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Experimental and kinetic study of the nitration of 2-ethylhexanol in capillary microreactors

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ABSTRACT

The nitration process of 2-ethylhexanol (2-EH) with mixed acid was studied in different capillary microreactors. The conversion of 2-EH and selectivity to 2-ethylhexyl nitrate (EHN) were investigated by varying reaction temperature, molar ratio of nitrate to 2-EH, residence time and water content in mixed acid. Under optimized conditions, the conversion of 2-EH and selectivity to EHN could be up to 99% in less than 10 seconds, indicating great potential of microreactors in process intensification. Moreover, with an assumption of homogeneous reaction, a kinetic model based on first order kinetics for nitric acid and 2-EH was proposed to determine both the apparent and intrinsic reaction kinetics. By taking into account the activity of solutes that depend on the acidity (M_c), the intrinsic kinetic was obtained, which is independent of the sulfuric acid concentration. The reaction model can well predict the conversion of 2-EH.

1. Introduction

2-Ethylhexyl nitrate (EHN) is an excellent cetane improver in diesel fuel [1,2]. Its main role is to reduce the ignition temperature and shorten the ignition delay time, hence improving the dynamic performance of engine. Currently, industrial production of 2-EHN is generally through nitration of 2-ethylhexanol (2-EH) with mixed solutions of sulfuric acid and nitric acid in stirred tanks. The reaction mechanism is shown by Eqs. (1)-(3) and the overall reaction shown by Eq. (4). It is a typical alcohol nitration reaction, which is fast and highly exothermic. The products are usually temperature-sensitive energetic materials [3] that are highly decomposable and explosive. Therefore, a precise control over reaction temperature and mixing is of great importance during production.

$$HNO_3 + 2H_2SO_4 \leftrightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \quad (1)$$

$$C_8H_{17}OH + NO_2^+ \leftrightarrow C_8H_{17}ONO_2 + H^+ \quad (2)$$

$$2HSO_4^- + H_3O^+ + H^+ \leftrightarrow 2H_2SO_4 + H_2O \quad (3)$$

$$C_8H_{17}OH + HNO_3 \leftrightarrow C_8H_{17}ONO_2 + H_2O \quad (4)$$

Conventionally, the reaction is operated in stirred tanks with limited mass and heat transfer rate. In order to prevent the oxidation [4,5] that may result in serious decomposition of 2-EHN, the nitration temperature is kept at low temperatures in the range of −10 ~ 10 °C [6]. In addition, the mixed acid is usually fed by dropping into the reactant to avoid hot spot and regional over-nitration [6,7]. Obviously, such conditions induce large amount of coolant and long reaction time, leading to very low efficiency. To improve the reaction performance, two main approaches have been developed. One approach is using additives such as urea [8] to prevent side reaction or using large amount of inert solvent [9] to prevent fast heat accumulation. This method, however, increases the energy consumption in refining and acid recycling. The other approach is to develop high efficient reactors such as static reactor and spinning disk. Yan et al. [4] employed a jet reactor to improve the mixing and a large reduction in the acid usage and reaction time was obtained. However, the reaction heat can only be removed by the cooling jacket that large amount of coolant is still needed. The above research results suggest that the current methods are still with low efficiency and there is huge need of improvement.

Among the emerging novel reactors, microreactors hold great promises for process intensification, especially in fast and highly exothermic reaction [10–13]. With characteristic size in the range of tens to hundreds of microns, microreactors have huge specific surface area, providing both excellent heat and mass transfer rate [14–18]. Therefore, it allows fast mixing and quick heat removal during reaction. For the nitration of 2-EH, the reaction can be conducted at higher temperatures to increase the reaction rate while keeping the process safety. In this case, the usage of acid, as well as coolant, can be dramatically reduced. Moreover, microreactors can improve process

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Nomenclature

2-EH	2-ethylhexanol
EHN	2-ethylhexyl nitrate
$C_{2\text{-}EH}$	the concentration of 2-EH (mol/L)
C^0_{2-EH}	the initial concentration of 2-EH (mol/L)
$C^t_{HNO_3}$	the total concentration of nitric acid (mol/L)
$C_{NO_2^+}$	the concentration of nitronium ion (mol/L)
C_{HNO_3}	the concentration of nitric acid (mol/L)
C_{H^+}	the proton concentration in the mixed acid (mol/L)
$C_{H_2SO_4}$	the concentration of sulfuric acid (mol/L)
$n_{2\text{-}EH}$	the amount of substance of 2-EH (mol)
$v_{2\text{-}EH}$	the flow rate of 2-EH (ml/min)
$v_{mixed\ acid}$	the flow rate of mixed acid (ml/min)
$\rho_{2\text{-}EH}$	the density of 2-EH (g/ml)
$M_{2\text{-}EH}$	the relative molecular mass of 2-EH (g/mol)
a	activity (mol/L)
K_{HNO_3}	the equilibrium constant of nitric acid
$K_{NO_2^+}$	the equilibrium constant of nitronium ion
ΔG_{HNO_3}	the Gibbs free energy of HNO_3 (KJ/mol)
M	the initial concentration ratio of nitric acid to 2-EH
x	the conversion rate of 2-EH
t	reaction time (s)
k_{app}	the apparent reaction rate constant (L mol^{-1} s^{-1})
k°	the intrinsic rate constant (L mol^{-1} s^{-1})
n	thermodynamic parameter defined in Eq.11
M_c	activity coefficient function
A	pre-exponential factor (L mol^{-1} s^{-1})
E_a	activation energy (J mol^{-1})
R	gas constant (J K^{-1} mol^{-1})
T	reaction temperature (K)

