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Supporting Information

Continuous flow synthesis of β-hydroxyethyl hydrazine in microreactors: Process behavior and impurities formation mechanism

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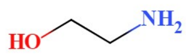
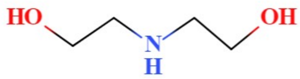
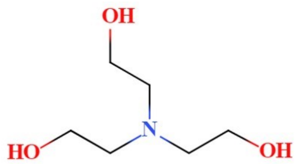
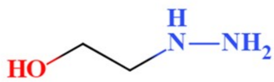
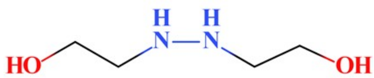
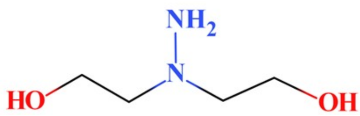
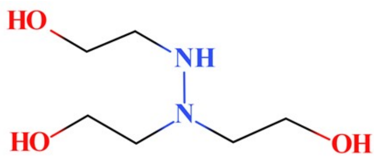
Table S1. MS characterization data of products.

Abbr.	Retention time (min)		MS main fragments (m/z)	Formula
	GC	GC/MS		
Ethanolamine	1.31	1.323	61 (M+), 42, 30, 28.	
Diethanolamine	2.238	2.238	74 (M+), 56, 45, 42, 30, 28.	
Triethanolamine	3.417	3.402	118 (M+), 88, 74, 56, 45, 30.	
Hydroxyethyl hydrazine	1.527	1.501	76 (M+), 57, 45, 43, 31, 30, 28.	
1,2-Bis(β-hydroxyethyl) hydrazine	2.543	2.438	120 (M+), 89, 71, 45, 42, 30, 28.	
1,1-Bis(β-hydroxyethyl) hydrazine	2.727	2.817	120 (M+), 89, 71, 45, 30, 28.	
Tri(β-hydroxyethyl)hydrazine	3.863	3.858	164 (M+), 133, 89, 74, 56, 45, 42, 30, 28.	

