Density modelling

NH_3-CO_2-H_2O liquid mixtures

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Liquid density model in Aspen Plus

Clarke model (for aqueous electrolyte molar volume)

- Molar volume for electrolyte solutions (V_m^l), applicable to mixed solvents
- Based on apparent components

$$V_m^l(298.15K) = \underbrace{x_w V_w^{*,l} + x_{am} V_{am}^{*,l} + 2x_w x_{am} K_{w,am} \left(V_w^{*,l} V_{am}^{*,l}\right)^{0.5} + 2x_w x_c K_{w,c} \left(V_w^{*,l} V_c^{*,l}\right)^{0.5} + 2x_{am} x_c K_{am,c} \left(V_{am}^{*,l} V_c^{*,l}\right)^{0.5}}_{V_s^l \equiv liquid\ molar\ volume\ for\ solvent\ mixtures\ based\ on\ liquid\ volume\ quadratic\ mixing\ rule} + \underbrace{x_{BC} V_{BC} + x_{CM} V_{CM} + x_{CB} V_{CB}}_{V_e^l \equiv liquid\ molar\ volume\ for\ electrolytes}$$

$$V_m^l(T) = V_m^l(298.15K) \frac{V_s^l(T)}{V_s^l(298.15K)}$$

  - Non-electrolyte apparent components (molecular solvents):
    - H_2O (w)
    - NH_3 (am)
    - CO_2 (c)

DIPPR equation for the computation of the pure component liquid molar volume: $V_W^{*,l}$, $V_{am}^{*,l}$ and $V_c^{*,l}$

  - Electrolyte apparent components (ca):
    - NH_4HCO_3 (BC)
    - NH_4NH_2COO (CM)
    - $(NH_4)_2CO_3$ (CB)

$V_{ca} = V_{ca}^{\infty} + A_{ca} \frac{\sqrt{x_{BC}+x_{CM}+x_{BC}}}{1+\sqrt{x_{BC}+x_{CM}+x_{BC}}}$, with $x_w + x_{am} + x_c + x_{BC} + x_{CM} + x_{CB} = 1$ and where x_i is computed from the true ionic concentrations

- 9 parameters to be estimated: $K_{w,am}$, $K_{w,c}$, $K_{am,c}$, V_{BC}^{∞}, A_{BC}, V_{CM}^{∞}, A_{CM}, V_{CB}^{∞}, A_{CB}

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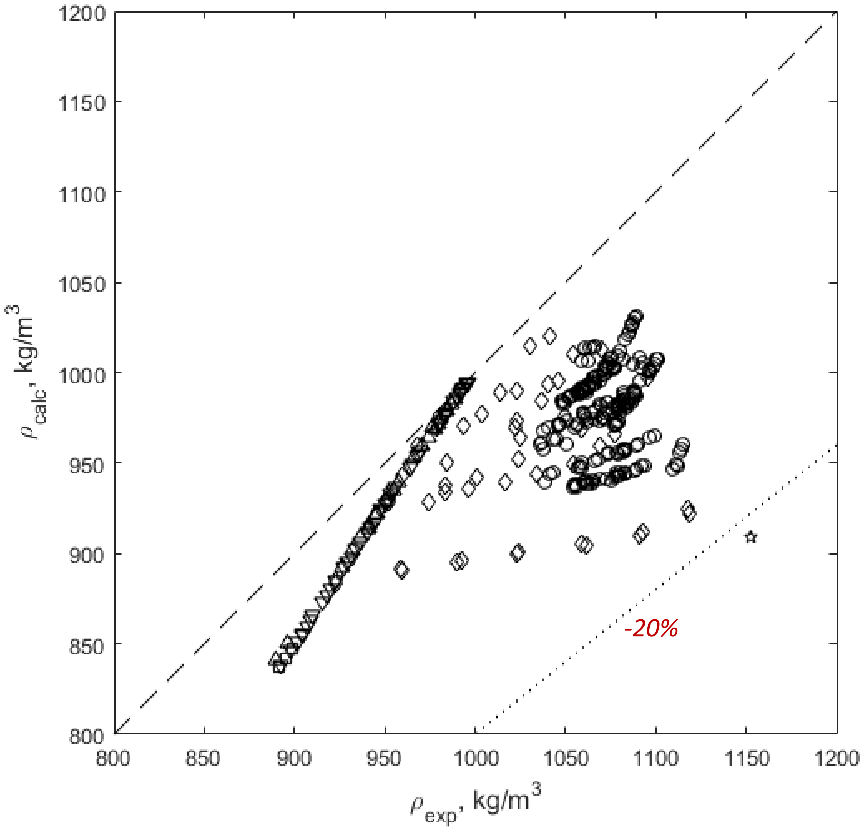
Default (Aspen Plus) liquid density model validation

Default value of parameters:

$$K_{w,am} = 0 \qquad V_{BC}^{\infty} = 0.0047\,\frac{\mathrm{m}^3}{\mathrm{kmol}} \qquad V_{CM}^{\infty} = -0.0012\,\frac{\mathrm{m}^3}{\mathrm{kmol}} \qquad V_{CB}^{\infty} = -0.0387\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$$

$$K_{w,c} = 0;\, K_{am,c} = 0 \qquad A_{BC} = 0.020\,\frac{\mathrm{m}^3}{\mathrm{kmol}} \qquad A_{CM} = 0.020\,\frac{\mathrm{m}^3}{\mathrm{kmol}} \qquad A_{CB} = 0.020\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$$



If experimental data obtained at $P_{vap} > P_{atm}$ and $T < 0°C$ are not considered, the density is underestimated up to 20%

☐ Perkin (1889)

$3.9 \leq T(°C) \leq 15.0$ $\qquad m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) = 26.5$ $\qquad CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) = 0$

▽ Perry's chemical engineers' handbook

$0 \leq T(°C) \leq 25.0$ $\qquad 0.6 \leq m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) \leq 25.2$ $\qquad CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) = 0$

△ Liu et al. (2012)

$10.0 \leq T(°C) \leq 50.0$ $\qquad 1.5 \leq m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) \leq 24.3$ $\qquad CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) = 0$

◇ Lichtfers (2000)

$39.9 \leq T(°C) \leq 80.1$ $\qquad 1.9 \leq m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) \leq 12.2$ $\qquad 0 \leq CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) \leq 0.82$

☆ This work (Lab samples)

$T(°C) = 27.0$ $\qquad m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) = 17.7$ $\qquad CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) = 0.5$

○ This work (Pilot plant samples)

$11.9 \leq T(°C) \leq 22.3$ $\qquad 2.9 \leq m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) \leq 10.6$ $\qquad 0.28 \leq CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) \leq 0.71$

Perkin. *J Chem Soc* 55 (1889) 680
Perry et al. *Perry's chemical engineers' handbook*, 8th ed.; McGraw-Hill: New York, 2008

Liu et al. *J Chem Eng Data* 57 (2012) 2387-2393
Lichtfers (2000)

