

行政院國家科學委員會專題研究計劃成果報告

逆流與順流式多段臭氧化處理程序之研究: (I)

Study on the countercurrent and cocurrent multistage operations of
ozonation process (I)

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一、中文摘要

本計畫針對普遍使用的臭氧化氣液反應系統,探討逆流式與順流式氣泡塔反應器 (bubble column reactor, BCR)及多段連續攪拌槽反應器(continuous stirred tank reactor, CSTR)之系統參數對臭氧化效能之影響。所考慮的臭氧化效能包括:臭氧利用率、污染物去除率及臭氧尾氣排放之濃度等。針對氣泡塔反應器,本研究加入前人所忽略之因子,例如:臭氧自解及臭氧與污染物反應對臭氧質量傳輸之影響(即增進因子)、壓力變化、及延散(dispersion)等。本研究應用已完成之 O_3 逆流式單段BCR及逆流式多段CSTR模式,將之延伸至 O_3 逆/順流式多段BCR及順流式多段CSTR。多段的CSTR將可提高臭氧的利用率、降低臭氧氣體排放濃度、及減少總反應器之體積。逆流與順流式之CSTR(s)其臭氧化效能相近。就BCR臭氧化系統而言,多段之臭氧化效能則與單段相近;而逆流與順流式之臭氧化效能亦相近。研究成果可提供合理設計臭氧化處理程序之參考,對於臭氧應用於污染物處理甚為有用。

關鍵詞：臭氧化反應、氣泡塔反應器、連續攪拌槽反應器、多段操作、逆流及順流操作

英文摘要

An analysis is performed for countercurrent and cocurrent multistage bubble column reactors (BCRs) as well as cocurrent multistage continuous stirred tank reactors (CSTRs) of gas-liquid ozonation systems. The effects of system variables on the ozonation performance are examined. The system variables under consideration include the utilization efficiency of ozone, the removal efficiency of pollutants, and the emission concentration of ozone gas. This analysis includes the effects of ozone decomposition and the ozonation of pollutants on the ozone mass transfer (i.e., enhancement factor, E_r), the variation of pressure along the column, and the dispersion effect. The application of multistage CSTRs has the advantages to increase the utilization efficiency of ozone, to decrease the emission concentration of ozone gas, and to reduce the total volume of reactor. The ozonation performances of countercurrent and cocurrent CSTRs are about the same. For BCR system, the ozonation performance of multistage is close to that of single stage. Both countercurrent and cocurrent BCRs give nearly the same ozonation performance. The results of this study can provide the useful information for the rational design of ozonation contactor, and are of importance for the treatment of

pollutants via ozonation.

Keywords: ozone, ozonation, multi-stage reactor, countercurrent operation

二、計畫緣由與目的

臭氧應用於水及廢水處理時，其效力受氣液質量傳輸、臭氧自解反應及臭氧與污染物反應之影響。而在設計臭氧/水/廢水處理程序時，上述三種因子均必需加以考量。此三種因子中，氣液質量傳輸又受後兩種因子之影響。其影響程度可以增進因子 (enhancement factor) E_r 來表示。此 E_r 定義為 N_{Ar}/N_A ； N_{Ar} ， N_A 分別為伴有化學反應吸收與純物理吸收時之質量傳送通量 (Danckwert, 1970)。Bollkky (1981)、Hawash et al. (1990)、Chang et al. (1995, 1996 a and b) 指出臭氧自解反應及臭氧與污染物的反應均會促進氣液間的質量傳送，即 E_r 值有顯著之影響。

臭氧化氣液反應系統中的半連續及連續攪拌槽反應器、及氣泡塔反應器的質量傳送及反應物的轉化率曾被很多學者加以探討 (semibatch continuous reactor: Yocum, 1980; Anselmi et al., 1984; Chiu et al., 1997; continuous stirred tank reactor (CSTR): Bollyky, 1981; Sheffer and Esterson, 1982; Farooq and Ahmed, 1989; Hawash et al., 1990; bubble column reactor (BCR): Hayashi et al., 1993; Marinas et al., 1993; Zhou et al., 1994; Smith and Zhou, 1994; Roustan et al., 1996; Huang et al., 1998)。以上學者除了 Chiu et al. (1997) 及 Huang et al. (1998) 之外，並未在定量上探討化學反應對 E_r 值 ($=k_L/k_L^0$) 的影響，也未對 k_L (化學吸收之液相質量傳送係數) 及 k_L^0 值加以區分。當系統之氣相及液相之濃度隨時間(如半連續攪拌槽反應器)或位置(如氣泡塔反應器)變化時，亦將影響 E_r 值。嚴謹的考量應當將 E_r 值的變化予以納入 (Chiu et al., 1997; Huang et al., 1998)。

