Electronic Supplementary Material (ESI) for Green Chemistry.


**Supplementary information**

# An assessment of electrified methanol production from an environmental perspective

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**Table S-1.** Process conditions and flows of the major streams in plasma-assisted methanol production process.

| | | DMR in | DMR out | SCMR in | SCMR out | Syngas | MeOH-R in | MeOH |
|---|---|---|---|---|---|---|---|---|
| Mass Flows | kg/hr | 30026 | 30026 | 53229 | 53229 | 19826 | 68791 | 16353 |
| $CO_2$ | kg/hr | 22005 | 12595 | 12595 | 14171 | 1051 | 12726 | 31 |
| CO | kg/hr | | 8095 | 8095 | 16445 | 16273 | 45030 | |
| $H_2$ | kg/hr | | 647 | 647 | 2503 | 2502 | 9530 | |
| Natural gas | kg/hr | 8021 | 3979 | 3979 | | | 5 | |
| $C_2H_6$ | kg/hr | | 75 | 75 | | | | |
| $C_2H_4$ | kg/hr | | 175 | 175 | | | | |
| $C_2H_2$ | kg/hr | | 879 | 879 | | | | |
| $C_3H_8$ | kg/hr | | 14 | 14 | | | | |
| Water | kg/hr | | 2450 | 26771 | 20110 | | 5 | 1 |
| MeOH | kg/hr | | | | | | 1495 | 16321 |
| Coke | kg/hr | | 1117 | | | | | |
| Pressure | bar | 1 | 1 | 1 | 1 | 30 | 30 | 1 |
| Temperature | °C | 25 | 200 | 1000 | 1000 | 250 | 250 | 30 |

**Table S-2.** Process conditions and flows of the major streams in thermocatalytic methanol production process.

| | | DMR in | DMR out | WGS in | WGS out | SMR in | SMR out | Syngas | MeOH-R in | MeOH |
|---|---|---|---|---|---|---|---|---|---|---|
| Mass Flows | kg/hr | 18766 | 18766 | 25979 | 25979 | 22351 | 22351 | 44052 | 218976 | 3557 |
| $CO_2$ | kg/hr | 13753 | 1315 | 1315 | 7739 | | 71 | 7806 | 85723 | 87 |
| CO | kg/hr | | 15246 | 15246 | 12281 | | 18068 | 30348 | 90041 | |
| $H_2$ | kg/hr | | 1039 | 1039 | 1576 | | 3914 | 5490 | 28607 | |
| Natural gas | kg/hr | 5013 | 750 | 750 | 107 | 10528 | 154 | 260 | 8451 | |
| $C_2H_6$ | kg/hr | | | | | | | | | |
| $C_2H_4$ | kg/hr | | | | | | | | | |
| $C_2H_2$ | kg/hr | | | | | | | | | |
| $C_3H_8$ | kg/hr | | | | | | | | | |
| Water | kg/hr | | 377 | 7629 | 4276 | 11823 | 144 | 148 | 253 | 2 |
| MeOH | kg/hr | | | | | | | | 5901 | 35468 |
| Coke | kg/hr | | 39 | | | | | | | |
| Pressure | bar | 1 | 1 | 1 | 1 | 1 | 1 | 30 | 30 | 1 |
| Temperature | °C | 750 | 750 | 750 | 750 | 1000 | 1000 | 250 | 250 | 30 |

**Table S-3.** Detailed material and energy flows of the plasma-assisted DMR-to-MeOH process utilizing natural gas as carbon source.

| Plasma-assisted DMR-to-MeOH ; feed: natural gas + $CO_2$ | | | | | |
|---|---|---|---|---|---|
| | | **kg/h** | **$m^3$/h (25°C; 1bar)** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| **Raw material** | Natural gas ($CH_4$) | 8021 | 12376 | 0.49 | 0.76 |
| | $CO_2$ | 8701 | ($CO_2$ from 2nd flash drum is recycled) | 0.53 | |
| | Water | 4221 | (water from 1st flash drum is recycled) | 0.26 | |
| | | **MW** | | **$MJ/kg_{MeOH}$** | |
| **Utility** | Hot utility (oil) | 30.7 | | 6.75 | |
| | Cold utility (water) | -39.6 | | 393 | **$kg/kg_{MeOH}$** |
| | Cold utility (refrig.) | -23.9 | 47 | 1 | **$kWh/Kg_{MeOH}$** |
| | | **kW** | | **kWh/kgMeOH** | |
| | Electricity | 103594 | | 6.3 | |
| | | 4088 | | 0.25 | **CW recirculation (20 bar loss)** |
| | Make-up water | | | 7.9 | **$kgwater/kg_{MeOH}$ (5% loss)** |
| | | **kg/h** | **$kg/k_{gcat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| **Catalyst Bi** | $Mg(NO_3)_2 \cdot 6H_2O$ | $1.3 \cdot 10^{-3}$ | 1.68 | $7.8 \cdot 10^{-8}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $3.7 \cdot 10^{-3}$ | 4.87 | $2.3 \cdot 10^{-7}$ | |
| | $Ni(NO_3)_2 \cdot 6H_2O$ | $3.8 \cdot 10^{-4}$ | 0.50 | $2.3 \cdot 10^{-8}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $3.1 \cdot 10^{-5}$ | $4 \cdot 10^{-2}$ | $1.9 \cdot 10^{-9}$ | |
| | $NH_4OH$ ($L/kg_{cat}$ ; density = 0.88 kg/L) | $1.3 \cdot 10^{-3}$ | 1.76 | | $8.2 \cdot 10^{-8}$ |
| | Catalyst demand Kg (4 $mol_{CO}/s/Kg_{cat}$) | 20 | | | |
| | Catalyst lifetime $Kg_{cat}/h$ (3 years) | $8.0 \cdot 10^{-4}$ | | | |
| | | **kg/h** | **$kg/k_{gcat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| **Catalyst MeOH** | $Cu(NO_3)_2 \cdot 3H_2O$ | $7.9 \cdot 10^{-2}$ | 2.41 | $4.8 \cdot 10^{-6}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $4.4 \cdot 10^{-2}$ | 1.33 | $2.7 \cdot 10^{-6}$ | |
| | $Zn(NO_3)_2 \cdot 6H_2O$ | $3.4 \cdot 10^{-2}$ | 1.03 | $2.1 \cdot 10^{-6}$ | |

