

Supplementary material to

Application of response surface methodology to optimize the treatment process of high conversion of free fatty acids using (1R)-(-)-camphor-10-sulfonic acid and iron(III) sulphate

Adeeb Hayyan^{1,2}, Khalid M. Abed^{1,3}, Mohammed A. Al-Saadi⁴, Amal A. M. Elgharbawy^{5,6}, Yousef Mohammed Alanazi⁷, Jihad Saleh⁷, Nur Hanie Mohd Latiff⁸, Sharifah Shahira Syed Putra⁹, Mohd Roslan Mohd Nor¹⁰ and Shareef Fadhil Mahel Alhashemi¹¹

¹Department of Chemical Engineering, Faculty of Engineering, Universiti Malaya, Kuala Lumpur, Malaysia

²Sustainable Process Engineering Centre (SPEC), Faculty of Engineering, Universiti Malaya, Kuala Lumpur, Malaysia

³Department of Chemical Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq

⁴National Chair of Materials Science and Metallurgy, University of Nizwa, Nizwa, Oman

⁵International Institute for Halal Research and Training (INHART), International Islamic University Malaysia, Kuala Lumpur, Malaysia

⁶Bioenvironmental Engineering Research Centre (BERC), Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia (IIUM), Kuala Lumpur, Malaysia

⁷Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia

⁸Global Centre for Environmental Remediation (GCER), College of Engineering, Science, and Environment (CESE), University of Newcastle, Callaghan, Australia

⁹Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang Al-sultan Abdullah, Lebuhraya Tun Abdul Razak, 26300 Gambang, Pahang, Malaysia

¹⁰Halal Research Group, Academy of Islamic Studies, Universiti Malaya, Kuala Lumpur, Malaysia

¹¹Department of Chemistry, College of Science, Sultan Qaboos University, Muscat, Oman

Hem. Ind. **79(2)** 79-92 (2025); <https://doi.org/10.2298/HEMIND240515003H>

Table S1. Box-Behnken design for optimizing (1R)-(-)-camphor-10-sulfonic acid catalyzed esterification

Run	Factor 1 A: Catalyst dosage, wt.%	Factor 2 B: Methanol-to-oil molar ratio	Factor 3 C: Reaction temperature, °C	Factor 4 D: Reaction time, min	Response F / wt.%
1	1.25	14	60	50	0.75
2	1.25	14	60	50	0.72
3	1.25	14	40	30	1.73
4	1.25	14	40	30	1.7
5	2.25	8	60	10	1.57
6	2.25	8	60	10	1.5
7	1.25	8	40	10	2.76
8	1.25	8	40	10	2.8
9	1.25	8	40	50	1.78
10	1.25	8	40	50	1.77
11	2.25	2	60	30	4.1
12	2.25	2	60	30	4.3
13	2.25	14	60	30	0.44
14	2.25	14	60	30	0.4
15	0.25	2	60	30	5.1
16	0.25	2	60	30	4.9
17	2.25	8	40	30	1.88
18	2.25	8	40	30	1.81
19	1.25	8	80	50	1.8
20	1.25	8	80	50	1.79
21	1.25	14	80	30	0.96
22	1.25	14	80	30	1
23	0.25	8	80	30	3.72
24	0.25	8	80	30	3.7
25	1.25	8	60	30	1.39
26	1.25	8	60	30	1.41
27	1.25	2	60	50	3.31



Run	Factor 1 A: Catalyst dosage, wt. %	Factor 2 B: Methanol-to-oil molar ratio	Factor 3 C: Reaction temperature, °C	Factor 4 D: Reaction time, min	Response F / wt. %
28	1.25	2	60	50	3.29
29	0.25	8	60	50	3.86
30	0.25	8	60	50	3.85
31	2.25	8	80	30	1.6
32	2.25	8	80	30	1.56
33	1.25	8	60	30	1.39
34	1.25	8	60	30	1.41
35	0.25	8	40	30	4.87
36	0.25	8	40	30	4.8
37	2.25	8	60	50	0.44
38	2.25	8	60	50	0.42
39	1.25	8	80	10	2.98
40	1.25	8	80	10	3
41	1.25	8	60	30	1.39
42	1.25	8	60	30	1.41
43	0.25	8	60	10	5.99
44	0.25	8	60	10	6.2
45	1.25	8	60	30	1.39
46	1.25	8	60	30	1.41
47	1.25	14	60	10	2.12
48	1.25	14	60	10	2
49	1.25	8	60	30	1.39
50	1.25	8	60	30	1.41
51	0.25	14	60	30	3.74
52	0.25	14	60	30	3.69
53	1.25	2	60	10	5.05
54	1.25	2	60	10	5.15
55	1.25	2	40	30	4.14
56	1.25	2	40	30	4
57	1.25	2	80	30	2.68
58	1.25	2	80	30	2.8

