Selection of sustainable technologies for reducing emission of volatile organic compounds and greenhouse gases

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Abstract

Selection of sustainable and environmental friendly technologies is very important in meeting strict environmental regulations on industrial emissions of volatile organic compounds and greenhouse gases. Many of the industrial volatile organic compounds are toxic and carcinogenic, and they are regulated under Clean Air Act for hazardous air pollutants. Similarly, global environmental agreements such as European Union's 2015 Paris Agreement and Kyoto Protocol restrict carbon emission, which is responsible for global warming, sea-level rise, flooding, and ecological imbalance. It is essential that industries choose suitable technologies that reduce not only toxic volatile organic compounds in the air but also greenhouse gas emissions. In this communication, biotechnological methods are discussed and compared with conventional processes, which are used for control of volatile organic compounds. The readers may find this article useful in the selection of an appropriate technology for their application while minimizing the greenhouse gas emissions.

Introduction

Nearly most manufacturing processes, paint shops, contaminated soil sites, and industrial wastewater treatment plants emit waste gases containing abundant of toxic and carcinogenic volatile organic compounds (VOCs). The presence of VOCs in the air even in trace quantities is an environmental and health hazard. Because of the reactivity as precursors to ozone, VOC control has become the target of the 1990 Clean Air Act Amendments (CAAA).

Greenhouse gases (GHGs), principally carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), from the combustion of fossil fuels are viewed as contributing to human-induced global climate change, which is one of the most challenging environmental issues facing the world today (Zhao et al., 2019). The GHGs act as a blanket that increases the temperature of the earth. CO_2 has been identified as the major GHG because of its abundance in the atmosphere (Davis and Cornwell, 2013). Effects of global warming include sea-level rise, polar ice melting, flooding, damage to structures, and effects on ecosystems (Field et al., 2014). Scientists, researchers, academicians, and politicians, irrespective of their professional and partisan interest, agree that reduction of GHG emission is critically important for saving the people from destructive climate change. The Kyoto protocol identifies fuel combustion as one of the major sources of GHG emissions and sets targets for industrialized countries to reduce GHG emissions, and the protocol was ratified by 192 countries (European Environment

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Agency (EEA), 2012). Integration of innovative biotechnological processes in industrial systems can significantly reduce GHG emissions while removing toxic VOCs.

Conventional technologies used in industries to reduce VOC emissions are thermal oxidation, condensation, absorption, chemical scrubbing, and adsorption. In thermal oxidation, the VOCs are completely eliminated; however, in all the other conventional technologies, VOCs are simply transferred from one phase to another. GHG, mainly CO_2, emissions generated from the combustion are largely responsible for global warming. VOCs are typically treated by thermal oxidation, which requires consumption of heat from a fuel source. To increase the efficiency of thermal oxidation and reduce fuel requirement for combustion, several forms of this technology (i.e. recuperative, regenerative, and catalytic) are practiced. Thermal oxidation can remove VOCs with 99.99% efficiency but produces the highest amount of GHGs resulting from burning of fossil fuels (Bannai et al., 2006; Nevers, 2017). This method is also expensive due to high temperature requirements, equipment, and the catalyst costs. On the contrary, biological process (i.e. biofiltration, biotrickling filtration, and bioscrubbing) is an alternative technology for VOC reduction, and it does not require fuel for oxidation and relies on microbial transformation of pollutants under ambient conditions.

Biological processes for removal of VOCs are based on microbial reduction of VOCs in biofilms which are formed on solid media particles. Biofiltration involves biological oxidation in a bioreactor, which is packed with media such as compost, wood bark, lava rock, or synthetic media. In biotrickling filters, the packing media require nutrients for biofilm growth. In this process, nutrients are continuously supplied. In biofiltration, bacteria rely on the nutrients present in the media. In bioscrubbing unit, bacteria are suspended in the liquid phase reactor. There are other VOC control methods and variations of biological systems (i.e. rotating biological reactors, membrane biological reactors, etc.) (Revah and Morgan-Sagastume, 2005). In addition to VOC removal, biological processes can also biodegrade GHG such as CH_4 (Helen et al., 2018). In general, the operating cost of biological process is much lower as compared to the existing conventional technologies such as thermal oxidation, adsorption, or chemical scrubbing.