| | | | | |
|---|---|---|---|---|
| | Catalyst demand Kg (2.7 $mol_{MeOH}/s/Kg_{cat}$) x 10 (catalyst guard) | 575 | | |
| | Catalyst lifetime $Kg_{cat}/h$ (2 years) | $3.3 \cdot 10^{-2}$ | | |
| | | **kg/h** | **Molecular weights (kg/koml)** | **kg/kgMeOH** |
| | $CO_2$ (purge flaring+Waste 1/vapor distillate) | 2144 | 44.1 $CO_2$ | 0.13 |
| | $H_2O$ (purge flaring+vapor distillate) | 2144 | 18.0 $H_2O$ | 0.13 |
| **Wastes** | $CO_2$ biogenic | - | 2498 demand for flaring | - |
| | Carbon | 1117 | | 0.07 |
| | Water (Waste 2/Bottom liquid) | 1685 | | 0.10 |
| | Catalysts | $3.0 \cdot 10^{-2}$ | | $2 \cdot 10^{-6}$ |
| | | **kg/h** | | |
| **Product** | MeOH | 16353 | | |

**Table S-4.** Detailed material and energy flows of the plasma-assisted DMR-to-MeOH process utilizing biogas as carbon source.

| Plasma-assisted DMR-to-MeOH ; feed: biogas | | | | | |
|---|---|---|---|---|---|
| | | **kg/h** | **$m^3/h$ (25°C; 1bar)** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| **Raw material** | Natural gas ($CH_4$) | - | - | - | - |
| | Biogas | 30026 | | 1.84 | |
| | Water | 4221 | (water from 1st flash drum is recycled) | 0.26 | |
| **Utility** | | **MW** | | **$MJ/kg_{MeOH}$** | |
| | Hot utility (oil) | 30.7 | | 6.75 | |
| | Cold utility (water) | -39.6 | | 393 | **$kg/kg_{MeOH}$** |
| | Cold utility (refrig.) | -23.9 | 47 | 1 | **$kWh/Kg_{MeOH}$** |
| | | **kW** | | **kWh/kgMeOH** | |
| | Electricity | 103594 | | 6.3 | |
| | | 4088 | | 0.25 | **CW recirculation (20 bar loss)** |
| | Make-up water | | | 7.9 | **$kgwater/kg_{MeOH}$ (5% loss)** |
| **Catalyst Bi** | | **kg/h** | **$kg/k_{gcat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| | $Mg(NO_3)_2 \cdot 6H_2O$ | $1.3 \cdot 10^{-3}$ | 1.68 | $7.8 \cdot 10^{-8}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $3.7 \cdot 10^{-3}$ | 4.87 | $2.3 \cdot 10^{-7}$ | |
| | $Ni(NO_3)_2 \cdot 6H_2O$ | $3.8 \cdot 10^{-4}$ | 0.50 | $2.3 \cdot 10^{-8}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $3.1 \cdot 10^{-5}$ | $4 \cdot 10^{-2}$ | $1.9 \cdot 10^{-9}$ | |
| | $NH_4OH$ ($L/kg_{cat}$ ; density = 0.88 kg/L) | $1.3 \cdot 10^{-3}$ | 1.76 | | $8.2 \cdot 10^{-8}$ |
| | Catalyst demand Kg ($4\ mol_{CO}/s/Kg_{cat}$) | 20 | | | |
| | Catalyst lifetime $Kg_{cat}/h$ (3 years) | $8.0 \cdot 10^{-4}$ | | | |
| **$H_2S$ removal** | | **kg/h** | **$kg/k_{gcat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| | ZnO | | | | |
| | Material demand Kg/h (13.9 kgbiogas/ZnO) | 2160 | | 0.13 | |

