Choosing the Correct Emission Control Technology

Increasingly stringent clean air standards and heightened concerns over greenhouse gas emissions are driving technology enhancements in the chemical processing industry. The air pollution control landscape is changing for manufacturers of petroleum derivatives like Pure Terephthalic Acid (PTA). Those that adapt are seeing the environmental and economic benefits but many questions still remain. Which CPI processes favor each abatement device? What are the operating cost advantages to each technology? How have technologies changed to accommodate the new greenhouse gas standards? Here are some of the straightforward answers.

Today, most manufacturers in the United States Chemical Processing Industry (CPI) are required to be compliant with regulations like the National Emission Standard for Hazardous Air Pollutants (NESHAP) for Miscellaneous Organic Chemical Manufacturing (MON). Similar regulations are being adapted worldwide. Many of the exhaust gas emissions from this industry include Volatile Organic Compounds (VOCs) as well as Hazardous Air Pollutants (HAPs). When left untreated, these emissions degrade in the presence of sunlight and contribute to low-lying ozone, or smog. In addition to their harmful effects on plants and trees, VOCs and HAPs are known to cause respiratory ailments, heart conditions, birth defects, nervous system damage and cancer in humans. Often times, these hydrocarbon-based pollutants are best destroyed through the use of thermal and catalytic oxidizer systems.

*CPI’s Abatement History…*

The concept of oxidation for emission abatement has been around since the early 1970’s when air pollution control regulations were first developed. Emissions are burned or oxidized at a prescribed temperature for a minimum time period with some turbulence resulting in an extremely high percentage of the pollutants converted to carbon dioxide and water vapor.

Not long ago, an oxidizer sales pitch would begin with the proud claim that, “Our oxidizers will convert your harmful VOCs into harmless carbon dioxide and water vapor.” Needless to say, harmless carbon dioxide is not a phrase used often today. With all the recent attention given to global climate change from greenhouse gases, one may start to wonder about the future of a class of equipment that generates carbon dioxide and nitrous oxidizes as a desired end product. The objectives have changed from simply destroying target emissions to also include the minimization of these harmful byproducts of combustion.

Process emissions from batch and continuous chemical manufacturing applications can vary greatly in volume and composition. This has resulted in a variety of different abatement technologies being applied in this industry. Depending on the process conditions, chemical processors have used flares, vapor combustors, thermal oxidizers and catalytic systems.

On the production side, many chemical manufacturers employ industrial catalysts to promote or provide a chemical reaction that can generate products from various reactants. For that reason, the environmental personnel at these plants felt very comfortable widely applying another type of catalyst for environmental control. Namely the use of catalysis to remove the VOCs and HAPs from their process
exhaust gases. Like industrial catalysts, these environmental catalysts are used to promote a chemical reaction but in the case of air emission control equipment, the environmental catalyst promotes the oxidation or combustion of the emissions at lower temperatures. This will generally lead to lower energy consumption than if these environmental catalyst were not used.

Catalytic oxidation has been used extensively in the chemical process industry for many years. Even with advances in other oxidation technologies, there are still numerous applications where environmental catalysts are the preferred solution to emission removal — and for good reason. For example, carbon monoxide, aromatic compounds and alkenes are often easily removed by passing the exhaust gas emissions over a heated catalyst. This catalyst will continue to perform at a high level of removal efficiency for many years with minimal operational issues. Formaldehyde emissions are currently controlled to a very high degree with many years of proven success. These systems represent an industrial version of the catalytic convertor in automobiles, but often with additional heat input and heat recovery since the industrial exhaust gas flow is so much higher.

Catalyst life is theoretically unlimited, but in actual practice deactivation typically occurs in three to eight years. Aging mechanisms include poisoning, masking and sintering. Precious metal catalysts like platinum are deactivated by exposure to certain chemical poisons, such as mercury, lead and cadmium, which form inactive alloys with the platinum. The catalyst sites can be covered up or masked by accumulation of inorganic scale, phosphorous (from lube oils), dirt, etc. Various forms of sintering can occur at high temperature, in which the catalyst particles, and catalyst substrate that the metals are deposited onto, tend to agglomerate into larger crystals with a resulting decrease in activity. The precious metal catalyst for emission removal represents the largest component cost for a catalytic oxidizer. Depending on the rate of deactivation, this component could be replaced numerous times during the life of the system.

