Optimal design of a CO_2 absorption unit and assessment of solvent degradation

Progress Review Presentation

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26th July 2012

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1. Progress Review

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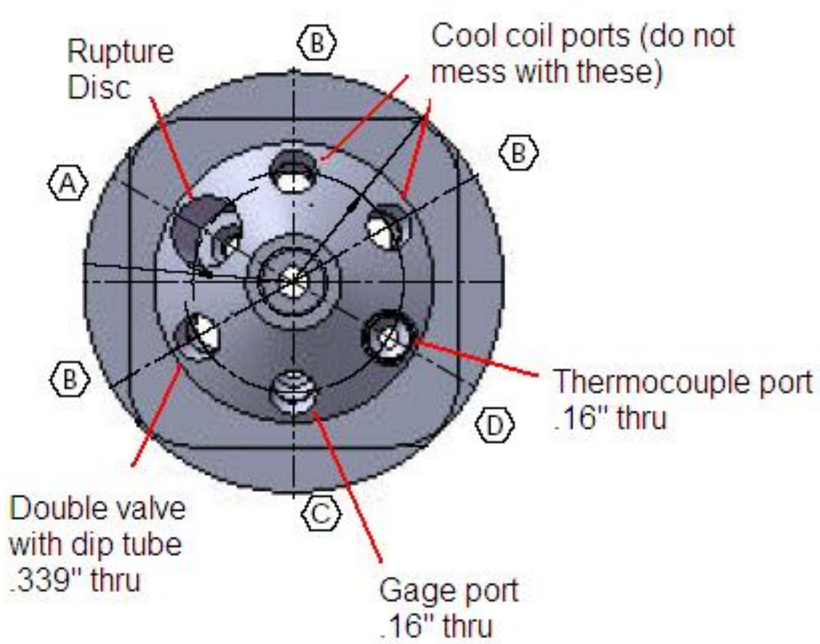
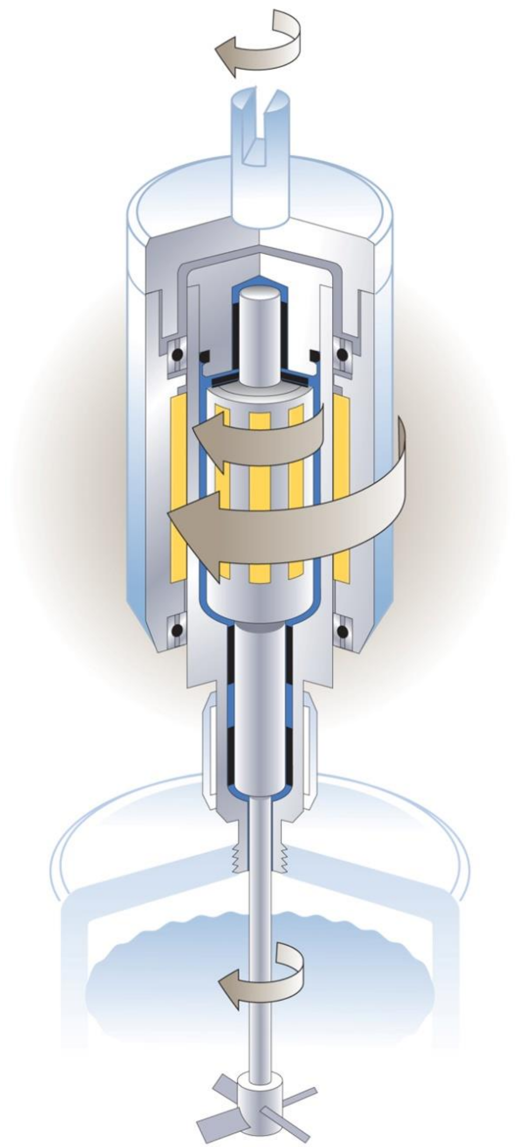
1. Progress review

Test bench improvements:

- Agitation improvements, new bushings
- Heating mantle repaired
- Larger connection for the condenser
- Mass balance ensured





1. Progress review

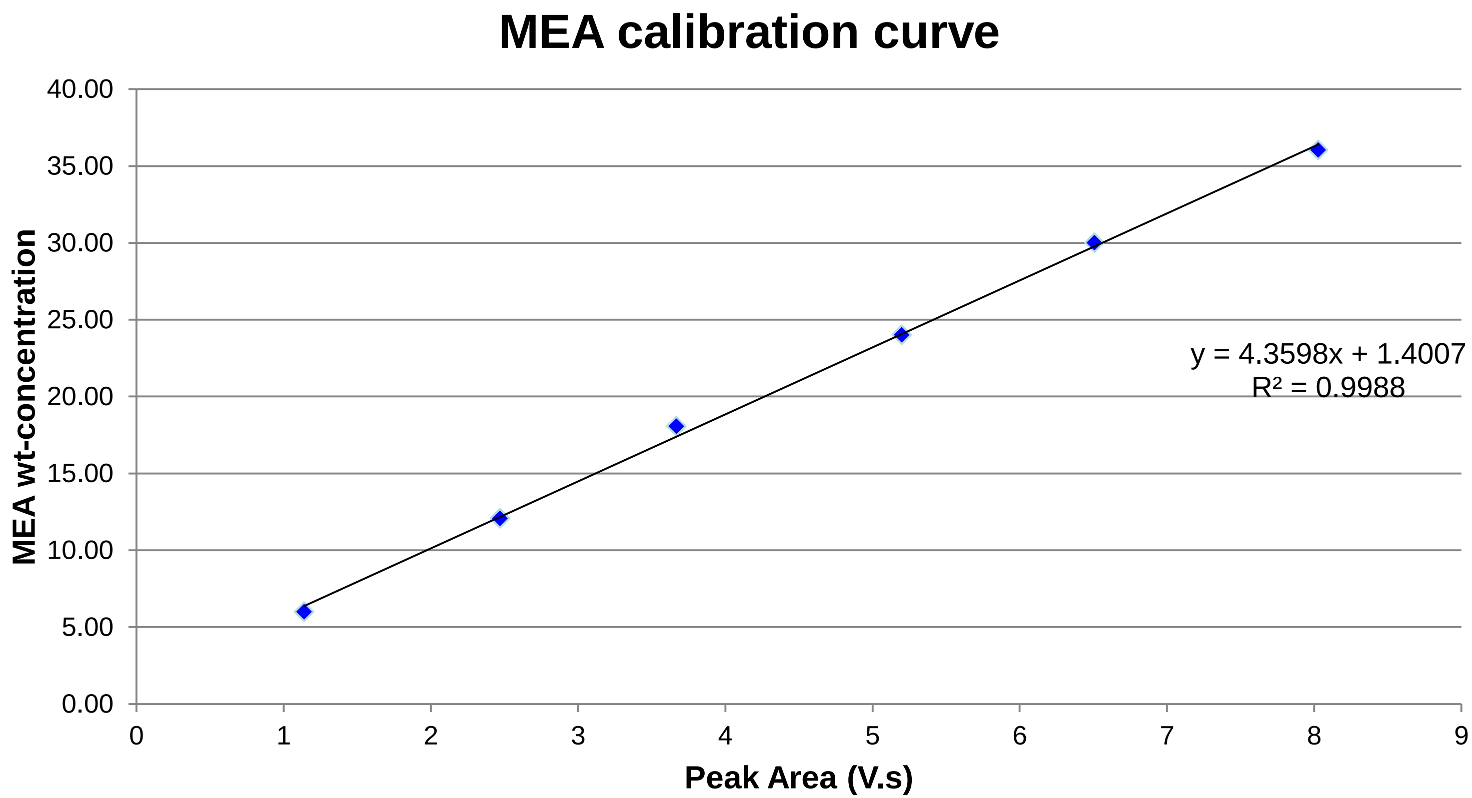
Test bench improvements:

