**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

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

| Run | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Response |
|---|---|---|---|---|---|
| | A: Catalyst dosage, wt.% | *B*: Methanol-to-oil molar ratio | *C*: Reaction temperature, °C | D: Reaction time, min | 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 |
| 28 | 1.25 | 2 | 60 | 50 | 3.29 |
| 29 | 0.25 | 8 | 60 | 50 | 3.86 |
| 30 | 0.25 | 8 | 60 | 50 | 3.85 |

| Run | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Response |
|---|---|---|---|---|---|
| | A: Catalyst dosage, wt.% | *B*: Methanol-to-oil molar ratio | *C*: Reaction temperature, °C | D: Reaction time, min | F / wt.% |
| 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 S.****: Box-Behnken design for optimising iron (III) sulphate catalysed esterification*

| Run | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Response |
|---|---|---|---|---|---|
| | A: Catalyst dosage, wt.% | *B*: Methanol-to-oil molar ratio | *C*: Reaction temperature, °C | D: Reaction time, min | 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 |
| 22 | 0.25 | 8 | 60 | 10 | 5.99 |
| 23 | 1.25 | 8 | 60 | 30 | 1.39 |
| 24 | 1.25 | 14 | 60 | 10 | 2.12 |

| Run | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Response |
|---|---|---|---|---|---|
| | A: Catalyst dosage, wt.% | *B*: Methanol-to-oil molar ratio | *C*: Reaction temperature, °C | D: Reaction time, min | F / wt.% |
| 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

