

Effect of types of catalyst. Reaction conditions: 120 °C, 5-HMF solution (5 g/L) flow rate of 0.06 ml/min, acetonitrile as solvent, oxygen gas flow rate of 10 ml/min and catalyst amount of 0.05 g.

Ru/Al₂O₃ 120C/100psi/0.06flow/0.05cat/1002/ACE

| | Vol.AQ | 5-HMF g | HMFCA g | DFF g | FFCA g | FDCA g | Yield HMFCA | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity | Carbon balance |
|---|--------|-----------|---------|-----------|-----------|--------|-------------|-----------|------------|------------|------------|-------------|----------------|
| 1 | 1.8 | 0.001194 | 0 | 0.0063266 | 0.0007067 | 0 | 0.00 | 56.81 | 7.07 | 0.00 | 86.73 | 65.50 | 78.03 |
| 2 | 1.8 | 0.0016345 | 0 | 0.0061622 | 0.0009367 | 0 | 0.00 | 55.33 | 9.37 | 0.00 | 81.84 | 67.61 | 78.71 |

Ru/C 120C/100psi/0.06flow/0.05cat/1002/ACE

| | Vol.AQ | 5-HMF g | HMFCA g | DFF g | FFCA g | FDCA g | Yield HMFCA | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity | Carbon balance |
|---|--------|-----------|---------|-----------|-----------|-------------|-------------|-----------|------------|------------|------------|-------------|----------------|
| 1 | 1.8 | 0.003519 | 0 | 0.0044546 | 0.0002002 | 7.72926E-06 | 0.00 | 40.00 | 2.00 | 0.07 | 60.90 | 65.68 | 51.45 |
| 2 | 1.8 | 0.0035431 | 0 | 0.004251 | 0.0001889 | 6.75435E-06 | 0.00 | 38.17 | 1.89 | 0.06 | 60.63 | 62.96 | 49.05 |

Pt/C 120C/100psi/0.06flow/0.05cat/1002/ACE

| | Vol.AQ | 5-HMF g | HMFCA g | DFF g | FFCA g | FDCA g | Yield HMFCA | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity | Carbon balance |
|---|--------|-----------|---------|-----------|-----------|--------|-------------|-----------|------------|------------|------------|-------------|----------------|
| 1 | 1.8 | 0.0063854 | 0 | 0.0002514 | 1.834E-05 | 0 | 0.00 | 2.26 | 0.18 | 0.00 | 29.05 | 7.77 | 2.36 |
| 2 | 1.8 | 0.0064827 | 0 | 0.0002203 | 1.349E-05 | 0 | 0.00 | 1.98 | 0.13 | 0.00 | 27.97 | 7.07 | 1.95 |

Effect of solvent. Reaction conditions: 120 °C, 5-HMF solution (5 g/L) flow rate of 0.06 ml/min, oxygen gas flow rate of 10 ml/min and Ru/Al₂O₃ 0.05 g.

Acetonitrile 120C/100psi/0.06flow/0.05cat/1002/ACE

| | Vol.AQ | 5-HMF g | HMFCa g | DFF g | FFCA g | FDCA g | Yield HMFCa | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity | Carbon balance |
|---|--------|-----------|---------|-----------|-----------|-------------|-------------|-----------|------------|------------|------------|-------------|----------------|
| 1 | 1.8 | 0.0025316 | 0 | 0.0060926 | 0.0007232 | 1.50984E-05 | 0.00 | 54.71 | 7.24 | 0.14 | 71.87 | 76.12 | 75.65 |
| 2 | 1.8 | 0.0028098 | 0 | 0.0058677 | 0.0005836 | 1.50726E-05 | 0.00 | 52.69 | 5.84 | 0.14 | 68.78 | 76.61 | 71.57 |