- New condenser (larger and vertical)
- Chiller and heating rope
- FTIR sample line

1. Progress review

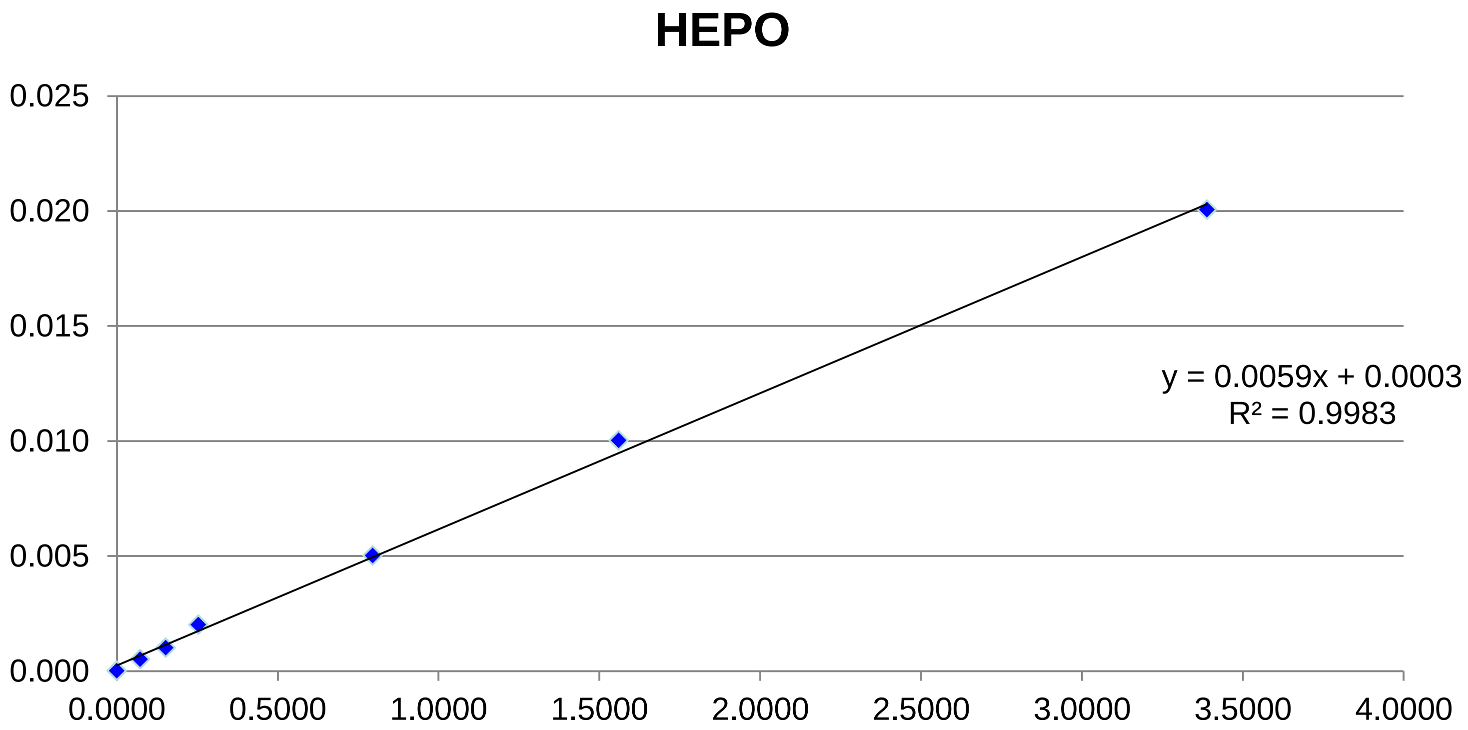
Development of analytical methods

- **HPLC-RID**: method optimization using a polar reversed phase (3-months internship)



