# Supporting Information

# Next Generation Multiphase System for Homogeneous Catalyst Recycling:

# Overcoming the Reactivity vs. Separation Dilemma

**Authors: Tim B. Riemer,[a] + Anna Kampwerth,[a] + Tim Sinnhoffer,[a] Moritz Prange,[a] Marc Häusler,[a] Dieter Vogt,[a] and Thomas Seidensticker*[a]**

Tim B. Riemer, + Anna Kampwerth, + Tim Sinnhoffer, Moritz Prange, Marc Häusler, Dieter Vogt, and Thomas Seidensticker*, TU Dortmund University, Department for Biochemical and Chemical Engineering, Laboratory of Industrial Chemistry, Emil-Figge-Straße 66, 44227 Dortmund, Germany.

Email: thomas.seidensticker@tu-dortmund.de

Tel: +49 231 7552310

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# 1. Experimental Procedures

## 1.1 Chemicals

**Table S1**: List of Chemicals used in this work.

| Chemical | Supplier | Purity |
|---|---|---|
| 1-Decene | Alfa Aesar | 96 |
| Argon | Messer | 99.996 |
| Carbon monoxide | Messer | 98 |
| Diethylamine | Carl Roth | >99.5 |
| Dibutyl ether | TCI | >99 |
| Ethylene glycol | Fischer Scientific | 99 |
| Hydrogen | Messer | 99.999 |
| Isopropanol | TCI | >99 |
| Methanol | Carl Roth | 99 |
| Nitrogen | Messer | 99.5 |
| Rh(acac)(cod) | Umicore | >99 |
| SulfoXantphos | MOLISA | - |
| Ultrapure Water | Generated with PURELAB flex 3 | - |

## 1.2 Analytics

Offline analysis of the sample was performed using an Agilent Technologies (7890A) gas chromatograph (GC) equipped with an HP-5 column (30 m x 0.32 mm x 0.25 µm). All samples were prepared by mixing 0.5 g of isopropanol with 0.05 g of the internal standard di-*n*-butyl ether and 0.45 g of the reaction solution. A thermal conductivity detector (TCD) with helium as carrier gas (injection volume 1 µL, split ratio 1:100) was used to determine the water concentration, while all other components were measured with a flame ionization detector (FID) and nitrogen as carrier gas (injection volume 1 µL, split ratio 1:100). An identical GC, column and detector, but with helium as carrier gas (1 µL injection volume, split ratio 1:400) was used for performing the online measurements of the decanter product phase. The inlet of the GC was directly connected to the decanter *via* a capillary, which enabled automatic measurements every hour.
The concentrations of rhodium and phosphorus were measured by inductively coupled plasma emission spectroscopy (ICP-OES, Analytik Jena (Plasma Quant 9000)). Samples with rhodium or phosphorus concentration under the detection limit of 1 ppm were concentrated *via* evaporation under vacuum prior to analysis.

**Table S2**: Temperature profile of the offline and online Gas Chromatographs.

| | Offline GC FID | Online GC FID | Offline GC TCD |
|---|---|---|---|
| $T_{Start}$ | 40 °C<br>(hold 1 min) | 40 °C<br>(hold 2 min) | 30<br>(hold 2.9 min) |
| Ramp 1 | 25 °C/min to 140 °C | 20 °C/min to 110 °C (hold 3 min) | 30 °C/min to 110 °C |
| Ramp 2 | 5 °C/min to 180 °C | 2.5 °C/min to 140 °C | 10 °C/min to 130 °C |
| Ramp 3 | 40 °C/min to 320 °C<br>(hold 6 min) | 50 °C/min to 320 °C (hold 8 min) | 20 °C/min to 152 °C |
| Ramp 4 | | | 12 °C/min to 198 °C |

| | |
|---|---|
| Ramp 5 | 50 °C/min to 320 °C (hold 4 min) |

**Table S3**: Retention times and response factors for the offline and online GC analysis.

| | Offline GC | | Online GC | |
|---|---|---|---|---|
| Substance | Retention [min] | Response Factor | Retention [min] | Response Factor |
| Methanol | 2.29 | 0.4153 | 2.3 | 4.54E-05 |
| Diethylamine | 2.6 | 0.903 | 2.71 | 3.22E-05 |
| Ethylene glycol | 3.14 | 0.3865 | 3.65 | 3.72E-05 |
| 1-Decene | 5.07 | 1.3277 | 6.48 | 1.45E-05 |
| Decane | 5.12 | 1.339 | 6.57 | 1.45E-05 |
| Iso-decenes | 5.16 – 5.22 | 1.3277 | 6.63 – 6.73 | 1.53E-05 |
| b-Undecanal | 7.15 | 0.8639 | 11.54 | 2.05E-05 |
| l-Undecanal | 7.56 | 0.8639 | 12.79 | 2.05E-05 |
| b-Amine | 9.46 | 1.1789 | 18.49 | 1.56E-05 |
| b-Enamine | 9.56 | 1.1789 | 18.78 | 1.56E-05 |
| l-Amine | 10.8 | 1.1789 | 21.39 | 1.56E-05 |
| l-Enamine | 11.44 | 1.1789 | 21.81 | 1.56E-05 |
| Aldol condensate | >16.51 | 1.1333 | >24.48 | 2.03E-05 |
| Water[a] | 2.65 | 0.994 | - | - |

[a] Only on offline GC *via* TCD.

### 1.3 Safety Statement

Strict safety precautions must be taken when carrying out high-pressure experiments with compressed $H_2$ and CO, and only with the appropriate equipment.