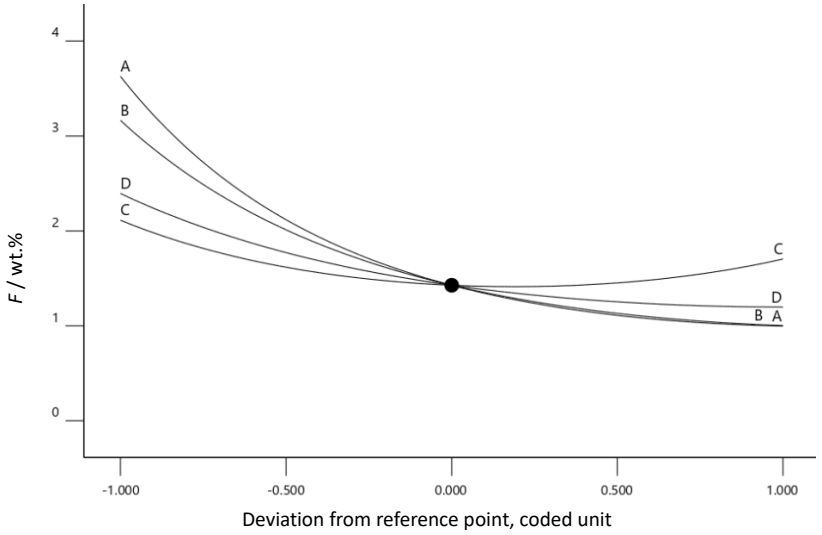


***Figure S1.*** *The perturbation plot for optimizing 10-CSA-catalyzed esterification*

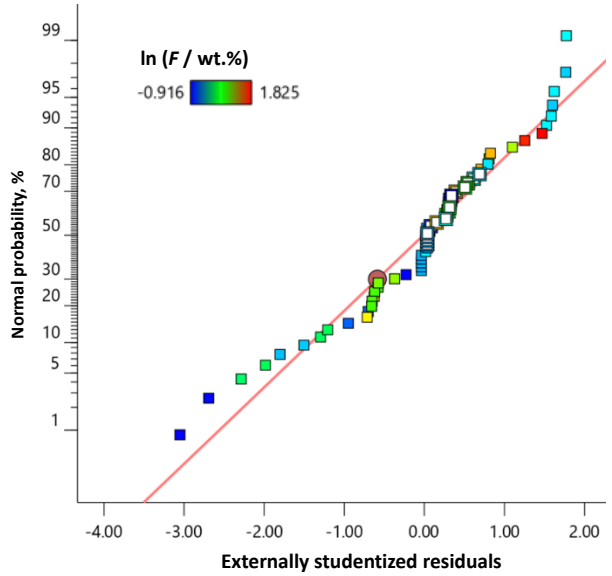


***Figure S2.*** *Normal plot of residuals for optimizing 10-CSA- catalysed esterification*

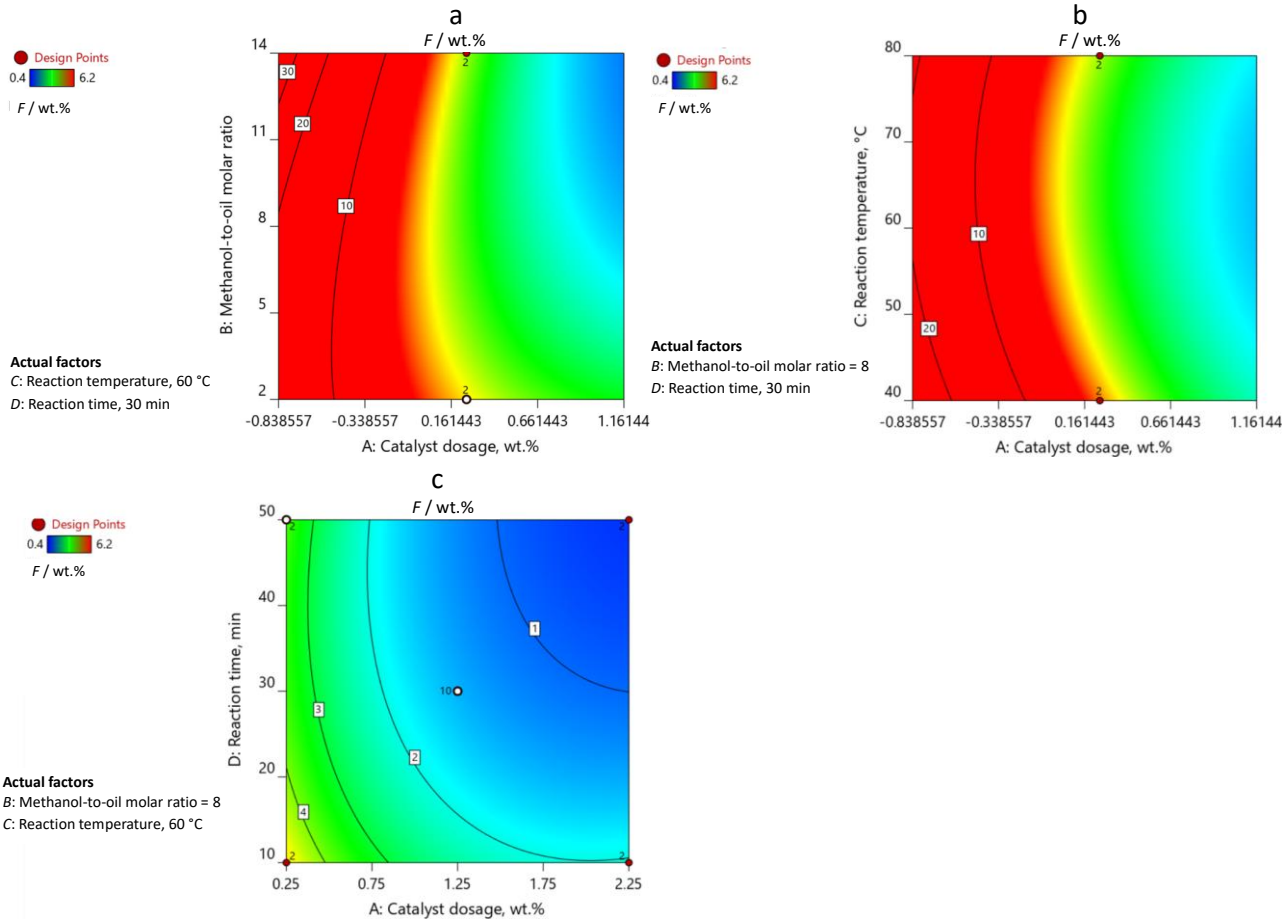


***Figure S3:*** *Contour plots for timising 10-CSA-catalysed esterification: (a) catalyst dosage and methanol-to-oil molar ratio, (b) catalyst dosage and reaction temperature, (c) catalyst dosage and reaction time*