| | | kg/h | kg/k$_{gcat}$ | kg/kg$_{MeOH}$ | m$^3$/kg$_{MeOH}$ |
|---|---|---|---|---|---|
| | $Cu(NO_3)_2 \cdot 3H_2O$ | $7.9 \cdot 10^{-2}$ | 2.41 | $4.8 \cdot 10^{-6}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $4.4 \cdot 10^{-2}$ | 1.33 | $2.7 \cdot 10^{-6}$ | |
| **Catalyst MeOH** | $Zn(NO_3)_2 \cdot 6H_2O$ | $3.4 \cdot 10^{-2}$ | 1.03 | $2.1 \cdot 10^{-6}$ | |
| | Catalyst demand Kg (2.7 mol$_{MeOH}$/s/Kg$_{cat}$) x 10 (catalyst guard) | 575 | | | |
| | Catalyst lifetime Kg$_{cat}$/h (2 years) | $3.3 \cdot 10^{-2}$ | | | |
| | | **kg/h** | **Molecular weights (kg/koml)** | **kg/kgMeOH** | |
| | $CO_2$ (purge flaring+Waste 1/vapor distillate) | 2144 | 44.1 $CO_2$ | 0.13 | |
| | $H_2O$ (purge flaring+vapor distillate) | 2144 | 18.0 $H_2O$ | 0.13 | |
| **Wastes** | $CO_2$ biogenic | 13304 | 2498 demand for flaring | 0.81 | |
| | Carbon | 1117 | | $7.0 \cdot 10^{-2}$ | |
| | Water (Waste 2/Bottom liquid) | 1685 | | 0.10 | |
| | Catalysts | $3.0 \cdot 10^{-2}$ | | $2 \cdot 10^{-6}$ | |
| | | **kg/h** | | | |
| **Product** | MeOH | 16353 | | | |

**Table S-5.** Detailed material and energy flows of the thermocatalytic DMR-to-MeOH process utilizing natural gas as carbon source.

| **Thermocatalytic DMR-to-MeOH ; feed: natural gas + $CO_2$** | | | | | |
|---|---|---|---|---|---|
| | | **kg/h** | **$m^3$/h (25°C; 1bar)** | **kg/$kg_{MeOH}$** | **$m^3$/kgMeOH** |
| **Raw material** | Natural gas ($CH_4$) | 15541 | 23978 | 0.44 | 0.67 |
| | $CO_2$ | 13753 | | 0.39 | |
| | Water | 14797 | (water from 1st, 2nd & 3rd flash drum is recycled) | 0.42 | |
| **Utility** | | **MW** | | **MJ/$kg_{MeOH}$** | |
| | Hot utility (oil) | 100.3 | | 10 | |
| | Cold utility (water) | -103.7 | | 475 | **$kg_{water}$/$kg_{MeOH}$** |
| | Cold utility (refrig.) | -6.6 | 13 | 0.13 | **$kWh_{cooling}$/$Kg_{MeOH}$** |
| | | **kW** | | **kWh/$kg_{MeOH}$** | |
| | Electricity | 38225 | | 1.1 | |
| | | 10667 | | 0.3 | **CW recirculation (20 bar loss)** |
| | Make-up water | | | 9.5 | **$kg_{water}$/$kg_{MeOH}$ (5% loss)** |
| **Catalyst DMR** | | **kg/h** | **kg/$kg_{cat}$** | **kg/$kg_{MeOH}$** | **$m^3$/$kg_{MeOH}$** |
| | $Mg(NO_3)_2 \cdot 6H_2O$ | $2.5 \cdot 10^{-3}$ | 1.68 | $6.9 \cdot 10^{-8}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $7.1 \cdot 10^{-3}$ | 4.87 | $2.0 \cdot 10^{-7}$ | |
| | $Ni(NO_3)_2 \cdot 6H_2O$ | $7.3 \cdot 10^{-4}$ | 0.50 | $2.1 \cdot 10^{-8}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $5.9 \cdot 10^{-5}$ | 0.04 | $1.6 \cdot 10^{-9}$ | |
| | $NH_4OH$ (= 2 L/kgcat) (considering density = 0.88 kg/L) | $2.6 \cdot 10^{-3}$ | 1.76 | | $7.0 \cdot 10^{-5}$ |
| | **Catalyst demand Kg** (5.9 $mol_{CO}$/s/$Kg_{cat}$) | 26 | | | |
| | **Catalyst lifetime Kgcat/h** (2 years) | $1.5 \cdot 10^{-3}$ | | | |
| **Catalyst MeOH** | | **kg/h** | **kg/$kg_{cat}$** | **kg/$kg_{MeOH}$** | **$m^3$/$kg_{MeOH}$** |
| | $Cu(NO_3)_2 \cdot 3H_2O$ | $1.6 \cdot 10^{-1}$ | 2.41 | $4.5 \cdot 10^{-6}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $8.8 \cdot 10^{-2}$ | 1.33 | $2.5 \cdot 10^{-6}$ | |
| | $Zn(NO_3)_2 \cdot 6H_2O$ | $6.8 \cdot 10^{-2}$ | 1.03 | $1.9 \cdot 10^{-6}$ | |
| | **Catalyst demand Kg** (2.7 $mol_{MeOH}$/s/$Kg_{cat}$) x 10 (catalyst guard) | 1154 | | | |

