Simultaneous disposal of acrylic acid (ester) wastewater and residue with high efficiency and low energy consumption

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ABSTRACT

The acrylic acid (ester) production wastewater and residue were simultaneously treated by a novel two-stage fluidized-bed/fixed-bed catalytic system. The effects of fluidized-bed temperature, flow rate of wastewater or residue, and oxygen excess rate (OER) on the disposal efficiency were investigated to certify the feasibility. The chemical oxygen demand of effluent was less than 100 mgO_2 L^{-1} when the temperature exceeded 380°C, the OER was greater than 2, and the flow rate of distillation residue was less than 1.5 mL h^{-1}. By utilizing the high calorific value of residue, the energy balance of the system can be achieved by regulating the flow rates of wastewater and residue with the guarantee of the treatment efficiency, which was verified by the theoretical simulation calculations. The technology employed in our research shows obvious advantages on purification of the acrylic acid (ester) production wastewater and residue for its high efficiency and can make the most use of the energy in wastes to reduce energy consumption.

Keywords: Acrylic wastewater; Residue; Fluidized-bed/fixed-bed; Energy balance

1. Introduction

Acrylic acid (ester) is an important raw material for chemical production [1–3]. It is mainly used as surfactant, leather finishing agent, filler, and antifouling agent to improve the quality of leather in the leather production process [4]. It also can be used as paper reinforcer and paper adhesives in paper industry to improve paper strength, cohesiveness and mechanical stability in paper-making industry [5]. In textile industry, acrylic ester emulsion is mainly used as thickener and fabric adhesive in pigment printing [5]. The global acrylic acid market size was 5.75 million tons in 2014, and the demand for acrylic acid and esters is estimated to reach 8.75 million tons by 2022 [6]. The wastewater and residue are inevitably generated in the production of acrylic acid and its ester. It is reported that 0.05 tons wastewater and 0.003 tons distillation residue are discharged for every ton of product [7,8]. The composition of the heavy distillation residual liquid is complex and it is difficult to effectively recover the available resources. Similarly, the production wastewater has strong acidity, high toxicity and high chemical oxygen demand (COD) (20,000–90,000 mgO_2 L^{-1})

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[9] because the main components are acrylic acid, formaldehyde, acetic acid, methacrylic acid and acetaldehyde [9,10]. Therefore, detrimental effects of the wastewater and residue on environment and human health will be aroused if the wastewater and residue lack proper treatment.

It has been reported that the main disposal methods of acrylic acid and ester production wastewater and residue mainly include biological process [11,12], incineration [13,14], supercritical water oxidation [10,15], wet catalytic oxidation [16,17] and advanced oxidation techniques (AOPs) [18,19]. The biological treatment often has a large installation area, a long processing cycle and low efficiency. The incineration method operated at high temperature can reduce the secondary pollution but lead to high operating cost due to the high energy consumption. The supercritical water oxidation technology requires a special reactor to resist high pressure and corrosion. The harsh operation conditions, precious metal oxidants, and long residence time increase the cost of wet catalytic oxidation process. The purification performance of single AOPs is poor, although the operating temperature and pressure are modest. Overall, it is difficult to reduce the treatment cost of acrylic acid and ester production wastewater and residue under the premise of the high treatment efficiency.

The main problem in the existing high-efficient treatment of acrylic acid production wastewater and distillation residue is high energy consumption. The energy consumed in China's wastewater treatment for one year is 1×10^{11} kWh, and it consumes approximately 4% of all electrical power produced in the United States [20]. In recent years, there have been various studies on the energy balance of high calorific value waste treatment devices [21,22]. For example, Jimenez-Espadafor et al. [23] studied the supercritical water oxidation of oily wastes at pilot plant to recover the energy. The recovery of waste heat was between 71% and 45.6% of the energy content of the organic compound, which can be considered as a high thermal efficiency. Ding and Jiang used the co-pyrolysis of sludge and waste biomass such as sawdust and rice husk to treat sludge, and high calorific value oil was produced during the process, which can be used as an energy source during the co-pyrolysis. This process can achieve self-heating when the feed mass fractions of sawdust and rice husk were 49.6% and 74.75%, respectively [24]. The anaerobic digestion of food waste was treated by Tampio et al. [25] to produce liquid fertilizer. Meanwhile, the biogas from the waste was used to generate electricity and heat, and the energy conversion efficiencies for electricity and heat were 38% and 48% in the system of anaerobic digestion plant. The use of high calorific value waste in industrial installations to achieve an energy balance of the purification plant is feasible and economical. It will provide us with a new idea for simultaneous treatment of acrylic acid (ester) production wastewater and residue using the characteristics of high calorific value of residue, so as to achieve the energy balance.

The distillation residue and wastewater are both oxidizable organic pollutants, and gaseous phase is the most easily oxidized phase. Catalytic oxidation has attracted great attention for the investigation organic pollutants purification [26–28] due to the advantages of simple process and low energy consumption [29]. The energy released by oxidation of pollutants can be employed to the transformation of pollutants from liquid phase to gaseous phase in the process of simultaneous treatment of wastewater and residue. In this work, a simultaneous treatment of acrylic acid and ester production wastewater and residue was carried out by a novel two-stage fluidized-bed/fixed-bed catalytic system [30]. The effects of fluidized-bed temperature, flow rates of wastewater or residue and oxygen excess rate (OER) on COD of outlet water and volatile organic compounds concentration (VOC) of the emission gas were investigated to certify the feasibility of the simultaneous treatment of acrylic acid (esters) production wastes. By utilizing the high calorific value of residue, the energy balance of the system can be achieved by adjusting the flow rates of wastewater and residue while guaranteeing the treatment efficiency, which was confirmed by the theoretical simulation.

2. Experiments and simulation

2.1. Experimental section

2.1.1. Materials

The main components of the acrylic wastewater and acrylate distillation residue are acrylic acid and polymer of acrylate. Therefore, the acrylic acid and acrylic resin (polymethyl methacrylate) were chosen as the objects of acrylic acid production wastewater and distillation residue in this study. Acrylic acid was bought from Jinan Hongxin Chemical Co. Ltd., (Zibo, Shandong Province, China) and acrylic resin was obtained from China Petroleum and Chemical Corporation (Nanjing, Jiangsu Province, China). The acrylic acid production wastewater was prepared by the mixture of acrylic acid and water, and the COD was normally between 20,000–90,000 mgO_2 L^{-1}. The acrylic resin was dissolved in a mixed solution consisting of *n*-butanol, ethylene glycol and isopropanol.

