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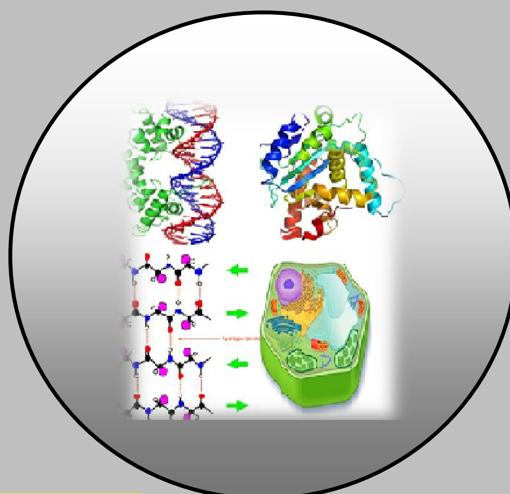

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RESEARCH PAPER

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Supercritical Extraction of Aroma/ Flavor and Essential Oil from Nagpur mandarin (*Citrus reticulata* Blanco) Peel

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ABSTRACT

Supercritical fluid extraction is an advantageous alternative process for refining citrus oils due to its low operating temperature and the absence of solvent residues. In this work aroma and essential oil of dried Nagpur mandarin peel were extracted by supercritical carbon dioxide. In supercritical extraction, the parameters evaluated were temperature, pressure, and dynamic time. The best results for supercritical extraction of aroma was found to be 400 bar vessel temperature (Vt) 35^oC and valve temperature (Vlt) 40^oC , resulted in maximum aroma recovery of 2.79% in 300 minutes dynamic time with constant 20 min. static time. The optimum recovery condition for peel oil was 2.26 % peel oil in 350 minutes dynamic time 100 bar pressure, 45^oC (Vt), 50^oC Vlt. at 30 min. of sample held at static condition and 350 min dynamic time of step. The fractional study of aroma and oil is in progress in processing lab of NRC for Citrus, Nagpur, Maharashtra.
Key words: Citrus, Nagpur mandarin, supercritical carbon dioxide, peel aroma, peel oil.

INTRODUCTION

In recent years great deal of interest has been devoted to the extraction of different high value molecules and active compounds from the citrus processing waste used as natural source. Among the large number of active substances in the focus- aroma, flavor and essential oil have received particular attention in the present era. The common commercial methods to produce the oils from citrus fruits and peels are machine-cold pressing and distillation. However, the oils obtained by distillation deteriorate easily and develop off-flavors due to the instability of the terpenes hydrocarbons present, particularly *d* limonene (Yamauchi and Sato, 1990). Among the several extraction methods, application of SFE for extraction of high value active compound, color and oil in citrus gaining momentum nowadays because processes based on supercritical fluids (SFE) are an environment-friendly alternative to traditional solvent extraction techniques (TSE) which often requires long are the high compressibility and diffusivity of the supercritical fluid.

Supercritical fluid extraction is an advantageous alternative process for refining citrus oils due to its low extraction time and consumes large amount of organic solvents that may remain as residues in the final extract. Overall the most discernible features that differentiate the SFE from TSE operating temperature and the absence of solvent residues (Iwai *et al*., 1994). Studies with mandarin oils have shown good yield in comparison to other extraction processes (Atti Santos *et al*., 2000). These oils are used in the pharmaceutical, perfumery and food industries (Huet, 1991), and the quality of the oils is related to the value of total aldehydes, basically citral content, which is between 4-5%. The most widely used supercritical fluids (SFs) is carbon dioxide (SC CO_2) because of the low critical temperature (31.18 °C) and pressure (7.4 MPa), inexpensiveness, non-toxicity, non-flammability, recyclability and environmental benignity. The Nagpur mandarin fruit is one of the important Citrus fruit containing about 50-60% waste as peel, pomace, rag and seeds, which are thrown away after juice extraction. But various value added products can be developed out of this processing waste employing an advanced, economical and eco friendly technique. Therefore, the study on supercritical extraction for aroma and essential oil from the Nagpur mandarin peel was important to standardize the SFE operational condition like, pressure, temperature and dynamic time at processing laboratory of NRC for Citrus, Nagpur.

