Supercritical Fluid Extraction of Natural Products: A Review

Priyanka* and Shabina Khanam**
*Research Scholar and **Assistant professor
Department of Chemical Engineering,
Indian Institute of Technology Roorkee, Roorkee - 247 667, India

Abstract: The present paper deals with literature review on different aspects of supercritical extraction. A brief introduction and literature review on two aspects such as types of solute available for extraction and design of experiment for the optimizing the experimental runs are provided. Type of solute/extractable solid can be divided into 13 categories and found that maximum work has been done on seed category. By literature review on type of species available for extraction, categories having least work done can be identified. Root and leaves categories are less investigated category in which ginger root, turmeric root, mango leaves, guava leaves are the option for the future study. Different designs of experiment techniques available for the optimization of experimental runs have been reviewed. Four types of designs are Factorial design (full or fractional), Mixture design, Response surface method (RSM) and Taguchi method in which RSM has been found best design technique. Three type of design comes under RSM design: (1) Three-level factorial design (FD), (2) Central composite design (CCD) and (3) Box-Behnken design (BBD). Among all three designs, CCD has been found best design techniques because CCD provides less number of experiments for given factors and central points.

Keywords: SFE, CCD, RSM, Factorial Design.

I. INTRODUCTION

Recently more attention has been paid to the healthy way of life, mainly to the importance of healthy nutrition intake. That means the general use of natural products, food supplements and different natural medical preparations at homes[1).]The supercritical fluid extraction (SFE) substitutes the traditional organic solvent extraction such as hexane extraction in an increasing area. The official regulations motivate the producers to manufacture products less harmful to the people and environment, and to initiate new environment friendly technologies. The authorative FDA (Food and Drug Administration, USA), EMEA (European Agency for the Evaluation of Medicinal Products, EU) and EPA (Environmental Protection Agency, USA) regulations promote the spreading of the techniques, which do not use organic solvents. Comparing the traditional organic solvent extraction with the supercritical fluid extraction (SFE), which uses CO_2 as solvent for extraction of active substances from plants, it is observed that one of the most significant advantages of SFE is to separate the solvent from the extract without leaving any residue[2)].

A supercritical fluid (SCF) has physical and thermal properties between those of the pure liquid and gas[3)]. The properties of supercritical fluid (SCF) change sharply with very little change in pressure, particularly in the vicinity of the critical temperature and pressure. Some commonly used solvents for SFE are Carbon dioxide, Ethane, Ethylene, Propane, Propylene, Benzene, Toluene, Methanol etc. Several applications for the supercritical fluid extraction have been described in bioprocessing, including, extraction of fermentation products, bio-oil production[4)], production of pharmaceutical ingredients[5)] removal of biostatic agents and organic solvents from fermentation broth, SCF disruption of yeasts[6)] and bacteria[7)], destruction of industrial waste[8)], fractionation and purification of biopolymers[16)], removal of chlorinated compounds from water and treatment of lingo-cellulosic materials [8)].

II. Different aspects of SFE

Supercritical fluid extraction (SFE) is a unique extraction process which embodies several features of conventional solvent extraction while, at the same time, having important features of its own such as use of non-toxic solvent, no residual solvent in extract. Literature on supercritical fluid extraction can be divided into several aspects as:

1. Extraction of different species
2. Pretreatment of seed
3. Mathematical modelling of supercritical extraction process
4. Design of experiment
5. Selection of co-solvent (modifier)
6. Selection of solvent
7. Data availability
8. Kinetics of supercritical extraction process
9. Computational fluid dynamics of supercritical extraction process
10. Effect of operating parameters
11. Effect of seed matrix
12. Economics of supercritical extraction process
13. Pollution abatement of Contaminated soil

Amongst all these aspects detailed literature on Extraction of different species and Design of experiment are reviewed in this paper.

