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Kinetic Study of Supercritical Fluid Extraction of Essential oil from Cumin (C.*cyminum*) Seeds

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Abstract—*This study involves the evaluation of the performance of supercritical fluid extraction unit by extracting oil from cumin seeds using SC-CO_2 as a solvent in dynamic mode. The solubility of sample oils was studied at 45^0C & 50^0C temperature, 200-500 barpressure and 0.2l pm, 0.4l pm & 0.8l pm solvent flow rate.The study revealed that the temperature, pressure and solvent flow rate process parameters significantly affected the extraction rate. Composition of cumin seeds were analysed by GC-MS by equating their retention times with those of reference samples. A total of 7 fatty acids and 33 volatile compounds were identified in the oil obtained from cumin seeds by using supercritical fluid extraction.The sustainable conditions of 300 bar and 45°C allowed us to obtain the highest amount of extracted oil yield with maximum volatile content. The study of the results showed that at a very high pressure of 500 bar extraction yield was affected and clearly brought out possibility of loss of valuable compounds.*

1. INTRODUCTION

CUMIN (C. cyminum or JIRA), a native from the east Mediterranean to Indiais a flowering plant belonging to the family Apiaceae. It is used in the cuisines of many different cultures.Cumin seeds containstwo mericarps with a single seed along eight ridges with oil canals andare 4–5 mm (⅙–⅕ inch) in length [1]. For itscharacteristic flavour and aroma cumin seeds are used as a spice. Cumin has abundant medicinal benefits like protection against heart disease, poor digestion, tastelessness, vomiting, swellings and chronic fever along with many pharmacological effects such as anti-diabetic, anti-tumor, immunologic, anti-epileptic, and antimicrobial activities[2].A study by researchers at Mysore University in India reported the potential anti-diabetic properties of cumin [3].

Efraim Lev and Zohar Amar [4] reviewed the medicinal properties of cumin and stated that cumin seeds and warm jeera water is believed to improve saliva secretion, provide relief in digestive disorders.

The major volatile components of cumin seeds includes cuminaldehyde, cymene and terpenoids.The cumin seeds possesantioxidant activity due to the presence ofphenoliccompounds [5] and the antimicrobial and antifungal activity as well [6].Cumin seeds contain more than hundred different volatile components like γ-terpinene, safranal, p-cymene andβ-pinenewhich have different useful properties discussed in various studies.SFE is an alternative process to traditionally used solvent extraction and hydrodistillation techniques which suffer from several diadvantages as essential oils undergo chemical alteration and results in loss of some heat sensitive compounds. Using solvents like CO_2, water and ethanol under pressure offers safety and economical processing for the extraction of several essential oils, volatile components from natural products [7].Supercritical fluids produces solvent residue free products and has very less processing cost in comparison to other methods.The aim of this research work was to extract essential oil from cumin (*Cuminumcyminum)* by supercritical fluid extraction method.The influence of extraction conditions on yield and volatile oil composition of cumin seeds has been discussed in this paper.

2. MATERIALS AND METHODS

2.1 Plant material

C. cyminum(cumin) seeds were collected from the local market of Aligarh (U.P), India.Cleaned seeds were pulverized into a fine powder before extraction to enhance the extraction efficiency and the powder was sealed and stored at a room temperature 25°C for further use.

2.2 Chemicals

Food grade CO_2 cylinder (99.9% purity) was obtained from Trilok Gases Company Aligarh (U.P), India.

2.3 Supercritical fluid extraction procedures

The extraction experiments were carried out in a high pressure laboratory scale extractor (M/S Applied Separation, Pennsylvania18101, USA), capable of working to the maximum pressure of 10,000 psig and at temperatures up to 240°C. Food grade CO_2 was pumped into the system by diaphragm pump until to set required pressure. The extraction unit also contains heat exchanger to heat to the specific temperature, flow meter to monitor the flow rate of CO_2 circulating in the system, manometers for flow Control and valves.Experiments were carried out at 200, 250& 300 bar pressure and 45, 50°C temperature with solvent flow rate of 0.2, 0.4, 0.8 lpm.