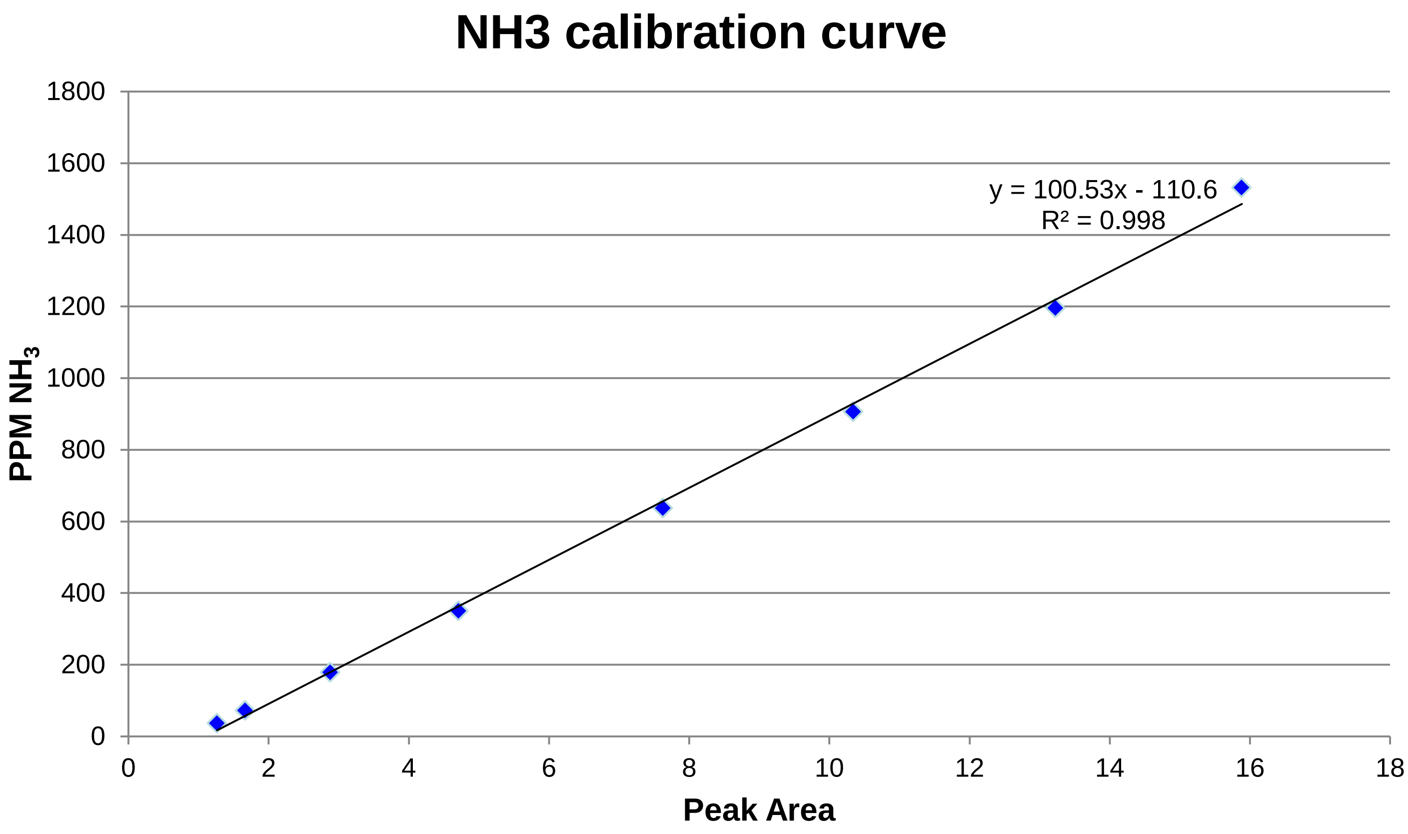
Development of analytical methods

- **GC-FID**: method available, calibration for MEA and degradation products: OZD, HEI, HEPO, BHEOX



Development of analytical methods

- **FTIR**: method developed, calibration for NH_3 at two different dilutions



Performed experiments (MEA 30wt-%):

Experi-ment	Start	End	Days	Test	**Rpm**	T° (C)	P_{tot} (bar)	O_2 (%)	CO_2 (%)	N_2 (%)	Gas flow (mln/min)
11	11/04/12	25/04/12	14	Base case repetability	**1000**	120	4	5	15	80	160
12	30/04/12	14/05/12	14	Influence of CO2	**1000**	120	4	0	15	85	160
13	22/05/12	5/06/12	14	Influence of O2	**1000**	120	4	5	0	95	160
14	8/06/12	15/06/12	7	Influence of Temperature	**1000**	140	4	5	15	80	160
15	20/06/12	4/07/12	14	Base Case at lower rpm	**400**	120	4	5	15	80	160
16	12/07/12	26/07/12	14	Influence of O2	**400**	120	4	5	0	95	160

Conclusions:

1. Test bench improved

=> Experimental problems appear to be definitely under control; repetability has been evidenced

2. Analytical methods further developed

=> Reliable quantification of MEA, liquid degradation products, and NH_3

3. Experiments are running

2. Degradation results

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2. Degradation results

2[nd] test campaign with MEA 30 wt-%

=> Mass losses avoided!

Experiment	Days	Test	Rpm	T° (C)	P_{tot} (bar)	O_2 (%)	CO_2 (%)	N_2 (%)	Mass balance
11	14	Base case repetability	1000	120	4	5	15	80	3.53%
12	14	Influence of CO_2	1000	120	4	0	15	85	-39.83%
13	14	Influence of O_2	1000	120	4	5	0	95	5.47%
14	7	Influence of temperature	1000	140	4	5	15	80	2.17%
15	14	Base Case at lower agitation rate	400	120	4	5	15	80	-1.33%
16	14	Influence of O_2 at lower agitation rate	400	120	4	5	0	95	-

2. Degradation results

Test of repetability: comparison with Experiment 10

- Repetability achieved at 400 rpm (Exp. 10 and 15) !
- High degradation rate when rotating at 1000 rpm!
- Mass balance problems in Experiment 12

Experiment	10	11	12	13	14	15
MEA wt-% HPLC	21,73	4.02	52.45	4.76	3.71	21.72
MEA wt-% GC	19.94	1.65	79.67	1.75	1.8	18.94

2. Degradation results

Quantification of degradation products

- First experiment campaign:

Concentration	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	LTTE
MEA	20.34	8.97	14.49	17.90	18.78	21.93	8.88	29.66	26.97	19.94	19.68
OZD	0.08	0.13	0.14	0.07	0.05	0.09	0.06	0.00	0.00	0.08	0.05
HEI	0.13	0.09	0.48	0.05	0.13	0.39	0.08	0.01	0.01	0.20	0.08
HEPO	5.43	0.37	0.62	0.22	1.21	0.21	0.03	0.05	0.05	0.60	0.31
BHEOX	0.11	0.00	0.43	0.00	0.00	0.00	3.00	0.00	0.00	0.17	0.06

2. Degradation results

Quantification of degradation products

- Second experiment campaign:

Concentration	LTTE	10	11	12	13	14	15	16 (1w)
MEA	19.68	19.94	1.65	79.67	1.75	1.80	18.94	19.48
OZD	0.05	0.08	0.14	0.19	0.33	0.08	0.05	0.01
HEI	0.08	0.20	4.17	0.01	4.85	0.96	0.04	0.08
HEPO	0.31	0.60	0.07	0.08	0.10	0.16	0.58	0.06
BHEOX	0.06	0.17	0.00	0.00	0.04	0.05	0.10	0.02

- Good repetability except for HEI (Exp. 10-15)
- Base case seem to be closer to LTTE than other Exp.

