In the present work, the influence of pressure and temperature on the yield and composition of extracts was investigated, while the seeds of CM used in the experiments originated from two different locations, Bosnia and Montenegro.

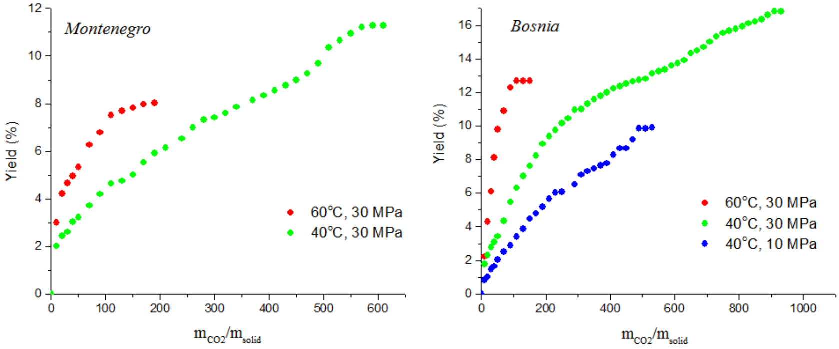

Figure 1: Results of SFEs from seeds of Cornelian cherry.

The results from the SFE experiments, shown in Figure 1., show that the kinetics of the extraction were practically the same at 30 MPa for seeds from both locations. The extraction rate was higher at higher temperature, but the overall yield was substantially higher at lower temperatures. This result indicates that the composition of the extracts should be quite dependent on the temperature, which was expected to be confirmed with qualitative analysis. An additional experiment was performed at 10 MPa and 40°C with seeds from Bosnia. Expectedly, the yield was lower compared to the one obtained at the same temperature and higher pressure. For the purpose of comparison, conventional Soxhlet extractions were performed with seeds from Bosnia. The yields were 6.57% and 23.65% with hexane and ethanol as the solvent, respectively, indicating that the extract constituents were mainly polar compounds. The main conclusions from the present study are that the SFE is a process that can be competitive with conventional extraction processes for obtaining extracts from CM seeds. Moreover, the results indicate clearly the potential for selective extraction with the appropriate choice of operating conditions. These first results of a planned larger study are highly optimistic regarding the potential of SFE as a *green* process for obtaining extracts suitable to be constituents of added value products.

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SSI of PLA-based surgical sutures with thymol

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Due to the high use and misuse of antibiotics over the years, microbes have developed resistance to a significant number of drugs (so-called antimicrobial resistance - AMR) [1]. Therefore, the necessity has been recognized for the development of natural antimicrobial agents to overcome growing bacterial resistance against synthetic antibiotics. Thymol is a natural monoterpenoid, with proven anti-inflammatory, antioxidant, and antimicrobial properties, and it has been recognized as safe by the FDA (it has GRAS status).

With the aim to fabricate material with antibacterial activity, supercritical solvent impregnation (SSI) was applied for loading of commercial PLA-based absorbable surgical sutures with thymol in a green medium, supercritical CO_2. The operating temperature and pressure were set to 35 °C and 10 MPa, while the contact time was varied between 1 and 6 h. The SSI process was performed under mild processing parameters, to obtain an effective amount of loaded thymol against the tested bacteria, keeping in mind the recommended safe content of thymol for human blood cells (in terms of cytotoxicity and mutagen effect) [2]. The selected process conditions enabled thymol loadings of 3.9–5.6% (Fig. 1) [3]. SEM analyses was used to monitor the sutures' morphological change from swelling to agglutination, induced by the increased amount of thymol in the material.

FTIR analyses confirmed the presence of thymol on the surface of the impregnated sutures. The antibacterial activity of the thymol-loaded surgical sutures was proven against *E. coli* and *S. aureus*. The range of sutures' antibacterial activity was measured by the width of the inhibition zones [3]. The release of bioactive compounds from the impregnated carriers into the surrounding liquid medium supports a decrease in the spread of bacterial growth [4]. The initial burst effect, desirable to provide an immediate antibacterial effect in contact with the impregnated material, was observed for all the tested samples after exposure to the medium simulating body fluids (PBS, 37 °C), since the release of loaded thymol from the material was fast in the first 4 h, while prolongation of the release experiment led to gradual thymol release [3].

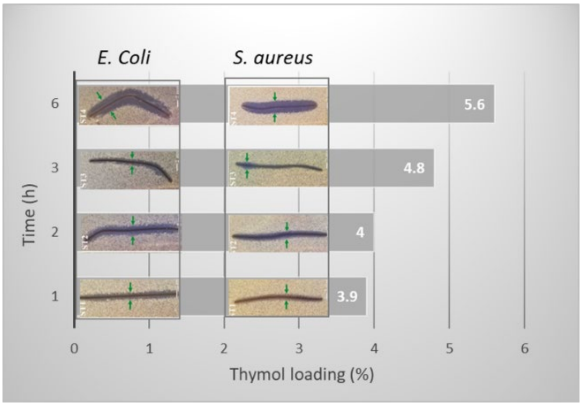

Figure 1: Kinetic of the SSI process with corresponding antibacterial effect of thymol loaded samples.