Table S2. Box-Behnken design for optimising iron (III) sulphate catalysed esterification

Run	Factor 1 A: Catalyst dosage, wt. %	Factor 2 B: Methanol-to-oil molar ratio	Factor 3 C: Reaction temperature, °C	Factor 4 D: Reaction time, min	Response F / wt. %
1	1.25	14	60	50	0.75
2	1.25	14	40	30	1.73
3	2.25	8	60	10	1.57
4	1.25	8	40	10	2.76
5	1.25	8	40	50	1.78
6	2.25	2	60	30	4.1
7	2.25	14	60	30	0.44
8	0.25	2	60	30	5.1
9	2.25	8	40	30	1.88
10	1.25	8	80	50	1.8
11	1.25	14	80	30	0.96
12	0.25	8	80	30	3.72
13	1.25	8	60	30	1.39
14	1.25	2	60	50	3.31
15	0.25	8	60	50	3.86
16	2.25	8	80	30	1.6
17	1.25	8	60	30	1.39
18	0.25	8	40	30	4.87
19	2.25	8	60	50	0.44
20	1.25	8	80	10	2.98
21	1.25	8	60	30	1.39

Run	Factor 1 A: Catalyst dosage, wt. %	Factor 2 B: Methanol-to-oil molar ratio	Factor 3 C: Reaction temperature, °C	Factor 4 D: Reaction time, min	Response F / wt. %
22	0.25	8	60	10	5.99
23	1.25	8	60	30	1.39
24	1.25	14	60	10	2.12
25	1.25	8	60	30	1.39
26	0.25	14	60	30	3.74
27	1.25	2	60	10	5.05
28	1.25	2	40	30	4.14
29	1.25	2	80	30	2.68
30	1.25	14	60	50	0.73
31	1.25	14	40	30	1.7
32	2.25	8	60	10	1.5
33	1.25	8	40	10	2.8
34	1.25	8	40	50	1.75
35	2.25	2	60	30	4
36	2.25	14	60	30	0.42
37	0.25	2	60	30	5
38	2.25	8	40	30	1.89
39	1.25	8	80	50	1.82
40	1.25	14	80	30	1
41	0.25	8	80	30	3.75
42	1.25	8	60	30	1.4
43	1.25	2	60	50	3.2
44	0.25	8	60	50	3.9
45	2.25	8	80	30	1.58
46	1.25	8	60	30	1.4
47	0.25	8	40	30	4.8
48	2.25	8	60	50	0.42
49	1.25	8	80	10	3
50	1.25	8	60	30	1.4
51	0.25	8	60	10	6
52	1.25	8	60	30	1.4
53	1.25	14	60	10	2.2
54	1.25	8	60	30	1.4
55	0.25	14	60	30	3.75
56	1.25	2	60	10	5
57	1.25	2	40	30	4.2
58	1.25	2	80	30	2.7

Table S3. Optimization constraints for (1R)-(-)-camphor-10-sulfonic acid-catalyzed esterification

Name	Goal	Lower limit	Upper limit	Importance
A: catalyst dosage, wt. %	Minimise	0.25	1.5	2
B: molar ratio	Is in range	2	14	2
C: Temperature, °C	Minimise	50	60	2
D: Time, min	Is in range	10	50	2
F / wt. %	Minimize	0.44	1	5

Table S4. Solutions of optimization for (1R)-(-)-camphor-10-sulfonic acid-catalyzed esterification

Number	Catalyst dosage, Wt. %	Molar ratio	Temperature, °C	Time, min	F / wt. %	Desirability	
1	1.50	12.67	59.58	33.11	0.43	1.000	Selected
2	1.48	13.65	56.47	35.85	0.44	1.000	
3	1.50	12.76	53.68	42.04	0.43	1.000	
4	1.48	12.88	59.23	46.75	0.43	1.000	
5	1.49	13.54	59.63	33.44	0.43	1.000	

Table S5. Optimisation constraints for iron(III) sulphate used for esterification of ACPO