2.1.2. Equipment

The schematic diagram of the two-stage fluidized-bed/fixed-bed experimental apparatus used for the experiment is illustrated in Fig. 1. The fluidized-bed reactor is 30 mm in diameter and 610 mm high. The Cu/K/Ce catalyst of 26 g was used in the fluidized-bed, and its particle size distributed from 110 to 170 meshes [31,32]. The catalyst applied in fluidized-bed had both pyrolytic active component and oxidized active component, which enables it to have catalytic cracking and catalytic oxidation functions. In addition, it could greatly reduce the toxic gases containing ester groups and increase the rate of carbon dioxide formation. The fixed-bed reactor is 36 mm in diameter and 380 mm length. The copper-based composite oxide catalyst of 32 g was used, and its particle size distributes from 5 to 10 mesh. The copper species on the catalyst surface are highly dispersed, which leads to high catalytic oxidation activity because of high oxygen vacancy concentration on the catalyst surface. These two catalysts used in the experiment were provided by Nanjing TOP Chemical Co. Ltd., (Nanjing, Jiangsu Province, China). In our hypothesis, the thermos-oxidative pyrolysis [33] and catalytic oxidation of the residue occurred in fluidized-bed. Macromolecular substances were cracked into
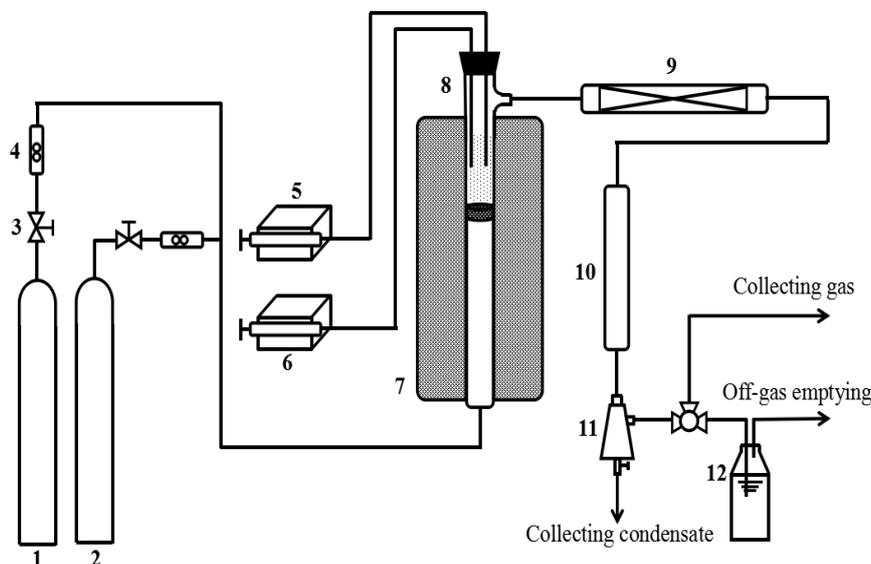
Fig. 1. Schematic diagram of purification equipment. 1. Nitrogen cylinder, 2. Oxygen cylinder, 3. Pressure reducing valve, 4. Mass flowmeter, 5. Acrylic acid production wastewater syringe pump, 6. Acrylic ester residue syringe pump, 7. Heating furnace, 8. Fluidized-bed reactor, 9. Fixed-bed reactor, 10. Condenser, 11. Gas-liquid separator, 12. Absorption bottle.

small molecules, and most of them were oxidized into CO_2 and H_2O. The rest was further oxidized in fixed-bed. On the basis of catalysis in the single stage fluidized-bed reactor, the second staged fixed-bed introduced for deep oxidation makes the treatment of the organic pollutants were treated more thoroughly [30], which also allows the energy contained in organics to be released and utilized more completely. On the other hand, the operation temperature of catalytic oxidation reactor is low compared with that of thermal oxidation [34]. Therefore, this process has lower energy consumption. During the purification process, the acrylic ester residue gives off a lot of heat, and the acrylic acid production wastewater transferred excess heat to keep the reactor in an appropriate temperature. Suitable flow rates of residue and wastewater can make the treatment at thermal balance in the homeostatic process. The residue and wastewater were continuously fed near the top of the bed using measuring pump, and gas was fed near the bottom of the bed. Some preliminary experiments were carried out to determine the necessary gas flow for the fluidization under the operating conditions of our experiments. The total gas flow rate was kept at 500 mL min^{-1}. Then, gases after the fluidized-bed/fixed-bed were condensed into liquid and non-condensable gases in gas-liquid separator. Finally, the non-condensable gases were collected by gas sample bag, and the VOC of off-gas was measured by SP-6890 gas chromatography (Shandong LuNan RuiHong chemical instruments Co. Ltd., (Zaozhuang, Shandong Province, China)). The COD of condensate was measured by a COD rapid digestion apparatus 6B-200 (Jiangsu ShengAoHua Environment Protection Technology Co. Ltd., (Changzhou, Jiangsu Province, China)).

2.1.3. Simulation

It is generally impossible to realize the self-heating of the reactor in our laboratory test no matter what kind of

heat preservation method adopted because of the high heat loss of the reactor and little heat generation. Therefore, it is necessary to estimate the energy balance by simulation under the experimental operation conditions.

2.1.4. Calculation of OER

Oxygen consumption (OC, g h^{-1}) of acrylic acid production wastewater can be obtained based on COD value as below, V_{wwt} (mL h^{-1}) represents wastewater flow.

$$OC_{wwt} = \frac{V_{wwt} \times COD}{1000} \tag{1}$$

COD is defined as the amount of oxygen consumed by oxidizing reducing substances in 1 L water sample. Therefore, the OC_{wwt} can be obtained according to the V_{wwt}.