2.4 Determination of SC-CO_2 extract yield

The extraction yield (*Y*) in supercritical carbon dioxide extraction (SC-CO2) was calculated by equation:

$$\% \, Yield = \frac{\text{Mass of extract} * \ (\text{g})x\ 100}{Mass\ of\ raw\ material\ (g)}$$

Mass of extract = wt of sample initially – wt of sample after extraction*

***% Error** or lost during extraction is calculated by:*

$$= \frac{(wt. of\ sample\ before\ extraction - wt. of\ sample\ after\ extraction) - \ wt. of\ extract}{(wt. of\ sample\ before\ extraction - wt. of\ sample\ after\ extraction)}$$

2.5 Chromatographic analysis

The analysis of volatile components and essential fatty acids in the sample were analysed in the Instrument- GC-MS (Agilent technology) GC- Model 7890, MS- Model5975. The chromatographic analysis for both volatiles and fatty acidswas done using DB-WAX (30M×250μm×0.25mm) column. The oven temperatureprogram was a 1-5 C/min temperature rampfrom 60˚ to 200˚C for analyses of volatile and 1-13C/mintemperature ramp from 60˚ to 240˚C for fatty acid profile analyses present in the extract with inletheater temperature 240 and pressure-8.2 psi.

3. RESULT AND DISCUSSION

SFE KINETICS

Experiment was carried out at two different temperature 45^{0}C & 50^{0}C at constant solvent flow rate of 0.2 lpm (leter per minute) by varying pressure from 200 bar to 500 bar. Percentage yield and error lost during process were calculated during each experiment [Table 1].The results showed that highest yield obtained was 14.3% at 45^{0}C temperature, 300 bar pressure and solvent flow rate of 0.2 lpm.

Table 1: Calculated Percentage yield and Error in different experimental condition during SFE of cumin

Mass of extract = 40 gm					
Solvent flow rate = 0.2 lpm					
Exp.no	**P (bar)**	**% yield at T = 450C**	**% yield at T = 500C**	**% Error at T = 450C**	**% Error at T = 500C**
1	200	12.46	11.91	7.4	10.69
2	250	13.19	12.37	5.86	9.93
3	300	14.3	12.55	4.17	12.63
4	400	12.89	12.64	6.49	11.69
5	500	11.86	12.32	4.63	8.44

3.1 Effect of pressure on extraction rate and % yield of extract

Fig.1 & 2 shows the effect of change in pressure on the extraction rate and % yield at constant temperature of 45°C and 50°C respectively at constant volumetric flow rate of 0.2 lpm. The figure clearly shows that increase in pressure from 200 bar to 300 bar, resulted in increased extraction rate. At given temperatures,solubility of oil in the solvent increased with increase in the extraction pressure due to increase in the solvent density which results in increased extraction rate [7 & 8].But at higher temperature of 50^{0}C percentage yield of extract was decreased due to the loss of some volatile compounds.

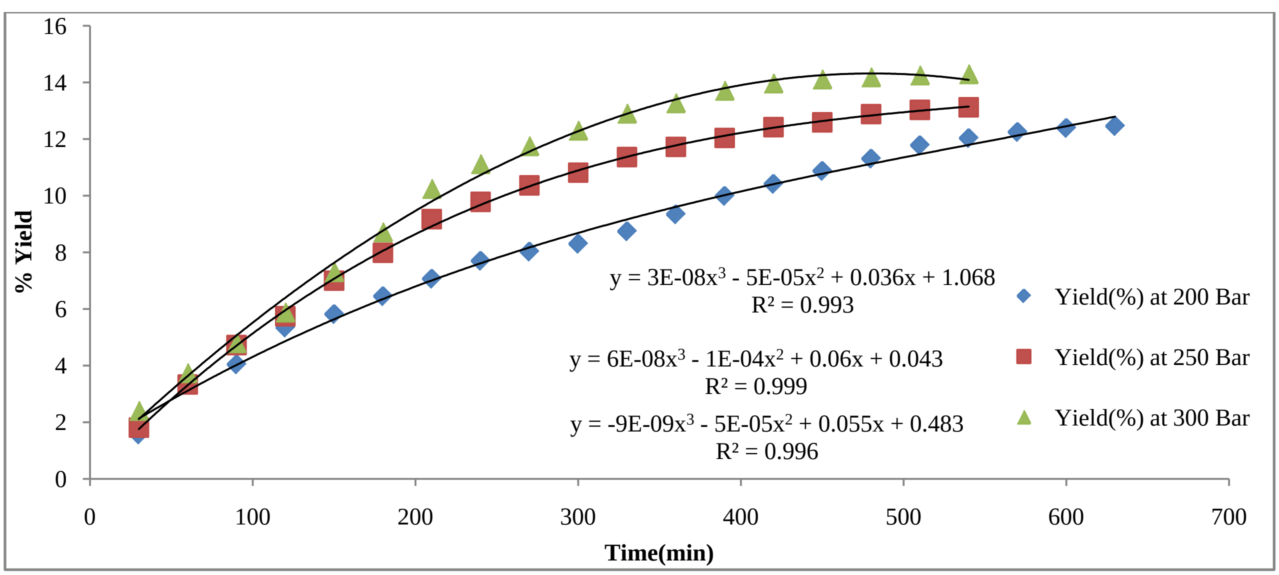

Fig. 1: Accumulated yield of extraction obtained through SFE of CUMIN at 45^{0}C and 200, 250, 300 bar Pressure.