The present study revealed successful application of SSI for functionalization of surgical sutures with the biological agent thymol, with the aim to fabricate material with anti-bacterial properties. The mild process conditions (35 °C, 10 MPa, 1–6 h) allowed thymol loadings up to 5.9%. The thymol loaded sutures expressed antibacterial effect against the tested bacteria strains (E. coli and S. aureus). Thel release of Thymol from the impregnated sutures in PBS media exhibited gradual release, whereby the sample subjected to the SSI during 4 h retained the highest thymol amount (41.2%) after 10 days of exposure to PBS.

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CO_2 supercritical extraction of antioxidant compounds from tangerine leaves (*Citrus reticulata*) and their application as an antioxidant in soybean oil

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The negative effect of synthetic antioxidants on health, together with consumers' interest in purchasing natural products, have contributed to replacing synthetic additives with natural antioxidants [1]. In this sense, agro-industrial waste and by-products` valorization represents an economical and environmental alternative for obtaining bioactive compounds. Therefore, this study aimed to extract bioactive compounds from tangerine leaves (TL) (*C. reticulata* var. Arrayana), to act as an antioxidant ingredient in preserving oil oxidation. First, Soxhlet extraction was evaluated using hexane, ethyl acetate, and ethanol; the most significant protective effect against lipid oxidation was observed in the oil added with the extract obtained with hexane. After the Schaal oven test, this oil presented lower peroxide and p-anisidine index values, showing that non-polar compounds obtained using hexane preserved the oil better. Therefore, considering the greenness of CO_2 supercritical extraction and its potential to improve the recovery of this class of compounds, this study optimized the operational parameters of pressure (100, 200, and 300 bar) and temperature (40, 50, and 60ºC) on the extraction of TL compounds. The effects of the extraction technique on the total phenolic content (TPC), measured by the Folin-Ciocalteu method and antioxidant capacity, were investigated using 2,2-azinobis (3-ethylbenzothiazoline- 6-sulfonic acid) radical cation (ABTS), 2,2-diphenil-1-picrylhydrazyl radical scavenging capacity (DPPH), and oxygen radical absorbance capacity (ORAC). The oxidation was quantified and monitored each 5 days for 20 days, using accelerated methods such as Rancimat and the Schaal oven storage test at 60ºC (AOCS M. Cg 5-97) measuring acid (% oleic acid), peroxide and p-anisidine values. Fig. 1 presents the CO_2 supercritical conditions on extraction yield, showing a significant influence of pressure and temperature on the yield. Gas chromatography-mass spectrometry, GC-MS, characterized the terpene profile of the extracts. The main terpenoids identified in the extracts were linalool, α-pinene, β-pinene, and phytol. The best oxidative stability values were found at 288 bar and 36ºC. The optimized CO_2 extraction conditions allowed obtaining extracts more able to protect soybean oil against lipid oxidation than the hexane Soxhlet extract. Thus, the developed CO_2 extraction method can be considered a sustainable alternative in valorizing waste from tangerine agro-industrial by using it as antioxidant.

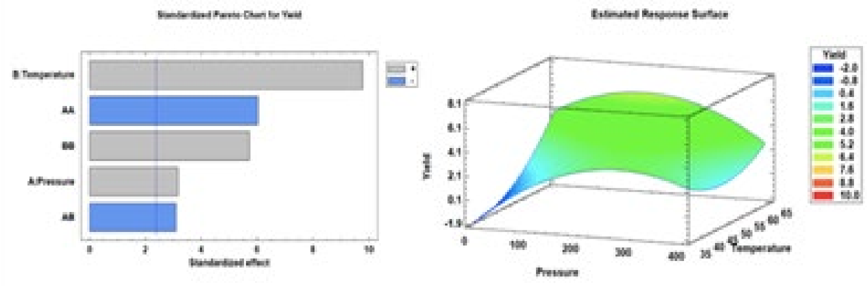

Figure 1: Effects of CO_2 supercritical conditions on extraction yield.

Acknowledgments

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Functional hydrogels and aerogels based on barley straw and chitosan by high-intensity ultrasound processing and supercritical CO_2 drying

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Canada is the fourth largest producer of barley after Russia, France and Germany [1]. Large quantities of straw are produced after harvesting that can be used to obtain carbohydrates and phenolic compounds [2]. The high content of cellulose (30-40%) in barley straw makes it a good source for isolating cellulose and producing cellulose nanofiber (CNF), which can be used to prepare hydrogels and aerogels due to their properties, such as high strength, stiffness, crystallinity, sustainability, and biodegradability [3]. In the last two decades, hydrogels have been studied as attractive materials in the biomedical field, due to their ability to retain a high volume of water in their cross-linked network, thereby providing sufficient nutrients for cell growth in tissue engineering applications. However, pure CNF hydrogels exhibited poor mechanical stability due to weak hydrogen bond crosslinking, which limited their applications. Therefore, natural modifiers like chitosan (CS) can be considered as a reinforcing agent, based on the high compatibility of CNF with CS. Furthermore, to extend the shelf life, hydrogels can be dried to obtain aerogels, with low bulk density, high porosity, thermal insulation, and mechanical properties.

