

# Camet<sup>®</sup> CO Oxidation Catalysts

## CO vs VOC – The Catalyst’s Perspective

BASF’s Clean Air Group has been servicing the power generation industry for over 25 years with over 810 units operating. Our customers value our experience and technical expertise as the premier supplier of oxidation catalyst solutions to the Power Generation industry.

The breadth of our experience encompasses virtually every make, model and turbine configuration. BASF’s R&D, application and project engineering staff expertise ensure maximum performance for both new source applications and replacement catalyst for existing applications.

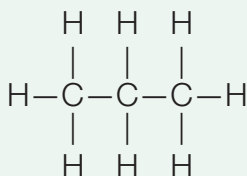
The stringent VOC conversion requirements for CO catalysts in gas turbine power generation often cause confusion. Typically, the design basis for VOC conversion in a CO oxidation catalyst is based on “NON-METHANE / NON-ETHANE 50% Saturated”.

This VOC definition results in VOC conversions typically about 50% at temperatures of approximately 700°F.\* The immediate challenge for the customer (i.e. system providers; turbine suppliers; regulators) is to define the VOCs present in a given exhaust stream.

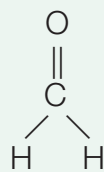
The term “VOC” represents a class of compounds:

*EPA CFR 51.100(s) Definition – Volatile organic compounds (VOC): “...any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.”*

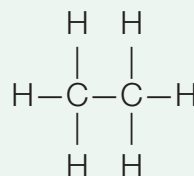
*EPA CFR 51.100(s) (1) “[VOC includes] ...any such compound other than the following, which have been determined to have negligible photochemical reactivity: methane, ethane...”*



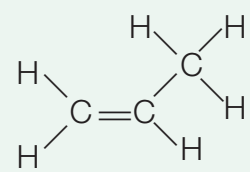
**Propane**  
VOC & Saturated HC



**Formaldehyde**  
VOC but not a HC



**Ethane**  
HC but not a VOC



**Propylene**  
VOC & Unsaturated HC

\*Dependent on inlet VOC concentration; space velocity and temperature – can vary widely.

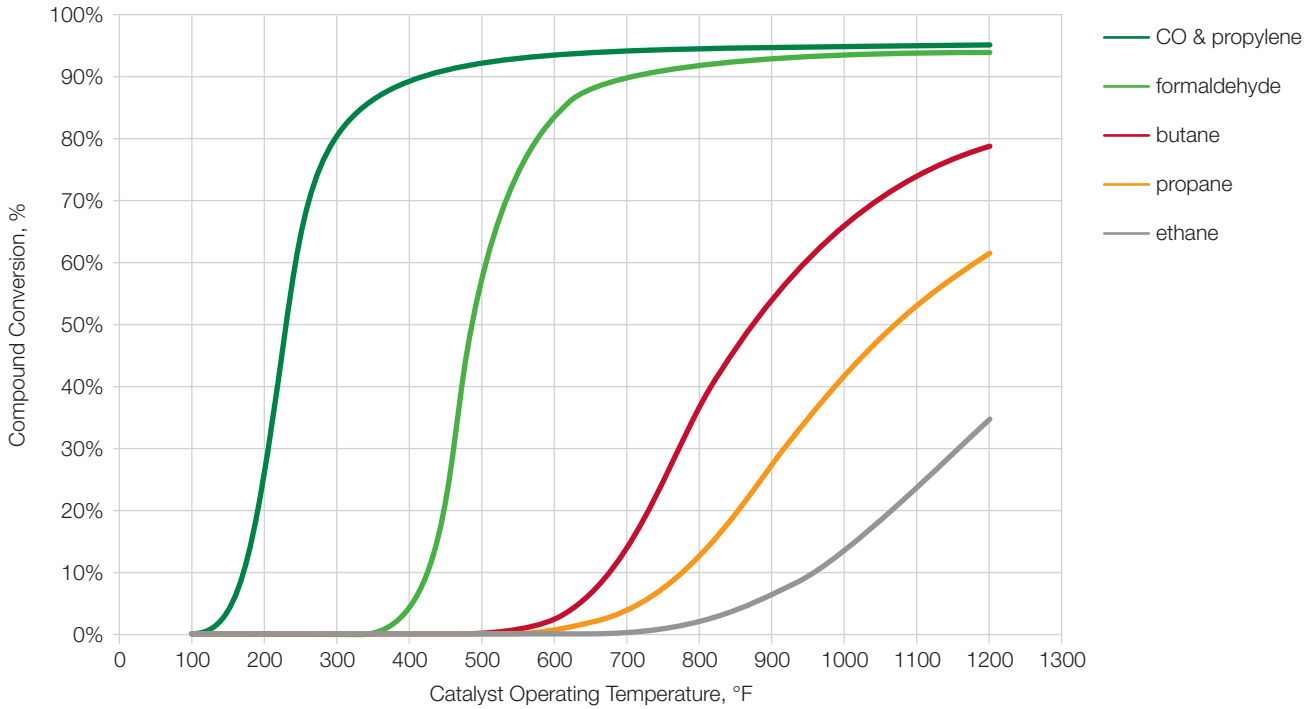
**How VOCs are measured and reported have a significant impact on the conversion requirement of the oxidation catalyst.**