Liquid density modelling NH_3-H_2O mixtures

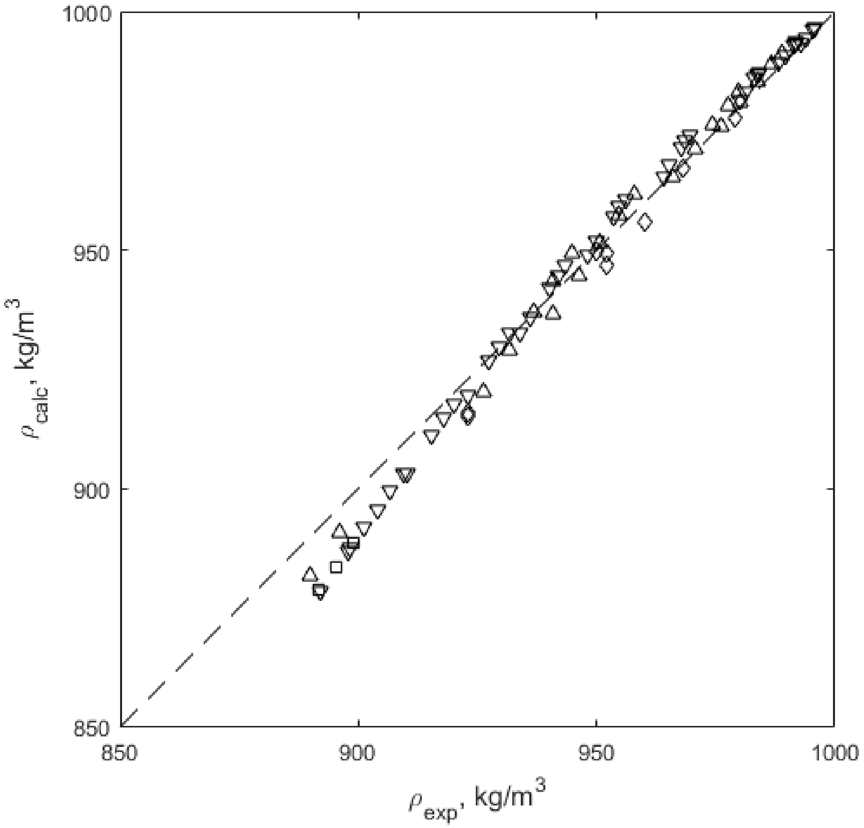
Regressed parameter:

$K_{w,am} = -0.202 \pm 0.003$

$K_{w,c} = 0;\ K_{am,c} = 0$

Average absolute relative deviation: $AARD(\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{|\rho_{exp,i}-\rho_{calc,i}|}{\rho_{exp,i}}$

Absolute average deviation: $AAD\left(\frac{kg}{m^3}\right) = \frac{1}{N}\sum_{i=1}^{N}|\rho_{exp,i}-\rho_{calc,i}|$



Density regression of unloaded aqueous NH_3 solutions from the literature[1,2,3,4] using experimental data obtained at $T \geq 0°C$ and with $P_{vap} < P_{atm}$

□ Perkin (1889)

$3.9 \leq T(°C) \leq 15.0$ $m_{NH_3}\left(\frac{mol_{NH_3}}{kg_{H_2O}}\right) = 26.5$ $CO_2\ loading\left(\frac{mol_{CO_2}}{mol_{NH_3}}\right) = 0$

▽ Perry's chemical engineers' handbook

$0 \leq T(°C) \leq 25.0$ $0.6 \leq m_{NH_3}\left(\frac{mol_{NH_3}}{kg_{H_2O}}\right) \leq 25.2$ $CO_2\ loading\left(\frac{mol_{CO_2}}{mol_{NH_3}}\right) = 0$

△ Liu et al. (2012)

$10.0 \leq T(°C) \leq 50.0$ $1.5 \leq m_{NH_3}\left(\frac{mol_{NH_3}}{kg_{H_2O}}\right) \leq 24.3$ $CO_2\ loading\left(\frac{mol_{CO_2}}{mol_{NH_3}}\right) = 0$

◇ Lichtfers (2000)

$40.0 \leq T(°C) \leq 60.1$ $1.9 \leq m_{NH_3}\left(\frac{mol_{NH_3}}{kg_{H_2O}}\right) \leq 12.2$ $CO_2\ loading\left(\frac{mol_{CO_2}}{mol_{NH_3}}\right) = 0$

$\boldsymbol{AARD = 0.4\%}$ $\boldsymbol{max(ARD) = 1.5\%}$

$\boldsymbol{AAD = 3.6\,\frac{kg}{m^3}}$ $\boldsymbol{max(AD) = 13.5\,\frac{kg}{m^3}}$

[1] Perkin. *J Chem Soc* 55 (1889) 680

[2] Perry et al. *Perry's chemical engineers' handbook*, 8th ed.; McGraw-Hill: New York, 2008

[3] Liu et al. *J Chem Eng Data* 57 (2012) 2387-2393

[4] Lichtfers (2000)

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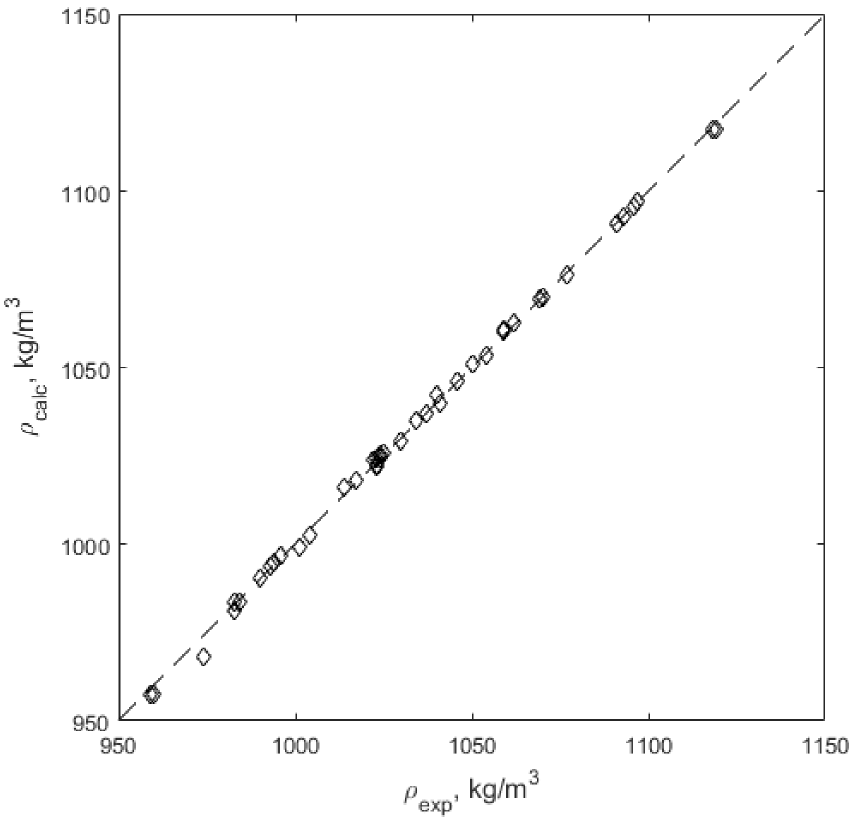
Liquid density modelling CO_2-NH_3-H_2O mixtures