In this study, cellulose-rich residue (purity of 90.2%) removed from barley straw was used to obtain CNF hydrogels (1-2 wt.%) by high-intensity ultrasound (HIUS) treatments at 1200 W for 10-30 min (Fig. 1). The highest water retention value (WRV) (82.9±0.8 g/g) and fibrillation yield (62.12±0.13 wt.%) of the hydrogels were obtained by 1 and 2 wt.% CNF, respectively, after HIUS treatment at 1200 W for 20 min. Also, CS (1-3 wt.%) was added to the CNF hydrogels by HIUS treatment at 1200 W for 20 min. The addition of CS reduced the WRV and fibrillation yield. All the hydrogels exhibited a typical elastic gel-like behavior, determined using a rotational rheometer. Then, the hydrogels were dried using supercritical CO_2 to form aerogels, and their properties (bulk density, porosity, stiffness, morphology, and thermal behavior) were determined by the gravimetric method, texture analyzer, scanning electron microscope, and thermal gravimetric analyzer, respectively. The lowest bulk density and the highest porosity were achieved using 1 wt.% CNF without the addition of CS. However, the addition of CS increased aerogel stiffness.

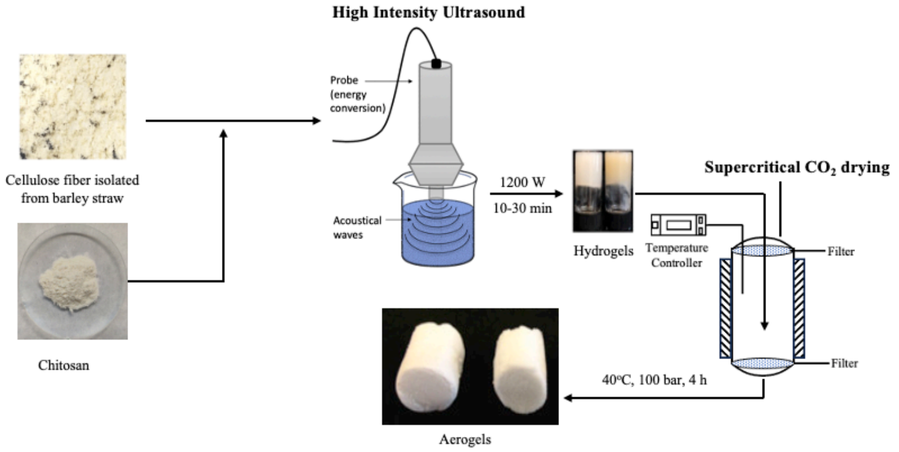

Figure 1: Functional aerogels and hydrogels from barley straw and chitosan.

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Supercritical carbon dioxide extraction and characterization of elderberry flower lipophilic bioactive components

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Many innovations in the field of Medicinal Plant Extraction have emerged with the introduction of the green chemistry concept. For the isolation of lipophilic fractions on the industrial scale, traditional techniques like Soxhlet extraction can no longer meet all the safety requirements for the environment. Therefore, the scientific literature is supporting the application of alternative techniques strongly, among which supercritical carbon dioxide extraction is a leading example. To date , the solvent properties of carbon dioxide in the supercritical state have been proven and confirmed experimentally in a number of scientific articles [1]. Therefore, supercritical carbon dioxide extraction has been applied, followed by gas chromatography (GC) analysis, on elderberry flowers, which, to our knowledge, have not been investigated and characterized yet.

Belonging to the *Adoxaceae* family, elderberry (*Sambucus nigra* L.) is a small tree or shrub that is native to the regions of Europe and North Africa. Elderberry is utilized widely in the food and health industries, due to the diverse chemical composition and high nutritional value. Recent studies indicated that elderberry flowers, in addition to being exceptional sources of polyphenolic compounds, exhibit high antibacterial activity. Additionally, elderberry flowers exhibit anti-inflammatory, antipyretic, diaphoretic, emetic, immunostimulant, and antiviral activity [2].

In order to determine the best process conditions for the supercritical carbon dioxide extraction of elderberry flowers, five different extraction pressures were applied (100, 150, 200, 250 and 300 bar), while the temperature was kept constant at 40 °C. The yield of the extraction was in the range from 1.59 to 2.54%. Additionally, to increase the yield of extraction further, two types of pretreatments were introduced, enzymatic and microwave. Enzymatic pretreatment was conducted at two different concentrations of cellulolytic enzyme mixture (2 and 4% concentrations of viscozyme), while the microwave pretreatment was conducted at 800W during 2 min. The introduction of pretreatments had a substantial impact on the yield of extraction, with achieved yields of 7.51, 6.34% for enzymatic and 5.26% for microwave pretreatment. The GC analysis showed that the content of most bioactive components increases with the increase in extraction pressure up to 250 bar, with the highest content of hexanoic acid, terpendiol, nonadecane and henaicosane.

