

Two-step continuous synthesis of tetraethylthiuram disulfide in microstructured reactors

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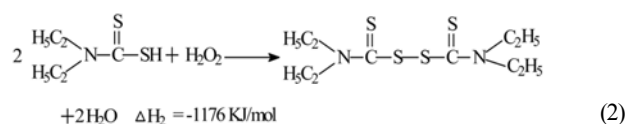
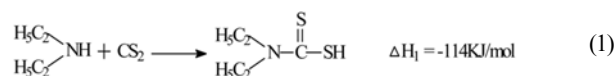
Abstract—We present two-step continuous synthesis of tetraethyl thiuram disulfide using microstructured reactors, starting with the formation of N, N-diethyldithiocarbamic acid from carbon disulfide and diethylamine in the first microstructured reactor, and the oxidation of N, N-diethyldithiocarbamic acid by hydrogen peroxide in the second one. We studied the effects of reaction temperature, LHSV and total flow rate on the yield of the product. In the first microstructured reactor assembled with an HPIMM micromixer and a stainless steel capillary as the delay loop, the yield of N, N-diethyldithiocarbamic acid reached 96.3% in the 40 wt% diethylamine ethanol solution under reaction conditions of the CS₂/(C₂H₅)₂NH molar ratio of 1.1 : 1, total flow rate of 4 mL/min, LHSV of 42.4 h⁻¹, and reaction temperature of 25 °C. Consequently, the obtained N, N-diethyldithiocarbamic acid solution was reacted with H₂O₂ solution in another microstructured reactor assembled with SIMM-V2 and a PTFE capillary as the delay loop, the yield of the high purity tetraethylthiuram disulfide reached 89.3% under the optimized reaction conditions.

Key words: Microstructured Reactor, N, N-diethyldithiocarbamic Acid, Tetraethylthiuram Disulfide, Vulcanization Accelerator, Strongly Exothermal

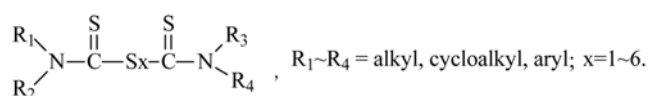
INTRODUCTION

The vulcanization of natural or synthetic rubber, a very important process for improving the mechanical strength and chemical resistance by cross-linking individual rubber polymer chain via sulfide and disulfide bridges, has garnered much attention from the modern rubber industry [1]. Many vulcanization accelerators have been developed, including dithiocarbamates, thiurams, thiourea, thiazoles, and sulfenamides. Among them, thiurams (tetraalkyl thiuramdisulfites, TATD) (Scheme 1) can vulcanize rubber in the absence of sulfur, and are one of the most effective materials for rubber vulcanization [2]. Generally, a two-step method is used to synthesize tetraalkyl thiuram disulfides. In the first step, secondary amine and base react with carbon disulfide to give dithiocarbamate. In the second step, the dithiocarbamate is oxidized to the corresponding thiuram disulfide by H₂O₂. Both steps are exothermic reactions and may encounter difficulty in accurate control of temperature, leading to low yield and selectivity of final products [3]. Thus, one of the reactants is always dropwisely added in the reaction system, resulting in low operation efficiency. Furthermore, the immiscibil-

ity of the reactants of secondary amine and carbon disulfide can result in the inefficient mixing. Although other synthesis methods, such as usage of a catalyst [4], electrolytic oxidation [5], have been developed for synthesis of TATD, they are still too complex for practical application.



Microstructured reactors have been known as efficient reaction systems for exothermic reactions and immiscible reactions, resulting from their excellent heat and mass transfer rates [6-19]. Obvious advantages are observed in reactions, such as Michael additions of amines to α , β -unsaturated carbonyl compounds [20], the Moffatt-Swern oxidation [21], nitration and bromination electrophilic reactions [22], enzyme reactions [23], esterification [24], and so on. These demonstrations motivated us to synthesize tetraalkylthiuram disulfides in microstructured reactors. We took tetraethylthiuram disulfide (TETD) as an example for the synthesis of TATD using carbon disulfide, diethylamine, and hydrogen peroxide as raw materials. The thermodynamic unsteady N, N-diethyldithiocarbamic (DTC acid) was first synthesized in one microstructured reactor (reaction 1), and then the solution of DTC acid was oxidized by H₂O₂ in the next microstructured reactor (reaction 2). A versatile and high efficient continuous flow microreactor unit capable of improving the



Scheme 1. General molecular structure of thiuram.

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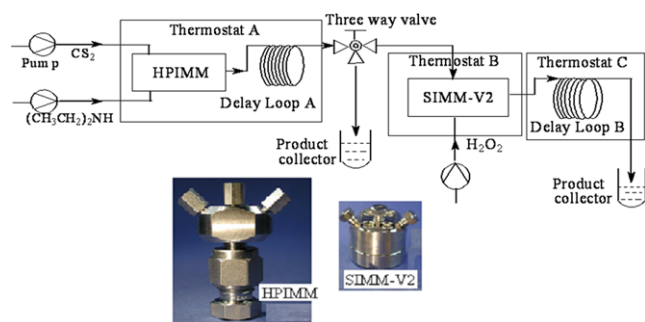


Fig. 1. Schematic of the experimental setup for the production of tetraethylthiuram disulfide using microstructure reactors.

yield and selectivity of the desired product has been developed.