BCR 及 CSTR 均為臭氧化系統常用的反應器。主持人於前一計畫中已針對單段逆流式 BCR 及多段逆流式 CSTRs 考量臭氧化反應對 E_r 值得影響，並對 k_L 及 k_L^0 加以區分。本計畫應用單段逆流式 BCR 及多段逆流式 CSTR 之結果延伸至多段逆/順流式 BCRs 及多段順流式 CSTRs。此外並就逆/順流式 BCRs 系統考量臭氧化反應、壓力變化、延散、及氣相與液相濃度變化之影響。

三、氣液接觸的理論分析

3.1 臭氧在水溶液中的反應

臭氧在水溶液中的反應包括了臭氧的自解反應及臭氧與有機物的反應。其反應速率通式為，可描述如下。

(1). 臭氧自解反應：

Chang et al. (1995) 綜合了 Weiss (1935), Sotelo et al. (1987), Nadezhdin (1988), Miyahara and Hirokawa (1994) 所提出的臭氧自解速率式，將臭氧自解反應速率 ($-r_{O_3}$) 以通式表示為

$$-r_{O_3} = k_{am}[O_3]^m + k_{bn}[O_3]^n. \quad (1)$$

在方程式(1)中， k_{am} 和 k_{bn} 代表酸性和鹼性的自解反應速率常數，且 k_{bn} 為 $[OH^-]$ 之函數； m ， n 為反應次數。

(2). 臭氧在水溶液中與有機物的作用：

臭氧(A)在水溶液中的自解和與有機物(B)反應之系統可以通式表示如下 (Chiu et al., 1999)。臭氧的分解速率 ($-r_{AL}$) 包括了臭氧的自解反應及與污染物的反應，其速率式為

$$-r_{AL} = -dC_{AL}/dt = k_{am} \cdot C_{AL}^m + k_{bn} \cdot C_{AL}^n + k_R C_{AL}^a C_{BTL}^b. \quad (2)$$

而有機物(B)的反應，其反應速率 ($-r_{BTL}$) 為

$$-r_{BTL} = -dC_{BTL}/dt = \beta_R k_R C_{AL}^a C_{BTL}^b. \quad (3)$$

上列二式中，反應速率常數 k_{bn} 、 k_R 均為 $[OH^-]$ 與 C_{BTL0} (B 之起始濃度) 之函數。

3.2 增進因子的影響

氣體在吸收的過程中伴隨著化學反應，會影響氣體被吸收的質量傳

送速率。化學反應可能會發生在液相中(慢反應)或發生在液膜中(快反應)，其影響可由增進因子 E_r 值來顯示。

考慮包含臭氧自解及其與污染物反應時的增進因子，因反應較為複雜，文獻上並無直接可使用以求出增進因子之模式。因此利用本研究室先前以薄膜理論為基礎所推估之模式(Chiu et al., 1999)，考慮臭氧水溶液中臭氧的吸收、自解、及其與有機物的反應(反應以前述的反應通式表示)，並以有限差分法的數值方法求出。

3.3 臭氧與污染物反應之系統控制方程式

3.3.1 逆流式BCR反應系統

考慮臭氧在氣液氣泡塔中吸收、自解和與污染物反應的質量傳送；臭氧與污染物的反應速率通式，如方程式(2)、(3)。由氣泡塔反應器之質量平衡與吸收平衡並考慮增進因子、壓力變化及延散(dispersion)性，可得無因次化後之系統控制方程式。

$$(1/Pe_L) d^2\theta_{ALb}/dZ^{*2} + d\theta_{ALb}/dZ^* + E_r St_L (\theta_{AH} - \theta_{ALb}) - D_{am} \theta_{ALb}^{m'} - D_{bn} \theta_{ALb}^{n'} - D_R \theta_{ALb}^{a'} \theta_{BTLb}^{b'} = 0, \quad (4)$$

$$(1/Pe_L) d^2\theta_{BTLb}/dZ^{*2} + d\theta_{BTLb}/dZ^* - \beta_R D_R C_{ALb}^{a'} C_{BTLb}^{b'}/k_q = 0, \quad (5)$$

$$(1/Pe_G) d^2\theta_{AH}/dZ^{*2} - U_G d\theta_{AH}/dZ^* - (\alpha/\beta) U_G \theta_{AH} - E_r St_G (1 - (1+\alpha) y_0 \theta_{AH}/\beta) (\theta_{AH} - \theta_{ALb}) = 0, \quad (6)$$

$$dU_G/dZ^* - (\alpha/\beta) U_G + E_r St_G ((1+\alpha) y_0/\beta) (\theta_{AH} - \theta_{ALb}) = 0. \quad (7)$$

