Experimental Investigation on efficient Supercritical CO_2 Extraction of Essential Oil from Turmeric Rhizomes: Effects of Geometric and other Operation Parameters

Sutapa Roy, Chandan Guha, Asit Kumar Saha, Somak Jyoti Sahu

Abstract*: Supercritical carbon dioxide extraction experiments were carried out to isolate essential oil from turmeric rhizomes efficiently using extractors of annulus bed geometry and conventional cylindrical geometry using the same operating conditions of pressure 24.5 MPa, temperature 50^0C and particle size 0.3 mm keeping the time of extraction constant. A faster rate of extraction and improved yield was obtained in annulus bed geometry than conventional cylindrical geometry. The effect of pressure, temperature and particle size within the range of 21.6 MPa to 27.5 MPa, 40^0C to 60^0C and 0.3 mm to 0.9 mm respectively in annulus bed geometry were studied using response surface methodology. Full face central composite design method of statistical analysis was applied to find the interactions of all these parameters on oil yields and the optimum conditions. It was found that optimum oil yields of 4.454 gm oil/100 gm turmeric powder were obtained at a temperature of 59.96^0C and a pressure of 27.097 MPa for an average particle size of 0.3 mm. Model equations predicting the oil yields with operating parameters were also proposed.

Keywords: Supercritical carbon dioxide extraction, turmeric oil, extractor bed performance, oil yield, central composite design.

I. INTRODUCTION

Turmeric rhizomes are finger-like underground storage organs obtained from a perennial, tuberous herb (*Curcuma longa L.*) belongs to the Zingiberaceae family [1]. Its uses in traditional Chinese medicine and ayurvedic medicine of India were reported as more than thousands of years older [2]. Among different warmer parts of the world where turmeric is cultivated extensively, India is one of the largest producers of commercial turmeric products like turmeric powder, essential oil, oleoresin, etc. [3] and exporter as well [4]. The dark yellow powder product processed from dried matured rhizomes is used as a daily spice by almost one billion populations over the world for its natural color pigments, flavor, aroma, and food preservation characteristics [5]. There are several amazing benefits of daily use of raw turmeric rhizomes. Major industries who consume turmeric in many ways include foods, pharmaceuticals, confectionery, cosmetics and textiles [4, 6].

This golden spice plant extracts may contain more than 200 bioactive components [7]. These active ingredients of turmeric consist of mainly essential oil (volatile aromatic fractions) and nonvolatile saffron color polyphenol curcumin (probably the strongest antioxidant of turmeric) [5]. The volatile oil of Curcuma from Indian origin was reported to contain mainly four different sesquiterpenes (ar-turmerone, α-turmerone, turmerol, and β-turmerone) [8]. The benefits of these secondary metabolites were enlisted as having anti-oxidative, anti-inflammatory, antifungal, antibacterial, anti-carcinogenic, anti-mutagenic, antiviral, insect repellant, anticoagulant, ant diabetic, antiprotozoal, antivenom, antiulcer, antifibrotic, antifertility, hypotensive and hypocholesteremic properties [9, 6].

The extracts from various parts of *C. longa* are possible to recover by various extraction methods such as Soxhlet extraction [10-11], steam distillation [12] , hydro-distillation [1, 8], microwave-assisted extraction [13] and supercritical fluid extraction (SFE) using supercritical carbon dioxide (SCO_2) [14-16, 6]. Among them, two mostly used laboratory and industrial grade traditional methods, hydro-distillation, and steam distillation, are suffering from producing good quality yields [16]. Supercritical carbon dioxide extraction (SCO_2E) is a robust technology to produce good quality yield with abundant bioactive components [15], provide oxygen-free extraction environment, minimize extraction time and solvent consumption, reduce secondary treatment steps, and diminish solvent contamination of the product to zero levels [14]. Various research works were reported to study the effect of various operating parameters such as pressure, temperature, particle size, solvent flow rate, the addition of co-solvent, and material drying conditions on the extraction of turmeric oil from different plant parts using SFE. Gopalan, Priyanka, and their co-workers recommended a pressure range from 20MPa to 40MPa and temperature range from 313K to 333K for SCO_2E of turmeric rhizomes to obtain good quantity oil yield [14, 6].

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Chang and others suggested an operating pressure of at least 26MPa and the temperature range of 320K-350K is suitable for turmeric oil extraction using SCO_2E without applying any co-solvent [15].

Some studies on the effect of particle size indicate that particles smaller than 0.45 mm enhance the rate and yield of extraction using SCO_2 [6, 15]. Angel L. Chassagnez-Me´ndez studied the kinetics of SCO_2E of curcumins and essential oil from the turmeric rhizomes [17]. Another important factor that has considerable influence on the extraction process along with various operating conditions of SFE is the design of extractor. The effects of design variations of the extractor (in terms of bed volume, bed height to diameter ratio, etc.) on SFE of various plant materials were reported in some works of literature [18-24]. The variation in bed geometry interferes in the extractor performance by affecting the distribution pattern of solid feed, the tortuous path for solvent flow, mass and heat transfer rates. These factors influence the overall extraction curves (OEC) and corresponding extraction kinetics. Conventionally cylindrical geometry is used in designing the extractor vessel. In the present work, a special type of annular extractor bed design, introduced earlier by us to study the effect of geometrical modification of extractor on supercritical carbon dioxide extraction of clove bud oil [25], is used for turmeric oil extraction. It aims mainly to establish the effect of this design concept in the extraction of biomass like turmeric rhizomes which is not enriched with essential oils like clove buds. The effects of operating parameters like pressure, temperature and particle size using modified bed geometry are also studied. Then the performance of modified extractor beds in the extraction of turmeric oil was compared and verified with the results obtained earlier in the case of clove oil extraction.

