#### **ORIGINAL PAPER**



# Direct conversion of terminal alkenes to aldehydes via ozonolysis reaction in rotating zigzag bed

Zhengyong Liang<sup>1</sup> · Tong Wei<sup>1</sup> · Jun Xie<sup>1</sup> · Hua Li<sup>1</sup> · Hui Liu<sup>2</sup>

Received: 9 December 2019 / Accepted: 6 April 2020 © Iranian Chemical Society 2020

#### Abstract

In this study, continuous ozonolysis of terminal alkenes in a rotating zigzag bed was developed. Rotating zigzag bed is a new type high gravity unit relative to the previous rotating packed bed and can intensify mass transfer remarkably. The rotating zigzag bed takes advantage of centrifugal force to mix liquid and gas phase effectively. The H<sub>2</sub>O in acetone acts as an in situ reducing agent for the carbonyl oxide intermediate, providing aldehydes directly from the reaction mixture. Critical factors were investigated and achieved optimum reaction conditions. Under these conditions, the yields of series aldehydes ranged from 72.3 to 95.8%. The discrepancy in product yields among different olefin substrates likely originates from the electronic stability of the carbonyl oxide intermediate, which is longer lived for aryl olefines with electron donor group and longer carbon chain alkene ( $C_nH_{2n}$ ,  $n \ge 10$ ).

Keywords Ozonolysis · Terminal alkene · Rotating zigzag bed · Flow chemistry

#### List of symbols

G	Gas volumetric flow rate, m <sup>3</sup> /h	
L	Liquid volumetric flow rate, L/h	
С	Substrate concentration of the liquid phase,	
	mol/L	
$\beta = \frac{N^2 r}{900}$	Super gravity factor	
$N \int \sqrt{\sqrt{2+n^2}}$	Rotational speed, rpm	
$r = \sqrt{\frac{r_{\rm i}^2 + r_{\rm o}^2}{2}}$	Geometric radius, m	
$r_{\rm i}$	Inner radius of RZB rotor, m	
r <sub>o</sub>	Outer radius of RZB rotor, m	

# Introduction

Ozone is a highly reactive oxidant and applied widely in modern organic chemistry with the advantages of high atom economy, absence of metals or hypervalent iodine and the straightforward synthesis of ozone from  $O_2$ . So, ozonolysis is a popular method for the oxidative cleavage of alkene to produce aldehyde and ketone [1, 2]. However, on the traditional

Zhengyong Liang lzy781103@126.com

<sup>2</sup> Luoyang Petrochemical Engineering Corporation Ltd/SINOPEC, Luoyang 410300, People's Republic of China conditions, the ozonolysis of alkenes generates ozonides and other peroxidic ozonolysis products, which must be reduced in a separate step to form the desired aldehydes [3, 4]. The common reductants, such as Me<sub>2</sub>S, PPh<sub>3</sub>, Pt/H<sub>2</sub>, Zn/HOAc and NaHSO<sub>3</sub>, often have troublesome problem of low electrical selectivity or complex product separation, which limits the large-scale process of ozonolysis of alkenes.

To solve these drawbacks, trapping of carbonyl oxides by reagents, such as water and N-oxides, had been introduced in ozonolysis reaction and achieved great progress [5–7]. But batch reactions and water-miscible polar organic solvents in this method had difficulties in industrial scale, which was the most significant deficiencies [8].

It is generally known that high gravity technology, which was invented by New Science Group in Imperial Chemical Industries, has developed into one of the most promising branches of process intensification [9]. Rotating zigzag bed (RZB) is a new high gravity unit with the advantages of multilayer rotors in one unit, high mass transfer efficiency and service durability than traditional rotating packed bed (RPB) [10]. According to the reports in the current literature, RZB has been widely used in absorption and distillation, but it was seldom utilized for ozonolysis of mass transfer limited gas–liquid reacting systems. To expand the approach of in situ carbonyl oxide reduction with water, while taking advantages of the safety and scalability of flow ozonolysis,

<sup>&</sup>lt;sup>1</sup> School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, People's Republic of China

we developed a high-throughput flow method using a RZB in this paper.