**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

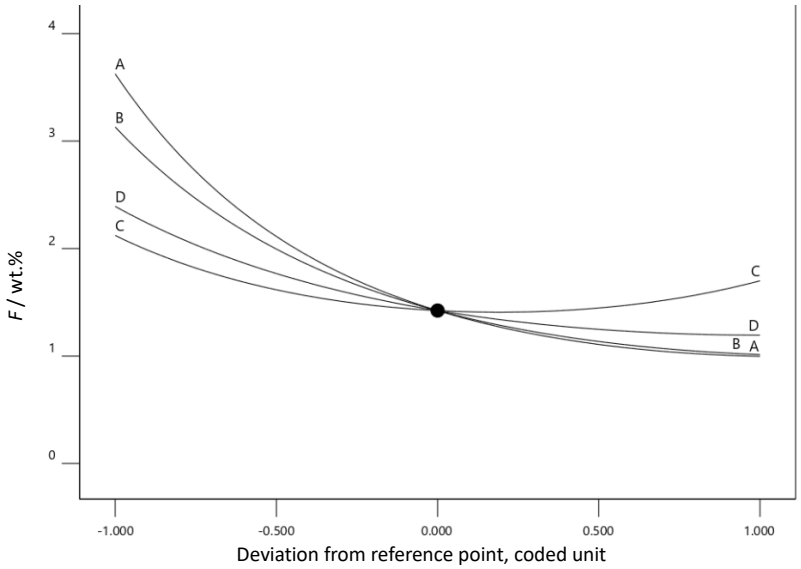


***Figure S4.*** *The perturbation plot for optimising iron(III) sulphate catalysed esterification*

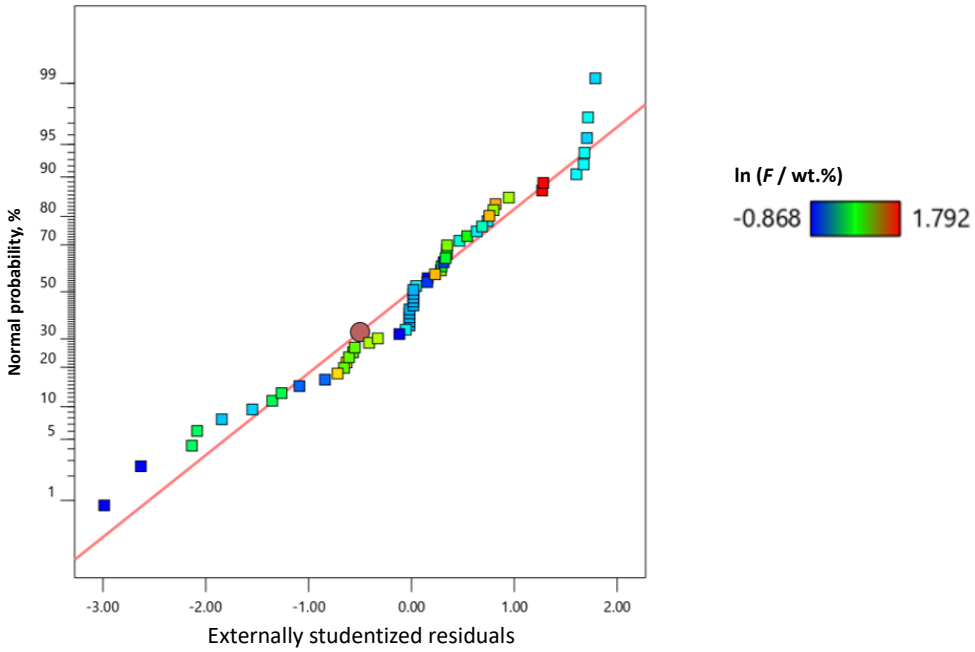


***Figure S5.*** *Normal Plot of Residuals for optimising iron III