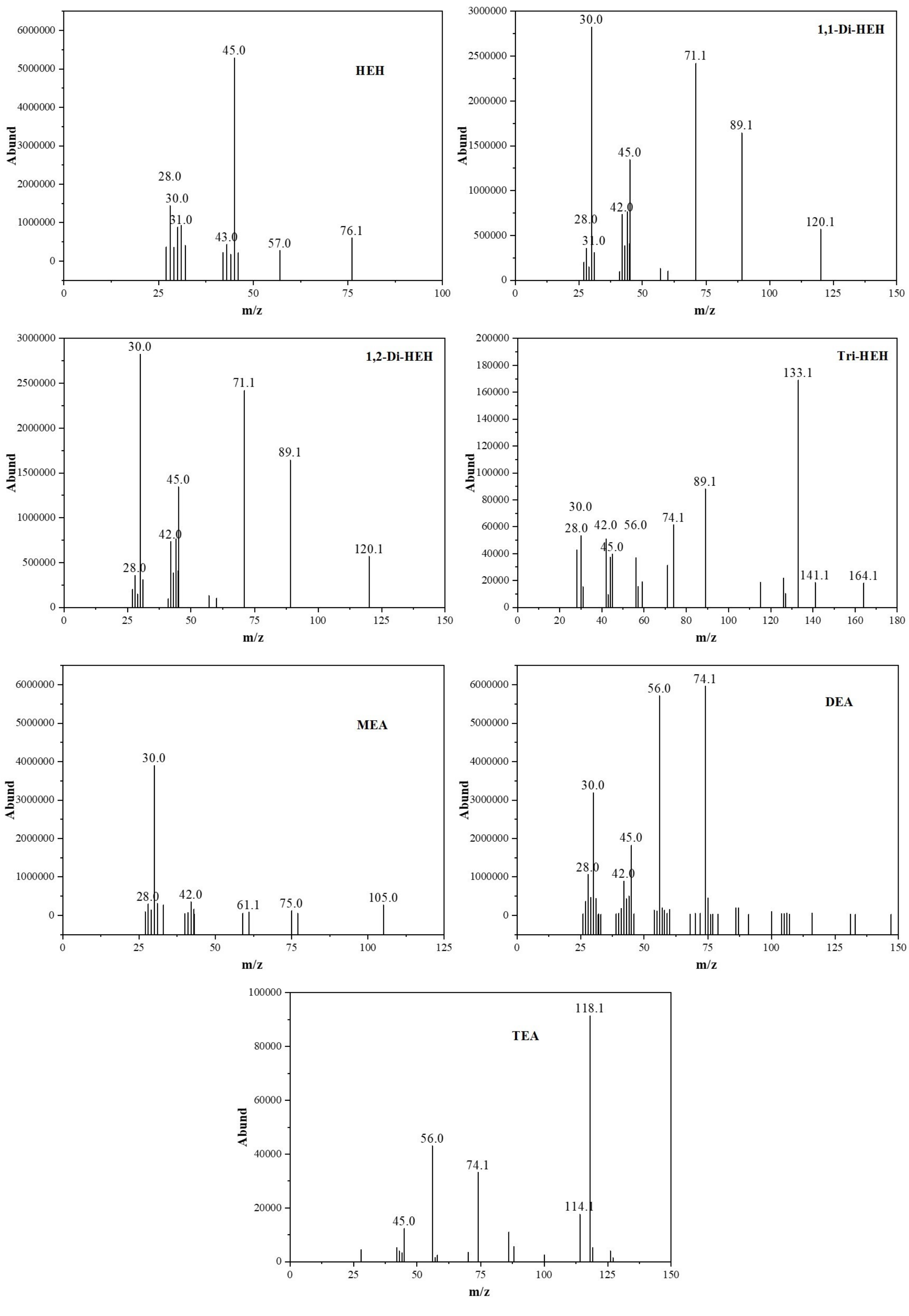
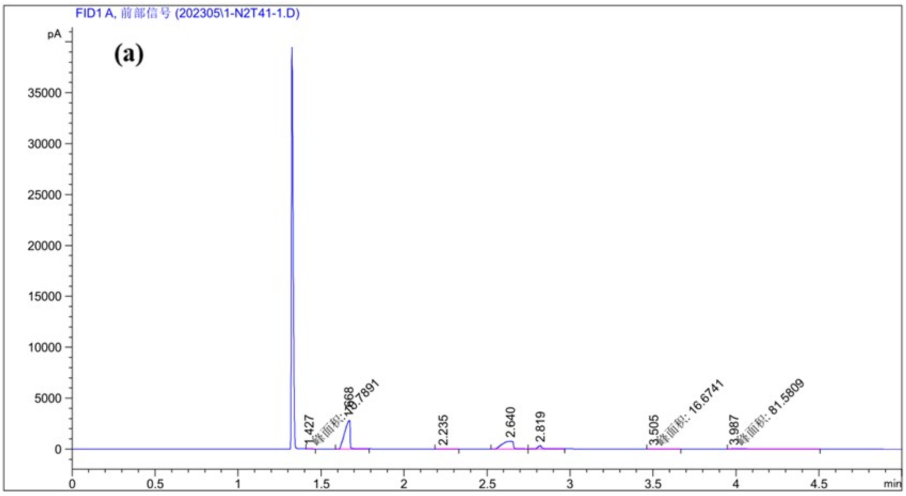


Figure S1. Mass spectrogram of the products.