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Supercritical carbon dioxide extraction and characterization of *Curcuma longa L.* bioactive components

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Curcuma longa L., commonly known as turmeric, is a perennial herbaceous plant that is native to Southeast Asia, but is now cultivated worldwide. Its dried rhizome, which has been revered in traditional Indian and Chinese medicine for centuries, is used widely in cooking and herbal products [1]. Turmeric is known for its anti-inflammatory properties, and has been used to treat digestive and liver disorders, as well as to accelerate skin health and wound healing [2]. Research on the nutrient compounds in turmeric demonstrates its potential for various therapeutic possibilities. There is a wide range of extraction techniques that can be used to isolate certain bioactive components, of which supercritical extraction is recognized as sustainable and environmentally friendly. It can isolate non-polar components with supercritical CO_2 as a solvent, and more polar components with the addition of a polar co-solvent.

Supercritical extractions were first performed using supercritical CO_2. Another set of experiments has followed by the addition of a co-solvent to modify the polarity of the extraction medium. Due to the distinct polarity of the solvents, the mixture of non-polar and polar components has been isolated from turmeric. The total phenolic content and antioxidant activity of the individual extracts (SCE and SCE+EtOH) and the extract in which both polar and non-polar solvents were used (SCE MIX), were analyzed and compared using the spectrophotometric method (UV-VIS) [3,4].

The aim of this study is to present the influence of the polarity of the solvent at a pressure of 250 bar and a temperature of 60 °C on the yield and content of bioactive components in SCE, SCE+EtOH, and SCE MIX extracts. The use of a co-solvent contributed to a higher extraction yield (7.71 wt.%), and to the isolation of a higher proportion of bioactive components. For the SCE MIX extract, the second extraction step contributed the most (more than 90% of the total inhibition) to the high antioxidant activity measured by the $DPPH^{\cdot}$ radical scavenging method. In contrast, the $ABTS^{+\cdot}$ method showed that SCE and SCE+EtOH extracts contributed approximately equally to the final value of antioxidant activity (for SCE: 54 mg Trolox/g DW and for SCE+EtOH: 60 mg Trolox/g DW). From these results it can be summarized that $ABTS^{+\cdot}$ determined both hydrophilic and lipophilic antioxidants, due to its single positive charge and its solubility in aqueous and organic solvents.

Acknowledgement

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Supercritical fluid extraction from native and defatted milk thistle, dandelion, and chamomile seeds

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The supercritical fluid extraction (SFE) technique that employs supercritical carbon dioxide (SC-CO_2) has been reported to be superior (compared to mechanical and extractions with organic solvents) for the separation of oils from seeds [1]. The current work aims to show that, beside oils, additional valuable extracts can be recovered from defatted seeds. Seeds of milk thistle, dandelion and chamomile grown in Poland have been tested for that purpose.

Initially, SFE for oil separation from seeds was tested by variation in pressure (from 100 to 450 bar) and temperature (from 40 to 80 °C) [2–4]. The yield and composition of oils indicated optimal conditions for the separation of extracts from defatted seeds using SC-CO_2 with ethanol.

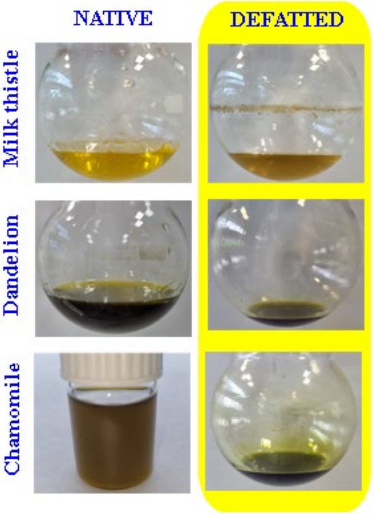

Figure 1: Images of oils and extracts obtained by SFE.

It was determined that neat SC-CO_2 enabled separation 146–315 mg, 6–250 mg, and 24–186 mg of oil per g of native milk thistle, dandelion, and chamomile seeds, respectively. On the other hand, SC-CO_2 with the co-solvent ethanol (performed at optimized pressure and temperature conditions) enabled separation of 31.0 mg, 9.1 mg, and 26.5 mg of extract per g of defatted milk thistle, dandelion, and chamomile seeds, respectively. Images of the obtained oils and extracts can be seen in Figure 1. The content of dominant unsaturated fatty acids was influenced slightly by the selection of native compared to defatted seeds. The linoleic acid and oleic acid contens were in the range of 54.1–77.8% and 8.6–29.5%, respectively. On the other hand, the total flavonoid content (TFC) and antioxidant activity were significantly higher in extracts obtained from defatted seeds. The TFC increased from 0.1 to 0.3 mg QE/g for milk thistle, from 1.3 to 6.4 mg QE/g for dandelion, and from 0.3 to 1.8 mg QE/g for chamomile when SFE was performed from defatted seeds compared to native seeds. The initial removal of oils from seeds and the use of a polar co-solvent increased the separation of polar compounds such as flavonoids.