EXPERIMENTAL

1. Chemicals

Hydrogen peroxide (50 wt%) was supplied by Nanjing Xiongwei Chemical Co. Ltd.. Bromothymol blue (AR-grade) was purchased from Tianjin Kernel Chemical Reagent Co. Ltd. Hydrochloride, sodium hydroxide and carbon disulfide (AR-grade) were purchased from Sinopharm Chemical Reagent Co. Ltd.. Diethylamine (AR-grade) and acetonitrile (HPLC-grade) were purchased from Shanghai Lingfeng Chemical Reagent Company.

2. Experimental Processes

The synthesis of TETD was performed in two sequential microstructured reactors; each of them is assembled with a micromixer and a delay loop (Fig. 1). The excessive carbon disulfide and a specified concentration of diethylamine ethanol solution were, respectively, fed by two high-performance liquid chromatograph (HPLC) pumps (Beijing Chuang Xin Tong Heng Science & Technology Co. Ltd.) into the first microstructured reactor composed of the micromixer HPIMM (channel dimensions: width×height=40×37 μm, IMM, Germany) and the Delay Loop A (0.6-mm-i.d. 316 L stainless steel capillary, 20 m length) at a set molar ratio. As Chen et al. [25] reported, the high yield of intermediate DTC Acid would not be obtained unless the molar ratio of carbon disulfide to secondary amine is 1 : 1-1.25 : 1. Herein, we adopted a CS₂/(C₂H₅)₂NH molar ratio of 1.1 : 1. The reaction temperature was controlled by immersing the microstructured reactor into the thermostat A. The residence time was controlled by adjusting the total flow rates of the feed pumps. The outlet of Delay Loop A was connected to a three-way valve. The other two outlets of the three-way valve were, respectively, connected to a product collector and the next microstructured reactor. When the yield of DTC acid was to be examined, the three-way valve was turned to the collector side to collect reaction products from the first reactor. The concentration of DTC acid solution was determined by the HPLC, and the diethylamine in the DTC acid solution was determined by titration, as described in section 2.3.

The three-way valve was turned to the second reactor to carry out the second reaction. At the same time, a hydrogen peroxide solution was fed into the second microstructured reactor assembled with the micromixer SIMM-V2 (channel dimensions: width×height=45×200 μm, IMM, German) and the Delay Loop B (1.5-mm-i.d. PTFE tube, 2 m length). The temperatures of the micromixer and

the Delay loop B were controlled by thermostat B and thermostat C, respectively. The suspension of TETD was collected at the outlet of the Delay Loop B. Solid TETD could be obtained after filtrating and oven drying at 50 °C.

3. Analyses

The concentration of diethylamine in the DTC acid solution was determined by a titration method. 1.0 mL of the obtained DTC acid solution from the first microstructured reactor was precisely shifted to a flask containing 20-30 mL of distilled water. 2-3 drops of 0.01% bromothymol was added into the flask. The solution in the flask was thus titrated with a 0.1mol/L hydrochloride standard solution until its color turned to light yellow from blue. The content of diethylamine X₁ (%) is calculated by the following formula:

$$X_1 = \frac{C_1 \cdot V_1 \cdot 0.07314}{M} \cdot 100\% \quad (3)$$

where, C₁ is molar concentration of hydrochloride stand solution (mol/L); V₁ is volume of hydrochloride standard solution for the titration (mL); M is mass of the supernatant sample solution (g).

The content of DTC acid was determined by the HPLC (Agilent 1100 Series, USA, ZORBAX Eclipse XDB-C18, 5 μm, 4.6 mm × 250 mm column) equipped with a programmable variable wavelength UV-VIS detector and an auto-sampler injector. Chromatographic separations were performed at 35 °C. The mobile phase consisting of acetonitrile-water (70 : 30) was delivered in isocratic mode at a flow rate of 1 mL/min. To obtain a maximal sensitivity, a programmable variable wavelength UV-VIS detector was operated at λ_{max} for DTC acid (275 nm) at their retention times for data acquisition. The heat unstable property of the DTC acid was analyzed by simultaneous thermal analyzer (STA 409, Netzsch Co. Ltd. Germany). A small amount of TETD crystals was taken to diffract by Brucker-Smart-1000 meter (Germany). Information of unit cell parameters, bond length, bond angle, conformation, intermolecular stacking interaction, crystallographic data and final refinement details is shown in supporting information. The purity of the TETD achieved 100%. The yield of TETD was determined by weighting. The melting point of TETD is 68-72 °C as determined by X-4 digital display micro melting point apparatus (Beijing Taike Instrument Co. Ltd.). The results are consistent with the melting point of 70-74 °C reported in the literature.