III. Extraction of Different Species

Different species for which Supercritical fluid extraction is used are categorized as:

Seeds, Roots, Flowers, Leaves, Herbs, Meat, Algee, Stem, Fractionation of Oil components

No of papers available in different types of species is shown in Fig.1 and can be seen that out of all type of solutes, maximum work has been done on seed category followed by herbs, leaves, flowers, roots, algee, meat, oil and stem. As can be seen from literature that most of the work has been done on seed category i.e. Sunflower, Corn germ, Black pepper, Watermelon. It can be concluded from above dicussion that least work has been done on root, leaves, algee and stem category.Ginger root and turmeric root are least investigated according to literature, similarily in leaves category,neem leaf, guava leaf and mango leaf are least investigated as shown in Fig.2,3,4. In stem category, Eucalyptus globulus bark and wood, white fir sapwood and cedarwood chips are least investigated so all these species can be taken for the future work as they have many health and nutrition benefits. The abbreviations used in Figures are given in Appendix A.

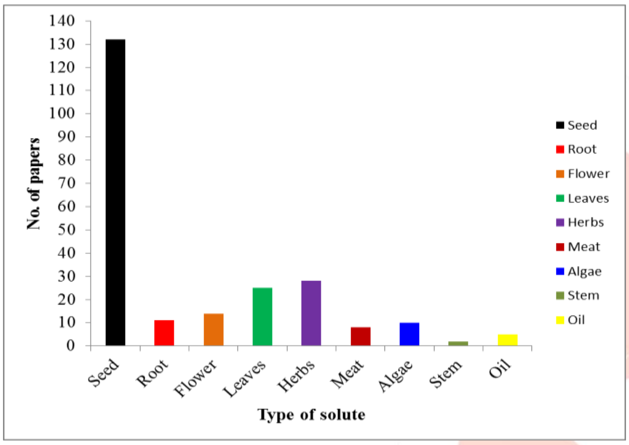

Fig.1 No of papers in different types of species

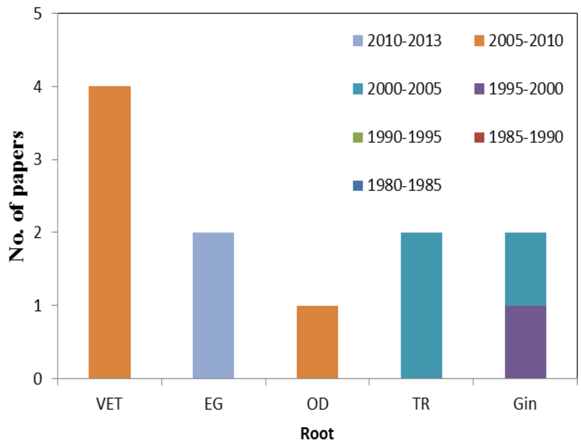

Fig.2 No of papers in Root category.

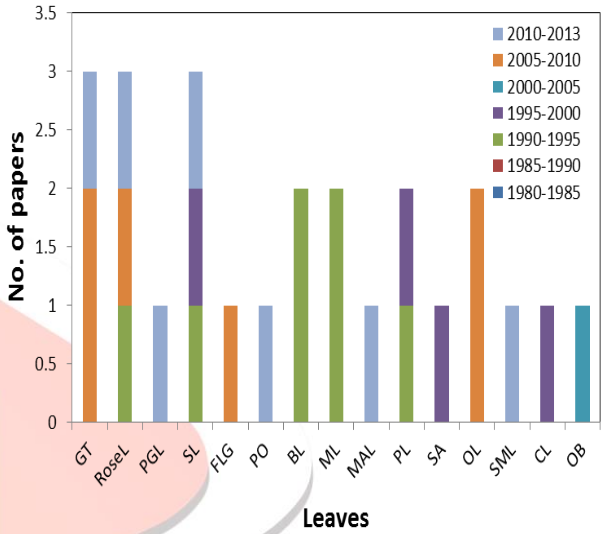

Fig. 3 No of papers in Leaves category.

