EXTRACTING LYCOPENE FROM TOMATO POWDERS BY SUPERCRITICAL PROPANE AND CARBON DIOXIDE WITH INDUSTRIAL SCALE PILOT

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Abstract: A series of experiments were carried out to develop a method to extract lycopene from tomato powders by supercritical fluids CO_2 and propane. At first the operating conditions for CO_2 and propane were searched respectively in a laboratory instrument with 2L capacity extractor and one with 1L extractor. The influence of temperature, pressure, flowrate and powder size on the yields of oleoresin and lycopene recovery rate was studied. It was found both CO_2 and propane can effectively extract lycopene from tomato powders, but very high operating pressure are needed to get high enough lycopene recovery by CO_2. A pilot with 3*50L was then used to confirm CO_2 result, while a 3*300L pilot was applied to verify data for propane extraction. It was shown that laboratory results can be reproducible and lycopene could be recovered to 90% at optimized conditions. When different feeds were tested, lycopene content in extracts are found proportional to its content in feed but yields of lycopene resin does not vary much. The results show that extracting lycopene from tomato powders by supercritical propane under mild conditions may be a promising process.

Keywords: supercritical fluid extraction, lycopene, propane, industrial scale

Introduction

Lycopene, which has an intense red color, is the most abundant carotenoid in tomatoes, accounting for about 85% of the pigments present. Its concentration can vary considerably: from 30 to 200 mg/kg of fresh fruit or 430 to 2950 ppm on a dry basis. It has received great attention in recent years because of its beneficial effect in the treatment of diseases such as skin cancer [1] and prostate cancer [2]. Several recent studies including cell culture, animal and epidemiological investigations have indicated the effect of dietary lycopene in reducing the risk of chronic diseases such as cancer and coronary heart disease. At the plasma level, lycopene has be found to be incorporated in low-density lipoproteins in which it decreases the oxidation of cholesterol and of other lipids, thus preventing vascular damage. The antioxidant properties of lycopene and other mechanisms such as intercellar gap junction communication, hormonal and immune system modulation and metabolic pathways may also be involved [3].

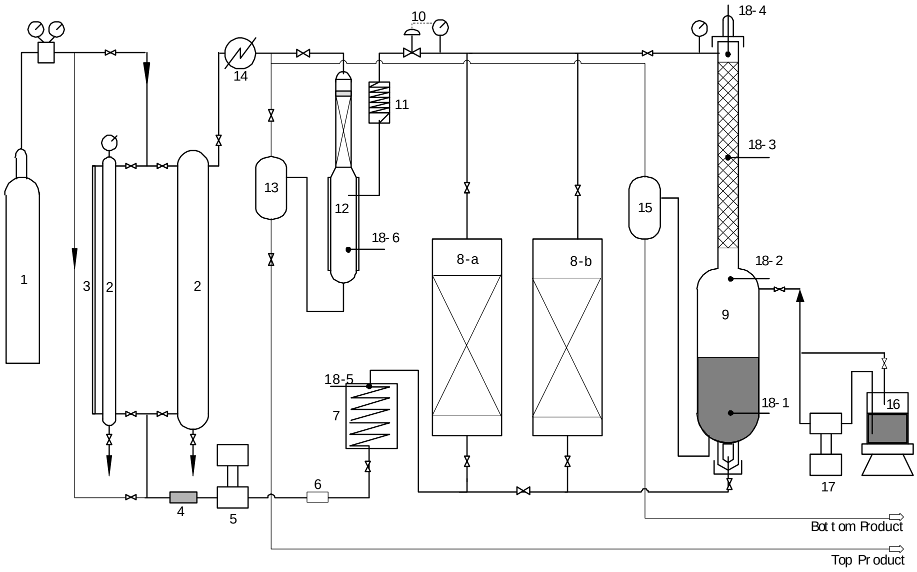
Lycopene can be extracted from the sources it occurs naturally by different extraction processes. A number of processes have been proposed and are currently used for the extraction of oleoresins, e.g., by using hexane as the extraction solvent [4]. The pulp obtained after the separation of waste materials and of tomato serum is fed to an extraction stage, where it is extracted to provide tomato oleoresin. Such oleoresin contains about 2-10% of lycopene, depending on the original concentration of lycopene in the tomato. However, evaporating organic solvent needs heating and Lycopene is thermally liable and also sensitive to light illumination [5].

Supercritical fluid extraction, showing many advantages, has been widely used in many fields. Carbon dioxide, a most popular supercritical solvent, can be used to extract thermally labile materials because of its low critical temperature. Extracting lycopene from dried ripe tomato skins and seeds by supercritical CO_2 has been carried out [6]. It was found at low temperature, even with high pressure up to 27MPa, lycopene could not be detected in the extract. High enough recovery rate for lycopene could be obtained with temperature up to 80? . Entrainers such as chloroform may help enhancing solving power of CO_2, but removing trace harmful entrainer from product is another problem.