# Experimental

## Mechanism of ozonolysis reaction with water as zwitterion

The mechanism is shown in Fig. 1, and during the course of ozonolysis reaction, carbonyl oxides **4** and **5** are active intermediates, which can be trapped by water which is a common nucleophile. The oxygen atom of water can be used as a nucleophilic center, which attacks the carbonyl oxide and generates a gem-hydroperoxy alcohol. Under the reaction conditions, the intermediate decomposes with liberation of the aldehyde or ketone and  $H_2O_2$  [11, 12].

#### Continuous operation of ozonolysis reaction in RZB

#### Structure of the RZB

The RZB has two rotors with an inner diameter of 11.8 cm and outer diameter of 28.5 cm and a height of 5.0 cm, with a casing of diameter 38.0 cm and height 21.0 cm and a liquid distributor located at the center of rotor. The nine stationary baffles with the height of 3.8 cm have diameters of 13.0, 15.8, 18.0, 20.0, 1.8, 23.6, 25.3, 26.8, 28.5 cm. In addition, there is a layer of stainless steel packing with a thickness of 4 mm sticking to the inside surface of every stationary baffle. The nine rotational baffles with the height 4.3 cm have diameters 11.8, 14.5, 16.9, 18.9, 20.8, 22.8, 24.3, 26.0, 27.5 cm. Every rotating baffle is 4.3 cm and comprises two regions: The upper region is 2.8 cm high and perforated with small holes of 0.15 cm diameter and 0.25 cm distance between holes, and the lower region was blank with a height of 1.5 cm.

#### Specification of ozone generator and main reagents

HD-500 ozone generator (ozone output is 500 g/h, average concentration of ozone is about 100 mg/L, power is 4.5 kw) was provided by Yinhe Ozone Equipment Co., Ltd (Zhuhai, China). Commercially available reagents, such as styrene, 4-methylstyrene, 4-methoxystyrene, 4-nitrostyrene, 1-decene, 1-dodecene and 1-hexene, were purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai, China) and used directly without further purification. Standard product samples such as benzaldehyde, 4-methylbenzaldehyde, 4-methoxybenzaldehyde, 4-nitrobenzadehyde, 1-nonanal, 1-undecanal and valeraldehyde were purchased from Merck Chemical Technology (Shanghai) Co., Ltd. Product yield was determined by Agilent 4890 gas chromatograph.

#### **Experimental procedure**

Figure 2 shows the diagram of experimental setup for the ozonolysis reaction. The major components include a RZB, a ozone generator, a heat exchanger, a gas–liquid separator, a liquid pump, a  $O_2$  cylinder, two liquid tanks and other auxiliary equipment.

Preparation of olefin solutions: Taking styrene solution (1.5 mmol/L) for an example, 9.37 kg styrene and 4.86 kg deionized water were used as trapping agent and reductant was added into storage tank. Then, acetone solvent was added into storage tank slowly and constant volume to 60 L. The other terminal alkenes are listed in Table 1, and different concentration solutions were obtained by referencing this method.

Typical ozonolysis operation: The  $O_2$  valve was opened and adjusted flow to 5.0 m<sup>3</sup>/h when the ozone generator was kept switch off. Then, conveying pump and heat exchanger were started successively, and the substrate flow was adjusted to 6.0 L/h and 5 °C. After a period of stabilization, the switch of ozone generator was shifted.



Fig. 1 Ozonolysis reaction mechanism of terminal alkenes with water as zwitterion derived from references [11, 12]



Fig. 2 Schematic diagram of the experimental apparatus

Entry	Alkene	Aldehyde (%)	Acid (%)
1		94.7	2.1
2	H <sub>3</sub> C	95.8	2.7
3	СН3О	92.6	4.3
4	O <sub>2</sub> N	74.8	Trace
5	$CH_2 = CH(CH_2)_7 CH_3$	89.7	6.8
6	$CH_2 = CH(CH_2)_9CH_3$	91.8	3.7
7	$CH_2 = CH(CH_2)_3CH_3$	72.3	16.9

 Table 1
 Ozone reaction effects of different substrates

Conditions:  $G=5.0 \text{ m}^3/\text{h}$ , L=6.0 L/h, T=5 °C, N=1200 rpm, C=1.5 mol/L

The ozonization of substrate occurred at the same time. The samples were collected from product flow by a sampler at 10-min intervals (10 min, 20 min, 30 min) and detected by GC. The measurements of the samples were averaged to obtain the corresponding yields of aldehyde and acid.