### 1.4 Miniplant Setup

The miniplant setup mainly consists of the CSTR (B1), a decanter (B2), and a membrane unit (M1). The reaction solution continuously leaves the reactor, is cooled to 10 °C, and settles in B2. Here, the product phase is released into a product tank after phase separation. The online GC automatically takes a GC sample from the product phase every hour to determine the reaction yields. The polar catalyst phase flows from the decanter into a buffer tank (B3), which decouples the recycle catalyst stream of the CSTR from the membrane loop. This configuration ensures a high feed flow velocity over the membrane even with low reactor throughputs and, thus, small recycle streams. To counter the accumulation of water in the process, water is continuously removed from the process via the organic solvent nanofiltration (OSN) membrane. Since the permeability of molecules through the OSN membrane is mainly dependent on their polarity, besides water, the polar solvents are leaving the process over M1, too. Therefore, a solvent makeup is pumped into the buffer tank to maintain a constant mass and ratio of solvents. The mentioned makeup pump can also be used to adjust the solvent ratio in the process. The gas ratio of hydrogen and carbon monoxide in the CSTR is controlled over two mass flow controllers. The gas phase concentration is measured via GC TCD over the miniplant operation to verify their ratio further. Additionally, offline samples of the recycle, permeate, and product streams are taken and analyzed every few hours via GC FID and TCD. The concentration of rhodium and ligand is determined via ICP-OES.

### 1.6 Batch Recycling Experiments

Figure S1: Setup for the recycling experiments in the 300 mL autoclave.

### 1.8 Phase Investigation Experiments:

*Phase Investigations at 10 °C for the ternary phase diagrams:*

To determine the ternary phase diagrams, the compositions to be investigated were filled in screw-cap tubes on a scale of 2.5 mL, filling them to about one-third of their capacity. The tubes were closed and sealed with parafilm. For 1 hour, the samples were then placed in an ultrasonic bath, which was occasionally cooled with ice to maintain a temperature well below the boiling point of methanol at all times. The samples were then placed in a temperature-controlled bath at 10 °C for 20 minutes. Samples that were monophasic at this point were discarded. From the two-phase samples, a small amount of the upper phase was first carefully removed, followed by the lower phase, using a fine cannula. These two samples were then analyzed by gas chromatography.

*Phase Investigations with miniplant solutions:*

In order to get reliable information about the real phase behavior during the miniplant operation, phase investigations were performed in a stainless steel sight reactor under reaction conditions. The influences of all components on the phase behavior were included since these investigations were performed with real miniplant solutions of the recycle and product phases. First, the sight reactor is filled with the solution to be investigated. After the sight reactor has been pressure-sealed, it is pressurized with 6 bar hydrogen. Then, the reactor is heated to the desired temperature *via* a thermostat while the solution is mixed using an overhead stirrer. When the desired temperature was reached, the stirrer was turned off. After 15 minutes, the phase conditions were checked *via* the sight glasses. If the solution in the sight reactor was biphasic, a sample of the polar and the nonpolar phase was taken *via* two sampling valves. The compositions of these two phases (which are both located on the binodal curve of the LLE diagram) were determined *via* GC FID and GC TCD. Afterward, a solution consisting of methanol and the miniplant product phase solution was pumped into the sight reactor *via* an HPLC pump. The reactor was stirred again for 15 minutes and heated to the desired temperature. Again, after allowing the phases to settle for 15 minutes, the phase conditions in the reactor were verified via the sight glasses. If the solution was still biphasic, the above-mentioned procedure was repeated. If the solution in the sight reactor was monophasic, a GC sample was taken from the reactor solution. Then, ethylene glycol or a product phase solution was pumped into the reactor to shift the composition of the mixture into the biphasic area. Again, the reactor was stirred for 15 minutes and heated to the desired temperature. After allowing the phases to settle for 15 minutes, the phase conditions in the reactor were verified again *via* the sight glasses. Then, the procedure, which depends on the monophasic or biphasic nature of the solution, is repeated until sufficient data points are obtained.

## 2. Results and Discussion

### 2.1 Side product identification N,N-diethyl-4-hydroxypentanamide

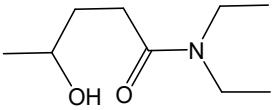


**Figure S2.** Chemical structure of N,N-diethyl-4-hydroxypentanamide.

**GC-MS:**
The samples for MS were diluted to 100 µg/mL with dried methanol as solvent and measured with an Agilent Technologies 7890B gas chromatograph equipped with an Agilent 5977 MSD module.

**HPLC-HRMS:**
The samples for MS were diluted to 100 µg/mL with dried methanol as solvent. The HPLC separation was performed with an Agilent 1200-series and the mass analysis was performed with LTQ-Orbitrap from Thermo Fisher Scientific. The MS samples were measured in DR. ZÜHLKE's workgroup at TU Dortmund.

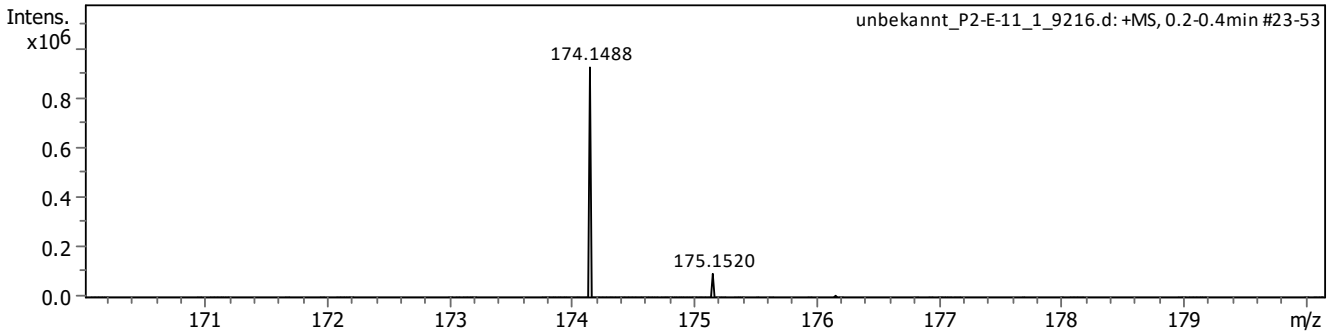


**Figure S3.** LC-HRMS of N,N-diethyl-4-hydroxypentanamide [M+H]+: calculated: 174.1494; detected: 174.1488 (3.4 ppm deviation)

