

Chapter 8: Pollution from combustion

Objectives

The objectives of this Chapter are:

- To sensitise the student on the very important technological and social problem of air pollution.
- To present the nature of pollutants emitted from combustion sources.
- To discuss some features of the chemistry of pollutant generation.
- To present typical techniques used to reduce pollution.

Introduction

The combustion of fossil fuels results in exhaust gases that contribute to air pollution. *Air pollution* is the presence of undesirable material in the air, in quantities large enough to cause harmful effects. It has become increasingly evident that we cannot continue generating energy at the rate and in the manner we do now, without causing serious environmental damage. We will describe in this Chapter the various pollutants that may be emitted from combustion sources and what can be done to reduce them.

The levels of pollutants emitted from cars, airplanes, factories, power generation, and virtually anywhere we use fuels are strictly *limited by legislation*. Today, the need to generate energy efficiently, while at the same time abiding to legislation and ensuring no harm to the environment, motivates huge investments from industry and governments on research and development and finally on the use of new, environment-friendlier technologies. Combustion science plays a major role in this effort. For most pollutants, we could say that, in very general terms:

$$\begin{aligned} (\text{pollutant emission}) &= (\text{population}) \times (\text{economic activity per person}) \\ &\quad \times (\text{pollutant per unit economic activity}) \end{aligned}$$

The control of the population or the economic activity involve political and social decisions, but combustion technology can help minimize how much pollutant is released per unit of energy. In the next Section, we discuss various pollutants and their sources and we give some common methods to reduce their formation or to remove the pollutant after it has been generated.

Some comments on air pollution

Why do we care?

There are various reasons why we must fight air pollution. We could categorize these reasons as:

- economic, e.g. destruction of property by a particular chemical;
- aesthetic, e.g. destruction of monuments from acid rain and the unsightly haze in the atmosphere;
- related to sustainability: carbon dioxide contributes to the greenhouse effect and acid rain destroys forests; and

- related to health: some pollutants cause serious harm, either immediately upon exposure or long-term, and even death.

Smog

This word comes from “smoke” and “fog” and is used, sometimes loosely, to describe serious atmospheric pollution over cities. Smog is the manifestation of air pollution that more than anything else has forced society to act and control pollutants. Smog is usually a “cocktail” of chemicals (NO_x, organic vapours, ozone) and solid particles. If the meteorological conditions are such that the gases above the cities are not replenished, serious respiratory and other health problems may result. The typical brown colour over polluted cities with smog is due to solid particles and NO₂.

Pollutants: effects, sources, solutions

An overview

The total emissions of the *regulated* pollutants (i.e. controlled by legislation) have been categorized according to sectors of economic activity in Table 8-1, with the percentage contribution of each sector being typical for all industrialized countries. As we can see, transportation and electricity generation make the highest contribution for almost all pollutants and most of it is related to combustion. More information and explanations for each of these pollutants, including some not shown in Table 8-1, is given next.

Table 8-1. Estimates of the US emissions of the major regulated pollutants for 1991 (million tons per year) per category of source. (From de Nevers, 1995).

Source category	CO	SO _x	NO _x	PM ₁₀	VOC
Transportation	43.49	0.99	7.26	1.51	5.08
Electricity generation	4.67	16.55	10.59	1.10	0.67
Industrial processes	4.69	3.16	0.60	1.84	7.86
Solid waste disposal	3.06	0.02	0.10	0.26	0.69
Miscellaneous	7.18	0.01	0.21	0.73	2.59
Total	62.09	20.73	18.76	5.44	16.89

Fuel contributions

When we burn fuels, we have to deal with the impurities they may *already* contain, but also with pollutants that may be *generated during combustion*, for example nitric oxides (NO_x) and soot. *Clean fuels* like natural gas, propane, and good-quality gasoline or kerosene do not contain impurities. In contrast, some fuels contain substances that, either directly or in modified form after passing through the flame, may cause harm when released. For example:

- some heavy oils and diesels may contain *sulphur* and traces of *metals* (e.g. from the refining process);
- coal contains sulphur and *nitrogen* (which contributes to NO_x, see later);
- refuse-derived fuel (RDF), i.e. fuel briquettes derived from municipal waste, may contain *chlorine* or *heavy metals*;
- various fuel-like substances used in incinerators (e.g. car tyres, plastics, municipal waste, hazardous wastes) may release hundreds of toxic substances if burned in the wrong way.

