Chapter 5:
Flame extinction – the well-stirred reactor

Objectives

The objectives of this Chapter are:
- To develop a theory for a model combustion problem: the well-stirred reactor (WSR).
- To identify the conditions under which the WSR extinguishes.
- To explore the theory to explain the phenomenon of flame extinction.

Introduction

It is our everyday experience that flames extinguish, for example blowing at a candle causes combustion to cease. In technical applications of combustion, we would like to know the maximum amount of fuel that can be burnt in a given burner or, in other words, the maximum flow rate that a flame can sustain. In this Chapter, we present an idealization that describes quite adequately many combustion devices and helps answering the question of when a flame extinguishes. It is called the well-stirred reactor. The theory developed will be explored to calculate the conditions under which combustion is not possible due to an over-supply of reactants. The phenomenon of extinction is very important for the operation of any type of burner. It is chemistry-influenced, like autoignition, and depends, as we shall see, on a balance between the rate of heat generation by the reaction and the rate at which heat is removed from the reactor by bulk fluid motion.

The well-stirred reactor

Basic description and assumptions

Consider a vessel of volume V with one inlet and one outlet. Reactants flow in, they mix with the gases inside the reactor, and products flow out. The total mass flow rate through the reactor is $\dot{m}$. Figure 5-1 shows a schematic of a well-stirred reactor, also called the "Longwell bomb". Although shown as spherical, it need not be of a particular geometrical shape. The properties inside the reactor are denoted by symbols without a subscript for simplicity. We assume that:

- All properties are uniform inside the reactor (mass fractions, temperature, pressure). This is achieved by very intense mixing, for example by allowing the reactants to flow in through many small holes producing jets that mix very fast with the background fluid inside the reactor.
- The gas leaving the reactor has the composition and temperature of the reactor (i.e. $T_{out}=T$ and $Y_{i,out}=Y_i$).
- There are no heat losses (the reactor is adiabatic).
- The pressure is constant.
- All quantities are steady (i.e. no changes with time).
- We use the simple one-step chemistry and constant c_p model of Chapter 4 (i.e Eqs. 4.4, 4.5, 4.6).
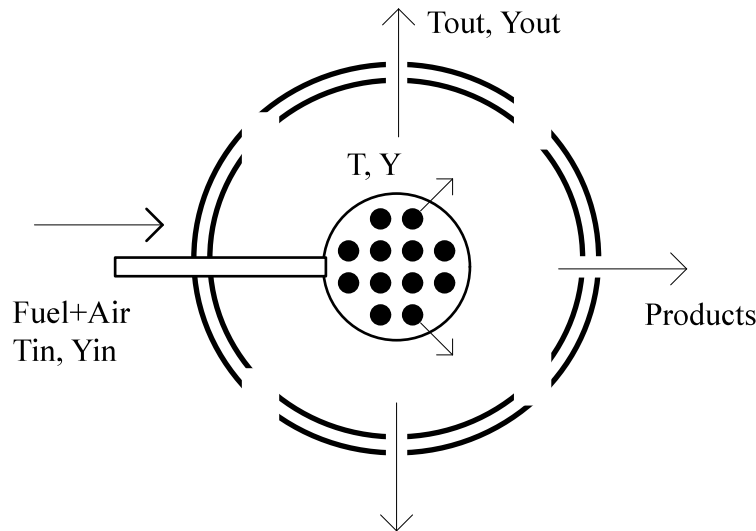
Figure 5-1. Schematic of a well-stirred reactor. This device is also called "Longwell bomb".

Governing equations

Based on these assumptions, the species conservation equation becomes:

$$\dot{m}\left(Y_{i,out} - Y_{i,in}\right) = \dot{w}_i\, V \tag{5.1}$$

Equation (5.1) can be very easily derived considering the mass balance of species i for a CV enclosing the reactor and using the fact that, since the species and temperature are uniform, $\dot{w}_i$ is uniform. Using our simple one-step chemical model for combustion (Chapter 4, Eq. 4.4), the reaction rate for fuel is given by

$$\dot{w}_{fu} = -A\,\frac{MW_{fu}}{MW_{fu}\,MW_{ox}}\,\rho^2\,Y_{fu}\,Y_{ox}\,\exp\left(-E/R^0 T\right) \tag{5.2}$$