**GC-MS** (EI 70 eV) m/z (%): 55 (29.6), 56 (12.2), 57 (12.2), 58 (100.0), 59 (10.0), 70 (5.5), 72 (37.5), 73 (8.8), 74 (18.0), 83 (11.3), 85 (6.8), 86 (11.6), 87 (7.3), 100 (42.3), 101 (5.6), 114 (5.3), 115 (52.4), 128 (16.9), 129 (7.2), 158 (4.6)

## 2.2 Further investigations of the γ-Valerolactone solvent system

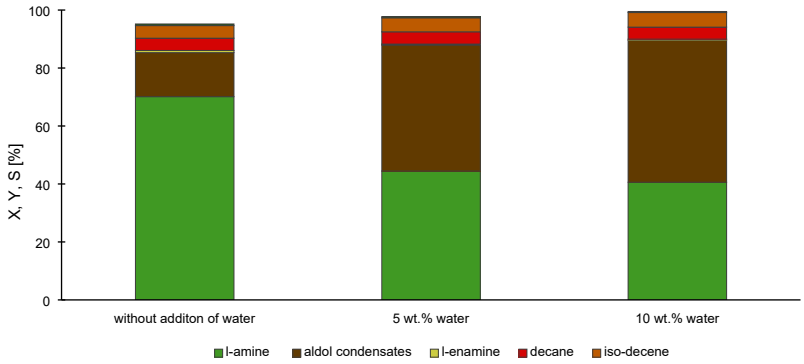


**Figure S4** Hydroaminomethylation of 1-decene with diethylamine in the γ-valerolactone solvent system with the addition of water before the reaction. Conditions: $n_{1\text{-decene}}$ = 88.4 mmol (11.2 w%), $n_{DEA}/n_{1\text{-decene}}$ = 1, 0.1 mol% Rh(acac)(cod), $n_{Lig}/n_{Cat.}$= 3.5, T = 125 °C, p = 36 bar, $p_{H2}/p_{CO}$ = 2, γ-valerolactone, $m_{total}$ = 100 g, $T_{Separation}$ = 10 °C.

*Product Composition in γ-Valerolactone TMS and Leaching values:*

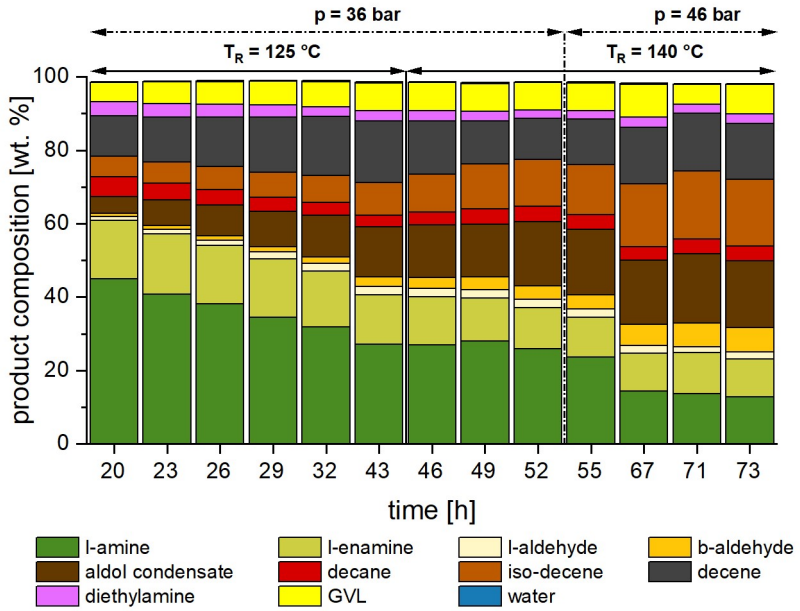


**Figure S5.** Product composition in continuous miniplant operation for GVL TMS. Conditions: $T_{decanter}$ = 10 °C.

**Table S4:** Rhodium (Rh) and SulfoXantphos (SX) losses of the miniplant experiments of the γ-Valerolactone TMS *via* the product phase of the TMS in the decanter. The losses of Rh and SX were measured via inductively coupled plasma-optical emission spectrometry.

| Species | Loss per hour [%/h][a] | Loss per product [mg/kg] |
|---|---|---|
| Rh | 0.028 | 8.3 |
| SX | 0.012 | 92.6 |

[a] Percentage losses refer to the initial mass of Rh and SX in the miniplant.

## 2.3 Recycle Composition in γ-Valerolactone, Water/Methanol, Ethylene Glycol/Methanol TMS

The recycle composition throughout continuous miniplant operation is shown in Figure S6 for the γ-valerolactone solvent system, Figure S7 for the methanol/water TMS and in Figure S8 for the methanol/ethylene glycol TMS.