II. MATERIALS AND METHOD

A. Plant Materials and Chemicals

The quality matured dried turmeric rhizomes as available in local market were obtained from Haldia (West Bengal, India), checked minutely to remove any other impurity (if any) and dried under controlled condition in a laboratory drying unit having air evacuated system for 12 h. This is done in order to avoid the opposing effect of moisture content of the sample above 12% on the rate of mass transfer and solubility of the volatile matter in the solvent CO_2 used for SFE [26].

The dried turmeric sample was then milled in a mixture grinder (Philips Mixer Grinder HL7720) and separated into three fractions with the help of a sieve shaker assembled with 16 - 80 mesh sieves from Tyler standard screen series. The average particle sizes (D_P) of different fractions were determined following the mass mean diameter calculation and the ground turmeric (to be used later for SCO_2E experiments) was stored after packaging in air-tight polyethylene bags in cold and dark place since curcuminoids, the natural pigment of turmeric, degrade in contact with light, heat and oxidative conditions [27].

CO_2 (commercial grade with above 99% purity) used in the extraction experiments was acquired from a local supplier, Bharat Oxytech Pvt. Ltd., Haldia (West Bengal, India).

B. Moisture Content of Turmeric Rhizomes

The moisture content of both, the raw turmeric bought from the market and moisture controlled turmeric after laboratory drying, were measured using the “SARTORIUS MA45C” moisture analyzer. The moisture analysis results were provided after triplicate measurements.

C. Determination of the Global Yield (Total Amount of Extractable Material)

In the present study, the traditional Soxhlet extraction method was applied to obtain the entire extractable aromatic oil content from the turmeric sample. For the experiment 30 gm of the dried and comminuted sample from the feedstock having 0.6mm average particle size was loaded in a glass thimble after wrapping in Whatman filter paper. The thimble was connected with a round bottom reflux flux (500 mL capacity) of the Soxhlet apparatus. The extraction was carried out using 200 mL n-hexane as a solvent and the apparatus was kept under reflux condition for 8hrs. Then the final extract was separated by removing the solvent at 50^0C with the help of a rotary vacuum evaporator.

D. Modified Externally Loaded Solid Bed

It is common practice to fill the ground plant material externally in a shell (conventionally cylindrical in geometry) having perforated surface and placed it inside the cylindrical extractor vessel for solid-fluid SCO_2E. In this study, a concentric tube extractor shell was used to study the effect of this modified bed geometry on turmeric oil extraction as a continuation of our previous published work [25]. This special type of extractor shell is an assembly of two concentric perforated tubes. The smaller diameter tube which has one blind end at the upstream side was surrounded by the main shell of fixed diameter 5.5cm (same as the internal diameter of the extractor vessel) and groundmass of plant matrices was loaded in the annulus. The internal tube was designed for two different diameters (0.75cm and 1.5cm). Experimental studies on turmeric oil extraction using supercritical carbon dioxide (SCO_2) were conducted under same operating conditions using modified extractor bed of two different dimensions (AB1, Annulus Bed designed with 1.5cm diameter inner channel & AB2, Annulus Bed designed with 0.75cm diameter inner channel) and conventional solid bed without any annulus (CB) to co-relate the bed performances with previous study using same alteration of bed geometry [25]. The figure of annulus bed loaded inside the extractor was available in the previous publication [25].

E. SFE Experimental Set-up

All the experimental investigations related with the evaluation of the annulus extractor bed performance in turmeric oil extraction by SFE were conducted using a semi-batch type SFE unit (Model No: CSL/SCF/1L2/400) supplied by M/s Chemtron Science Laboratories Pvt. Ltd. (Navi Mumbai, India), and described elsewhere [25].

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It consists mainly of a high-pressure pump, a SCO_2 generation vessel, two 1000mL Extractors (each of 42cm height and 5.5cm inside diameter), and two low-pressure 1000mL Separators, and a low-temperature CO_2 Storage and a Control Unit to view and change the system settings. The schematic of the SFE module used in the present study is the same as published earlier [25].

F. Operational Procedure

The operational procedure used in this SFE module was described in detail by S.Roy et al [25]. Initially, a particular type of feed shell (designated as AB1, AB2 or CB) was filled in full with comminuted turmeric samples and placed inside the extractor vessel to carry out the runs. Pressurized solvent CO_2 from the pump was allowed to enter the extractor vessel through SCO_2 generation vessel to attain the desired extraction pressure. Once the extractor pressure was stabilized, the extract laden SCO_2 was expanded to reduce the pressure and recover the essential oil through two successive separators. In all the experiments extraction was continued for a period (t_E) of 240 minutes and the samples were collected and weighed at intervals (of 15, 30, 45, 60, 90, 120, 150, 180, 210, & 240 minutes) using separate sampling bottles and recorded to construct OECs. This SFE unit was equipped with a solvent CO_2 recovery system and the recovered solvent was returned back to the low-temperature CO_2 storage vessel for reuse. After extraction total yield was centrifuged and the pure essential oil part was separated and stored in a refrigeration unit for further analysis.