Xin Jiang, locating in China Northwest, has very special geography and weather conditions, which favor producing many kinds of nutrition rich fruits. A few kinds of tomatoes are believed in the rank of highest lycopene content in world. Tomato industry has been well established there. This work was aimed at a possible utilization of the by-products of the tomato industry. In fact, the by-products such as wastes from the production of peeled tomatoes and tomato concentrate could be an excellent source. Propane, with mild critical temperature 96.7? and low critical pressure 4.25MPa, having strong solving power for non polar or weak polar compounds, was considered a proper solvent for extracting lycopene. As well, extraction by SC-CO_2 was carried out as comparison.

1. Experiments

Extracting lycopene oleoresins from tomato powders by propane were carried out in near critical and supercritical conditions with a 1L extractor instrument to search operating conditions for industrial pilot. The pilot is a self-designed multifunctional instrument with 2 *300L solid extractors and 1*300L liquid extractor. During operation for solid matrix, feed is packed in the autoclaves, solvent propane was pumped and preheated to desired temperature and pressure to the extractor. The product oleoresin was separated from propane in solvent recovery tower. Remained solvent is further stripped by nitrogen in top product collector to obtain final product. And a bottom product may also be obtained when liquid feed is handled. High purity propane(>99.5 wt%) was used, in which the only minorities are ethane and butane and no harmful substance exists. Supercritical CO_2 extracting lycopene from tomato powders was carried out in an instrument with 2L extractor and pilot with 2*50L in Xin Jiang University. A HPLC method for lycopene analysis in oleoresins was established as described in [7]. A supercritical fluid chromatograph (SFC) method was established as described in the proceedings. The HPLC method used mobile phase of methanol: THF: water=67:27:6 and Hpepersil BDS C_{18} (5μ) column with UV-Vis detection at 472nm. Both methods were found accurate.



1- N_2, 2- solvent cylinder, 3- solvent level indicator, 4- filter, 5- solvent pump, 6-flow rate meter , 7-preheater, 8-solid extractor, 9- liquid extractor with column, 10- back pressure adjust system, 11- heater, 12-solvent recovery tower, 13- top product collector, 14- cooler, 15-bottom product coillector, 16-liquid feed tank, 17-liquid feed pump, 18-thermal couple

Figure 1 Schematic flowsheet of 3*300L pilot

2. Results and Discussion

At the beginning, tests were designed to find pronounced factors influencing SFE by CO_2. Tomato powder size of 5, 20 and 60 mesh, extracting temperature of 30,40 and 50? and pressure of 15,25 and 35 MPa were chosen and cross combined. Table 1 illustrate that smaller powder size, higher temperature and pressure favor higher oleoresin yields. Small powder size will help overcoming mass transfer barrier while many researchers claimed there is no such barrier for SFE. The results show 60 mesh size, pressure at 35 MPa and temperature of 50 ? might be best combinations. In subsequent experiments 60 mesh powder size was used for SEF by CO_2. Figure 2 shows that oleoresin yield increases as pressure increase until 25MPa when extraction was carried out at 40? and run time 1.5hr. Further rising pressure will not get more oleoresin. Temperature was found having significant effect on extraction as shown in figure 3. Sufficient run time are necessary to obtain a complete recovery, see figure 4. In fact, the ratio of recycled solvent to feed (S/F) up to 90 (wt/wt) is necessary to get a full extraction of oleoresin.

Extracting lycopene oleoresin by subcritical and supercritical propane was then studied with one tomato feed containing less oleoresin. The powder size was kept 30 to 60 mesh. Lycopene content in feed was measured for each run. Data in table 2 show that extraction temperature up to 100? does not cause much lycopene loss. In fact, the recovery rate could reach 90% at higher temperature with more

Table 1 Influence of tomato power size and operating conditions on oleoresin yield

No	Pressure MPa	Temperature ?	Flow rate kg/ h	Powder size mesh	Oleoresin Yield, %
1	25	40	15	20	1.9
2	15	30	15	5	0.3
3	35	50	15	60	2.59
4	25	30	20	60	2.47
5	15	50	20	20	2.21
6	35	40	20	5	0.83
7	25	50	25	5	0.42
8	15	40	25	60	2.17
9	35	30	25	20	1.87