邊界條件為

在 $Z^* = 0$, (bottom of column, inlet of gas)

$$d\theta_{ALb}/dZ^* = 0,$$

$$d\theta_{BTLb}/dZ^* = 0,$$

$$\theta_{AH} = \theta_{AH,inf} + (1/Pe_G) d\theta_{AH}/dZ^*, \quad \theta_{AH,inf} \rightarrow 1$$

$$U_G = 1. \quad (8)$$

在 $Z^* = 1$, (top of column, inlet of liquid)

$$\theta_{ALb} = \theta_{ALb,inf} - (1/Pe_L) d\theta_{ALb}/dZ^*,$$

$$\theta_{ALb,inf} \rightarrow 0$$

$$\theta_{BTLb} = \theta_{BTLb,inf} - (1/Pe_L) d\theta_{BTLb}/dZ^*,$$

$$\theta_{BTLb,inf} \rightarrow 1$$

$$d\theta_{AH}/dZ^* = 0. \quad (9)$$

上列各式中 $Z^* = z/L$ 、 $\theta_{ALb} = C_{ALb} / (C_{AGi}^0 / He)$ 、 $\theta_{BTLb} = C_{BTLb} / C_{BTL0}$ 、 $\theta_{AH} = (C_{AGi} / He) / (C_{AGi}^0 / He) = \beta y / [(1+\alpha) y_0]$ 、 $U_G = u_G / u_G^0$ 、 $Pe_L = u_L L / (\epsilon_L D_L)$ 、 $Pe_G = u_G^0 L / (\epsilon_G D_G)$ 、 $St_L = k_L^0 a_e L / u_L = k_L^0 S / Q_L = k_L^0 a_e V / Q_L$ 、 $St_G = k_L^0 a_e L / (u_G^0 He) = k_L^0 S / (Q_L He) = k_L^0 a_e V / (Q_L He)$ 、 $\alpha = \epsilon_L \rho_L g L / P_t$ 、 $\beta = 1 + \alpha (1 - Z^*) = P / P_b$ 、 $D_{am} = k_{am} \epsilon_L (C_{AGi}^0 / He)^{m-1} L / u_L$ 、 $D_{bn} = k_{bn} \epsilon_L (C_{AGi}^0 / He)^{n-1} L / u_L$ 、 $D_R = k_R \epsilon_L (C_{AGi}^0 / He)^{a-1} (C_{BTLb0})^{b'} L / u_L$ 。符號中， y 為氣相臭氧 mole 分率， 0 表進流， inf 表進流， H 表滯留氣體， S 為氣液接觸面積， $a_e = S / (V_L + V_H) = S / V$ ， V_L 、 V_H ：液體、滯留氣體之體積， L ：塔高。由於臭氧與污染物的反應及臭氧的自解反應均會影響臭氧的質量傳送速率，其影響反應在方程式(4)、(6)及(7)中的 E_r 上，因此如果要解方程式(4)~(9)，必須先解出 E_r 。

3.3.2 順流式BCR反應系統

考慮臭氧在氣液氣泡塔中吸收、自解和與污染物反應的質量傳送；臭氧與污染物的反應速率通式，如方程式(2)、(3)。由氣泡塔反應器之質量平衡與吸收平衡並考慮增進因子、壓力變化及延散(dispersion)性，可得無因次化後之系統控制方程式。

$$(1/Pe_L) d^2\theta_{ALb}/dZ^{*2} - d\theta_{ALb}/dZ^* + E_r St_L (\theta_{AH} - \theta_{ALb}) - D_{am} \theta_{ALb}^{m'} - D_{bn} \theta_{ALb}^{n'} - D_R \theta_{ALb}^{a'} \theta_{BTLb}^{b'} = 0, \quad (10)$$

$$(1/Pe_L) d^2\theta_{BTLb}/dZ^{*2} - d\theta_{BTLb}/dZ^* - \beta_R D_R C_{ALb}^{a'} C_{BTLb}^{b'}/k_q = 0, \quad (11)$$

$$(1/Pe_G) d^2\theta_{AH}/dZ^{*2} - U_G d\theta_{AH}/dZ^* - (\alpha/\beta) U_G \theta_{AH} - E_r St_G (1 - (1+\alpha) y_0 \theta_{AH}/\beta) (\theta_{AH} - \theta_{ALb}) = 0, \quad (12)$$

$$dU_G/dZ^* - (\alpha/\beta) U_G + E_r St_G ((1+\alpha) y_0/\beta) (\theta_{AH} - \theta_{ALb}) = 0. \quad (13)$$

邊界條件為

在 $Z^* = 0$, (bottom of column, inlet of gas and liquid)

$$\begin{aligned}\theta_{ALb} &= \theta_{ALb,inf} + (1/Pe_L) d\theta_{ALb} / dZ^*, \quad \theta_{ALb,inf} \rightarrow 0 \\ \theta_{BTLb} &= \theta_{BTLb,inf} + (1/Pe_L) d\theta_{BTLb} / dZ^*, \quad \theta_{BTLb,inf} \rightarrow 1 \\ \theta_{AH} &= \theta_{AH,inf} + (1/Pe_G) d\theta_{AH} / dZ^*, \quad \theta_{AH,inf} \rightarrow 1 \\ U_G &= 1.\end{aligned}\quad (14)$$