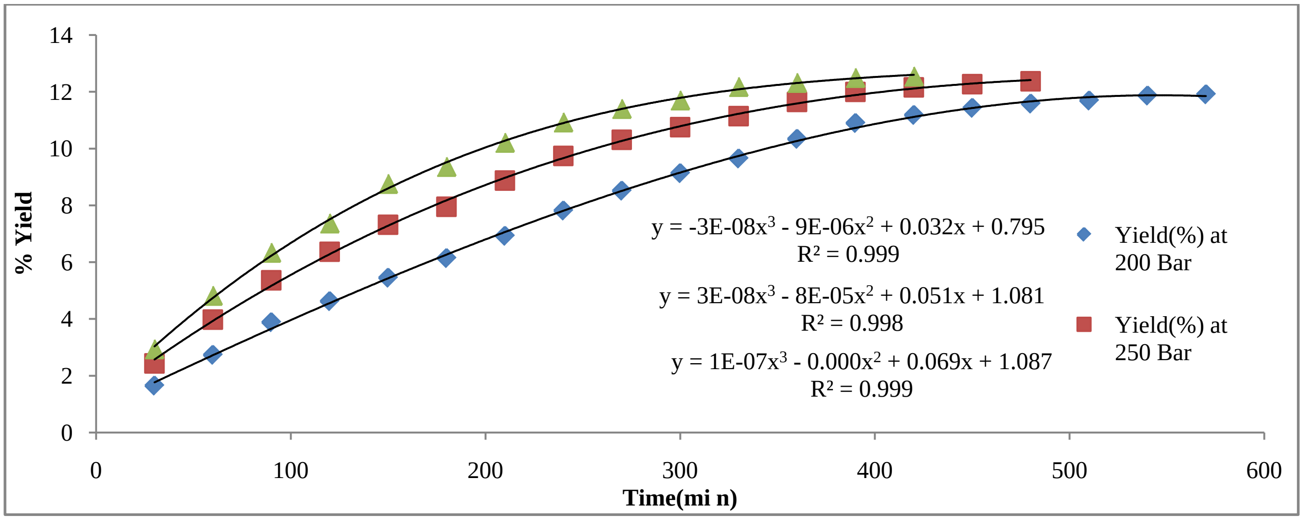

Fig. 2: Accumulated yield of extraction obtained through SFE of CUMIN at 50^{0}C and varying pressure of 200,250 & 300 bar.

The fig. 3 & 4 represents the curves obtained at 45^{0}C & 50^{0}C temperature and 300-500 bar pressure. Both the figures and Table 1 shows that with pressure increase up to 500 bar at constant temperature, percentage yield of extract was decreased because at higher pressure weak bonds between atoms gets ruptured which in turn resulted in loss of different pressure sensitive compounds. Loss of compounds also favoured by Lee-Chatelier's principal [9],which states that on applying pressure system gets disturbed and trys to minimize the effect of pressure and decrease the volume thus system favoures the loss of compounds.

3.2 Effect of temperature on extraction rate and % yield of extract

Fig 3, Fig 4 & Fig 5shows the effect of temperature on extraction rate at constant pressure of 200 bar, 250 bar & 300 bar respectively. The figures depicts that with increase in temperature from 45°C to 50°C extraction yield decreased due to the loss of some temperature sensitive volatile compounds whereas extraction rate increased at higher temperature. Li *et al.* [10]andP. Maheshwari[11] investigated that the extraction rate increased with increase in temperature at 25 MPa (250 bar) or aboveWith an increase in temperature the extraction rate increases due to increase in solubility of oil in the solvent. These compounds on forming solution with solvent absorbs heat i.e. the process is endothermic and thus by Lee-Chatelier's principle [9] as the temperature increased, solubility increased and hence extraction rate increased.