The present study indicated the high potential of milk thistle, dandelion, and chamomile seeds processed by SFE technology. Namely, solvent-free oils recovered from native seeds can find an application in the food industry, while extracts recovered from defatted seeds can be applied in the pharmaceutical industry.

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CO_2 supercritical extraction of hydrophobic compounds from almond co-product employing hydrophobic deep eutectic solvent as co-solvent

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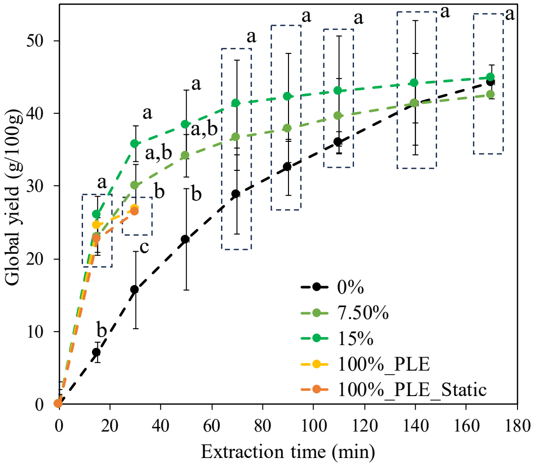
The plant-based milk market is growing, due to the increase in consumers who are lactose intolerant, allergic to milk proteins, or adopting more plant-based lifestyles [1, 2]. Almond is among the nuts most used to produce these milk substitutes, due to its high protein, monounsaturated fatty acids content, and bioactive compounds such as α-tocopherol, vitamin A, and manganese [3]. Considering the significant growth of this industry, it is also a large generator of solid waste. Solids after aqueous extraction, commonly done by wet milling using mechanical energy, present a high fat and protein content that can be separated and used as food and pharmaceutical ingredients. Therefore, this study aimed to recover the fat content of the solid material acquired after producing almond-based milk, speeding up the CO_2 supercritical extraction employing a hydrophobic deep eutectic solvent (HDES) as a co-solvent. An HDES (eucalyptol-menthol of molar ratio 1:1) was chosen, based on preliminary tests to be used as a co-solvent in supercritical extraction. The extractions were performed at 50 °C and 200 bar, employing a solvent flow of 4 mL/min. The HDES used as a co-solvent was employed at 0, 7.5, and 15%. Kinetic extractions were performed, and, for comparison purposes, pressurized liquid extraction (PLE) employing the DES was performed, using static and dynamic methods. Figure 1 presents the global yields acquired by increasing the HDES (from 0 to 15%) as a co-solvent in CO_2 supercritical extractions, and in PLE using 100% HDES in continuous and static mode. Typical kinetic curves can be observed in Figure 1 for supercritical extractions, including the three extraction phases: constant extraction rate, falling extraction rate, and diffusional controlled [3]. HDES, as a co-solvent, accelerated the extraction of hydrophobic compounds from almond waste. The most efficient methodology for extracting the compounds was supercritical extraction with 15% HDES. Under these conditions, approximately 2.3 and 1.3 × more compounds were recovered than in the conditions employing only CO_2 and PLE in 30 min. The almond extracts presented the primary fatty acids: oleic, linolenic, palmitic, and stearic, and minor bioactive compounds such as α-tocopherol and campesterol. In this sense, using co-solvents, composed of natural compounds that could be included in food and pharmaceutical formulations, presents an economic advantage regarding process time.



(A)

Figure 1: HDES percentage effects on global yield.

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Sustainability indicators for supercritical fluids assisted applications: A comprehensive assessment

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In recent years, the use of supercritical fluids has gained significant attention across various industrial applications, owing to their unique properties and environmental advantages. This work presents a comprehensive exploration of sustainability indicators associated with supercritical fluid-assisted processes, aiming to provide a systematic framework for evaluating and enhancing the overall performance of such applications. The study addresses key aspects of sustainability, including energy efficiency, resource utilization, and environmental impact, by considering diverse SCF applications such as extraction, synthesis, and cleaning.

The assessment of sustainability indicators involves a multi-faceted approach, that applies for a different way of re-designing the classic life cycle analysis and techno-economic analysis methodologies. The paper discusses the intricacies of each indicator, highlighting the importance of selecting appropriate metrics and benchmarks for a holistic process evaluation. Moreover, the research delves into the identification of critical factors influencing the sustainability of SCF-assisted processes, examining the role of critical process parameters, feedstock selection, and the development of green solvents.