MATERIALS AND METHODS

The mature Nagpur mandarin fruits were collected from local farmers orchard which was brought into the processing laboratory for washing the peel surface with tap water followed by rinsing with distilled water to remove the dust particle etc, and then, the peel was removed manually and dry it at 60^{o}C temperature for 72 hrs in tray dryer, and was grinded in grinder to get the fine and uniform size particles of 200 mesh for the study. The 22 gm sample of peel powder retaining <5% moisture level for each trial was loaded into a thick-walled stainless steel vessel having 25 ml internal volume. These SFE apparatus fitted with single vessel manufactured by Applied Separations module was used to perform the experiments to extract the peel aroma and peel oil. At the experimental pressure, carbon dioxide was passed through the extraction column to start the extraction and the exit fluid (CO2 with citrus volatiles) was expanded at ambient pressure in the collection tube. The vessel temperature were kept to ranges between 30 to 40ºC at 400 bar for aroma and 45 to 60ºC, at 100 bar for peel oil extraction, respectively. The static time for uniform blending of CO_2 into samples was fixed constant 20 minutes for aroma extraction for while it was 30 minutes for peel oil. The dynamic time was varied from 60 to 540 minutes for peel aroma and 100 to 500 minutes for peel oil in each step. Vessel temperature and valve temperature was kept changed for each set of experiment to optimize the operational extraction condition both for the aroma and essential oil extraction studies. The dynamic time has played crucial role in optimization studies for determining the optimum recovery of final product. The extracts were collected into a vial of 60 ml volume to determine the aroma and essential oil yields in each case. The CO_2 gas was used as super critical fluid in the current research. The oil was collected and the gas was vented through the dry gas meter.

Extractions of all the samples in closed vessels were carried out for about 6 hours at constant rates of 3 ml per minute flow of carbon dioxide for all the experimental runs at the studied temperatures and pressures. The result of aroma and oil were expressed in percent recovery of extract.

RESULTS AND DISCUSSION

Extraction of peel aroma/flavor

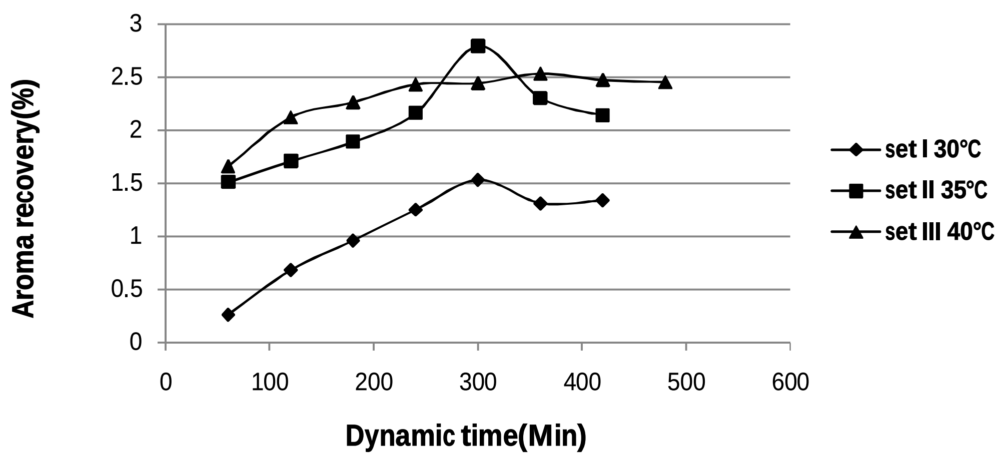
The influence of different operational conditions was analyzed constantly at 400 bar pressure and 35, 45 and 55°C varying temperatures with 20 minutes static time for all the three set of peel sample experimentation. As the dynamic time has played crucial role in optimization of final product recovery.

Table. 1 Effect of different SFE operational condition on aroma extraction from peel of Nagpur mandarin fruit.

Samples run steps for peel aroma extraction	SFE Operational Conditions					
	Pressure (Bar)	Vessel Temp. (˚C) (Vt)	Valve Temp. (˚C) (Vlt)	StaticTime (min)	Dynamic Time (min)	Aroma recovery (%)
Set I						
Run Step 1	400	30	35	20	60	0.26
Run Step 2	400	30	35	20	120	0.68
Run Step 3	400	30	35	20	180	0.96
Run Step 4	400	30	35	20	240	1.25
Run Step 5	400	30	35	20	300	1.53
Run Step 6	400	30	35	20	360	1.31
Run Step 7	400	30	35	20	420	1.34
CD(P=0.05)	-	-	-	-	-	0.50
Set II						
Run Step 1	400	35	40	20	60	1.51
Run Step 2	400	35	40	20	120	1.71
Run Step 3	400	35	40	20	180	1.89
Run Step 4	400	35	40	20	240	2.16
Run Step 5	400	35	40	20	300	2.79
Run Step 6	400	35	40	20	360	2.30
Run Step 7	400	35	40	20	420	2.14
CD(P=0.05)	-	-	-	-	-	0.25
Set III						
Run Step 1	400	40	45	20	60	1.66
Run Step 2	400	40	45	20	120	2.12
Run Step 3	400	40	45	20	180	2.26
Run Step 4	400	40	45	20	240	2.43
Run Step 5	400	40	45	20	300	2.44
Run Step 6	400	40	45	20	360	2.53
Run Step 7	400	40	45	20	420	2.47
CD(P=0.05)	-	-	-	-	-	0.15

However, in Set III the set of vessel temperature (Vt) 40 °C and valve temperature (Vlt) 45 °C showed the maximum aroma recovery of 2.43% in 240 minutes dynamic time compared to other sets of different run steps. The results of the three set of experimental performed in 8 run step on SFE apparatus are presented in Table 1 & Fig. 1, which indicated that the vessel pressure 400 bar and vessel temperature (Vt) 35°C and valve temperature (Vlt) 40°C in Set II, resulted significantly maximum aroma recovery of 2.79 % in 300 minutes among all the three set of run steps.