sulphate acid catalysed esterification*

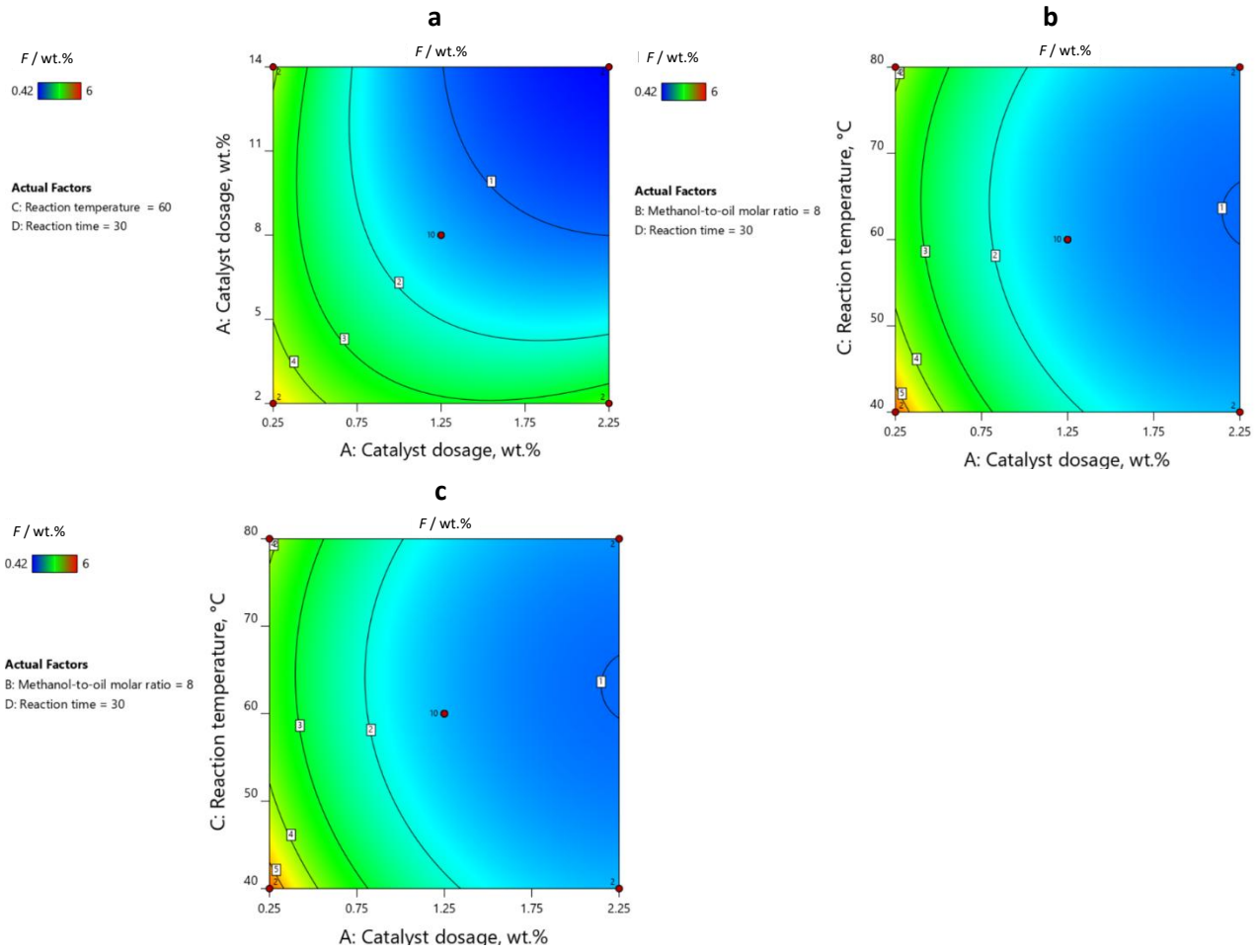


***Figure S6.*** *Contour plots for optimising iron III sulphate catalysed esterification: (a) catalyst dosage and methanol-to-oil molar ratio, (b) catalyst dosage and reaction temperature, (c) catalyst dosage and reaction temperature*