RESULTS AND DISCUSSION

1. Synthesis of N, N-diethyldithiocarbamic Acid

1-1. Effect of the Flow Rate

The effect of total flow rate (sum of the flow rate of diethylamine solution and carbon disulfide) was investigated with a diethylamine concentration of 40 wt%, a LHSV of 42.4 h⁻¹, and a reaction temperature of 25 °C. The results are presented in Fig. 2. It shows that with the increase of the total flow rate from 2 to 3 mL/min (corresponding to the increase of delay loop length from 10 to 15 m), the DTC acid yield increases slightly with an increment of 1.8%. Further increase of the flow rate to 4 and to 6 mL/min (corresponding to the increase of delay loop length from 20 to 30 m) results in the increase of DTC acid yield to 96.3% and 98.9%, respectively. This may be ascribed to the fact that the fluid flow and inner wall shear stress promote the fluid mixing and heat transfer with the increase

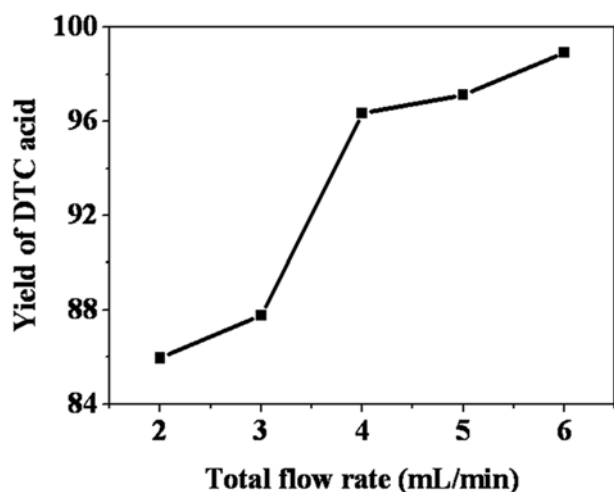


Fig. 2. Effect of the total flow rate on the yield of DTC acid. The experiments were carried out with a 40 wt% diethylamine, a $\text{CS}_2/(\text{C}_2\text{H}_5)_2\text{NH}$ molar ratio of 1.1 : 1, a LHSV of 42.4 h^{-1} and a temperature of 25°C .

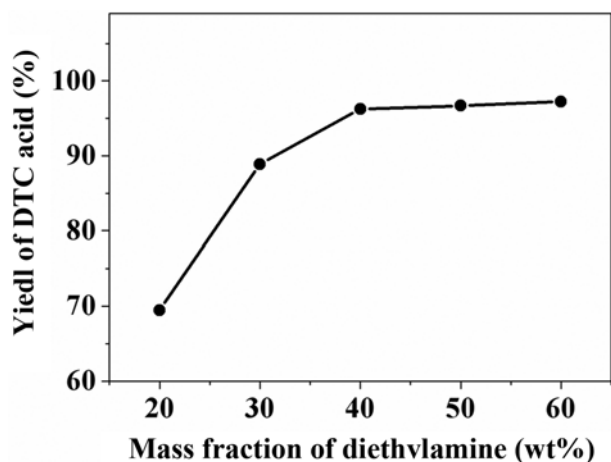


Fig. 3. Effect of the concentration of diethylamine ethanol solution on the yield of DTC acid. The experiments were carried out in the first microstructured reactor with a $\text{CS}_2/(\text{C}_2\text{H}_5)_2\text{NH}$ molar ratio of 1.1 : 1, a LHSV of 42.4 h^{-1} , a total flow rate of 4 mL/min and a temperature of 25°C .

of the flow rate.

1-2. Effect of the Diethylamine Concentration

The effect of diethylamine concentration on the yield of DTC acid was examined with a $\text{CS}_2/(\text{C}_2\text{H}_5)_2\text{NH}$ molar ratio of 1.1 : 1, a LHSV of 42.4 h^{-1} , a total flow rate of 4 mL/min and reaction temperature of 25°C . The results are presented in Fig. 3. It shows that the yield of DTC acid increases sharply when the diethylamine concentrations are less than 30 wt%. Further increasing the diethylamine concentration from 30 to 40 wt% results in the slight increase of DTC acid yield from 89.0% to 96.2%. High concentration of diethylamine can move the chemical equilibrium to the positive direction, and thus get a high yield of DTC acid. However, further increasing the diethylamine concentration from 40 to 60 wt% does not have significant influence on the yield of DTC acid. Under such circumstances, we observed blockage of the capillary. This may be