The objective of this work is to compare any technology which is based on biological processes for removal of VOCs against a conventional treatment process, namely, thermal oxidation, in terms of GHG emission reduction. It should be mentioned that comparison is limited to VOCs that are biodegradable only.

Methods and calculations

In biological processes, microorganisms (bacteria), which have capabilities to biodegrade VOCs, are acclimatized and immobilized onto packing media (i.e. biofiltration and biotrickling filers) or suspended in liquids (i.e. bioscrubbers). As the VOCs are consumed, the bacteria grow either on the media particles or in liquid suspensions under ambient conditions. The biomass generated in the process acts as a biocatalyst to enhance the biological oxidation process.

A typical composition of the biomass has molecular formula of $CH_{1.8}O_{0.5}N_{0.2}$ (Shareefdeen and Baltzis, 1994), and thus a portion of the carbon content in the VOCs is converted into biomass due to metabolic reactions. In comparison to thermal oxidation, biological methods do not require fuel and do not generate undesirable by-products. Final products after complete mineralization of a VOC are biomass, small quantities of CO_2, and water. GHG emission rates can be calculated based on biological oxidation and biomass formation.

Commercial biological treatment systems used for VOC control can handle air flow volume as high as half a million cfm (ft^3/min) or about 850,000 m^3/h. For illustration of GHG emission calculation for a biological system, let us take a case in which 50,000 cfm or about 85,000 m^3/h air contaminated with 0.5 g/m^3 VOC (toluene) is treated. By simple mass balance, it can be easily deduced that the amount of toluene that needs to be biodegraded annually is about 370 metric ton as follows

$$\text{Rate of toluene input}\left(\text{metric ton/year}\right)$$
$$= 85,000\,\frac{m^3}{h}\left|\frac{0.5\,g}{m^3}\right|\frac{24\,h}{day}\left|\frac{360\,day}{year}\right|\frac{0.001\,\text{metric ton}}{1000\,g}$$
$$= 370\,\text{metric ton/year}$$

Biological process for toluene (C_7H_8) is as follows (not balanced)

$$C_7H_8 + air + nutrients \rightarrow$$
$$\text{biomass }(CH_{1.8}O_{0.5}N_{0.2}) + H_2O + CO_2 \qquad (1)$$
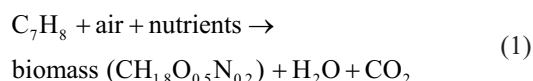
The rate of biomass (molecular weight of biomass $[CH_{1.8}O_{0.5}N_{0.2}] = 24.6\,g$) produced to the pollutant consumed is known as the yield coefficient. Assuming a typical value of yield coefficient as 0.25 (Shareefdeen and Baltzis, 1994), we can calculate the amount of carbon that will be converted into biomass for one mole of toluene as follows

$$\text{Yield coefficient} = 0.25$$
$$= \frac{\text{Biomass produced}}{\text{One mole of toluene consumed}} =$$
$$\frac{\text{Biomass produced}}{92\,g\,(\text{molecular weight of toluene})}$$
$$\text{Biomass produced (mole)}$$
$$= \frac{23.0\,g}{24.6\,g\,(\text{molecular weight of biomass})} = 0.94\,\text{mole}$$

Thus, when one mole of toluene is biologically oxidized, CO_2 produced will be (7.0–0.94=6.06) 6.06 moles or 267 g of CO_2. Thus, the abovementioned equation can be written as follows (the equation is now carbon balanced)

$$C_7H_8 + air + nutrients \rightarrow$$
$$0.94(CH_{1.8}O_{0.5}N_{0.2}) + H_2O + 6.06CO_2 \qquad (2)$$
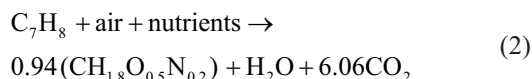
Now for the specific condition (85,000 m^3/h, 0.5 g/m^3 of toluene), assuming complete removal of toluene, we can calculate the amount of CO_2 produced per year as follows

$$CO_2 \text{ production rate}$$
$$(metric \ ton \ / \ year) = \frac{370 \ metric \ ton \ toluene}{year}$$
$$\left| \frac{267 \ metric \ ton \ CO_2}{92 \ metric \ ton \ toluene} \right| = 1075 \ metric \ ton \ /year$$

Thus, if biological method is used for VOC removal, under the process condition specified, 1075 metric ton of CO_2 will be produced annually. Based on this balance, with the knowledge on the yield coefficients and chemical equations, one can easily estimate the annual GHG emission rates for any VOCs that are biodegraded in a biological process.