| | | | | | |
|---|---|---|---|---|---|
| | **Catalyst lifetime $Kg_{cat}$/h** (2 years) | $6.6 \cdot 10^{-2}$ | | | |
| **Catalyst SMR** | | **kg/h** | **$kg/kg_{cat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| | $Mg(NO_3)_2 \cdot 6H_2O$ | $1.8 \cdot 10^{-3}$ | 1.68 | $5.0 \cdot 10^{-8}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $5.1 \cdot 10^{-3}$ | 4.87 | $1.4 \cdot 10^{-7}$ | |
| | $Ni(NO_3)_2 \cdot 6H_2O$ | $5.2 \cdot 10^{-4}$ | 0.50 | $1.5 \cdot 10^{-8}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $4.2 \cdot 10^{-5}$ | 0.04 | $1.2 \cdot 10^{-9}$ | |
| | $NH_4OH$ (= 2 L/$kg_{cat}$ ; density = 0.88 kg/L) | $1.8 \cdot 10^{-3}$ | 1.76 | | $5.0 \cdot 10^{-5}$ |
| | **Catalyst demand Kg** (3.9 $mol_{CO}/s/Kg_{cat}$) | 46 | | | |
| | **Catalyst lifetime $Kg_{cat}$/h** (5 years) | $1.0 \cdot 10^{-3}$ | | | |
| **Catalyst WGS** | | **kg/h** | **$kg/kg_{cat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| | $La(NO_3)_3.6H_2O$ | $4.7 \cdot 10^{-2}$ | 2.20 | $1.3 \cdot 10^{-6}$ | |
| | $(NH_4)_2Ce(NO_3)_6$ | $1.7 \cdot 10^{-2}$ | 0.80 | $4.9 \cdot 10^{-7}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $1.6 \cdot 10^{-2}$ | 0.72 | $4.4 \cdot 10^{-7}$ | |
| | Glycerol | $4.1 \cdot 10^{-2}$ | 1.90 | $1.2 \cdot 10^{-6}$ | |
| | **Catalyst demand Kg** (0.4 $mol_{CO}/s/Kg_{cat}$) | 378 | | | |
| | **Catalyst lifetime $Kg_{cat}$/h** (2 years) | $2.2 \cdot 10^{-2}$ | | | |
| **Wastes** | | **kg/h** | **Molecular weights (kg/koml)** | **$kg/kg_{MeOH}$** | |
| | $CO_2$ (purge flaring+Waste 1/vapor distillate) | 7103 | 44.1 $CO_2$ | 0.20 | |
| | $H_2O$ (purge flaring+vapor distillate) | 7515 | 18.0 $H_2O$ | 0.21 | |
| | $CO_2$ biogenic | - | *8473 kg/h $O_2$ demand for flaring | - | |
| | Carbon | 39 | | $1.1 \cdot 10^{-3}$ | |
| | Water (Waste 2/Bottom liquid) | 2363 | | $7.0 \cdot 10^{-2}$ | |
| | Catalysts | $9.0 \cdot 10^{-2}$ | | $2.5 \cdot 10^{-6}$ | |
| **Product** | | **kg/h** | | | |
| | MeOH | 35557 | | | |

**Table S-6.** Detailed material and energy flows of the thermocatalytic DMR-to-MeOH process utilizing biogas as carbon source.