在 $Z^* = 1$, (top of column, outlet of gas and liquid)

$$\begin{aligned}d\theta_{ALb} / dZ^* &= 0, \\ d\theta_{BTLb} / dZ^* &= 0, \\ d\theta_{AH} / dZ^* &= 0.\end{aligned}\quad (15)$$

3.3.3 Nt段CSTRs的逆流式串接

將Nt個CSTR逆流式串聯。且Nt段CSTR中的任一個反應器均符合單段CSTR其氣液間的質量傳送。考慮逆流式串接的Nt段CSTR間的質量平衡與吸收平衡，並無因次化後可得以下系統控制方程式。

第1個CSTR

$$\theta_{ALb,0} - \theta_{ALb,1} + E_{r,1} St_{L,1} (\theta_{AH,1} - \theta_{ALb,1}) - [(m'+1)/2] St_{L,1} Sh_1 M_{Am',1} \theta_{ALb,1}^{m'} - [(n'+1)/2] St_{L,1} Sh_1 M_{Bn',1} \theta_{ALb,1}^{n'} - [(a'+1)/2] St_{L,1} Sh_1 M_{R,1} \theta_{ALb,1}^{a'} \theta_{BTLb,1}^{b'} = 0,$$

$$\theta_{BTLb,0} - \theta_{BTLb,1} - \beta_R [(a'+1)/2] St_{L,1} Sh_1 M_{R,1} \theta_{ALb,1}^{a'} \theta_{BTLb,1}^{b'} / k_q = 0,$$

$$\theta_{AH,2} - \theta_{AH,1} - E_{r,1} St_{G,1} (\theta_{AH,1} - \theta_{ALb,1}) = 0,$$

$$\theta_{AH,1} = \theta_{AF,1}.$$

第2個CSTR

$$\theta_{ALb,1} - \theta_{ALb,2} + E_{r,2} St_{L,2} (\theta_{AH,2} - \theta_{ALb,2}) - [(m'+1)/2] St_{L,2} Sh_2 M_{Am',2} \theta_{ALb,2}^{m'} - [(n'+1)/2] St_{L,2} Sh_2 M_{Bn',2} \theta_{ALb,2}^{n'} - [(a'+1)/2] St_{L,2} Sh_2 M_{R,2} \theta_{ALb,2}^{a'} \theta_{BTLb,2}^{b'} = 0,$$

$$\theta_{BTLb,1} - \theta_{BTLb,2} - \beta_{DB} [(a'+1)/2] St_{L,2} Sh_2 M_{R,2} \theta_{ALb,2}^{a'} \theta_{BTLb,2}^{b'} / k_q = 0,$$

$$\theta_{AH,3} - \theta_{AH,2} - E_{r,2} St_{G,2} (\theta_{AH,2} - \theta_{ALb,2}) = 0,$$

$$\theta_{AH,2} = \theta_{AF,2}.$$

...
第N個CSTR

$$\theta_{ALb,N-1} - \theta_{ALb,N} + E_{r,N} St_{L,N} (\theta_{AH,N} - \theta_{ALb,N}) - [(m'+1)/2] St_{L,N} Sh_N M_{Am',N} \theta_{ALb,N}^{m'} - [(n'+1)/2] St_{L,N} Sh_N M_{Bn',N} \theta_{ALb,N}^{n'} - [(a'+1)/2] St_{L,N} Sh_N M_{DB,N} \theta_{ALb,N}^{a'} \theta_{BTLb,N}^{b'} = 0,$$

$$\theta_{BTLb,N-1} - \theta_{BTLb,N} - \beta_{DB} [(a'+1)/2] St_{L,N} Sh_N M_{R,N} \theta_{ALb,N}^{a'} \theta_{BTLb,N}^{b'} / k_q = 0,$$

$$\theta_{AH}^0 - \theta_{AH,N} - E_{r,N} St_{G,N} (\theta_{AH,N} - \theta_{ALb,N}) = 0,$$

$$\theta_{AH,N} = \theta_{AF,N}.$$

$$\theta_{AH,N} = \theta_{AF,N}.$$

聯立解(16)~(27)時，還同時配合增進因子的求解，即可求得串接的Nt段CSTR的濃度變化及增進因子。

上列各式中 $\theta_{ALb0} = C_{ALb0} / (C_{AGi}^0 / He)$ 、 $\theta_{BTLb0} = C_{BTLb0} / C_{BTLb0}$ 、 $\theta_{AH0} = (C_{AGi}^0 / He) / (C_{AGi}^0 / He)$ 、 $\theta_{AF} = (C_{AGe} / He) / (C_{AGi}^0 / He)$ 、 $Sh = k_L V_L / (D_{AL} S_{GL})$ 、 $M_{Am'} = 2D_{AL} k_{am'} (C_{AGi}^0 / He)^{m'-1} / [(m'+1) (k_L^0)^2]$ 、 $M_{Bn'} = 2D_{AL} k_{bn'} (C_{AGi}^0 / He)^{n'-1} / [(n'+1) (k_L^0)^2]$ 、 $M_R = 2D_{AL} k_R (C_{AGi}^0 / He)^{a'-1} C_{BTL0}^{b'} / [(a'+1) (k_L^0)^2]$ 、 $k_q = C_{BTL0} / (C_{AGi}^0 / He)$ 。符號中，H表滯留氣體，F表攪拌槽上方空間之氣體，e表出口。

