

Anne Himmelberg, Aron Katz, and Victor Hoffman, John Zink Hamworthy Combustion, USA, assess vapour control options and introduce a suitable technology where vapour combustion technology is selected.

apour control equipment is used to control the release of volatile organic compounds (VOCs). VOCs can be harmful to the environment if released into the atmosphere, as they are chemical precursors to ozone and smog formation. Worldwide, a wide breadth of regulations require that the VOCs be captured or destroyed to prevent their release.

Technologies utilised to control VOC emissions are typically classified into two main categories. Vapour recovery units (VRUs) capture VOCs and turn them back into a liquid product (Figure 1), whereas vapour combustion units (VCU) destroy the VOCs through combustion (Figure 2). Each technology has its own benefits and shortcomings.

For certain applications, VRUs are the greenest form of emission control. Unlike VCUs, VRUs do not produce nitrogen oxide (NO_x) or carbon monoxide (CO) and do not require a supplemental fuel gas for efficient operation. While VRUs are very green, they are not suitable for all applications. VRUs utilise activated carbon for VOC removal. Activated carbon is not chemically compatible with all VOCs including, but not limited to, strong oxidisers such as ketones and aldehydes. These compounds can cause heat-ups in the

carbon media which can increase the risk of hydrocarbon autoignition in the carbon bed. Activated carbon also has difficulty capturing small volatile molecules, such as methane. VCUs have the benefit of being able to simultaneously handle a larger range of VOCs compared to VRUs.

Other than being green, VRUs have the economic benefit of recovering vapour and turning it back into a liquid product. In certain applications, selling the recovered liquid product can lead to a significantly

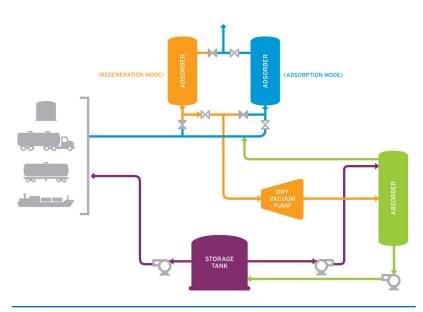
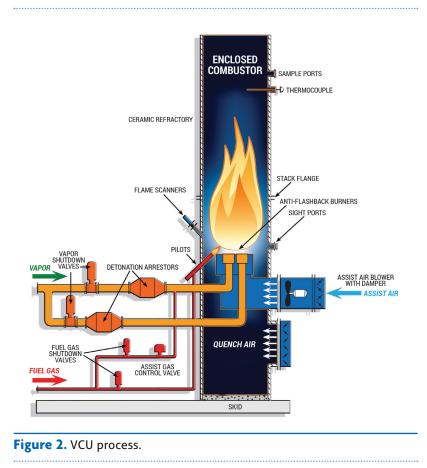


Figure 1. VRU process.



positive return on investment. Complications with the recovered product can also lead to a shortcoming of VRUs. Typically, all of the vapour sent to the VRU gets recovered into a single liquid product stream. In applications where high purity is required for the recovered product, mixed loading may not be suitable. VCUs can better handle mixed loading because the vapour is destroyed rather than recovered.

Other than component and process compatibility, a major reason for a VCU to be selected over a VRU is

capital cost. VRUs have a significantly larger capital cost compared to VCUs. This difference in capital cost is increased for vapour streams containing less than 6% hydrocarbon. Such units often require a vapour saturation step to allow the VRU to effectively recover the product. This pre-treatment device increases the overall size of the VRU significantly.

Where vapour combustion technology is employed, the John Zink Hamworthy Combustion NOx $STAR^{TM}$ VC System is an excellent vapour control technology. The system maintains or improves upon many of the benefits of a traditional VCU, including offering destruction efficiency (DE) up to 99.99% and CO emissions as low or lower than 0.015 lbs/million Btu, while also achieving ultra-low NO_x emissions.

Controlling NO_x

Low NO_x vapour destruction in a petroleum products terminal setting presents many technical challenges. A variety of techniques often employed in ultra-low NO_v process burner designs cannot be utilised in vapour combustion service. For example, in contrast to process burners, the waste gas in VCU service tends to be available at very low pressure, resulting in a poor amount of energy available for mixing. Additionally, the flow rate and composition of the waste gas can vary considerably. In terminal and marine service, hydrocarbon vapours can fluctuate from very lean to very rich, they may have an inert balance gas or air as a balance gas (non-inert), and they may span an extremely wide range of flow rates necessitating high turndown capability.

To understand how the technology produces lower NO_x than traditional VCU technology, it is important to understand how the most prevalent, individual NO_x compounds in the combustion process are formed. NO_x derived from the combustion process

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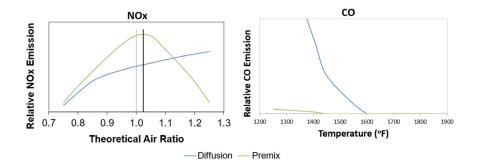


Figure 3. NO_{χ} , CO vs theoretical air graph.



Figure 4. ZULE[®] Flare System.

comes from three distinct categories: Thermal NO_x, Fuel NO_x , and Prompt NO_x .