2. Degradation results

Quantification of degradation products: 2nd test campaign

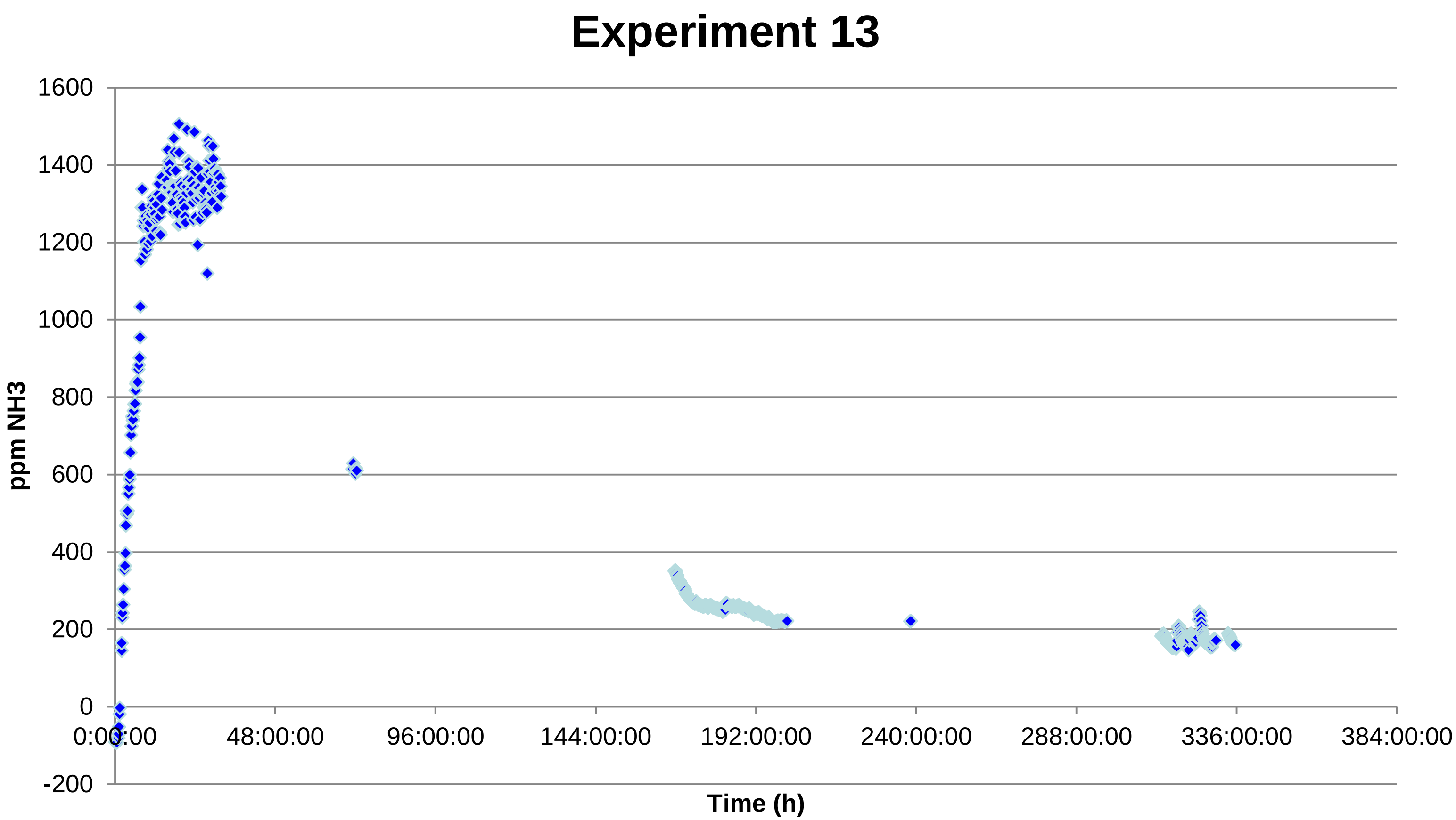
Concentration	LTTE	10	11	12	13	14	15	16 (1w)
MEA	19.68	19.94	1.65	79.67	1.75	1.80	18.94	19.48
OZD	0.05	0.08	0.14	0.19	0.33	0.08	0.05	0.01
HEI	0.08	0.20	4.17	0.01	4.85	0.96	0.04	0.08
HEPO	0.31	0.60	0.07	0.08	0.10	0.16	0.58	0.06
BHEOX	0.06	0.17	0.00	0.00	0.04	0.05	0.10	0.02

- Nearly no degradation under CO_2
- HEPO major degradation product at 400 rpm and in LTTE
- HEI major degradation product at 1000 rpm, less present at higher T°

2. Degradation results

Quantification of NH3: first results

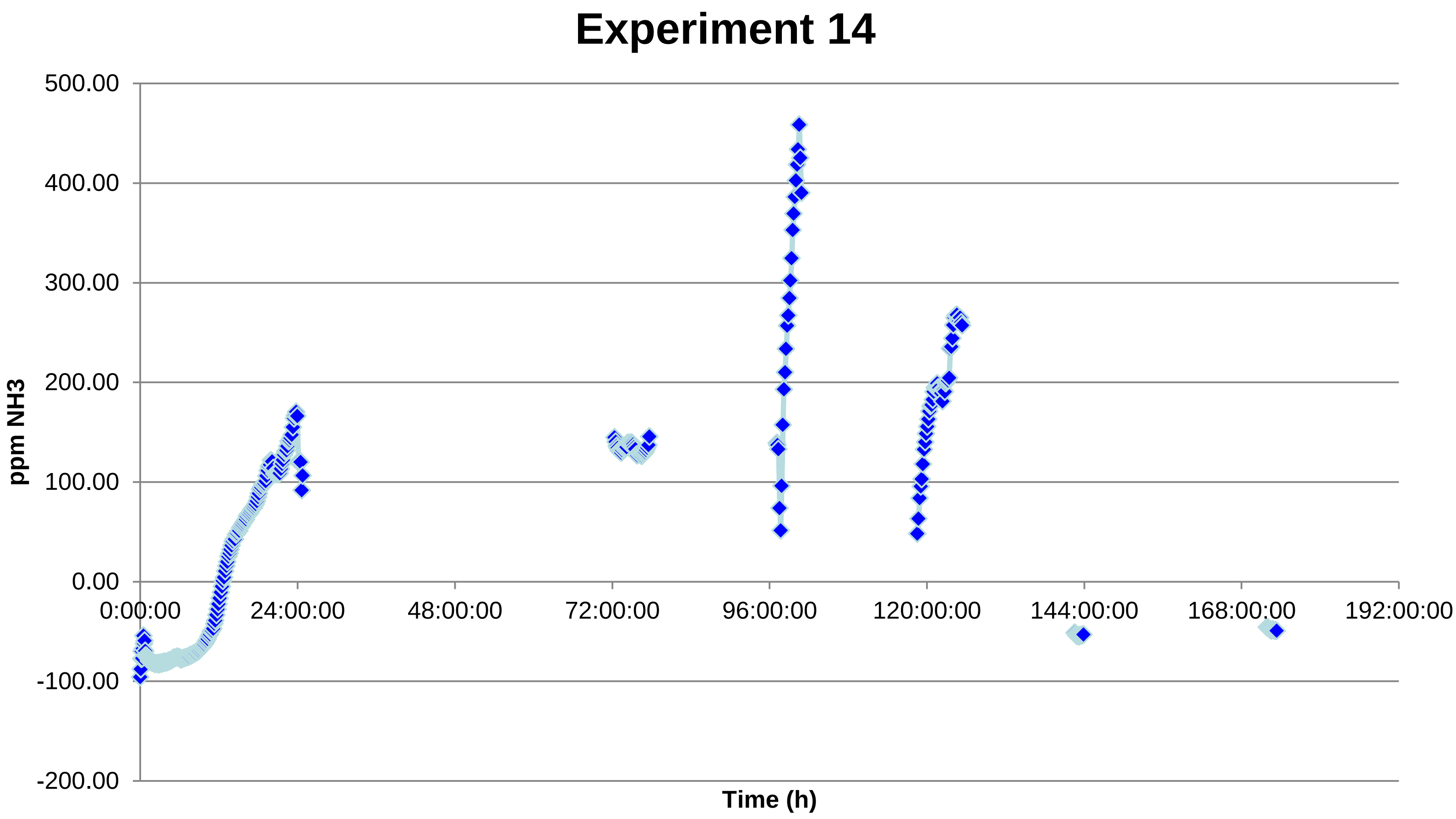
=> Typical curve, but has to be confirmed



