

THERMAL AND CATALYTIC COMBUSTION

A. Buekens

Department of Chemical Engineering – CHIS 2, Vrije Universiteit Brussel, Belgium

Keywords: Flare, Postcombustion, Products of Incomplete Combustion (PICs), Safety, Self-Ignition Temperature, Static Electricity, Volatile Organic Compounds (VOCs)

Contents

1. Survey of VOCs treatment methods
 2. Thermal combustion
 - 2.1. Technology
 - 2.2. Ignition Temperature
 - 2.3. Design Calculations
 - 2.4. Case Study: Elevated Flares
 - 2.5. Case Study: Products of Incomplete Combustion (PICs) in Incinerators
 - 2.6. Formation of Dioxins, or PCDD/F, in Incineration
 3. Catalytic post-combustion
 - 3.1 Scope and Applications.
 - 3.2. Physical and Chemical Phenomena
 - 3.3. Catalytic Chemical Reactions
 - 3.4. Diffusion Control
 - 3.5 Design of Catalytic Units
 - 3.6 Case Study: Commercial Catalytic Units
 - 3.7 Case Study: Catalytic Treatment Unit for Dioxins Removal
 - 3.8 Economic Aspects
 4. Process control optimization and improved firing technique
 - 4.1 Emission Control
 - 4.2 Flue Gas Treatment
 5. Combustion, Safety and Environmental Pollution
 6. Conclusions
- Acknowledgement
Glossary
Bibliography
Biographical Sketch

Summary

This chapter presents a survey of Volatile Organic Compounds (VOCs) Treatment Methods.

Condensation applies to relatively concentrated flows of VOCs, e.g. solvents in air. Concentration may be enhanced beforehand, by suitable treatment, e.g. a cyclic operating adsorber/desorber. The efficiency of condensation is severely restricted by the

residual vapor pressure at treatment temperatures, as well as by the possible formation of fog or aerosols. It is enhanced by operating under cryogenic conditions, featuring a direct or indirect contact with boiling nitrogen, or by combining condensation proper with absorption into an auxiliary liquor.

Adsorption allows an almost unlimited deep reduction in VOCs concentration: the residual concentration after adsorption mainly depends on imperfections in gas/adsorbent contacting. Since it is limited by the adsorption capacity of the amount of adsorbent used, it may be used as an add-on to condensation units or as a police filter after any treatment method: in these cases it is treating only low residual concentrations, reduced by preliminary treatment.

Biological treatment mostly proceeds on trickling bed filters. Its limitations are (as usual in biochemistry): temperature dependence (freezing in wintertime!), slow conversion rates, presence of recalcitrant molecules, and sensitivity to toxicants.

Combustion of VOCs and other combustible compounds is an advantageous, safe treatment method, since the oxidation products are mainly water and carbon dioxide and conversion is quite fast. Thermal combustion of VOCs proceeds at temperatures of 800° C or more. However, at these temperatures harmful by-products, such as nitrogen oxides and carbon monoxide are also formed and care must be taken to attain a high combustion efficiency under variable input conditions.

Catalysts can lower the required combustion temperature to 200 - 400° C so that:

- fuel consumption is lower or even nil (*auto-thermal* operation).
- formation of secondary pollutants is negligible.
- less CO₂ is formed, since the auxiliary fuel consumption is lower.
- inexpensive construction materials such as plain carbon steel can be used.

The cleaning efficiency by catalytic combustion is high. Some 10 g per normal cubic meter of VOCs are easily reduced to the typical emission threshold of 20 mg per normal cubic meter or lower - a cleaning efficiency of 99.8 percent, or more, depending on the ratio of amount of catalyst provided per unit of flow rate to be treated. Technically, the latter is often expressed as GHSV, standing for Gaseous Hourly Space Velocity. A GHSV of 20 means that 1 cubic meter of catalyst can treat 20 cubic meter of gas per hour.

1. Survey of VOCs Treatment Methods

Volatile Organic Compounds (VOCs) originate in a variety of processes, involving e.g.

- Solvents, paints, varnishes, lacquers, inks, glues...
- Miscellaneous organic compounds, their production, storage, and application,
- Monomers, migrating from polymers,
- Biological and biochemical processes, such as fermentation, digestion, and putrefaction, and
- Thermal treatment, e.g. of coffee beans, smoking of fish and meat.

Somewhat similar compounds may appear as Products of Incomplete Combustion (PICs). Such effluents can be treated by (see *Control of Gaseous Emissions*):

- Condensation,
- Adsorption,
- Biological treatment, or
- Thermal treatment.