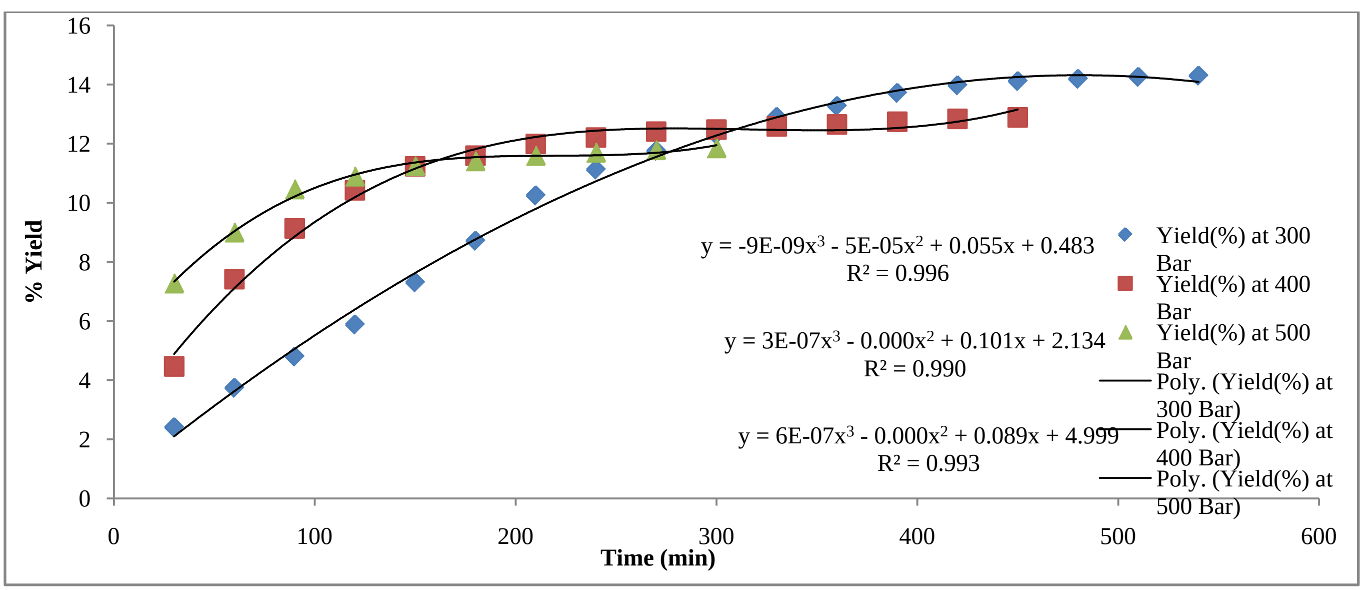

Fig. 3: Accumulated yield of extract obtained through SFE of CUMIN at 45^{0}C and varying pressure of 300,400 & 500 bar.

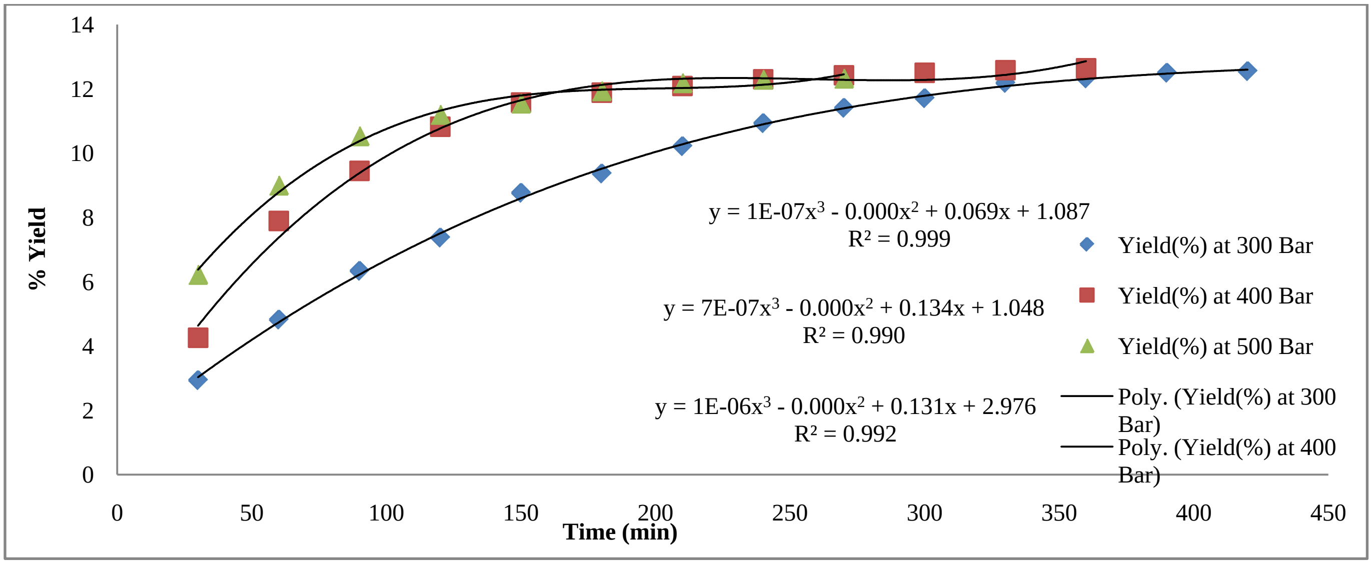

Fig. 4: Accumulated yield of extract obtained through SFE of CUMIN at 50^{0}C and varying pressure of 300,400 & 500 bar.