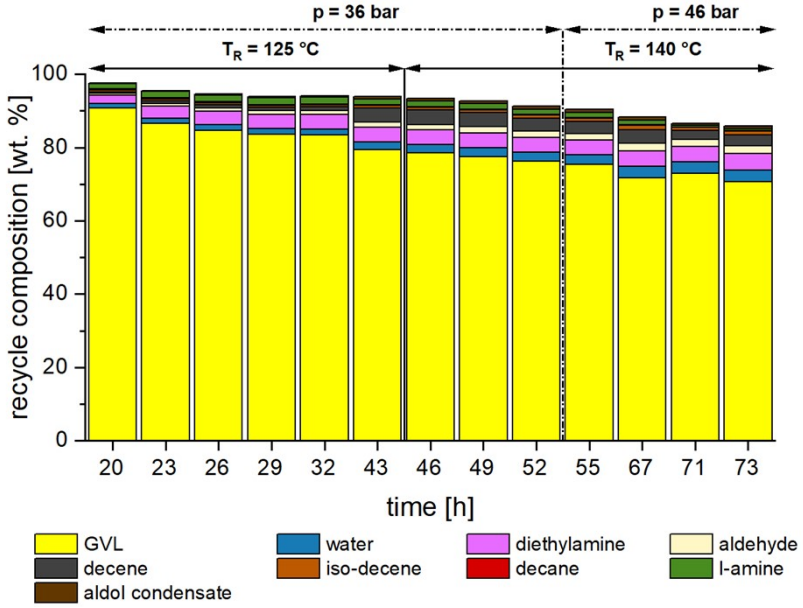


**Figure S6.** Recycle composition in continuous miniplant operation for GVL TMS. Conditions: $T_{decanter}$ = 10 °C, $T_{buffer\ tank}$ = 35 °C. The accumulation of the by-product N,N-diethyl-4-hydroxypentanamide, formed from GVL, is represented by the rising gap from the sum of the recycle composition to 100 wt.%.

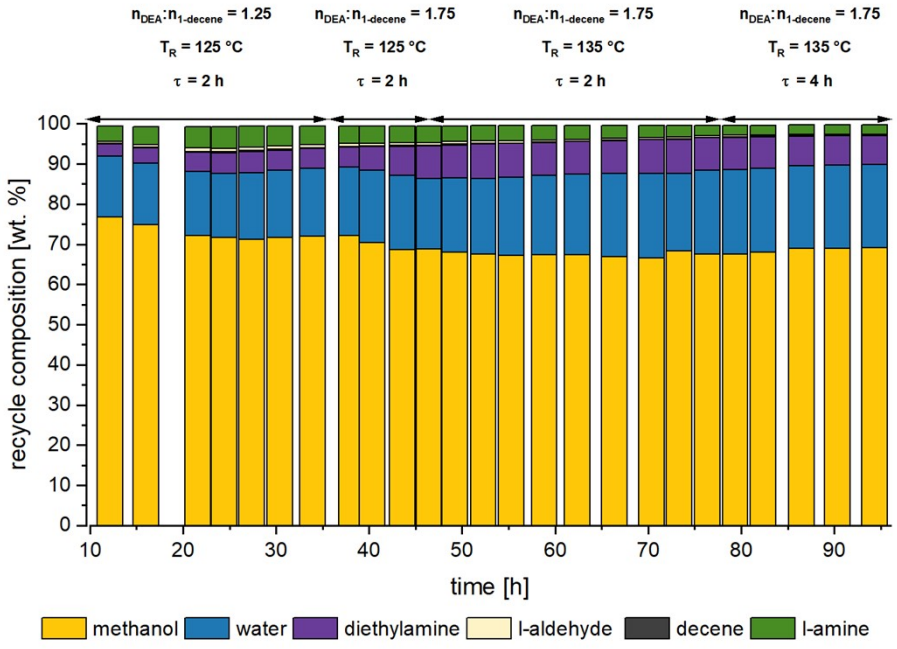


**Figure S7.** Recycle composition in continuous miniplant operation for water/methanol TMS. Conditions: $T_{decanter}$ = 10 °C, $T_{buffer\ tank}$ = 35 °C.

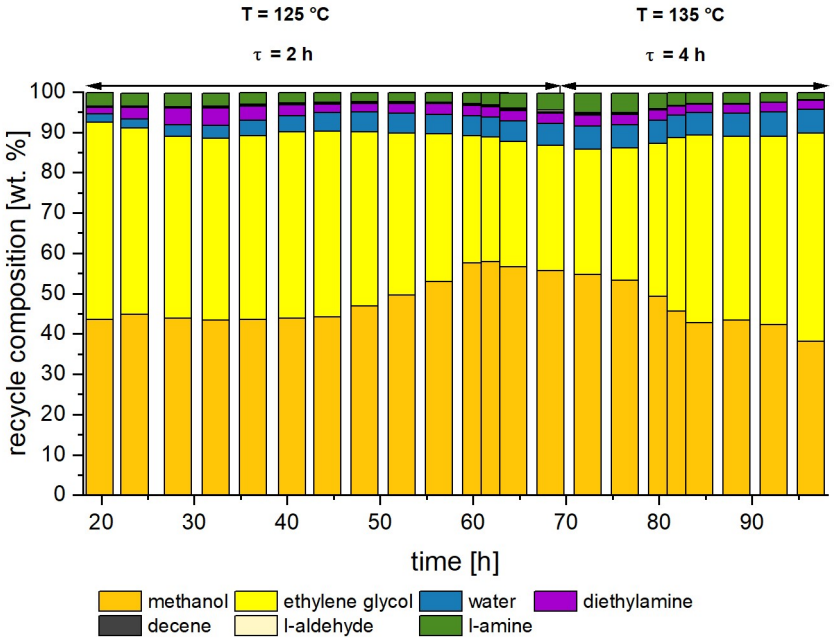


**Figure S8.** Recycle composition in continuous miniplant operation for ethylene glycol/methanol TMS. Conditions: $T_{decanter}$ = 10 °C, $T_{buffer\ tank}$ = 35 - 55 °C.

