Estimate Solubility of Canola oil (Oleic Acid) in Supercritical Carbon dioxide - Experimental and Modeling

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Abstract: Extraction by using supercritical fluids is one of the procedures for separating specific substances which are not separable by common methods. (Like separating bimolecular from foods).one of the most important properties of bimolecular which makes using supercritical fluids method useful to separate them is great change of solubility in supercritical solvents with change in pressure and temperature. Intermolecular energy parameters, critical properties, acenteric factor, and molecular interactions are some parameters that restrict us in using thermodynamic simple equations in modeling supercritical interactions. In this research, four state equations (third order) was used in modeling colza oil extraction (oleic oily acid) by supercritical carbon dioxide that consisted of Vandervalse, Redlish-Quang,Ping-Robinson and Mohsen nia-Mansori- Modares(MMM) corrected equation. [Journal of American Science 2010;6(10):606-611]. (ISSN: 1545-1003).

Keywords: Supercritical fluid, Extraction, Canola Oil, Thermodynamic model.

1. Introduction

Fluids in super critical condition have some properties which in some aspects are like gas and in some other aspects are like liquid. A super critical fluid is like a liquid in some physical properties such Density and in some transition properties such permeability, viscosity and low surface tension is like a liquid [1]. Supercritical fluids because of low viscosity and high permeability solve all the substances in specific pressure and temperature in supercritical region and because of high volatility separated simply from extracted substances.

One of the specific properties of supercritical solvent is high isothermal compressibility of them in compare to liquids, while those are same to liquids in density. Good solvability for supercritical fluid is cause high density of them. Moreover, with change in pressure and temperature, we can change the solubility of this in a broad range. For this purpose, after solving the extracted substance in solvent, we can separate it from solvent by change in pressure or operational temperature under critical point. Also, with use of supercritical fluids with low critical temperature, we can extract substances which are sensible to temperature (like medicinal material in foods) without any destruction. Carbon dioxide gas is used as supercritical solvent in extraction processes because of non flammable and non poisonous properties, inexpensiveness, availability and low supercritical condition and is one of the most common and appropriate substances gas. Thus, with regard to these properties, an appropriable potential is used for this kind of fluid (especially carbon dioxide) in separation process. Therefore, considering these special properties of supercritical fluids we use from extrication system with supercritical fluids (SCFE-supercritical fluid extrication) to extract and separate some specific, sensible, expensive, scarce subschema, this is an appropriate method.

2. Application of supercritical extraction

In early of 1970s, energy price increase unexpectedly, because of some events in the world that it was a great problem for industrial countries.

Therefore most of the research centers and universities, concentrated on processes with lower energy consumptions. Use of supercritical fluids to separating and extraction of plant extract was one of these processes. In this process, solvent recycle is performed by using of sudden expansion, and for example, such liquid- liquid extraction, there is no need of distillation operation (sox ell operation) thus this subject is due to considerable decrease in energy consumption and also high quality of extracted substance. Some of diverse usages of supercritical technology are:

Pharmaceutical industry, Bioenvironmental industry, food industry, such as oily extract, Medicinal and herbal extract (subject of this research), Protein, vitamin, and….

In this research, oil extraction from oily extract from colza oily grain (canola) has been investigated.

Plant oils, from the health protection and adoption to human body, have priority over animal oils because they have a lot of unsaturated oily acids

and those are considerable especially in recent decade. Generally plant oils extract from corn, Soya, canola, sunflower, olive, safflower, and grape seeds.

In comparison with oil extracted from these seeds, with increase in saturated oily acids, the quality of that oil and it's resistance against temperature rise, will be increase. Also, from an economical point of view, the amount of oil in oily grain is of special importance. In selecting a high quality oily grain for oil extraction, some important factors such as quality of oil from physical and chemical point of view, the amount of oil in oily grain, easy extraction, inexpensiveness of oily grain, easiness in planting seeds, availability in all seasons are importance. Colza in European language is famous with these names: rapeseed, colza and raps.