OC of various substances in mixed solution can be obtained according to their constitution of carbon, hydrocarbon and oxygen. The oxidation reaction of organics is given by Eq. (2):

$$C_n H_m O_p + \frac{2n + 0.5m - p}{2} O_2 = nCO_2 + \frac{m}{2} H_2O \tag{2}$$
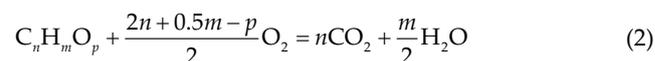
The mass fraction of acrylic resin, *n*-butanol, ethylene glycol and isopropanol in mixed solution are 45%, 15%, 35% and 5%. According to Eq. (2), the oxygen consumption per mole of acrylic resin, *n*-butanol, ethylene glycol and isopropanol are 19/2, 6, 5/2 and 9/2 mol g^{-1}. Therefore, OC of various substances in mixed solution which can be calculated by Eq. (3):

$$OC_{res} = V_{res} \times \rho_{res} \times \left(\frac{45\%}{174} \times \frac{19}{2} + \frac{15\%}{74} \times 6 + \frac{35\%}{62} \times \frac{5}{2} + \frac{5\%}{60} \times \frac{9}{2} \right) \times 32 \tag{3}$$

V_{res} (mL h⁻¹) represents residue; ρ_{res} (0.883 g mL⁻¹) denotes the density of acrylic ester residue.

The OC_{tot} (total oxygen consumption) can be calculated by Eq. (4). Oxygen supply (OS) is constant at certain oxygen feed rate, which can be calculated by Eq. (5). The OER is affected by the residue and wastewater flow flows, which represent the ratio of surplus oxygen to oxygen demand for complete oxidation of the organic pollutants; it was given by Eq. (6):

$$OC_{tot} = OC_{wwt} + OC_{res} \tag{4}$$

$$OS = \frac{V_{oxy}}{V_m} \times 32 \tag{5}$$

$$OER = \frac{OS - OC_{tot}}{OC_{tot}} \tag{6}$$

V_{oxy} denotes the oxygen flow rate (L h⁻¹); V_m represents molar volume of gas (22.4 L mol⁻¹).

2.1.5. Thermal balance

In this system, air and wastewater absorb heat, while the residue releases heat. When the heat absorbed by the system is equal to the heat released, thermal balance can be established by Eq. (7).

$$Q_{air} + Q_{wwt} = Q_{res} \tag{7}$$

Q_{res} (kJ h⁻¹), Q_{air} (kJ h⁻¹) and Q_{wwt} (kJ h⁻¹) denote the amount of heat produced from the catalytic oxidation of distillation residue, heat required for gas heating, and heat required for wastewater heating, respectively. The fluidized-bed reactor can be considered as the isothermal operation system, and the excess heat can be removed timely.

The heat produced from the catalytic oxidation of residue Q_{res} can be calculated in Eq. (8).

$$Q_{res} = H_{res} \times \rho_{res} \times V_{res} \tag{8}$$

H_{res} (30,800 kJ kg⁻¹, determined by calorimeter) represents the combustion heat of distillation residue. There are only a small number of organic compounds left after treatment, so the heat released by their oxidation can be ignored. The residue can be considered to be decomposed completely during the calculation of the released heat of residue.

Heat required for air heating can be calculated in Eq. (9). Since the heat capacity of the gas changes significantly with the change of temperature, the product of the heat capacity and the temperature change amount is expressed as an integral formula of the heat capacity in a certain temperature range. The same treatment is applied to water vapor in Eq. (10).

$$Q_{air} = \frac{V_{air}}{V_m} \times \int_{T_0}^{T_{flu}} C_{air} dT \times 10^{-3} \tag{9}$$

T_{flu} (K) and T_0 (K) represent fluidized-bed temperature and feed temperature in the fluidized-bed, respectively.

Air heat capacity C_{air} (J mol⁻¹ K⁻¹) can be calculated as follows, $C_{air} = 27.50 + 6.241 \times 10^{-3} \times T - 0.9080 \times 10^{-6} \times T^2$.

Due to the low content of organics in the wastewater, the flow rate of wastewater entering the system is regarded as the same flow rate of water. Heat required for wastewater heating can be calculated in Eq. (10), and every item in Eq. (10) represents heat of vaporization, heat absorbed by liquid water with the change of temperature, heat absorbed by water vapor with the change of temperature and heat release of organics oxidation in turn.

$$Q_{wwt} = r_{wat} \times \rho_{wat} \times V_{wwt} + C_{p_{wat}} \times \rho_{wat} \times V_{wwt} \times (T_{100} - T_0)$$
$$+ \frac{\rho_{wat} \times V_{wwt}}{M_{wat}} \times \int_{T_{100}}^{T_{flu}} C_{vap} dT - H_{COD} \times COD \times 10^{-3} \times V_{wwt} \tag{10}$$

r_{wat} (2,257.6 kJ kg⁻¹) is the latent heat of water; ρ_{wat} (1,000 kg m⁻³) denotes the density of wastewater; $C_{p_{wat}}$ (kJ kg⁻¹ K⁻¹) is the heat capacity of water; M_{wat} (18 g mol⁻¹) denotes the molar mass of water; C_{vap} (J mol⁻¹ K⁻¹) represents heat capacity of water vapor, it can be calculated as follows, $C_{vap} = 29.16 + 14.49 \times 10^{-3} \times T - 2.022 \times 10^{-6} \times T^2$. Energy contained in acrylic acid production wastewater can be calculated according to the value of COD. Most organics will release about 14 kJ while consuming 1 g oxygen when they are oxidized [35,36], so it is recorded as H_{COD} (14 kJ g⁻¹) in the Eq. (10).

The simulation method is based on the energy balance model established by Eqs. (7)–(10). The temperature and OER were calculated by adjusting wastewater and residue flow rates, and another steady state operation under thermal equilibrium would be obtained when the operation conditions were changed. In addition, it was assumed in this simulation that the organic materials were completely oxidized in the outlet gas and the heat loss was ignored.