Fig: 1 Effect of dynamic time and temprature on aroma recovery of Nagpur mandarin peel under SFE condition



The maximum aroma recovery in Set III was found to be 2.53% at 360 minutes of dynamic time, 40°C vessel temperature (Vt) and 45°C valve temperature (Vlt) SFE operational condition but in Set I, it was found to be 1.53 % at 300 minutes dynamic time, 30 ° C Vt and 35 ° C Vlt operational condition. Thus the percent aroma recovery indicated that the operational condition in Set II run at 300 minutes of dynamic time was better than recovery at other dynamic time trials with very little changes in aroma recovery possibly due to the uniform blending of CO_2 in the peel samples as it was not proportionate increase in recovery as demonstrated in the study. In another study with mandarin peel has shown good yield at 60° C/ 90 bar operating condition (Atti Santos *et al*., 2005). The optimal operational conditions was based on the percentage of aroma extract indicated that this could be the optimum operational condition for optimum peel aroma extraction on reduced level of CO_2 gas and dynamic time. In almost all three set of trials, study indicated that increase in percent recovery was found to be increased with increase in dynamic time but significant changes were not observed in peel aroma recovery. As it was found to range between 0.26 to1.53%, 1.51 to 2.79% and 1.66 to 2.53% of aroma content in all 7 run step of Set I, II and III study, respectively. The pressure dependent extraction studies need to be continued in order to obtain the optimum SFE operating condition for temperature and pressure. Further ,the graphical presentation of aroma content between three sets of temperature 30˚C,35˚Cand 40˚C and varying degree of dynamic time indicated clearly that set II operating condition for peel aroma extraction was found to be superior over set III and set I operating condition under constant flow of CO_2 gas at supercritical state of analysis(Fig.1).

In general study indicated the operating conditions had shown the significant recovery in peel aroma extraction in all 8 run step of time set of experimentation but that of quantum yield recovery was found to be changes to reduce for set II and III respectively.

Extraction of peel oil

Based on the literature available information nationally and internationally, the vessel pressure (100 bars) and static time (30 min.) were kept constant for oil extraction all the time. The results of the four set of experimental condition performed in 9 run steps on SFE apparatus for corresponding recovery were shown in Table 2 & Fig.2. Which indicated that the operating conditions of 100 bar vessel pressure and 45^{o}C vessel temperature (Vt) and 50^{o}C valve temperature (Vlt) in set I yielded simultaneously 2.26 % peel oil in 350 minutes dynamic time followed by 1.81% in 300 minutes among all the four sets of 9 run step. However, in set II, III and IV of trials comparatively recovery was less than that of set I. The oil recovery trend showed that operating condition in set I was recorded to be superior to those in set II, III and IV, respectively. The maximum of 2.26% peel oil was extracted in 200 minutes of dynamic time. Similarly, other studies have shown good yield of lime oil with super critical extraction methods at operational conditions of 60^{o}C/ 90 bar pressure at 1 ml/min CO_2 flow rate for 30 minutes run time (Atti Santos *et al*., 2005). Study also indicated that number of run steps of set II, III and IV experimentation of operating condition showed such quantum of peel oil recovery in Nagpur mandarin fruits. On the contrary all these sets of operational condition showed the poor recovery ranges between 0.53 to 1.63%, 0.04 to 1.85% and 0.28 to 1.29% in set II, III and IV operating condition, respectively. In general the trend of peel oil recovery in set IV operating condition indicated that the increase in dynamic time had shown the increase in oil recovery to the maximum strength of 1.29% which was much lower than that of 2.26%, 1.63%, 1.85% in set I, set II and set III operating condition, respectively. It may be concluded that the optimum conditions for peel oil recovery was found to be 100 bar pressure, 45 ^{o}C (Vt), 50 ^{o}C Vlt., for 30 min static time and 350 min dynamic time.