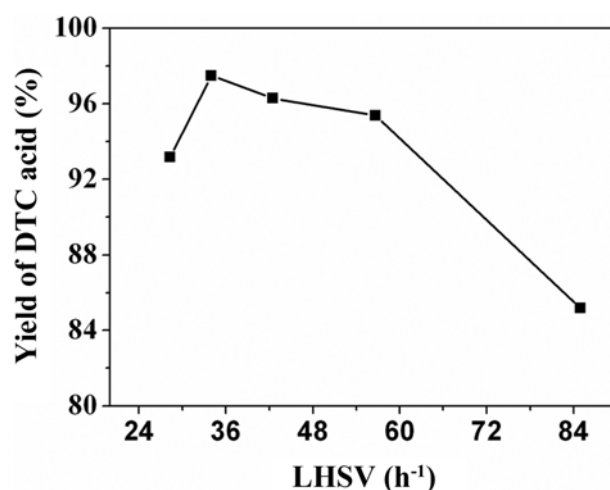


Fig. 4. Effect of the LHSV on the yield of DTC acid. The experiments were carried out in the first microstructured reactor with a 40 wt% diethylamine, a molar ratio of $\text{CS}_2/(\text{C}_2\text{H}_5)_2\text{NH}$ of 1.1 : 1, a total flow rate of 4 mL/min and a reaction temperature of 25°C .

attributed to the partial education of diethylamine from its ethanol solution in the delay loop.

1-3. Effect of the LHSV

The effect of the LHSV on the yield of DTC acid was investigated with a $\text{CS}_2/(\text{C}_2\text{H}_5)_2\text{NH}$ molar ratio of 1.1 : 1, total flow rate of 4 mL/min , reaction temperature of 25°C in 40 wt% diethylamine ethanol solution. The results are shown in Fig. 4. It can be seen that the yields of DTC acid reach 93.2% and 98.0% with the increase of the LHSV from 28.3 to 34.0 h^{-1} . However, the yield slightly decreased from 98.0% to 96.3% and to 95.4% when the LHSV was further prolonged from 34.0 to 42.4 and to 56.6 h^{-1} . This may result from the decreases in the residence times.

1-4. Effect of the Reaction Temperature

The effect of the reaction temperature on the yield of DTC acid was investigated with a $\text{CS}_2/(\text{C}_2\text{H}_5)_2\text{NH}$ molar ratio of 1.1 : 1, a LHSV of 42.4 h^{-1} and a total flow rate of 4 mL/min in 40 wt% diethylamine solution. The results showed that the yield of DTC acid slightly increases from 94.2% to 96.3% as the reaction temperature changed from 5 to 25°C . Further increase of the temperature to 35°C resulted in the slight decrease of the yield of DTC acid, possibly resulting from decomposition of DTC acid at higher temperature.

The above results indicated that over 96.3% DTC acid yield could be obtained at a diethylamine concentration of 40 wt%, a $\text{CS}_2/(\text{C}_2\text{H}_5)_2\text{NH}$ molar ratio of 1.1 : 1, a LHSV of 42.4 h^{-1} , a total flow rate of 4 mL/min and a reaction temperature of 25°C . Diethylamine was not detected in the DTC acid solution by titration method when the excessive carbon disulfide was used, indicating complete conversion of diethylamine in the reaction system. In the following experiments, the above reaction conditions were applied for the production of DTC acid in the first microstructured reactor.

In step (1), the ethanol solution of DTC acid was collected at the outlet of a three-way valve. The solution was crystallized at low temperatures, filtrated, washed and low-temperature vacuum drying procedures to get the light yellow solid product. The TG-DSC curves of DTC acid indicated that the intermediate would be de-

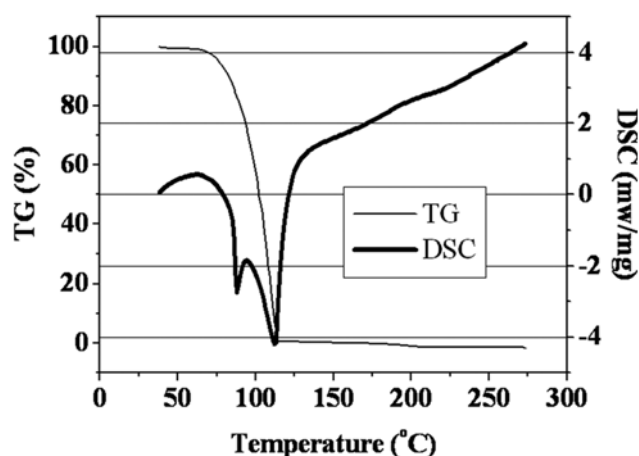


Fig. 5. TG-DSC curves of DTC acid.

composed even at 50 °C (Fig. 5). The side products remain in the solution would seriously affect the yield and purity of TETD if the reaction temperature is out of control.

