OPTIMIZATION OF CONIDITIONS FOR EXTRACTION OF GLYCEROL ACETATES by SCCO$_2$

M. Rezayat and H.S. Ghaziaskar *

Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I.R. Iran,
E-mail: ghazi@cc.iut.ac.ir, +98-311-3912500

ABSTRACT

In this work the conditions for partially selective extraction of triacetin (TA) from a mixture of TA, diacetin (DA), and monoacetin (MA) have been optimized using a semi-continuous supercritical CO$_2$ extraction technique. We applied a central composite design (CCD) to evaluate the optimum conditions for four variables (pressure, temperature, solvent flow rate, and extraction time) at three levels of 109 bar, 56 °C, 0.86 mL/min, and 61 min, respectively. At the predicted conditions, about 62.6 % TA was extracted while accompanied with 16.8 % DA and 0 % MA from the feed composition with 1:2:1 ratio for TA, DA, and MA, respectively.

INTRODUCTION

Glycerol acetates (TA, DA, and MA) have been synthesized via esterification of glycerol with acetic acid or acetic anhydride with or without a homogeneous or heterogeneous catalyst using an organic solvent and inbatch or continuous processes [1]. Usually, the product is the mixture of TA, DA, and MA accompanied with some by-products, which change its color and odor. MA or glycerol monoacetate is used in the manufacture of explosives, as tanning agent, and as solvent for dyes. DA or glycerol diacetate is used as a plasticizer and softening agent and solvent [2]. Glycerol triacetate or TA is used as a solvent for dissolving or diluting drugs and organic compounds. Also DA and TA are valuable additives that cause either improved properties when used as a supplement to diesel fuel as antiknocking agent when added to gasoline [3]. Melero et al have reported the synthesis of mixture of MA, DA, and TA with 90% conversion and over 80% of combined selectivity toward DA and TA, and 20% selectivity for MA that is not desired due to its high solubility in water. Then, it's necessary to separate MA from the mixture of DA and TA. In addition, purification and decolonization of glycerol esters have been done using different methods including passing the crude esters over activated carbon, or using a relatively strong oxidant, or using a typical liquid-liquid extraction in multistage, or using distillation for separation of products from impurities [4]. Using reactive chromatography, a technique was described by employing a chromatographic packed column to synthesis and separate one or more produced esters simultaneously [5].

Enormous efforts have been done to replace conventional methods for extraction of natural materials especially in food grade with supercritical fluid extraction (SFE) technique [6]. The most gifted features that make scCO$_2$ so attractive are being chemically inert, non-flammable, non-toxic, environmentally friendly and easily removable from products, tunable solvent power, and shorter extraction time at lower working temperature.

In this study, we applied a central composite design (CCD) to evaluate optimum conditions for continuous extraction of MA, DA, and TA, separately, from a three components mixture of them with molar ratio of 1:2:1, respectively. This mixture was selected since the two commercial standards available for DA had nearly the same ratio for MA, DA, and TA. Thus this work is the first step towards the development of a supercritical fluid process for separation of MA, DA, and TA mixture. The main variables which were investigated in this study were pressure, temperature, solvent flow rate, and extraction time.

MATERIALS AND METHODS
MATERIALS

Carbon dioxide with purity of 99.95% was supplied from Zam Zam Co. Ltd (Isfahan, Iran). TA (purity > 99%) and DA (purity = 50% verified by GC-FID) were purchased from Fluka. Absolute ethanol was purchased from Temad Co. (purity > 99%, Tehran, Iran). 1-hexanol was purchased from Riedel-deHaën (purity > 98%). Since, we did not find commercial MA it was synthesized via a previously reported method reported in 11th international European meeting on Supercritical Fluids [7].