Thermal oxidation leads to complete destruction of the VOC pollutants, and this technology has been widely used and accepted by industry; however, it is an expensive process due to high-energy consumption. The main form of energy used in oxidizing VOCs is fossil fuel. For example, natural gas gives 55.5 kJ (or 52.6 Btu) of energy per gram of gas burned (Felder and Rousseau, 2000). In thermal oxidation, in addition to the CO_2 emission due to oxidation of VOCs, fuels (i.e. hydrocarbons) also emit significant amounts of CO_2. Furthermore, thermal oxidation also leads to NO_x gaseous emissions, which contribute to GHGs. Global warming potential for N_2O resulting from thermal oxidation process is 310 times more than that of CO_2 (Lashof and Ahuja, 1990). In biological processes, only oxygen in the air is consumed and nitrogen in the air is unreacted due to the low temperature (ambient conditions) of biological oxidation. For the same condition (85,000 m^3/h process air flow, 0.5 g/m^3 toluene), annual CO_2 emission from a thermal oxidation process can be easily calculated using the complete combustion balance equation

$$C_7H_8 + 9O_2 \rightarrow 4H_2O + 7CO_2 \qquad (3)$$
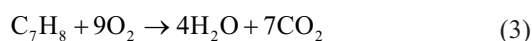
Thus, for the same toluene input rate of 370 metric ton/year, CO_2 production rate based on the stoichiometric ratios in equation (3) is about 1239 metric ton/year. For combustion reaction (3), the energy requirement for raising the temperature of 370 metric ton of toluene/year alone up to a combustion temperature of 1000°C is about 4.06×10^5 MJ/year. The process air of 85,000 m^3/h is equivalent to 8.66×10^5 metric ton/year in mass flow rate. Since the process air and toluene are mixed, substantial portion of the heat energy (9.61×10^8 MJ/year) will be consumed for heating the process air. Thus, calculations show that the energy consumed for heating the process air is about three orders of magnitude higher than the energy that is used for combustion of toluene. The total energy consumption (the sum of two heat quantities) is 9.62×10^8 MJ/year. In many cases, substantial portion of the heat can be recovered. Assuming 90% heat recovery (Revah and Morgan-Sagastume, 2005), the total energy required will be as high as 9.62×10^7 MJ/year. In combustion process, energy needed for the process is supplied by a fuel such as natural gas-CH_4 which mainly contains CH_4. The heat of combustion for CH_4 is about 55.5 kJ/g (Felder and Rousseau, 2000). Thus, the total fuel required to generate 9.62×10^7 MJ/year of energy is calculated to be 1733 metric ton of CH_4/year. The amount of CO_2 generated due to combustion of this fuel according to the following combustion reaction is about 4765 metric ton/year

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \qquad (4)$$
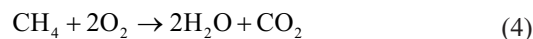
Thus, the total CO_2 emission rate for thermal oxidation process will be (1239 + 4765)=6004 metric ton/year, which is the sum of CO_2 emission rate due to thermal oxidation of toluene and required fuel (CH_4) combustion.

Results and discussion

The calculations show that even with 90% heat recovery assumption, thermal oxidation produces 5.6 times more CO_2 than biological process for the selected case study. Thus, emission of 4929 metric ton CO_2/year (i.e. 6004 – 1075=4929) can be avoided if biological methods are used instead of thermal process for controlling VOCs.

The amount of GHG (i.e. CO_2) generated also depends on concentrations, flow rate, temperature of thermal oxidation process, type of compounds, and the type of fuels used. Figure 1 shows comparison of CO_2 emission rate as a function of air flow rate for toluene concentration of 0.5 g/m^3. In Figure 1, emission rates of both biological process and thermal technology are compared. The CO_2 emission rate increases with the flow rate due to increase in the VOC mass loading. The graph can be used to estimate the difference in CO_2 emission rates (in metric ton/year) between the biological and thermal technologies. From this figure, CO_2 emission rate is estimated to be 0.02 and 0.12 metric ton/year/cfm (or 0.013 and 0.071 metric ton/year per 1 m^3/h of air flow treated) for biological process and thermal oxidation, respectively.

