

## Wet air oxidation of polyether solutions

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### ARTICLE INFO

#### Article history:

Received 8 December 2009

Received in revised form 29 June 2010

Accepted 1 July 2010

Available online 31 July 2010

#### Keywords:

Polyether

WAO

Temperature

Fatty acid

Acetic acid

### ABSTRACT

This paper studied the characteristics of wet air oxidation (WAO) on polyether as non-ionic surfactant and analyzed its main intermediates. The results showed that, WAO was an effective method to treat non-ionic surfactants like polyether; temperature played a decisive role throughout the process: the COD removal percentage within 2 h was only 33.5% at 160 °C, 57.2% at 200 °C, and 94.4% at 240; fatty acid was the major intermediate, and oxidation of acetic acid was the key rate-determining step during fatty acid oxidation, and the oxidation of fatty acid could be accelerated by rising the temperature as well as elongating the reaction time. Meanwhile, oxidative decomposition of polyether and oxidation on fatty acid were the rate-determining steps to the whole WAO process, the oxidation of polyether was relatively more limited at lower temperature; on the contrary, the oxidation of fatty acid and other organics was obviously more limited at higher temperature.

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### 1. Introduction

Polyoxyethylene polyoxypropylene ether (GPE2035, abbreviated as GPE or polyether) serves as a typical non-ionic surfactant and has been widely applied in industries. It is a segmented copolymer formed by addition reaction of propylene oxide and epoxy ethane by using propanediol as the initiative reactant and its general formula is  $\text{HO}(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c$ , thereinto  $b$  is at least 15, which means that the relative molecular weight of hydrophobic polyoxypropylene will ranges from 1000 to 2000. Polyether possesses such properties as emulsification, penetration, dispersion, solubilization and the like. Its been used as detergents in machine-building industries. The emulsification wastewater is one kind of refractory organic wastewater (COD: 53570–74110 mg/L,  $\text{BOD}_5/\text{COD}$ : 0.072–0.12) [1], in which 53.0% of the total COD is attributed to the polyether that derives from the usage of detergents containing non-ionic surfactants in the process of cutting, stamping and washing in aluminum industry. The treatment of emulsification wastewater both inland and outland mainly focuses on conventional physiochemical and chemical methods [2–5]. The former is efficient in pollutants separation but will also easily entail secondary pollution; the latter can decompose the pollutants but it consumes so many agents as to make the method unaffordable.

The highlight of WAO is that it can be properly used to treat refractory organic wastewater with high concentration and poisons at a time when biochemical method and incineration are not working out. That is the reason why WAO gets so much attention nowadays [6–9]. The documents and reports about WAO have increased significantly in recent 20 years, with the focus not only on the traditional WAO but also on the catalytic WAO, from the initial homogeneous catalytic WAO to the latter heterogeneous catalytic WAO. Its mechanism as well as kinetics has made great progress in this field [10–16].

WAO is effective to the treatment of emulsification wastewater for its high organic removal efficiency [17–19]. In order to fully understand its mechanism, the main organic (GPE) in emulsification wastewater was used to prepare solution in certain concentration so as to study the properties of WAO, its main intermediates and their contents from the outlet were detected by gas chromatography to further analyze the process or mechanism.

### 2. Experiments

#### 2.1. Devices

The reactor was a FYX-2a permanent magnet-agitated autoclave composed of vessel, stirring device, heating furnace, cooling and operating system. In the reaction kettle, the direct current (DC) speed-controlling motor drives the magnetic coupling machine to do the churning; a director controls the rotation speed. The temperature was controlled by heating furnace through intelligent controller ( $\pm 2$  °C), which could cut off the heating circuit in case of over-high temperature or start the cooling system when necessary.

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**Table 1**  
Analysis condition of preliminary fatty acids using gas chromatography (HP5890).

Series	Chromatographic analysis condition
1	Chromatographic column: FFAP capillary column, 0.53 mm × 30 m
2	Detector: flame ionization detector (FID)
3	Column temperature: 110 °C (5 min) → 10 °C/min → 220 °C (10 min)
4	Gasification room temperature: 180 °C
5	Detector temperature: 240 °C
6	Supporting gas: helium gas
7	Sample size: 5 μL

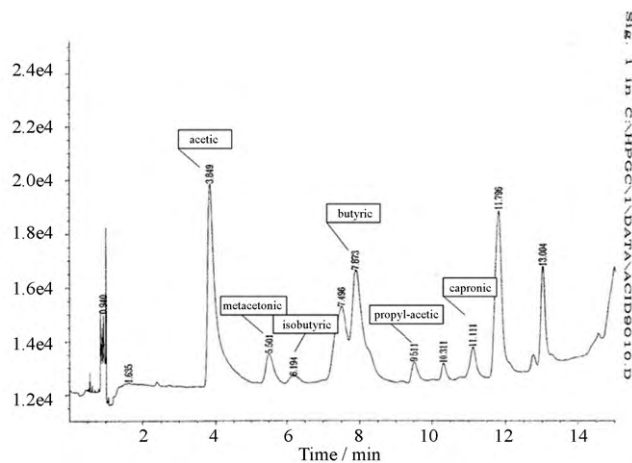
The pressure was read on manometer. A blast valve was installed to ensure safety for fear that the system might lose control under overpressure.