Since the reactor is adiabatic, the mass fractions of fuel and oxygen are related to the temperature by

$$Y_{fu} = Y_{fu,in} - c_p(T - T_{in})/Q \tag{5.3}$$

$$Y_{ox} = Y_{ox,in} - Sc_p(T - T_{in})/Q \tag{5.4}$$

that are, essentially, statements of the First Law (if fuel is depleted, the temperature must go up accordingly). Recall that in the context of this thermochemical model, the adiabatic flame temperature is

$$T_f = Y_{fu,in}Q/c_p + T_{in} \tag{5.5}$$

and that Eqs. (5.3) and (5.4) imply that <u>fuel is present</u> if the reactor does not have the adiabatic flame temperature (i.e. if complete combustion has not been achieved). This model does not allow for dissociation, which we know (Chapter 3) will result always in unused chemical energy in the flame products. Neglecting dissociation helps us to obtain analytical results – including dissociation

only changes the numbers, not the physics for the present problem. The density inside the reactor is given by the equation of state:

$$\rho = \frac{P\,\overline{MW}}{R^0 T} \tag{5.6}$$

Finally, the energy equation is given by

$$\dot{m}\,c_p\left(T_{out} - T_{in}\right) = -\dot{w}_{fu}\,VQ \tag{5.7}$$

which is a simple statement of the First Law for the whole reactor assuming constant heat capacity and steady operation. Note that our energy equation (5.7) is not independent of the species equation (5.1) if relations (5.3) and (5.4) are used. Hence we should not use both (5.1) and (5.7), but only one of them, e.g. (5.7).

Manipulation

Employing Eqs. (5.2). (5.3) and (5.4) in Eq. (5.7) gives:

$$\dot{m}\,c_p\left(T_{out} - T_{in}\right) = VQ\ A\,\frac{MW_{fu}}{MW_{fu}\,MW_{ox}}$$
$$\times\ \rho^2\left(Y_{fu,in} - c_p(T - T_{in})/Q\right)\left(Y_{ox,in} - Sc_p(T - T_{in})/Q\right)\ \exp\!\left(-E/R^0 T\right) \tag{5.8}$$

Since $T_{out}{=}T$ (i.e. the outlet has the temperature of the reactor), Eq. (5.8) becomes of the form:

$$\frac{\dot{m}}{V\rho}\left(T - T_{in}\right) = C\ f(T) \tag{5.9}$$

where

$$C = \frac{Q}{c_p}\ A\,\frac{MW_{fu}}{MW_{fu}\,MW_{ox}}\,\frac{P\,\overline{MW}}{R^0} \tag{5.10}$$

$$f(T) = \frac{1}{T}\left(Y_{fu,in} - c_p(T - T_{in})/Q\right)\left(Y_{ox,in} - Sc_p(T - T_{in})/Q\right)\ \exp\!\left(-E/R^0 T\right) \tag{5.11}$$

So the temperature of the reactor (and hence the mass fraction of fuel and oxygen) will be determined by: the inlet conditions (T_{in}, $Y_{fu,in}$, $Y_{ox,in}$) and pressure P, the mass flow rate $\dot{m}$, the volume of the reactor, the thermochemistry of the fuel (E/R^0, A, Q), and the mixture properties (MW, c_p). We have tried to isolate the effects of temperature and inlet mass fractions (Eq. 5.11) from all the others (Eq. 5.10) and we have created the group $V\rho/\dot{m}$, that appears in Eq. (5.9). This group has the units of time and we call it the *residence time* – it is a measure of how long, on average, the fluid spends inside the reactor:

$$t_{res} \equiv \frac{V\rho}{\dot{m}} \tag{5.12}$$

Equation (5.9) is the governing equation for the well-stirred reactor. Unfortunately it is not easy to solve analytically. It can be solved numerically (see "Internet-based Learning"). However, <u>very important physical insight</u> can be obtained by a <u>graphical</u> solution, which is presented next.

<u>Solution of Eq. (5.9)</u>

The RHS of Eq. (5.9) can be thought of as a <u>heat generation</u> term. The LHS can be thought of as a <u>heat transfer</u> term that represents how much energy leaves the reactor per unit time. The two terms are shown in Fig. 5-2.