At very higher pressure of 500 bar when the temperature increased from 45^{o}C to 50^{o}C, % yield of extract slightly increased(fig8 & 9) because at this higher temperature-pressure combination solubility of fatty acids in the solvent increased. At this higher pressure temperature combination solubility of fatty acid were increased due to the higher bond polarisation between the atoms which enhance the solute – solvent interaction [12].

4.3 Effect of Solvent flow rate on extraction rate and % yield of extract

Fig 4.10 presents the effect of solvent flow rate on the extraction rate of cumin oil and the effect was measured at 45^{0}C temperature and pressure of 300 bar. The figure depicts that as the solvent rate increased from 0.2 to 0.8 lpm extraction rate increased because the concentration driving force between solute and solvent phase got increased [13&14].Thus from the kinetic study of the SFE ofcumin it is clear that the operating parameters such as temperature, pressure and solvent flow rate did affect the extraction rate and the process yield and thus these parameters must be carefully determined for the maintenance of quality aspects of the product (extract) and the process efficiency.

4.4 Qualitative and Quantitative analysis of sample

Highest yield of cumin oil was obtained at P = 300 bar and T = 45^0 C and this sample was analysed with GC/MS (Chromatogram 4a & 4b). The result of GC/MS analysis of the extract obtained from cumin oil contained saturated, unsaturated fatty acids and organic volatiles which were analysed by comparing their retention times with those of reference samples (4c). The composition of the oil with maximum % yield obtained from the seeds contained around 33 different volatile components and their concentration varied by changing experimental temperature & pressure conditions. Volatile oil of the extract contained 6 important compounds namely o-Cymene (Benzene, 1-methyl-2-(1-methylethyl)-), γ-Terpinene [1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-], α-pinene, cis-β-Terpineol [Cyclohexanol, 1-methyl-4-(1-methylethenyl)-], cis limonene, 1-Terpinenol [3-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-] and γ-Terpinene [1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-], o-Cymene[Benzene, 1-methyl-2-(1-methylethyl)-] p-Cumic aldehydes Benzaldehyde p-isopropyl, α,β-Dihydroxyethylbenzene/ 1,2-Ethanediol, 1-phenyl-/ Styrene glycol, p-Cymen-7-ol were present in highest amount.

The fatty acid compositions (% of total fatty acid) of extract of cumin oil are shown in Table 5.The most abundant fatty acid present in cumin extract was oleic acid (C18:1) which gave 64.18% of total fatty acid. The other major fatty acids was linoleic acid (C18:2), which produced the 30% of total fatty acids. From the results obtained, the major fatty acids of cumin oil were palmitic acid (4.5%), stearic acid (0.87%) and butyric acid (0.3%) as saturated fatty acids. Furthermore, linoleic acid (30%), α- linoleic acid (0.2%) and oleic acid (64.18%) were the main unsaturated fatty acids. The total amount of saturated fatty acid was 5.67% and total amount of unsaturated acid was 94.61% in which 64.18% was mono unsaturated while 30.2% was poly unsaturated acids.