Fixed parameters:

$$K_{w,am} = -0.202 \pm 0.003$$
$$K_{w,c} = 0$$
$$K_{am,c} = 0$$

Regressed parameters:

$$V_{BC}^{\infty} = 0.041 \pm 0.003 \frac{\mathrm{m}^3}{\mathrm{kmol}} \quad V_{CM}^{\infty} = 0.027 \pm 0.007 \frac{\mathrm{m}^3}{\mathrm{kmol}} \quad V_{CB}^{\infty} = 0.12 \pm 0.05 \frac{\mathrm{m}^3}{\mathrm{kmol}}$$
$$A_{BC} = 0.030 \pm 0.016 \frac{\mathrm{m}^3}{\mathrm{kmol}} \quad A_{CM} = 0.09 \pm 0.04 \frac{\mathrm{m}^3}{\mathrm{kmol}} \quad A_{CB} = -0.2 \pm 0.3 \frac{\mathrm{m}^3}{\mathrm{kmol}}$$



Density regression of CO_2-loaded aqueous NH_3 solutions from the literature[1] using experimental data obtained at $T \geq 0°C$ and with $P_{vap} < P_{atm}$

◇ Lichtfers (2000)

$39.9 \leq T(°C) \leq 80.1 \quad 1.9 \leq m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) \leq 12.2 \quad 0.09 \leq CO_2\ loading \left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) \leq 0.82$

$$\boldsymbol{AARD = 0.1\%} \qquad \boldsymbol{max(ARD) = 0.6\%}$$
$$\boldsymbol{AAD = 1.0 \frac{kg}{m^3}} \qquad \boldsymbol{max(AD) = 5.8 \frac{kg}{m^3}}$$

But highly correlated parameters with high standard deviation in some cases ➔ Additional experiments might be required for modelling

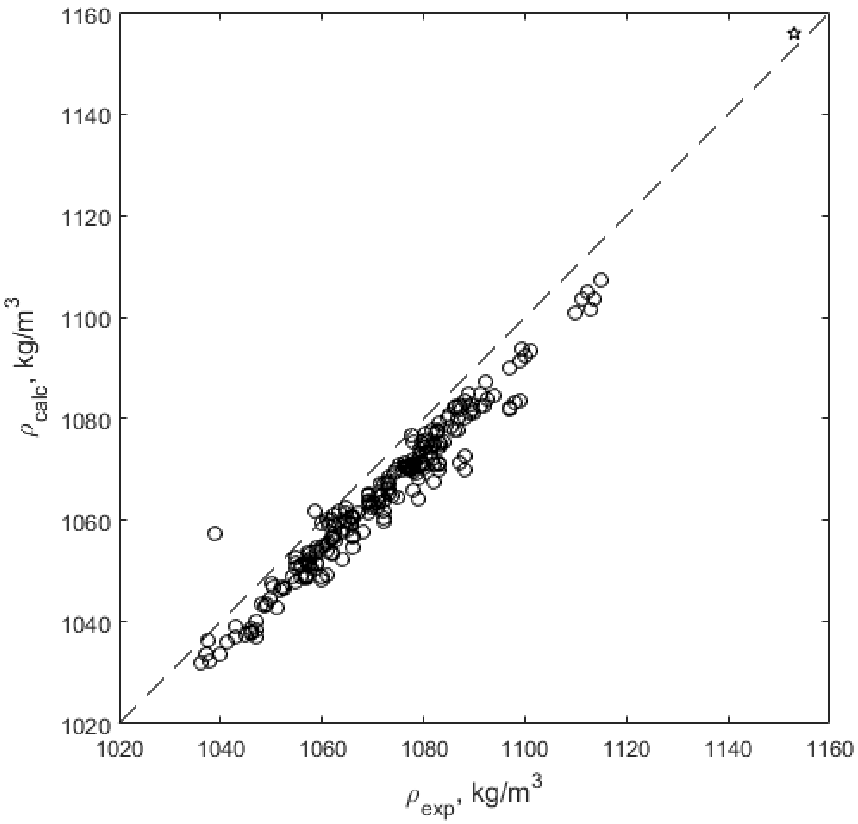
[1] Lichtfers (2000)

Liquid density model validation

Regressed parameters:

$K_{w,am} = -0.202$ $V_{BC}^{\infty} = 0.041\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$ $V_{CM}^{\infty} = 0.027\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$ $V_{CB}^{\infty} = 0.12\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$

$K_{w,c} = 0;\ K_{am,c} = 0$ $A_{BC} = 0.030\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$ $A_{CM} = 0.09\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$ $A_{CB} = -0.2\,\frac{\mathrm{m}^3}{\mathrm{kmol}}$



Model validation with independent liquid density measurements of the samples taken during the pilot plant tests of the CO_2 absorber

☆ This work (Lab samples)

$T(°\mathrm{C}) = 27.0$ $m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) = 17.7$ $CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) = 0.5$

○ This work (Pilot plant samples)

$11.9 \le T(°\mathrm{C}) \le 22.3$ $2.9 \le m_{NH_3}\left(\frac{\mathrm{mol_{NH_3}}}{\mathrm{kg_{H_2O}}}\right) \le 10.6$ $0.28 \le CO_2\ loading\left(\frac{\mathrm{mol_{CO_2}}}{\mathrm{mol_{NH_3}}}\right) \le 0.71$

The **model** consistently **underpredicts** the experimental **liquid density** values, **but always below 2%**

$\boldsymbol{AARD = 0.6\%}$ $\boldsymbol{max(ARD) = 1.8\%}$

$\boldsymbol{AAD = 6.9\,\frac{kg}{m^3}}$ $\boldsymbol{max(AD) = 18.5\,\frac{kg}{m^3}}$

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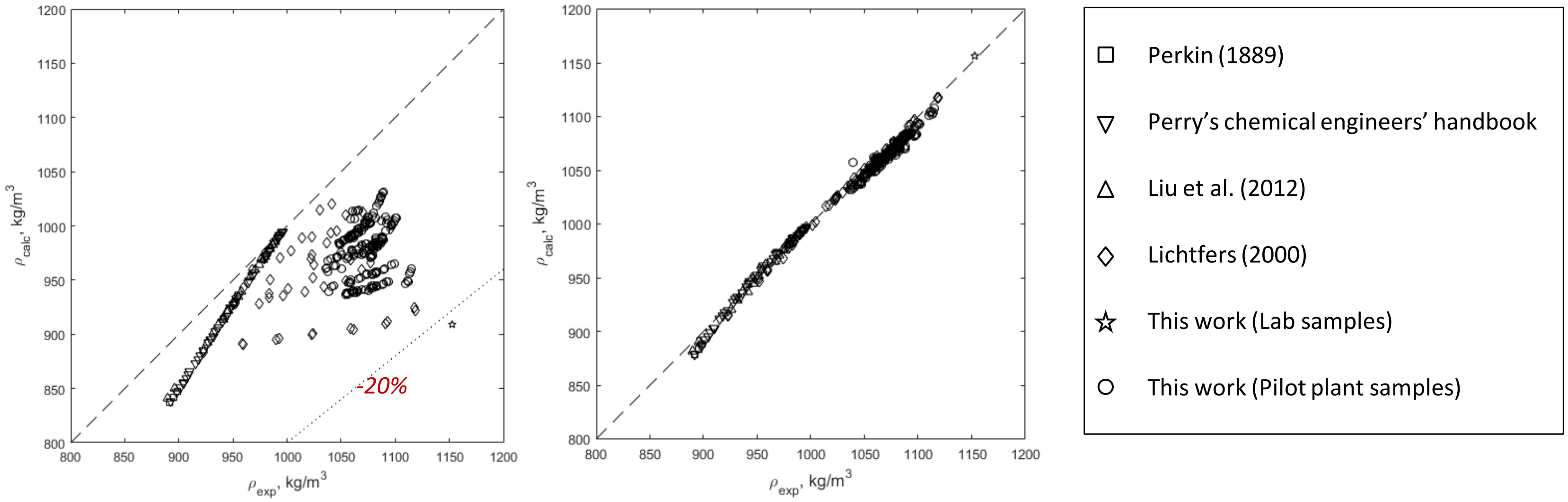
Density model for CO_2-NH_3-H_2O liquid mixtures



