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# SUSTAINABLE DEVELOPMENT OF GREEN SOLVENT SEPARATION PROCESS

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***Abstract:*** *Solvents define a major part of the environmental performance of processes in the chemical industry and impact on cost, safety and health issues. The idea of green solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production.*

*In spite of conventional separation methods, precise process green technologies are based on the application of modern processes and process equipment as well as control and management systems. These processes are optimized in order to produce maximal profitability with minimal environmental impact.*

*Non-conventional separation procedure - supercritical fluid* $CO_2$ *extraction (SFE-*$CO_2$*) conforms to the strict demands of the precise process eco-technologies. It represents a perspective method especially in obtaining eco-friendly extracts from vegetable and animal raw materials. Implementation of SFE-*$CO_2$ *as a green solvent, for isolation of vegetable extracts results in obtaining high quality and high purity total extract and excludes the presence of organic solvents, heavy metals and some microorganisms.*

*This work provides proper analysis of the sustainable development of alternative separation processes that are based on the implementation of supercritical* $CO_2$ *as a green solvent.*

***Keywords:*** *green solvent, green technology, supercritical fluids, sustainable development*

## INTRODUCTION

The process industry is used in large amounts different type's solvents. In particular, in fine-chemical and pharmaceutical production, large amounts are used per mass of final products. Therefore, solvents define a major part of the environmental performance of a process and also impact on cost, safety and health issues. The idea of ''green'' solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production [1].

In this respect, in the last years the development of new, unconventional precise technology gains the upper hand over. The extracted products are with high purity and quality. Extraction using gases under pressure ($CO_2$) in high extent represents solid separation process for isolation not only plant but animal active components [4,7].

Supercritical extraction (supercritical fluid extraction) is a process of fluid extraction, which are found in supercritical condition, on temperature and pressure above critical levels. This kind of extraction is particularly efficient for isolation of substances with average molecule mass and relatively low polarity. The solubility of polar compounds could be improved by adding co-solvents in the main supercritical fluid.

The main priority of the supercritical fluid extraction is that the process could be carried out in favorable working conditions (low temperatures) and the extract is uncontaminated with heavy metals and microorganisms. Supercritical fluid extraction is with high applicability in food industry processing, chemical and pharmaceutical industry [2].

### Green chemistry and green process engineering

Green Chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products . The basic principles of green chemistry and green process engineering are based on reducing of the : waste , materials, hazard, risk , energy and cost. Green chemistry looks at pollution prevention on the molecular scale and is an extremely important area of Chemistry due to the importance of Chemistry in our world today and the implications it can show on our environment. The Green Chemistry program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances [1].

The basic objective of the green process engineering is to combine and integrate the fundamental principles of chemical engineering to design commercial products and processes that are safe, economical and environmentally friendly. There is a pool of technologies that are becoming the most widely studied or used in seeking to achieve the goals of Green Chemistry [1,3]. The major "clean technologies" are summarized in Fig. 1.

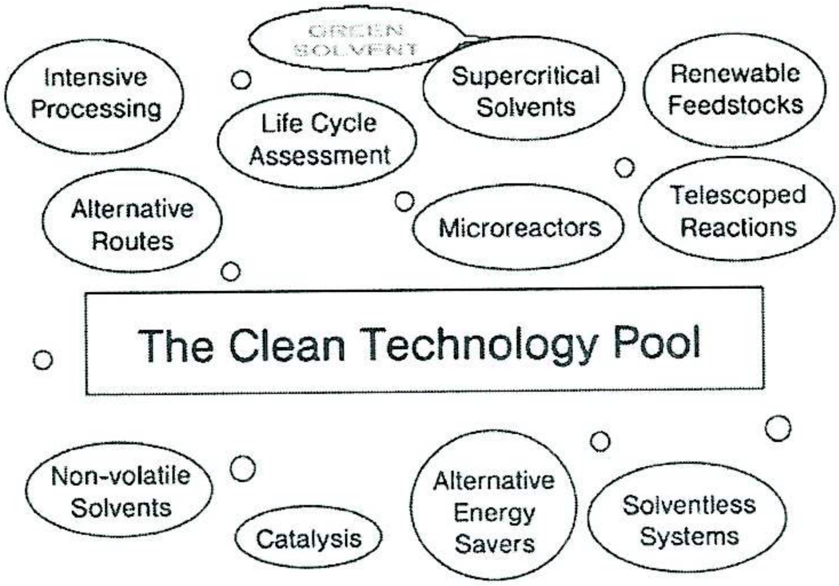



*Fig. 1. The major green technologies*

### Supercritical fluids – green solvents

A substance is at supercritical state i.e. a supercritical fluid, when its temperature and pressure are simultaneously higher than the critical values. A supercritical fluid exists in a single fluid phase possessing characteristics between those of gasses and liquids. Figure 2 illustrates lines of sublimation, melt and saturation. Two phases-saturation and melting are presented and in the "triple point" where tree phases goes altogether (T - 56.6°C and P- 5.2 bar).In the critical point (T-31.1°C and P-73.8 bar) liquid and gas phase goes into one aggregate phase. The other spots on the diagram only one phase presented (Fig.2).