2. Synthesis of Tetraethylthiuram Disulfide

2-1. Effect of Temperature of the Mixer and the Delay Loop

In step (2), the DTC acid solution obtained under the reaction conditions of step (1) mentioned above and H_2O_2 were, respectively, fed into the second microstructured reactor assembled with SIMM-V2 and a $\varnothing 3.0$ mm stainless steel tube (i.d.=2.0 mm) or PTFE tube (i.d.=1.5 mm) for production of TETD. The experiments were initially carried out with an H_2O_2 concentration of 10 wt%, a $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio of 1.8 : 1, a LHSV of 92.3 h^{-1} and at 0 °C for both the mixer and delay loop B. The results showed that the PTFE tube was suitable for the continuous production of TETD, while the stainless steel tube was always blocked by the TETD deposition. This may be due to the hydrophobic and elastic prosperities of PTFE tube, which avoids TETD deposition. The yield of TETD was just 45.6%. It is reported that the suitable reaction temperature for oxidation of DTC acid is 20–30 °C [26]. Thus, we examine the effect of temperature of the delay loop B while keeping the temperature of SIMM-V2 at 0 °C. The results are listed in Table 1. It shows that increase in the temperature of Delay loop B results in obviously an increase in the yield of TETD. The highest TETD yield was obtained at the delay loop temperature of 35 °C. Afterwards, the effect of the temperature of SIMM-V2 was also investigated when the temperature of Delay Loop B was set at 35 °C with a H_2O_2 concentration of 10 wt%, a LHSV of 92.3 h^{-1} and a total flow rate of 6.43 mL/min. The results showed that the yield of TETD hardly changed when the temperatures of SIMM-V2 were in the range of –10–0 °C. Further increasing the temperature of SIMM-V2 caused significant decrease in the yield of TETD. This is quite possibly

Table 1. Effect of the temperature of the delay loop B on the yield of TETD with a LHSV of 92.3 h^{-1} , a H_2O_2 concentration of 10 wt%, a $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio of 1.8 : 1, a total flow rate of 6.43 mL/min and a SIMM-V2 temperature of 0 °C

Temperature (°C)	0	20	30	35	40
Yield of TETD (%)	45.6	72.6	83.4	86.5	78.3

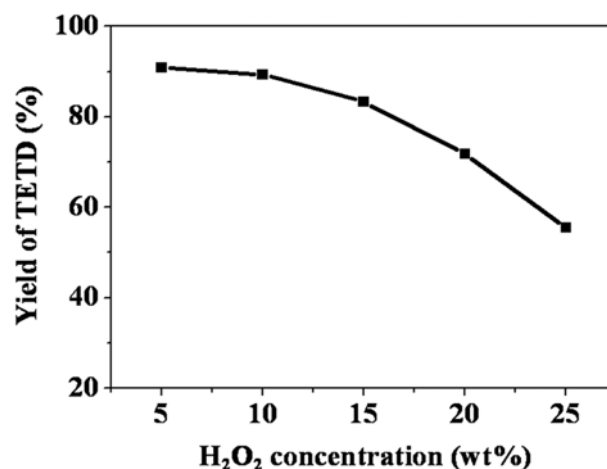


Fig. 6. Effect of H_2O_2 concentration on the yield of TETD. The experiments were carried out with a $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio of 1.8 : 1, a LHSV of 92.3 h^{-1} , a total flow rate of 6.43 mL/min and at oxidation reaction temperatures of –5 °C, 35 °C respectively.

due to the highly exothermic nature of this oxidation reaction, a large amount of heat was released at the moment of mixing of DTC acid and H_2O_2 in SIMM-V2, leading to over heating of the reactants in SIMM-V2 at a slight high SIMM-V2 temperature. The temperature of SIMM-V2 was controlled lower to assure most of the heat transferred timely; the relative high temperature of delay loop B can accelerate the oxidation rate, thus increasing the yield of TETD product.

2-2. Effect of H_2O_2 Concentration

The effect of H_2O_2 concentration on the yield of TETD was investigated with a $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio of 1.8 : 1, a LHSV of 92.3 h^{-1} , a total flow rate of 6.43 mL/min. The temperatures of the micromixer and the delay loop B were controlled at –5 °C and 35 °C, respectively. Fig. 6 shows the results. It can be seen that the

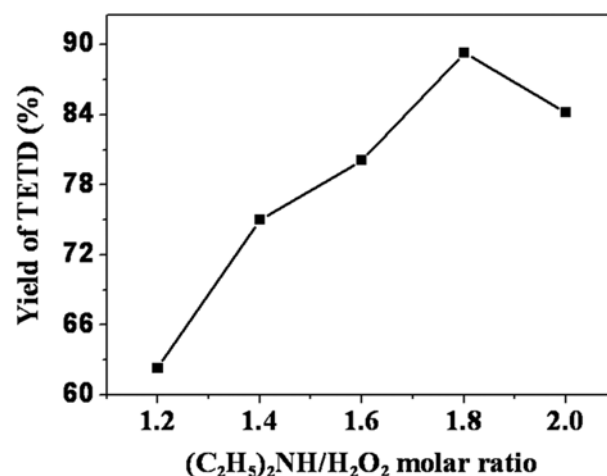


Fig. 7. The effect of $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio on the yield of TETD. The experiments were carried out with a $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio of 1.8 : 1, a LHSV of 92.3 h^{-1} , a total flow rate of 6.43 mL/min and at oxidation reaction temperatures of –5 °C, 35 °C respectively.

yield of TETD decreases from 90.8% to 89.3% when the H_2O_2 concentration increases from 5 to 10 wt%. Further increasing the H_2O_2 concentration causes almost linear decrease of the yield of TETD, which is attributed to the vigorous heat release at high H_2O_2 concentration, resulting in decomposition of unstable DTC acid and hydrogen peroxide, as well as alternation of flow patterns of liquid phase and gas-liquid phase [27].