	Default Aspen (Thomsen)	**This work (Thomsen)**
AARD, % (*max*)	**7.3** (*21.1*)	**0.5** (*1.8*)
ARD, kg/m^3 (*max*)	**77.2** (*243.6*)	**5.5** (*18.5*)

Average absolute relative deviation: $AARD(\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{|\rho_{exp,i}-\rho_{calc,i}|}{\rho_{exp,i}}$

Absolute average deviation: $AAD\left(\frac{kg}{m^3}\right) = \frac{1}{N}\sum_{i=1}^{N}|\rho_{exp,i}-\rho_{calc,i}|$

Perkin. *J Chem Soc* 55 (1889) 680
Perry et al. *Perry's chemical engineers' handbook*, 8th ed.; McGraw-Hill: New York, 2008

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Lichtfers (2000)

CAP pilot testing
CO_2 absorber tests

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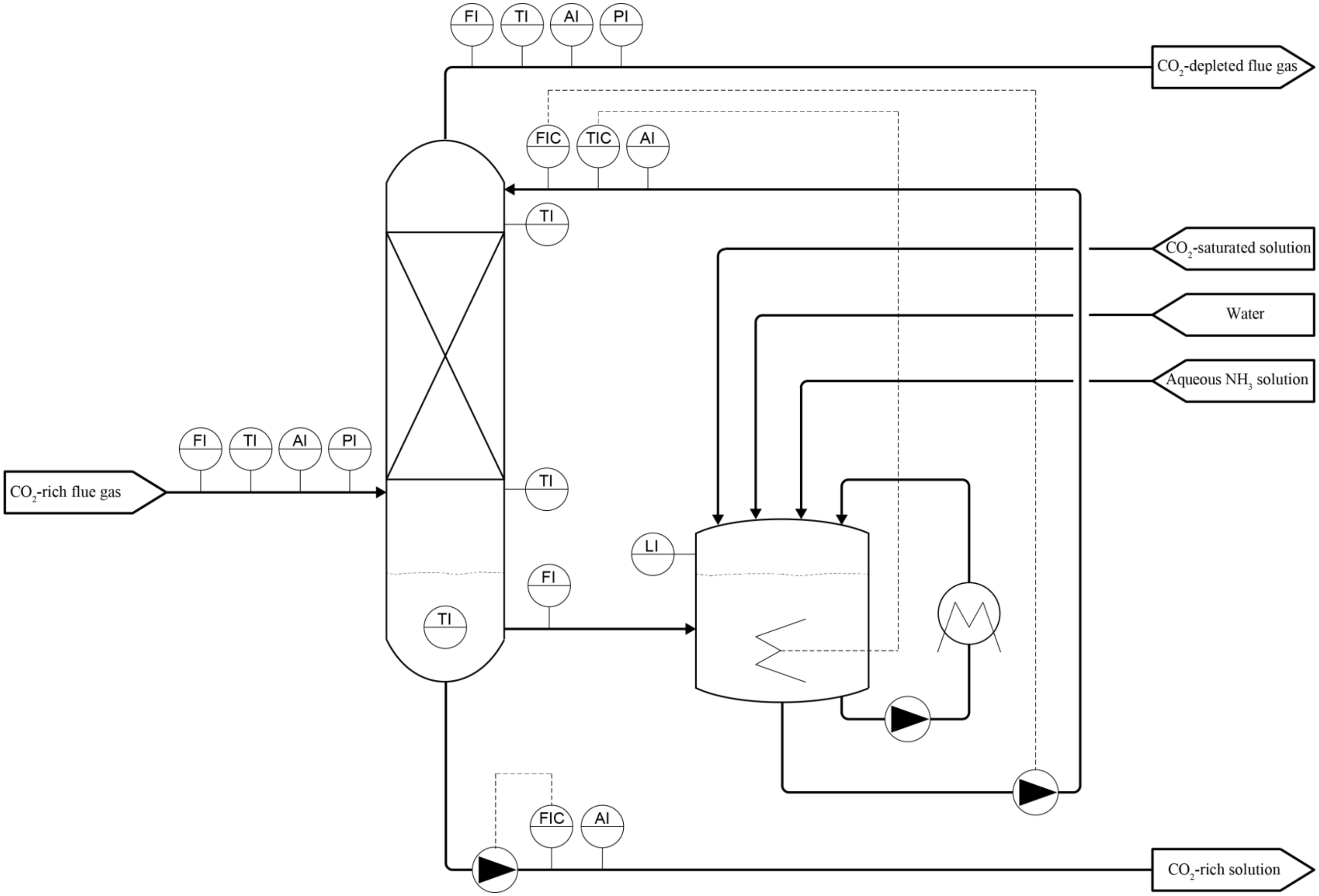
Test rig – CO_2 absorber



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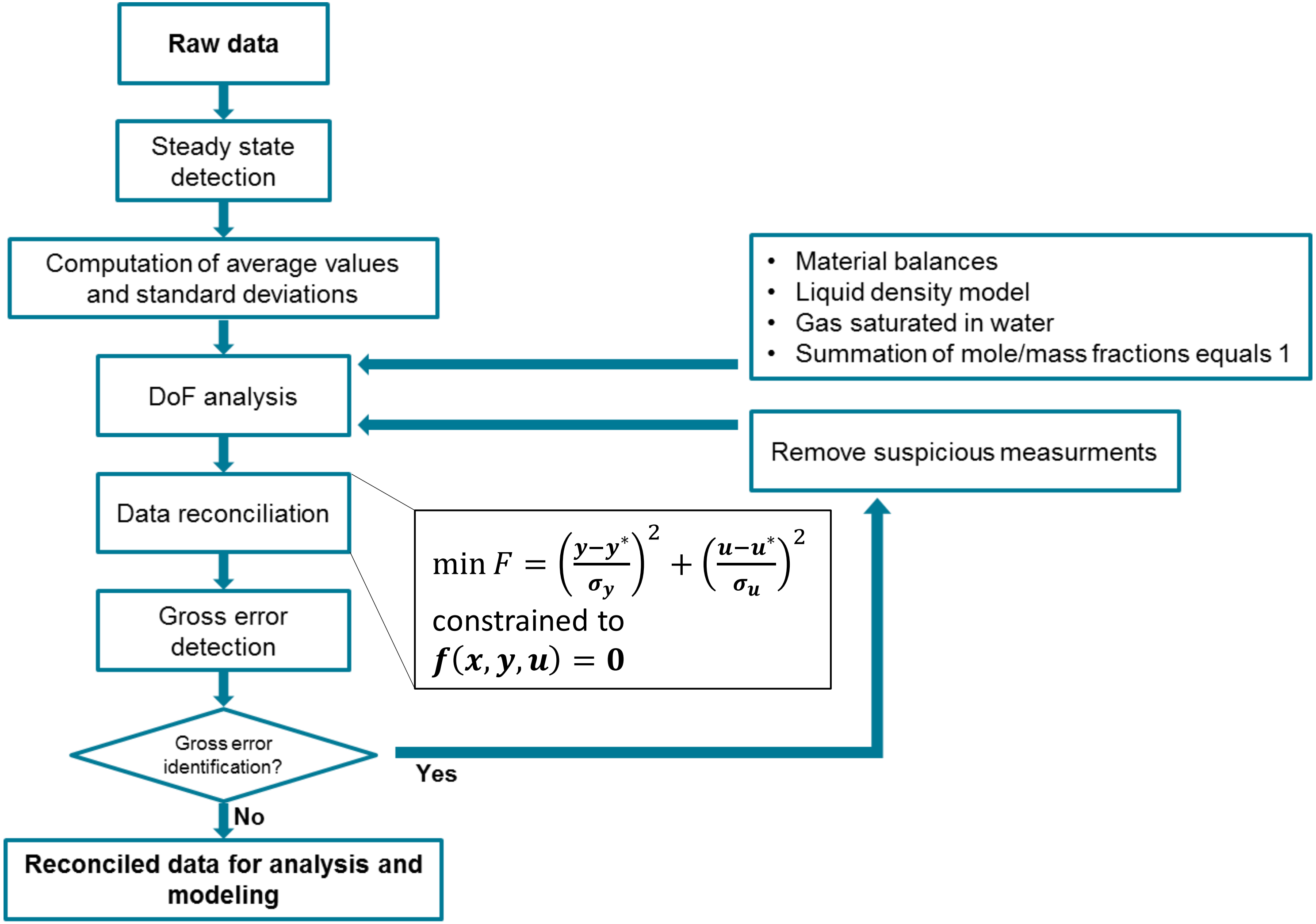
Systematic treatment of raw data from pilot plant tests