Furthermore, the study explores emerging technologies and innovations that contribute to advancing the sustainability profile of SCF applications. This includes the exploration of alternative energy sources for SCF generation, the development of eco-friendly and bio-based solvents, and process optimization strategies. The integration of these innovations is discussed in the context of achieving a balance between environmental stewardship and economic feasibility.

Through a synthesis of current literature, case studies, and experimental findings, this paper aims to establish a foundation for future research and development in the field of Sustainable SCF Applications. The proposed framework provides researchers, engineers, and policymakers with valuable insights into the critical parameters influencing the sustainability of SCF processes, facilitating the design and implementation of environmentally responsible solutions for a wide range of industrial applications.

Figure 1: Sustainable environment from different points of view.

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Cell disruption of medical mushrooms mycelium using conventional and unconventional methods

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Due to their rich composition with bioactive compounds that exhibit a spectrum of medicinal properties, medicinal mushrooms are increasingly gaining ground as a natural source of medicinal agents. Several studies have shown that medicinal mushrooms such as *Pleurotus ostreatus* and *Ganoderma lucidum* contain antioxidant agents and different intra and extracellular enzymes. Recent research has shown that medicinal mushrooms are a rich source of bioactive compounds that exhibit anti-tumor, antioxidant, antimicrobial, antiviral, and anti-inflammatory properties, in addition to strengthening the immune system, anti-cancer, preventing neurological diseases and regulating blood sugar, cholesterol, and blood pressure levels. The most important enzymes that reduce and prevent oxidative stress in living organisms are superoxide dismutase (SOD) and catalase [1]. These are intracellular enzymes in the fungi *P. ostreatus* and *G. lucidum*. Various cell disruption methods (homogenization and cell exposure in supercritical carbon dioxide (SC CO_2)) have been used to obtain intracellular enzymes from mushrooms. When opening the cells with SC CO_2, the sample is incubated in SC CO_2 at high pressure, which allows the supercritical fluid to diffuse into the interior of the cells. This is followed by sudden and rapid decompression, i.e., a decrease in pressure, during which cells saturated with SC CO_2 burst [2]. In this case, the cells are exposed to minimal shearing forces, and no generation of heat could affect the temperature-sensitive material [3]. The influence of each method was studied for obtaining intracellular components from mushroom mycelium (homogenization or exposure in SC CO_2 (exposed time and pressure)) on the concentration of proteins and the activity of the mentioned enzymes in the obtained samples. The results showed that both disruption methods (homogenization or exposure of mushroom mycelium to SC CO_2) opened the fungal cells successfully, since a higher concentration of proteins in these samples was detected in comparison with the protein concentration obtained in the samples prepared by conventional extraction of the mushroom mycelium with a buffer (comparative sample). The concentration of proteins in the samples increased with the homogenization time, and with an increase in incubation time and pressure in SC CO_2. The highest specific activities of SOD were determined after a 30-minute homogenization (171 U/mg in the extract from *P. ostreatus* and 129 U/mg in the extract from *G. lucidum*), and after a 5-hour incubation in SC CO_2 at 200 bar (243 U/mg in the extract from *P. ostreatus* and 170 U/mg in the extract from *G. lucidum*). The results showed that the cell disruption method using SC CO_2 is more efficient than homogenization, and, in addition, represents a green, sustainable technology.

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Towards the purification of the extracted electrolyte from LiB waste materials using supercritical carbon dioxide

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The recovery and full removal of the electrolyte solvents from Li-ion battery (LiB) waste is an ongoing challenge in current recycling processes [1]. Generally, the electrolyte is a combination of non-polar and polar organic solvents used to dissociate the conductive salt, while achieving low viscosity. Many additives are added to enhance the overall performance of the LiB [2]. The composition of the multi-component system becomes more complex after cycling, as several degradation products are formed [1]. After the lifetime of a LiBs, it is not uncommon to detect more than 30 different components in the residual electrolyte.

LiB waste side streams containing residues of the electrolyte are classified as hazardous waste, and thus entail a financial burden for the recycling industry. Once successfully recovered from the LiB waste, extensive purification of the collected products is required to be saleable for repurpose in other industries, or reuse in the battery manufacturing process [3].

The tunable solvent characteristic of supercritical CO_2 ($scCO_2$) makes the latter a promising method for targeted electrolyte extraction and purification. However, extensive knowledge of the extraction behavior, i.e., a phase diagram and kinetics, of the different electrolyte solvents using $scCO_2$ is required to design these processes. Although these are available in the literature for some of the components, the required information is not existent for, i.e., ethylene carbonate, which is one of the most used solvents to dissociate the conductive salt, and often the remaining product in the LiB waste side streams.

Thus, the extraction behavior and kinetics of ethylene carbonate and other electrolyte solvents were studied using $scCO_2$ at different critical process parameters, including temperature, pressure, flowrate, and time. The composition of the extract was analyzed qualitatively and quantitively using gas chromatography-mass spectrometry (GC-MS), inductively coupled plasma - optical emission spectrometry (ICP-OES), and ion chromatography (IC).