From a capital equipment cost perspective, catalytic oxidizers can be quite expensive. The chemical processing applications typically incorporate a round oxidation chamber design to withstand the process exhaust pressures from equipment like reactors and absorbers. These pressurized units require construction materials and internal components made almost entirely out of expensive metals. The internal heat exchangers are generally built with stainless steel to prevent corrosion and withstand high
temperatures. Considering that some catalytic designs incorporate numerous heat exchanger bundles for higher energy recovery, this can add up.

While catalytic oxidizers achieve emission destruction at lower temperatures, they must operate above 570°F (300°C) or higher. Integral heat recovery with 65-70% efficiency is used to reduce the auxiliary fuel requirement but this equipment must be equipped with additional burners and fuel trains to supplement the oxidation process. The additional auxiliary energy maintains proper temperature across the oxidation catalyst to ensure high rates of destruction efficiency. It represents a major operating expense for catalytic systems and significant source of greenhouse gas emissions for the operating company.

*When might a catalytic oxidizer still be the right technology?*

- Catalysts have been successfully applied in the past.
- When the catalyst maintenance cost does not offset the reduced operational cost.
- Plant managers feel more comfortable with catalyst.
- Very clean airstreams where catalyst life is higher.

To further reduce auxiliary fuel consumption and the secondary emissions such as CO₂ and NOₓ, the CPI is looking to alternative technologies to the catalytic oxidizer. Enter the Regenerative Thermal Oxidizer (RTO). Abatement equipment using catalysis can represent a significant capital investment, ongoing maintenance and operating costs.

When you take into account the higher capital cost, maintenance concerns, potential for higher operating expenses and subsequent greenhouse gas emissions, it seems clear why the CPI is looking for an alternative to the conventional catalytic oxidizer.

*Enter the Regenerative Thermal Oxidizer…*

Over the years, chemical production companies have focused mainly on new process technologies to streamline production and increase profits. It was not until recently that newer, more efficient technologies were designed to meet the varying process emissions of the chemical processing industry. The Regenerative Thermal Oxidizer (RTO) is an abatement technology widely used on industrial air pollution control applications because of its ability to reuse up to 97% of the thermal energy from combustion to preheat incoming, untreated pollutants.

In operation, the solvent laden air (SLA) enters into one of the RTO energy recovery chambers where the high temperature, ceramic heat transfer media preheats the SLA prior to introduction into the oxidation chamber. As the SLA passes up through the bed, its temperature rapidly increases. After the chemical oxidation purification reaction occurs, the hot, clean, outgoing gas heats the outlet energy recovery bed.
In order to maintain optimum heat recovery efficiency of the beds, the SLA flow direction is switched at regular intervals by the automatic diverter valves on demand from the programmable logic control system. This periodic shift in flow direction provides a uniform temperature distribution throughout the entire oxidizer. With sufficient concentration of hydrocarbons in the process air stream, the heat energy content of the hydrocarbons will self-sustain the oxidation process, and no additional heat energy will be required.

Early RTO designs were established for process exhaust gases containing very low emission concentrations but current designs have evolved to handle much higher concentrations. Likewise, new features enable the RTO to handle challenging conditions such as emission spikes by incorporating a Hot Gas Bypass (HGB). The HGB prevents the unit from overheating and damaging the insulation or ceramic heat recovery media. So they can be applied to many more process exhaust conditions. The early RTO designs were also able to obtain only 90-95% destruction rate efficiencies, whereas current designs can achieve greater than 99% removal efficiency on a consistent basis. Even higher destruction efficiencies are achievable with specially designed, multi-chamber units.

Since oxidizers are designed around the emission type, concentrations, temperature and airflow they must be built for worst-case scenario conditions. The RTOs can be built with a larger unit size than catalytic systems resulting in lower overall capital cost for control equipment. This is especially significant as processes expand and require more exhaust gas treatment or as additional processes are controlled with fewer numbers of air pollution devices.

The primary benefit of RTOs is the high heat recovery, which correlates to low operational costs. There is also a lower capital equipment cost since the RTO utilizes a ceramic media for heat recovery as opposed to the stainless steel heat exchangers of the catalytic counterparts. The high thermal efficiency of the RTO results in the stack outlet temperatures not much higher than the oxidizer inlet temperatures when the emission concentrations are low. This can result in the potential for dewpoint corrosion concerns if there are acidic gases being handled. However, this corrosion potential can be mitigated by using special alloys of construction, or by preheating the process gas into the RTO so that the acid gas dewpoint temperature is never reached. This technique has been used successfully on hundreds of RTOs over the last 10 years for process gases with corrosive constituents, or where corrosive gases can be formed during oxidation.

