OXIDATION OF PROPYLENE OXIDE IN SUBCRITICAL AND SUPERCRITICAL WATER

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Abstract

The production of propylene oxide generates waste water containing mainly methanol, propylene oxide, glycols and methoxy-propanols. This paper studies the degradation pathway of these effluents when treated by oxidation under subcritical and supercritical conditions using air and/or hydrogen peroxide. Furthermore, biodegradability of the reaction products, which include acetone and carboxylic acids, has been studied in order to determine the most suitable post-treatment.

Introduction

The direct production of propylene generates wastewaters with content in methanol and propylene oxide. These waste waters can be treated by subcritical and supercritical water oxidation. In this manuscript the degradation pathway has been identified.

Experimental

The reaction was carried out in 1.5 mL batch reactors made of AISI 316L. Every reactor was filled with 1 mL of initial solution 50%mol H_2O, 48%mol methanol and 2%mol Propylene Oxide. Reactors were introduced in a forced convection oven at 200 ºC. Decomposition products were analysed by Mass Spectroscopy Gas Chromatograph.

Results

Propylene oxide (PO) decomposition

A total of 15 runs were carried out between 25 and 200 ºC at reactions times between 5 and 75 min. The ratio H_2O_2 to propylene oxide was between 1:1 and 1:2.

It was found that propylene oxide is oxidised at 99% at 200 ºC in 10 min.

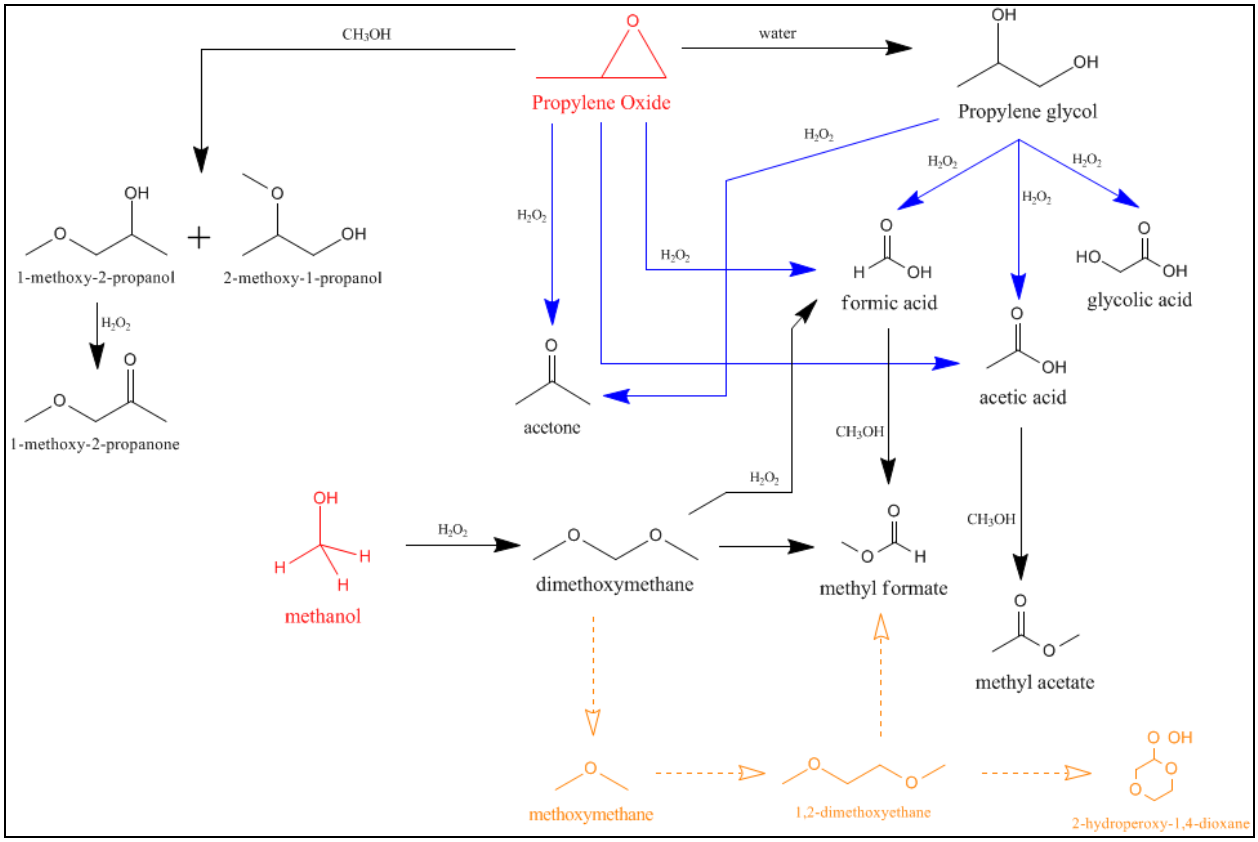
Degradation pathway

- After 20 min at 200 ºC we obtained 1-methoxy-2-propanol (1MP), 2-methoxy-1-propanol (2MP) and propylenglycol (PG). Methoxypropanols come from the reaction of propylene oxide with methanol. The glycol is formed by propylene oxide and water.
- The reaction between water and methanol with H_2O_2 during 20 min at 200 ºC gave dimethoxymethane (DMM).
- The reaction between water and propylene oxide with H_2O_2 during 20 min gave formic acid and acetic acid.
- The degradation of PG (200 ºC and 20 min) with water and methanol ad H2O2 gave formic acid and acetic acid. These two acids were thought to come from the degradation of PG.
- Commercial DMM was oxidized with H_2O_2 (200 ºC and 20 min) obtaining methyl formate (MF) and formic acid.

From these results we can induce that:

- The main oxidation products of propylene oxide are formic acid, acetic acid and acetone.
- PG is formed from PO and H_2O and is degraded to carboxylic acids.
- Acetone is the oxidation product of PO and PG if methanol is present.
- Methoxypropanols come from PO and methanol
- Methanol oxidizes to DMM.

The proposed degradation pathway is shown in Scheme 1. The reagents are printed in red colour. Oxidation reactions with H2O2 are in blue. Reactions in orange show the proposal of products and relations.



Scheme 1. Degradation pathway for propylene oxide using H_2O_2

More results for the degradation in a continuous flow reactor under subcritical conditions using H_2O_2 and O_2 will be presented in the conference.

Conclusions

The degradation pathway of the oxidation of propylene oxide has been proposed in this manuscript. This pathway will help designers of the post-treatment in a biological step.

References

No references cited in the manuscript.