## 2.4 Ternary phase diagram of ethylene glycol/methanol TMS

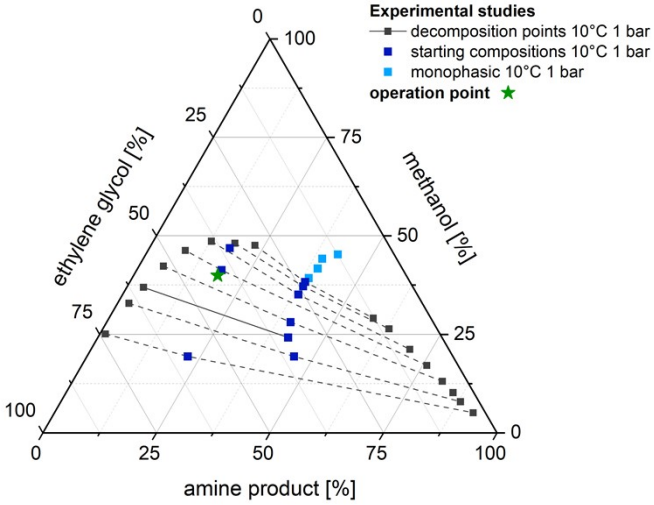


**Figure S9.** Ternary diagram of the ethylene glycol/methanol solvent system. Conditions: 10 °C, 1 bar, N = 0-200 rpm.

The recycling reactions of the third solvent system, ethylene glycol/methanol, were performed in a liquid biphasic regime. In previous investigations, our group[1] already experienced other switchable solvent systems, which showed high reaction performance even under biphasic conditions since, despite its biphasic character, sufficient mass transport was accomplished with the proper solvent ratio. To be able to determine the effects of the mono- or biphasic character of the ethylene glycol/methanol TMS investigated here, the real phase behavior of this system, including the influence of all substrates and products of the hydroaminomethylation, was determined in dependency of the solvent ratio. For this purpose, phase investigations with solutions of previous miniplant experiments were performed for the ethylene glycol/methanol solvent system. Since we are dealing with real solutions with far more than three components, pseudo-

components are introduced, which still allow visualization in the ternary diagram. For this purpose, ethylene glycol and water were summarized into one pseudo-component, as they have a segregating effect on the phase behavior. Methanol and diethylamine are summarized as the second pseudo-component, as these have a homogenizing effect on the phase behavior. The third pseudo-component combines 1-decene and all derived products, which make up the majority of the product phase. The resulting ternary diagram at the reaction temperature of 125 °C is shown in Figure S10 A).

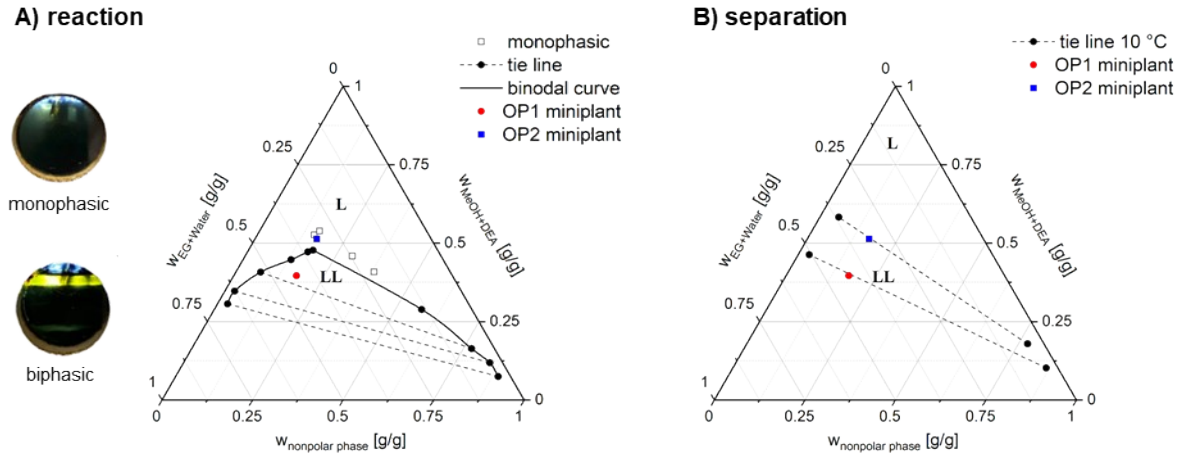


**Figure S10.** Ternary diagram **A)** of the ethylene glycol/methanol solvent system at reaction temperature. **B)**: Ternary diagram with the stationary product and catalyst phase compositions after phase separation via decanter during miniplant operation and their resulting tie lines. Conditions: A): 125 °C, 12 bar of hydrogen, N = 0-200 rpm, B): 10 °C, 36 bar $CO/H_2$. Assumption made for B): At the considered stationary points, the difference between the recycle phase composition in the buffer tank of the membrane loop and the recycle phase composition in the decanter is negligible, as the recycle stream is significantly larger than the permeate stream.

The operating point 1 (Figure S10 A, OP1) of the recycle experiments and starting point of the miniplant experiment is located in the biphasic area at a methanol/ethylene glycol ratio of 0.96. In the continuous process, the operating point is then shifted into the monophasic area (Figure S10 A, OP2) by increasing the methanol/ethylene glycol ratio to 1.8. The stationary phase compositions of the product and catalyst phases obtained after phase separation in the decanter and their resulting tie lines are shown in Figure S10, B.