Note: Extraction time 1.5hr

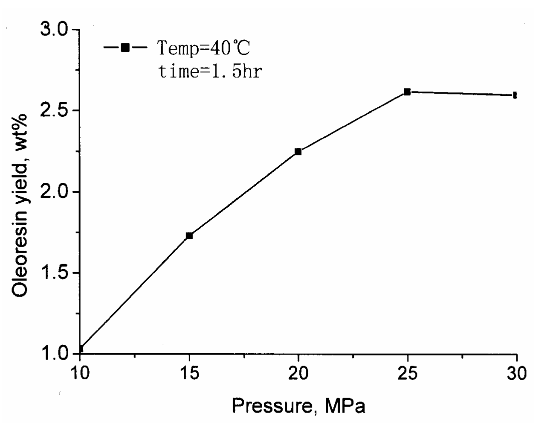


Figure 2 Pressure effects on oleoresin yield by CO_2

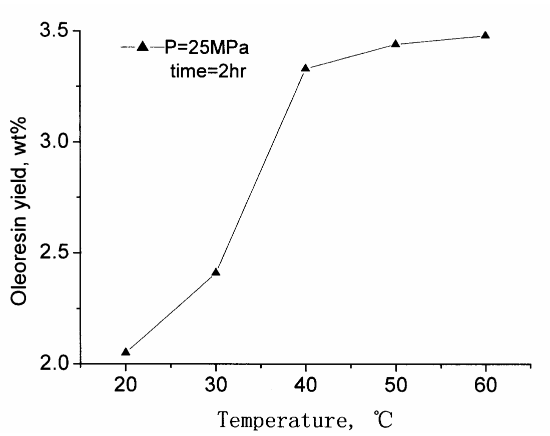


Figure 3 Temperature effects on oleoresin yield by CO_2

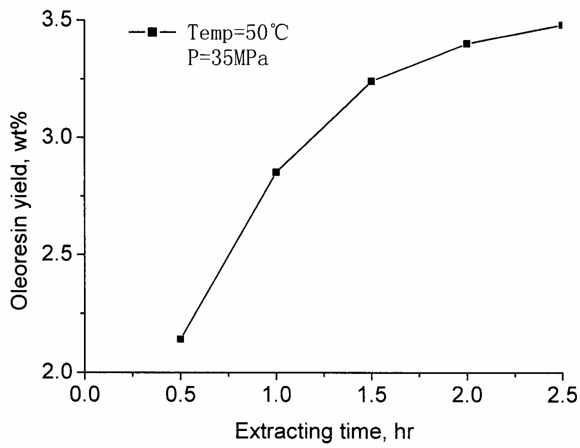


Figure 4 Oleoresin yield as a function of extraction time by CO_2

oleoresin produced. Oleoresin product contains lycopene 5.5 to 7.6wt%. But when the lycopene powder which contain 8wt% water was dried at 105 ? for 2 hour under vacuum to dry all the moisture out, the recovery rate reduces to only 56.3%. When moisture content was reduced to 5% at room temperature under vacuum, no significant reduction in both oleoresin yield and lycopene recovery is observed. Hence the reason is obvious that degradation occurs at higher temperature without protection of solvent. Because flow rate is limited by pump capacity to only 6L/hr, longer time was used. But corresponding S/F is 30(wt/wt) only, a much smaller number than 90 for SFE by CO_2. Hence, the operating conditions at temperature 100? and pressure 12 MPa and S/F 30 (wt/wt) might be an optimized condition for lycopene extraction by supercritical propane.

Table 2 Results for sub- and supercritical propane extraction

No.	Extr. Temp. ?	Pressure MPa	Time hr.	Yield %	Lycopene content wt %	Lycopene recovery wt%
l	60-100	15	4	1.47	5.5	93.8
2	80	5-12	5	1.00	6.6	82.5
3	100	5-12	5	1.40	7.6	83.2
4	60-100	5-12-15	6	1.40	5.9	88.8
5[a]	80	5-12	4	0.90	4.8	56.3

Note: a- sample was dried at 105 ? for 2 hr under vacuum.

3.2 Pilot tests

After optimized operating conditions had been set. Industrial scale tests were ran by using CO_2 and propane respectively. The data is listed in table 3. For propane, extraction was kept at l00? , pressure 12MPa. Necessary recycled solvent to get complete extraction was found much less than laboratory runs, a S/F 7.6

Table 3 Comparison of pilot tests

		CO_2		Propane	
		Lab.	Pilot	Lab.	Pilot
Feed	Mass(g)	400	65,000	300	100,000
	Lycopene content mg/ 100g	111	200	86	69.8
Oleoresin	Mass (g)	6.8	950	4.4	1350
	Lycopene content mg/ 100g	5440	12657	5500	4630
Residue	Mass (g)	393	64,000	295	97,800
	Lycopene content mg/ 100g	20	2.5	5.0	7.5
Oleoresin, %		1.7	1.46	1.47	1.35
Lycopene recovery rate, %		83	92.5	93.8	89.55

(wt/wt) being recorded. SFE with both solvents could obtain good recovery up to 90%

and oleoresin yield of 1.35 to 1.7wt%. But a number of S/F 50 (wt/wt) and high pressure up to 35MPa for CO_2 pilot tests was found necessary. Thus propane extraction could dramatically reduce the operating cost. The research also found that lycopene content in oleoresin is proportional to its content in feed. In fact, it is enriched 50 to 65 folds in oleoresin products. If the feed contain lycopene over 200 mg/100g, its content in oleoresin product could be over 10%.

3.Conclusion

Both supercritical CO_2 and propane could effectively extract lycopene from tomato powders by laboratory experiments and pilot tests. Higher temperature, pressure and longer run time or higher S/F favor high lycopene recovery. Small powder size may help overcoming mass transfer barrier. It was found that laboratory data could be reproducible in industrial experiments. Lycopene could be recovered 90% at optimized conditions, but its content in oleoresin is proportional to that in feed. As compared to CO_2 n, lycopene oleoresin extraction by propane could be realized under much lower pressure and smaller S/F, thus reducing operating cost efficiently.

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