Controlling Nitrogen Oxides (NO_x) Emissions from Exothermic Nitrogen Generating Systems (NGS) for Application in Subsea Environments

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SUPPORTING INFORMATION

1) Paired t-test

Table S1 – Experimental conditions selected to validate the NO_x measurement methodology by ATR-FTIR.

Experimental condition	Temperature (°C)	$[NH_4^+]$ (mol L^{-1})	$[NO_2^-]$ (mol L^{-1})	[HAcO] (mol L^{-1})
I	5.00	2.67	2.67	0.13
II	5.00	2.40	3.20	0.13
III	12.50	2.40	3.20	0.10
IV	12.50	2.86	2.29	0.04
V	8.75	2.67	2.67	0.07

Table S2 – Paired t-test for comparison of NO_x measurements by ATR-FTIR ant titration for the experimental conditions highlight in Table S1. Measurements performed after 11 h of reaction.

Experimental condition	$[NO_x]_{titration}$	$[NO_x]_{infrared}$	$d = [NO_x]_{titration} - [NO_x]_{infrared}$
I	1.84×10^{-1}	1.70×10^{-1}	1.40×10^{-2}
II	3.25×10^{-1}	2.95×10^{-1}	3.01×10^{-2}
III	2.77×10^{-1}	2.53×10^{-1}	2.44×10^{-2}
IV	1.31×10^{-1}	1.41×10^{-1}	-1.03×10^{-2}
V	1.50×10^{-1}	1.53×10^{-1}	-3.16×10^{-3}
Variance			3.02×10^{-4}
Standard deviation			1.74×10^{-2}
Comparison of techniques			
$t_{critical}$ (significance level: $\alpha = 0.05$)			2.776
$t_{experimental}$			1.415

2) Central composite design

Table S3 – Central composite design performed to study the responses selected. R, C, T and P are the coded values of the factors $[NH_4^+]/[NO_2^-]$, [HAcO], temperature and partition, respectively. y_1, y_2 and y_3 are the responses yield after 11 h, yield after 1.5 h and NO_x generation, respectively.

Assay	R	C	T	P	y_1 (%)	y_2 (%)	y_3 (%)
1	-1	-1	-1	-1	50.14	11.56	4.24
2	1	-1	-1	-1	48.38	13.03	4.75
3	-1	1	-1	-1	62.56	25.62	6.65
4	1	1	-1	-1	64.17	26.51	5.59
5	-1	-1	1	-1	69.69	24.63	2.47
6	1	-1	1	-1	58.51	21.09	5.91
7	-1	1	1	-1	77.55	39.38	6.77
8	1	1	1	-1	73.67	39.19	8.97
9	-1	-1	-1	1	50.14	10.45	3.92
10	1	-1	-1	1	49.98	11.45	3.29
11	-1	1	-1	1	65.05	23.04	5.87
12	1	1	-1	1	64.07	27.43	5.00
13	-1	-1	1	1	63.50	23.52	2.38
14	1	-1	1	1	57.21	19.37	5.65
15	-1	1	1	1	82.36	37.74	4.38
16	1	1	1	1	71.65	38.44	8.20
17	0	0	0	0	55.09	21.03	3.53
18	0	0	0	0	50.60	19.58	3.60
19	0	0	0	0	53.77	18.87	3.91
20	0	0	0	0	49.86	21.62	3.47
21	0	0	0	0	52.37	19.60	3.93
22	-2	0	0	0	81.22	34.72	11.09
23	2	0	0	0	76.52	31.88	12.95
24	0	-2	0	0	8.83	2.21	0.06
25	0	2	0	0	56.32	25.20	6.45
26	0	0	-2	0	46.30	13.72	1.93
27	0	0	2	0	84.68	46.47	5.34
28	0	0	0	-2	49.04	23.09	5.74
29	0	0	0	2	51.24	17.34	3.17

The models for the responses were evaluated by multiple multivariate linear regression. The models initially contained first and second-order terms, with interactions between variables and quadratic terms of each factor. ANOVA was performed to analyze the generated models and the least contributing variables were eliminated by backward elimination with $\alpha = 0.05$.

a) Modelling of yield after 11 h (y_1)

$$y_1 = 52.98 - 1.78R + 8.69C + 7.35T - 1.92RT + 7.58R^2 - 3.99C^2 + 4.24T^2 \quad \text{Eq. S1}$$

Table S4 – ANOVA of the quadratic model adjusted to the yield after 11 h (Eq. S1).