## 2.5 Water separation through OSN Membrane

**Water/methanol TMS:**

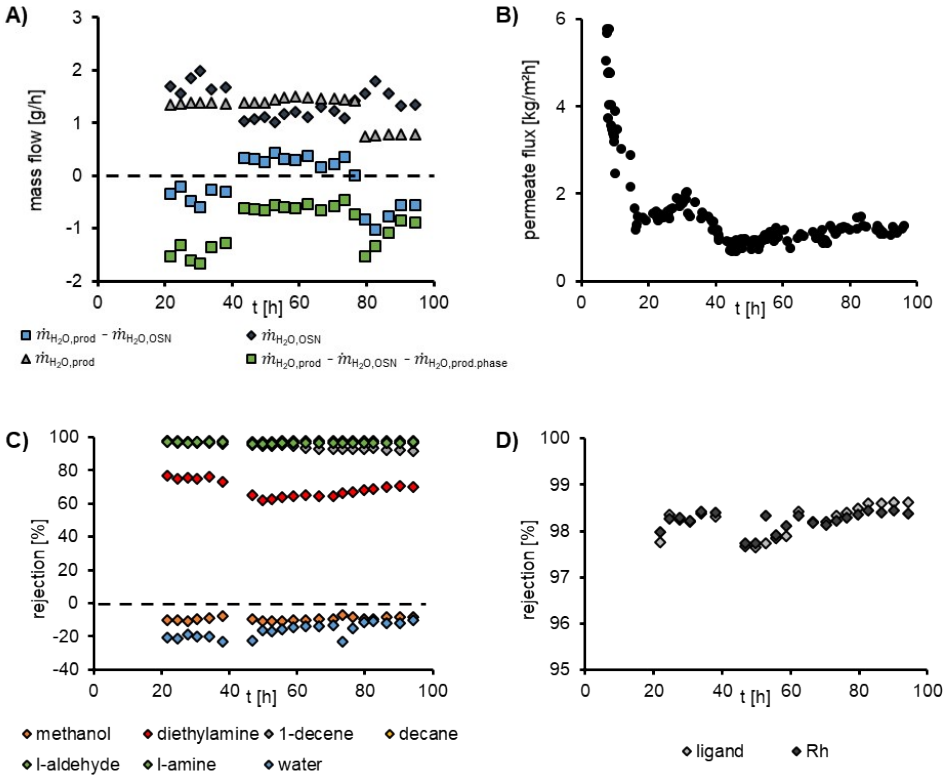


**Figure S11.** In **A),** the water accumulation/discharge is shown for the water/methanol TMS miniplant operation. Here, $\dot{m}_{H2O,prod}$ refers to the water mass produced in the reaction, $\dot{m}_{H2O,OSN}$ to the water mass leaving the process via organic solvent nanofiltration membrane and $\dot{m}_{H2O,prod.phase}$ to the water mass leaving the process over the product phase. In **B),** the permeate flux over the miniplant operation is shown. The rejections of the liquid components and of the catalyst are displayed in **C)** and **D)**. Conditions: Membrane: Nanopro S-3012, $A_{mem}$ = 52 cm², $T_{feed}$ = 35 °C, $p_{feed}$ = 36 bar, and $V_{feed}$ = 50 L $h^{-1}$. The compositions of feed and permeate were determined via GC-FID and GC-WLD measurements.

**Ethylene glycol/methanol TMS:**

In order to investigate the suitability of the organophilic nanofiltration membrane Nanopro S-3012 for the ethylene glycol/methanol solvent system, preliminary membrane experiments were carried out with a model feed solution prior to the miniplant experiment (see Figure S12). These experiments were performed in the membrane loop section of the miniplant.

Experimental procedure of membrane experiments:
First, the membrane feed solution (ethylene glycol, methanol, water, decane, DEA, l-amine, 1-decene, and l-aldehyde) with a realistic recycle composition was degassed with argon for 30 min in an ultrasonic bath. Then, the ligand SulfoXantphos was dissolved in the degassed solution. The system was flushed several times with nitrogen, and the membrane module with the NanoPro S-3012 OSN membrane sheet was connected in nitrogen crossflow. The feed solution is pumped into the membrane buffer tank, and the system is pressurized with syngas. After opening the membrane loop, the membrane pump is started. The feed temperature is controlled via a heating jacket attached to the membrane buffer tank. Every 3 hours, samples of the permeate and recycle are taken for GC-FID/TCD and ICP-OES analysis. To ensure a constant membrane feed concentration, the permeate is pumped back into the buffer tank of the membrane loop.

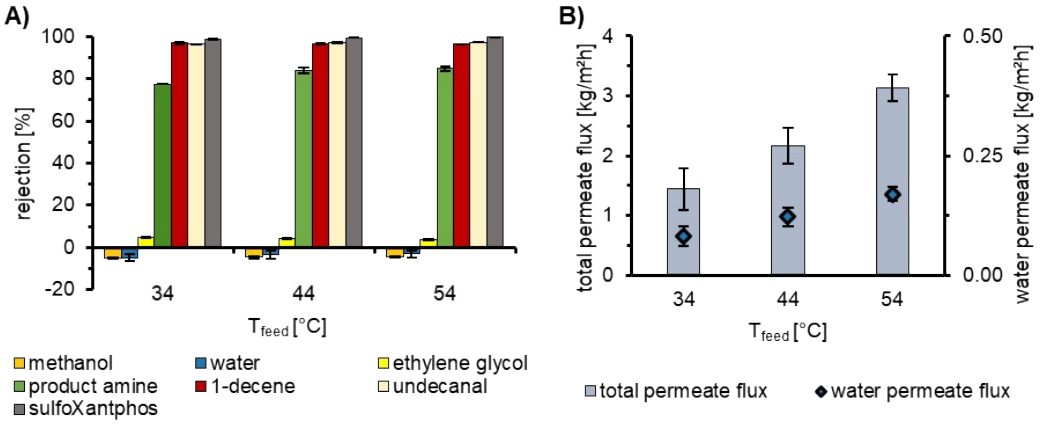


**Figure S12.** Influence of the membrane feed temperature on the rejections A) and permeate flow B). Conditions: Membrane: Nanopro S-3012, $A_{mem}$ = 52 cm², $T_{feed}$ = 34 -54 °C, $p_{feed}$ = 36 bar, and $V_{feed}$ = 50 L $h^{-1}$. The compositions of feed and permeate were determined *via* GC-FID and GC-WLD measurements. Error bars represent the standard deviation estimated from at least two GC samples. The permeate flow was averaged over 4 hours.