Condensation applies only to relatively high concentrations of VOCs, e.g. solvents in air. Its efficiency is severely restricted by residual vapor pressure, as well as by the possible formation of fog or aerosols. It is enhanced by operating under cryogenic conditions or by combining condensation with absorption.

Adsorption allows an almost unlimited reduction in VOCs concentration. Since it is capacity-limited, it may be used as an add-on to condensation or as a police filter.

Biological treatment mostly proceeds on trickling bed filters. Its limitations are as usual in biochemistry: temperature dependence (freezing!), slow conversion rates, recalcitrant molecules, and sensitivity to toxicants.

Combustion of VOCs and other combustible compounds is advantageous, since the main oxidation products are water and carbon dioxide and conversion is fast. Thermal combustion of VOCs proceeds at temperatures of 800° C or more. However, at these temperatures harmful by-products, such as nitrogen oxides and carbon monoxide are formed and care must be taken to attain high efficiency under variable input conditions.

Catalysts can lower the required combustion temperature to 200 - 400° C so that:

- fuel consumption is lower or even nil (auto-thermal operation).
- formation of secondary pollutants is negligible.
- less CO₂ is formed, since the auxiliary fuel consumption is lower.
- inexpensive construction materials such as normal carbon steel can be used.

The cleaning efficiency by catalytic combustion is high. Some 10 g per Nm⁻³ of VOCs are easily reduced to the typical emission threshold of 20 mg per Nm³ or lower - a cleaning efficiency of 99.8 percent, or more.

2. Thermal Combustion

2.1. Technology

Incineration of VOCs, PICs and hydrocarbon fumes is usually accomplished in an afterburner or post-combustor. Typically, such an afterburner consists of a steel shell lined internally with refractory material, such as firebrick. The refractory lining and a layer of thermal insulator protect the steel shell. Sometimes, heat is stored in a refractory mass, piled in the combustion chamber and serving as a thermal flywheel, if the supply of gas to be treated is irregular or variable. Such a refractory mass is also

used in **hot stoves**, operating in a cyclic mode, first storing heat of combustion from hot gases, later transferring this heat to the incoming gas to be fired.

To achieve almost complete combustion, the afterburner must provide appropriate levels of burning time, temperature and turbulence (the 3 T's). Direct-flame incineration is used when the waste gas is combustible (after sufficient preheating) and does not need additional fuel or air, a situation involving, however, very serious safety issues.

The thermal combustion unit is composed of:

- a burner, first firing auxiliary fuel to preheat the furnace and thus raising the temperature up to the ignition temperature,
- a mostly empty combustion chamber to provide appropriate mixing conditions and,
- a heat exchanger to preheat the gas stream to be treated and save fuel.

Off-gas is extracted by a fan, preheated in the heat exchanger and injected into the furnace, where it is rapidly brought to combustion temperature. There are several alternative arrangements to this scheme, e.g. regarding the method of:

- Injecting the flow of vitiated gas to be treated into the combustion chamber, i.e.
 - Radially into the flame,
 - Tangentially to it,
 - At an angle with the wall, or
 - Through the burner, either as air, giving a whirling flow to the flame, and possibly even
 - Premixed with gaseous fuel.

The last option is seldom used, because of evident safety problems, i.e. a possible flame flashback into the duct, if the outlet gas velocity descends below the flame propagation rate.

- The method of exchanging heat, featuring
 - a gas/gas heat exchanger,
 - a fixed (hot stoves), or
 - a mobile (Ljungström type) regenerative heat exchanger, to preheat the off-gas with heat derived from the treated gas.

Firing auxiliary fuel is required to maintain and control the temperature of combustion in the most usual case that it is not self-sustaining. Moreover, a process in which combustion is more or less self-sufficient, after recycling heat from the hot combustion gases to the incoming flows, still needs facilities for starting up the process and navigate it through possible plant upsets. Prerequisites to a smooth thermal post-combustion are:

- Attaining an adequate temperature for ignition, so that combustion becomes self sustaining,

- Sufficient reaction time, so that combustion is complete,
- Adequate oxygen levels,
- Good mixing between the off-gas and the hot combustion gas.

2.2. Ignition Temperature

Gases are flammable only within a specific domain of concentrations, situated between a lower explosion limit (LEL), below which the mixture is too lean in fuel to sustain combustion, and an upper explosion limit (UEL), above which the mixture is too rich in oxygen. The flammability limits for a mixture methane/oxygen/air are represented in the triangle diagram of Figure 1.