APPARATUS AND PROCEDURE

The schematic experimental set up for the semi-continuous SFE process is shown in Figure 1 as detailed elsewhere [8]. The $scCO_2$ were delivered to the sample cell (a 10.3 mm (ID), 12 cm length, 316-stainless steel reactor with an internal volume of about 10 mL) which was contained glass beads mixed with an specific amount of sample, then the solute-loaded $scCO_2$ flowed up through the extraction column (a 9.8 mm (ID), 25 cm length, 316-stainless steel tubing with an internal volume of about 19 mL) packed with glass beads (3-4 mm). Each sample was collected in a cold trap and analyzed by GC-FID. In a typical run, about 1.0 g of the standard mixture of acetins was mixed with glass beads and transferred to the sample cell. When system was established at the desired pressure and temperature, $scCO_2$ at a set flow rate was introduced to the system. The extracted sample was delivered in a cold trap while the CO_2 was expanded in atmospheric pressure, at different times and prepared for analyses. Analyzing the collected samples was carried out using a GC (Agilent Technologies model 6890N) [7]. Data were analyzed in terms of selectivity, extraction yield for DA and TA which was defined as the percent weight of the extracted compound from each 1.0 g of the loaded sample.
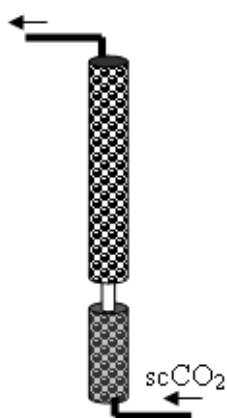

Figure 1: The schematic diagram for semi-continuous SFE process.

EXPERIMENTAL DESIGN

The effect of four factors, pressure, temperature, solvent flow rate, and extraction time on the extraction of each acetins was investigated by using a partial factorial design, CCD. The central composite design was mostly used for a second-order model [9]. We used the MINITAB software package to design and evaluate these four independent variables at three levels on the responses according to the following equation (1), also Table 1 shows the three levels for the variables.

Table 1: The levels of the factors were selected in the experimental design.

Variables	Low level (-1)	Medium level (0)	High level (+1)
Pressure (bar)	100	120	140
Temperature (^{o}C)	48	60	72
Flow rate[a] (mL/min)	0.5	0.8	1.1
Time (min)	30	45	70

[a] flow rate of CO_2 in liquid form at 60 bar and 0°C.

$$(1)$$

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i}^{i<j} \sum_{j} b_{ij} x_i x_j + e$$

Where the response Y includes linear effects for factors x_i, their interactions $x_i x_j$ and their quadratic components x_i^2 and e is the random error.

RESULTS AND DISCOSION

Table 2 shows the 31 runs which were designed by MINITAB in accompany with obtained and predicted responses for DA and TA. As already stated, the response is the selective extraction yield for DA and TA. However, the standard sample was the mixture of MA, DA and TA. It is worthy to mention that we could detect any response for MA by GC analysis in all of the collected samples. Besides, owing to difficulties in quantitative collection of the raffinate from the extraction cell in each experiment, we couldn't analyze it. As it is shown in Table 2, the maximum TA extracted which is 95.6%, obtained when pressure, temperature, solvent flow arte, and extraction time were respectively 140 bar, 48 °C, 1.1 mL/min, and 60 min. Moreover, the maximum DA extracted at this condition was96.9%.

The experimental data were analyzed by response surface design (RSD) using the Minitab software. The results of the statistical analysis including, the estimated regression coefficients, t-values (t-test) and p-values of DA% and TA% is tabulated in Table 3. In each run, the predicted results for DA% and TA% were calculated by substituting the coefficients and numerical values of the variables in equation 1, shown in Table 2. The analysis of variance (ANOVA) confirms the suitability of the fitted models. The R^2 adjusted of the DA% and TA% were 93.2% and 92.4%, respectively. It means that the disability of the developed models to predict the percent extraction of DA and TA is only 6.8% and 7.6% of the total variations. In addition, Figure 2 shows the plots of the obtained results versus predicted data for both DA% and TA%. The linear regression coefficients, R^2, of these plots denote a good agreement between obtained and predicted responses.

Table 2: Experimental matrix design for three-level-four factors CCD and comparison between obtained and predicted extraction data for DA and TA.