The reporting of VOC as methane significantly impacts the conversion requirement, and puts the burden on the turbine manufacturer to clearly identify the VOC. Simply stating, the ppmv of the VOC is not sufficient for a catalyst oxidation supplier to provide guarantees of performance. As an example, if the requirement is to go from 3 ppmv VOC to 0.8 ppmv VOC, that would appear to 73% conversion. However, if the inlet VOC is 3 ppmv of butane (5 carbons per molecule), it will be measured as 15 ppmv in the inlet if reported as methane; and

if 0.8 ppmv is required in the outlet, that conversion is 94%. If the inlet VOC is 3 ppmv of propane (3 carbons per molecule), that will be measured as 9 ppmv as methane in the inlet; if 0.8 is required in the outlet that conversion will be 91% conversion.

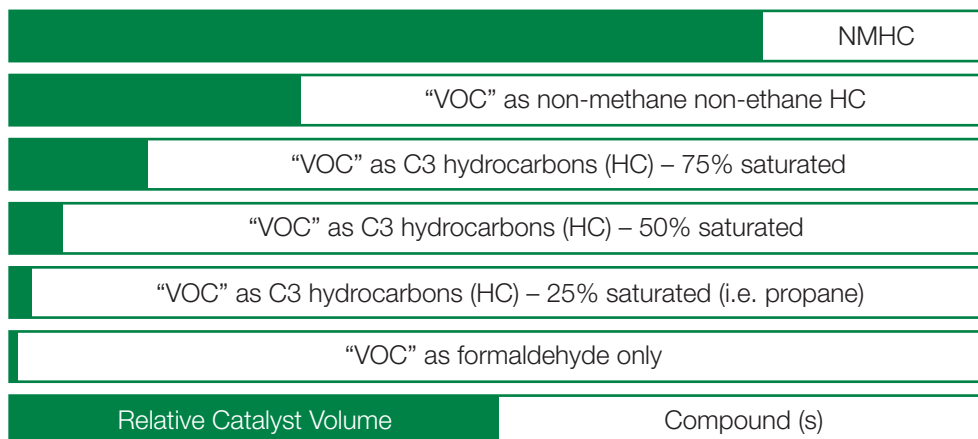
The variable composition of natural gas due to seasonal and source impacts can also alter the VOC composition from the turbine at all operating conditions. *Therefore, the guarantee can only be based upon a well-defined inlet VOC composition, and a clearly defined measurement technique.*

Each "VOC" compound has a unique, temperature-dependent conversion curve:



The following chart indicates how the differences in VOC definition impact the expected relative catalyst volume of the CO oxidation catalyst designed for 50% VOC conversion at a fixed temperature. As the table below shows, if the VOC is defined as formaldehyde only the relative volume (represented by the green portion of the bar) is relatively small. However, as the definition of VOC changes with increasing portions of the VOC

as saturated hydrocarbons, the relative volumes (or surface area) increase by orders of magnitude at the typical operating conditions in a gas turbine. Therefore, the design limiting condition becomes VOC conversion, and it may not be possible to achieve the conversion at the operating conditions available in the heat recovery steam generator.



With the standard catalyst formulations designed for CO conversion, and at the temperatures in the typical CO oxidation catalyst location in the HRSG, ignition is the issue for VOC conversion. Some hydrocarbons will not ignite at the temperatures where the CO catalyst is located. The ignition temperature of VOC differs depending upon the test methodology used, but in general the table below highlights generally accepted light-off temperatures (the temperature at which 50% conversion of the VOC is met).

	Tg °F
Methane	920
Ethane	810
Propane	770
Butane	575
Formaldehyde	300

Ignition of VOC can be improved by changing the catalyst formulation and increasing the precious metal and composition of the catalyst. However, this can only have a limited impact and can greatly increase the catalyst cost. It may also have an impact on SO<sub>2</sub> to SO<sub>3</sub> conversion, as well as NO to NO<sub>2</sub> conversion, both of which need to be controlled.

Increasing surface area (generally higher volume) also improves VOC conversion, but also raises the cost.

For example, tripling the catalyst volume may double the VOC conversion, but at the expense of increased pressure drop, increased SO<sub>2</sub> to SO<sub>3</sub> conversion, and increased NO to NO<sub>2</sub> conversion.

The conversion of VOC has become an increasingly more difficult problem for catalyst vendors because:

1. Gas turbine manufacturers provide guarantees regarding VOC emission that provide the least degree of risk to meet their guarantees.
2. VOC conversion requirements have become more stringent without any consideration as to the definition of VOC.

*This lack of VOC definition pushes the problem to the HRSG and catalyst manufacturers who now must design the emission control system to a much higher conversion requirement with no clear definition of what is being controlled. The most costly solution is to push all of the uncertainty (What really are the VOC's? How will they be measured? (etc.)) on to the CO catalyst design.*

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