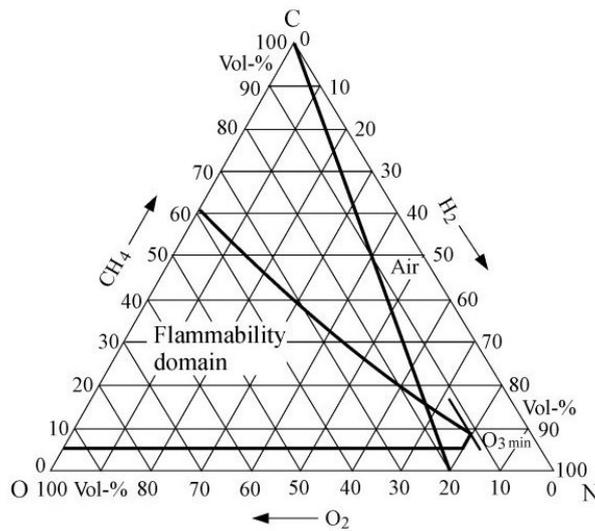


Figure 1: Triangle Diagram indicating the flammability domain in a methane – oxygen – nitrogen mixture

The ignition temperature for a series of stoichiometric fuel/air mixtures at atmospheric pressure increases with the stability of the compound:

Compound	Ignition Temperature, ° C
n-octane	210
n-pentane	285
Ethane	425
Propane	470
Benzene	555
Hydrogen	560
carbon monoxide	605
Methane	610

Table 1: The ignition temperature for a series of stoichiometric fuel/air mixtures at atmospheric pressure

Non-stoichiometric fuel/air mixtures require even higher temperatures to react.

2.3. Design Calculations

The design calculations of a thermal post-combustor are based on:

- Stoichiometric equations, relating the amount of fuel to that of oxygen; in dilute streams oxygen is only rarely in short supply,
- Heat balances, allowing to estimate the operating temperature; cf. computation of adiabatic temperatures; relevant thermo-chemical data are discussed in *Combustion Research and Computer Fluid Dynamics*,
- Residence times, derived from the simple relationship

$$(\text{Residence time, s}) = (\text{Volume of the Combustion Chamber, m}^3)/(\text{Volumetric Flow, m}^3/\text{s})$$

The Volumetric Flow is calculated at combustion chamber temperature and pressure. Since the temperature is not constant the volume must be split into quasi-isothermal segments, and the resulting fractional times integrated.

A sufficient residence time is required to guarantee adequate **destruction efficiency**. A lower residence time can somewhat be compensated by a higher temperature, as far as mixing between reactants is adequate. Some pollution codes specify:

- minimum residence times at a given combustion temperature (850° C),
- maximum residual CO-contents,
- maximum residual content of specific organic compounds,
- maximum residual VOC-values.

It is a common fallacy that temperature and time together determine (non-)ideal combustion conditions. Often mixing of streams of different temperature, density, oxygen content, and origins, etc. is the real key to adequate destruction efficiency. Computer Fluid Dynamics allows prediction of such mixing patterns (see *Combustion Research and Computer Fluid Dynamics*).

2.4. Case Study: Elevated Flares

A practical environmentally important example of a diffusion flame is that of **elevated flares**, erected to great height in oil fields, refineries, petrochemical plants, or landfills, to dispose safely of excess amounts of flammable gases. In case of equipment failure volatile hydrocarbons in oil and/or organics should be purged from operating equipment, so that it can be serviced. Since these volatile compounds form explosive mixtures with air they are delivered by closed piping systems to the flare, and burned in a controlled manner. Under normal conditions only a pilot flame light, maintained by a small base flow, is visible (see *Control of Pollution in the Petroleum Industry*)

Elevated flares feature a refractory-lined tubular furnace mounted on a platform. **Ground flares** consist of an arrangement of small burners, activated progressively with

increasing flare gas load, and contained in a refractory-lined enclosure, screening most of the light, diminishing radiant heat losses, and promoting turbulent mixing by creating artificial draft. In both cases a continuous observation of the flame (generally based on its UV-radiation and monitoring flaming combustion) and the presence of a pilot flame, situated right in the tip of the flare, are essential. Eigenfrequencies are a property of flames, related to their flame stability: flames show a characteristic wave effect, the amplitude and frequency of which characterizes flame stability.