Name	Goal	Lower Limit	Upper Limit	Importance
A: Catalyst dosage, wt.%	Minimise	2	6	1
B: Molar ratio	Is in range	8	12	2
C: Temperature, °C	Minimise	60	80	1
D: Time, min	Minimise	100	200	1
F / wt.%	Minimize	0.75	3.7	5

Table S6. Solutions of optimisation for iron (III) sulphate-catalysed esterification

Number	Catalyst dosage wt.%	Molar ratio	Temperature, °C	Time, min	F / wt.%	Desirability	
1	3.14	12.00	60.00	178.59	1.037	0.771	Selected
2	3.12	12.00	60.00	178.81	1.036	0.771	
3	3.17	12.00	60.00	178.60	1.031	0.771	
4	3.11	12.00	60.00	178.36	1.047	0.771	
5	3.14	12.00	60.00	179.18	1.024	0.770	

Table S7. Specifications of biodiesel produced from ACPO compared with the standard limits

Properties	Biodiesel from ACPO	EN 14214		ASTM D6751	
		Test method	Limit	Test method	Limits
Ester content, mol.%	96.3	EN 14103	min 96.5	-	-
Monoacylglycerol content, mol.%	0.05	EN 14105	max 0.80	-	-
Diacylglycerols content, mol.%	0.025	EN 14105	max 0.20	-	-
Triacylglycerols content, mol.%	<0.01	EN 14105	max 0.20	-	-
Free glycerol content, mol.%	<0.01	EN 14105	max 0.02	ASTM D 6584	max 0.020 wt.%
Total glycerol content, mol.%	0.050	EN 14105	max 0.25	ASTM D 6584	max 0.240 wt.%
Water content, mg kg ⁻¹	473	EN ISO 12937	max 500	ASTM D 2709	max 0.050 vol.%
K content, mg kg ⁻¹	max 1	EN 14108	max 5.0	UOP 391	max 5.0
P content, mg kg ⁻¹	max 7.10	EN 14107	max 10.0	ASTM D 4951	max 0.001 wt.%
Density (at 15 °C), kg m ⁻³	867	EN ISO 3675	860 - 900	-	-
Flash point, °C	182	EN ISO 3679	120 °C min	ASTM D 93	130 - min
Cloud point, °C	16	-	-	ASTM D 2500	Not specified
Content of sulphated ash, wt.%	<0.005	ISO 3987	Max 0.02 mol.%	ASTM D 874	Max 0.020
Total contamination, mg kg ⁻¹	0.008	EN 12662	24 - max	-	-
Copper strip corrosion (3 h at 50 °C)	Class 1	EN ISO 2160	Class 1 rating	ASTM D130	No. 3 max

Table S8. Effect of recycling catalysts on the FFA reduction and conversion of FFA to FAME

Reused runs	(1R)-(-)-camphor-10-sulfonic acid		Iron (III) sulphate	
	F / wt. % (final)	FFA conversion, %	FFA content reduction, wt. %	FFA conversion, %
1	2.09	75.20	3.51	58.36
2	3.67	56.46	4.88	42.11
3	4.23	49.82	4.39	47.92
4	5.46	35.23	4.70	44.24
5	5.48	34.99	5.36	36.41