2. Degradation results

Quantification of NH3: first results

=> Maximum at 24h; measure errors



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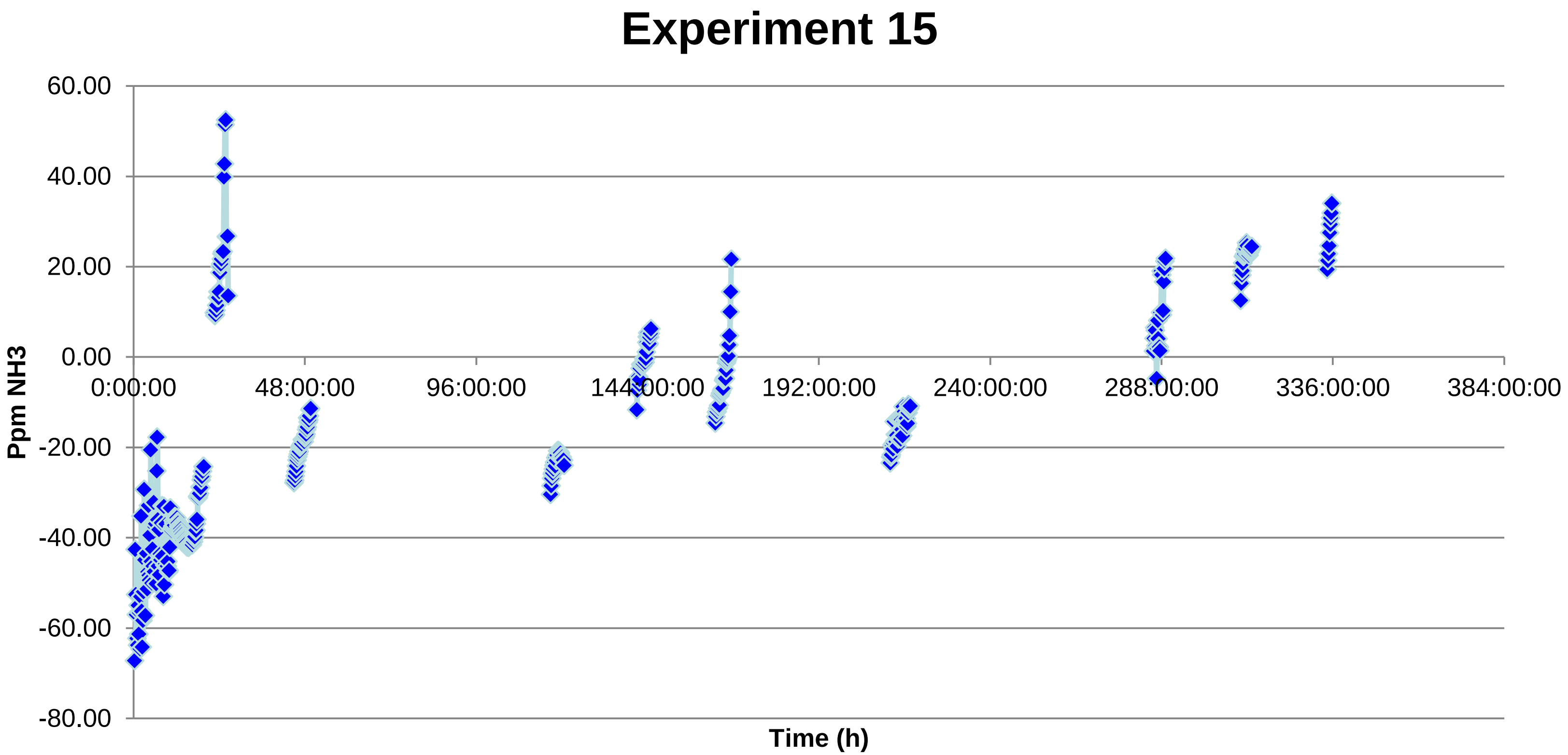
Quantification of NH3: first results