Curve G, the heat generation term is described essentially by Eq. (5.11) (to within the constant C). This term has a shape already discussed in Chapter 4. It starts at practically negligible values at low temperatures (i.e. T_{in}), peaks close to the adiabatic flame temperature (T_f), and drops to zero at T_f, because at least one of the reactants mass fractions becomes zero there. It is very important to note that the peak occurs <u>close to</u>, but <u>not at</u>, T_f. Curve G is determined by the nature of the fuel, the inlet conditions, and the pressure.

The LHS of Eq. (5.9) is a straight line with slope equal to $1/t_{res}$, i.e. it is <u>steep when the residence time is short</u>. Such lines are drawn as HT1 to HT3 in Fig. 5-2. The well-stirred reactor will operate at the intersection of such a line with curve G. Let us describe the various possibilities.

1. Very low flow rates / very long residence times:

This situation is denoted by Curve HT1. The reactor can operate only at point S1, at a temperature very close to T_f. Hence, from Eq. (5.3), the amount of unburnt fuel escaping the reactor is very small and we achieve almost complete combustion.

2. Low flow rates / long residence times:

This situation is shown by Curve HT2. Now, there are three intersections.
- (i)   The point at low temperatures (point S4) corresponds to negligibly small reaction rates and temperature increments. It represents an un-ignited flow through the vessel.
- (ii)   The point S2 corresponds to a burning reactor, operating at high temperatures. However, the reactor temperature is now <u>lower</u> from the temperature point S1. Decreasing the residence time lowers the temperature and increases the amount of unburnt fuel leaving the reactor.
- (iii)   Point S3 is not physically realizable, as any small excursion (e.g. due to fuel supply unsteadiness) will make the system go to S4 or to S2.

3. Very high flow rates / very short residence times:

This situation corresponds to Curve HT3. Now, the reactor can only operate at the low-T solution (S4). Therefore, no high-temperature operation is possible, <u>the reactor has been quenched</u>. <u>At very short residence times, the flame extinguishes completely</u>. The reactants just pass through the vessel unreacted.

4. Critical conditions:

Curve HTcr shows the critical condition. For a given type of fuel, fuel and oxygen mass fractions, pressure, and inlet temperature (i.e. for a given Curve G), if the mass flow rate increases beyond this point, the reactor will extinguish and will shift to the low-T intersection (cold, unreacted flow through vessel). Hence, point C corresponds to the *blow-off* limit of the reactor. Any point between C and S4 (such as S3) is unstable (not physically realisable). Any point to the right (such as S2 or S1) is stable, but can occur only at smaller flow rates.
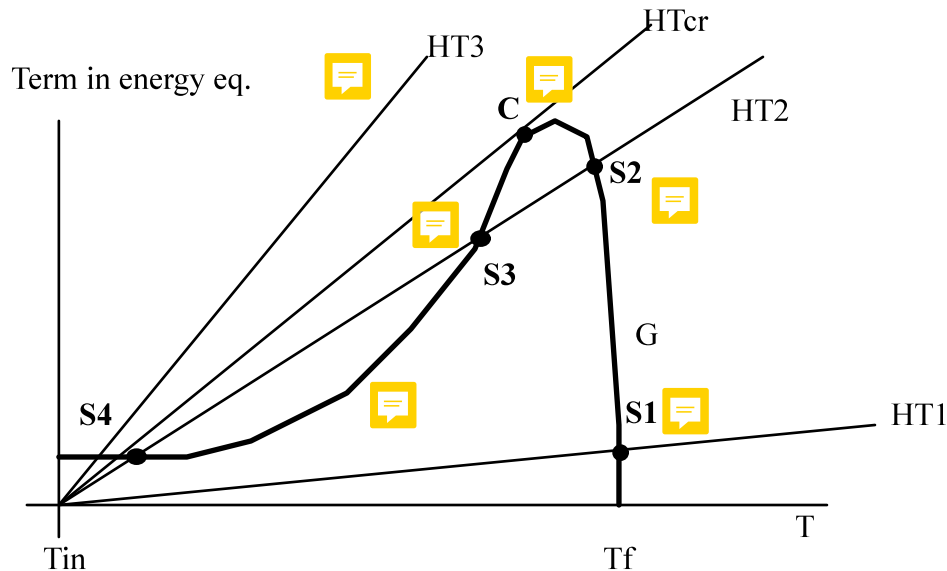
Figure 5-2. The heat generation (G) and the heat transfer term (HT) for the WSR.