Oily colza is the most important species of brassica type and probably wild species of it limited to Europe and North Africa.

The most probable habitation of it is where brassica campetris and brassica oleraces overacts grew adjacent, since, canola (brassica napus) is created by compounding these two species and equalize hypoid chromosome. In remainder trace of Neolithic age in Egypt and in hendo writing, which is found between 1500 - 2000 AD, and especially in Greece, Rome and Chinese inscriptions, which is remained from 200-500AD, refer to oily plants of brassica species their medicinal valve.

Canola oily grain entered Iran in last year's. And several researches have done on it. In recent years, because of more attention and advances in under cultivation canola, the amount of it shows considerable increase and in 2001, 2002, under cultivation of canola reaches 70000 heaters.

Specific characteristic and adoption of canola to different climatic, made this product more important and it is a promising product in providing necessary edible oils in our country. In this regard we can say:

- ✓ We can cultivate canola with barley and wheat, which cause decrease in plant disease and weeds and also increase in seeds Activity.
- ✓ Autumn and winter and moderate types provide possibility of cultivating canola in different climate.
- ✓ In autumn cultivation need less irrigation and rain and raining in autumn and winter is enough for it.
- ✓ Canola has a high activate, potential and among oily grain has the highest oil (40 to 45 percent).
- ✓ In rice field, after harvesting the rice, we can use cultivable premature colza.
- ✓ Growth season of canola is different from other oily grains, and when extraction units are out of capacity, this plant harvested.
- ✓ Because canola harvest is early in summer, we can use the land for cultivating wheat.
- ✓ With right managing and use of simple methods, provide possibility of cultivating, storage, and harvest, in different conditions and with local facilities.
- ✓ This plant is useful because of favorable plant leftover and positive effect on amount of organic matter of soil in providing required provender for farmers.
- ✓ This plant has important role in expansion of beekeeping industry.
- ✓ Canola is an autumn plant and don't compete with spring profitable products. Lack of water in some regions, make cultivating premature canola a good choice and solve the problem of shortage of water.
- ✓ With cultivating premature canola in dry farming regions that have appropriate rain in autumn and dryness in spring. There is a better result of cultivating.

Considering mentioned instances, canola oily grain because of high oil percentage, high physical and chemical quality, inexpensiveness, high under cultivating in all seasons and all regions, was subject of attention in recent years. Here we compare the extracted oil of some oily grains with each others.

As you see in table 4 Canola oil with 94% unsaturated fatty oil, has highest quality and high edible value among other foods.

Most of the oily grains have 12 to 65 percent of oil and with regard to existence of oil in oily grains, to extract this oil, two methods of extraction by press and extraction by solvents was used. For grains that have more than 20 percents oil, only extraction by solvent was used and for grains with high percent of oil, first extraction by press and then extraction by solvent was used. In fact, the mechanism of extraction process, is like leaching of extracting inside solid by liquid (solvent) and it means that oil before that solvent solubility that is hexane normal is not saturated in it and exit of porosities of oily grains and when solubility in hexane is saturating, an equilibrium existed between outside liquids (Misla) and liquid inside solid (oil and misla), so that oil molecules enter solid phase.

Two basis methods of immersion and percolation were used to extract oil. Factors such as temperature, time of extraction, amount of solvent, grain humidity, geometric figure, and size of flake particles effect on extraction process. One of the most important problems in using this method is use of poisonous solvent of normal hexane and

inseparability of oil from denude phase of process (sox ell) and this process cause small amount of hexane normal enter the extracted oil and cause low quality of it. In extracting method by supercritical fluids cause of complete separating of carbon dioxide (solvent) from extracted oil, gain high quality of oil and healthiness of it. Thus, in this research, we want to use a thermodynamic model, calculate best condition of oil extraction from colza grain, and compare suggested model with experimental data. To extract experimental data from supercritical fluids extractions, this equipment is designed (SCFE-supercritical fluids extractions).