Hence fuel-switching is an obvious method to reduce the amount of a particular pollutant emitted (e.g. from sulphur-containing coal to natural gas). Of course, this may lead to the emission of more of another pollutant.

Carbon dioxide

All the carbon in the fuel will eventually be transformed to carbon dioxide in the atmosphere. Even if we have incomplete combustion (hence emitting CO from the flame), the CO will be oxidized to CO₂ in the atmosphere. Carbon dioxide is a major contributor to the *greenhouse effect*, which is a term denoting the warming of the atmosphere due to the CO₂ absorbing part of the radiation emitted by the earth surface. This may then lead to *global warming*. Using fossil fuels will invariably lead to CO₂ production and hence, at the very least, we should make sure we burn fuels as efficiently as possible. Power generation is an important player in the public debate concerning global climate change.

Carbon monoxide

Incomplete combustion results in CO formation. Carbon monoxide is extremely dangerous and can cause death if inhaled in large concentrations. It is mostly emitted by cars (Table 8-1) and is caused by engines with rich flames, incomplete mixing, flame quenching close to the cylinder walls, and in general by combustion with too short residence times (Chapter 5). The use of catalysts has helped to reduce the problem considerably by ensuring the oxidation of CO to CO₂. The CO emission from industrial sources is minimized by using excess air and ensuring good mixing between the fuel and the air. Because the CO-O₂-CO₂ equilibrium is attained quickly, an equilibrium calculation of the combustion products will very often give a reasonable estimate for the amount of CO emitted (see “Internet-based learning” and Chapter 3).

Sulphur oxides

When burning fuels with sulphur, like coal and diesel, all of the sulphur will be oxidised in the flame into SO₂ and SO₃, collectively called SO_x. This poses serious problems because: (i) SO_x dissolves in clouds to form sulphuric acid, which can then be deposited to the earth by rain. This is called “acid rain” and has caused deforestation in Europe and North America and serious damage to structures (monuments, steel buildings). (ii) SO_x is a respiratory irritant and in large concentrations can cause death. Sulphur-rich coal combustion for domestic use (e.g. for cooking or heating) has been responsible for thousands of deaths in London over the past centuries, notably during the “Great London Smog” in December 1952, in which about 4,000 people died.

Current emission standards on sulphur oxide emissions are very strict and are met by post-combustion treatment of the exhaust gases. This is based mostly on scrubbing: mixing the exhaust gases with water droplets that contain limestone, which reacts with the oxide according to $\text{CaCO}_3 + \text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2$. The cost of the scrubbers is a very large percentage of a modern coal power station.

Nitrogen oxides

Two of the most serious pollutants attributed to combustion sources are nitric oxide (NO) and nitrogen dioxide (NO₂), collectively called NO_x. Usually, only NO is emitted, but this will react in the atmosphere to create NO₂. Nitrogen oxides will form acid rain, by a similar mechanism to SO_x, and will participate in the formation of solid particles during smog episodes. At ground level

and under sunlight, NO_2 will release an oxygen atom which can then form ozone (O_3). Ozone is very irritating for the respiratory system and causes impaired vision. In addition, NO emitted by high-altitude airplanes participates in ozone destruction and hence contributes to the ozone hole problem. Nitrogen oxides are strictly regulated and low- NO_x combustion equipment has become today a huge business.

There are three mechanisms by which NO is formed in combustion: the *fuel* NO, the *prompt* NO, and the *thermal or Zel'dovich* NO. These are discussed below.

1. Fuel NO

Various coals and oils may contain up to 2% N_2 (by mass). During combustion, from 10 to 50% of this nitrogen will react with hydrocarbon radicals like CH or CH_3 and will form HCN, which will then lead to NO. There is not much we can do to stop the generation of the fuel NO.

2. Prompt NO

By approximately the same mechanism as above, the nitrogen contained in the air will be attacked by the hydrocarbon radicals CH to form HCN, which then leads almost invariably to NO. This is called “prompt” NO because it forms as quickly as the combustion reactions and, again, we cannot do anything to limit its generation.