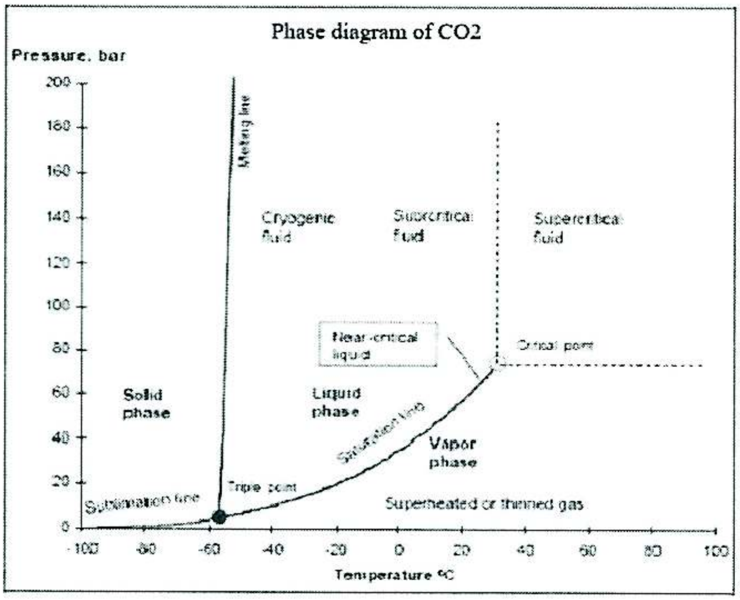



*Fig. 2. Phase diagram of $CO_2$*

Above the critical temperature a liquid phase will not appear regardless of how much the pressure increased. The critical pressure is the pressure, which causes the gas to become a liquid at the critical temperature. The density of a compound at the critical point is called the critical density [2].

The compressibility of supercritical fluid just above the critical temperature is large compared to the compressibility of ordinary liquids. A small change in the pressure or temperature of a supercritical fluid generally causes a large change in its density. A commonly accepted opinion is that the solvent power of supercritical fluids mainly related to its density in the critical point region [5.6]. A high density generally implies a strong solvating capacity. The unique property of a supercritical fluid is that its solvating power can be tuned by changing either its temperature or pressure [2].

A significant cost factor for many conventional liquid-liquid extraction processes ids the recovery of the spent extraction solvent. If a supercritical solvent is applied, the solute can be separated from the mixture by e.g. lowering the pressure of the mixture. One should remember that to recycle the supercritical solvent, it must be compressed again. This can be significant cost factor, if the difference between the pressure in the extraction vessel and the pressure in the separator is relatively large. Even though the density of a supercritical fluid increases with pressure and becomes liquid-like, the viscosity and diffusivity remain between liquid-like and gas-like values [7]. Additionally, supercritical fluids exhibit almost zero surface tension, which allows facile penetration into micro porous materials. As a result of the advantageous combination of physicochemical properties, the extraction process can often be carried out more efficiently with a supercritical solvent than it can with an organic liquid one [4].

The critical temperature ($T_c$) of the compound depends on the polarity of the compound. The critical temperatures of non-polar gases, such as carbon dioxide or ethane are below 50°C, whereas for polar compounds, such as methanol and water, the critical temperatures are well above 200°C. In practice, especially in food-related industries, it is usually desirable that the critical temperatures of solvent are below 100°C [5]. Therefore, the solvents commonly used for supercritical operations are low molecular weight gases, such as carbon dioxide, ethane and propane. (Tab. 1)

Tab.1. Density, viscosity and diffusion coefficient of gas, liquid and supercritical fluid (SCF)

| | Density ($kg/m^3$) | Viscosity cP ($10^{-3}$ $Ns/m^2$) | Diffusion coefficient ($cm^2/s$) |
|---|---|---|---|
| Gas | 1 | 0.01 | $10^{-1}$ |
| Liquid | 1000 | 0.5 – 1.0 | $10^{-5}$ |
| SCF | 200 – 700 | 0.03 – 0.1 | $10^{-4}$ – $10^{-3}$ |

Carbon dioxide is the most commonly used solvent in industrial practice for several reasons.

- Carbon dioxide has a technically convenient critical pressure and temperature of 73.8 bar and 31.1°C, respectively. It is non-toxic, non-flammable, non-reactive, no-corrosive, and abundant. Furthermore, it is the second least expensive solvent after water and it does not leave any solvent residue after extraction.
- Carbon dioxide is a relatively good solvent for hydrocarbons and non-polar solids. However, owing to the unique properties of supercritical solvents, supercritical carbon dioxide will dissolve many relatively volatile polar compounds.