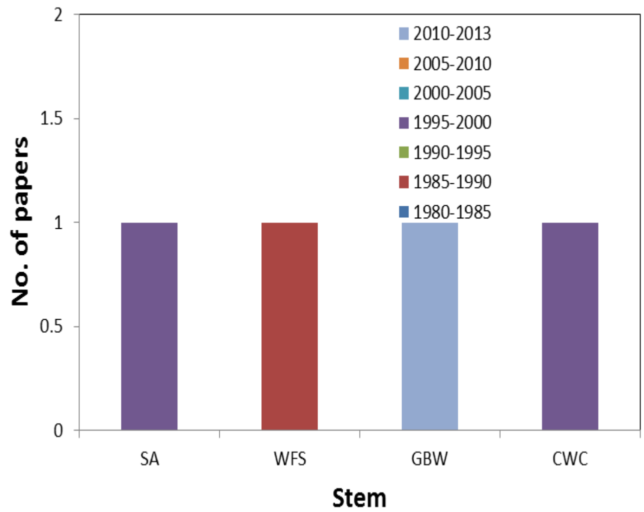

Fig. 4 No. of papers in Stem category.

IV. Design of experiments

Design of Experiment (DOE) is a well-planned, systematic and organized method used to determine the functional relationship between the various input parameters (Xs) that affect the output parameters (Ys) of the process as:

$$Y = f(X_i)$$

Where, Y= output, X_i = input where i= 1, 2, 3…..

Building a design through DOE helps to carefully select a small number of experiments that are to be performed under controlled conditions. This design is obtained in such a way that its analysis will lead to valid statistical inferences. There are a few interrelated steps in building a design as:

I. To define an objective for the research e.g. sort out important input and output variables for a process.
II. To define the important input design variables those will be controlled during the experiment and its maximum and minimum levels.
III. To define the response variables e.g. how to measure the response that will describe the results of experimental runs (response variables).
IV. One design has been chosen from all the available standard designs which suits to the objective e.g. number of input design variables and can be performed at a reasonable cost.

There are various well-known classes of standard designs available for DOE. Once, the objective, number and nature of design variables, nature of the responses and number of experimental runs are decided, the experimental design can be generated using various software like Minitab, Matlab, Design Expert, etc.

DOE has been mainly classified into four categories such as:

- Factorial design(full or fractional)
- Mixture design
- Response surface method
- Taguchi method

Amongst all the categories of DOE, RSM is essentially a set of mathematical and statistical methods for experimental design. RSM is capable of evaluating the effects of variables and searching optimum conditions of variables required to predict targeted responses. It is also used extensively in industrial research where large number of variables affect the process[9)]. It is a well suited approach to study the primary and interactive effects of distinct variables and also for optimization of the process. Many authors followed the RSM for the optimization of extraction of vegetable oil from the various seed materials with supercritical carbon dioxide [10)]

Various design techniques, which fall under RSM, are

- Three-level factorial design (FD)
- Central composite design (CCD) and
- Box-Behnken design (BBD)

The three-level design is denoted as 3^k factorial design and used by several authors to optimize the experimental runs[11)]. It means that 'k' factors are considered, each at three levels. Usually, these are referred to as low, intermediate and high levels as -1, 0 and +1, respectively.

Central composite design (CCD)[12,13)] is another design of the RSM, which is often recommended when the design plans for sequential experimentation. CCD consists of factorial or cube points, axial or star points and center points. There are supercritical fluid extraction method[14)].

2k cube points, where k is the number of factors/input parameters. The cube portion and its center points may serve as a preliminary stage where first-order linear model can be fitted. However, these points can also be used for the fitting of a second-order (quadratic) model.