Figure 2 shows fuel demand ($) for thermal oxidation as a function of process air flow rate (m^3/h). This figure
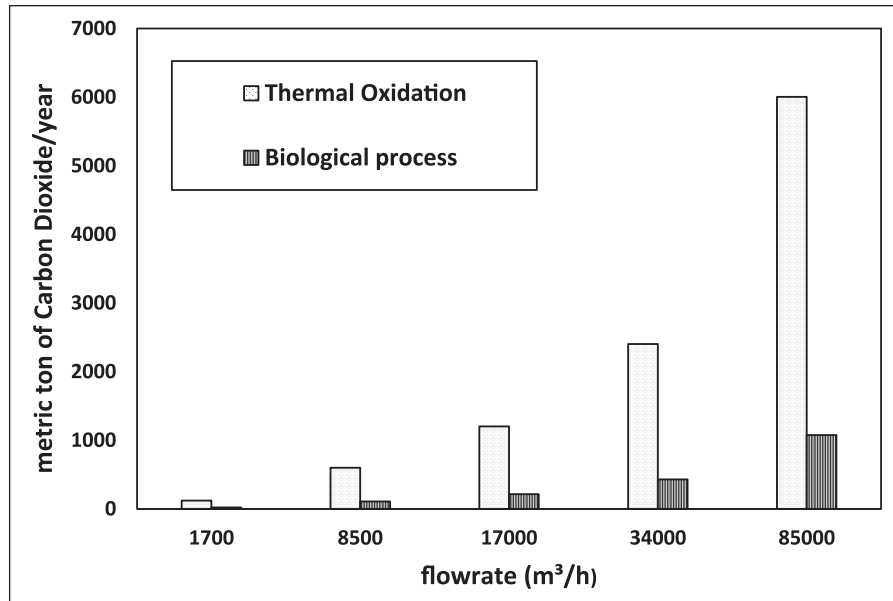
Figure 1. Annual CO_2 emission rate (metric ton/year) as a function of airflow rate (m³/h).
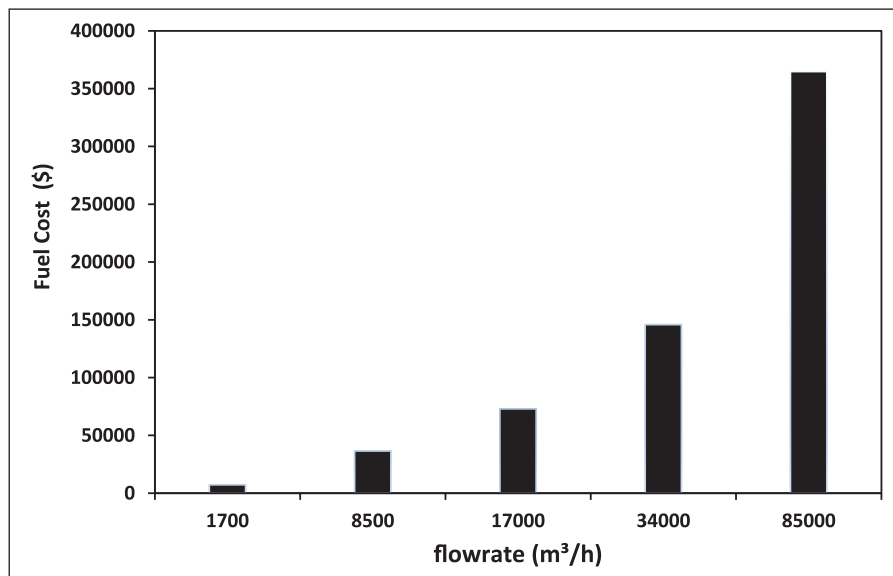

Figure 2. Cost of fuel ($) (at $4/MBtu) as a function of air flow rate (m³/h) if thermal oxidation process is selected.

shows that fuel cost as much as $365,000 per year is required to treat 85,000 m³/h air. In calculating fuel cost, a value of $4/million British thermal unit (MBtu) is used based on values of natural gas price (US Energy Information, 2019; Figure 3), and combustion temperature of 1000°C is assumed. Figure 3 shows that natural gas price varies over the years; however, average over the last 3 years (2015–2018) remains around $143.85/1000 m³ (or $4.11/1000 ft³). The heating value for natural gas varies from 32 to 39 MJ/m³ (or 850–1050 Btu/ft³). These values justify our assumption of about $4/MBtu. Chemical Plant