G. SCO_2E using Different Bed Geometry

SFE runs to isolate essential oil from turmeric rhizomes using extractors of annulus bed geometry (AB1 & AB2) and conventional cylindrical geometry (CB) was conducted to see the impact of annulus bed geometry over conventional cylindrical geometry and compared with the results as obtained in case of clove oil extraction using SCO_2 in the previous study [25]. Extraction experiments of milled turmeric powder of the same particle size were carried out in the same experimental setup, applying the same operating conditions and the same period of extraction, varying only the bed geometry of extractor vessel. All the experimental data such as mass of feed (F), extraction pressure (P), extraction temperature (T), particle size (D_P), solvent flow rate (Q_{CO2}), initial static period of extraction (t_S), period of extraction (t_E), yield of extract (as %OY) are provided in Table-1. The extract of oil was expressed as percentage oil yield [%OY = (gm of oil extract /100 gm of extractable mass]. All the assays were replicated twice for double sanguine. Finally, the OECs for all these three-bed geometries were plotted and compared.

Table-1: Experimental Data from the Extractor Performance Study

F (gm)	D_P (mm)	Q_{CO2} gm/min	T in E (^0C)	P in E (MPa)	T in S_1 (^0C)	P in S_1 (MPa)	T in S_2 (^0C)	P in S_2 (MPa)	t_s (min)	t_E (min)	Q_{CO2} gm/min
500	0.3	10	50	24.5	30	≈6	25	≈5	20	240	18.5

F - Mass of feed, Q_{CO2} - Solvent flow, T – Temperature, P - Pressure, E – Extractor, S_I – Separator-I, S_{II} – Separator-II, t_s - Static period, t_E period of extraction

H. Experimental Design and Statistical Analysis

The performance of an extraction process to produce essential oil from various plant parts is evaluated in terms of the quantity of extract obtained from the process and the quality of the yield measured in terms of the presence of important bioactive components in dense form. The quantity and quality of oil extracted from vegetable matrix by SFE are influenced by various operating parameters, such as temperature, pressure, particle size, solvent flow rate, time of extraction, use of co-solvent, level of moisture in the feed, porosity of feed bed, extractor bed geometry [28], and their roles on the process may be direct/indirect also independent/interactive in nature [29]. In the present work, the extractor with high performance as obtained from the experimental results of Section-G was chosen for the parametric study of SFE process on turmeric. Three parameters, (i) pressure (X1), (ii) temperature (X2), and (iii) particle size (X3) were chosen to analyze their role in producing turmeric oil efficiently and optimize them to maximize the yield.

For SCO_2E processes, the statistical optimization procedures were applied extensively to find out optimal operating conditions that ensure either the maximum oil yield or yield with the maximum targeted bioactive component. The methods of statistical analysis examine various possible interactions of the process variables during optimization [30]. In statistics, central composite design (CCD) is a useful tool under Response Surface Methodology (RSM) for modeling various technological processes by fitting a second-order mathematical relation between the process variables and one or more response variable(s). In this work, face-centered central composite design (FC-CCD) strategy was applied to build a statistical model equation that explores the relations between optimizing parameters X1, X2 and X3 of SCO_2E (for a particular bed geometry) and dependent response %OY of turmeric. For experimental design, values of three process parameters X1, X2, and X3 were expressed at three levels as (−1), (0) and (+1) and FC-CCD required responses (%OY) resulting from the experiments conducted for twenty different combinations of these three independent process variables. Three levels of the process variables pressure, temperature and particle size of the present study are given in Table-2. The temperature levels were chosen following the previously published works [6, 15]. In selecting pressure levels, (i) highest pressure of 27.5MPa was chosen considering the design pressure of the extractor (29.42 MPa) and (ii) lowest pressure of 21.6 MPa was selected considering the favorable pressure data recommended for turmeric extraction (at least 26MPa) [15]. Two particle sizes were selected above the recommended size (≈0.45mm) of previous researchers [6, 15] to study the influence of modified bed geometry to overcome the negative impact of larger particle size.

All the 20 experiments of FC-CCD generated combinations were

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performed and the analysis of variance (ANOVA) was done using the Design Expert-11 software package [31]. Thus, the influence of each independent factor and their interactions were examined and estimated statistically. All the runs were performed fixing other parameters such as mass of feed (F), solvent flow rate (Q_{CO2}) and period of extraction time (t_E) same as provided in Table-1.

Table-2: Three levels of selected variables chosen for FC-CCD

Pressure, X1 (MPa)	Temperature, X2 (^{0}C)	Particle size, X3 (mm)
21.6 (-1)	40 (-1)	0.3 (-1)
24.5 (0)	50 (0)	0.6 (0)
27.5 (+1)	60(+1)	0.9 (+1)

I. Characterization of Turmeric Extract: GC/MS analysis

The compositions of volatile substances present in the turmeric extract were identified in an advanced standard gas chromatograph *mass* spectrometer, *GCMS*-QP2010 SE (SHIMADZU, Kyoto, Japan). The capillary column, DB - 1 MS UI with specification length 60m, inside diameter 0.25m, internal film width 0.25µm, used for separating the components was supplied by Agilent. The sample of essential oil of turmeric rhizomes was diluted using acetone in 1:4 ratios and injected with the help of an auto injector. 1 µL volume of diluted sample was injected in the split mode (1:50). The other details are given elsewhere [25]. The total run time was 90 min.

The settings of MS detector used in the analysis of turmeric oil were – (i) Ion source temperature 220^{0}C, (ii) interface temperature 300^{0}C. The mass spectra developed by the detector were analyzed to identify the chemical species using GCMS solution software (version 4) build with MS library - NIST, Wiley, and SHIM. All the testing of turmeric samples was done in quality control laboratory of M/s Imperial Fragrances & Flavours Pvt. Ltd., Howrah, West Bengal, India.

III. RESULTS AND DISCUSSIONS

A. Moisture and Global yield

In Table-3, the moisture content of raw and dried milled samples of turmeric rhizomes and the global yield resulted from Soxhlet extraction experiments are provided. The result of the global yield was found to agree well with literature values [32, 6].