| | | | | | |
|---|---|---|---|---|---|
| | **Thermocatalytic DMR-to-MeOH ; feed: biogas** | | | | |
| | | **kg/h** | **$m^3$/h (25°C; 1bar)** | **kg/$kg_{MeOH}$** | **$m^3$/kgMeOH** |
| **Raw material** | Natural gas ($CH_4$) | 10528 | 16243 | 0.30 | 0.46 |
| | Biogas | 18766 | | 0.53 | |
| | Water | 14797 | (water from 1st, 2nd & 3rd flash drum is recycled) | 0.42 | |
| **Utility** | | **MW** | | **MJ/$kg_{MeOH}$** | |
| | Hot utility (oil) | 100.3 | | 10 | |
| | Cold utility (water) | -103.7 | | 475 | **$kg_{water}$/$kg_{MeOH}$** |
| | Cold utility (refrig.) | -6.6 | 13 | 0.13 | **$kWh_{cooling}$/$Kg_{MeOH}$** |
| | | **kW** | | **kWh/$kg_{MeOH}$** | |
| | Electricity | 38225 | | 1.1 | |
| | | 10667 | | 0.3 | **CW recirculation (20 bar loss)** |
| | Make-up water | | | 9.5 | **$kg_{water}$/$kg_{MeOH}$ (5% loss)** |
| **Catalyst DMR** | | **kg/h** | **kg/$kg_{cat}$** | **kg/$kg_{MeOH}$** | **$m^3$/$kg_{MeOH}$** |
| | $Mg(NO_3)_2 \cdot 6H_2O$ | $2.5 \cdot 10^{-3}$ | 1.68 | $6.9 \cdot 10^{-8}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $7.1 \cdot 10^{-3}$ | 4.87 | $2.0 \cdot 10^{-7}$ | |
| | $Ni(NO_3)_2 \cdot 6H_2O$ | $7.3 \cdot 10^{-4}$ | 0.50 | $2.1 \cdot 10^{-8}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $5.9 \cdot 10^{-5}$ | 0.04 | $1.6 \cdot 10^{-9}$ | |
| | $NH_4OH$ (= 2 L/kgcat) (considering density = 0.88 kg/L) | $2.6 \cdot 10^{-3}$ | 1.76 | | $7.0 \cdot 10^{-5}$ |
| | **Catalyst demand Kg** (5.9 $mol_{CO}$/s/$Kg_{cat}$) | 26 | | | |
| | **Catalyst lifetime Kgcat/h** (2 years) | $1.5 \cdot 10^{-3}$ | | | |
| **Catalyst MeOH** | | **kg/h** | **kg/$kg_{cat}$** | **kg/$kg_{MeOH}$** | **$m^3$/$kg_{MeOH}$** |
| | $Cu(NO_3)_2 \cdot 3H_2O$ | $1.6 \cdot 10^{-1}$ | 2.41 | $4.5 \cdot 10^{-6}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $8.8 \cdot 10^{-2}$ | 1.33 | $2.5 \cdot 10^{-6}$ | |
| | $Zn(NO_3)_2 \cdot 6H_2O$ | $6.8 \cdot 10^{-2}$ | 1.03 | $1.9 \cdot 10^{-6}$ | |
| | **Catalyst demand Kg** (2.7 $mol_{MeOH}$/s/$Kg_{cat}$) x 10 (catalyst guard) | 1154 | | | |

| | | | | | |
|---|---|---|---|---|---|
| | **Catalyst lifetime $Kg_{cat}$/h** (2 years) | $6.6 \cdot 10^{-2}$ | | | |
| | | **kg/h** | **$kg/kg_{cat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| **Catalyst SMR** | $Mg(NO_3)_2 \cdot 6H_2O$ | $1.8 \cdot 10^{-3}$ | 1.68 | $5.0 \cdot 10^{-8}$ | |
| | $Al(NO_3)_3 \cdot 9H_2O$ | $5.1 \cdot 10^{-3}$ | 4.87 | $1.4 \cdot 10^{-7}$ | |
| | $Ni(NO_3)_2 \cdot 6H_2O$ | $5.2 \cdot 10^{-4}$ | 0.50 | $1.5 \cdot 10^{-8}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $4.2 \cdot 10^{-5}$ | 0.04 | $1.2 \cdot 10^{-9}$ | |
| | $NH_4OH$ (= 2 $L/kg_{cat}$ ; density = 0.88 kg/L) | $1.8 \cdot 10^{-3}$ | 1.76 | | $5.0 \cdot 10^{-5}$ |
| | **Catalyst demand Kg** (3.9 $mol_{CO}/s/Kg_{cat}$) | 46 | | | |
| | **Catalyst lifetime $Kg_{cat}$/h** (5 years) | $1.0 \cdot 10^{-3}$ | | | |
| | | **kg/h** | **$kg/kg_{cat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| **Catalyst WGS** | $La(NO_3)_3.6H_2O$ | $4.7 \cdot 10^{-2}$ | 2.20 | $1.3 \cdot 10^{-6}$ | |
| | $(NH_4)_2Ce(NO_3)_6$ | $1.7 \cdot 10^{-2}$ | 0.80 | $4.9 \cdot 10^{-7}$ | |
| | $Fe(NO_3)_3 \cdot 9H_2O$ | $1.6 \cdot 10^{-2}$ | 0.72 | $4.4 \cdot 10^{-7}$ | |
| | Glycerol | $4.1 \cdot 10^{-2}$ | 1.90 | $1.2 \cdot 10^{-6}$ | |
| | **Catalyst demand Kg** (0.4 $mol_{CO}/s/Kg_{cat}$) | 378 | | | |
| | **Catalyst lifetime $Kg_{cat}$/h** (2 years) | $2.2 \cdot 10^{-2}$ | | | |
| | | **kg/h** | **Molecular weights (kg/koml)** | **$kg/kg_{MeOH}$** | |
| **Wastes** | $CO_2$ (purge flaring+Waste 1/vapor distillate) | 7103 | 44.1 $CO_2$ | 0.20 | |
| | $H_2O$ (purge flaring+vapor distillate) | 7515 | 18.0 $H_2O$ | 0.21 | |
| | $CO_2$ biogenic | - | *8473 kg/h $O_2$ demand for flaring | - | |
| | Carbon | 39 | | $1.1 \cdot 10^{-3}$ | |
| | Water (Waste 2/Bottom liquid) | 2363 | | $7.0 \cdot 10^{-2}$ | |
| | Catalysts | $9.0 \cdot 10^{-2}$ | | $2.5 \cdot 10^{-6}$ | |
| | | **kg/h** | **$kg/k_{gcat}$** | **$kg/kg_{MeOH}$** | **$m^3/kg_{MeOH}$** |
| **$H_2S$ removal** | ZnO | | | | |
| | Material demand Kg/h (13.9 kgbiogas/ZnO) | 1350 | | 0.13 | |
| | | **kg/h** | | | |
| **Product** | MeOH | 35557 | | | |