3. Experimental pilot plant and experiments

The following picture indicate supercritical extraction pilot which was used in this research. This apparatus was used to extract liquid from solid in supercritical conditions. This apparatus also has capacity to work in 1000 Psi pressure and temperature of 100 degree of centigrade. As you saw in figure, this apparatus has capacity to work in dynamic and static conditions with distinct characteristics. In designing and manufacturing this experimental pilot, specific capacity was planned such as:

1: Possibility of work in dynamic and static conditions

2: Possibility of observing how supercritical phase forms considering specific design of extraction container (equipped with lateral glass)

3: Great decrease in energy consumption in addition not using of compressor to compress the solvent.

4: Possibility of changes in operational condition and simultaneous sampling without need to opening the system.

5: Unique designs of high pressure pump to move supercritical fluids in two phase state.

6: Lack of pressure oscillation in system with regard to unique design of pressure supplying system in pilot

7: Possibility of change in solvent flow rate with the use of setting approaches of pump.

In this research with the extraction equipment, more than 50 experimental data in relation to extraction of oil from canola oily grain by supercritical carbon dioxide solvent were obtained which was in different operational conditions, temperature of 35 to 60 degree of centigrade, pressure of 1500 to 2750 Psi, supercritical carbon dioxide flow rate of 2 lit/min to 7/5 lit/min, size of colza oily particles 80 to 200 micrometer, and after data evaluating, size of 120 micrometer, solvent flow rate of 5/5 lit/min, pressure of 2250 Psi and temperature of 55 degree of centigrade, was specified as the best most appropriate operational condition in extracting. In table 1, experimental data has shown.

4.Thermodynamic modeling

To estimate phase equilibrium between supercritical phase and extracted phase (density phase), knowing the fugacity coefficients of each component in each phase is necessary. The solubility of extracted substances in gas phase in sup ercritical conditions (y_i) was calculated from below equation [walas 1985]:

$$y_i = \left(\frac{P_i^{sat}}{P}\right)\left(\frac{\phi_i^S}{\phi_i^V}\right)\exp\left\{\int_{P_i^{sat}}^{P}\frac{v_i^S}{RT}\,dP\right\} \qquad (1)$$

To simplifying this formula, we assume that supercritical solvent dose not solve in density phase at all. Saturated pressure of extracted substances (density phase) was very low (P_i^{sat}) and thus we can assume the fugacity coefficient is one $(\phi_i^S \approx 1)$

If we assume that molar volume of density phase (υ_i^S) is independent of pressure, equation 1 changes to this equation:

$$y_i = \left(\frac{P_i^{sat}}{\phi_i^V P}\right)\exp\left\{\frac{v_i^S(P-P_i^{sat})}{RT}\right\} \qquad (2)$$

Fugacity coefficient of extracted substances in gas phase (ϕ_i^V) was shown by using thermodynamic state equation in this equation:

$$RT\ln\phi_i^V = \int_V^\infty\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \frac{RT}{V}\right]dV - RT\ln Z \qquad (3)$$

Which in this equation:

$$Z = P\upsilon/RT$$

In table 2, three types of thermodynamic state equations (third order) listed to calculate fugacity coefficient.

Considering present component of canola oil based on analysis on extracted sample, more than 85% of canola oil components are oleic acid. Thus in this research, we assume that colza oil is single part and all the physical and chemical parameters and is equal to oleic acid.

Considering present data, supercritical properties of oleic acid and carbon dioxide is presented in table 2.

Critical properties of oleic acid were calculated by using JOBACK method, and υ^S obtained from Schulz reference (1991). To

calculate oleic acid gas pressure, the method presented by Hasan Orbey (1998) and final formula was explained as this:

$$Lnp^{Sat} = 21.45008842 - 158003.0917 / T^{1.5} \quad (4)$$

That in this formula, gas pressure was based on Pascal and temperature was based on Kelvin. Also to calculate oleic acid density, JAVA method was used. All critical properties of carbon dioxide were obtained from TRC reference. Finally with using thermodynamic state equations and applying correction factor on MMM state equation solubility of oleic acid in supercritical carbon dioxide solvent is estimated and compare with experimental data.