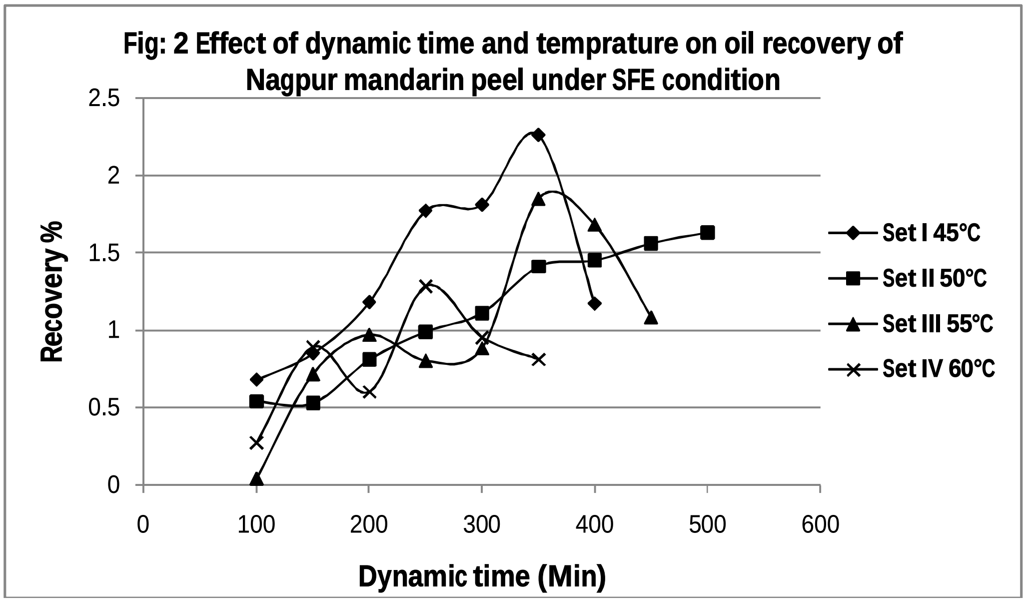
Further the graphical presentation between dynamic time and four sets of temperature at 45°C, 50°C, 55°C and 60°C of set I, II,III and IV under SFE condition showed maximum oil recovery between 150 to350 minutes of dynamic time .This is the dynamic time at which the highest peak of oil recovery was recorded except in set IV at vessel temperature 60°C which showed increasing trend of oil content with increase in dynamic time under constant flow of CO_2 gas at supercritical state of analysis(Fig.2).

CONCLUSION

During Super critical Fluid Extraction of Aroma/flavor and essential oil from Nagpur mandarin fruits (*C. reticulata* Blanco) peel, the solubility of CO_2 were found to be declined when the operating condition of dynamic time and temperature increases from 100-500 minutes and 30-50° C, respectively. The use of CO_2 at super critical state in this extraction has beneficial effect on the extractant yield and quality. Regarding the sensitivity of CO_2 to the high pressure and temperature, it is preferable to perform the extraction at temperature less than 45°C.

Table 2. Effect of different SFE operational condition on oil extraction from peel of Nagpur mandarin fruit.

Samples run steps for peel oil extraction	SFE Operational Conditions					
	Pressure (Bar)	Vessel Temp. (˚C) (Vt)	Valve Temp. (˚C) (Vat)	Static Time (min)	Dynamic Time (min)	Oil Recovery (%)
Set I						
Run Step 1	100	45	50	30	100	0.68
Run Step 2	100	45	50	30	150	0.85
Run Step 3	100	45	50	30	200	1.18
Run Step 4	100	45	50	30	250	1.77
Run Step 5	100	45	50	30	300	1.81
Run Step 6	100	45	50	30	350	2.26
Run Step 7	100	45	50	30	400	1.17
CD(P=0.05)	-	-	-	-	-	0.65
Set II						
Run Step 1	100	50	55	30	100	0.54
Run Step 2	100	50	55	30	150	0.53
Run Step 3	100	50	55	30	200	0.81
Run Step 4	100	50	55	30	250	0.99
Run Step 5	100	50	55	30	300	1.11
Run Step 6	100	50	55	30	350	1.41
Run Step 7	100	50	55	30	400	1.45
Run Step 8	100	50	55	30	450	1.63
Run Step 9	100	50	55	30	500	1.56
CD(P=0.05)	-	-	-	-	-	0.36
Set III						
Run Step 1	100	55	60	30	100	0.41
Run Step 2	100	55	60	30	150	0.72
Run Step 3	100	55	60	30	200	0.97
Run Step 4	100	55	60	30	250	0.80
Run Step 5	100	55	60	30	300	0.88
Run Step 6	100	55	60	30	350	1.85
Run Step 7	100	55	60	30	400	1.68
Run Step 8	100	55	60	30	450	1.08
CD(P=0.05)	-	-	-	-	-	0.33
Set IV						
Run Step1	100	60	60	30	100	0.28
Run Step2	100	60	60	30	150	0.89
Run Step3	100	60	60	30	200	0.60
Run Step4	100	60	60	30	250	1.29
Run Step5	100	60	60	30	300	0.96
Run Step6	100	60	60	30	350	0.81
CD(P=0.05)	-	-	-	-	-	0.40



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