## **Results and discussion**

It is well known that ozonization of terminal alkene is gas–liquid phase reaction. So, improving the capacity of heat and mass transfer between phases is a effective measure. Taking ozonization of styrene as an example, some important factors such as rotation speed, reaction temperature, liquid volumetric flow and the concentration of substrate were discussed in detail.

### **Rotation speed**

The rotational speeds ranged from 800 to 1600 rpm, with an interval of 200 rpm. The yields of benzaldehyde (main product) and benzoic acid (by-product) are shown in Fig. 3.

Figure 3 shows the rotational speed has great influence on ozonization. When the rotation speed was low, the super gravity factor was small, the liquid material was not dispersed enough, and the mass transfer rate between phases was small. With the increase in rotation speed, thinner liquid film and better dispersion of liquid cause the mass transfer rate to increase, so the yield of benzaldehyde also increases [13]. When the rotation speed reached 1200 rpm, the yield of benzaldehyde reached the peak value of 94.7% (the super gravity factor  $\beta$  reached 340.2 at this moment). But further increase in the rotation speed can cause the oxidation of benzaldehyde, which leads to the amount of benzoic acid.



and C=1.5 mol/L

**Fig.3** Effect of rotational speed on yield of benzaldehyde and benzoic acid. Conditions:  $G=5.0 \text{ m}^3/\text{h}$ , L=6.0 L/h, T=5 °C and C=1.5 mol/L

#### Influence of temperature

Figure 4 illustrates the influence of reaction temperature. It is well known that ozonization is a strong exothermic reaction [14], so temperature has great influence on it. Because of the good heat transfer effect in this reaction system, it seldom forms local hot spots. So, ozonization can be carried out at a higher temperature than traditional batch reaction mode to obtain a higher reaction rate and shorten the reaction time. From Fig. 4, it can be found that the side reaction had not been occurred remarkably when reaction was carried out at about 5 °C. But, when temperature is higher than 10 °C, side reaction would occur significantly, and the yield of benzaldehyde was dropped remarkably.

#### Change of liquid flow rate

The ozone output of the ozone generator we used is about 500 g/h regardless of input change of  $O_2$ , so we mainly discussed the relationship between yield of products and the change of liquid flow rate, and the results are shown in Fig. 5.

From Fig. 5, it can be found that when the liquid phase flow was <4.5 L/h, the ozone in the gas phase was in large excess, which would lead to excessive oxidation of benzaldehyde, so the product yield was lower. With the increase in liquid phase flow rate, more liquid jets and tinier liquid droplets leaving the rotational baffles were produced, thus increasing mass transfer rate. At the same time, the trend of peroxidation gradually decreases. When the liquid phase flow rate increases to 6.0 L/h, the mole ratio of O<sub>3</sub> and substrate obtains a optimal value, and the yield of benzaldehyde can reach the peak of 94.7%. If the liquid flow continues to increase, the styrene was in an excessive state conversely, which could basically eliminate the excessive oxidation side reaction and improve the selectivity of benzaldehyde. However, the larger liquid volumetric flow rate reduces the





**Fig. 4** Influence of temperature on yield of benzaldehyde and benzoic acid. Conditions: N=1200 rpm, G=5.0 m<sup>3</sup>/h, L=6.0 L/h and C=1.5 mol/L

**Fig. 5** Influence of liquid flow rate on yield of benzaldehyde and benzoic acid. Conditions: N=1200 rpm, G=5.0 m<sup>3</sup>/h, T=5 °C and C=1.5 mol/L



Fig. 6 Influence of substrate concentration on the yield of benzaldehyde and benzoic acid. Conditions: N=1200 rpm, G=5.0 m<sup>3</sup>/h, T=5 °C and L=6.0 L/h

dispersion effect, leading to a decrease in the reaction efficiency and a significant decrease in the yield of benzaldehyde [15].

#### Change of substrate concentration in liquid flow

The liquid and gas volumetric flow rates were held constants of 6.0 L/h and 5.0 m<sup>3</sup>/h, respectively. That is to say, the ratio of gas to liquid was maintained under the condition of optimization, and the mass transfer coefficient between liquid gas phases remained basically unchanged. Under this major premise, the relationship between substrate concentration variation and product yields was investigated. Concentration variation ranged from 1.0 mol/L to 2.0 mol/L. The results are shown in Fig. 6.