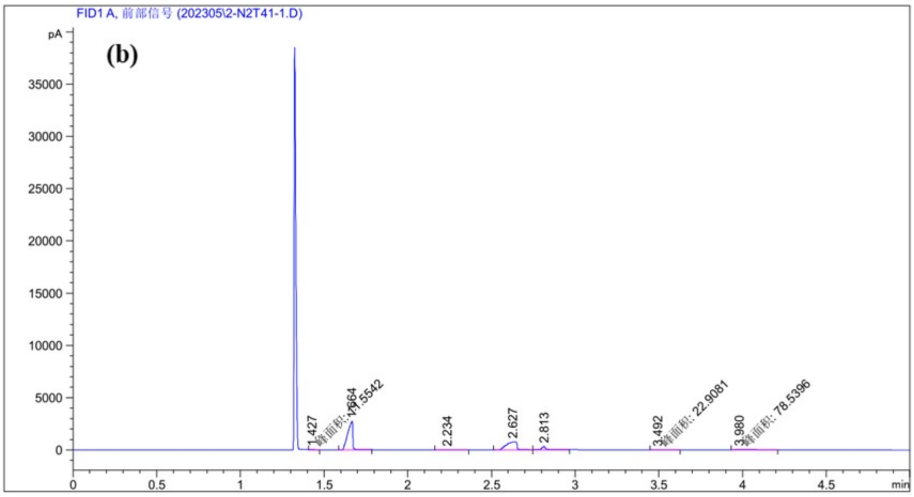


Figure S2. Gas chromatogram of the products.

Run conditions: (a) $N_2H_4 \cdot H_2O$/EO= 2.0, [$N_2H_4 \cdot H_2O$] 80 wt.%, 70 ^{o}C, 0.2 MPa. (b) $N_2H_4 \cdot H_2O$/EO= 2.0, [$N_2H_4 \cdot H_2O$] 80 wt.%, 70 ^{o}C, 0.3 MPa, t=0.69 min.

Figure S2 shows the results of a certain sample in the given conditions. Gas chromatograms clearly showed the existence of MEA, DEA, TEA, HEH, 1,2-Di-HEH, 1,1-Di-HEH and Tri-HEH.

Table S2. The vapor pressure of NH_3 under different temperatures.

Temperature /^oC	Pressure /MPa	Temperature /^oC	Pressure /MPa
0	0.43	10	0.61
20	0.85	30	1.16
40	1.55	50	2.03
60	2.61	70	3.32
80	4.16	90	5.14

Table S3. The vapor pressure of EO under different temperatures.

Temperature/^oC	Pressure/kPa	Temperature/^oC	Pressure/kPa
0	67.23	10	101.69
20	149.07	30	212.50
40	289.28	50	392.53
60	521.93	70	681.21
80	874.44	90	1105.46

Comparison of addition reaction in the microreactor and in a batch reactor

Utilizing the optimized process conditions obtained in the microreactor, we conducted a comparison between the microreactor and the semi-batch reactor. Table S4 displays that the microreactor achieved a 95% HEH yield in 0.7 min, while the batch reactor only achieved 43% in 10 min. The superior performance of the microreactor system for addition reaction could be attributed to the enhanced gas-liquid mass transfer efficiency. Additionally, Table S4 provides several examples on HEH production. In the process developed by Olin Corporation, a raw material ratio ($N_2H_4 \cdot H_2O$/EO) of 12:1 is employed, and the content of HEH in the crude product can reach 90%, although the yield is not mentioned. In the study of Zhu et al., an HEH yield of 89% was achieved by using magnetic stirrers to enhance the gas-liquid reaction. It is worth noting that the HEH synthesis process in the semi-batch reactor is achieved by introducing ethylene oxide

(EO) gas into hydrazine hydrate. A slower rate of ethylene oxide (EO) feed was necessary to enhance the selectivity of HEH, but it also considerably extended the reaction time. Therefore, compared to batch reactors, microreactors exhibit significantly enhanced reaction efficiency, with notable enhancements observed not only in yield but also in space-time yield.

Table S4. The HEH synthesis in different reactors.

	Reactor Type	Volume	$N_2H_4\cdot H_2O$/EO	Times	Temperature	Yield	Reference
		mL	/	min	°C	%	
1	Microreactor	12	12	0.7	70	95.0	This work
2	Three-neck flask	200	10	10	70	43.0	Self-experiment
3	Tube reactor	—[a]	12	—[a]	70	—[a]	Olin Corporation[1]
4	Three-neck flask	2000	10	—[a]	70	89.0	Zhu et al.[2]

a: not mentioned in the text.

1. Olin Corporation, *US Patent* 5 433 802, 1995.

2. Y. F. Zhu, H. S. Tian and H. L. Pan, *Shanghai Chemical Industry (In Chinese)*, 2001, 23, 13-15.