Raw data

Steady state detection

Computation of average values and standard deviations

DoF analysis

- Material balances
- Liquid density model
- Gas saturated in water
- Summation of mole/mass fractions equals 1

Remove suspicious measurments

Data reconciliation

$$\min F = \left(\frac{y-y^*}{\sigma_y}\right)^2 + \left(\frac{u-u^*}{\sigma_u}\right)^2$$

constrained to

$$\boldsymbol{f}(\boldsymbol{x},\boldsymbol{y},\boldsymbol{u}) = \boldsymbol{0}$$

Gross error detection

Gross error identification?

Yes

No

Reconciled data for analysis and modeling

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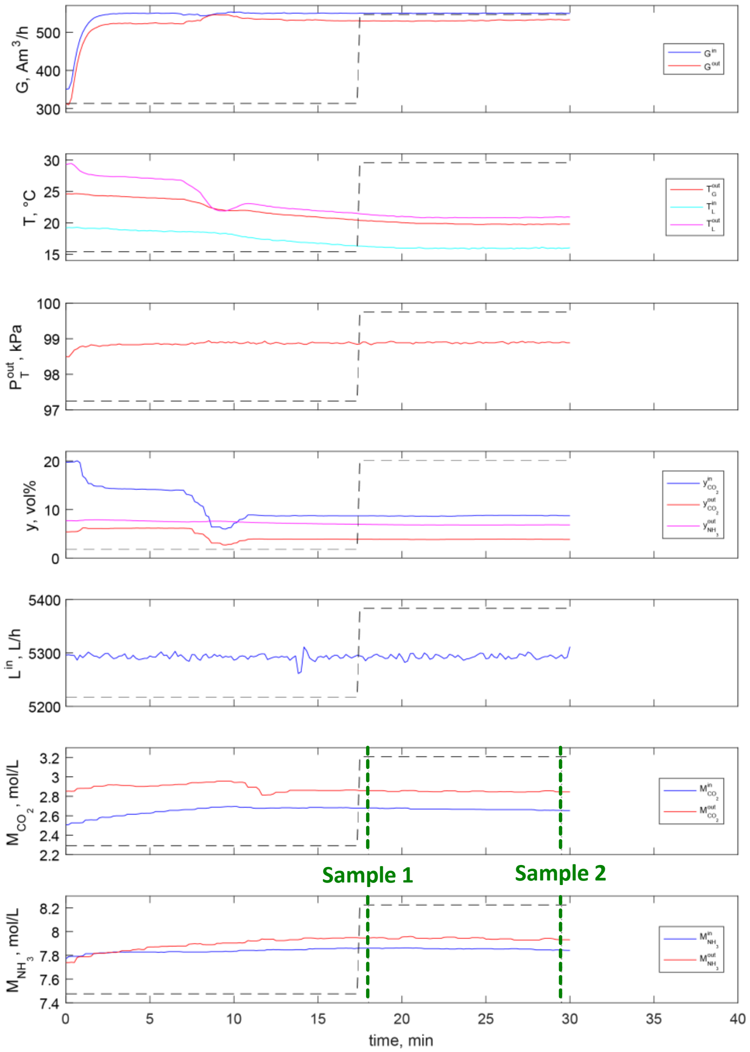
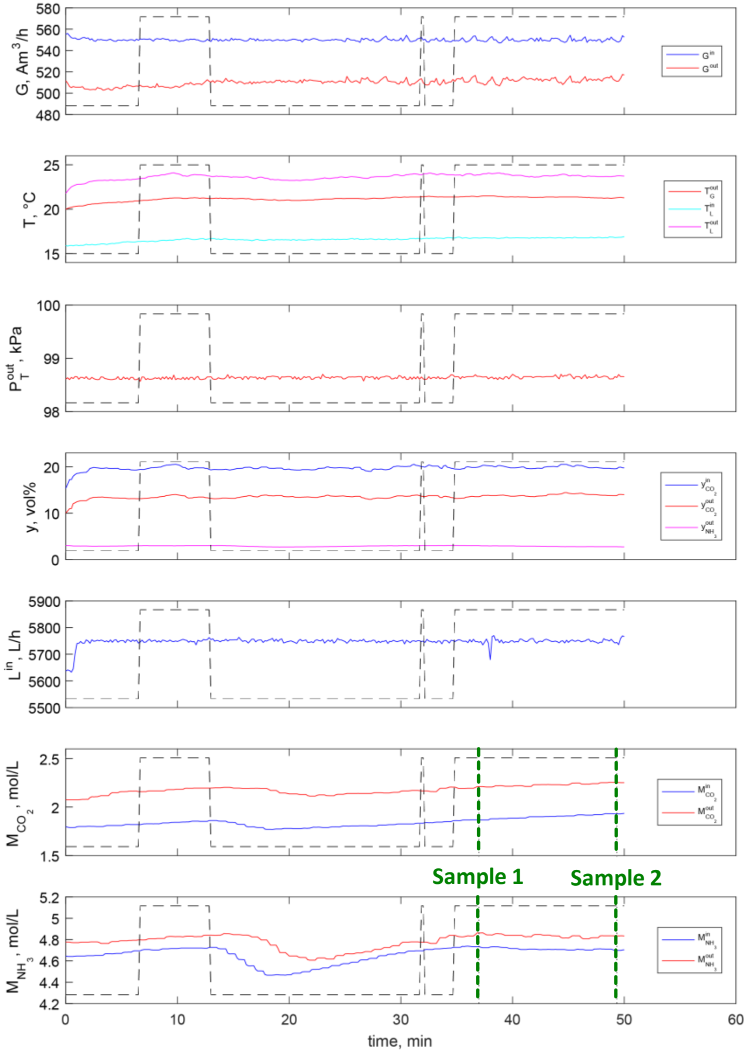
Automatized steady state detection