Table-3: Moisture Content and Global yield

The moisture content of raw milled Turmeric (wt %)	The moisture content of dry milled Turmeric (wt %)	Global Yield (gm oil / 100 gm feed)
12.34	4.29	5.42

B. *Effect of Bed Geometry Modification on Extractor Performance*

Fig 1 shows that the bed geometry modification from conventional cylindrical type (CB) to annulus type (AB1 & AB2) influenced the OECs significantly in terms of the rate and yield of extraction while other conditions including extraction time (t_E) were kept constant. The yield (%OY) was maximum in the case of AB1 type extractor and lowest in the case of CB type extractor for a fixed extraction period of 240min. Since operational cost is increased with increasing period of extraction (t_E) to recover at least 90% of the volatile fraction of plant material, the design concept of any extractor that may increase the rate of extraction during constant extraction rate (CER) period in OEC (indicated by the initial steeper portion of the curves) must play a positive role on the process. In the present study on turmeric oil extraction by SCO_2, annulus bed arrangement (AB) revealed that this geometrical modification had some positive impact on the performance of the extractor as reported in the case of clove oil extraction [25]. It is due to the fact that the annulus bed reduces the molecular diffusive path for all the molecules and also induces turbulence in the supercritical fluid bulk that increases convective diffusion. Thus, the mass and heat transfer resistance for oil extraction decreases yielding higher oil mass [25]. During the design of the annulus bed, the detrimental effect of larger voids on channeling must come under consideration.

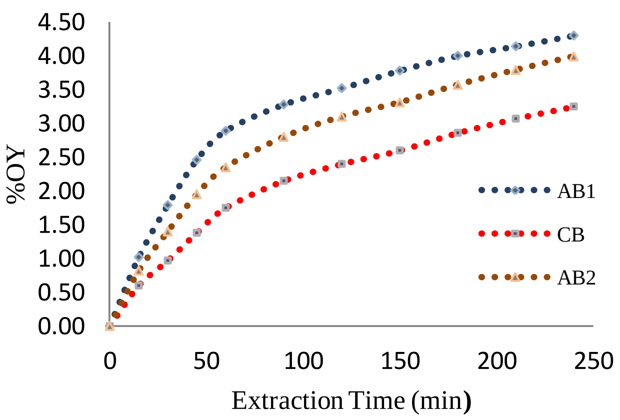

Fig 1: Variation in OECs of turmeric extract under varying bed geometry AB1, AB2, and CB (Process Parameters: Temperature (50^{0}C), Pressure (24.5 MPa), Particle Size (D_p = 0.3 mm)

C. Analysis of Variance (ANOVA)

In this work, RSM was applied to find out the quadratic model equation to optimize three process variables (X1, X2, and X3) and maximize extract [expressed as (%OY)] of turmeric oil extraction process using annulus bed extractor AB1 and SCO_2. Based on the FC-CCD for three factors, a total of 20 experiments of turmeric oil extraction were performed with 20 sets of values of X1, X2, X3 (three factors of CCD). The yield, %OY, obtained from each experiment was reported as the response of CCD along with corresponding values of X1, X2, and X3 in Table- 4.

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Table -4: FC-CCD data of three factors and response oil Yield (%OY) of Turmeric rhizome

	Factor 1	Factor 2	Factor 3	Response 1
Run	A:Pressure (MPa)	B:Temperature (^{0}C)	C:Particle Size (mm)	%OY (gm oil/100 gm Feed)
1	24.5 (0)	40(-1)	0.6(0)	3.25
2	21.6 (-1)	40(-1)	0.3(-1)	3.76
3	24.5 (0)	50(0)	0.6(0)	3.51
4	24.5 (0)	50(0)	0.6(0)	3.5
5	27.5 (+1)	50(0)	0.6(0)	3.74
6	24.5 (0)	50(0)	0.6(0)	3.5
7	24.5 (0)	50(0)	0.6(0)	3.52
8	21.6 (-1)	60(+1)	0.3(-1)	4.3
9	27.5 (+1)	60(+1)	0.9(+1)	3.2
10	21.6 (-1)	60(+1)	0.9(+1)	2.7
11	27.5 (+1)	60(+1)	0.3(-1)	4.45
12	24.5 (0)	50(0)	0.6(0)	3.5
13	27.5 (+1)	40(-1)	0.9(+1)	2.65
14	27.5 (+1)	40(-1)	0.3(-1)	4.23
15	24.5 (0)	50(0)	0.3(-1)	4.3
16	21.6 (-1)	50(0)	0.6(0)	3.23
17	24.5 (0)	50(0)	0.9(+1)	2.62
18	24.5 (0)	60(+1)	0.6(0)	3.72
19	21.6 (-1)	40(-1)	0.9(+1)	1.84
20	24.5 (0)	50(0)	0.6(0)	3.5

To explore the model equation, all convenient models such as linear, two-factor interaction (FI) and quadratic were examined for the responses %OY of all runs based on R^2 [33], standard deviation, adjusted R^2, predicted R^2, "PRESS" values, F-values, p-values, and lack-of-fit tests results. The higher order quadratic model was chosen as best for the data from the fit summary [larger F-value (25.69), negligible p-value <0.0001, low value of standard deviation (0.0256), high value of R^2 (0.9992) , lowest "PRESS" value and larger Adjusted R^2 (0.9984) and largest Predicted R^2 (0.994), and (Adjusted R^2 - Predicted R^2) < 0.2]. ANOVA test results as illustrated in Table-5 provided the information about significant fitting of all linear terms (X1, X2, X3), all FI terms (X1X2, X1X3, X2X3) and all quadratic terms ($X1^2$, $X2^2$,$X3^2$) from their individual P value (most of them are less than 0.0500). The Model F-value of 1348.94 implies that the quadratic model equation is significant. The larger value of adequate precision (144.879>>4) obtained in ANOVA was the desirable condition to describe the true behavior of the system by the selected model in comparison to the linear model and 2FI models.