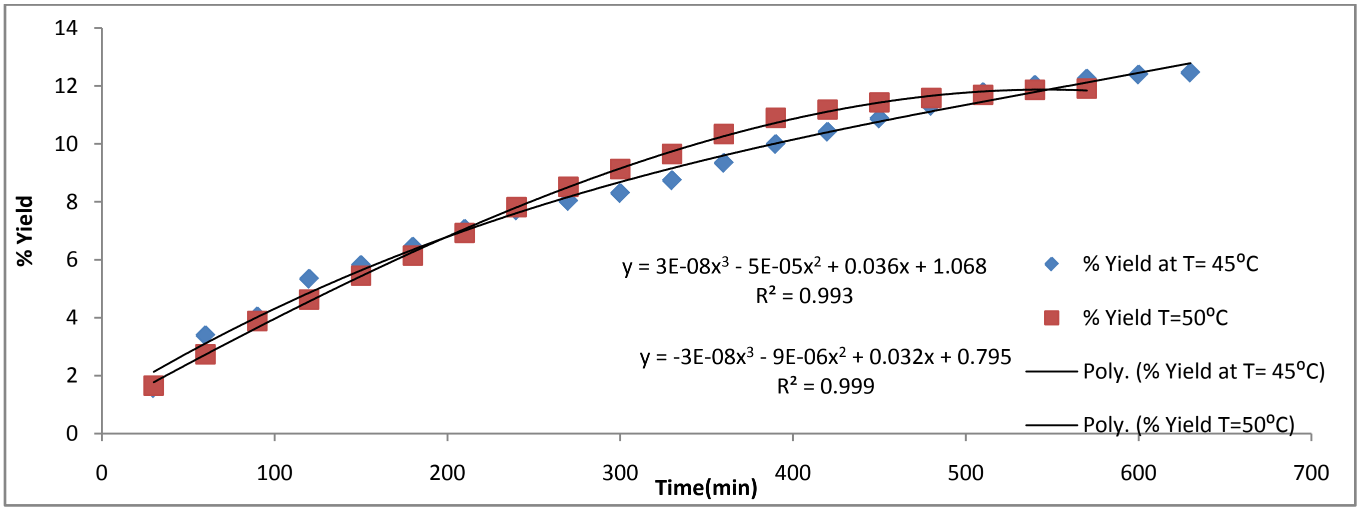

Fig. 5: Accumulated yield of extraction obtained through SFE of CUMIN at 200 bar pressure and 45°C & 50°C temperature.

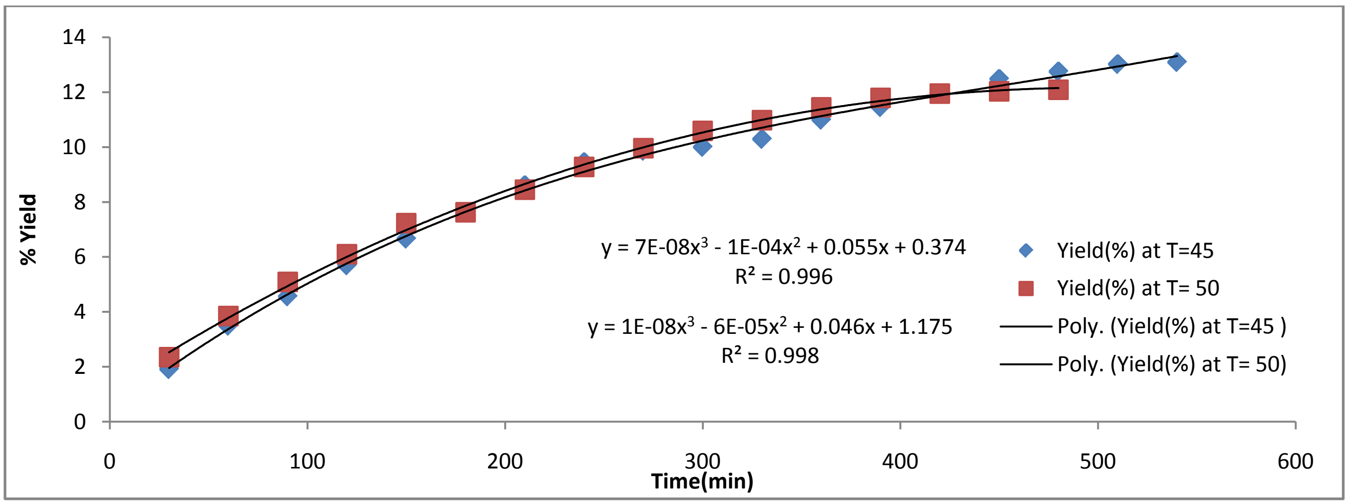

Fig. 6: Accumulated yield of extraction Obtained through SFE of CUMINat 250 bar pressure and 45°C & 50°C temperature.