## 2.2. Experiment process

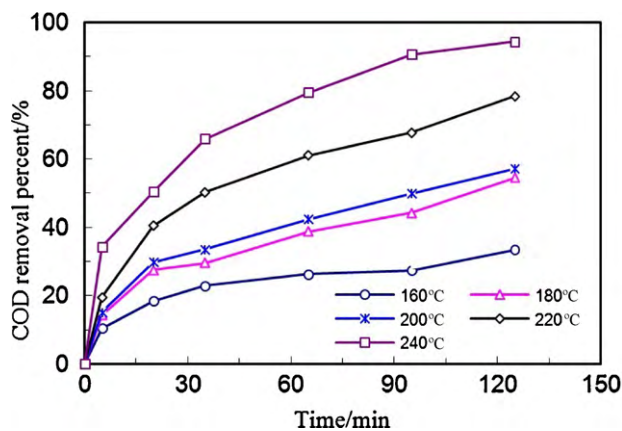
2000 mg/L commercial pure polyether solution (average molecular weight is 3000) was prepared as water sample with COD at 3933, TOC at 1172 mg/L and pH value at 6.00. 400 mL sample of wastewater was added to the reaction kettle. Nitrogen was used to replace the air in the kettle at room temperature. Slow agitation ( $n = 100$  rpm) was running as temperature rose, to avoid coking or carbonization caused by the overheating of the kettle wall. Excessive oxygen ( $PO_2 = 0.40$  MPa at 25 °C) was pumped immediately when it reached the preset temperature. Then agitation was accelerated and time was measured on the spot.

## 2.3. Water quality analysis

The COD analysis was carried out using the potassium-dichromate method. The pH value analysis was measured using PHS 3DC Precise Digital Display Acidimeter (Tian Da Instrument Co. Ltd., Shanghai, China); TOC was analyzed using TOC Analyzer (Shimadzu Co. Ltd., Japan); and non-ionic surface active agents were measured using the colorimetry of complex-extraction of ammonium cobaltous thiocyanate (UV 2201 ultraviolet and visible spectrophotometer, Himadzu Co. Ltd., Japan). Gas chromatography tests were adopted for preliminary fatty acid analysis. The characterization was determined by the retaining time of the master sample and quantification was determined by the specification curve. Gas chromatography analysis condition was shown in Table 1. Fig. 1 was one representative GC chromatogram of WAO outlet of polyether at 220 °C (polyether: 2000 mg/L,  $PO_2 = 0.40$  MPa at 25 °C, 2 h).



**Fig. 1.** GC chromatogram of WAO outlet of polyether at 220 °C (polyether: 2000 mg/L,  $PO_2 = 0.40$  MPa at 25 °C, 2 h).



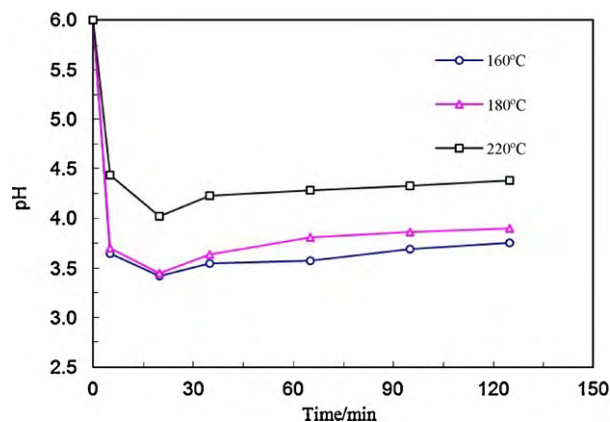
**Fig. 2.** Time-COD removal percentage relationship under different temperatures.

## 3. Results and discussions

### 3.1. The influence of temperature on WAO

The experimental temperatures ranging from 160 °C to 240 °C were studied and the results were shown in Figs. 2 and 3. Conclusions can be drawn as below:

- (1) With sufficient oxygen supply, temperature exerted decisive impact on WAO, the oxidation rate was higher at higher temperatures. For example, the COD removal percentage was only 33.5% at 160 °C in 2 h. Combining research on its kinetics [20], we concluded that the decomposition and direct oxidation of polyether were pretty slow, and the intermediates were hard to be oxidized; the oxidation rates at the first and the last period were accelerating to some extent within 2 h at 180 °C and the removal percentage reached 54.6%; and it could reach 57.2% at 200 °C; the oxidation rate at the first period was more significantly accelerated at 220 °C, so that the removal percentage increased to 78.4% within 2 h, at this point, the decomposition and direct oxidation of polyether (including the unsteady products) were also notably promoted; when the temperature rose to 240 °C, the oxidation rate at the first and the last period had both notably increased; the removal percentage within 1 h was greater than that within 2 h at 220 °C, with the final result to be 94.4% after 2 h.
- (2) The variation in pH values of the outlet basically embodied the concentration changes of organic acid as intermediate: at the temperature of 160 °C pH value slowly increased with the passage of time, whereas the oxidation of organic acid slowed



**Fig. 3.** Time-pH of the outlet relationship under different temperatures.

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