**Table S-7.** Ecoinvent dataset used for each mass and energy flow in the LCI modelling.

| | |
|---|---|
| *Inputs from Technosphere* | |
| Natural gas | Natural gas, high pressure {Europe without Switzerland}\| market group for \| Cut-off, U |
| Biogas | Biogas {CH}\| anaerobic digestion of manure \| Cut-off, U |
| Water | Water, deionised {Europe without Switzerland}\| market for water, deionised \| Cut-off, U |
| Hot utility | Heat, central or small-scale, natural gas {RER}\| market group for \| Cut-off, U |
| Electricity, low voltage | Electricity, low voltage {RER}\| market group for \| Cut-off, U |
| Electricity, high voltage | Electricity, high voltage {RER}\| market group for \| Cut-off, U |
| Cold utility, makeup water | Water, decarbonised {RER}\| water production, decarbonised adapted |
| Catalyst DMR/BiMR/SMR | Catalyst Fe-Ni/$MgAl_2O_4$ |
| Catalyst MeOH | Catalyst Cu-Zn-Al |
| Catalyst WGS | Catalyst La-Ce-Fe |
| ZnO for $H_2S$ removal | Zinc oxide {GLO}\| market for \| Cut-off, U |
| *Emissions to air* | |
| $CO_2$ from flaring | Carbon dioxide |
| $H_2O$ form flaring | Water |
| *Outputs to Technosphere* | |
| Waste water | Wastewater, unpolluted {RoW}\| treatment of, capacity 5E9l/year \| Cut-off, U |
| Carbon waste | Inert waste, for final disposal {CH}\| treatment of inert waste, inert material landfill \| Cut-off, U |
| Catalyst waste | Spent catalyst base from ethylene oxide production {GLO}\| market for \| Cut-off, U |

**Table S-8.** Key performance indicators (KPI) as function of $CH_4$ conversion (x) in the DMR reactor. The KPI's were normalized to functional unit: Electricity, HV and LV ($y_1$ and $y_2$) = $kWh/kg_{MeOH}$; Heat, fossil-based ($y_3$) = $MJ/kg_{MeOH}$; Heat, electrically conductive ($y_7$) = $kWh/kg_{MeOH}$; Natural gas ($y_4$) = $m^3/kg_{MeOH}$; Biogas ($y_5$) = $m^3/kg_{MeOH}$; Direct $CO_2$ ($y_6$) = $kg_{CO2}/kg_{MeOH}$. X ranges from 0.38-0.63 and 0.76-0.92 for the plasma-assisted and thermocatalytic DMR-to-MeOH process, respectively.