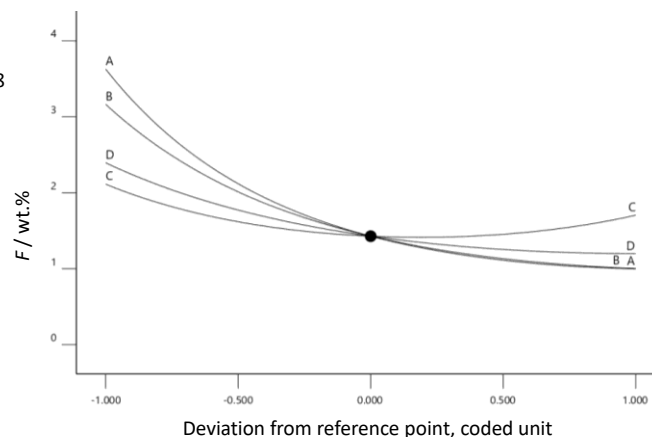
Actual factors

A: Catalyst dosage = 1.25 wt. %

B: Methanol-to-oil molar ratio = 8

C: Reaction temperature, 60 °C

D: Reaction time, 30 min

**Figure S1.** The perturbation plot for optimizing 10-CSA-catalyzed esterification

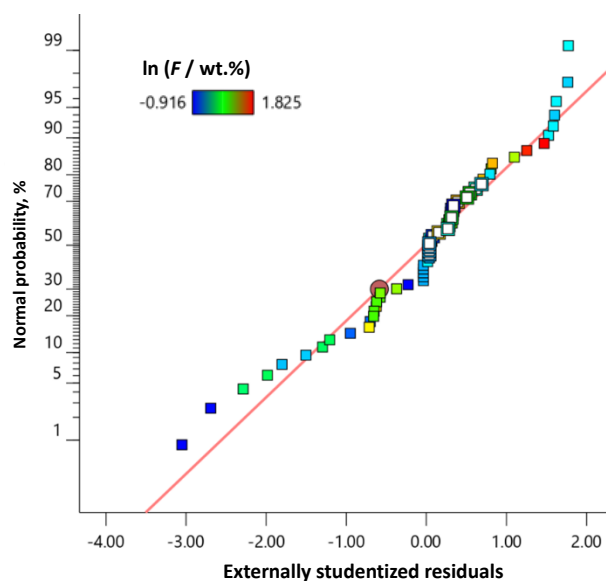


Figure S2. Normal plot of residuals for optimizing 10-CSA- catalysed esterification