The flow rate of air and residue were maintained at 500 mL min⁻¹ and 2 mL h⁻¹, and the flow rate ratio of wastewater (20,000–90,000 mgO₂ L⁻¹) to residue was calculated under the temperature from 300°C to 420°C. For the simulation of the control of OER, the air flow rate was set at 500 mL min⁻¹, and the temperature was set at 380°C. The flow rate of wastewater (20,000–90,000 mgO₂ L⁻¹) was calculated by changing the residue flow rate from 1.5 to 3.5 mL h⁻¹.

3. Results and discussion

3.1. Influence factors of purification effect

3.1.1. Effect of temperature

The effect of fluidized-bed temperature on the COD of outlet water and the VOC of off-gas is investigated in Fig. 2. The acrylic acid production wastewater and acrylic ester residue flow rates were kept at 5 and 2 mL h⁻¹. Oxygen and nitrogen flow rates were also maintained at 105 and 385 mL min⁻¹, respectively. It can be seen from Fig. 2 that the COD decreased sharply from 320°C to 380°C, while it decreased slowly after 380°C. It could be considered that high temperature was more beneficial for the purification, but the function of temperature on the reduction of COD was less obvious at a high temperature. The VOC data displayed the same trend, which first decreased sharply and then slowly with the increase of temperature. The VOC was
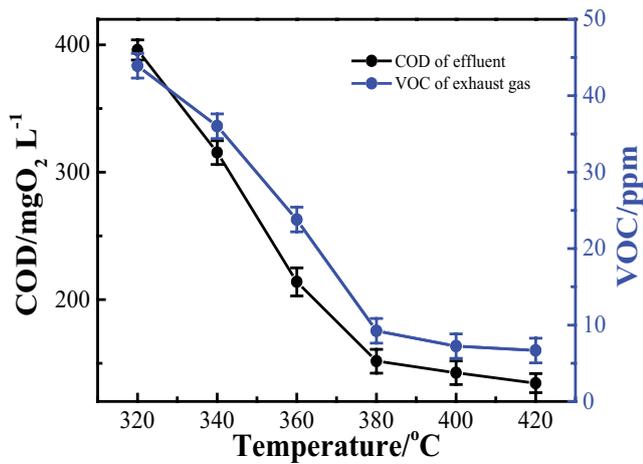
Fig. 2. Effect of fluidized-bed temperature on the acrylic acid (ester) production wastewater and residue purification.

always lower than 50 ppm. Among several thermodynamic methods, incineration was used to treat distillation residue at temperatures above 1,000°C [37], and supercritical water oxidation was used to treat acrylic acid production wastewater at temperatures between 400°C–500°C [10,15]. Comparatively speaking, the temperature of the catalytic oxidation method used in this study is lower than 400°C, and the heat source is the distillation residue with high calorific value under steady-state operation. From the point of view of the reactor requirements and long-term operation, the catalytic oxidation method with lower operating temperature in this paper is more advantageous.

3.1.2. Effect of flow rate of wastewater and residue

The different acrylic ester residue flow rate (1, 1.5, 2, 2.5 and 3 mL h^{-1}) and acrylic acid production wastewater flow rate (3, 4, 5, 6 and 7mL h^{-1}) were performed to investigate

their effects on the COD of effluent and VOC of exhaust gas in Fig. 3. The oxygen fraction in gas feed was changed to ensure that OER was constant at 1.9 under different conditions. It can be seen from Fig. 3a that the COD value of condensate decreased from 306.5 to 23.96 mgO$_2$ L^{-1} as residue flow rate decreased from 3 to 1 mL h^{-1} when the flow rate of wastewater was 5 mL h^{-1}. It indicates that lower air-speed is more beneficial to the treatment of pollutants [38]. The COD decrease in the purification process was because the residence time was much longer at lower flow rate and pollutants were decomposed more thoroughly. When the residue flow rate was kept at 3 mL h^{-1} and the wastewater flow rate increased from 3 to 7 mL h^{-1}, the COD of outlet water decreased from 386.0 to 264.4 mgO$_2$ L^{-1}. Generally speaking, the treatment efficiency will decrease as the contaminant flow rate increases [39], but it can be noticed that organics concentration in the wastewater with higher flow rate was lower. It is shown from Table 1 that the theoretical calculation of outlet condensate increased from 6.83 to 10.83 mL h^{-1}, leading to the additional residual organics amount increased from 2.63 to 2.86 mgO$_2$ h^{-1} as the wastewater flow rate increased from 3 to 7 mL h^{-1}.

As shown in Fig. 3b, VOC of off-gas was always lower than 25 ppm at 380°C when OER was 1.9. VOC decreased from about 24 to 3 ppm gradually with the decrease of residue flow rate, while it had a little change under different wastewater flow rate.

3.1.3. Effect of OER

The oxygen flow rate of 36, 72, 108, 144 and 180 mL min^{-1} (the rest gas was nitrogen, and the total flow rate was kept at 500 mL min^{-1}) was performed to investigate the effect of OER (0–4) on the purification at 380°C in Fig. 4. The flow rates of acrylic acid production wastewater and acrylic ester residue were maintained at 5 and 1.5 mL h^{-1}. It can be seen from Fig. 4 that the COD of effluent decreased gradually with the increase of OER. The increase of the proportion of oxygen
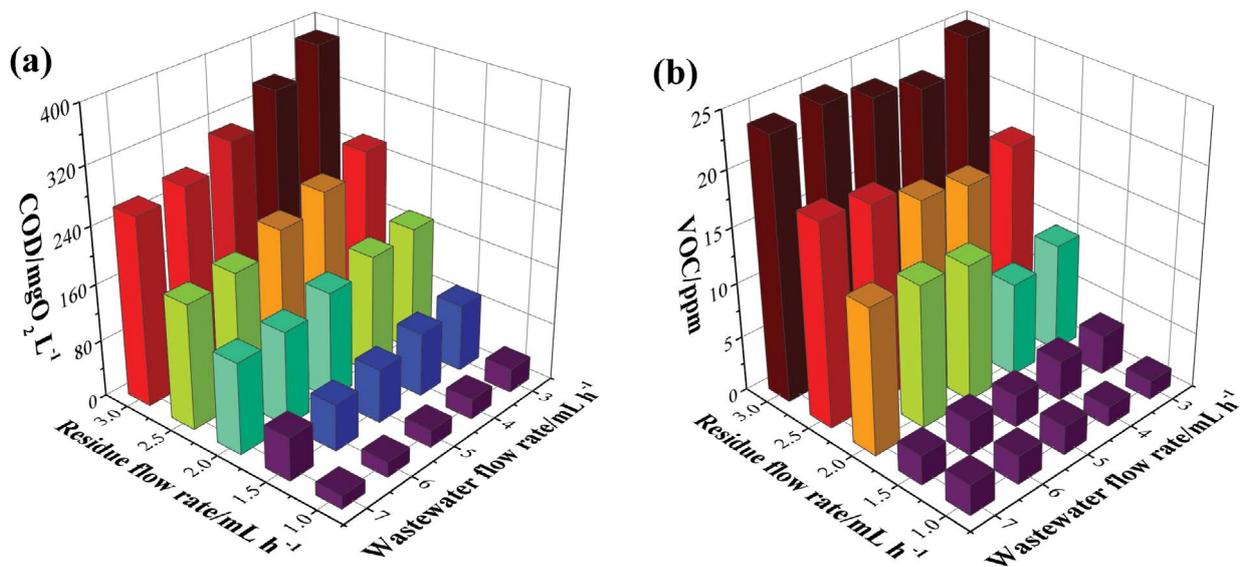
Fig. 3. Effect of flow rate on the acrylic acid (ester) production wastewater and residue purification.