- Measurement errors ?
- Almost no NH3

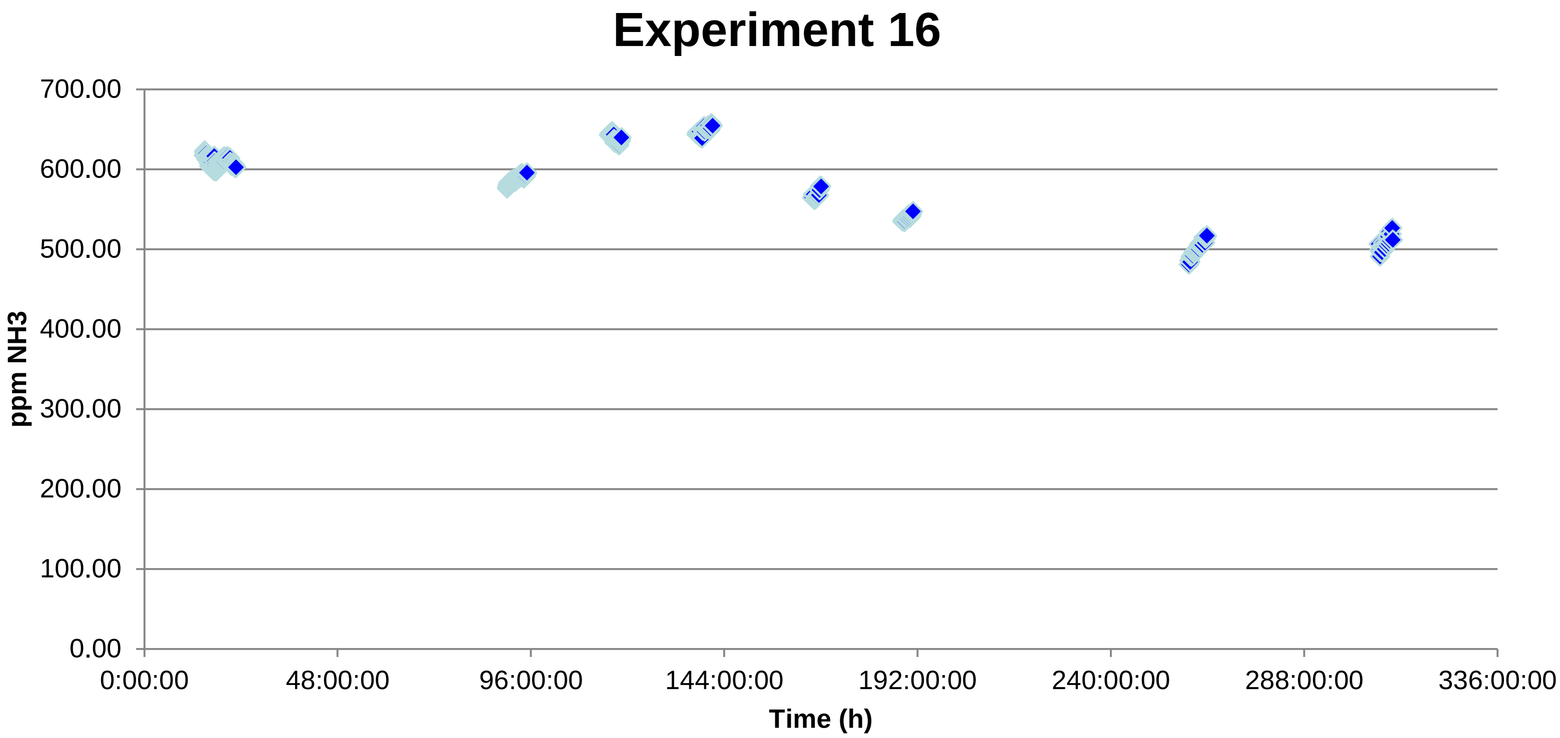


2. Degradation results

Quantification of NH3: first results

=> New calibration method, lower dilution

=> Beginning of the curve is missing



2. Degradation results

Metal Follow-up

=> Possibility of quantifying NH_4 by capillar electrophoresis

Experiment	Fe (ppm)	Cr (ppm)	Ni (ppm)	F (ppm)	Mn (ppm)	NH_4 (ppm)
10	3.46	6.41	0.87	557.55	n.o.	n.o.
11	37.3	7.38	4.31	n.o.	0.63	6 448
12	29.0	5.20	4.66	n.o.	0.51	530
13	15.2	5.29	3.57	n.o.	0.37	5 568
14	39.4	9.22	9.81	n.o.	0.80	4 931

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3. Degradation Modeling

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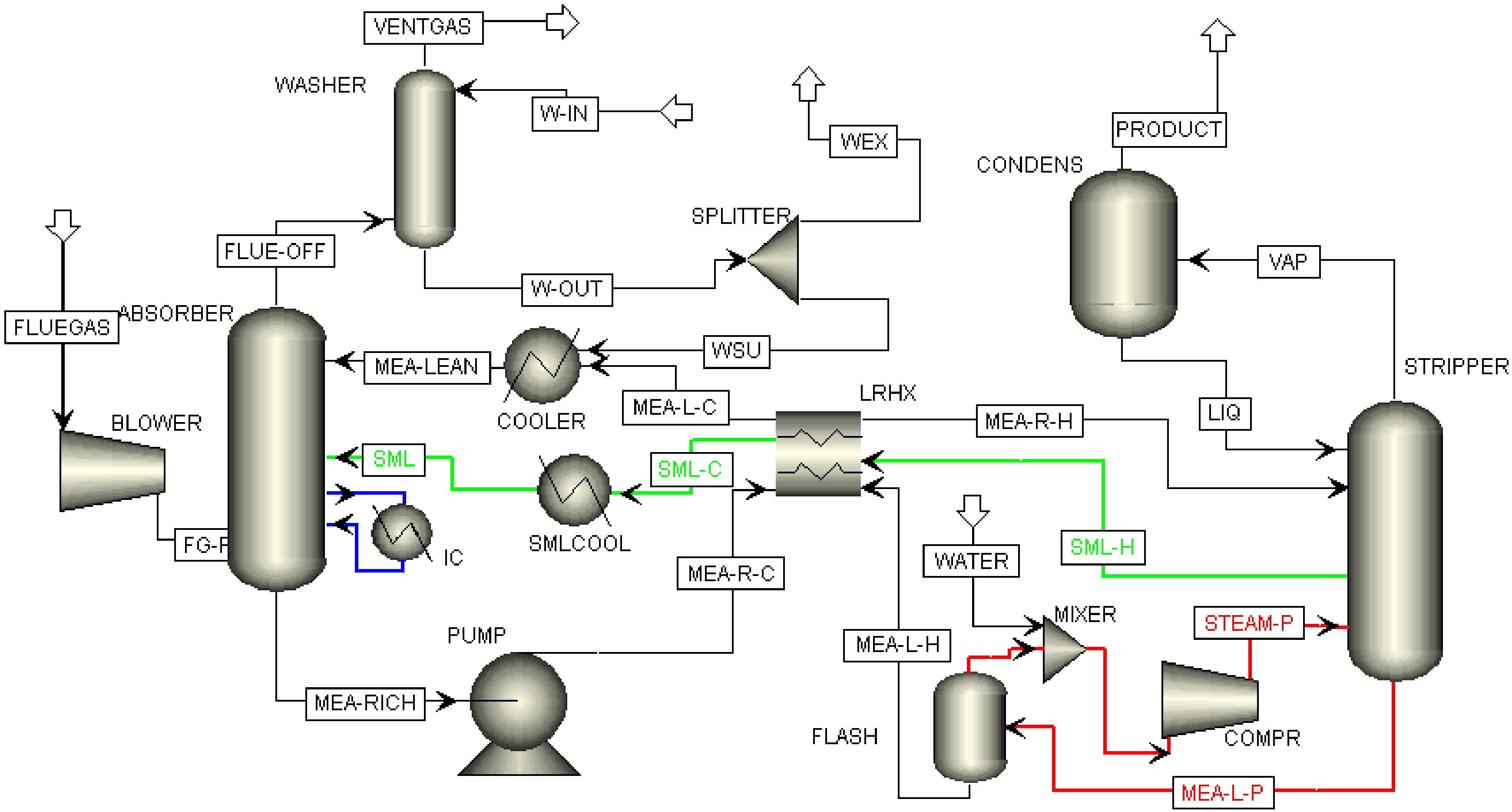
Former flowsheet