Discussion

The important physical intuition provided by Fig. 5-2 is that:
- The reactor will be either burning vigorously at high *T* or the mixture just flows through, cold and virtually unreacted.
- Decreasing the residence time reduces the reactor temperature.
- Hence, from Eq. 5.12, increasing the mass flow rate or decreasing the volume, reduces the temperature.
- There is a critical value of mass flow rate above which a given reactor cannot sustain a flame at all.

The analysis brought out, as in Chapter 4, that successful combustion occurs only if the heat transfer term is not excessive compared to the heat generation term. Here, we also showed that these phenomena have associated *timescales*: combustion will be successful only if the residence time is long compared to the time needed to complete the reactions. As Fig. 5-2 shows, if we do not give enough time to our reactants, unburnt fuel will escape our reactor, the temperature will drop, and if we over-do it, the flame will extinguish.

Important physics

It is a general conclusion that flames extinguish when the reaction cannot keep up with the supply of reactants. The exact point when this occurs depends on the speed of the reaction (in Eq. 5.10, the pre-exponential factor; in Eq. 5.11 the mass fractions and the activation energy), the pressure (Eq. 5.10), and the residence time (Eq. 5.12). Although the present theory may not produce numerically very accurate results for realistic flames (due to spatial inhomogeneities, non-adiabatic or unsteady operation, and due to the fact that our chemical model is too simple), the trends predicted are correct. These trends are explored in Example 5-1 and in the following text.
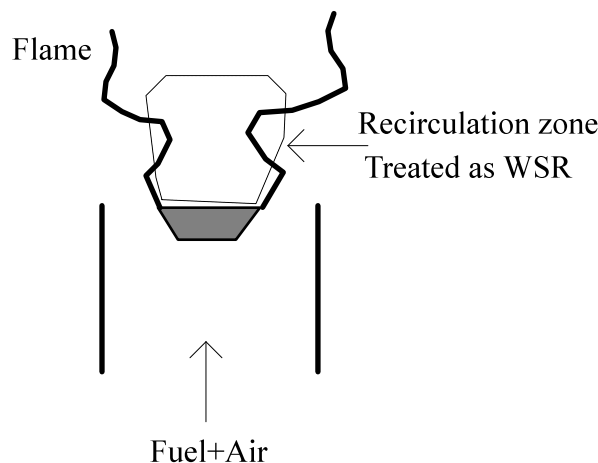
Figure 5-3. A schematic of a bluff-body stabilised flame. The dashed line represents the recirculation zone, which can be approximated as a WSR.

<u>Relevance to practical situations - stabilisation</u>

<u>Bluff-body stabilisers</u>

In most combustion devices, the flow is turbulent and fast and the flame cannot propagate against the reactants. *Stabilization* with *recirculation zones* induced by bluff bodies, sudden expansions or vigorous swirl, is employed to keep the flame anchored in the burner. A bluff-body, apart from creating a low-velocity region, creates a region of <u>hot</u> gases immediately downstream of the stabiliser, because the recirculating flow picks-up hot products from the flame and moves them back at the root of the flame, hence providing a continuous ignition source. This region is very turbulent, well mixed, and hence may be approximately represented by a well-stirred reactor (Fig. 5-3). The blow-off limits of the bluff-body stabilised flame are then determined by the conditions under which the WSR extinguishes. Stabilisation is always employed in industrial burners, gas turbines, and afterburners in military aircraft engines. The blow-off limits of all these devices are predicted by the present theory, hence allowing engineers to know up to how much fuel can be burnt in a given burner or combustor.

A quite crude criterion of flame stability can be derived based on the concept of competition between flow and reaction that has been presented in this Chapter: extinction will occur if the residence time (in the combustor, recirculation zone, flame zone etc.) is less than a characteristic time needed for reactions to be completed. This idea is explored further in Chapter 6 through a rigorous definition of "reaction time".