Table 1
COD with different wastewater flow rate

V_{res}/mL h^{-1}	V_{wwt}/mL h^{-1}	COD/mgO$_2$ L^{-1}	Q_{eff}/mL h^{-1}	COD × Q_{eff}/mgO$_2$ h^{-1}
3	3	386.0	6.83	2.63
3	4	347.7	7.83	2.72
3	5	306.5	8.83	2.70
3	6	282.2	9.83	2.77
3	7	264.4	10.83	2.86
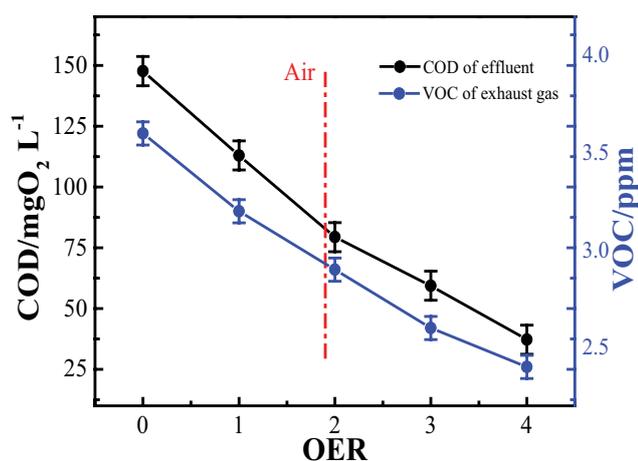
Fig. 4. Effect of OER on the acrylic acid (ester) production wastewater and residue purification.

in the gas feed decreased the COD of condensate obviously. Generally speaking, the increase of oxygen ratio is indeed more advantageous to the oxidation process [40]. When the fraction of oxygen in the gas feed was the same as that in air, and OER was 1.9. Under the above conditions, the COD value of effluent was lower than 100 mgO$_2$ L^{-1}. Therefore, air can be used to treat wastewater and residue based on the economic problem.

3.2. Simulation of temperature and OER control based on energy balance

3.2.1. Reaction temperature

By controlling the acrylic ester residue and acrylic acid production wastewater flow rates to change the temperature of the reactor, it is clear that the OER will also change at the same time. The influence of flow rate on the self-heating reactor is various and needs comprehensive consideration. The impact of wastewater flow rate on the purification effect was much smaller than temperature according to the results of the experiment. On the other hand, there is much more organic matter in the residue than that in the wastewater. Therefore, the wastewater flow rate has little effect on the OER. The temperature control was simulated by keeping residue flow rate constant, and the key point to consider is the change of temperature.

The flow rate ratio of the wastewater to residue can affect the steady-state operating temperature. Feeds of air

and residue were maintained at 500 mL min^{-1} and 2 mL h^{-1}, respectively. Temperature regulation was studied by calculating the flow rate ratio of wastewater with different COD values to residue under different temperature; the whole results are given by Fig. 5. Taking wastewater with 20,000 mgO$_2$ L^{-1} as an example, when the requisite temperature increased from 320°C to 420°C, the required flow rate ratio decreased from 2.805 to 1.895. As a result, for the same batch of wastewater (with the same COD value), when higher operating temperature is required to achieve better purification effect, the flow rate ratio of wastewater to residue should be reduced to maintain the system's self-heating at higher temperature.

As mentioned earlier, the COD of wastewater has a certain influence on the regulation of temperature under energy balance. Flow rate ratio of wastewater with different COD values to residue was calculated at 380°C, when COD of wastewater increased from 20,000 to 90,000 mgO$_2$ L^{-1}, it can be known from Fig. 5 that the ratio increased from 2.25 to 3.42. Therefore, if keeping reactor at a designed temperature, for the wastewater with higher COD value, handling capacity of the wastewater with higher COD value will increase when the residue flow rate remains constant.
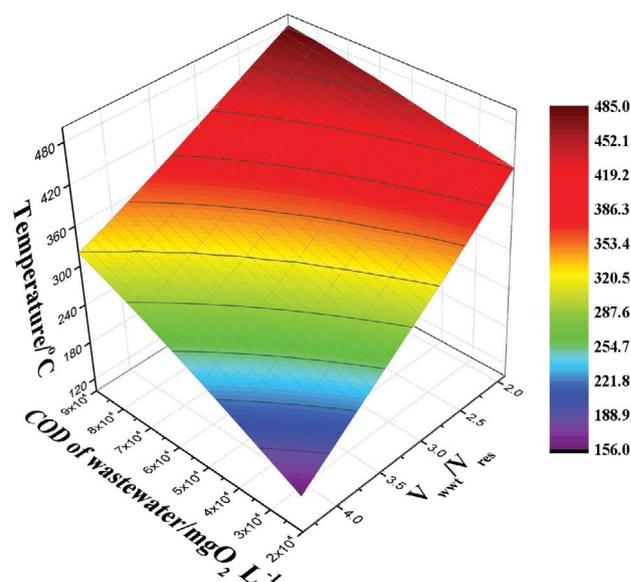
Fig. 5. Effect of feed low rate of acrylic acid (ester) production wastewater with different COD values to residue on the fluidized-bed temperature.