5. Discussions

Considering experimental data with using data mathematics conformity with MMM model, all coefficients in equation is investigated and finally equation explained as this:

$$C-MMM: P = \frac{RT(\upsilon+1.4286b)}{\upsilon-b} - \frac{a}{T^{0.5}\upsilon(\upsilon+\sum y_i b_{ii})}, \quad a = \sum_i \sum_j y_i y_j a_{ij}, \quad b = 0.25(3\sum_i \sum_j y_i y_j b_{ij} + \sum y_i b_{ii})$$

$$a_{ii} = 0.48748R^2T_{cii}^{2.5}/P_{cii}, \quad b_{ii} = 0.064623RT_{cii}/P_{cii} \quad (5)$$

With regard to corrected state equation, solubility of oleic acid in supercritical carbon dioxide with using state equations VdW ،RK ،PNG ،MMM ، C-MMM estimated and calculated and obtained result compare with experimental data shown in Fig1 and Fig2.

As you can see in Figure 1 and 2, in high pressure, solubility of oleic acid in carbon dioxide with high temperature has little changes and solubility is under control the pressure completely.

The reason of this is increase in neighborhood number in high pressure and tangible increase in solvent density and finally is increase in solubility. Also high pressure of 2250 Psi, is cause increase in solubility and after this pressure, increase in pressure dose not effect on solubility.

As you see in used state equations in this research, these equations have two adjustable parameters (a and b) and have a molecular interaction parameter K_{ij}. Extract calculation of adjustable parameters and appropriate selection of K_{ij} parameter, has effect on data adjusting with mathematical model and total error of system changes considerably. To adjust K_{ij} parameter, in each state equation, decrease in total error of system was used as the following:

$$AD = \frac{1}{N}\sum_{i=1}^{N} \left| y_i^{calc} - y_i^{\exp} \right| \quad (6)$$

So in this equation; N presents the number of experimental data. Total error of all state equations, is presented in Figure 3. As you see in Figure 3, thermodynamic model of C-MMM has the least error and the best adjusting with experimental data.

Table 1: Extracted oily concentration experimental data with pressure and temperature difference in operational conditions

Concentration gr Oil/gr (CO_2)	Temperature (C°)	Pressure (Psi)	Run	Concentration gr Oil/gr (CO_2)	Temperature (C°)	Pressure (Psi)	Run
0.00698828	35	2250	19	0.005544703	35	1500	1
0.007078656	40	2250	20	0.005261361	40	1500	2
0.007169032	45	2250	21	0.004242797	45	1500	3
0.007315588	50	2250	22	0.003424526	50	1500	4
0.007281392	55	2250	23	0.002887154	55	1500	5
0.007274064	60	2250	24	0.002808991	60	1500	6
0.006871035	35	2500	25	0.006243287	35	1750	7
0.006927215	40	2500	26	0.005930634	40	1750	8
0.007046902	45	2500	27	0.005520277	45	1750	9
0.00728872	50	2500	28	0.00534441	50	1750	10
0.007274064	55	2500	29	0.005068396	55	1750	11
0.007269179	60	2500	30	0.004907184	60	1750	12
0.006871035	35	2750	31	0.006289696	35	2000	13
0.0069321	40	2750	32	0.00643381	40	2000	14
0.007032247	45	2750	33	0.006617005	45	2000	15
0.007286277	50	2750	34	0.006890576	50	2000	16
0.007271622	55	2750	35	0.006878363	55	2000	17
0.007266736	60	2750	36	0.006890576	60	2000	18

Other conditions:

- Particles size 120 micrometer
- Solvent flow rate 5/5 liter per minute
- Consumption gas volume 2017/38 cubic centimeter
- Static time 60 minute