Experiment 14



Experiment 21



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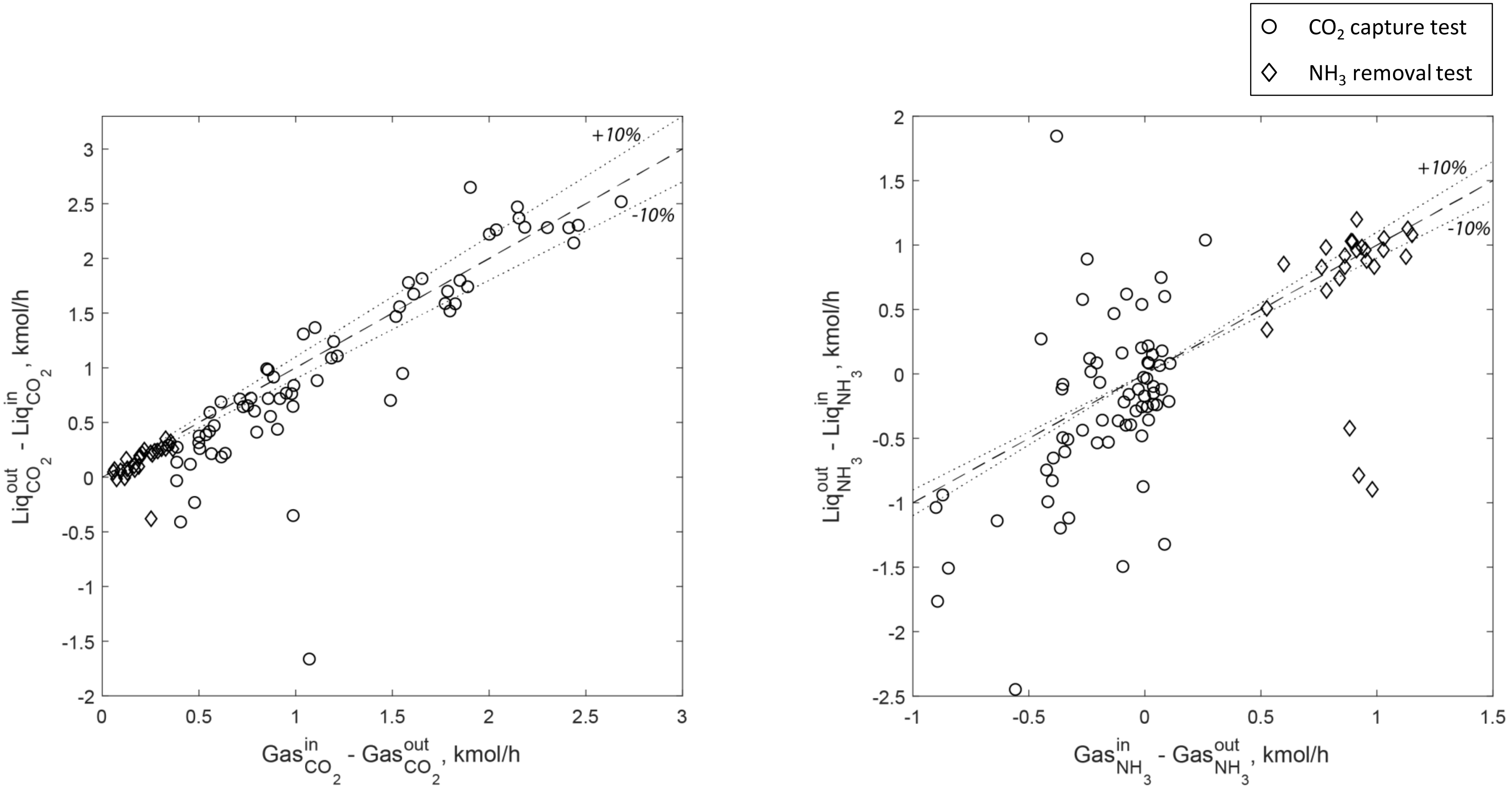
Mass balances before data reconciliation