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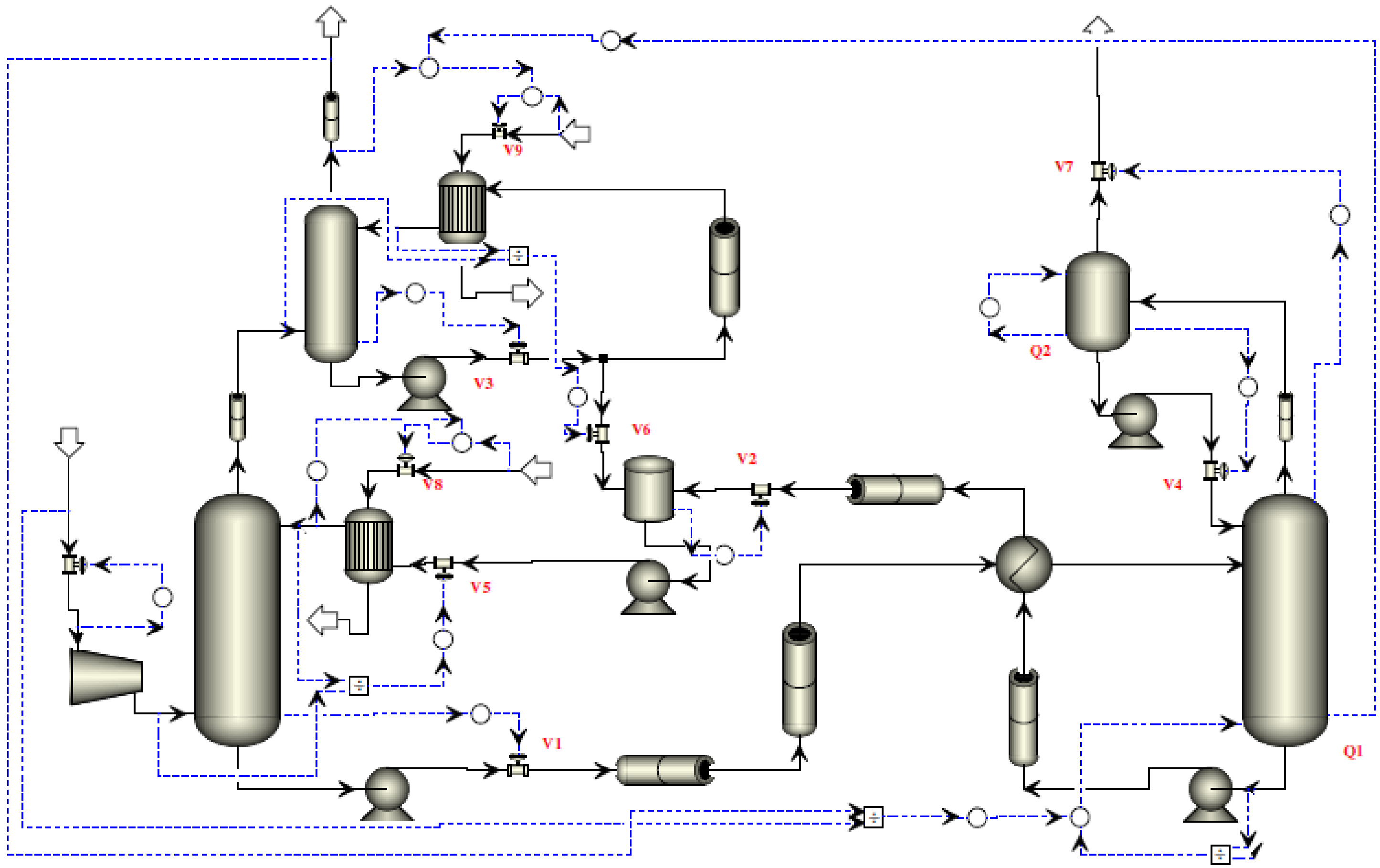
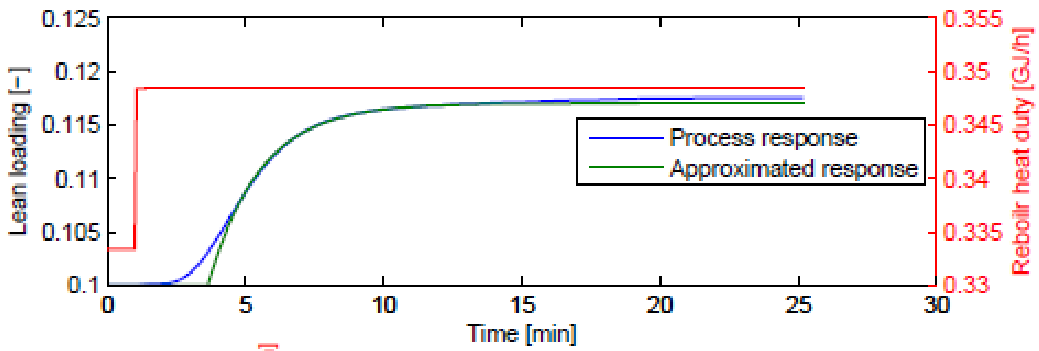
Recent modeling efforts have focussed on the follow-up of a master thesis about dynamic process modeling

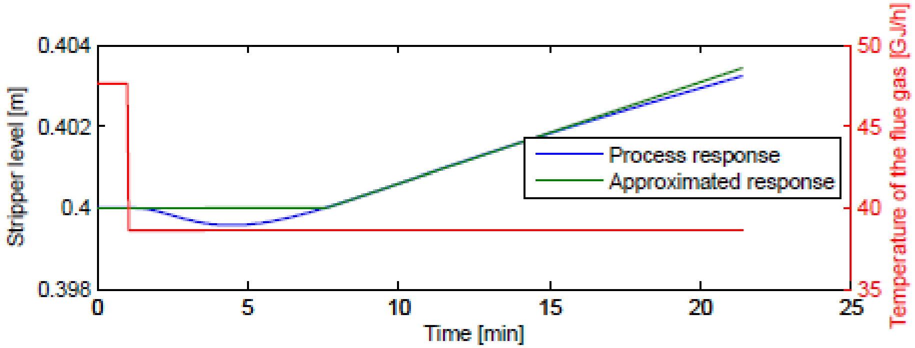


3. Degradation Modeling

Master Thesis in brief

- Rigourous design of the washing section
- Innovative control strategy
- Study of some process disturbances and regime transition





3. Degradation Modeling

- New version Aspen 7.3.2 available, with new databanks for MEA: pure components data as well as reaction data
- Model is currently being upgraded
- Work on dynamic simulation is going on: Bruno Cabeza Mogador and Ségolène Belletante

3. Degradation Modeling

- First attempts to take degradation into account in the model

$$2\ NH_2CH_2CH_2OH + 5\ O_2 \longleftrightarrow 2\ NH_3 + 4\ CO_2 + 4\ H_2O$$

=> Convergence is achieved with default values, but production of CO_2 is unrealistic

- Formation of formate salts seems more realistic

$$NH_2CH_2CH_2OH + 1.5\ O_2 \longleftrightarrow NH_3 + 2\ HCOOH$$

$$3\ NH_2CH_2CH_2OH + 1.5\ O_2 \longleftrightarrow NH_3 + 2\ HCOO^- + 2\ NH_3^+CH_2CH_2OH$$

=> Not converged yet

3. Degradation Modeling

- Required parameters for degradation reactions

$$NH_2CH_2CH_2OH + 1.5\ O_2 <--> NH_3 + 2\ HCOOH$$

$$3\ NH_2CH_2CH_2OH + 1.5\ O_2 <--> NH_3 + 2\ HCOO^- + 2\ NH_3^+CH_2CH_2OH$$

$$K_{eq,\ 1}(T)=[NH_2CH_2CH_2OH]*[O_2]^{1.5} / [NH_3]*[HCOOH]^2$$

$$K_{eq,\ 2}(T)=[NH_2CH_2CH_2OH]^3*[O_2]^{1.5} / [NH_3]*[HCOO^-]^2*[NH_3^+CH_2CH_2OH]^2$$

1. Stoechiometry regarding O_2
2. Inhibiting influence of CO_2
3. Temperature dependency

3. Degradation Modeling

1. Stoechiometry regarding O_2

- Transfer limited reactions
- MEA in excess

$K'_{eq,1}(T) = [O_2]^{1.5} / [NH_3]*[HCOOH]^2$

2. Inhibiting influence of CO_2

- Lower O_2 absorption in CO_2 loaded MEA
- May already be considered in Aspen?