The properties of the SC-$CO_2$ as a green solvent are:

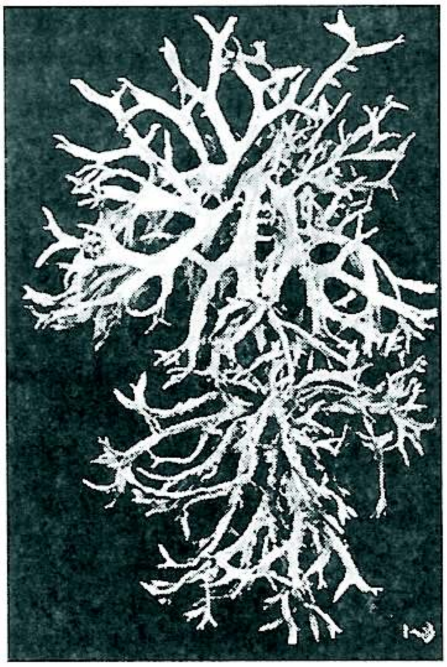
- ➢ High compressibility ;
  - Large change in solvent properties for relatively small change in pressure – infinite range of solvent properties available ,
  - Ability to tune solvent to favour a particular reaction pathway simply by optimising temperature or pressure.
- ➢ Small amounts of co-solvents can further modify solvent properties ;
- ➢ High diffusion rates offer potential for increased reaction rates ;

- Potential for homogeneous catalytic processes ;
    - High solubility of light gases, some catalysts and substrates; bring all together in single homogeneous phase.
- Inert to oxidation; resistant to reduction ;
    - Excellent medium for oxidation and reduction reactions.

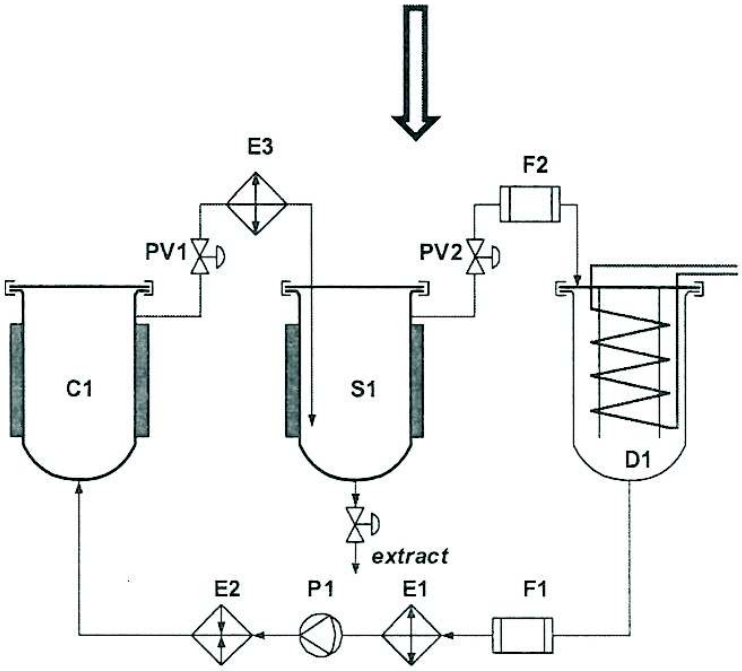
**Green solvent separation of eco-fixatives**

In the frame of this work separation of eco-fixatives for perfume industry from the lichen ***Evernia prunastri L.*** was performed.

The obtained eco-fixatives with application of this green solvent separation process are characterized with high yield of total extract and degree of quality for perfume industry [2]. (Fig. 3).



*Oak moss Evernia prunastri L*




Schematic flow sheet of supercritical extraction apparatus (Uhde.Germany)

( $C_1$ – extractor ; $S_1$ –separator ; $D_1$ – $CO_2$ tank)

**Fixatives – perfume industry**

**Usnic acid – cosmetic industry**

*Fig. 3. Process scheme for separation of eco-fixatives with SC- $CO_2$ as a green solvent*

## Conclusion

The green separation process - supercritical fluid $CO_2$ extraction (SFE-$CO_2$) conforms to the strict demands of the precise process eco-technologies. It represents a perspective method especially in obtaining eco-friendly extracts from vegetable and animal raw material.

Supercritical carbon dioxide is a nearly ideal solvent. Under normal conditions, carbon dioxide is not a very good solvent for organic substances Supercritical carbon dioxide readily dissolves many of these substances, including perfumes fixatives from oak moss.

Generally, the implementation of SFE-$CO_2$, as a green solvent, in process engineering is very important for sustainable development of green separation processes.

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