3. Thermal NO

The Zel'dovich mechanism has been discussed in Chapter 1, where a reduced model for the rate of generation of NO by this mechanism was discussed. The mechanism is composed of the elementary reactions (I) and (II) and we supplemented it by the (sometimes) partially-equilibrated reaction (III):



Writing the thermal NO global reaction as $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$, we derived the following expression for the net rate of NO formation (Chapter 2, Eq. 2.10):

$$\frac{d[\text{NO}]}{dt} = 2k_I \left(\frac{k_{III,f}}{k_{III,b}} \right)^{1/2} [\text{O}_2]^{1/2} [\text{N}_2] \quad (8.1)$$

The forward and backward rates of the equilibrium reaction (III) can be related to the equilibrium constant (Chapter 3). It is evident that the rate of formation of NO depends on the amounts of N_2 and O_2 and on the temperature (through the Arrhenius expression for the reaction rate constant k_I and the equilibrium constant for the $\text{O}_2=2\text{O}$ dissociation reaction). Both the dissociation of O_2 and the rate constant k_I increase very fast with temperature. Thermal NO is important only for temperatures higher than about 1800K and is relatively slow compared to combustion reactions. Hence shortening the residence time at high temperatures decreases the final NO emitted. This is the basis of various strategies to reduce NO, which has been a major preoccupation of the combustion engineering industry for the past two decades (and still is).

The NO emitted from coal combustion is controlled by reacting it with a reducing agent, e.g. ammonia, in a variety of techniques. A successful technique called “reburn” is essentially the inverse of the prompt mechanism: extra fuel is used after the flame for extra power and to transform the NO back to N_2 . The NO emitted from gasoline engines is reduced by a catalyst in the exhaust,

while for all types of flames, burning at reduced temperatures is the means of choice to decrease thermal NO production. These techniques can be understood by reference to Eq. (8-1) and include:

- *Lean burn*: use lean premixed combustion, which has a low flame temperature.
- *Use of exhaust gas recirculation* (EGR): this reduces the flame temperature for both premixed and non-premixed flames (e.g. Chapter 7, Ex. 7-1).
- *Oxy-fuel combustion*: burn with oxygen-enriched air, so that $[N_2]$ is reduced. This technique is used in glass furnaces that must be kept very hot and would otherwise result in huge amounts of thermal NO.
- *Rich-Quench-Lean*: a technique used in gas turbines, where a rich flame is used in the primary zone of the combustor (for stability), rapid mixing with air lowers the temperature suddenly, and extra fuel then burns lean. Various variants are used in all low- NO_x burners. The aim always is to minimize the residence time in the high temperature region.
- *Use of high air preheat*: preheated air for the same flame temperature allows very lean operation and hence prompt NO decreases.

Particulate matter

Combustion in non-premixed mode may lead to *soot* formation. By “soot” we mean solid particles of size less than $1\mu m$, which result in the yellow colour of flames and in the smoke emitted from diesel engines and some older gas turbines. Apart from the presence of unburnt carbon in the exhaust, which implies incomplete combustion and hence lower efficiency, this particulate matter may cause lung diseases and is hence controlled by legislation. The particulates are usually denoted by PM_{10} , which means “particulate matter of size less than $10\mu m$ ”.

Coal also contains inorganic mineral matter that cannot react and escapes the flame as solid particles (called “fly ash”). The ash particles are collected in filters before the exhaust gases are released to the atmosphere. PM_{10} from diesel engines and gas turbines is controlled by careful flame adjustments (including overall very lean operation and good mixing with air), by ensuring fine atomization, and by *soot traps* (i.e. filters) in the exhaust.

VOC and UHC

The term VOC refers to “volatile organic compounds”. By VOC we mean evaporated gasoline from petrol filling stations, vapours from refineries, organic solvents from paint, and many others. The term UHC means “unburnt hydrocarbons” and usually denotes any hydrocarbon that exists in the flame products. These organic species are major contributors to smog and may be toxic or carcinogenic for humans. Their emissions are strictly regulated.

Combustion itself does not contribute much VOC to the atmosphere, although the fuel preparation and processing stages do. Since VOC is organic, it can be burnt and there are special combustion techniques to incinerate VOC before release to the atmosphere, e.g. by passing the solvent-containing fumes through a flame or a catalyst.

UHC species in the exhaust almost never include the fuel itself, as the high temperature of the flame always causes chemical transformations to the fuel. The origin of UHC is flame quenching in solid walls, pockets of reactants that are rich or unburnt, or too short residence times. From spark-ignition and diesel engines, UHC is also due to the lubricant oil. The UHC emission standard for spark-ignition engines is met by fitting a catalyst, while diesel engines need fine atomization and good mixing with air inside the cylinder. Release of UHC from industrial burners is not very serious because ample residence time can usually be given to the reactants and solid surfaces are usually far from the flames.