Source of variation	**Sum of squares**	**Degrees of freedom**	**Mean square**
Regression	5931.40	7	847.34
Residual error	463.69	21	22.08
Lack of fit	444.85	17	26.17
Pure error	18.84	4	4.71
Total	6395.09	28	
Percentage of variation explained: 92.75%			
$MS_{regression}/MS_{residual\ error} = 38.38$		$F_{critical} = 2.49$ ($\alpha = 0.05$)	
$MQ_{lack\ of\ fit}/MQ_{pure\ error} = 5.56$		$F_{critical} = 5.83$ ($\alpha = 0.05$)	

b) Modelling of yield after 1.5 h (y_2)

$$y_2 = 20.21 + 7.01C + 6.66T - 0.88P - 0.93RT + 3.31R^2 - 1.59C^2 + 2.51T^2 \qquad \text{Eq. S2}$$

Table S5 – ANOVA of the quadratic model adjusted to the yield after 1.5 h (Eq. S2).

Source of variation	Sum of squares	Degrees of freedom	Mean square
Regression	2839.64	7	405.66
Residual error	79.84	21	3.80
Lack of fit	74.65	17	4.39
Pure error	5.19	4	1.30
Total	2919.47	28	
Percentage of variation explained: 97.27%			
$MS_{regression}/MS_{residual\ error} = 106.71$		$F_{critical} = 2.49$ ($\alpha = 0.05$)	
$MQ_{lack\ of\ fit}/MQ_{pure\ error} = 3.39$		$F_{critical} = 5.83$ ($\alpha = 0.05$)	

c) Modelling of NO_x generation (y_3)

$$y_3 = 3.67 + 0.60R + 1.32C + 0.51T - 0.49P + 0.92RT + 0.31CT + 1.99R^2 - 0.20C^2 \qquad \text{Eq. S3}$$

Table S6 – ANOVA of the quadratic model adjusted to the NO_x generation (Eq. S3).

Source of variation	Sum of squares	Degrees of freedom	Mean square
Regression	192.99	8	24.12
Residual error	8.07	20	0.40
Lack of fit	7.88	16	0.49
Pure error	0.19	4	0.05
Total	201.06	28	
Percentage of variation explained: 95.99%			
$MS_{regression}/MS_{residual\ error} = 59.81$		$F_{critical} = 2.45$ ($\alpha = 0.05$)	
$MQ_{lack\ of\ fit}/MQ_{pure\ error} = 10.40$		$F_{critical} = 5.84$ ($\alpha = 0.05$)	

3) Maximization of function f (y_1/y_3)

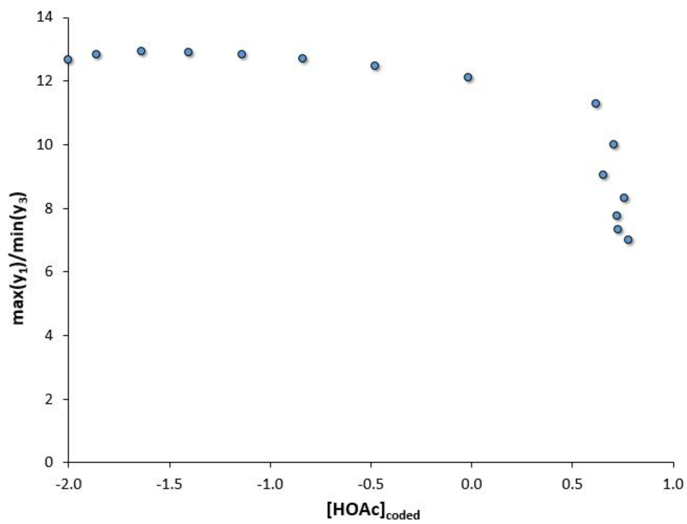

Figure S1 - Maximization of function f (y_1/y_3) for maximum overall conversion with minimum NO_x generation