3.3.4 Nt段CSTRs的順流式串接

第1個CSTR

$$\theta_{ALb,0} - \theta_{ALb,1} + E_{r,1} St_{L,1} (\theta_{AH,1} - \theta_{ALb,1}) - [(m'+1)/2] St_{L,1} Sh_1 M_{Am',1} \theta_{ALb,1}^{m'} - [(n'+1)/2] St_{L,1} Sh_1 M_{Bn',1} \theta_{ALb,1}^{n'} - [(a'+1)/2] St_{L,1} Sh_1 M_{R,1} \theta_{ALb,1}^{a'} \theta_{BTLb,1}^{b'} = 0,$$

$$\theta_{BTLb,0} - \theta_{BTLb,1} - \beta_R [(a'+1)/2] St_{L,1} Sh_1 M_{R,1} \theta_{ALb,1}^{a'} \theta_{BTLb,1}^{b'} / k_q = 0,$$

$$\theta_{AH,2} - \theta_{AH,1} - E_{r,1} St_{G,1} (\theta_{AH,1} - \theta_{ALb,1}) = 0,$$

$$\theta_{AH,1} = \theta_{AF,1}.$$

$$\theta_{AH,1} = \theta_{AF,1}.$$

第2個CSTR

$$\theta_{ALb,1} - \theta_{ALb,2} + E_{r,2} St_{L,2} (\theta_{AH,2} - \theta_{ALb,2}) - [(m'+1)/2] St_{L,2} Sh_2 M_{Am',2} \theta_{ALb,2}^{m'} - [(n'+1)/2] St_{L,2} Sh_2 M_{Bn',2} \theta_{ALb,2}^{n'} - [(a'+1)/2] St_{L,2} Sh_2 M_{R,2} \theta_{ALb,2}^{a'} \theta_{BTLb,2}^{b'} = 0,$$

$$\theta_{BTLb,1} - \theta_{BTLb,2} - \beta_{DB} [(a'+1)/2] St_{L,2} Sh_2 M_{R,2} \theta_{ALb,2}^{a'} \theta_{BTLb,2}^{b'} / k_q = 0,$$

$$\theta_{AH,3} - \theta_{AH,2} - E_{r,2} St_{G,2} (\theta_{AH,2} - \theta_{ALb,2}) = 0,$$

$$\text{Sh}_2 M_{R,2} \theta_{ALb,2} a' \theta_{BTLb,2}^{b'} = 0, \quad (33)$$

$$\theta_{BTLb,1} - \theta_{BTLb,2} - \beta_{DB} [(a'+1)/2] \quad (34)$$

$$\text{St}_{L,2} \text{Sh}_2 M_{R,2} \theta_{ALb,2} a' \theta_{BTLb,2}^{b'} / k_q = 0, \quad (35)$$

$$\theta_{AH,1} - \theta_{AH,2} - E_{r,2} \text{St}_{G,2} (\theta_{AH,2} - \theta_{ALb,2}) = 0, \quad (36)$$

$$\theta_{AH,2} = \theta_{AF,2}, \quad (37)$$

$$\dots$$

$$\text{第} N \text{個 CSTR}$$

$$\theta_{ALb,N-1} - \theta_{ALb,N} + E_{r,N} \text{St}_{L,N} (\theta_{AH,N} - \theta_{ALb,N}) - [(m'+1)/2] \text{St}_{L,N} \text{Sh}_N M_{Am',N} \theta_{ALb,N}^{m'} - [(n'+1)/2] \text{St}_{L,N} \text{Sh}_N M_{Bn',N} \theta_{ALb,N}^{n'} - [(a'+1)/2] \text{St}_{L,N} \text{Sh}_N M_{R,N} \theta_{ALb,N}^{a'} \theta_{BTLb,N}^{b'} = 0, \quad (38)$$

$$\theta_{BTLb,N-1} - \theta_{BTLb,N} - \beta_R [(a'+1)/2] \text{St}_{L,N} \text{Sh}_N M_{R,N} \theta_{ALb,N}^{a'} \theta_{BTLb,N}^{b'} / k_q, \quad (39)$$

$$\theta_{AH,N-1} - \theta_{AH,N} - E_{r,N} \text{St}_{G,N} (\theta_{AH,N} - \theta_{ALb,N}) = 0, \quad (40)$$