Heavy metals and dioxins

If the fuel contains metals, they will finish in the atmosphere (in pure form or in oxides) and they could be very dangerous (particularly Hg, Cd, Pb, As, Be, Cr, and Sb). This is a serious problem for municipal, toxic, and hospital waste incinerators. If the fuel contains chlorine, for example if it includes plastics (PVC), then there is a danger that *dioxins* may be formed – not at the flame, but on medium-temperature metal surfaces in the stack or inside the waste itself. Dioxins are chlorinated aromatic organic compounds whose chemistry is not very well known. They are extremely dangerous because they are carcinogenic even in the part per trillion range. Municipal waste incinerators are needed to decrease the volume of waste going to landfills and to generate some power, but their use is controversial because of the danger of dioxins. If the plant operates at the design point, the exhaust is probably free of dangerous substances because a lot of attention has been given to the clean-up stage. However, open, uncontrolled burning of any waste or plastic material is extremely dangerous.

Catalysis

A very common technique to reduce pollutants (especially UHC, CO, and NO) is to pass the exhaust over a (usually precious) metal surface (e.g. platinum, nickel, rhodium). The action of the metal is to catalyze a particular reaction, for example UHC oxidation, CO oxidation, and NO reduction back to N_2 , so that its rate is high even at low temperatures (in the range 400-900K). Catalysis is a very difficult topic because it involves heat and mass transfer and surface reactions, which are very complex. The mechanism of catalysis is discussed very briefly below.

The reactants diffuse towards the surface, they are *adsorbed* by the metal and reside in the *active sites*, the reactants meet in the active sites, the product is formed, which is then *desorbed* back to the gas phase, to be removed away by mass transfer (diffusion). By “adsorption” we mean a temporary chemical binding between the reactant molecule and the metal (“desorption” is the breaking of this bond). The rate of the overall process depends on the nature of the catalyst, the temperature, and the mass transfer rates. In addition, the age of the catalyst plays a role, as impurities may block the active sites. Lead and sulphur in the mixture are especially powerful catalyst *poisoning agents* and are hence removed from gasoline for catalyst-fitted cars.

Today, the pollutants emitted from cars are controlled by fitting a *three-way catalyst*, which achieves simultaneously the oxidation of UHC, CO and the reduction of NO. For this to be possible, the mixture has to be very close to stoichiometric, which motivates partly the complex electronic engine management control systems in modern cars.

Pollution control techniques in a nutshell

Table 8-2 summarises various techniques that can be used to reduce pollutants from common combustion devices (spark-ignition and diesel engines, gas turbines, industrial burners). Figure 8-1 indicates (very) roughly the dependence of the emission of various pollutants on the flame temperature. These trends are understood by reference to Chapters 2 and 3: thermal NO increases fast as $T > 1800K$; there is less chance for UHC to survive as the T increases; for some flames, CO will decrease with increasing T (but not if T is too high and dissociation of CO_2 begins). If the residence time becomes too short (Chapter 5), UHC and CO will appear due to unfinished reactions, and liquid droplets may not have enough time to evaporate (Chapter 7) fully, hence surviving in the exhaust.

Table 8-2. Techniques for reducing pollutant, per pollutant and combustion equipment. A “–” indicates no serious problem today.

Combustion Equipment	CO	SO _x	NO _x	PM ₁₀	UHC	Dioxins & Heavy Metals
Spark-ignition engines	Catalyst, avoid misfire	–	Catalyst, lean burn, EGR	–	Catalyst, avoid misfire	–
Diesel engines	Good mixing, fine droplets	Remove S from fuel	Good mixing, fine droplets, EGR	Good mixing, fine droplets, ensure high T, soot filters	Good mixing, ensure high T	–
Gas turbines	Good mixing, fine droplets	–	Lean burn, mixing strategy	Good mixing, fine droplets	Good mixing, ensure high T	–
Coal power stations	–	Scrubbing with limestone, switch to low-S coal	Reburn, EGR, react with ammonia	Filters	–	–
Industrial burners	Excess air	Switch to low-S fuel	Lean burn, mixing strategy	–	–	–
Incinerators	Excess air	As for coal	As for coal & diesel	Filters	Excess air, ensure high T	Chemical treatment of exhaust