Based on the retrieved thermodynamic and kinetic data, a process was developed to extract the electrolyte solvents stepwise from the LiB waste, and collect the purified electrolyte solvents. The results showed that low-density CO_2 extraction allowed the extraction of non-polar electrolyte solvents like dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate. The more polar electrolyte components, such as ethylene carbonate, and propylene carbonate were extracted selectively by increasing the pressure of the system gradually.

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20th European Meeting on Supercritical Fluids
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Methyl orange dye removal using nanostructured chitosan-based adsorbents produced by supercritical drying

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Dyes are generally synthetic compounds used to color textiles, paper, pulp, etc. Their disposal in wastewater, however, is not regulated by proper legislation, resulting in water bodies` contamination: indeed, they are suspected of being carcinogenic, mutagenic, and, overall, toxic [1]. **Adsorption represents the most effective choice when it comes to wastewater treatment**, being a well-known scaled-up unit operation, easy to perform and economically feasible [2]. The choice of the adsorbent is crucial to dye adsorption efficiency: the most promising choice as adsorbent material are aerogels, which are lightweight materials with outstanding surface areas. **Supercritical CO_2 (SC-CO_2) assisted drying** is the only way to produce **aerogels**, thanks to the supercritical fluids' near-zero surface tension and gas-like diffusivity, which avoids nanostructure collapse [3].

In this work, **chitosan (CH)-based aerogels** have been chosen as adsorbent materials, due to their eco-friendliness and functional groups` abundance; moreover, **Methyl Orange (MO)** has been picked as a reference anionic dye. Eventually, CH was functionalized using **Graphene Oxide (GO)**, to investigate the adsorption performances after compounding. CH-based adsorbents have been produced using SC-CO_2 drying (Figure 1), performed at **200 bar** and **35 °C**, and using a CO_2 flow rate of **0.8 kg/h**. Adsorption experiments have been carried out by weighing 50 mg of adsorbent, and changing the initial MO concentration (C_0), which ranged from 1 to 100 ppm. The **main scope** of this work was **to clear dyed wastewaters**, and to understand better the **effect of the driving force on nanostructure utilization** and mass transfer phenomena.

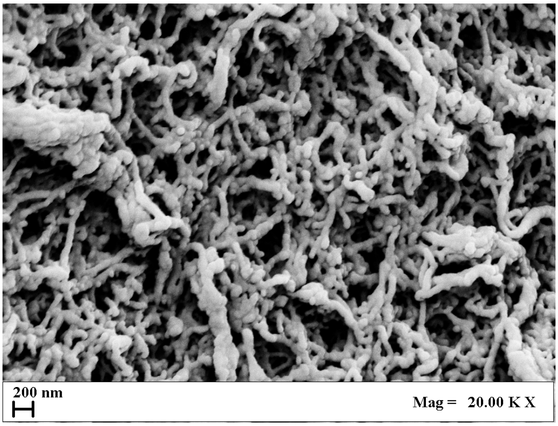

Figure 1: SEM image 3% w/w CH aerogel.

Collecting the data of equilibrium adsorbed MO per CH mass unit (q_e) vs. equilibrium concentration in the liquid phase (C_e), it emerged that **low-concentration** (C_0 from 1 to 10 ppm) **behavior differs from the high-concentration one** (C_0 from 25 to 100 ppm). Low driving forces did not employ the full potential of the nanostructure. The maximum experimental value of q_e was about **30 mg/g**; however, the Langmuir isotherm was used to fit such points, leading to a maximum adsorption capacity of about **360 mg/g** (R^2=0.97). Using CH-GO composites, the maximum q_e value obtained experimentally was of about **60 mg/g**: GO addition intensified the chemical interactions between MO and CH, improving the adsorption capacity.

In conclusion, **SC-CO_2 assisted drying allowed the production of a nanostructure rich in active sites**, available for adsorption; however, affinity between the MO and CH was improved by the addition of GO. In perspective, supercritical technologies should be investigated further, to produce eco-friendly and functionalized nanostructured materials for adsorption purposes.

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Bee pollen supercritical extract as a potential adjunctive medicine in skin cancer

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Melanoma poses a major challenge for treatment, due primarily to the aggressive behavior of human melanoma cells [1]. Therefore, researchers worldwide are working intensively on the development of new therapeutics to combat this malignant disease. Previous studies have shown the presence of bioactive components and secondary metabolites in natural resources, including bee pollen. Bee pollen has shown promise in laboratory experiments and animal studies, and has become a topic of interest due to its potential anti-cancer properties [2]. As they are rich in antioxidants, they can alleviate oxidative stress and inflammation, trigger apoptosis in cancer cells, modulate the immune response, and inhibit the proliferation of cancer cells [2–5].