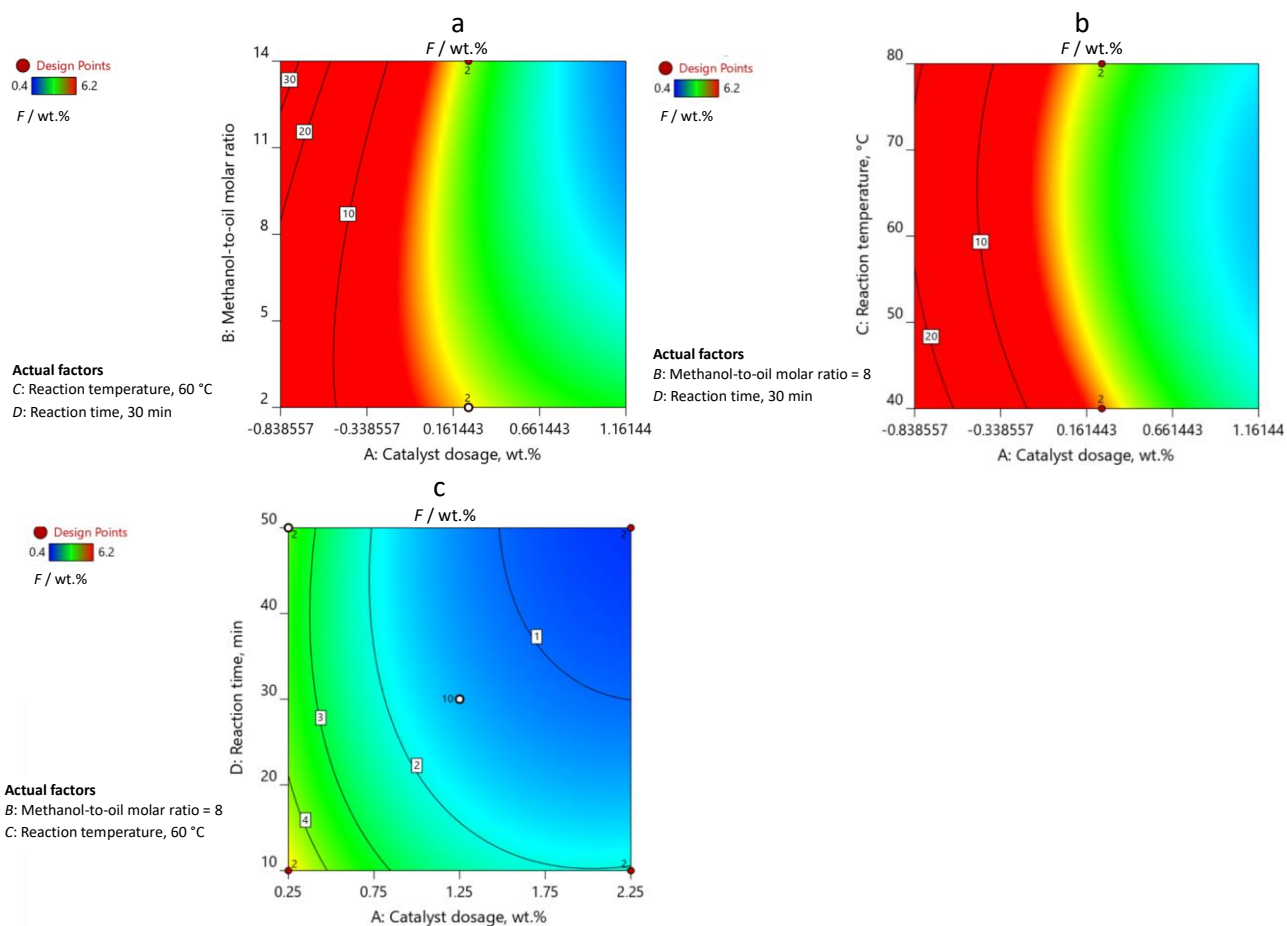


Figure S3: Contour plots for timising 10-CSA-catalysed esterification: (a) catalyst dosage and methanol-to-oil molar ratio, (b) catalyst dosage and reaction temperature, (c) catalyst dosage and reaction time

Actual factors

A: Catalyst dosage = 1.25 wt. %

B: Methanol-to-oil molar ratio = 8

C: Reaction temperature, 60 °C

D: Reaction time, 30 min

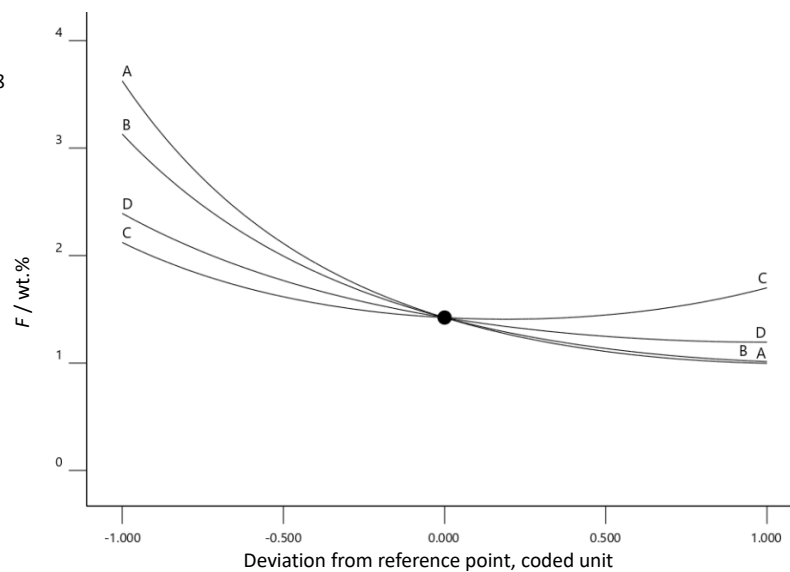


Figure S4. The perturbation plot for optimising iron(III) sulphate catalysed esterification

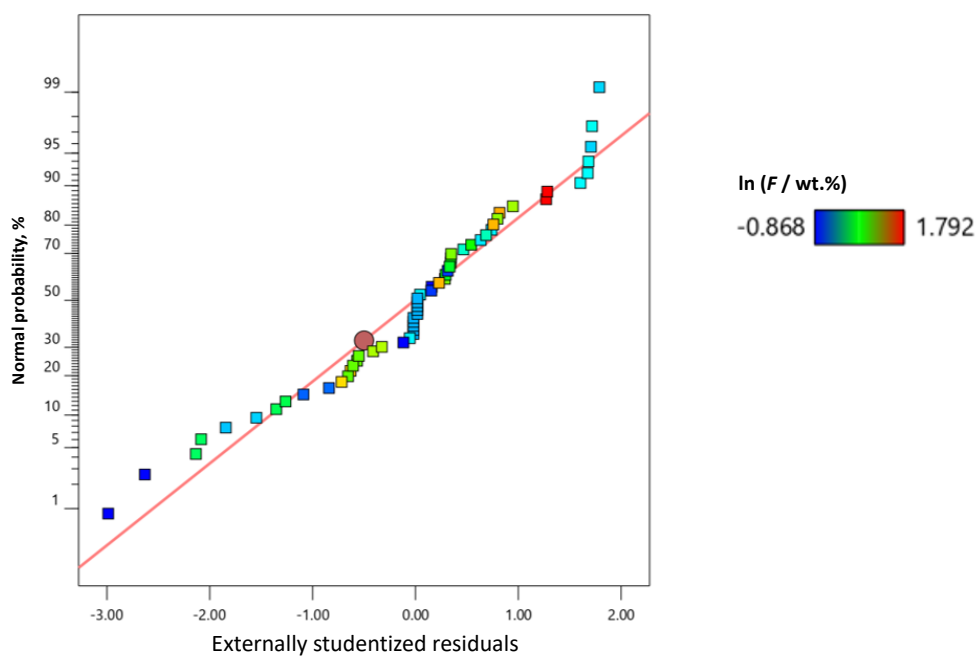


Figure S5. Normal Plot of Residuals for optimising iron III sulphate acid catalysed esterification