The effect of $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio on the yield of TETD was also investigated with a H_2O_2 concentration of 10 wt%, a LHSV of 92.3 h^{-1} , a total flow rate of 6.43 mL/min and the temperatures of the micromixer and the delay loop B were -5°C and 35°C , respectively. Fig. 7 shows the results. It can be seen that the yield of TETD increases from 62.3% to 89.3% when the $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ molar ratio increases from 1.2 to 1.8. Further increase in the $(\text{C}_2\text{H}_5)_2\text{NH}/\text{H}_2\text{O}_2$ stoichiometric molar ratio to 2.0 : 1 results in a decrease in the yield of TETD, possibly resulting from decomposition of H_2O_2 at higher temperature. The slight excessive H_2O_2 is appropriate for the production of TETD.

CONCLUSIONS

The TETD was successfully prepared in the two-step continuous-flow microstructured reactors assembled with micromixers and delay loops. In the synthesis of DTC acid from carbon disulfide and diethylamine, the yield of DTC acid increases with the increase of total flow rate of the reactants and the mass concentration of diethylamine. A relatively long residence time and higher reaction temperature lead to the decrease in the yield of DTC acid. In synthesis of TETD from DTC acid and H_2O_2 , it was beneficial to improve the yield of TETD when the SIMM-V2 and Delay Loop B were controlled at different temperatures because of the drastic exothermic reaction characteristics. In addition, low concentration of H_2O_2 and a short residence time were applied. Compared to the conventional batch synthesis, the microstructured reactor provides an efficient, safe, straightforward and high yield route for synthesis of TETD. This methodology is also successfully applied to synthesis of other thiuram derivatives, such as tetramethylthiuram disulfide (TMTD), dipentamethylenethiuram tetrasulfide (DPTT). Thus, the method developed in this paper is an alternative method for various thiuram vulcanization and its intermediates production with an easy adjustment of productivity according to the market demands.

ACKNOWLEDGEMENTS

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NOMENCLATURE

C_1	: molar concentrations of hydrochloride stand solution [mol/L]
i.d.	: inner diameter of the delay loop [mm]
M	: mass of the supernatant sample solution [g]
Φ	: outer diameter of the delay loop [mm]
R	: alkyl or cycloalkyl in the tetraalkyl thiuramdisulfites molecule [-]
V1	: volume of hydrochloride standard solution for the titration

[mL]	
x	: number of the s atom in the tetraalkyl thiuramdisulfites molecule [-]
ΔH	: enthalpy of reactions [KJ/mol]
LHSV	: liquid hourly space velocity [1/h]

Abbreviations

DPTT	: dipentamethylenethiuram tetrasulfide
DTC acid	: N, N-diethyldithiocarbamic acid
HPIMM	: High pressure micromixer
HPLC	: high-performance liquid chromatograph
PTFE	: polytetrafluoroethylene
SIMM-V2	: slit interdigital micro mixer version 2
TATD	: tetraalkyl thiuramdisulfites
TETD	: tetraethylthiuram disulfide
TMTD	: tetramethylthiuram disulfide
UV-VIS	: ultraviolet-visible

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SUPPORTING INFORMATION

Appendix Figure: Crystallographic Data of the TETD

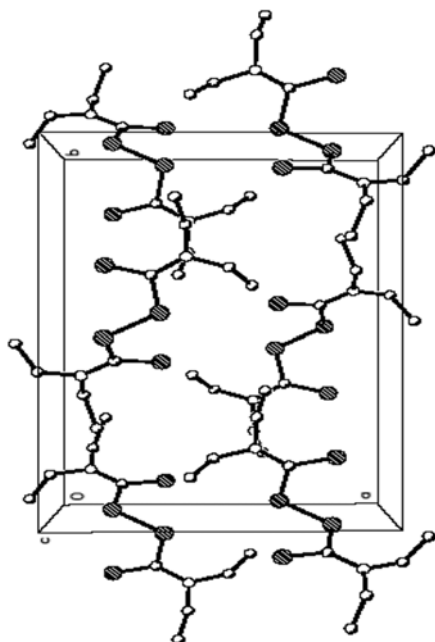


Fig. 9. Projection of the unit cell of TETD.

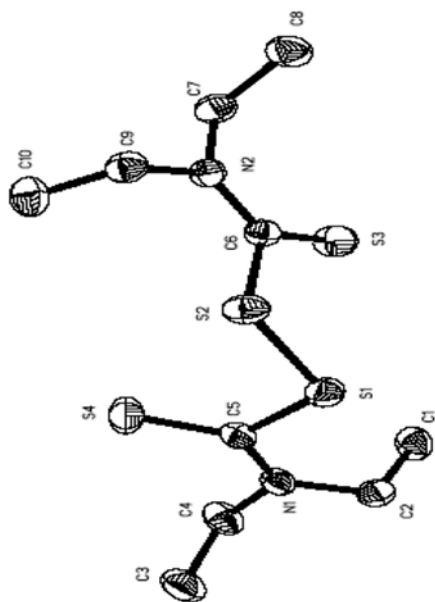


Fig. 10. Molecular structure for TETD with the atomic numbering scheme.