$$\theta_{AH,N} = \theta_{AF,N}. \quad (41)$$

3.3.5 Nt段BCRs的串接

分別將3.3.1及3.3.2兩節之系統方程式，設BCR高度 $(L_{Nt}) = L / Nt$ ，以有限差分法解Nt個BCRs之各格點方程式即可求解。

四、結果與討論

4.1 順/逆流式氣泡塔反應器

利用Marinas et al. (1993)的氣泡塔模擬甲酚(O-cresol)的臭氧化。模擬所應用的相關參數如Marinas et al. (1993)所引用，包括： $Q_L = 278 \text{ cm}^3/\text{s}$ ， $Q_G = 100 \text{ cm}^3/\text{s}$ ， $d_R = 16.20 \text{ cm}$ ， $L = 488 \text{ cm}$ ， $T = 286 \text{ K}$ ， $C_{O_3} = 0.0019 \text{ M}$ ， $C_{BTLb0} = 0.001 \text{ M}$ ， $y_0 = 0.03$ ， $k_{am'} = 0.00024 \text{ s}^{-1}$ ， $k_R = 12000 \text{ (M s)}^{-1}$ ， $He = 2.055$ ， $\beta_R = 0.5$ ，及利用Hughmark (1967)估計其 $k_L^0 = 0.015 \text{ cm s}^{-1}$ ， $a_e = 0.7$ 。經無因次群計算可得 $Pe_L = 8.19$ ， $Pe_G = 0.14$ ， $St_L = 3.88$ ， $St_G = 5.25$ ， $M_{am'} = 0.0000186$ ， $M_R = 0.93$ ， $D_{am'} = 0.085$ ， $D_R = 4240$ 。引用上述參數值於本模式中，則氣泡塔中包含有臭氧自解反應及臭氧與甲酚反應的模擬結果圖1(逆流式的氣液

接觸)及圖2(順流式的氣液接觸)。由圖1可看出，液相一進入氣泡塔中，即因為分散效果及污染物與液相臭氧反應，使得液相中的污染物濃度快速降低，例如圖1在塔頂液相中污染物由無因次濃度1快降低至0.96，而後液相中污染物隨著塔高位置的下降，濃度逐漸降低。而氣相中臭氧的濃度由塔底進入後隨塔高位置上升而逐漸降低。液相中臭氧因與污染物快速反應，而一直維持在低值(如圖1液相中的臭氧濃度為0.0003變化至0.0001)。而圖2為順流式操作，液相中污染物的濃度隨塔高位置的上升而濃度下降。由圖1及圖2中氣相出口的濃度可計算氣相臭氧的利用率或利用液相中污染物出口的濃度可計算污染物的去除率。在圖1逆流的BCR操作中，其臭氧的利用率為88.7%，污染物的去除率為29.9%；而圖2順流式的BCR操作中其臭氧的利用率為88.6%，污染物的去除率為29.6%。因此在BCR操作上逆流式的臭氧利用率及污染物的去除率僅稍高於順流式。

圖3及圖4為增進因子在逆、順流式BCR操作上隨塔高位置的變化，其使用的參數與圖1及圖2的操作條件相同。在逆流BCR操作上 E_r 隨塔高的位置升高而升高(由1.20升至1.28)，而順流BCR操作中 E_r 隨塔高而降低(由1.27降至1.20)，因此增進因子 E_r 在BCR的分佈上並不會維持一定值，因此在BCR的操作中必須考慮增進因子隨塔高的變化。在逆流操作中，若以塔底出口的液相濃度估算出的增進因子來計算BCR質量傳送量則會低估，但若以塔頂進口的液相濃度所估算出的增進因子來計算BCR質量傳送則會高估。

4.2 單/多段氣泡塔反應器

圖5與圖6為單段BCR與4段BCRs串聯的比較。圖5為逆流式操作，圖6為順流式操作，其操作的條件與圖1、圖2相同，但多段操作則限制其反應器

的總體積與單段相同。由圖中可看出多段串聯的BCRs操作中，其臭氧氣體的利用率與污染物的去除率均與單段BCR的操作結果相同。因此在BCR的操作中，單段BCR與多段BCRs的操作結果相同。但單段BCR在維修上因其塔僅有一個，當BCR有損壞或阻塞時，必須使BCR操作完全停頓。而多段BCRs只要抽換部分管件即可，其他管件仍可持續使用，因此多段BCRs的維護比單段BCR便利。