Table 5: ANOVA for the turmeric yield (% OY) in the FC-CCD

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7.95	9	0.8836	1348.94	< 0.0001	significant
A-Pressure (X1)	0.5954	1	0.5954	908.85	< 0.0001	
B-Temperature (X2)	0.697	1	0.697	1063.95	< 0.0001	
C-Particle Size (X3)	6.45	1	6.45	9843.39	< 0.0001	
AB	0.0496	1	0.0496	75.74	< 0.0001	
AC	0.0595	1	0.0595	90.85	< 0.0001	
BC	0.0528	1	0.0528	80.62	< 0.0001	
A^2	0.0026	1	0.0026	3.89	0.0767	
B^2	0.0026	1	0.0026	3.89	0.0767	
C^2	0.0085	1	0.0085	12.91	0.0049	
Residual	0.0066	10	0.0007			
Lack of Fit	0.0062	5	0.0012	17.72	0.0034	significant
Pure Error	0.0003	5	0.0001			
Cor Total	7.96	19				

Std. Dev.	0.0256					
R^2	0.9992					
Adjusted R^2	0.9984					
Predicted R^2	0.994					
Adeq Precision	144.8787					

X1, X2, and X3 relates the effects of main process parameters pressure (MPa), temperature (°C), and particle size (mm) on the response (%OY). $X1^2$, $X2^2$, and $X3^2$ produces the quadratic effects of the same input variables. X1X2, X1X3, and X2X3 express the interaction effects of three possible combinations of three factors (i) pressure and temperature; (ii) pressure and particle size, and (iii) temperature and particle size, respectively

D. Model Equation obtained from RSM

The quadratic mathematical model expression representing the percentage oil yield (% OY) of turmeric rhizomes as a function of the three independent process variables of RSM study in the range of their values under investigation is given by the following generalized equation:

$$\%OY = \beta_0 + \beta_1 X1 + \beta_2 X2 + \beta_3 X3 + \beta_{12} X1X2 + \beta_{13} X1X3 + \beta_{23} X2X3 + \beta_{11} X1^2 + \beta_{22} X2^2 + \beta_{33} X3^2$$

where %OY is the actual response; β_0 is the regression coefficient of intercept; β_1, β_2, and β_3 are the regression coefficients for linear fit; β_{12}, β_{13} and β_{23} are the regression coefficients for FI fit; and β_{11}, β_{22} and β_{33} are the regression coefficients for quadratic fit. The actual values of the regression coefficients of the final regression model were given in Table-6.

Table 6: Coefficient Table of ANOVA Test for turmeric

	β_0	β_1	β_2	β_3	β_{12}	β_{13}	β_{23}	$\beta_{11}{}^2$	$\beta_{22}{}^2$	$\beta_{33}{}^2$
%OY	3.50918	0.244	0.264	-0.803	-0.07875	0.08625	0.08125	-0.03045	-0.03045	-0.05545

E. Pressure, Temperature, and Particle size: Effects on the Oil Yield

Influence of individual process parameter on turmeric extract as (%OY) can be described with the help of perturbation plot shown in Fig. 2. The response surface plots are shown in Fig. 3 (a) -(c) were used to explain the two-factor interaction effects on the extract of turmeric in the range of values chosen for investigation. Analysis of both type plots indicates that pressure (in the range of 21.6-27.5 MPa) and temperature (in the range from 40^0C - 60^0C) both show a slightly positive impact on improving %OY. On the other side, particle size shows a significant effect on the extract. %OY was increased notably with decreasing the particle size from 0.9mm to 0.3 mm. Thus combined effect of pressure-temperature on %OY is lower than pressure – particle size interaction or temperature – particle size interaction. The increase of yield with increasing pressure is due to the increase of solubility of the solute with increasing pressure. Similarly, increasing temperature influences the yield positively due to the faster rate of mass transfer of solute attained from high diffusivity and vapor pressure value [28, 34-35].

The reduction of particle size to an optimal level is beneficial as milling of plant material to smaller particle size helps to rupture the cell walls and thus more molecules of volatile oil expose to the surface and come in direct contact with the solvent and easily extracted. In some literature, a range of particle size 0.2-0.45 mm was mentioned where yield increases gradually after which it declines significantly [6, 15]. Thus, a gradual reduction of yield for 0.6mm to 1.0mm particle size in the present study satisfies the literature. In this work RSM was applied in modified annulus bed geometry AB1and extraction was carried out without applying any co-solvent. In terms of percentage recovery of extractable oil at a faster rate annulus bed AB1 performance is remarkable as compared with CB performance under the same operating condition.