Thermal NO_x is the largest contributor to NO_x formation in the combustion process and is defined as NO_vthat is produced from the combustion air which contains atmospheric nitrogen (N_2) and oxygen (O_2) . N₂ and O_2 in the combustion air are further broken down into N and O radicals with the addition of high heat, which is above 1300°C (2370°F).¹ These N and O radicals can produce NO as follows:

$O + N_2 \rightarrow NO + N$
$N + O_2 \rightarrow NO + O$
$N + OH \rightarrow NO + H$

By reducing the peak flame temperature, NO_x formed from the Thermal NO_x process is reduced.

Fuel NO_x is defined as that NO_x produced from nitrogen that is chemically or organically bound in the fuel, such as ammonia (NH₃) or coal. When the nitrogen-bound compound is exposed to high heat, the N radical is broken from the molecule and readily attaches to an O radical. Once NO is formed, it is also possible to further combine with an N radical to form N_2 at low oxygen concentrations in the flue gas:

Fuel N + $O_2 \rightarrow NO + O$

Fuel N + NO \rightarrow N₂ + O

Since fuel-bound nitrogen compounds are not typically present in VCU applications, targeting the reduction of NO_v formation resulting from fuel-bound nitrogen by operating at lower oxygen concentrations in the flue gas is not a viable solution for NO_x reduction in this application. Prompt NO_x is formed in a

fuel-rich environment and is defined as NO_v formed in the initial portion of the flame zone when fuel and air react. For example, when methane (CH₄) is exposed to high heat, it is initially broken into CH/CH₂ plus some hydrogen (H) radicals. This CH and CH, then combine with N₂ to form HCN and NH, which now act as fuel-bound nitrogen:

$$N_2 + CH \rightarrow HCN + N$$

 $N_2 + CH_2 \rightarrow HCN + NH$

By combusting the fuel in a lean environment (air rich) the Prompt NO_x process is reduced. This effect can be seen in Figure 3. In most applications, Prompt NO_v is much less than Thermal NO_v.

With an understanding of the three mechanisms of NO_x formation, it is apparent that the critical factor in NO_x reduction is the reduction of peak flame temperature in an air rich environment, thus reducing the reactivity of the molecules involved, allowing them to more readily convert directly to carbon dioxide (CO_2) and water vapour (H_2O).

Designing a low NO_{χ} system

Building upon these principles, the NOxSTAR VC System is an adaptation of a similar John Zink technology, the ZULE® Flare System, which was first introduced to the landfill industry in 1999 (Figure 4).

Gas from the anaerobic digestion process which forms landfill or biogas is produced at a relatively constant flow rate and chemical composition, primarily methane and carbon dioxide. The ZULE Flare System operates by precisely mixing air with biogas based on a fixed methane concentration, pre-combustion. The primary challenge of safely and reliably adapting this system to the vapour control market is the variable flow rate and composition inherent to the vapour control applications.

To overcome this challenge, a NOxSTAR VC System utilises a total hydrocarbon analyser to measure and control the total hydrocarbons present, ensuring a consistently lean concentration of the waste gas just before combustion. By controlling the air and hydrocarbon mixture precisely, the technology can dynamically adapt to varying flow and composition while also optimising the combustion temperature,

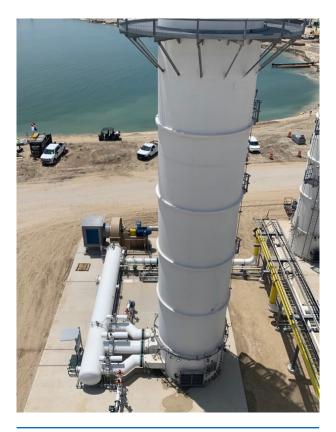


Figure 5. NOxSTAR VC System.

helping to ensure that destruction efficiencies are met (Figure 5).

Altogether, a NOx*STAR* VC System can attain NO_x emissions as low or lower than 0.02 lb/million Btu in most applications whereas traditional VCUs may only achieve NO_x emissions down to 0.12 – 0.15 lb/million Btu. Like traditional VCUs, the high heat capacity and significant turndown of the system often allows multiple types of streams to be combined into a single end control device. This can eliminate the need to stage multiple end control devices, making regulatory

compliance testing much easier, all while achieving the same performance standards.

The versatility of this technology also extends itself to multiple fuel gas types and many services including ship/barge loading, truck/railcar loading, and tank venting applications across crude, refined, petrochemical, and renewable product markets alike. Understanding that operational personnel in these markets place an extremely high demand on the safety and availability of the vapour control system, the NOx*STAR* VC System design places a similarly high priority on achieving these goals. John Zink employed computational fluid dynamics (CFD) analyses to help ensure even burner duct distribution and system self-diagnostics to avoid operation in unsafe conditions.

Implemented for decades now, users of traditional vapour combustion systems have come to depend on their end control device to be there when it is needed because, simply put, they just run. Among many others, some of the more common features and benefits include the fact that they are proven in a multitude of services and applications, they can handle a wide range of process conditions, they do not require special fluids or materials, and they completely hide the flame while combusting hydrocarbons in a safe and controlled manner.

Conclusion

Due to several potential technical or commercial constraints, vapour recovery technology cannot be universally employed to control VOC emissions. The system discussed in this article is a robust solution and a logical choice for applications requiring low NO_x and high destruction efficiency (less than 0.02 lbs NO_x/ million Btu, less than 0.015 lbs CO/million Btu, and destruction efficiencies of up to 99.99%).

Reference

1. https://www3.epa.gov/ttncatc1/dir1/fnoxdoc.pdf