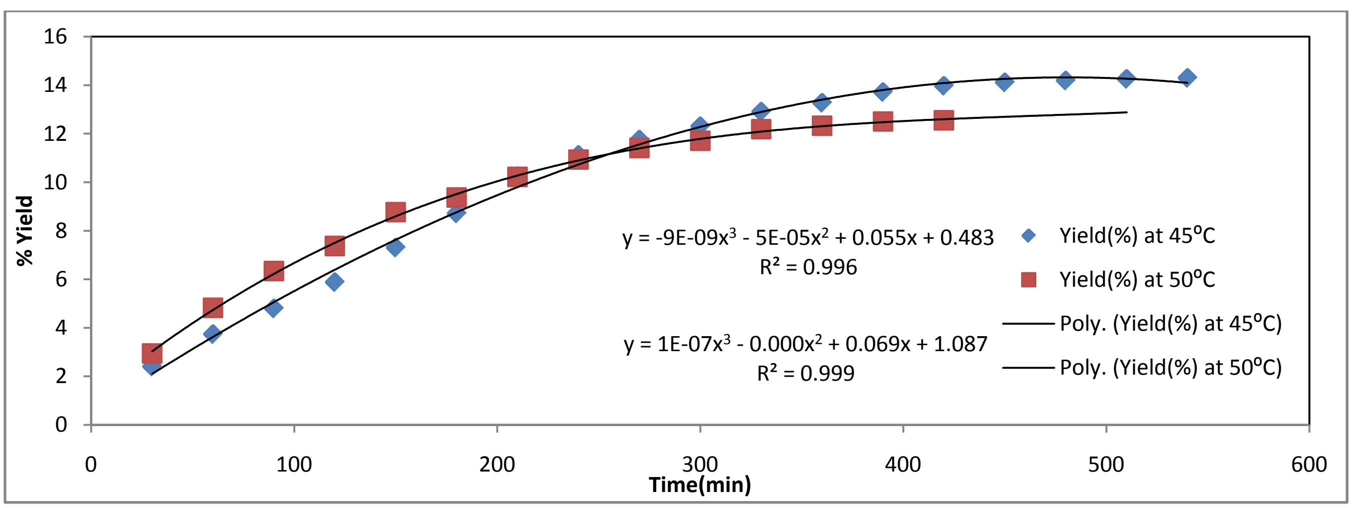

Fig. 7: Accumulated yield of extraction obtained through SFE of CUMIN at 300 bar pressure and 45°C & 50°C temperature.

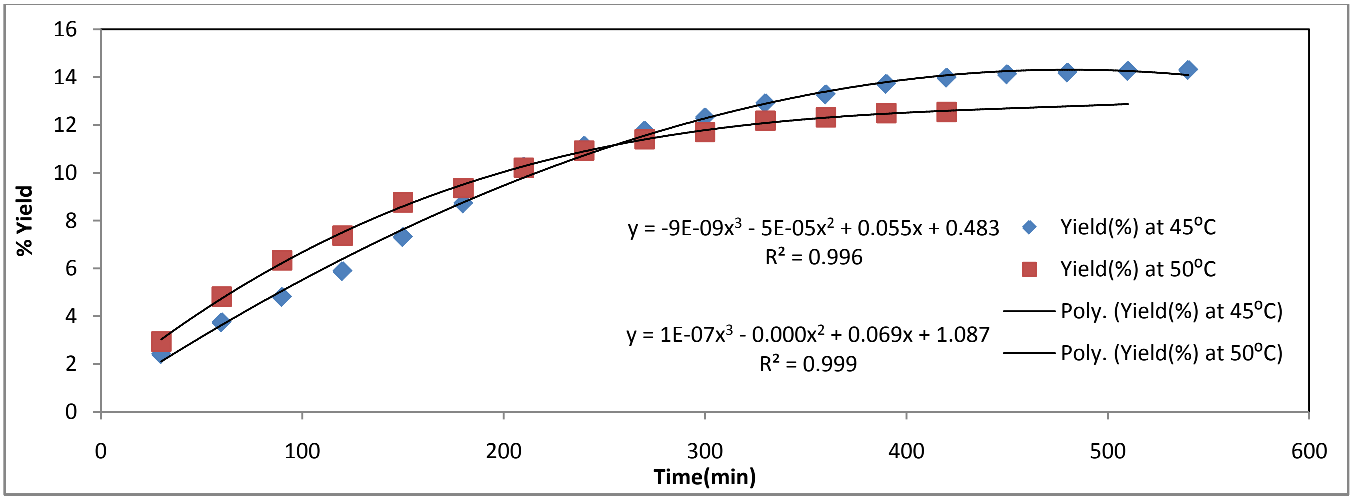

Fig. 8: Accumulated yield of extract obtained through SFE of CUMIN at 50^{0}C and varying pressure of 300,400 & 500 bar.