<u>Jet engines</u>

The highest flight altitude of an airplane is partly determined by flame extinction in the gas turbine combustor. At high altitudes, the pressure decreases and hence the chemical reaction slows down (Eq. 5.10; Ex. 5-1). Hence, for the same $\dot{m}$ through the gas turbine, flight at high altitudes makes the flame susceptible to blow-off (or "engine flame-out", as such events are called by pilots). The WSR theory predicts the correct trends with pressure and is used to relate ground-based tests in the engine factory to high altitude flight.

<u>Chemical engineering practice</u>

The fact that the residence time controls the conversion of reactants into products is a well-known concept in chemical process industries. When the reactions are very non-linear, as in

combustion, qualitatively different behaviour (combustion *vs.* no combustion) may occur if the residence time changes. The WSR model is used extensively in the chemical process industry to capture such phenomena.

Summary

- The well-stirred reactor is an idealization for combustion in many practical devices.
- The temperature of the reactor depends on a competition between residence time and reaction time.
- If the residence time is too short, combustion will extinguish.
- Bluff-body stabilisers are used to stabilize flames in high-speed flows and their stability limits are described by the well-stirred reactor theory.
- The theory predicts the trends of flame extinction with pressure, reactor volume, flow rate and mass fractions. Analytical results are not easy to get, however.

Suggested reading

Turns:
Ch. 6 (pp. 189-195).

Glassman:
Ch. 4, F (pp. 200-205, quickly 205-215).

Spalding:
Ch. 16.

Worked examples

Example 5-1. Find out how the blow-off limit of a well-stirred reactor changes with the pressure, the reactor volume, the fuel mass fraction, and the initial temperature.

Denote the mass flow rate at blow-off by $\dot{m}_b$. From Eq. (5.9), given T_{in} and $Y_{fu,in}$, $\dot{m}_b$ increases linearly with the volume V and with the square of the density ρ.

    (i)   Hence increasing the pressure by a factor of 2 increases the $\dot{m}_b$ by a factor of 4. Similarly, decreasing the pressure, drastically reduces $\dot{m}_b$.

    (ii)   Increasing the volume of the reactor by a factor of 2 increases $\dot{m}_b$ by a factor of 2.

    (iii)   Keeping P and T_{in} constant, a smaller amount of fuel will reduce $\dot{m}_b$. But the effect is very pronounced because reducing $Y_{fu,in}$ also reduces T_f, hence the temperature of operation of the reactor will be smaller, and hence the RHS of Eq. (5.9) will decrease (as the reaction rate decreases).

    (iv)   Increasing T_{in} results in an increase in the operating T of the reactor, hence an increase in the reaction rate, hence a resistance to extinction, i.e. higher $\dot{m}_b$.

Notes:

- In industrial burners, part of the reason why air preheat is used is to help stabilization of the flame.
- Jet planes may experience blow-off in the engine due to the steep reduction in $\dot{m}_b$ as both the pressure and the temperature decrease at high altitudes.

Example 5-2. Methane is burnt with air in a steel reheating furnace for annealing. The flame zone of the furnace is modelled as a WSR of volume 0.1m^3. The pressure is 1bar, the reactants enter the furnace at 300K at stoichiometric proportions and the WSR has a temperature of 2200K. Assume that $c_p=1.35\text{kJ/kgK}$, an average value between cold and hot gases. The reaction can be modelled by a one-step global mechanism with $A=1\text{x}10^9$ (kmol m^{-3})$^{-1}$s^{-1}, $T_{act}=20000\text{K}$. Calculate: (i) the fraction of unburnt fuel escaping the flame zone; (ii) the mass flow rate; (iii) the energy released; and (iv) the residence time.