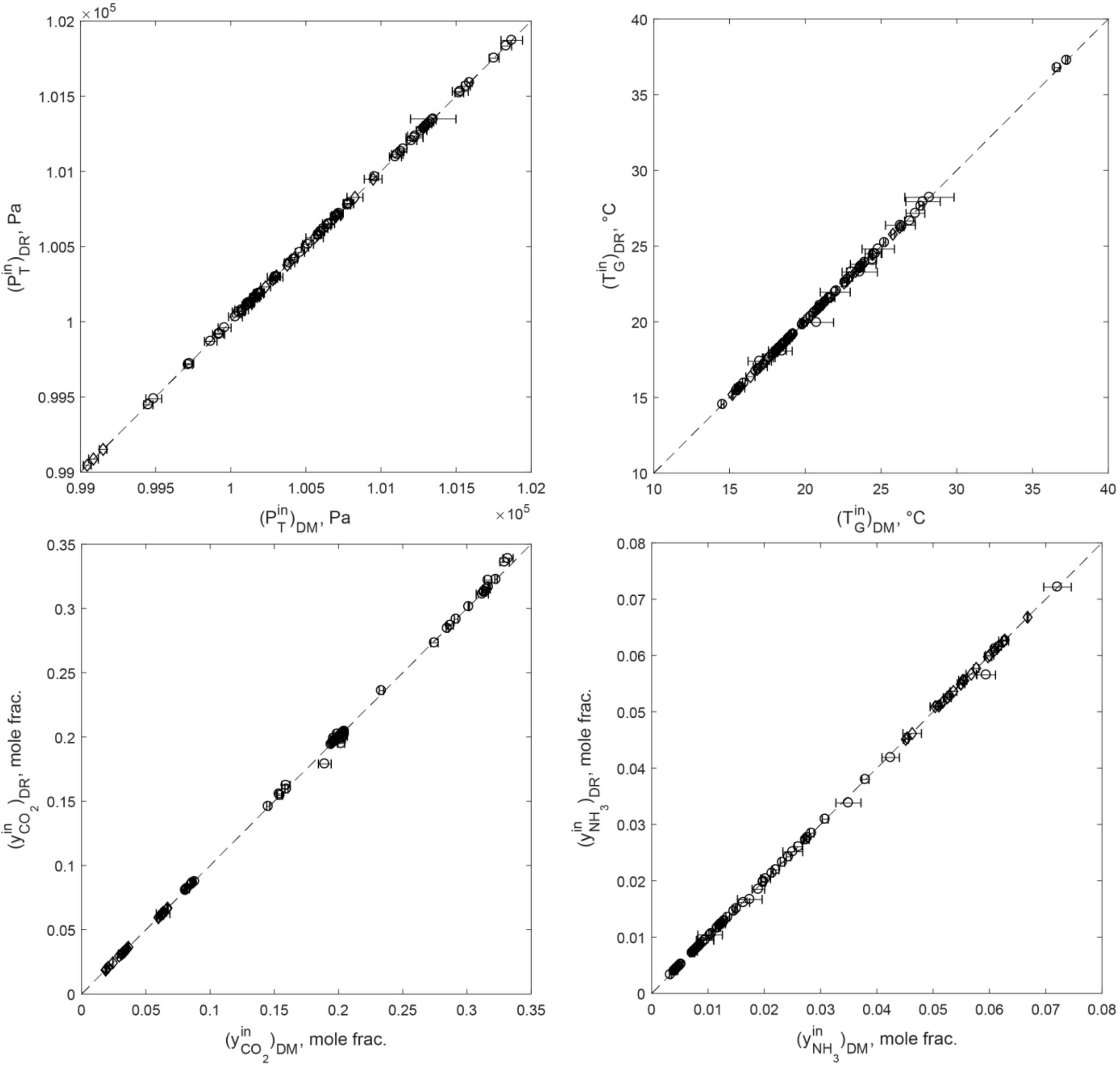


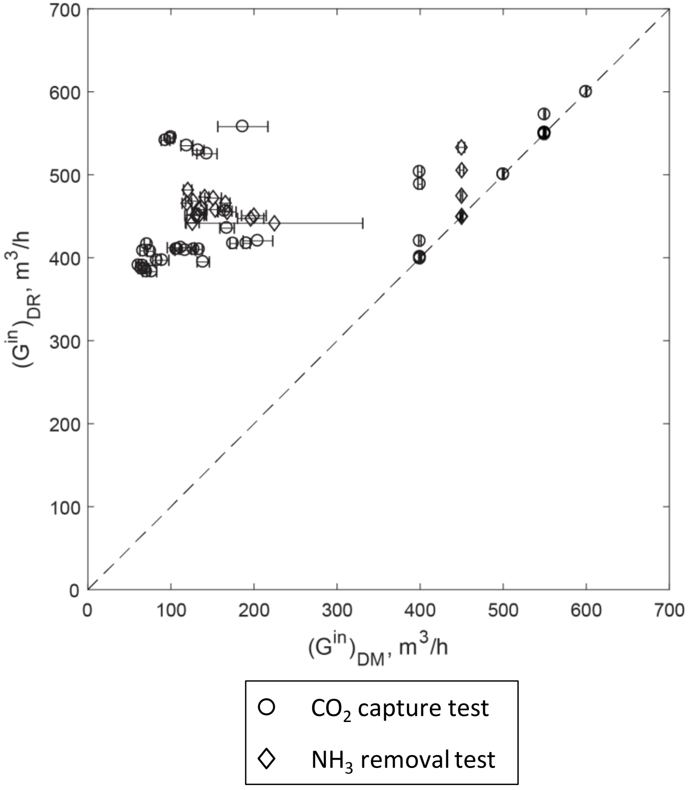
Composition and **flowrate** of **liquid streams** are **critical** for closing the **mass balances**

Reconciled data for analysis and modelling

Inlet gas

Failure in the in the inlet gas flowrate sensor during the tests





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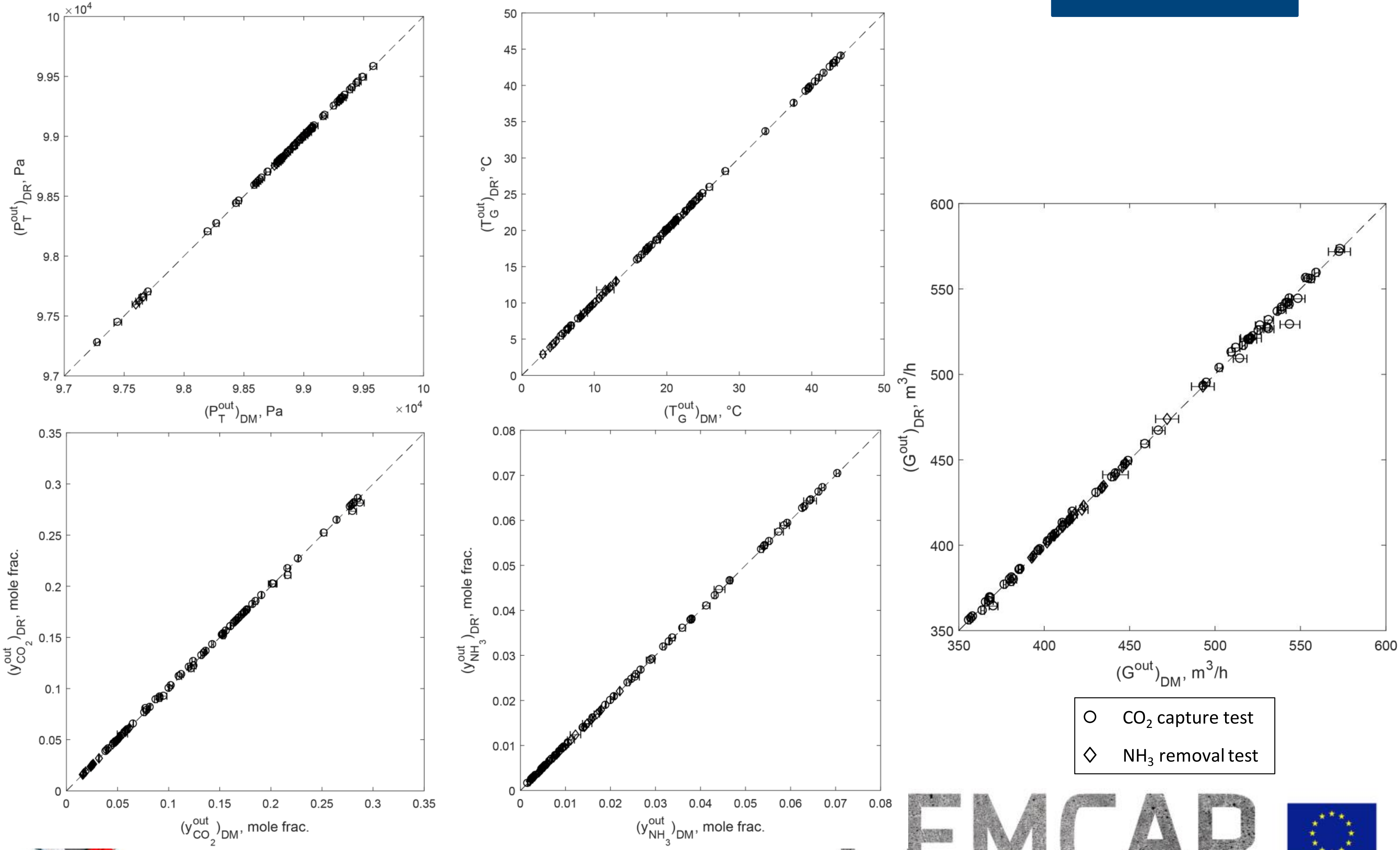
Reconciled data for analysis and modelling