| Exp. No.	Factors				DA%		TA%	
	Pressure (bar)	Temperature (°C)	Flow rate (mL/min)	Time (min)	Obtained	Predicted	Obtained	Predicted
1	100	48	0.5	30	3.40	5.80	28.34	25.24
2	100	72	0.5	30	0.00	2.12	2.94	-4.64
3	140	48	0.5	30	28.93	39.58	37.55	9.94
4	140	72	0.5	30	7.91	0.57	34.41	29.73
5	100	48	1.1	30	11.06	16.79	44.40	49.09
6	100	72	1.1	30	1.25	-1.97	6.54	1.25
7	140	48	1.1	30	79.50	75.81	87.06	82.49
8	140	72	1.1	30	18.76	22.12	60.41	62.38
9	100	48	0.5	60	7.02	11.52	48.41	51.37
10	100	72	0.5	60	0.92	1.08	7.11	8.41
11	140	48	0.5	60	63.99	63.69	78.53	72.51
12	140	72	0.5	60	16.19	18.32	49.00	49.23
13	100	48	1.1	60	21.09	25.24	66.83	68.25
14	100	72	1.1	60	2.37	-0.43	12.84	2.37
15	140	48	1.1	60	96.88	102.56	95.60	108.10
16	140	72	1.1	60	47.79	41.96	75.07	74.91
17	120	36	0.8	45	87.12	74.77	85.10	80.80
18	120	84	0.8	45	2.62	10.64	15.08	17.72
19	80	60	0.8	45	0.00	-4.34	2.51	0.85
20[a]	160	60	0.8	45	-	-	-	-
21	120	60	0.2	45	3.45	-1.37	16.06	24.14
22	120	60	1.4	45	32.86	33.34	83.40	73.66
23	120	60	0.8	15	3.67	1.01	25.07	29.97
24	120	60	0.8	75	28.34	26.66	75.18	68.66
25	120	60	0.8	45	15.91	15.06	57.79	58.31
26	120	60	0.8	45	16.78	15.06	57.79	58.31
27	120	60	0.8	45	15.92	15.06	48.23	58.31
28	120	60	0.8	45	16.47	15.06	54.02	58.31
29	120	60	0.8	45	6.97	15.06	66.72	58.31
30	120	60	0.8	45	16.97	15.06	66.72	58.31
31	120	60	0.8	45	16.41	15.06	56.90	58.31

[a] this run was misplaced.
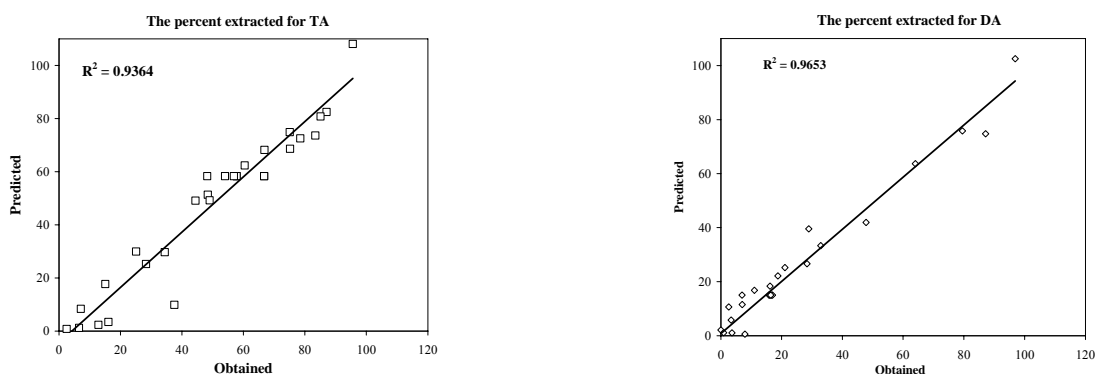
Figure 2: The plots of the obtained results versus predicted data calculated by fitting the models for both DA% and TA%.

Table 3: The regression coefficients, t-test, and significance p-value for the model estimated by Minitab software.

Term	DA%			TA%		
	Coefficient	t-value	p-value	Coefficient	t-value	p-value
Constant	128.401	1.269	0.224	-157.482	-1.388	0.185
Pressure	-1.180	-1.046	0.312	1.885	1.490	0.157
Temperature	-1.448	-0.969	0.348	0.520	-0.310	0.761
Flow rate	-45.396	-0.855	0.406	48.278	0.811	0.430
Time	-0.848	-0.788	0.443	2.300	1.905	0.076
Pressure*Pressure	0.012	2.754	0.015	-0.013	-2.689	0.017
Temperature*Temperature	0.048	5.328	0.000	-0.016	-1.557	0.140
Flow rate*Flow rate	2.579	0.179	0.860	-26.138	-1.619	0.126
Time*Time	-0.001	-0.239	0.814	-0.010	-1.551	0.142
Pressure*Temperature	-0.037	-5.147	0.000	0.020	2.569	0.021
Pressure*Flow rate	1.057	3.714	0.002	0.780	2.443	0.027
Pressure*Time	0.015	2.711	0.016	0.005	0.842	0.413
Temperature*Flow rate	-1.043	-2.198	0.044	-0.689	-1.295	0.215
Temperature*Time	-0.009	-0.978	0.343	-0.018	-1.707	0.108
Flow rate*Time	0.134	0.345	0.728	-0.387	-0.910	0.377