(i) Using the relationship between fuel mass fraction and temperature (Eq. 5.3), we have:

$$Y_{fu} = Y_{fu,in} - c_p(T - T_{in})/Q \Leftrightarrow Y_{fu}/Y_{fu,in} = 1 - (T - T_{in})/(Y_{fu,in}Q/c_p)$$
$$\Leftrightarrow Y_{fu}/Y_{fu,in} = 1 - (T - T_{in})/(T_f - T_{in})$$

For methane-air mixture at $\phi=1$ and writing the combustion equation, it is easy to show that $Y_{fu,in}=0.0552$ (and, by the way, $Y_{ox,in}=0.2201$). With $c_p=1.35\text{kJ/kgK}$ and $T_{in}=300\text{K}$, we get that $T_f=2343\text{K}$ (Eq. 5.5). Hence:

$$Y_{fu}/Y_{fu,in} = 1 - (2200 - 300)/(2343 - 300) = 0.07,$$ i.e. 7% of fuel escapes unburnt.

(ii) Using Eq. (5.9), we have that:

$$\frac{\dot{m}}{V\rho}(T - T_{in}) = \frac{Q}{c_p} A \frac{MW_{fu}}{MW_{fu} MW_{ox}} \frac{P\overline{MW}}{R^0} \frac{1}{T}$$
$$\times \left(Y_{fu,in} - c_p(T - T_{in})/Q\right) \left(Y_{ox,in} - Sc_p(T - T_{in})/Q\right) \exp\left(-E/R^0 T\right)$$

$$\Leftrightarrow \dot{m} = \frac{1}{T - T_{in}} V \frac{Q}{c_p} A \frac{MW_{fu}}{MW_{fu} MW_{ox}} \left(\frac{P\overline{MW}}{R^0 T} \right)^2$$

$$\times \left(Y_{fu,in} - c_p (T - T_{in})/Q \right) \left(Y_{ox,in} - Sc_p (T - T_{in})/Q \right) \exp\left(-E/R^0 T \right)$$

Recognising that $S = 2 \cdot 31.999/16.043 = 3.989$ (from the combustion equation; S is the mass ratio of oxygen to fuel at stoichiometry) and assuming a mean molecular weight equal to that of air (i.e. 28.85), putting numbers gives $\dot{m} = 9.51 \times 10^{-3}$ kg/s.

(iii) The energy released is equal to the amount of fuel burnt times the calorific value, i.e. $Q \dot{m} \left(Y_{fu,in} - Y_{fu} \right) = 24.38$ kW.

(iv) The residence time is given by Eq. (5.12), i.e. $t_{res} = V \dfrac{P\overline{MW}}{R^0 T \dot{m}} = 1.66$s.

Internet-based learning

Go to   http://diesel.ME.Berkeley.EDU/~gri_mech/cal22/

We first saw this Java applet in Chapter 4 concerning autoignition. Here, we will use its WSR option. This Java applet uses a detailed chemistry set, not our simple one-step model, and solves simultaneously many species conservation equations (5.1) in addition to the energy equation (5.7). The exercises below should take you about 30 mins and illustrate very well all the concepts discussed in this Chapter.

In the left of the page, click on "Reactor". Then select the buttons for "CSTR", "Energy Equation" and "Mass flow rate". (Chemical engineers call the well-stirred reactor a "continuously stirred tank reactor" and hence the CSTR acronym). Click "Set". Now, specify the reactor operating points and other parameters: try 1800K in "estimated temperature", 1 atm, 2 cm^3 reactor volume, 1 g/s mass flow rate, 300K inlet temperature, and zero for "heat loss". Click "Set".

Now input the percentage (by vol.) of natural gas in the reactants stream. Try 7%, Click "Set". Now, specify the natural gas composition. "Assign" 100% of CH_4. Specify the atmospheric air composition in the next window in a similar manner.

Click "Start Calculation". After a few seconds, you can examine the output, which consists of the reactor's temperature and the mole fractions of all species. Experiment now with increasing the mass flow rate in small steps until the reactor extinguishes (i.e. the output temperature is identical to the initial temperature of 300K). For the parameters above, this should happen between 2.6 and 2.7 g/s.

Plot the outlet temperature and fuel mole fraction against the mass flow rate. Examine these curves: as $\dot{m}$ increases, the temperature drops and the fuel mole fraction increases (i.e. unburnt fuel survives in the outlet of the reactor). These results are consistent with our simple theory in this Chapter. Experiment by increasing the pressure and/or the volume: the $\dot{m}$ for extinction should go up, as expected.

Computational codes very similar to the one in this applet are used extensively by gas turbine engineers to design new combustors.