3.2.2. Oxygen excess rate

The presence of oxygen is beneficial to the decomposition of organics, and the required oxygen is usually more than that by theoretical calculation for the purpose of the complete decomposition of the organics [40,41]. The OER will change accordingly when the flow rate of pollutants is changed. The air flow rate was set at 500 mL min^{-1}, and temperature was set at 380°C. The flow rate of acrylic acid production wastewater (COD between 20,000 to 90,000 mgO$_2$ L^{-1}) was calculated in turn with residue flow rate changed from 1.5 to 3.5 mL h^{-1}, the complete simulation result was obtained by Fig. 6. For instance, residue, air and wastewater flow rates were matched to make the reactor in a state of heat balance when residue flow rate was kept at 1.5 mL h^{-1}. It was shown that OER decreased from 1.98 to 1.75 while COD of wastewater increased.

If the COD value of the wastewater is kept constant, taking 20,000 mgO$_2$ L^{-1} wastewater for an example, as shown in Fig. 6, when the residue flow rate increased from 1.5 to 3.5 mL h^{-1}, the OER decreased from 1.98 to 0.25. OER is more affected by different residue flow rate than wastewater, this is because the amount of oxygen consumed by the complete oxidation of organics in residue is much greater compared to wastewater with the same volume.

The smaller the residue flow rate, the larger the OER. When adjusting the OER to make it favorable for catalytic pyrolysis and oxidation, the reduction of wastewater and residue flow rates is also beneficial to the purification process. However, there is a limit to the reduction of residue flow rate. Heat transfer process exists between the reactor and the outside world, a sufficient amount of residue flow rate should be ensured in order to compensate the heat loss and make the reactor remain self-heat balance. On the other hand, oversized OER is also unnecessary, which will reduce the amount of treatment.

3.2.3. Industrial application of the two-stage fluidized-bed/fixed-bed system

Fig. 7 shows the process of combined treatment of wastewater and distillation residue. The chemical energy in the residue is squandered with solid waste in conventional pathway [20]. In contrast, in the sustainable pathway, most of the chemical energy from distillation residue is effectively utilized by our novel treatment. In addition to pumps, fans and other equipment needing the input of conventional electrical energy, the fluidized-bed only relies on the energy released by the oxidation of organic pollutants to maintain
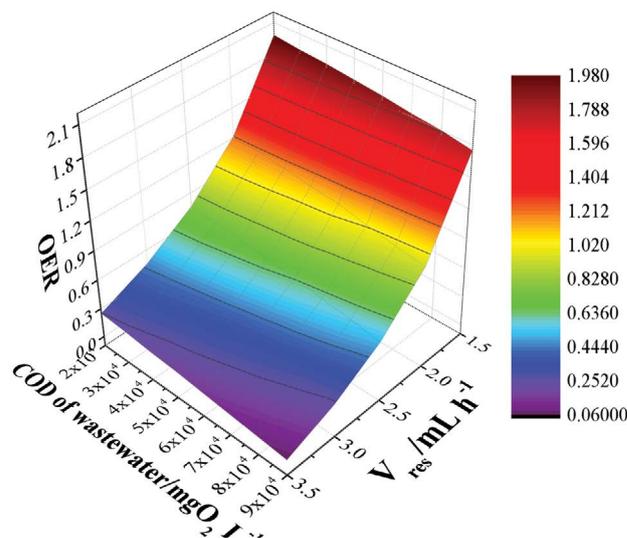
Fig. 6. Effect of acrylic acid (ester) production wastewater with different COD values and residue flow rate on the OER.
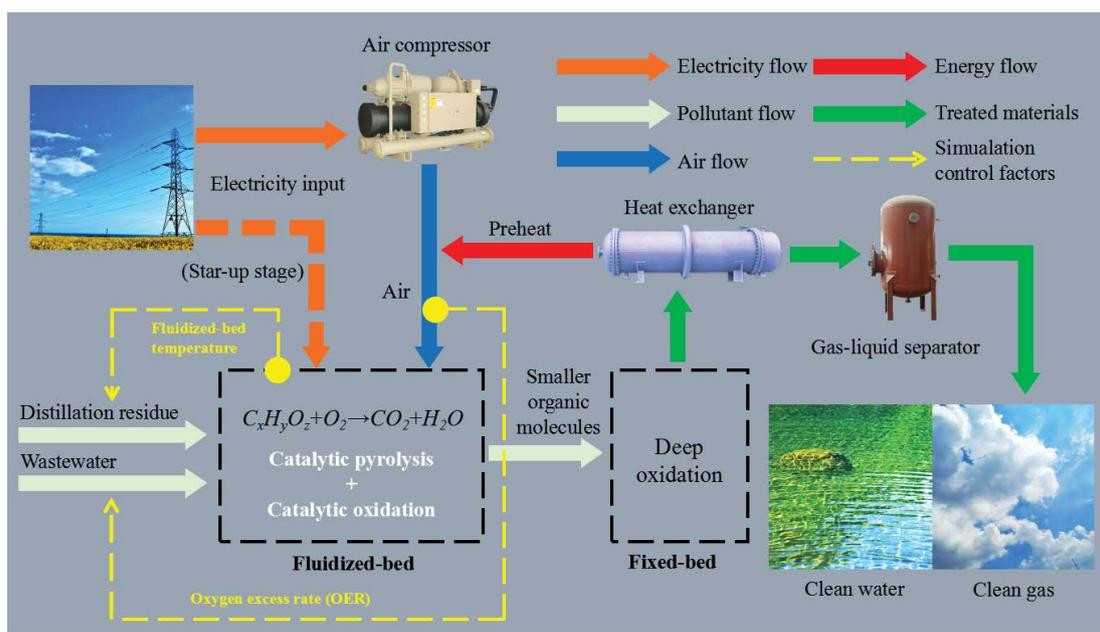
Fig. 7. Illustration of the purification technological process and the control factors.

thermal balance after the stable operation. And before the vapor-liquid separation, the feed is preheated by the heat exchanger at the outlet of the two-stage fluidized-bed/ fixed-bed catalytic system, which reduces part of the energy consumption. On the other hand, the extra energy provides more energy for the vaporization of wastewater and increases the wastewater throughput [24]. The yellow dotted line represents the factors that are controlled. By adjusting the flow rate of wastewater and residue, making the OER and temperature are as beneficial as possible to the removal of pollutants while ensuring a certain amount of treatment.