In point of view of the statistical results (ANOVA) with confidence level of 90%, the effect of each term in the models could be significant provided that it's p-value be smaller than 0.1 (p-value<0.1). As shown in the Table 3, the terms which have the strongest influence on the responses of DA% and TA% are different. Hence, the results belong to DA% in Table 3 indicate that the terms in linear form have any influence on the response of DA%, while pressure and temperature in quadratic form are very significant on the response. Among the interaction terms, interaction between pressure with temperature, flow rate and extraction time have high influence. In addition, the interaction term between temperature and solvent flow rate is as well as important. On the other hands, the results is owned to TA% in Table 3, denote that the terms in linear form are also insignificant except for the term of extraction time and only pressure in quadratic form has highly influence on the response of TA%. Between the interaction terms, the interaction terms of pressure with temperature and flow rate are important.

The polarity of a solute is an important characteristic which influences it's solubility in scCO$_2$. It could be proposed that the descending trend for the acetins solubility in scCO$_2$, is: TA>DA>MA which is opposite of their polarity trend. Therefore, we have tried to propose optimum conditions for partly selective extraction of TA from mixture of MA, DA, and TA. Referring to presented results in this study and by reason of no significant value was detected for MA in GC analyses, as stated previously; the optimized condition has only focused on TA, and DA. Using the response optimizer tools of Minitab software, the best conditions for partly separation of TA from DA was predicted when pressure, temperature, solvent flow rate and extraction time were 109 bar, 56 °C, 0.86 mL/min, 61 min, respectively. At the predicted conditions, about 62.6 %TA was extracted while accompanied with 16.8 % DA from the feed composition with 1:2:1 ratio for TA, DA, and MA, respectively. We have any experimental results at these conditions but, we are studying a continuous process for separation the acetins from each others using this result. The response surface plots could explain the interaction effects of variables on DA% and TA%. As shown in Figure 3, the effects of two variables were plotted while the two others were set up at the predicted optimum conditions.
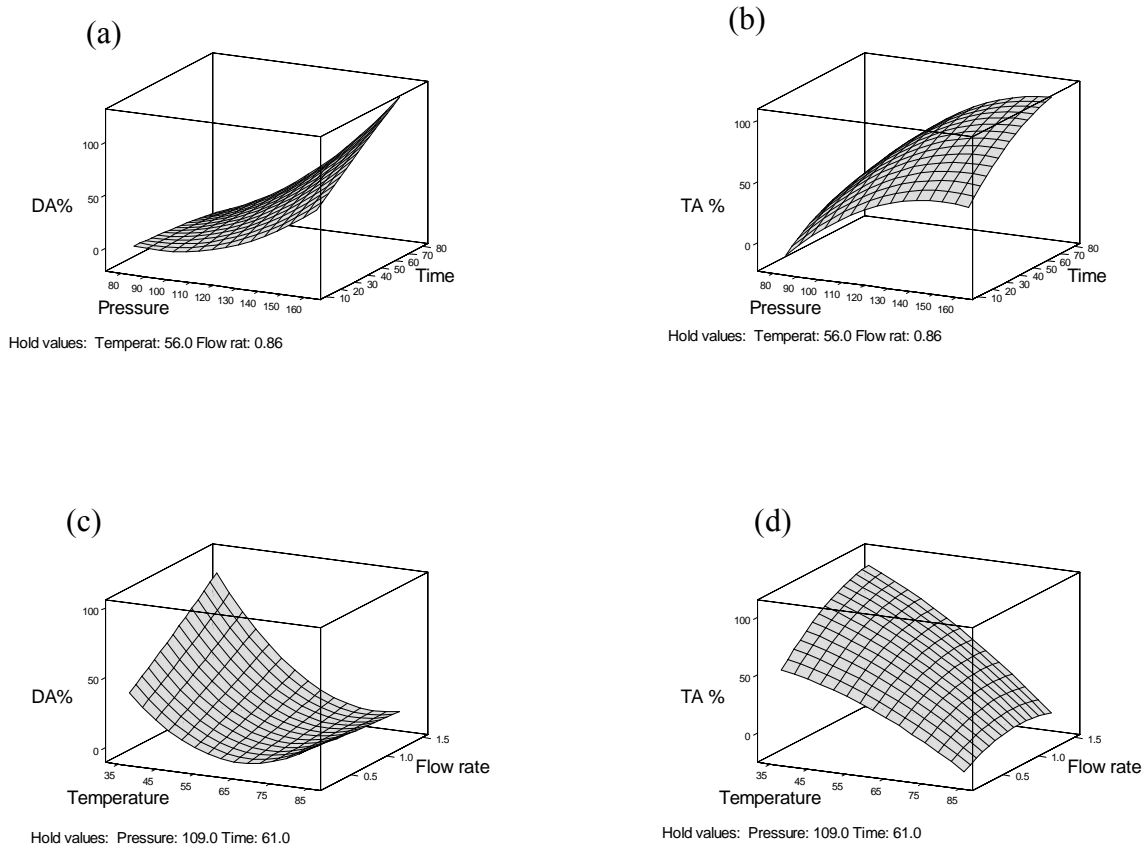
(a)