Toluene 120C/100psi/0.06flow/0.05cat/1002/TOL

| | Vol.AQ | 5-HMF g | HMFCa g | DFF g | FFCA g | FDCA g | Yield HMFCa | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity | Carbon balance |
|---|--------|-----------|---------|-----------|--------|--------|-------------|-----------|------------|------------|------------|-------------|----------------|
| 1 | 1.8 | 0.0024798 | 0 | 0.0061118 | 0 | 0 | 0.00 | 54.88 | 0.00 | 0.00 | 72.45 | 75.76 | 67.66 |
| 2 | 1.8 | 0.0022645 | 0 | 0.0056845 | 0 | 0 | 0.00 | 51.05 | 0.00 | 0.00 | 74.84 | 68.21 | 62.94 |

Water 120C/100psi/0.06flow/0.05cat/1002/water

| | Vol.AQ | 5-HMF g | HMFCa g | DFF g | FFCA g | FDCA g | Yield HMFCa | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity | Carbon balance |
|---|--------|-----------|---------|-----------|-----------|-------------|-------------|-----------|------------|------------|------------|-------------|----------------|
| 1 | 1.8 | 0.0044818 | 0 | 0.002294 | 0.0010744 | 5.63446E-05 | 0.00 | 20.60 | 10.75 | 0.51 | 50.20 | 41.03 | 37.60 |
| 2 | 1.8 | 0.0043382 | 0 | 0.0021826 | 0.000981 | 7.84217E-05 | 0.00 | 19.60 | 9.82 | 0.70 | 51.80 | 37.84 | 35.59 |

DMSO 120C/100psi/0.06flow/0.05cat/1002/DMSO

| | Vol.AQ | 5-HMF g | HMFCa g | DFF g | FFCA g | FDCA g | Yield HMFCa | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity | Carbon balance |
|---|--------|-----------|---------|-----------|-----------|--------|-------------|-----------|------------|------------|------------|-------------|----------------|
| 1 | 1.8 | 0.0055942 | 0 | 0.0015758 | 0.0001404 | 0 | 0.00 | 14.15 | 1.41 | 0.00 | 37.84 | 37.39 | 18.51 |
| 2 | 1.8 | 0.0057815 | 0 | 0.0015102 | 0.0001284 | 0 | 0.00 | 13.56 | 1.28 | 0.00 | 35.76 | 37.92 | 17.63 |

Box-Behnken design approach for optimization of DFF production

| StdOrder | RunOrder | PtType | Blocks | Temp | Oxy | Cat | yield | conversion | selectivity |
|----------|----------|--------|--------|------|-----|------|--------|------------|-------------|
| 1 | 1 | 2 | 1 | 100 | 10 | 0.1 | 46.490 | 89.505 | 51.941 |
| 2 | 2 | 2 | 1 | 140 | 10 | 0.1 | 71.700 | 97.043 | 73.884 |
| 3 | 3 | 2 | 1 | 100 | 30 | 0.1 | 55.810 | 88.478 | 63.077 |
| 4 | 4 | 2 | 1 | 140 | 30 | 0.1 | 69.850 | 93.467 | 74.732 |
| 5 | 5 | 2 | 1 | 100 | 20 | 0.05 | 43.310 | 67.865 | 63.818 |
| 6 | 6 | 2 | 1 | 140 | 20 | 0.05 | 65.710 | 92.774 | 70.828 |
| 7 | 7 | 2 | 1 | 100 | 20 | 0.15 | 54.110 | 96.586 | 56.023 |
| 8 | 8 | 2 | 1 | 140 | 20 | 0.15 | 81.750 | 99.865 | 81.860 |
| 9 | 9 | 2 | 1 | 120 | 10 | 0.05 | 53.490 | 69.426 | 77.046 |
| 10 | 10 | 2 | 1 | 120 | 30 | 0.05 | 62.690 | 77.033 | 81.381 |
| 11 | 11 | 2 | 1 | 120 | 10 | 0.15 | 66.970 | 99.426 | 67.357 |
| 12 | 12 | 2 | 1 | 120 | 30 | 0.15 | 65.610 | 99.163 | 66.164 |
| 13 | 13 | 0 | 1 | 120 | 20 | 0.1 | 58.770 | 98.046 | 59.941 |
| 14 | 14 | 0 | 1 | 120 | 20 | 0.1 | 58.910 | 97.324 | 60.530 |
| 15 | 15 | 0 | 1 | 120 | 20 | 0.1 | 58.550 | 98.235 | 59.602 |
| 16 | 16 | 2 | 2 | 100 | 10 | 0.1 | 44.295 | 93.562 | 47.343 |
| 17 | 17 | 2 | 2 | 140 | 10 | 0.1 | 72.715 | 99.806 | 72.857 |
| 18 | 18 | 2 | 2 | 100 | 30 | 0.1 | 55.984 | 87.741 | 63.806 |
| 19 | 19 | 2 | 2 | 140 | 30 | 0.1 | 69.275 | 99.391 | 69.699 |
| 20 | 20 | 2 | 2 | 100 | 20 | 0.05 | 44.591 | 69.774 | 63.907 |
| 21 | 21 | 2 | 2 | 140 | 20 | 0.05 | 62.473 | 94.952 | 65.794 |
| 22 | 22 | 2 | 2 | 100 | 20 | 0.15 | 56.927 | 90.544 | 62.873 |
| 23 | 23 | 2 | 2 | 140 | 20 | 0.15 | 83.436 | 99.264 | 84.055 |
| 24 | 24 | 2 | 2 | 120 | 10 | 0.05 | 51.756 | 63.506 | 81.498 |