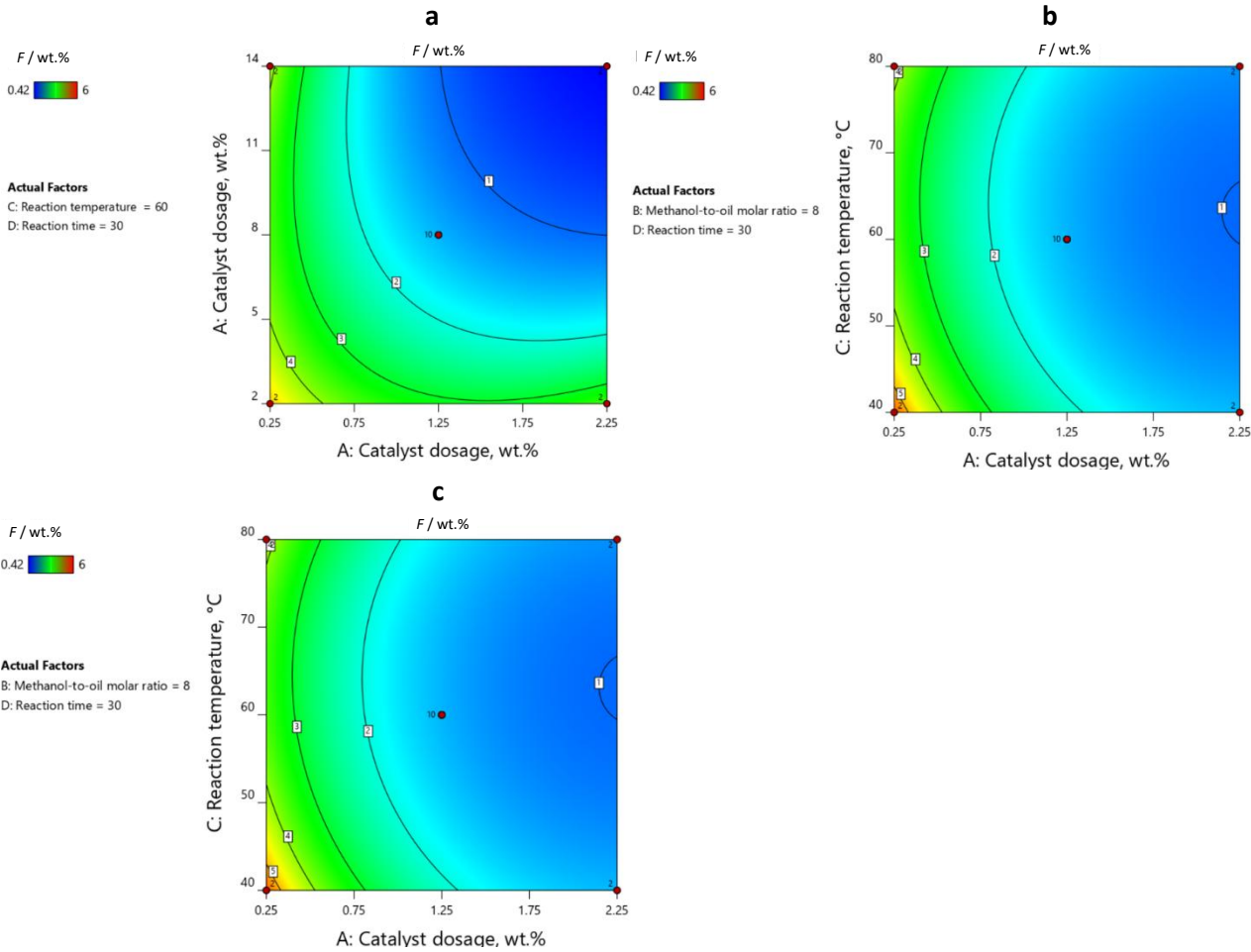


Figure S6. Contour plots for optimising iron III sulphate catalysed esterification: (a) catalyst dosage and methanol-to-oil molar ratio, (b) catalyst dosage and reaction temperature, (c) catalyst dosage and reaction temperature