DA%

Pressure   80 90 100 110 120 130 140 150 160

Time   10 20 30 40 50 60 70 80

Hold values: Temperat: 56.0 Flow rat: 0.86

(b)

TA %

Pressure   80 90 100 110 120 130 140 150 160

Time   10 20 30 40 50 60 70 80

Hold values: Temperat: 56.0 Flow rat: 0.86

(c)

DA%

Temperature   35 45 55 65 75 85

Flow rate   0.5 1.0 1.5

Hold values: Pressure: 109.0 Time: 61.0

(d)

TA %

Temperature   35 45 55 65 75 85

Flow rate   0.5 1.0 1.5

Hold values: Pressure: 109.0 Time: 61.0

Figure 3: The effect of pressure and time (a, b), temperature and flow rate (c, d) on the % DA and TA extracted.

CONCLUSIONS

The results presented in this study showed that the interactions between variables could have higher influence than their linear form on the responses. The effect of increasing the flow rate on DA% and TA% at high temperatures is different when the temperature is lower. The influence of interaction between pressure and time for DA% is not same as TA%. Also, the effect of interaction between temperature and solvent flow rate for DA% and TA% is not similar. The response surfaces have made possible the prediction of the conditions for selective extraction of acetins.

REFRENCES

[1] (a) J. B. Senderens, *Chem. Abs.*, **1914**, 8, 1752[2], (b) G. Janzso, L. Cegledi, L. Manya, and J. Kocsis, *Chem. Abs.*, **1992**, 116, 173576j, *US Pat.*, 4 381 407, **1983**.

[2] J. C. Kern, *Encyclopedia of Chemical Technology*, 3rd ed., **1978**, Vol. 11, p. 931.

[3] J. A. Melero, R. V. Grieken, G. Morales, M. Paniagua, *Energy& Fuels*, **2007**, 21, 1782-1791.

[4] (a) *US Pat.,* 6 153 773, **2000**, (b) *US Pat.*, 5 777 157, **1998**.

[5] *US Pat.,* 6 586 609 B2, **2003**.

[6] E. Reverchon, I. De Marco, *J. Supercritical Fluids*, 38, **2006**, 146-166, J. W. King, E. Sahle-Demessie, F. Temelli, J. A. Teel, *J. Supercritical Fluids*, 10, **1997**, 127-137.

[7] M. Rezayat, H.S. Ghaziaskar, 11th European Meeting on Supercritical Fluids, **2008**.

[8] S.M. Ghoreishi, R. Gholami Shahrestani, H.S. Ghaziaskar, Chem. Eng. Technol., 23, **2009**, 45.

[9] Yongxi, M., Hong, Z., *Chinese J. Chem. Eng.*, 14, **2006**, 223.