3. Temperature influence

- Equilibrium constant varies with the temperature
- $\ln(Keq) = A + B/T + C*\ln(T) + D*T + E*((P-P_{ref})/P_{ref})$
- Alternative: Gibbs free energy

3. Degradation Modeling

Conclusion:

- Need for measuring formate to be discussed!
- 3rd test campaign for measuring the influence of O_2 and CO_2 at different concentrations and temperatures:

- 3 different O_2 and CO_2 partial pressures
- 3 different temperatures

=> 9 experiments may be planned

4. Perspectives

4. Perspectives

- PhD till summer 2013
- => Few time for 14-days experiments

Experi-ment	Start	End	Days	Test	T° (C)	P_{tot} (bar)	O_2 (%)	CO_2 (%)	N_2 (%)	Additives
17	30/07/12	6/08/12	14	Influence of Temperature/1	55	4	5	15	80	-
18	8/08/12	22/08/12	14	Influence of Temperature/2	140	4	5	15	80	-
19	27/08/12	10/09/12	14	Influence of SS metals	120	4	5	15	80	Addition of stainless steel metals (0.4 mM Fe2+, 0.1 mM Cr3+, and 0.05 mM Ni2+, evtl. 0.1mM Mn2+)
20	12/09/12	26/09/12	14	Influence of inh. A	55	4	5	15	80	SS metals + 100 mM Inh. A
21	28/09/12	12/10/12	14	Influence of inh. A	120	4	5	15	80	SS metals + 100mM Inh. A
22	22/10/12	5/11/12	14	Influence of inh. A + HDPE	120	4	5	15	80	SS metals + 100 mM Inh A + HEDP 1wt-%
23	7/11/12	21/11/12	14	Test of metal additives/2	120	4	5	15	80	SS metals + HEDP 1wt-% + DTPA 0.4 wt-%
24	23/11/12	7/12/12	14	Influence of O2	120	4	10	15	75	-
25	10/12/12	24/12/12	14	Influence of O2	120	4	20	15	65	-

4. Perspectives

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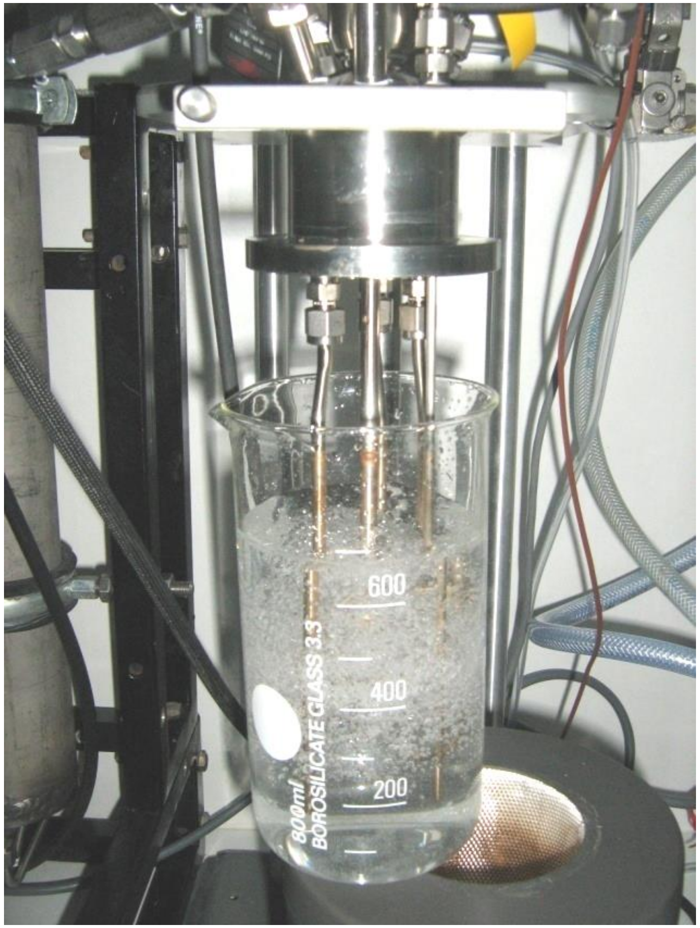
- 7 days may be enough!
- Degradation reactions are O_2-transfer limited

=> Varying the agitation rate has a large influence on the degradation



4. Perspectives

- Influence of time length not large!
- Comparison: P10-1w and P10-f, idem for P11 and P15
- Regarding degradation products, P10-1w is closer to LTTE than P10-f !
- Intermediate agitation rate could increase degradation within 1 week!

Concentration	LTTE	P10 1w	P10 f	P11 1w	P11 f	P12 1w	P12 f	P13 1w	P13 f	P14 f	P15 1w	P15 f
MEA	19.68	22.17	19.94	2.03	1.65	43.92	79.67	1.82	1.75	1.80	22.67	18.94
OZD	0.05	0.05	0.08	0.12	0.14	0.07	0.19	0.17	0.33	0.08	0.05	0.05
HEI	0.08	0.13	0.20	3.91	4.17	0.01	0.01	3.20	4.85	0.96	0.02	0.04
HEPO	0.31	0.26	0.60	0.07	0.07	0.05	0.08	0.09	0.10	0.16	0.28	0.58
BHEOX	0.06	0.03	0.17	0.00	0.00	0.00	0.00	0.01	0.04	0.05	0.04	0.10

4. Perspectives

- Alternative planning proposal

Experi-ment	Start	End	Days	Test	Rpm	T° (C)	P_{tot} (bar)	O_2 (%)	CO_2 (%)	N_2 (%)	Additives
17	30/07/12	6/08/12	7	Agitation rate	600	120	4	5	15	80	-
18	8/08/12	15/08/12	7	Agitation rate	800	120	4	5	15	80	-
19	17/08/12	24/08/12	7	Agitation rate	XXX	120	4	5	15	80	-
20	27/08/12	3/09/12	7	Repetability	XXX	120	4	5	15	80	-
21	5/09/12	12/09/12	7	Influence of O2	XXX	120	4	5	0	95	-
22	14/09/12	21/09/12	7	Influence of CO2	XXX	120	4	0	15	85	-
23	24/09/12	1/10/12	7	Influence of Temperature	XXX	140	4	5	15	80	-
24	3/10/12	10/10/12	7	Influence of Temperature	XXX	55	4	5	15	80	-
25	22/10/12	29/10/12	7	Influence of SS metals	XXX	120	4	5	15	80	Addition of stainless steel metals
26	31/10/12	7/11/12	7	Influence of inh. A	XXX	55	4	5	15	80	SS metals + Inh. A
27	12/11/12	19/11/12	7	Influence of inh. A	XXX	120	4	5	15	80	SS metals + Inh. A
28	21/11/12	28/11/12	7	Influence of inh. A + HDPE	XXX	120	4	5	15	80	SS metals + Inh A + HEDP 1wt-%
29	30/11/12	7/12/12	7	Metal + additives	XXX	120	4	5	15	80	SS metals + HEDP + DTPA

4. Perspectives

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- Analytical perspectives
  - HPLC: Quantification of formiate
    => New method development? What about LBE?
  - GC:
    - End of calibration for remaining degradation products (HEIA, HEA, HEF)
    - tests using less polar mobile phase for better peak separation
  - FTIR – CO_2 analyser:
    - Quantification of CO_2 in gas exhaust of the degradation reactor

4. Perspectives

- Project submitted to the FNRS: CO_2 Capt – PARSAD
- Impact of degradation on solvent properties
- Degradation and modeling at the ULg
- Characterisation of solvents at the UMons
- Decision in November

Thank you for your attention!

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