Table 2: Thermodynamic Models

EOS	Formula and parameters	Mixing rules	Fugacity coefficient
vdW	$P=\frac{RT}{\upsilon-b}-\frac{a}{\upsilon^2}$ $a_{ii}=27R^2T_{cii}^2/64P_{cii}$ $b_{ii}=RT_{cii}/8P_{cii}$	$a=\sum_i\sum_j y_i y_j a_{ij}$ $b=\sum_i y_i b_i$	$\phi_i=\exp\left(\frac{b_i}{\upsilon-b}-\ln[z(1-b/\upsilon)]-\frac{2\sum_j y_j a_{ij}}{RT\upsilon}\right)$
RK	$P=\frac{RT}{\upsilon-b}-\frac{a}{T^{0.5}\upsilon(\upsilon+b)}$ $a_{ii}=0.42748R^2T_{cii}^{2.5}/P_{cii}$ $b_{ii}=0.08664RT_{cii}/P_{cii}$	$a=\sum_i\sum_j y_i y_j a_{ij}$ $b=\sum_i y_i b_i$	$\phi_i=\exp\left(\frac{b_i}{b}(z-1)-\ln[z(1-b/\upsilon)]\right.$ $\left.+\frac{1}{bRT^{1.5}}\left[\frac{ab_i}{b}-2\sum_j y_j a_{ij}\right]\ln(1+b/\upsilon)\right)$
MMM	$P=\frac{RT(\upsilon+1.3191b)}{\upsilon-b}-\frac{a}{T^{0.5}\upsilon(\upsilon+\sum_i y_i b_{ii})}$ $a_{ii}=0.42748R^2T_{cii}^{2.5}/P_{cii}$ $b_{ii}=0.06466RT_{cii}/P_{cii}$	$a=\sum_i\sum_j y_i y_j a_{ij}$ $b=(1/4)\left(3\sum_i\sum_j y_i y_j b_{ij}+\sum_i y_i b_{ii}\right)$	$\phi_i=\exp\left(2.3191\left[\frac{3(2\sum_j y_j b_{ij}-\sum_i\sum_j y_i y_j b_{ij})+b_{ii}}{4(\upsilon-b)}-\ln\left(1-\frac{b}{\upsilon}\right)\right]-\ln Z\right.$ $\left.+\frac{a}{RT^{1.5}\sum_i y_i b_{ii}}\left[\left(\frac{b_{ii}}{\sum_i y_i b_{ii}}-\frac{2\sum_j y_j a_{ij}}{a}\right)\ln\left(1+\frac{\sum_i y_i b_{ii}}{\upsilon}\right)-\frac{b_{ii}}{\upsilon+\sum_i y_i b_{ii}}\right]\right)$

Table 3. Considering present data, supercritical properties of oleic acid and carbon dioxide is presented

ω	$\upsilon^c(L/mol)$	V_c (Cm^3/mol)	T_c (K)	P_c (bar)	Molecular weight	Chemical formula	Name
1.19	0.32716	991.5	919.24	14.03	282.46g/mol	$C_{18}H_{34}O_2$	Oleic acid

Table 4. Comparison between components in all kind of oral oil

Animal fat Oil	Olive oil	Sun flower oil	Cotton seed oil	Soya oil	Canol oil	Compositions of oily acids (%)
26.9	9	7	21.6	10.6	4.1	palmitic
12.1	2.7	4.5	2.6	4	1.8	acetearic
28.5	80.3	18.7	18.6	23.7	85.3	Oleic
3.2	6.3	67.5	54.4	54	5.1	linoleik
0.4	0.7	0.8	0.7	6.8	3.2	linolenik
65	12.1	12.8	25.6	15.4	5.9	Total of saturated oily acids
35	87.9	87.2	74.4	84.6	94.1	Total of unsaturated oily acids

