SUPPORTING INFORMATION

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Valorization of biodiesel derived glycerol to acetins by continuous esterification in acetic acid: focusing on high selectivity to diacetin and triacetin with no by-products

Hajar Rastegari[1], Hassan S. Ghaziaskar[*1] and Mohammad Yalpani[2]

[1] Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I.R. Iran

Email: ghazi@cc.iut.ac.ir, Tel: 0098-31-33913260, Fax: 0098-31-33912350

[2] R & D Department, Farzin Chemicals Sepahan Co., Montazerie Industrial Complex, Villashahr, Isfahan, 85131-14461 I.R. Iran. Email:moyalpani@gmail.com. Tel: 0098-31-42290748, Fax: 0098-31-42290746

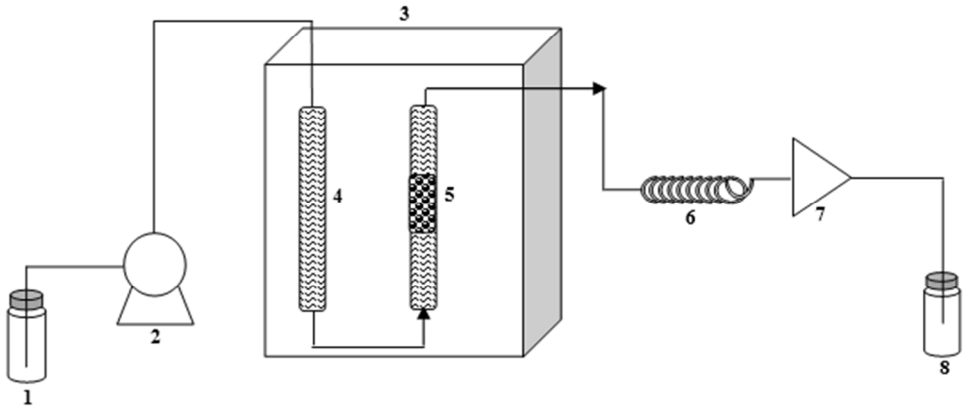

Fig. S1. The schematic diagram of the setup used for the esterification reaction; 1, feedstock reservoir; 2, HPLC pump; 3, air oven; 4, preheater; 5, reactor; 6, cooling jacket; 7, back pressure regulator; 8, collection vessel.

Table S1. Experimental MA, DA, TA and other by-products selectivity according to the experimental matrix design for a three-level-three factors CCD. Glycerol conversion was 100% in all experiments except in experiment no. 6 which was 95%.

No.	Variables			Selectivity (%)			
	X (Mole Ratio)	T (^{o}C)	P (bar)	MA	DA	TA	By-products
1	5	100	100	45	46	9	0
2	3	80	159	62	34	4	0
3	3	120	41	63	32	4	1
4	3	80	41	67	30	3	0
5	5	100	100	46	45	9	0
6	1	100	100	85	14	1	0
7	7	120	159	30	50	17	3
8	7	120	41	37	47	15	1
9	5	66	100	56	39	5	0
10	7	80	41	47	44	9	0
11	5	100	1	50	42	8	0
12	9	100	100	40	45	15	0
13	5	100	199	41	49	10	0
14	5	100	100	43	48	9	0
15	5	100	100	44	47	9	0
16	3	120	159	61	32	4	3
17	5	134	100	45	38	9	8
18	7	80	159	49	43	8	0
19	5	100	100	45	46	9	0
20	5	100	100	46	44	10	0

Table S2. Regression coefficients, T-values, and P-values for the models estimated by Minitab software for MA, DA and TA selectivity of the esterification reaction.

Term	Coefficient	T-value	P-value
MA Selectivity			
Constant*	44.875	47.722	0.000
X	-12.131	-19.445	0.000
T	-3.844	-6.161	0.000
P	-1.987	-3.185	0.010
$\mathbf{X^2}$	5.967	9.826	0.000
$\mathbf{T^2}$	1.725	2.841	0.018
P^2	-0.042	-0.070	0.946
XT	-3.000	-3.680	0.004
XP	0.250	0.307	0.765
TP	-0.750	-0.920	0.379
DA Selectivity			
Constant	45.934	43.087	0.000
X	7.918	11.194	0.000
T	0.362	0.513	0.000
P	1.301	1.840	0.096
$\mathbf{X^2}$	-5.408	-7.854	0.000
$\mathbf{T^2}$	-2.579	-3.747	0.004
P^2	0.248	0.361	0.726
XT	1.250	1.353	0.206
XP	-0.250	-0.271	0.792
TP	0.000	0.000	1.000
TA Selectivity			

Constant	9.168	29.643	0.000
X	4.286	20.891	0.000
T	1.737	8.467	0.000
P	0.319	1.557	0.150
X^2	-0.423	-2.122	0.060
$\mathbf{T^2}$	-0.777	-3.892	0.003
P^2	-0.703	-0.352	0.732
XT	1.625	6.061	0.000
XP	0.125	0.466	0.651
TP	0.375	1.399	0.192

*The significant parameters are shown in bold face.

Table S3. ANOVA to assess the effect of acetic acid to glycerol mole ratio, temperature and pressure on the selectivity of by-products at reaction conditions mentioned in Table S1.

Source	Degrees of freedom	Sum of squares	F-value	F-critical
Run no. 3 and 8				
Between groups	1	0.08	0.29	4.96
Within groups	10	2.83		
Total	11	2.92		
Run no. 7 and 16				
Between groups	1	0.75	3.46	4.96
Within groups	10	2.17		
Total	11	2.92		
Run no. 3 and 16				
Between groups	1	0.75	3.46	4.96
Within groups	10	2.17		
Total	11	2.92		
Run no. 16 and 17				
Between groups	1	75	281.25	4.96
Within groups	10	2.67		
Total	11	77.7		