In this study, the computer program Design Expert was used to plan the research and optimize the results. Supercritical processes in the temperature range of 40 °C to 60 °C and in the pressure range of 150 bar to 350 bar were used to obtain the extracts. Procedures for WM-266-4 cell cultivation, sub-cultivation of cells and planting in microtiter plates, suitable dilution of the extracts for application to cells and the WST 8 test to determine the metabolic activity of cancer cells were carried out as part of the testing of the anticancer effect.

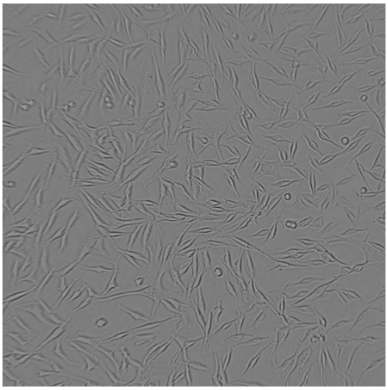

Figure 1: WM-266-4 cells.

Supercritical extraction with CO_2 and EtOH as co-solvents, was used to obtain the extracts. The Design Expert computer program was used to optimize the supercritical extraction conditions and solutions with different concentrations of these extracts applied to melanoma cells. The results showed that the extracts have a significant effect on the inhibition of melanoma cells when applied at a concentration of 0.005 mg/ml. The inhibition of melanoma cell division and function was inhibited more actively by extracts obtained at a pressure of 330 bar and a temperature of 40 °C. A decrease was observed in metabolic activity. A reduction was observed in the metabolic activity of melanoma cells of up to 78%. The study is an important starting point for further research into the positive effect of pollen on the inhibition of skin cancer.

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20TH EUROPEAN MEETING ON SUPERCRITICAL FLUIDS (EMSF 2024): BOOK OF ABSTRACTS

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The 20th European Meeting on Supercritical Fluids (EMSF 2024) was hosted by the Faculty of Chemistry and Chemical Engineering of the University of Maribor from 26 May to 29 May 2024 in Maribor, Slovenia. The EMSF 2024 was a joint event of the International Society for the Advancement of Supercritical Fluids (ISASF) and the European Federation of Chemical Engineering (EFCE) Working Party on High Pressure Technology (WP HPT) Event No. 807. This symposium provided an excellent opportunity for engineers, chemists, physicists, food technologists, and biologists to meet and discuss new ideas, review ongoing challenges, present potential solutions, and identify future issues related to high pressure technologies and supercritical fluids. The aim of the meeting was to deepen connections between researchers, establish new contacts, and promote synergies and partnerships between researchers. The symposium presented the latest advances in high-pressure process technologies that can contribute to the further development of the field.

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20TH EUROPEAN MEETING ON SUPERCRITICAL FLUIDS (EMSF 2024): KNJIGA POVZETKOV

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Ključne besede:
nadkritične tekočine,
fundamentalni podatki,
novi materiali,
industrijske aplikacije,
razvoj in raziskave

Fakulteta za kemijo in kemijsko tehnologijo Univerze v Mariboru je gostila 20. Evropsko srečanje o nadkritičnih tekočinah (EMSF 2024), ki je potekalo od 26. do 29. maja 2024 v Mariboru, Slovenija. EMSF 2024 je skupno srečanje Mednarodnega združenja za napredek madkritičnih tekočin (ISASF) in Evropske zveze za kemijsko inženirstvo (EFCE) za visokotlačno tehnologijo (WP HPT), dogodek št. 807. Ta simpozij je bil odlična priložnost, da se inženirji, kemiki, fiziki, živilski tehnologi in biologi srečajo in razpravljajo o novih idejah, pregledajo trenutne izzive, predstavijo možne rešitve in opredelijo prihodnja vprašanja, povezana z visokotlačnimi tehnologijami in nadkritičnimi tekočinami. Cilj srečanja je bil poglobiti povezave med raziskovalci, vzpostaviti nove stike ter spodbujati sinergije in partnerstva med raziskovalci. Na simpoziju so bili predstavljeni najnovejši dosežki na področju visokotlačnih procesnih tehnologij, ki lahko prispevajo k nadaljnjemu razvoju področja.

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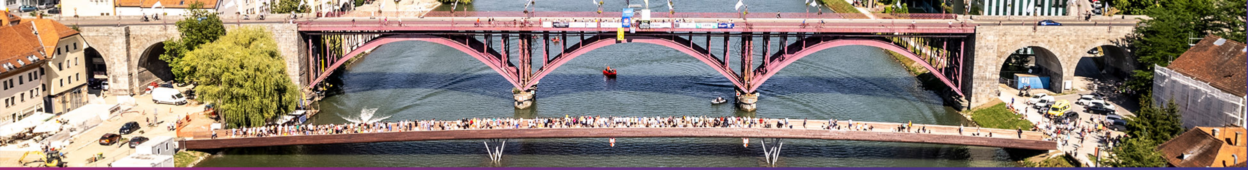

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