Cost Indices are 325.3 for 2003 and 390.6 for 2017 (Chemical Plant Cost Index, 2019). Using the chemical plant cost indices, the capital cost of a biological system (i.e. biofilter) for treating 85,000 m³/h air is approximately $1.50 M on the basis of $30/cfm or ($17.64 per m³/h) of air. It is worth noting that, fuel cost of $365,000 for thermal oxidation process alone accounts for 24% of the capital cost of a biological system. According to EPA report (EPA-456/R-03-003, 2003), annual operating costs for a recuperative thermal oxidizer and biofilter are $50,270 and $3309, per 1000 cfm (or $29,571 and $1947 per 1000 m³/h),
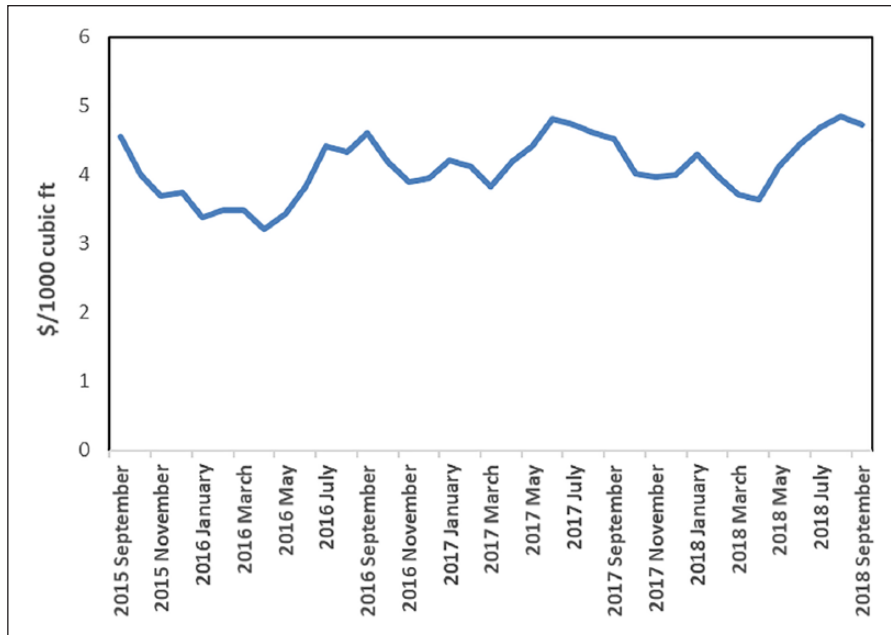
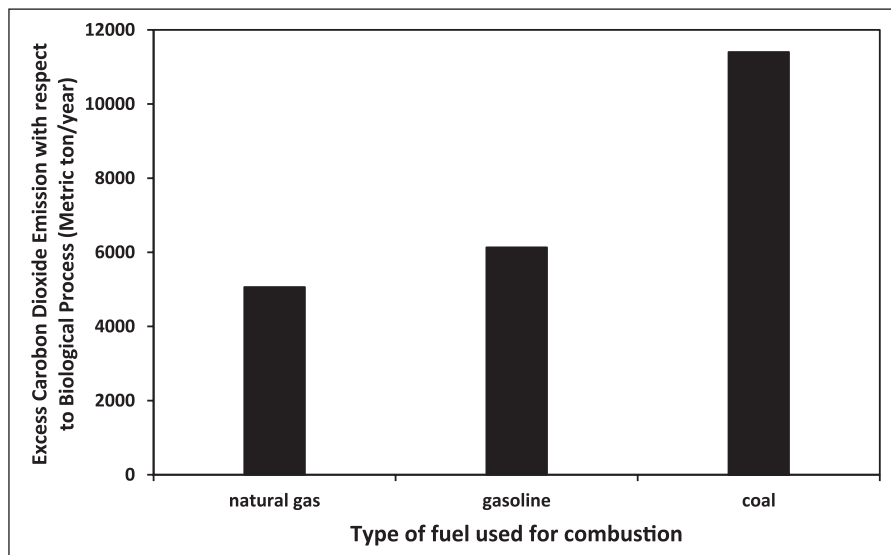**Figure 3.** Natural gas cost ($/1000 ft^3) from 2015 to 2018.