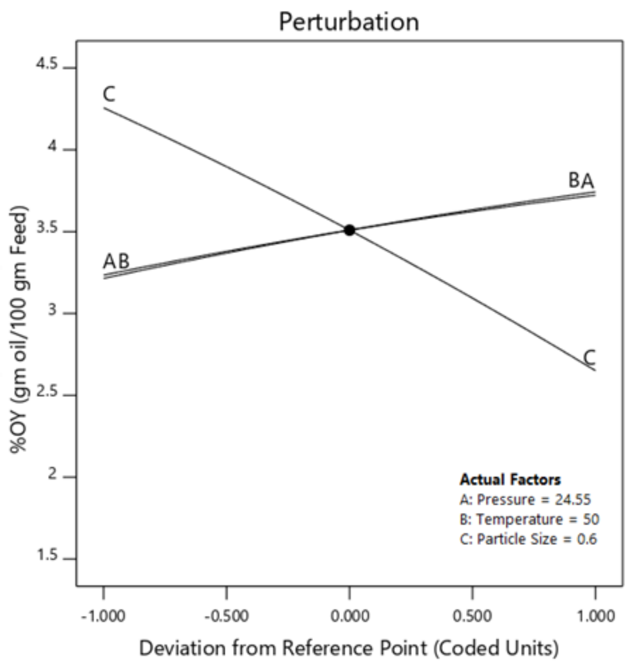

Fig 2: Effect of Individual Process Parameters on the %OY

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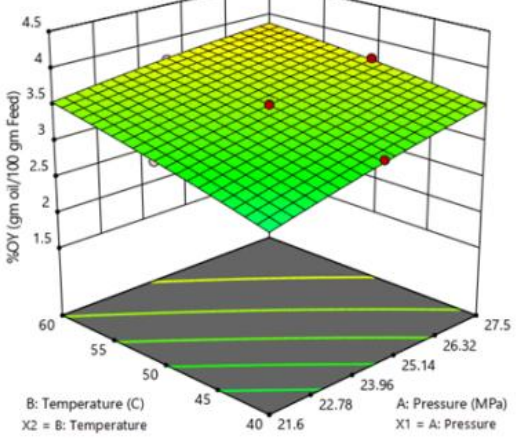

Fig. 3(a)

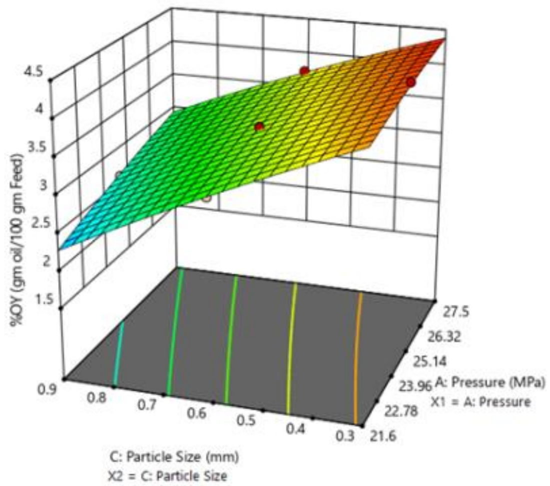

Fig. 3(b)

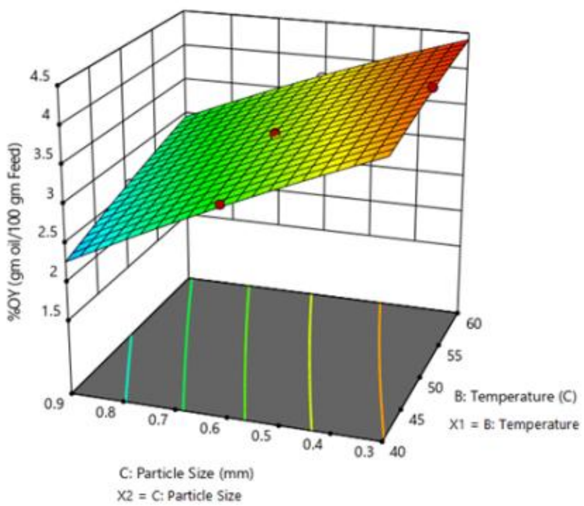

Fig. 3(c)

Fig. 3 Response surface plots (a-c) for turmeric oil Fig. 3(a) percent yield vs. extraction temperature and pressure at a constant particle size of 0.6 mm;

Fig. 3(b) percent yield vs. particle size and extraction pressure at a constant temperature of 50^{0}C
Fig. 3(c) percent yield vs. extraction particle size and extraction temperature at a constant pressure of 24.55 MPa

Fig. 4 is a graphical representation of the predicted response of ANOVA vs. actual response in terms of %OY obtained from various experiments of RSM study. Finally, numerical optimization of the operating variables was carried out to predict the optimal conditions of three factors towards the maximized yield of turmeric. The optimized values of 3 factors with corresponding with maximized %OY are reported in Table 7.

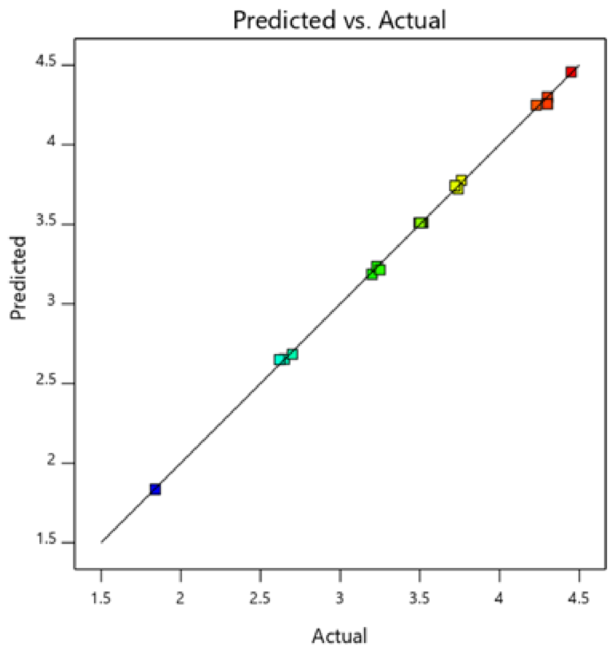

Fig. 4: Graphical representation of the predicted response of %OY vs. actual response of %OY

Table- 7 Optimum points of operating parameters to maximize the responses %OY

%OY	Pressure	Temperature	Particle Size
4.454	27.097	59.957	0.3

F. Chemical Analysis of Essential Oil Components of Turmeric Rhizomes

The volatile ingredients of the turmeric oil obtained from SCO_2E at optimal conditions using bed type AB1were analyzed. The full-length GC-MS chromatogram of turmeric oil was shown in Fig 5. The components identification methods were described in a previous study [25]. The identified compounds present in the turmeric oil sample were listed in Table 8. Some of the principal components detected are ar-Turmerone 57.21%, Curlone 14.63%, Curcumene 1.49%, Tumerone 1.21%, etc.