The membrane proved to be suited for water separation in the ethylene glycol TMS, as high rejections of the nonpolar components and especially of the ligand sulfoXantphos were achieved, as well as sufficient permeability of the polar solvents and, most importantly, water (Figure S12, A). An increase in the feed temperature is known to enhance the diffusion rates through the membrane and thus cause a faster separation of water through the membrane. Hence, the influence of temperature was also investigated in the membrane experiments. As expected, increasing the temperature from 34 to 54 °C resulted in a significant increase in water permeation, leading to a doubling of the water permeate flux to 0.18 kg/m²h.

The Membrane performance during the miniplant experiment is displayed in Figure S13.

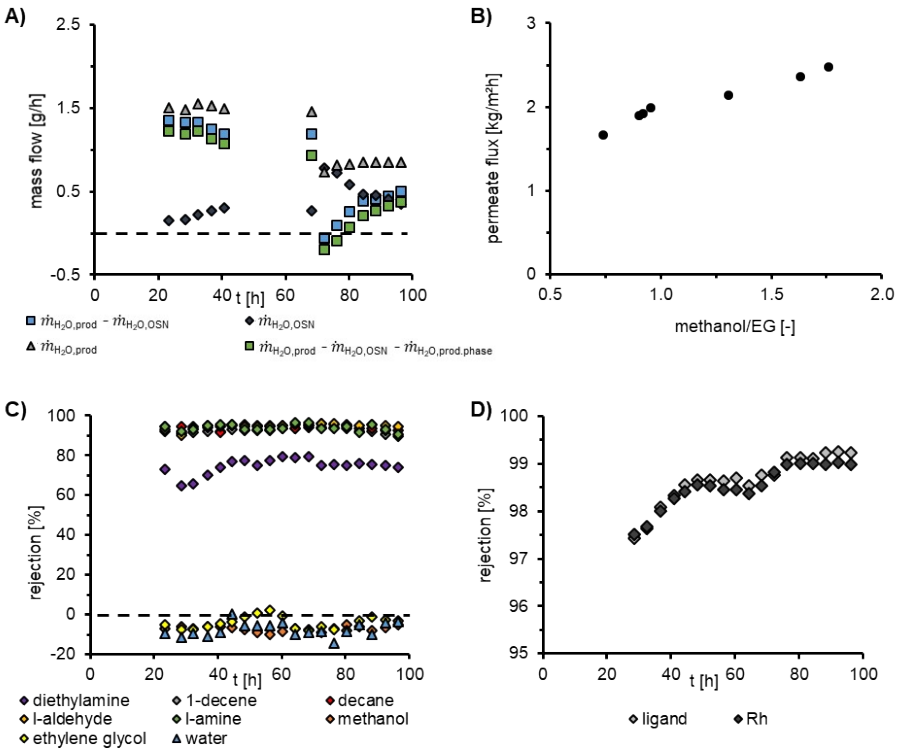


**Figure S13.** In **A)** the water accumulation/discharge in the miniplant operation is shown for the ethylene glycol (EG) and methanol (MeOH) TMS. Here, $\dot{m}_{H2O,prod}$ refers to the water mass produced in the reaction, $\dot{m}_{H2O,OSN}$ to the water mass leaving the process via organic solvent nanofiltration membrane and $\dot{m}_{H2O,prod.phase}$ and to the water mass leaving the process over the product phase. In **B)**, the permeate flux in dependency of the methanol/EG ratio in the polar catalyst phase (membrane feed) is shown. The rejections of the liquid components are displayed in **C),** and the rejections of the catalyst with the ligand sulfoXantphos in **D)**. Conditions: Membrane:

Nanopro S-3012, $A_{mem}$ = 52 $cm^2$, $T_{feed}$ (A, C and D) = 34-55 °C, $T_{feed}$ (B) = 55 °C $p_{feed}$ = 36 bar, and $V_{feed}$ = 50 L $h^{-1}$. The compositions of feed and permeate were determined *via* GC-FID and GC-WLD measurements.

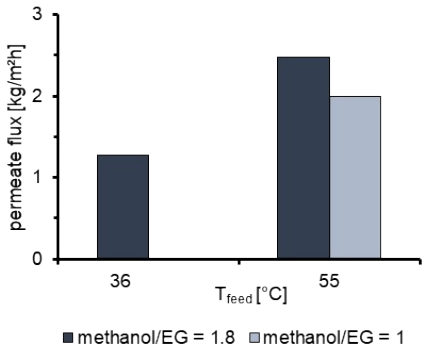


**Figure S14.** Feed temperatures influence on permeate flux during miniplant operation. Conditions: Membrane: Nanopro S-3012, $A_{mem}$ = 52 $cm^2$, $p_{feed}$ = 36 bar, and $V_{feed}$ = 50 L $h^{-1}$. The compositions of feed and permeate were determined *via* GC-FID and GC-WLD measurements.