| **KPI** | | **Proposed DMR-to-MeOH processes** | |
|---|---|---|---|
| | | **Scenario PNGG, PNGHVPV and PNGHVWM** | **Scenario PBGG** |
| HV electricity[1] | ($y_1$) | $y_1 = 0.0469x^2 - 0.1554x + 6.3384$; $R^2=1$ | $y_1 = 0.0469x^2 - 0.1554x + 6.3384$; $R^2=1$ |
| LV electricity[2] | ($y_2$) | $y_2 = 0.0172x^2 - 0.1296x + 1.3498$; $R^2=1$ | $y_2 = 0.0172x^2 - 0.1296x + 1.3498$; $R^2=1$ |
| Heat | ($y_3$) | $y_3 = 0.5481x^2 - 6.616x + 9.981$; $R^2=1$ | $y_3 = 0.5481x^2 - 6.616x + 9.981$; $R^2=1$ |
| Natural gas | ($y_4$) | $y_4 = -0.0659x + 0.7906$; $R^2=0.9992$ | |
| Biogas | ($y_5$) | | $y_5 = -0.139x + 1.6687$; $R^2=0.9992$ |
| Direct $CO_2$ | ($y_6$) | $y_6 = 0.0027x^2 + 0.0264x + 0.1156$; $R^2=1$ | $y_6 = 0.0027x^2 + 0.0264x + 0.1156$; $R^2=1$ |
| | | **Scenario TNG** | **Scenario TBG** |
| LV electricity | ($y_2$) | $y_2 = -0.0084x^2 + 0.0092x + 1.4295$; $R^2=0.9874$ | $y_2 = -0.0084x^2 + 0.0092x + 1.4295$; $R^2=0.9874$ |
| Heat | ($y_3$) | $y_3 = -1.8869x^2 + 2.4965x + 9.3912$; $R^2=0.9991$ | $y_3 = -1.8869x^2 + 2.4965x + 9.3912$; $R^2=0.9991$ |
| Natural gas | ($y_4$) | $y_4 = -0.0123x + 0.6847$; $R^2=0.9995$ | $y_4 = -0.0083x + 0.4638$; $R^2=0.9995$ |
| Biogas | ($y_5$) | | $y_5 = -0.0083x + 0.4638$; $R^2=0.9995$ |
| Direct $CO_2$ | ($y_6$) | $y_6 = -0.002\ln(x) + 0.1991$; $R^2=0.9340$ | $y_6 = -0.002\ln(x) + 0.1991$; $R^2=0.9340$ |
| | | **Scenario TNGG** | **Scenario TNGPV and TNGWM** |
| LV electricity | ($y_2$) | $y_2 = -0.5325x^2 + 0.7027x + 4.0382$; $R^2=0.9993$ | $y_2 = -0.0084x^2 + 0.0092x + 1.4295$; $R^2=0.9874$ |
| LV-H electricity[3] | ($y_7$) | | $y_7 = -1.8869x^2 + 2.4965x + 9.3912$; $R^2=0.9991$ |
| Natural gas | ($y_4$) | $y_4 = -0.0123x + 0.6847$; $R^2=0.9995$ | $y_4 = -0.0123x + 0.6847$; $R^2=0.9995$ |
| Direct $CO_2$ | ($y_6$) | $y_6 = -0.002\ln(x) + 0.1991$; $R^2=0.9340$ | $y_6 = -0.002\ln(x) + 0.1991$; $R^2=0.9340$ |
| | | **Scenario PNGWM** | **Scenario TNGWM** |
| HV electricity | ($y_1$) | $y_1 = 0.0469x^2 - 0.1554x + 6.3384$; $R^2=1$ | |
| LV electricity | ($y_2$) | $y_2 = 0.1694x^2 - 1.9674x + 4.1223$; $R^2=1$ | $y_2 = -0.5325x^2 + 0.7027x + 4.0382$; $R^2=0.9993$ |
| Natural gas | ($y_4$) | $y_4 = -0.0659x + 0.7906$; $R^2=0.9992$ | $y_4 = -0.0123x + 0.6847$; $R^2=0.9995$ |
| Direct $CO_2$ | ($y_6$) | $y_6 = 0.0027x^2 + 0.0264x + 0.1156$; $R^2=1$ | $y_6 = -0.002\ln(x) + 0.1991$; $R^2=0.9340$ |

[1] High voltage electricity only utilized in plasma reactor
[2] Low voltage electricity utilized for electrically conductive heating and fluids transfer
[3] Low voltage electricity utilized for electrically conductive heating in thermocatalytic reactor