4.3 單槽BCR與串聯多槽CSTR的比較

Levenspiel (1972)以追蹤劑(tracer)進行單相流體流動實驗並提出單相的分散性模式及下列方程式。

$$1/Nte = 2(1/Pe) - 2(1/Pe)^2 (1 - e^{-Pe}) \quad (40)$$

上式中， Pe 為 Pe_L 或 Pe_G ， Nte 為連續攪拌槽(continuous stirred tank, CST)的個數。式(40)可用來估計達到與氣泡塔相同的氣相或液相流體狀態所需要的串聯式CST的個數。因此若要描述氣相的狀態則可將 Pe_G 代入上式中，若要描述液相的狀態則可將 Pe_L 代入上式估算。將圖1 BCR模擬的出口污染物濃度與串聯的CSTR比較，結果如圖7。由圖中可看出BCR出口污染物的濃度明顯均比CSTR的濃度高。當 $Pe_L = 8.2$ 時($Nte = 4.67$)，若要描述BCR中液相的行為則需要以5個CSTRs來描述；若要描述BCR氣相的行為則只需要1個CSTR($Pe_G = 0.14$; $Nte = 1.05$)。因此若只利用1個CSTR來描述此時的BCR，顯然使液相中的行為不合。此時BCR污染物的出口濃度比1個CSTR出口的濃度僅高出約1.5% (BCR:0.7133, CSTR:0.7023)，但若有另一BCR其無因次群值除 Pe_G 外均與圖1相同，若其 $Pe_L = Pe_G = 8.2$ ，則利用此BCR與串聯的5個CSTR比較，其出口的污染物濃度亦僅高出約0.8%。因此在 $Pe_L > Pe_G$ 的BCR中，模擬BCR所需串聯CSTR的個數，應可由 Pe_G 決定。

五、結論

- 1.在BCR操作上逆流式的臭氧利用率及污染物的去除率稍較高於順流式。
- 2.在BCR中增進因子(E_r)會隨塔高而改變，尤其反應速率常數較大時，更必須考慮 E_r 及其對反應系統質量傳送之影響。
- 3.在逆流操作中，若以塔底出口的濃度估算出的增進因子來計算BCR質量傳送量則會低估，但若以塔頂進口的濃度所估算出的增進因子來計算BCR質量傳送則會高估。
- 4.多段串聯的BCR操作中其臭氧氣體的利用率與污染物的去除率均與單段BCR的操作結果相同。
- 6.隨著逆流式串聯CSTR之反應器數(Nt)的增加，出口處的污染物的濃度均隨 Nt 的增加逐漸降低。
- 7.在 $Pe_L > Pe_G$ 的BCR中，模擬BCR所需串聯CSTR的個數，可由 Pe_G 決定。

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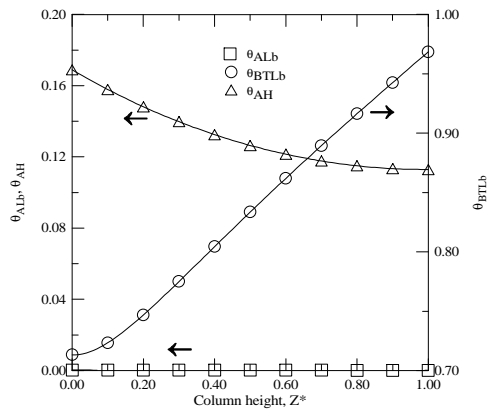


Figure 1. θ_{ALb} , θ_{BTLb} , θ_{AH} vs. column height for operation in countercurrent mode of one-stage bubble column reactor (BCR). $d_R = 16.20$ cm, $L = 488$ cm, $Q_L = 278$ cm³/s, $Q_G = 100$ cm³/s, $Pe_L = 8.20$, $Pe_G = 0.14$, $St_L = 3.88$, $St_G = 5.25$, $C_{AGi}^0 = 0.0019$ M, $C_{BTLb0} = 0.001$ M, $y_0 = 0.03$, $m^* = 1$, $n^* = 1$, $a^* = 1$, $b^* = 1$, $M_{am}^* = 0.000019$, $M_{bn}^* = 0$, $M_R = 0.929$, $D_{am}^* = 0.085$, $D_{bn}^* = 0$, $D_R = 4240$.

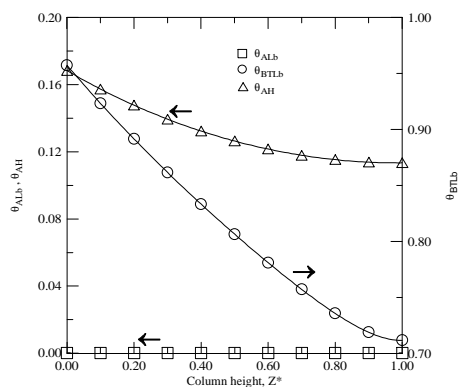


Figure 2. θ_{ALb} , θ_{BTLb} , θ_{AH} vs. column height for operation in cocurrent mode of one-stage bubble column reactor (BCR). Other notations and values of parameters are the same as Figure 1.