Since most RTOs do not have catalyst incorporated into the design, there is a significant savings in maintenance and replacement parts. And the VOC/HAP performance efficiency stays consistently high over the operational life since there is no catalyst present that can degrade with time. There is some
routine maintenance with RTOs but replacement parts are limited to thermocouples, actuators, flame sensors and fan belts. Although valves are constantly cycling to direct airflow in the RTO, they perform consistently for a million or more cycles. Most valves will operate for numerous years without operational issues.

RTOs have a distinct advantage over catalytic systems as the auxiliary fuel usage is lower under all low process exhaust concentrations. This has a direct correlation on greenhouse gas emissions from the auxiliary fuel combustion process, mainly CO\textsubscript{2} and NO\textsubscript{X} are also reduced compared to older emission control designs with the higher fuel usage. For example, the high thermal efficiency of the RTO can reduce the auxiliary fuel consumption by hundreds of dollars per hour for larger scale chemical plants. In the following section we demonstrate how one chemical supplier to the plastics industry saved nearly one million dollars.

**What RTO technology enhancements are increasing its applicability on CPI process emissions?**

- New RTO designs allow them to handle more concentrated streams.
- Thermal Rate Efficiencies (TRE) have increased to 97% through the use of ceramic heat recovery media making them more energy efficient.
- Destruction Rate Efficiencies (DRE) can reach 99%+ and remain relatively consistent.
- Only critical components within an RTO must be built with stainless steel or lined with internal coatings whereas most catalytic oxidizer internal metal components see higher temperatures and therefore must incorporate stainless steel.
- There are fewer consumable components in an RTO.
- RTOs have a smaller carbon footprint.

**Case in point...**

PTA is a white powder-substance used extensively in the production of plastics and polyester products like fibers or films. The material is produced in a pressurized reactor where acetic acid and xylene are combined chemically in the presence of catalyst. The majority of the PTA emissions come from this reactor, although there are small emissions sources from these facilities that could also emit VOCs and/or HAPs. Gas-phase byproducts of the PTA reaction are CO\textsubscript{2} (carbon dioxide), CO (carbon monoxide), water vapor, methyl acetate, unreacted xylene, acetaldehyde and small concentrations of methyl bromide. These gas phase emissions are routed to a pressurized absorber where the gases are
scrubbed with water to reduce emissions. The remaining air emissions are then routed to an abatement device.

A PTA plant in the Middle East was looking to expand production from 420 metric tons to 700 metric tons per year. An existing catalytic oxidizer with two reactor modules was only designed to treat a total flow of 67,000 SCFM (106,000 Nm$^3$/h). Rather than return to the catalytic style oxidizer they were familiar with, this plant decided that the RTO technology would be the better solution. In order to provide optimum performance they installed two RTOs with the capacity to handle 127,000 SCFM (200,000 Nm$^3$/h) of total airflow. The RTOs share some common components such as a main system stack and electrical controls but are capable of operating independently during routine maintenance or slow production.

When compared to the old catalytic oxidizer, the new RTOs collectively emit 5,000 fewer tons per year of CO$_2$ emissions and 5 tons each year of NO$_x$ emissions, which corresponds to approximately 10 MMBTU/hr of reduced auxiliary fuel consumption. The plant essentially doubled the capacity of the abatement device, lowered operating costs and reduced their carbon footprint all while achieving greater than 98% destruction of the targeted pollutants. In addition, there are no ongoing catalyst replacement costs, saving a significant amount of money maintenance expenditures.

Most of the recent PTA expansions have occurred in the Middle East, India and Asia where these plants are in close proximity to the plastic products made from the material. However, the low cost for carbon-based precursors will likely bring more of this PTA manufacturing back to the United States.
where manufacturers can also take advantage of the new air pollution control technologies and techniques.

**Conclusion**

Employing the proper abatement system for a given application can mean the difference between compliance and non-compliance, which in many cases translates to chemical production and a shutdown. Even under compliance, the improper application of an oxidizer technology can dramatically impact operating expenses and drive down profits.

This article covers many of the typical emission control applications found in the chemical processing and manufacturing industries. It is important to note that very few processes are identical and therefore no one technology choice can be applied on all applications. To maximize return on investment, plants should consult with a professional as each application is unique.

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