4. Conclusion

This study shows that it is a feasible strategy to treat acrylic acid production wastewater and distillation residue simultaneously by gas-solid catalytic oxidation. The COD of effluent was less than 100 $mgO_2 L^{-1}$, and the VOC of exhaust gas was always less than 100 ppm during the process. The treatment effect had been significantly improved with the increase of temperature, but the function of temperature was gradually weakened after 380°C. The reduction of distillation residue and wastewater flow rates was also beneficial to reducing the concentration of organics in effluent and off-gas. On the other hand, the COD and VOC values were also satisfactory when the oxygen concentration in gas feed satisfies that in air, which indicates that the process can use cheap and easily available air as oxidant. In the practical process, the control of temperature and OER fundamentally depended on residue and wastewater flow rates. The process conditions should be adjusted to ensure a good treatment performance under a relatively large throughput. According to the results of simulation, the flow rate ratio of wastewater to residue determines the temperature of reactor. OER increased with the decrease of wastes flow rates. For high calorific solid waste and exhaust gas, a similar approach may be used to treat it with wastewater to relieve the burden of energy consumption caused by environmental protection issues.

Acknowledgements

References

[1] U. Hasan, Investigation of acrylic acid extractability from aqueous solution using tridodecyl amine extractant, Desal. Wat. Treat., 28 (2011) 189–195.

[2] A.T. Owen, P.D. Fawell, J.D. Swift, The preparation and ageing of acrylamide/acrylate copolymer flocculant solutions, Int. J. Miner. Process., 84 (2007) 3–14.

[3] J. Hu, J. Ma, W. Deng, Synthesis of alkali-soluble copolymer (butyl acrylate/acrylic acid) and its application in leather finishing agent, Eur. Polym. J., 44 (2008) 2695–2701.

[4] S. Thamizharasi, G. Srinivas, N. Sulochana, B.S.R. Reddy, Copolymerization of 4-chlorophenyl acrylate with methyl acrylate: synthesis, characterization, reactivity ratios, and their applications in the leather industry, J. Appl. Polym. Sci., 73 (1999) 1153–1160.

[5] E. Princi, S. Vicini, E. Pedemonte, V. Arrighi, I.J. McEwen, New polymeric materials for paper and textiles conservation. II. Grafting polymerization of ethyl acrylate/methyl methacrylate copolymers onto linen and cotton, J. Appl. Polym. Sci., 103 (2007) 90–99.

[6] J. Kadar, N. Heene-Würl, S. Hahn, J. Nagengast, M. Kehrer, N. Taccardi, D. Collias, P. Dziezok, P. Wasserscheid, J. Albert, Acrylic acid synthesis from lactide in a continuous liquid-phase process, ACS Sustainable Chem. Eng., 7 (2019) 7140–7147.

[7] K.I. Suresh, M. Jaikrishna, Synthesis of novel crosslinkable polymers by atom transfer radical polymerization of cardanyl acrylate, J. Polym. Sci., Part A: Polym. Chem., 43 (2005) 5953–5961.

[8] J.S.F. Pereira, P.A. Mello, F.A. Duarte, M. de Fátima P. Santos, R.C.L. Guimarães, G. Knapp, V.L. Dressler, É.M.M. Flores, Feasibility of microwave-induced combustion for digestion of crude oil vacuum distillation residue for chlorine determination, Energy Fuels, 23 (2009) 6015–6019.

[9] A. Li, N. Dong, M. He, T. Pan, Evaluation of performance in a combined UASB and aerobic contact oxidation process treating acrylic wastewater, Environ. Technol., 36 (2015) 807–814.

[10] Y.M. Gong, S.Z. Wang, X.Y. Tang, D.H. Xu, H.H. Ma, Supercritical water oxidation of acrylic acid production wastewater, Environ. Technol., 35 (2014) 907–916.

[11] U. Durán, O. Monroy, J. Gómez, F. Ramírez, Biological wastewater treatment for removal of polymeric resins in UASB reactor: influence of oxygen, Water Sci. Technol., 57 (2008) 1047.

[12] C.C. Wang, C.M. Lee, A.S. Wu, Acrylic acid removal from synthetic wastewater and industrial wastewater using Ralstonia solanacearum and Acidovorax avenae isolated from a wastewater treatment system manufactured with polyacrylonitrile fiber, Water Sci. Technol., 60 (2009) 3011.

[13] L. Tao, G. Zhao, R. Sun, Q. Wang, Combustion characteristics of particles of hazardous solid waste mixtures in a fixed bed, J. Hazard. Mater., 181 (2010) 305–314.

[14] L. Zhou, X. Jiang, J. Liu, Characteristics of oily sludge combustion in circulating fluidized beds, J. Hazard. Mater., 170 (2009) 175–179.

[15] W. Gong, F. Li, D. Xi, Supercritical water oxidation of acrylic acid production wastewater in transpiring wall reactor, Environ. Eng. Sci., 26 (2009) 131–136.

[16] K. Kim, S. Ihm, Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review, J. Hazard. Mater., 186 (2011) 16–34.

[17] L. Oliviero, J. Barbier Jr., D. Duprez, A. Guerrero-Ruiz, B. Bachiller-Baeza, I. Rodríguez-Ramos, Catalytic wet air oxidation of phenol and acrylic acid over Ru/C and Ru–CeO$_2$/C catalysts, Appl. Catal., B, 25 (2000) 267–275.

[18] J. Wei, Y. Song, X. Meng, J.-S. Pic, Optimization and analysis of homogenous Fenton process for the treatment of dry-spun acrylic fiber manufacturing wastewater, Desal. Wat. Treat., 56 (2015) 3036–3043.