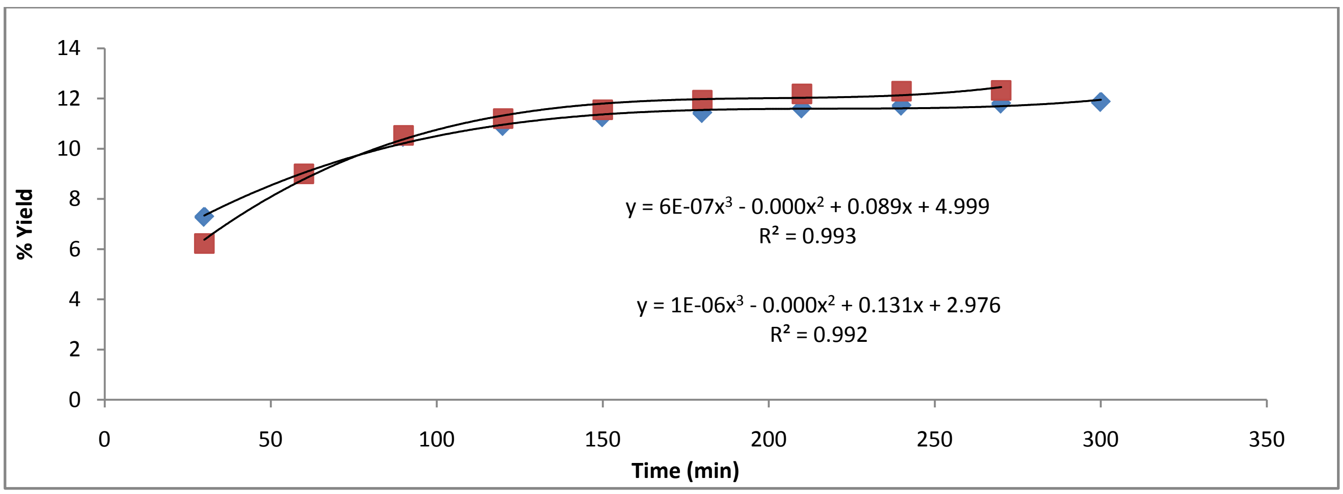

Fig.9 Accumulated yield of extract obtained through SFE of CUMIN at 500 bar Pressure and 45^{o}C & 50^{o}C temperature.

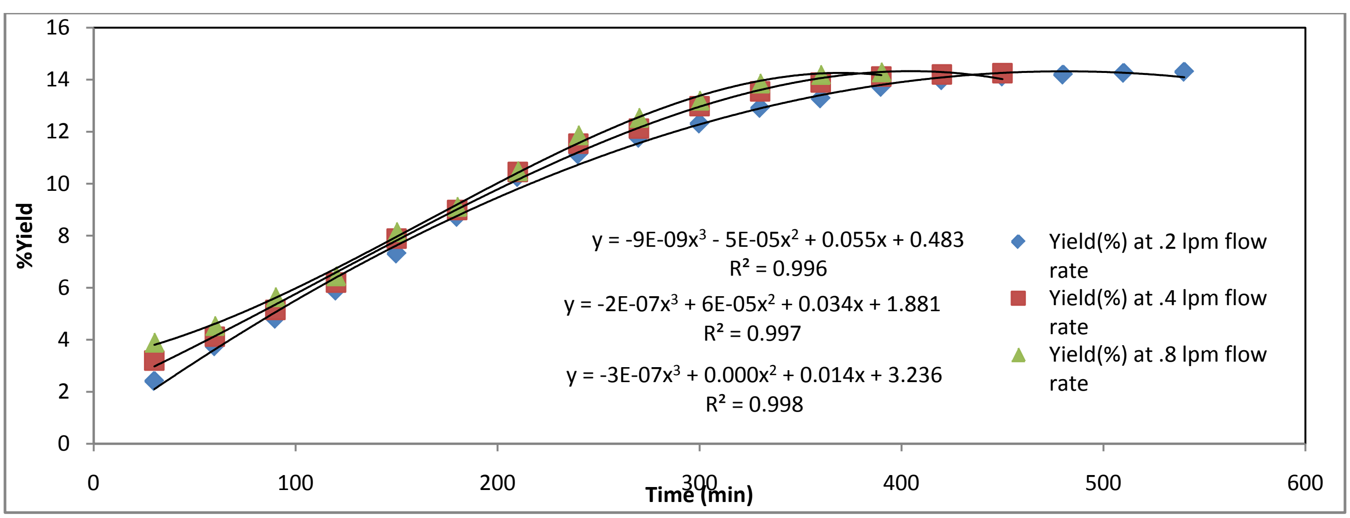

Fig. 10: Effect of flow rate on extraction rate at *T* = 45^{0}C K; *P* = 300 bar.

4. CONCLUSION

This study has brought out the possibilities to obtain higher percentage of volatiles through supercritical fluid extraction.From this study it is clear that the condition of 45^0C, 300 bar and solvent flow rate of 0.2 lpm were the favorable condition for the extraction of cumin oil which allowed us the extraction of highest quantity of cumin oil with maximum amount of valuable volatile compounds like γ-Terpinene, α-pinene and cis limonene.Thus from this study we conclude that on increasing pressure, extraction rate was increased and overall extraction yield was not affected up to 400 bar but at 450 bar or above extraction yield was decreased.On increasing temperature, extraction rate was increased while extraction yield was decreased.Extraction rate was increased by increasing solvent flow rate.Extraction of cumin should not be performed at a very high pressure of 500 bar because it effects the extraction yield and clearly brought out possibility of loss of valuable compounds as depicted from the results.

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