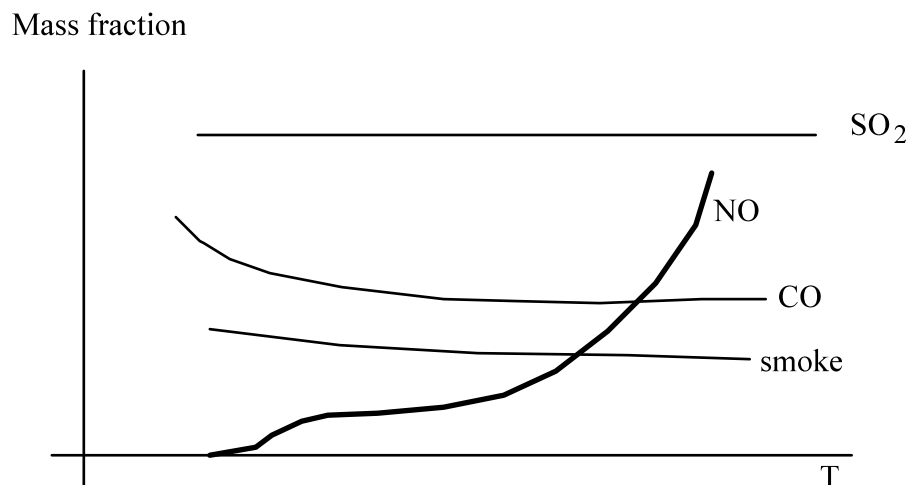


Figure 8-1. The evolution of some pollutants with flame temperature (not to scale).

Summary

- Air pollution has serious economic, social, and technological implications. Combustion science can contribute greatly to understanding how pollutants are generated from the use of fossil fuels and to developing techniques to reduce the amount of pollutants emitted.
- Table 8-2 summarizes the major pollutants and some of the techniques that can be used to decrease them. Equilibrium calculations are usually adequate for predicting CO emission.
- Nitric oxide is a major pollutant. It has three sources: fuel NO, prompt NO and thermal NO. For the latter, a global one-step mechanism has been developed (Chapter 1) and helps us understand various NO-reduction techniques.
- These techniques include lean burn and EGR and are based on reducing the flame temperature. Various low-NO_x burners use fuel-air mixing patterns in a way to minimize the residence time in the high temperature region.

Suggested reading

Turns:

Ch. 15

Glassman:

Ch. 8 (in particular: pp. 362-367; 399)

Additional reference on air pollution:

De Nevers, "Air Pollution Control Engineering", McGraw Hill, 1995: This is an excellent book for most air pollution problems, including sources and abatement technologies. It is not directly related to our course, but is a very useful reference.

Internet-based learning

Emissions from engines:

Revisit <http://www.wiley.com/college/ferguson> (described in Chapter 3) and launch the “Adiabatic Flame Temperature” Applet. For a given pressure (e.g. 20bar) and a given fuel (e.g. gasoline), experiment with the “Equivalence ratio” and the “Residual mass fraction” (equivalent to exhaust gas recirculation). Observe how the adiabatic flame temperature decreases with EGR. A crude criterion for no self-sustaining flame is when $T_f < 1500\text{K}$; at what EGR does that happen for gasoline?

For zero EGR and for a few values of the equivalence ratio, calculate the adiabatic flame temperature. Then, supply these to the “Equilibrium Combustion Solver” applet (launched from the same site) and observe the equilibrium CO and NO as a function of ϕ . Does the trend agree with your expectations?

Air pollution in general:

<http://www.epa.gov/students/>

The official site of the US Environmental Protection Agency, specifically made for University students. Explore the pages starting from “Air” and also try the “Motor Vehicle and Air Pollution” on-line quiz. The content is accurate and very useful. Highly recommended.

<http://europa.eu.int/comm/environment/air/>

The official site of the EU describing air pollution issues and policies. Explore the links for “Ground Level Ozone” and “Auto Oil II”.

http://news.bbc.co.uk/1/hi/english/sci/tech/newsid_1359000/1359917.stm

A news item from the BBC site that shows satellite pictures of air pollution.

Greenhouse effect:

<http://www.ieagreen.org.uk/index.htm>

An authoritative site from the International Energy Agency. Explore the links for “Tackling Climate Change” and “Reducing Emissions”.

<http://www.defra.gov.uk/environment/climatechange/index.htm>

The site of the Department for Environment, Food and Rural Affairs includes these pages that have a very concise and accurate description of the Greenhouse Effect.