Outlet gas



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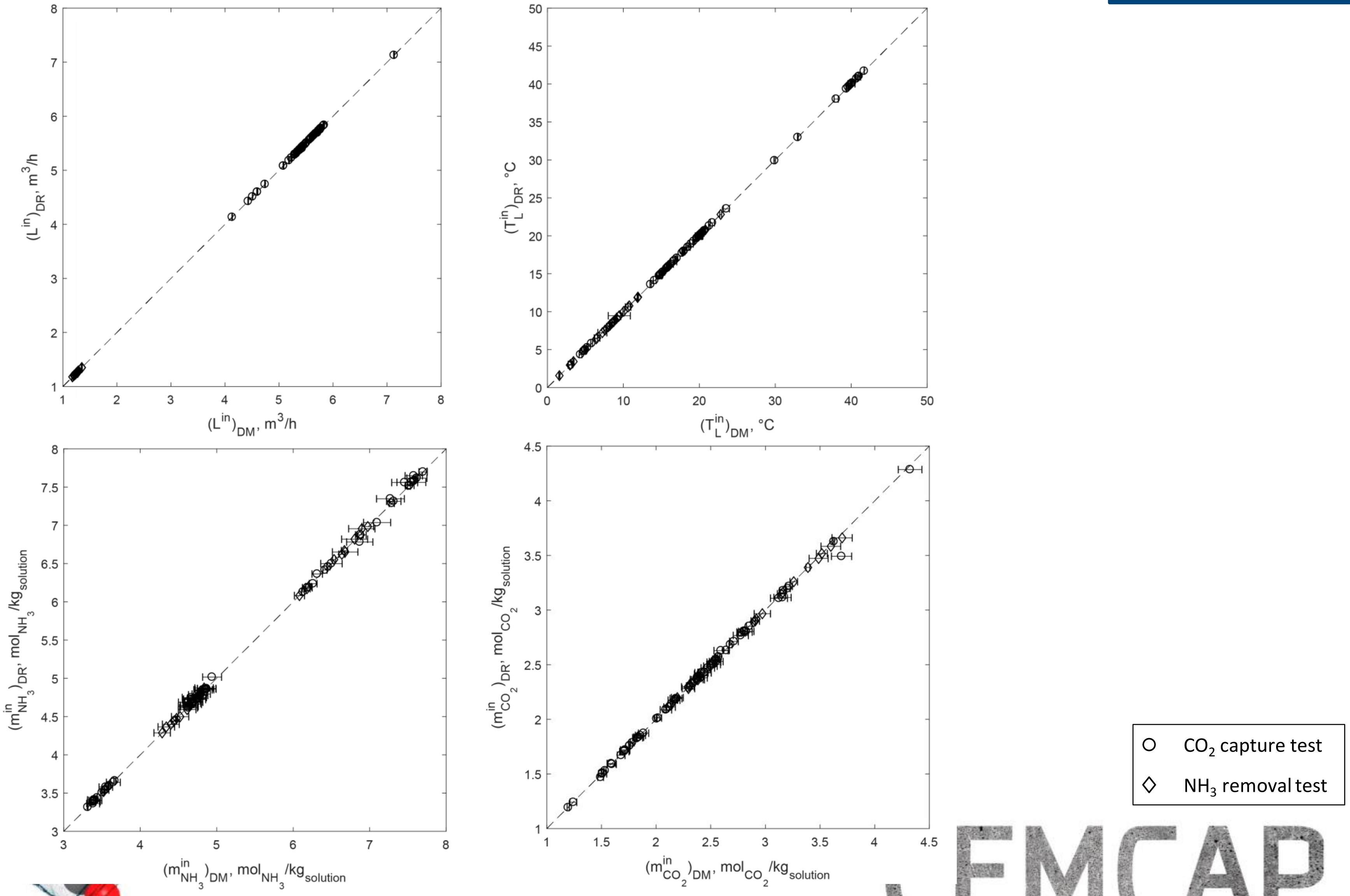
Reconciled data for analysis and modelling

Inlet liquid



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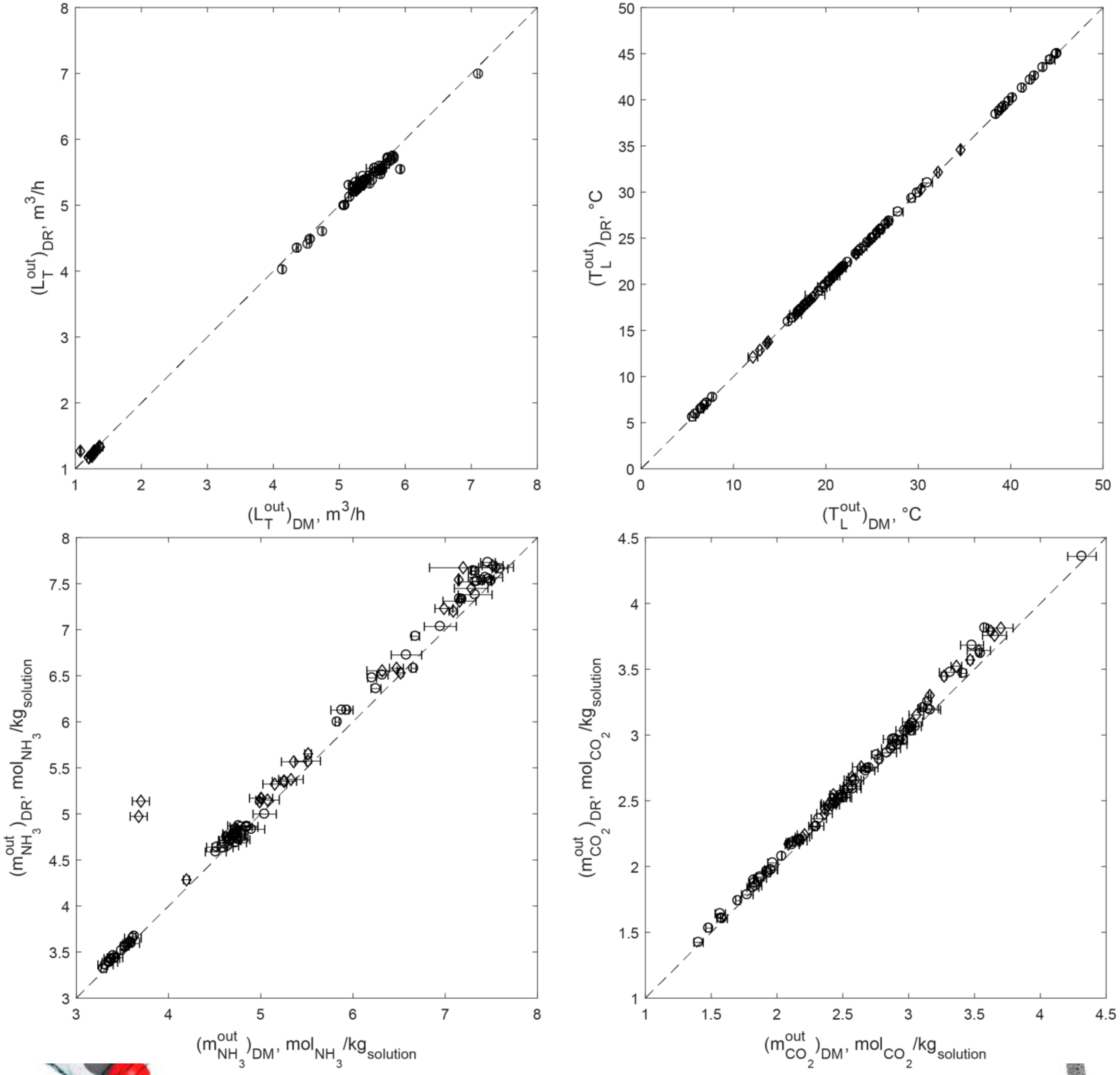
Reconciled data for analysis and modelling

Outlet liquid

Most **uncertainties** are in the measurement of the **flowrate** and **composition** of the **outlet liquid** stream



○ CO_2 capture test

◇ NH_3 removal test

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