| | | | | | | | | | |
|----|----|---|---|-----|----|------|--------|--------|--------|
| 25 | 25 | 2 | 2 | 120 | 30 | 0.05 | 61.473 | 76.711 | 80.135 |
| 26 | 26 | 2 | 2 | 120 | 10 | 0.15 | 66.747 | 97.688 | 68.326 |
| 27 | 27 | 2 | 2 | 120 | 30 | 0.15 | 65.241 | 99.678 | 65.452 |
| 28 | 28 | 0 | 2 | 120 | 20 | 0.1 | 58.519 | 98.742 | 59.264 |
| 29 | 29 | 0 | 2 | 120 | 20 | 0.1 | 58.227 | 92.516 | 62.937 |
| 30 | 30 | 0 | 2 | 120 | 20 | 0.1 | 58.545 | 96.435 | 60.709 |

Reaction performance of DFF synthesis over Ru/Al₂O₃ catalyst for extended period.

| Hour | Vol.AQ | 5-HMF g | HMFCA g | DFF g | FFCA g | FDCA g | Yield HMFCA | Yield DFF | Yield FFCA | Yield FDCA | Conversion | Selectivity |
|------|--------|----------|---------|----------|--------|--------|-------------|-----------|------------|------------|------------|-------------|
| 2 | 1.8 | 0.000635 | 0 | 0.023589 | 0 | 0 | 0.00 | 84.06 | 0.00 | 0.00 | 97.20 | 86.48 |
| 4 | 1.8 | 0.000534 | 0 | 0.024327 | 0 | 0 | 0.00 | 86.68 | 0.00 | 0.00 | 97.65 | 88.77 |
| 6 | 1.8 | 0.000266 | 0 | 0.024495 | 0 | 0 | 0.00 | 87.28 | 0.00 | 0.00 | 98.83 | 88.32 |
| 8 | 1.8 | 0.000317 | 0 | 0.024053 | 0 | 0 | 0.00 | 85.71 | 0.00 | 0.00 | 98.60 | 86.92 |
| 10 | 1.8 | 0.000292 | 0 | 0.023887 | 0 | 0 | 0.00 | 85.12 | 0.00 | 0.00 | 98.71 | 86.23 |
| 12 | 1.8 | 0.000575 | 0 | 0.021933 | 0 | 0 | 0.00 | 78.16 | 0.00 | 0.00 | 97.46 | 80.19 |