**Table S-9.** Environmental footprint results for all the scenarios

| **Indicator** | **Unit** | **PNGG** | **PBGG** | **TNG** | **TBG** |
|---|---|---|---|---|---|
| Climate change | kg $CO_2$ eq | 4.12E+00 | 7.46E+00 | 1.86E+00 | 2.82E+00 |
| Ozone depletion | kg CFC11 eq | 5.96E-07 | 4.28E-07 | 3.76E-07 | 3.28E-07 |
| Ionising radiation | kBq U-235 eq | 1.77E+00 | 1.86E+00 | 3.58E-01 | 3.85E-01 |
| Photochemical ozone formation | kg NMVOC eq | 8.69E-03 | 9.80E-03 | 3.14E-03 | 3.47E-03 |
| Particulate matter | disease inc. | 5.43E-08 | 5.80E-07 | 1.67E-08 | 1.68E-07 |
| Human toxicity, non-cancer | CTUh | 3.23E-08 | 4.53E-08 | 1.08E-08 | 1.46E-08 |
| Human toxicity, cancer | CTUh | 9.82E-10 | 1.21E-09 | 4.30E-10 | 4.98E-10 |
| Acidification | mol H+ eq | 1.93E-02 | 9.10E-02 | 5.43E-03 | 2.60E-02 |
| Eutrophication, freshwater | kg P eq | 3.14E-03 | 3.22E-03 | 6.49E-04 | 6.74E-04 |
| Eutrophication, marine | kg N eq | 3.33E-03 | 5.68E-03 | 9.62E-04 | 1.64E-03 |
| Eutrophication, terrestrial | mol N eq | 3.19E-02 | 3.49E-01 | 9.55E-03 | 1.01E-01 |
| Ecotoxicity, freshwater | CTUe | 4.14E+01 | 5.30E+01 | 1.48E+01 | 1.82E+01 |
| Land use | Pt | 1.51E+01 | 2.49E+01 | 3.83E+00 | 6.65E+00 |
| Water use | $m^3$ depriv. | 1.07E+00 | 1.10E+00 | 5.83E-01 | 5.92E-01 |
| Resource use, fossils | MJ | 1.04E+02 | 8.17E+01 | 5.15E+01 | 4.51E+01 |
| Resource use, minerals and metals | kg Sb eq | 1.13E-05 | 1.68E-05 | 6.38E-06 | 8.01E-06 |
| **Indicator** | **Unit** | **PNGHVPV** | **PNGHVWM** | **TNGG** | **TNGPV** |
| Climate change | kg $CO_2$ eq | 1.82E+00 | 1.71E+00 | 2.29E+00 | 1.79E+00 |
| Ozone depletion | kg CFC11 eq | 4.05E-07 | 3.91E-07 | 4.00E-07 | 3.60E-07 |
| Ionising radiation | kBq U-235 eq | 3.30E-01 | 3.35E-01 | 1.01E+00 | 6.81E-01 |
| Photochemical ozone formation | kg NMVOC eq | 4.04E-03 | 4.04E-03 | 5.14E-03 | 4.19E-03 |
| Particulate matter | disease inc. | 2.80E-08 | 3.57E-08 | 3.34E-08 | 3.06E-08 |
| Human toxicity, non-cancer | CTUh | 1.49E-08 | 3.77E-08 | 2.36E-08 | 2.11E-08 |
| Human toxicity, cancer | CTUh | 8.03E-10 | 1.28E-09 | 7.21E-10 | 6.55E-10 |
| Acidification | mol H+ eq | 6.45E-03 | 7.64E-03 | 1.15E-02 | 8.75E-03 |
| Eutrophication, freshwater | kg P eq | 6.39E-04 | 8.71E-04 | 1.82E-03 | 1.28E-03 |
| Eutrophication, marine | kg N eq | 1.25E-03 | 1.20E-03 | 1.95E-03 | 1.50E-03 |
| Eutrophication, terrestrial | mol N eq | 1.26E-02 | 1.23E-02 | 1.88E-02 | 1.46E-02 |
| Ecotoxicity, freshwater | CTUe | 2.08E+01 | 3.52E+01 | 2.77E+01 | 2.35E+01 |
| Land use | Pt | 1.72E+01 | 5.69E+00 | 9.45E+00 | 2.35E+01 |
| Water use | $m^3$ depriv. | 5.43E-01 | 5.70E-01 | 8.51E-01 | 8.14E-01 |
| Resource use, fossils | MJ | 5.42E+01 | 5.24E+01 | 6.53E+01 | 5.41E+01 |
| Resource use, minerals and metals | kg Sb eq | 9.58E-06 | 2.75E-05 | 1.36E-05 | 2.77E-05 |
| **Indicator** | **Unit** | **TNGWM** | **PNGWM** | **TNGWM** | |
| Climate change | kg $CO_2$ eq | 1.73E+00 | 1.21E+00 | 6.15E-01 | |
| Ozone depletion | kg CFC11 eq | 3.52E-07 | 3.47E-07 | 2.57E-07 | |
| Ionising radiation | kBq U-235 eq | 6.74E-01 | 3.58E-02 | 1.87E-02 | |
| Photochemical ozone formation | kg NMVOC eq | 3.98E-03 | 3.00E-03 | 1.70E-03 | |
| Particulate matter | disease inc. | 2.77E-08 | 3.06E-08 | 1.64E-08 | |
| Human toxicity, non-cancer | CTUh | 2.30E-08 | 3.71E-08 | 2.17E-08 | |
| Human toxicity, cancer | CTUh | 7.32E-10 | 1.28E-09 | 7.53E-10 | |
| Acidification | mol H+ eq | 8.65E-03 | 5.04E-03 | 2.96E-03 | |
| Eutrophication, freshwater | kg P eq | 1.28E-03 | 3.87E-04 | 2.23E-04 | |
| Eutrophication, marine | kg N eq | 1.43E-03 | 7.37E-04 | 4.18E-04 | |
| Eutrophication, terrestrial | mol N eq | 1.40E-02 | 8.01E-03 | 4.58E-03 | |

| | | | | |
|---|---|---|---|---|
| Ecotoxicity, freshwater | CTUe | 2.47E+01 | 3.25E+01 | 1.89E+01 |
| Land use | Pt | 6.86E+00 | 3.35E+00 | 1.74E+00 |
| Water use | $m^3$ depriv. | 7.27E-01 | 4.58E-01 | 4.82E-01 |
| Resource use, fossils | MJ | 5.32E+01 | 4.15E+01 | 2.94E+01 |
| Resource use, minerals and metals | kg Sb eq | 1.53E-05 | 2.91E-05 | 1.87E-05 |