Such flares typically dispose of excess refinery gas, composed of various hydrocarbons,. All these gases have a distinct sooting tendency, a consequence of hydrocarbon pyrolysis, which increases with rising molecular weight (methane \ll ethane $<$ propane $<$ etc.), rising chain branching, declining thermal stability according to the generic series:

aromatics $>$ *dienes* $>$ *olefins* $>$ *paraffins* (1)

or adopting IUPAC terminology (still little used in industry):

arenes $>$ *dienes* $>$ *alkenes* $>$ *alkanes* (2)

Methane, carbon monoxide and hydrogen burn without visible flame. Higher hydrocarbons burn with a yellow flame, due to the formation of soot, which enhances the thermal coupling between hot combustion zones and fuel, for soot is a prime absorber of heat radiating from the combustion zone. Carbon structures gradually grow initially from an aromatic nuclei, forming large sized polycyclic aromatic structures (PAHs) further condensing to soot particles that are problematic to burn out completely, if one of the values of the 3 T's is inadequate.

A safe height is required, not only to ensure adequate dispersion in case of flame failure, but also because of extremely high heat fluxes arising in case of an emergency. During emergency conditions the flare system disposes of large quantities of volatile gases, while steam and air suppress sooting of the flame by their well-timed addition and premixing with the flare gas. Air is aspirated into the tip by the suction effect of a ring of injection nozzles, operated with steam, fed from a manifold arranged around the flare tip. A circular steam line feeds a set of small steam nozzles located in holes pierced in the refractory-lined flame tip wall. Each nozzle entrains ambient air into the flame tip, creating turbulent mixing with the flare gas.

The use of flares creates several problems and hazards:

- Ignition loss creates dangerous operating conditions, particularly with ground flares. Pilot burners and flame detectors are hence basic equipment,
- Flashback of the flame into the burner tip must be prevented, by means of a continuous gas purge, a flame arrestor, a water seal, or a combination of these measures,
- Water seals maintain a positive pressure in all up-stream equipment and prevent air leaking in. Potential problems are freezing, corrosion by sour gas, and occurrence of periodic oscillations of the water level, causing rhythmical changes in flame intensity. Installing baffles or perforated plates acts as a

- damper on oscillations,
- Air leaking into ducts is a hazard, when part or all of the gas relief system is somewhat below atmospheric pressure, e.g. when vapors condense in the system or interconnected flares display siphon effects, during disposal of gases with different densities,
 - Flame impingement may damage the flare tip and its associated auxiliary equipment (pilot burner, steam lines, flame monitors),
 - Entrained liquid droplets give rise to ‘flaming’ rain. Hence, such droplets should be separated, before the flare gas enters the stack.

An alternative is a **ground flare**, where the heat of combustion can be shielded from the surroundings by firewalls.

Numerous views and drawings of flares and auxiliaries can be found at the site: <http://www.johnzink.com/products/flares/html/flare.htm>.

-
-
-

TO ACCESS ALL THE **25 PAGES** OF THIS CHAPTER,
Visit: <http://www.eolss.net/Eolss-sampleAllChapter.aspx>

Bibliography

BASF Aktiengesellschaft, Ludwigshafen, Company Brochures on "BASF DeNO_x Catalysts" and "The BASF Catalyst for Dioxin Decomposition" [Brochure showing BASF catalysts and their installation and usage]

Production of Large Volume Organic, Integrated Pollution prevention and chemical control. [Reference documentation best available techniques in the large volume organic chemical industry.] European Commission, February, 2003.

Verhulst D., Buekens A.G., Spencer P., Eriksson G. (1996), Thermodynamic Behaviour of Metal Chlorides and Sulfates under the Conditions of Incineration Furnaces, *Environ. Sci. Technol.*, Vol. 30, pp. 50-56, 1996 [Thermodynamic analysis of the influence of incinerator conditions on the volatilization of heavy metals]

<http://reports.eea.eu.int/EMEPCORINAIR3/en/B923vs1.3.pdf>. [Website discussing emission aspects of flares]

<http://www.epa.gov/ttn/chief/ap42/ch13/final/c13s05.pdf>. [Excellent summary of cardinal characteristics of flares]

<http://www.haldortopsoe.com/site.nsf/>. [Website with data on catalysts and their diverse uses]

<http://www.johnzink.com/products/flares/html/flare.htm>. [Website with numerous technical and safety aspects of flares, including auxiliaries and flame monitoring].

<http://www.uneptie.org/pc/apell/disasters/lists/disasterloc.html>. [Lists selected accidents involving hazardous substances, providing compelling evidence for the need for effective disaster prevention and response planning].

Biographical Sketch

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).