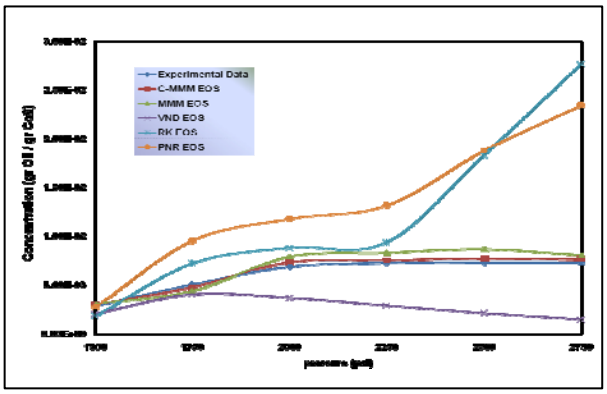

Fig 1: Solubility of oleic acid in supercritical carbon dioxide, with different equation $(K_{ij} \neq 0)$ in compare to experimental data in temperature of 55 degree of centigrade. equations $(K_{ij} \neq 0)$ in optimum state, pressure 2250 Psi and 55 degree of centigrade

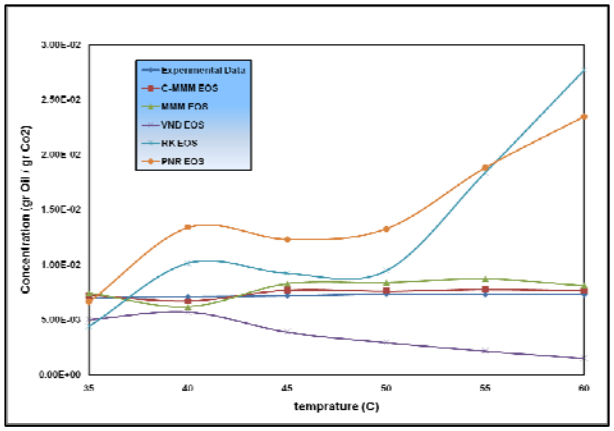

Fig 2: Amount of total error of estimation the oleic acid in supercritical carbon dioxide with use of thermodynamic state

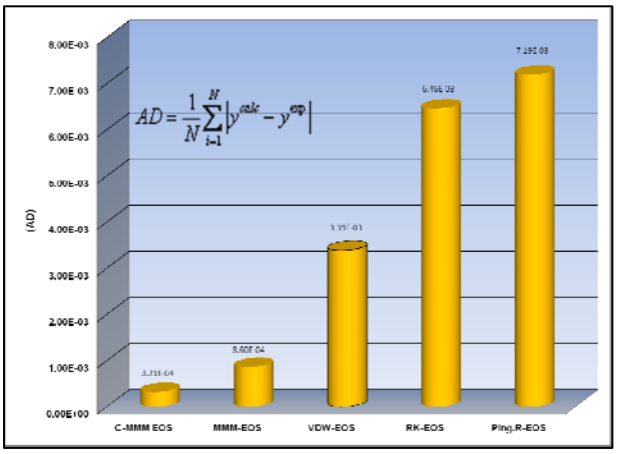

Fig. 3 Bar figure.

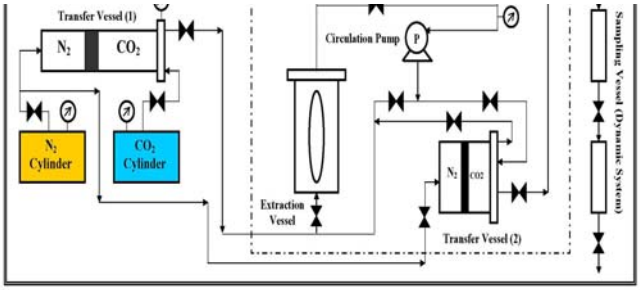

Fig 4: Schematic diagram of the Supercritical Fluid Extraction System (SCFE) for Extraction of oil from canola seed with supercritical carbon dioxide.

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