Box-Behnken design (BBD)[16,17,18)] is one of the classes of rotatable or nearly rotatable second-order designs, which is based on three-level incomplete factorial designs. The number of experiments (N) required for the development of BBD is defined as N=2k (k−1) +C_o, (where, k is number of factors and C_o is the number of central points). For comparison, the number of experiments for a CCD is N=2k +2k +C_0. Therefore, CCD provides less number of experiments for given factors and central points.

V. Conclusions

This review intends to document and systematize the progresses of supercritical fluid extraction research upon natural extract with emphasis on raw materials and optimizing techniques. The present study discusses the type of raw materials or solute available for the supercritical fluid extraction and optimization techniques to optimize the number of experimental runs. The major conclusions of the study are:

(1) The discussion on type of raw materials indicates that seed category is the exhausted category of solute for the supercritical extraction among all categories i.e. seed, leaves, flower, root, stem, meat, herbs, algae, oil.
(2) Amongst all solute categories, least work has been found in supercritical extraction of root, leaves and stem category. Oil, algae and meat category also less work but supercritical extraction of these species is not feasible because of availabily of species.
(3) By the literature review on supercritical fluid extraction of root and leaves, it can be concluded that ginger and turmeric root, mango leaves and guvava leaves have less work done but have a large scope in food industry, pharmaceuticals and as flavoring agents.
(4) Literature review on design of experiment shows that among all type of designs, RSM is the best suited design and CCD is the more accurate design in RSM category.

VI. References

[1]. Spilimbergo S., Bertucco A., "Non-thermal bacterial inactivation with dense CO_2",Biotechnology and Bioengineering, Volume 84, Issue 6, pages 627–638, 20 December 2003.
[2]. Bodmeier R., Wang H., Dixon D. J., Mawson S. and Johnston K. P., "Polymeric microspheres prepared by spraying into compressed carbon dioxide", Pharm. Res.,12(8): 1211-1217 (1995).
[3]. Mukhopadhyay, M. Natural extracts using supercritical carbon dioxide. CRC press 2000; Boca Raton, FL.
[4]. Naik, S.N., Goud, V.V., Rout, P.K. & Dalai, A.K. (2010). Production of first and second generation biofuels: A comprehensive review. Renewable and Sustainable Energy Reviews. Vol. 14, (February 2010), pp. 578–597, ISSN 1364-032.
[5]. Chattopadhyay and Gupta, 2001. Production of antibiotic nanoparticles using supercritical CO2 as antisolvent with enhanced mass transfer. Ndustrial & engineering chemistry research. Vol. 40 Issue 16,pp. 3530-3539.
[6]. Ho-Mu Lin, Err-Cheng Chan, Cheeshan Chen, and Li-Fu Chen, Disintegration of Yeast Cells by Pressurized Carbon Dioxide. Bbtechnol. Prog. 1991, 7, 201-204.
[7]. K. Khosravi-Darani and M. R. Mozafari (2011), "Supercritical Fluid Application in Food and Bioprocess