## 2.6 Influence of the MeOH/EG-ratio on reactivity in hydroaminomethylation:

Changing the solvent ratio to switch from the biphasic (0 to 45 h) to the monophasic phase regime (60 to 75 h) in the reactor showed no remarkable effect on the reaction performance in continuous miniplant operation and underlines the robustness of this system. However, to adjust the solvent ratio, more methanol was pumped to the buffer tank B3 of the miniplant, slightly reducing the catalyst concentration in the recycle phase. Since these two effects, the increasing methanol/ethylene glycol ratio and the slight decrease in catalyst concentration, could also potentially cancel each other out, we conducted additional batch experiments to investigate their isolated influences (see Figure S15). Here, an increase in the methanol/ethylene glycol ratio showed a minor increase in reaction conversion. The fact that no abrupt increase in reaction performance is seen when switching from the biphasic to the monophasic liquid phase regime in the CSTR suggests the absence of liquid-liquid mass transport limitations under biphasic conditions.

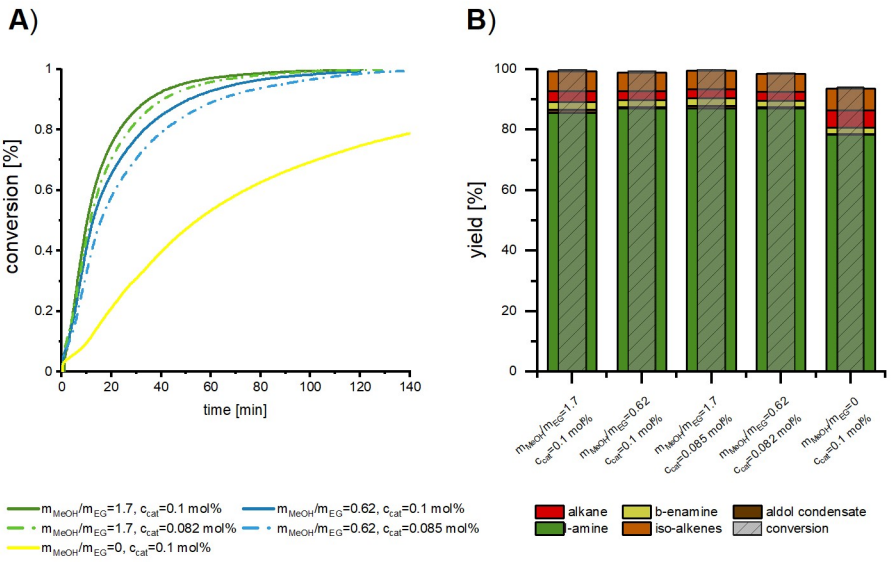


**Figure S15.** Batch autoclave investigation on the influence of catalyst concentration and the methanol/ethylene glycol ratio (MeOH/EG). A) Conversion-time plots determined over the gas consumption during the reaction. B) Final Conversion and yields of the batch autoclave experiments. The conversion-time plot was determined via the gas consumption during the reaction and the final conversion. The final yields and conversion were determined via the product phase composition using GC-FID with di-*n*-butyl ether as the internal standard. Conditions: T = 125 °C, p = 36 bar, $n_{stirrer}$ = 800 1/min, $H_2/CO$ = 2/1, $n_{SulfoXantphos}/n_{Rh(acac)(cod)}$ = 3.5, $n_{DEA}/n_{1\text{-decene}}$ = 1, $m_{methanol+EG}/m_{1\text{-decene}}$ = 7.15, $w_{1\text{-decene}}$ = 11.5 wt%, $t_{reaction}$ ($m_{MeOH}/m_{EG}$ = 1.7-0.62) = 120 -138 min, $t_{reaction}$ ($m_{MeOH}/m_{EG}$ = 0) = 4 h.

### 2.7 Heat duty required for heating and evaporating the solvents per kg of product amine

The heat duty required to evaporate the solvents in the product phases of the TMSs was estimated by calculating the heating and evaporation energy for each solvent *(i)* separately and then summing their contributions according to their mass fractions. The calculation is performed via the mass fractions of the solvents $w_i$, the mass of the product phase $m_{product\ phase}$, the enthalpy of evaporation at boiling temperature $T_{S,i}$ and the specific heat capacity $c_{p,i}(T)$.

$$Q_{solvents,TMS} = \sum (w_i\, x\, m_{product\ phase}\, x\, (h_{LV,i}(T_{S,i}) + \int_{10\ °C}^{T_{S,i}} c_{p,i}(T)\, dT))$$

The evaporation enthalpies and temperature functions of the specific heat capacities of the solvents were taken from the chemical properties handbook by Carl Yaws.[2]

The term $Q_{solv}/m_{prod}$ relates $Q_{solvents,TMS}$ to the mass of product amine, which is found in the product phase:

$$\frac{Q_{solv}}{m_{prod}} = \frac{\sum (w_i\, x\, m_{product\ phase}\, x\, (h_{LV,i}(T_{S,i}) + \int_{10\ °C}^{T_{S,i}} c_{p,i}(T)\, dT))}{w_{product\ amine} x\, m_{product\ phase}} = \frac{\sum (w_i\, x\, (h_{LV,i}(T_{S,i}) + \int_{10\ °C}^{T_{S,i}} c_{p,i}(T)\, dT))}{w_{product\ amine}}$$

# References


[1] T. Gaide, J. M. Dreimann, A. Behr, A. J. Vorholt, "Overcoming Phase-Transfer Limitations in the Conversion of Lipophilic Oleo Compounds in Aqueous Media-A Thermomorphic Approach", *Angew. Chem. Int. Ed.* **2016**, *55*, 2924.

[2] C. L. Yaws, "Chemical properties handbook. *Physical, thermodynamic, environmental, transport, and health related properties for organic and inorganic chemicals*, McGraw-Hill, New York, **1999**.