As can be seen from Fig. 6, when the substrate concentration was 1.5 mol/L, the mole ratio of ozone and styrene is about 1.05. In this case, suitable amount of ozone can not only oxidate alkene substrate sufficiently but also guarantee over-oxidation of benzaldehyde at a low level, so the yield of benzaldehyde can reach about 94.7%.

#### Ozonolysis results of various terminal alkenes

From Table 1, several terminal olefines can be efficiently converted to their corresponding aldehydes via ozonolysis operated in rotating zigzag bed. But there still have multifarious effects as a result of structure differences [16]. For the aromatic hydrocarbon terminal olefin, when there are electron donor groups on the ring, it is conducive to the oxidation reaction. However, the yield of aldehyde is abnormally reduced due to the easy oxidation of *p*-methoxy benzaldehyde into *p*-methoxybenzoic acid. An alkene with an electron-absorbing group, such as *p*-nitrostyrene, has low activity but very high selectivity, and the selectivity of aldehyde is about 100%. For aliphatic terminal alkenes, the primary ozonates of the long-chain alkenes whose carbon chain length is over 10 are dominant in the cleavage mode to produce the corresponding aldehydes, so the yields of aldehydes are higher. In contrast, while for short-chain aldehydes whose carbon chain length is < 6, their ozonide activity is too high, and it is easy to produce more stable acids and polymers.

## Conclusions

In this study, a novel kind of Higee device of rotating zigzag bed was applied to the continuous ozonolysis reaction of some terminal alkenes to produce aldehydes. Under the optimum conditions, the yields of corresponding aldehydes (main product) were between 72.3% and 95.8%, and only a small amount of acids (by-product) were produced simultaneously. The mixture of acetone and water is a suitable solvent with its excellent solubility and fast capture ability for carbonyl oxide intermediates. Rotational speed, ratio of liquid–gas and temperature all have great effect on the reaction and must be well matched each other. Generally speaking, the continuous ozonolysis reaction in RZB is a good example that high gravity can be used to intensify a chemistry reaction process.

**Acknowledgements** This work was supported by Key Technology Research Project of Henan Province (No. 152102210043) and Foundation of Henan Educational Committee (No. 16A430045).

## References

- P.S. Bailey, Ozonation in Organic Chemstry (Academic Press, New York, 1978)
- S.G. Vanonum, R.M. Champeau, R. Paria, J. Am. Chem. Soc. 106, 2990–3001 (2006)
- 3. R.L. Kuckow, Chem. Soc. Rev. 21, 79-83 (1992)
- 4. Y.S. Hon, S.W. Lin, Y.J. Chen, Synth. Commun. 23, 1543–1553 (1993)
- 5. C.E. Schiaffo, P.H. Dussault, J. Org. Chem. 73, 4688–4690 (2008)
- 6. H. Liu, Z.Y. Liang, Y.D. Zhang, Fine Chem. **29**, 303–307 (2012). in Chinese
- M.J. Newland, A.R. Rickard, M.S. Alam, Phys. Chem. Phys. 17, 4076–4088 (2015)
- A.J. Kendall, J.T. Barry, D.T. Seidenkranz et al., Tetrahedron Lett. 57, 1342–1345 (2016)
- G.Q. Wang, Z.C. Xu, YLYu. Chem, Eng. Process. 47, 2131–2139 (2008)
- 10. G.Q. Wang, Z.C. Xu, J.B. Ji, Chem. Eng. Res. Des. **89**, 1434–1442 (2011)

- 11. C.R. Willand, P.H. Dussault, J. Org. Chem. 78, 42-47 (2013)
- 12. T.J. Fisher, P.H. Dussault, Tetrahedron 73, 4233–4258 (2017)
- Y.M. Li, Y.S. Lu, X.J. Liu et al., Sep. Purif. Technol. 186, 156– 165 (2017)
- 14. L.B. Harding, W.A. Goddard, J. Am. Chem. Soc. **100**, 7180–7188 (1978)
- G.Q. Wang, Z.J. Zhou, Y.M. Li, Chem. Eng. Process. Process Intensif. 135, 141–147 (2019)
- 16. S.S. Tang, L. Du, N.T. Tsona, Atmos. Environ. 162, 23–30 (2017)