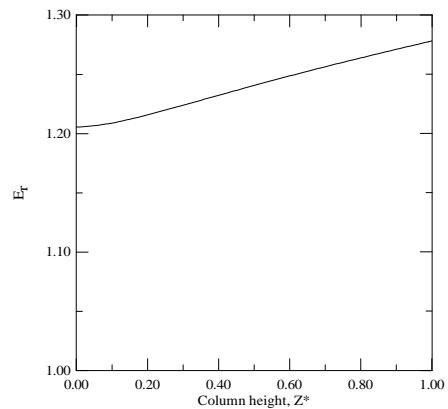


Figure 3. E_r vs. column height for operation in countercurrent mode of one-stage bubble column reactor (BCR). Other notations and values of parameters are the same as Figure 1.

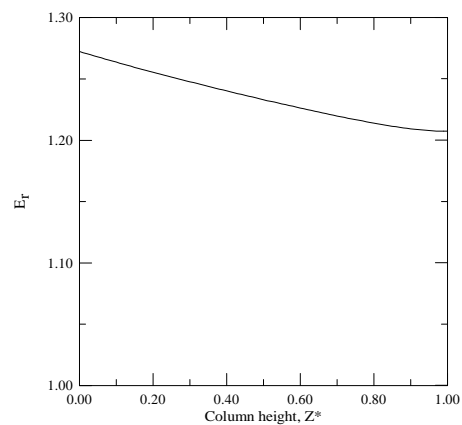


Figure 4. E_r vs. column height for operation in cocurrent mode of one-stage bubble column reactor (BCR). Other notations and values of parameters are the same as Figure 1.

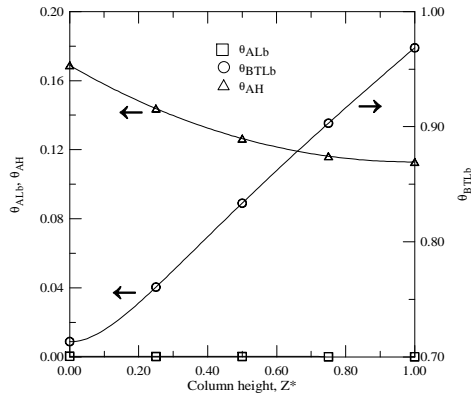


Figure 5. Comparison of predicted θ_{ALb} , θ_{BTLb} , θ_{AH} by one-stage BCR (—) and four BCRs in series (symbols) for operation in countercurrent mode. $L = 488$ cm for one-stage BCR, $L_4 = L/4$ for four-stage BCRs. Other notations and values of parameters are the same as Figure 1

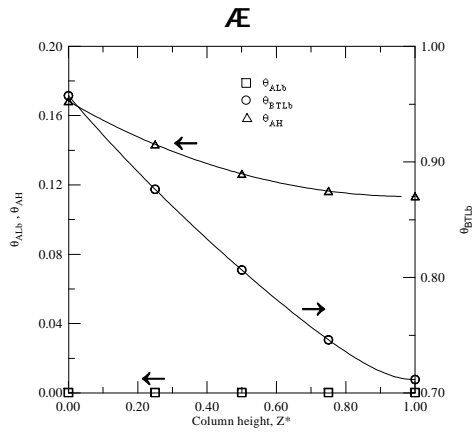


Figure 6. Comparison of predicted θ_{ALb} , θ_{BTLb} , θ_{AH} by one-stage BCR (—) and four BCRs in series (symbols) for operation in cocurrent mode. $L = 488$ cm for one-stage BCR, $L_4 = L/4$ for four-stage BCRs. Other notations and values of parameters are the same as Figure 1.

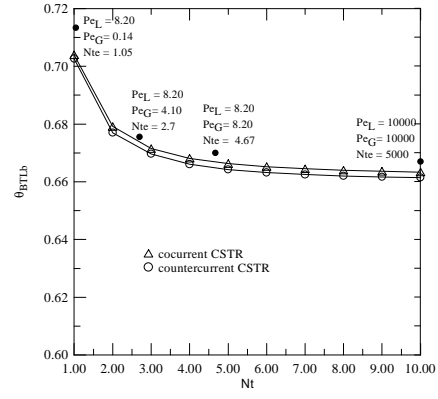


Figure 7. Comparison of θ_{BTLb} for cocurrent (Δ) and countercurrent (\circ) Nt -stage CSTRs in series with those for countercurrent one-stage BCR (\bullet). $d_R = 16.20$ cm, $L = 488$ cm, $Q_L = 278$ cm³/s, $Q_G = 100$ cm³/s, $St_L = 3.88/Nt$, $St_G = 5.25/Nt$, $C_{AGi}^0 = 0.0019$ M, $C_{BTLb0} = 0.001$ M, $y_0 = 0.03$, $m^* = 1$, $n^* = 1$, $a^* = 1$, $b^* = 1$, $M_{am}^* = 0.000019$, $M_{bn}^* = 0$, $M_R = 0.929$, $D_{am}^* = 0.085$, $D_{bn}^* = 0$, $D_R = 4240$. $Nt = Nte$ estimated by Eq. (40) with Pe_G .