Appendix Table: Crystallographic Data of Titled Product of TETD

Table 1. Crystal data and structure refinement for 090820b

Identification code	090820b
Empirical formula	C ₁₀ H ₂₀ N ₂ S ₄
Formula weight	296.52
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 (1)/c
Unit cell dimensions	a=11.1485(11) Å alpha=90 deg. b=15.9250(16) Å beta=92.583(6) deg. c=8.6645(7) Å gamma=90 deg.
Volume	1536.7(2) Å ³
Z, Calculated density	4, 1.282 Mg/m ³
Absorption coefficient	0.597 mm ⁻¹
F (000)	632
Crystal size	0.43×0.30×0.18 mm
Theta range for data collection	1.83 to 25.02 deg.
Limiting indices	-13≤h≤13, -18≤k≤8, -10≤l≤10
Reflections collected/unique	7873/2712 [R(int)=0.0349]
Completeness to theta=25.02	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9001 and 0.7833
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	2712/0/149
Goodness-of-fit on F ²	1.003
Final R indices [I>2sigma(I)]	R1=0.0368, wR2=0.0725
R indices (all data)	R1=0.0617, wR2=0.0791
Largest diff. peak and hole	0.266 and -0.240 e.Å ⁻³

Table 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for 090820b. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor

x	y	z	U (eq)	
S(1)	1738(1)	10148(1)	4140(1)	53(1)
S(2)	3293(1)	9530(1)	4482(1)	53(1)
S(3)	1688(1)	8279(1)	2729(1)	68(1)
S(4)	3268(1)	10782(1)	1568(1)	73(1)
N(1)	956(2)	11138(1)	1884(2)	48(1)
N(2)	4017(2)	8071(1)	3432(2)	43(1)
C(1)	-916(2)	10301(2)	1861(3)	67(1)
C(2)	-221(2)	11030(2)	2576(3)	55(1)
C(3)	1366(3)	12560(2)	871(4)	86(1)
C(4)	961(2)	11675(2)	487(3)	67(1)
C(5)	1956(2)	10745(1)	2383(3)	45(1)
C(6)	3030(2)	8541(1)	3465(2)	43(1)
C(7)	3980(2)	7220(2)	2755(3)	53(1)
C(8)	3707(2)	6557(2)	3924(3)	65(1)
C(9)	5224(2)	8361(2)	3980(3)	50(1)
C(10)	5885(2)	8794(2)	2703(3)	66(1)

Table 3. Bond lengths [Å] and angles [deg] for 090820b

S (1)-C (5)	1.821(2)
S (1)-S (2)	2.0040(9)
S (2)-C (6)	1.822(2)
S (3)-C (6)	1.653(2)
S (4)-C (5)	1.653(2)
N (1)-C (5)	1.333(3)
N (1)-C (2)	1.478(3)
N (1)-C (4)	1.483(3)
N (2)-C (6)	1.331(3)
N (2)-C (7)	1.478(3)
N (2)-C (9)	1.480(3)
C (1)-C (2)	1.513(3)
C (1)-H (1A)	0.9600
C (1)-H (1B)	0.9600
C (1)-H (1C)	0.9600
C (2)-H (2A)	0.9700
C (2)-H (2B)	0.9700
C (3)-C (4)	1.512(3)
C (3)-H (3A)	0.9600
C (3)-H (3B)	0.9600
C (3)-H (3C)	0.9600
C (4)-H (4A)	0.9700
C (4)-H (4B)	0.9700
C (7)-C (8)	1.503(3)
C (7)-H (7A)	0.9700
C (7)-H (7B)	0.9700
C (8)-H (8A)	0.9600
C (8)-H (8B)	0.9600
C (8)-H (8C)	0.9600
C (9)-C (10)	1.522(3)
C (9)-H (9A)	0.9700
C (9)-H (9B)	0.9700
C (10)-H (10A)	0.9600
C (10)-H (10B)	0.9600
C (10)-H (10C)	0.9600
C (5)-S (1)-S (2)	103.46(8)
C (6)-S (2)-S (1)	103.52(8)
C (5)-N (1)-C (2)	124.00(19)
C (5)-N (1)-C (4)	120.1(2)
C (2)-N (1)-C (4)	115.75(19)
C (6)-N (2)-C (7)	121.02(18)
C (6)-N (2)-C (9)	123.95(19)
C (7)-N (2)-C (9)	114.97(18)
C (2)-C (1)-H (1A)	109.5
C (2)-C (1)-H (1B)	109.5
H (1A)-C (1)-H (1B)	109.5
C (2)-C (1)-H (1C)	109.5
H (1A)-C (1)-H (1C)	109.5
H (1B)-C (1)-H (1C)	109.5
N (1)-C (2)-C (1)	111.8(2)
N (1)-C (2)-H (2A)	109.3