[19] Z.-w. Wu, X.-c. Xu, H.-b. Jiang, R.-y. Zhang, S.-n. Song, C.-q. Zhao, F.-l. Yang, Evaluation and optimization of a pilot-scale catalytic ozonation–persulfate oxidation integrated process for the pretreatment of dry-spun acrylic fiber wastewater, RSC Adv., 7 (2017) 44059–44067.

[20] P. Yan, R.-c. Qin, J.-s. Guo, Q. Yu, Z. Li, Y.-p. Chen, Y. Shen, F. Fang, Net-zero-energy model for sustainable wastewater treatment, Environ. Sci. Technol., 51 (2016) 1017–1023.

[21] M. Bermejo, F. Cantero, M. Cocero, Supercritical water oxidation of feeds with high ammonia concentrations: pilot plant experimental results and modeling, Chem. Eng. J., 137 (2008) 542–549.

[22] C. Bouted, C. Ratanatamskul, Effects of temperature and HRT on performance of a novel insulated anaerobic filter (IAF) system incorporated with the waste heat input for building wastewater treatment, J. Environ. Manage., 206 (2018) 698–706.

[23] F. Jimenez-Espadafor, J.R. Portela, V. Vadillo, J. Sánchez-Oneto, J.A.B. Villanueva, M.T. García, E.J.M. de la Ossa, Supercritical water oxidation of oily wastes at pilot plant: simulation for energy recovery, Ind. Eng. Chem. Res., 50 (2011) 775–784.

[24] H. Ding, H. Jiang, Self-heating co-pyrolysis of excessive activated sludge with waste biomass: energy balance and sludge reduction, Bioresour. Technol., 133 (2013) 16–22.

[25] E. Tampio, S. Ervasti, T. Paavola, S. Heaven, C. Banks, J. Rintala, Anaerobic digestion of autoclaved and untreated food waste, Waste Manage., 34 (2014) 370–377.

[26] Z. Xu, S. Deng, Y. Yang, T. Zhang, Q. Cao, J. Huang, G. Yu, Catalytic destruction of pentachlorobenzene in simulated flue gas by a V_2O_5–WO_3/TiO_2 catalyst, Chemosphere, 87 (2012) 1032–1038.

[27] Y. Fan, X. Lu, Y. Ni, H. Zhang, M. Zhu, Y. Li, J. Chen, Catalytic destruction of chlorinated aromatic pollutants over mesoporous $Cu_xMg_{1-x}Al_2O_4$ spinel oxides, Appl. Catal., B, 101 (2011) 606–612.

[28] J. Lichtenberger, M.D. Amiridis, Catalytic oxidation of chlorinated benzenes over V_2O_5/TiO_2 catalysts, J. Catal., 223 (2004) 296–308.

[29] D. Jecha, V. Brummer, P. Lestinsky, J. Martinec, P. Stehlik, Effective abatement of VOC and CO from acrylic acid and related production waste gas by catalytic oxidation, Clean Technol. Environ. Policy, 16 (2014) 1–10.

[30] Q. Liu, R. Chen, M. Zeng, Z. Fei, X. Chen, Z. Zhang, J. Tang, M. Cui, X. Qiao, High-efficiency treatment of benzaldehyde residue using two-stage fluidized-bed/fixed-bed catalytic system, Environ. Technol., (2019) doi: 10.1080/09593330.2019.1588382.

[31] X. Chen, X. Xu, Z. Fei, X. Xie, J. Lou, J. Tang, M. Cui, X. Qiao, CeO_2 nanodots embedded in a porous silica matrix as an active yet durable catalyst for HCl oxidation, Catal. Sci. Technol., 6 (2016) 5116–5123.

[32] Y. Dai, Z. Fei, X. Xu, X. Chen, J. Tang, M. Cui, X. Qiao, Oxygen consumption rate model in HCl oxidation over a supported CuO-CeO_2 composite oxide catalyst under lean oxygen condition, Can. J. Chem. Eng., 94 (2016) 1140–1147.

[33] V.F. Shvets, V.N. Sapunov, R.A. Kozlovskiy, A.I. Luganskiy, A.V. Gorbunov, F.S. Sovetin, T.N. Gartman, Cracking of heavy oil residues in a continuous flow reactor, initiated by atmospheric oxygen, Chem. Eng. J., 329 (2017) 275–282.

[34] L. Matejová, P. Topka, K. Jirátová, O. Solcová, Total oxidation of model volatile organic compounds over some commercial catalysts, Appl. Catal., A, 443 (2012) 40–49.

[35] I. Shizas, D.M. Bagley, Experimental determination of energy content of unknown organics in municipal wastewater streams, J. Energy Eng., 130 (2004) 45–53.

[36] E.S. Heidrich, T.P. Curtis, J. Dolfing, Determination of the internal chemical energy of wastewater, Environ. Sci. Technol., 45 (2011) 827–832.

[37] G. Mininni, A. Sbrilli, E. Guerriero, M. Rotatori, Dioxins and furans formation in pilot incineration tests of sewage sludge spiked with organic chlorine, Chemosphere, 54 (2004) 1337–1350.

[38] G.A. Jiang, Y. Zhao, B.Z. Li, H.S. Guo, Treatment of acid brilliant scarlet dye wastewater by ozone catalytic oxidation over activated carbon-based catalyst, Mod. Chem. Ind., 38 (2018) 124–127.

[39] X. He, M. Chen, R. Chen, X. Zhu, Q. Liao, D. Ye, B. Zhang, W. Zhang, Y. Yu, A solar responsive photocatalytic fuel cell with the membrane electrode assembly design for simultaneous wastewater treatment and electricity generation, J. Hazard. Mater., 358 (2018) 346–354.

[40] R.M. Serikawa, T. Usui, T. Nishimura, H. Sato, S. Hamada, H. Sekino, Hydrothermal flames in supercritical water oxidation: investigation in a pilot scale continuous reactor, Fuel, 81 (2002) 1147–1159.

[41] B.K. Gullett, K. Raghunathan, Observations on the effect of process parameters on dioxin/furan yield in municipal waste and coal systems, Chemosphere, 34 (1997) 1027–1032.