Figure 4. Excess CO_2 emission rate (metric ton/year) with respect to biological process when different types of fuels are used for combustion.

respectively, in 2003. Using the chemical plant cost indices for 2017, annual operating costs for a recuperative thermal oxidizer and biofilter are $60,361 and $3973 per 1000 cfm (or $35,485 and $2336 per 1000 m^3/h), respectively. Based on this analysis, one can deduce that substantial savings can be achieved by using a sustainable biological system for VOC removal. In Figure 4, for three different types of fuels, differences in annual CO_2 emission rates (excess CO_2) are presented. For estimating the excess CO_2 emission calculations, heating values of natural gas, gasoline, and coal were obtained from the study by Felder and Rousseau (2000). The excess CO_2 calculations show that coal emits 125% more CO_2 than natural gas. If compounds are non-biodegradable and thermal oxidation is the only option, then fuel selection is one of the critical factors in reducing CO_2 emission rates. In Figure 5, effect of combustion temperature on annual CO_2 emission rates is presented. By using catalytic oxidation, combustion temperature can be substantially (i.e.1000°C to 600°C) reduced and hence the amount of CO_2
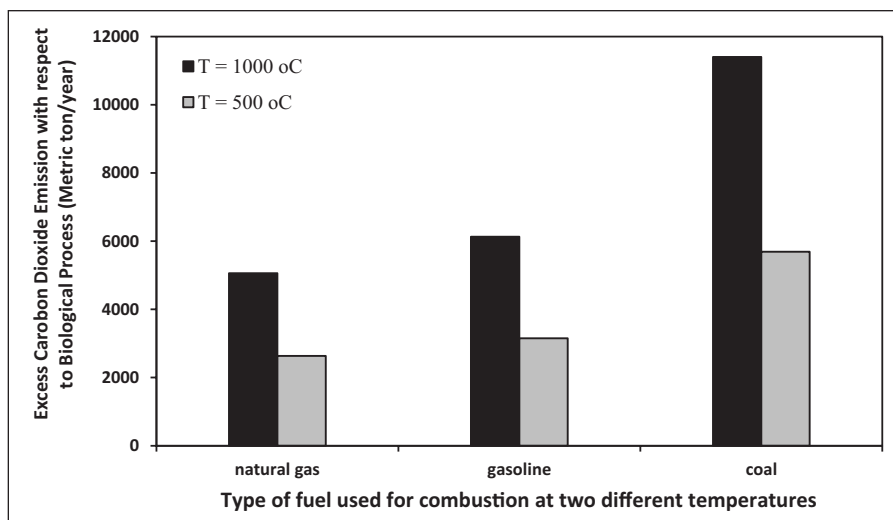
Figure 5. Excess CO_2 emission rate (metric ton/year) with respect to biological process at two different combustion temperatures.

generation can be reduced. However, the cost of catalyst in general is high, and even at lower temperatures the CO_2 emission rate as compared to biological processes will be still higher.

Conclusion

In summary, sustainable biological treatment systems and thermal oxidation methods for VOC treatment are discussed and compared with respect to annual emission of CO_2, which is one of the major GHGs. For an illustration purpose, an industrial case (85,000 m^3/h process air containing 0.5 g/m^3 toluene (a VOC)) is selected, and CO_2 emission rates are calculated. The results show that thermal oxidation emits 4930 metric ton of CO_2 per year more than the biological process. Even with the 90% heat recovery assumption, thermal oxidation emits higher level of CO_2 because of fuel usage. The results also show that the types of fuels used in combustion process, air flow volume treated, and temperature of operation can significantly influence the annual emission rate of CO_2. The results presented suggest that in addition to complying with environmental regulations, industries can benefit significantly from GHG emission reduction if a sustainable biological process is selected for VOC control. The European Union (EU) in a recent climate conference held in Paris agrees to reduce GHG emissions at least 40% by 2030 (Stua, 2017). Through in-depth evaluation of worldwide market share of technologies (i.e. thermal oxidation and biological methods) and information on a number of replacements of conventional technologies, total GHG emission reduction and cost savings on a global perspective can be estimated. With the increased interests in GHG emission reduction, this study will help to recognize biotechnological process as an alternative technology to thermal oxidation for VOC control

for biodegradable compounds at relatively low concentration levels. If compounds in the airstreams are not biodegradable, alternative methods that use other forms of energy (i.e. solar and wind power) should be explored.

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