Table 3. Continued

C (1)-C (2)-H (2A)	109.3
N (1)-C (2)-H (2B)	109.3
C (1)-C (2)-H (2B)	109.3
H (2A)-C (2)-H (2B)	107.9
C (4)-C (3)-H (3A)	109.5
C (4)-C (3)-H (3B)	109.5
H (3A)-C (3)-H (3B)	109.5
C (4)-C (3)-H (3C)	109.5
H (3A)-C (3)-H (3C)	109.5
H (3B)-C (3)-H (3C)	109.5
N (1)-C (4)-C (3)	111.7(2)
N (1)-C (4)-H (4A)	109.3
C (3)-C (4)-H (4A)	109.3
N (1)-C (4)-H (4B)	109.3
C (3)-C (4)-H (4B)	109.3
H (4A)-C (4)-H (4B)	107.9
N (1)-C (5)-S (4)	126.02(18)
N (1)-C (5)-S (1)	111.99(16)
S (4)-C (5)-S (1)	121.98(14)
N (2)-C (6)-S (3)	125.80(17)
N (2)-C (6)-S (2)	112.35(16)
S (3)-C (6)-S (2)	121.83(13)
N (2)-C (7)-C (8)	112.27(19)
N (2)-C (7)-H (7A)	109.1
C (8)-C (7)-H (7A)	109.1
N (2)-C (7)-H (7B)	109.1
C (8)-C (7)-H (7B)	109.1
H (7A)-C (7)-H (7B)	107.9
C (7)-C (8)-H (8A)	109.5
C (7)-C (8)-H (8B)	109.5
H (8A)-C (8)-H (8B)	109.5
C (7)-C (8)-H (8C)	109.5
H (8A)-C (8)-H (8C)	109.5
H (8B)-C (8)-H (8C)	109.5
N (2)-C (9)-C (10)	111.81(18)
N (2)-C (9)-H (9A)	109.3
C (10)-C (9)-H (9A)	109.3
N (2)-C (9)-H (9B)	109.3
C (10)-C (9)-H (9B)	109.3
H (9A)-C (9)-H (9B)	107.9
C (9)-C (10)-H (10A)	109.5
C (9)-C (10)-H (10B)	109.5
H (10A)-C (10)-H (10B)	109.5
C (9)-C (10)-H (10C)	109.5
H (10A)-C (10)-H (10C)	109.5
H (10B)-C (10)-H (10C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 090820b. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S (1)	55(1)	51(1)	53(1)	8(1)	7(1)	11(1)
S (2)	55(1)	45(1)	59(1)	-4(1)	-13(1)	6(1)
S (3)	47(1)	57(1)	99(1)	-5(1)	-15(1)	-6(1)
S (4)	50(1)	84(1)	85(1)	24(1)	16(1)	0(1)
N (1)	45(1)	42(1)	57(1)	12(1)	-2(1)	-2(1)
N (2)	41(1)	41(1)	47(1)	-2(1)	-2(1)	-1(1)
C (1)	48(2)	73(2)	80(2)	4(2)	0(1)	-11(2)
C (2)	48(2)	49(2)	67(2)	6(1)	2(1)	10(1)
C (3)	79(2)	55(2)	123(3)	28(2)	3(2)	-5(2)
C (4)	64(2)	64(2)	72(2)	27(2)	-12(2)	-7(2)
C (5)	46(2)	38(1)	49(1)	2(1)	-3(1)	-5(1)
C (6)	45(1)	40(1)	43(1)	3(1)	1(1)	2(1)
C (7)	57(2)	51(2)	52(2)	-11(1)	0(1)	7(1)
C (8)	69(2)	47(2)	77(2)	-5(2)	-2(2)	-3(1)
C (9)	43(1)	54(2)	52(2)	1(1)	-8(1)	5(1)
C (10)	51(2)	78(2)	68(2)	2(2)	0(1)	-12(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 090820b

	x	y	z	U (eq)
H (1A)	-1038	10393	770	101
H (1B)	-1680	10256	2323	101
H (1C)	-472	9791	2035	101
H (2A)	-687	11541	2432	66
H (2B)	-99	10934	3678	66
H (3A)	798	12820	1520	128
H (3B)	1418	12877	-65	128
H (3C)	2140	12543	1403	128
H (4A)	159	11692	5	80
H (4B)	1494	11432	-247	80
H (7A)	4749	7097	2324	64
H (7B)	3372	7203	1919	64
H (8A)	4320	6560	4739	97
H (8B)	3684	6017	3434	97
H (8C)	2943	6672	4347	97
H (9A)	5691	7884	4357	60
H (9B)	5145	8749	4833	60
H (10A)	5969	8411	1859	99
H (10B)	6666	8966	3096	99
H (10C)	5438	9278	2350	99