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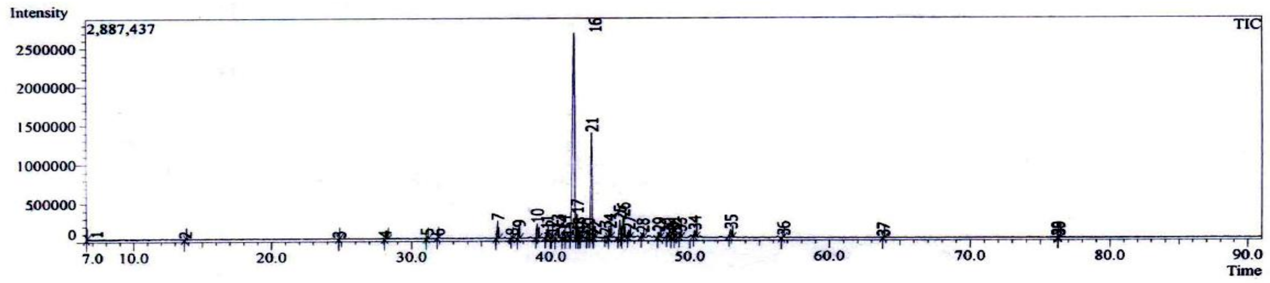

Fig 5: Gas chromatogram of bioactive components of turmeric essential oil

Table 8: Percentage chemical composition of the turmeric essential oil

Components Name	Molecular Formula	Molecular Weight	Retention Time	% Con.
Ethanol, 2-Methoxy-, Acetate	$C_5H_{10}O_3$	118.1311	6.551	0.27
ar-Turmerol	$C_{15}H_{22}O$	218.34	31.892	0.11
ar - Curcumene	$C_{15}H_{22}$	202.341	36.162	1.49
β-Sesquiphellandrene	$C_{15}H_{24}$	204.357	37.690	0.91
ar-Turmerol	$C_{15}H_{22}O$	218.34	39.012	2.05
ar-Turmerol	$C_{15}H_{22}O$	218.34	39.714	0.95
Lanceol	$C_{15}H_{24}O$	220.356	40.042	0.28
dihydro-ar-Turmerone	$C_{15}H_{22}O$	216.324	40.481	1.77
β-Biotol	$C_{15}H_{24}O$	220.356	40.910	1.18
Formic Acid, Benzoyl-,(8'-phenylmethyl) ester	$C_8H_8O_2$	136.15	41.250	0.29
ar Turmerone	$C_{15}H_{20}O$	216.324	41.680	57.21
Tumerone	$C_{15}H_{22}O$	218.34	41.868	1.21
1,5-Heptan-4-ol, 3,3,6-Trimethyl	$C_{10}H_{18}O$	154.253	41.995	0.61
β-Biotol	$C_{15}H_{24}O$	220.356	42.653	0.27
Curlone or β Tumerone	$C_{15}H_{22}O$	218.34	42.922	14.63
Turmerol	$C_{15}H_{22}O$	218.34	43.907	0.18
Bisabolone	$C_{15}H_{24}O$	220.356	44.257	1.31
ar-Turmerol	$C_{15}H_{22}O$	218.34	44.968	3.03
Atlantone	$C_{15}H_{22}O$	218.34	45.220	2.82
Atlantone	$C_{15}H_{22}O$	218.34	45.619	0.66
Tumerone	$C_{15}H_{22}O$	218.3346	46.603	0.43
Cyclohexane, (2-Nitro-2-Propenyl)	$C_9H_{15}NO_2$	169.2209	47.797	0.93
Atlantone	$C_{15}H_{22}O$	218.34	48.432	1.00
Cyclohexanecarboxylic acid, 3-phenylpropyl ester	$C_{16}H_{22}O_2$	246.35	48.787	1.03
Benzene, (1-cyclopenten-1-ylsulfonyl)	$C_{11}H_{12}O_2S$	208.277	48.975	0.30
α-Oxobisabolene	$C_{15}H_{24}O$	220.3505	49.317	0.88
5-Hydroxymethyl-1,1,4a-trimethyl-6-methylenedecahydronaphthalen-2-ol	$C_{15}H_{26}O_2$	238.371	50.100	0.24
Atlantone	$C_{15}H_{22}O$	218.34	50.412	1.42
2-Methyl-4-octenal	$C_9H_{16}O$	140.226	52.967	1.47
Atlantone	$C_{15}H_{22}O$	218.34	56.374	0.18
2,5-Heptadien-4-one,2,6-Dimethyl-	$C_9H_{14}O$	138.21	56.759	0.26

Rest components were present in the range of 0.01 - 0.14.