Greek letters

$\gamma_{NO_2^+}$	activity coefficient of nitronium ion
$\gamma_{2\text{-}EH}$	activity coefficient of 2-EH
γ^*	activity coefficient of the transition-state intermediate

safety because of low material hold-up, which has limited damage when hazardous situation happens. Other advantages such as miniaturization and the numbering-up mode can reduce the investment in R & D and commercial application. In accordance with these advantages, our previous work shown that the nitration of 2-EH in microreactors can be effectively enhanced, and the reaction was highly dependent on sulfuric acid concentration and temperature [10]. However, a deep understanding of the reaction with respect to reaction kinetics is rather limited, which is very important for process design, despite the fact that 2-EHN has been commercially produced for long time. Since excellent process control can be obtained in microreactors [19], they also serve as ideal tools for the determination of reaction kinetics [20–23], including apparent and intrinsic kinetics.

In this paper, the synthesis of EHN was studied in capillary microreactors. A microchemical system was designed to precisely control the reaction time and reaction temperature. The objective of this work was to determine the reaction kinetics of the nitration of 2-EH. Firstly, the effect of reaction temperature, residence time, HNO_3 to 2-EH molar ratio, water content in the mixed acid on nitration process was studied. Based on the experimental results, both the apparent and intrinsic kinetics were calculated with an assumption of homogeneous reaction.

2. Experimental

2.1. Chemicals

Fuming nitric acid (concentration of > 95%, Tianjin Kemiou Co.), concentrated sulfuric acid (concentration of > 98%, Tianjin Kemiou Co.) and 2-EH (purity of 98%, Sinopham Co.) were used. During preparation of the mixed acid, the water content was varied between 2-10% by mass, and the molar ratio of sulfuric acid to nitric acid (abbr. S/N) was kept at 2. The reason to choose the S/N of 2 is because it allows a maximum concentration of NO_2^+ for fixed water content [24]. The molar ratio of nitric acid to 2-EH (abbr. M-ratio) was set between 0.7-1.6.

2.2. Experimental setup

The experimental setup is shown in Fig. 1. 2-EH and mixed acid were delivered separately by metering pumps (America Lab Alliance Series II). The fluids were firstly mixed in a T-mixer with an inner diameter of 1.0 mm (stainless steel), and then reacted in stainless steel capillary with an inner diameter of 0.6 mm. The residence time was regulated by changing the length of the reaction tube. The feed tube, the mixer and the reaction tube were all immersed in a water bath to ensure a constant reaction temperature. After the reaction was quenched with ice-water mixture, the liquid samples were collected from the organic phase. For each condition, the samples were collected and analyzed for three times.

2.3. Sample analysis

For the current system, the fluid mixture was firstly a homogenous aqueous phase as 2-EH completely dissolves in mixed acid, whereas it turned to immiscible two phases as the product EHN had a very low solubility in the acid phase. After the reaction was quenched, the organic and acid phases were separated into layers by density difference. The acid phase included sulfuric acid, nitric acid and water. The organic phase included 2-EH, EHN and a small amount of by-products. The organic phase was treated with water and alkali solution until it reached neutral. Then, the organic phase was analyzed by gas chromatography.

3. Results and discussion

3.1. Effect of reaction temperature and residence time

The reaction temperature is a very important parameter that affects the reaction rate, product selectivity and heat release. To optimize the nitration reaction condition, the effect of reaction temperatures on the conversion of 2-EH and selectivity of 2-EHN is investigated. The reaction was performed at the nitric acid to 2-EH molar ratio of 1.26 and water content of 5% in the mixed acid. The results are shown in Fig. 2. As expected, 2-EH conversion increases with either increasing residence time or reaction temperature. This is because higher tem-

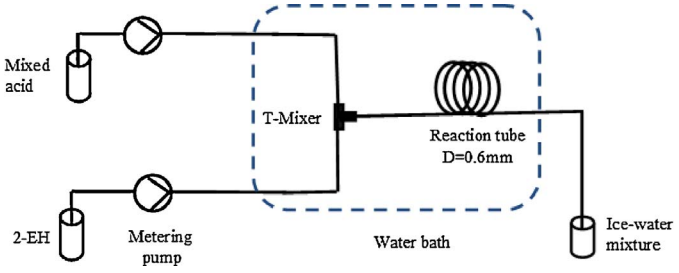

Fig. 1. The schematic overview of the experimental setup.