Technology, Mass Transfer - Advanced Aspects, Dr. Hironori Nakajima (Ed.), ISBN: 978-953-307-636-2.
[8]. Puri VP, Mamers H. Explosive pretreatment of lignocellulosic residues with high-pressure carbon dioxide for the production of fermentation substrates. Biotechnol Bioeng. 1983 Dec;25(12):3149-61.
[9]. Lazic ZR. Design of Experiments in Chemical Engineering, Wiley-VCH VerlaggmbH& Co., 2004, Weinheim, PP. 157-443.
[10]. Zhao S., Zhang D., Journal of separation and purification technology, A parametric study of supercritical carbon dioxide extraction of oil from MoringaOleifera using a response surface methodology 2013; 113:9-17.
[11]. Pederssetti M.M., Palú F., da Silva E.A., Rohling J.H., Filho L.C., Dariva C., "Extraction of canola seed (Brassica napus) oil using compressed propane and supercritical carbon dioxide", Journal of Food Engineering 102 (2011) 189–196.
[12]. Yothipitak W, Thana P, Goto M, Shotipruk A, Chiang Mai., Journal Science, Experiments and statistical analysis of supercritical carbon dioxide extraction 2008; 35: 109-115.
[13]. Danh L T, Mammucari R, Truong P, Foster N, Chemical engineering journal, Response surface method applied to supercritical carbon dioxide extraction of Vetiveriazizanioides essential oil, 2009;155:617-626.
[14]. Ferreira S.L.C., Bruns R.E., Ferreira H.S., Matos G.D., David J.M., Brando G.C., Silva E G P da, Portugal L A, Reis P S dos, Souza A.S., Santos W N L dos, Analyticachimicaacta, Box-Behnken design: an alternative for the optimization of analytical methods, 2007;597:179-186
[15]. Ozkal S.G., Yener M.E., Bayindirli L., "Response surfaces of apricot kernel oil yield in supercritical carbon dioxide", LWT 38 (2005) 611–616.
[16]. Kagliwal L.D., Patil S.C., Pol A.S., Singhal R.S., Patravale V.B., "Separation of bioactives from seabuckthorn seeds by supercritical carbon dioxide extraction methodology through solubility parameter approach", Separation and Purification Technology 80 (2011) 533–540
[17]. Wang L,Yang B, Du X, Yi C, Journal of food chemistry, Optimization of supercritical fluid extraction of flavonoids from Puerarialobata 2008;108:737-741

VII. **Appendices**:

S. No.	Solute	Code
1	Vetiver roots	VET
2	*Eucalyptus globulus* bark	*EG*
3	*Opuntia dillenii Haw.*	*OD*
4	*Turmeric rhizomes*	*TR*
5	Ginger	Gin
6	Green tea	GT
7	Green tea	GT
8	rosemary leaves	RoseL
9	Psidium guajava L.	PGL
10	sage leaves	SL
11	Fig leaf gourd	FLG
12	*Posidonia oceanica leaves*	*PO*
13	basil leaves	BL
14	marjoram leaves	ML
15	Mango Leaves (Mangifera indica L.)	MAL
16	Peppermint leaves	PL
17	rosemary leaves	Rose
18	*Andrographis paniculata*	*AP*
19	*Opuntia dillenii Haw.*	*OD*
20	Lavandin essential oil	LDO
21	Persea indica L.	PIL
22	German beech wood	GBW
23	Psidium guajava L.	PGL
24	sage leaves	SL
25	Fig leaf gourd	FLG
26	*Scutellaria baicalensis*	*SB*
27	*Spilanthes americana*	*SA*
28	Olive leaves	*OL*
29	coca leaves	CL
30	oregano bracts	OB
31	white fir sapwood	WFS
32	German beech wood	GBW
33	cedarwood chips	CWC

Acknowledgements:

Shabina Khanam is working as Assistant professor in Chemical Engineering Department of IIT Roorkee. The author has completed B.Tech degree from AMU Aligarh, Aligarh, Uttar Pradesh, India in 2000 and M.Tech and Ph.D. degree from IIT Roorkee, Uttarakhand, India in 2002 and 2007, respectively. The author's major field of study is process integration, energy management and modeling and simulation. She has 7 years experience in teaching and research. She has supervised 1 Ph.D., 9 M.Tech and many more B.Tech projects. 4 Ph.D and 5 M.Tech theses are in pipe line. She has published more than 20 papers in different refereed journals.

Priyanka is a research Scholar in Chemical Engineering Department of IIT Roorkee. The author has completed B.Tech degree from University Institute of technology, Kanpur, Uttar Pradesh, India in 2011 and M.Tech degree from IIT Roorkee, Uttarakhand, India in 2013. The author's major field of study is Chemical Reaction Engineering, Super Critical Fluid Extraction, Simulation and Modeling. She has published 2 papers in different referred journals.