G. Dynamic Mathematical Model of OECs

The OECs obtained from different experiments for RSM studies were found to fit in the Luo Denglin dynamic model type equation [36]. The model was expressed as-

$$Y = Y_{\propto}(1 - e^{-k.t})$$

where Y represents the amount oil extracted expressed as (%OY) at time t, $Y_{\propto}$ is a measure of the maximum value of Y after infinite time that is the maximum amount of extractable oil ($\%OY_{max}$) and k is a rate constant.

Y_α was substituted from the yield value obtained from Soxhlet extraction experiments.

The maximum oil yield obtained in the Soxhlet process was 5.42 ($which\ is\ equal\ to\ Y_{\propto}$). The rate constant, k, is found to be a function of reduced temperature and reduced pressure. It is defined as$\left[k = A.\frac{T/T_C}{P/P_C}\right]$,

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where A is proportionality constant; T_C is critical temperature (31.1^{0}C) and P_C is critical pressure (7.39MPa) of solvent CO_2. The value of the constant 'A=0.025' was evaluated with the help of Curve Expert 1.40. The final dynamic equation was thus found to take the form:

$$Y = 5.42\left(1 - e^{-0.025\frac{T/T_C}{P/P_C}.t}\right)$$

It described all the OECs (obtained from the RSM study on turmeric oil extraction) quite well (with R^2 ranges from 0.9-0.99). Fig 5(a) and 5(b) show two sample of model fitting curves obtained under operating conditions of SFE of turmeric rhizomes (a) P= 21.6 MPa, T= 60^{0}C, and D_P=0.3 mm, and (b) P= 24.55 MPa, T= 50^{0}C, D_P=0.3mm, using annulus extractor AB1.

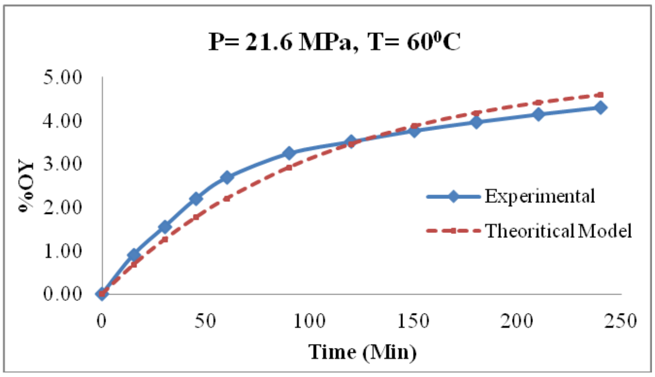

Fig. 5(a)

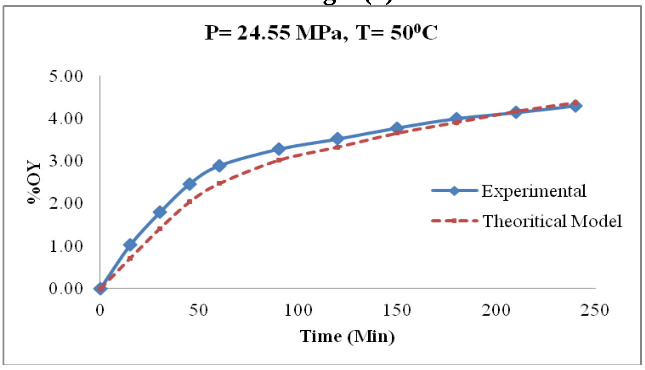

Fig. 5(b)

Fig 5 (a) & 5(b): Model Fitting Overall Extraction Curves of Turmeric Oil

IV. CONCLUSION AND FUTURE SCOPE

In the present study, turmeric oil was extracted from dried milled turmeric rhizomes using Soxhlet extraction and SCO_2E (without applying any co-solvent) methods. % OY obtained from the Soxhlet method was 5.42% and that obtained from SCO_2E (for an extraction period of four hours) was in the range of 1.84 to 4.45%.

Influence of individual process parameters like temperature, pressure, particle size and bed design geometry on turmeric oil-extract was studied thoroughly and the data were analyzed by using statistical response surface methodology (RSM). Annulus bed geometry shows a definite impact on the rate of extraction and %OY over conventional cylindrical geometry under the same operating conditions. Analysis of results of interaction plots indicates that pressure (in the range of 21.6-27.5 MPa) and temperature (in the range from 40^{0}C - 60^{0}C), both have a slightly positive impact on improving the %OY, whereas smaller particle size (0.3mm) has a significant effect on the %OY.

In RSM study using the FC-CCD method, a quadratic model exhibited the best fit to explore the relationship between operating parameters of SFE and the yield of turmeric rhizomes.

Chemical analysis of extract obtained from SFE applying optimum operating conditions and annulus bed geometry revealed the presence of 57.21% ar-Turmerone and 14.63% β –Turmerone, which indicates the good quality of the product.

Thus, it may be concluded that though the study of annular geometry in place of traditional cylindrical geometry of the extractor indicates an improvement of extractor performance in terms of increasing rate and yield of extraction for moderate extraction period or reduced extraction time to extract economically, further systematic studies with different bed geometries are necessary to correlate hydrodynamic behaviour for establishing a suitable criterion that can be used to predict extractor performance along with its economic gain.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AB	Annulus Bed
CB	Conventional Cylindrical Bed
CCD	Central composite design
CER	Constant extraction rate
D_P	Particle size
FC-CCD	Face centered central composite design
GCMS	Gas chromatograph mass spectrometer
OEC	Overall extraction curve
% OY	Percentage of oil yield
Q_{CO2}	Solvent flow rate
RSM	Response surface methodology
SCO_2	Supercritical CO_2
SCO_2E using CO_2	Supercritical fluid extraction technology
SFE	Supercritical fluid extraction
t_E	Period of Extraction
t_S	Static period of extraction

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