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Chapter 8
Jet-Stirred Reactors

Olivier Herbinet[1], Guillaume Dayma[2]

Abstract The jet-stirred reactor is a type of ideal continuously stirred-tank reactor which is well suited for gas phase kinetic studies. It is mainly used to study the oxidation and the pyrolysis of hydrocarbon and oxygenated fuels. These studies consist in recording the evolution of the conversion of the reactants and of the mole fractions of reaction products as a function of different parameters such as reaction temperature, residence time, pressure and composition of the inlet gas. Gas chromatography is classically used for the analysis of the species in the gas phase, but recent studies aimed at coupling new types of analytical devices to a jet-stirred reactor to observe new types of species and to gain accuracy in the identification and the quantification of species.

8.1 Overview of the Jet-Stirred Reactor

Gas phase kinetic studies are mostly performed using closed vessels, burners and continuous stirred-tank reactors. Among continuous stirred-tank reactors is the jet-stirred reactor. One of its major advantages relies on the efficient mixing of the gas phase which provides identical and homogeneous compositions of the outlet gas and of the gas inside the reactor. When operated at steady state and at constant residence time, temperature and pressure, this type of reactor is easily modelled by a very simple system of mass balances. Another advantage of this reactor is the possibility of being coupled with analytical techniques such as gas chromatography and mass spectrometry for the identification and the quantification of the species in the gas phase.

One of the best ways to achieve the mixing of the gas phase is to use turbulent jets obtained from nozzles. Despite the strong pressure drop in the nozzles, this technique provides very intense internal recycle streams. The material used for the manufacturing of the reactor is of great importance. The use of metal is not recommended because of possible large wall effects and the use of Pyrex glass or fused silica is preferred.

The jet-stirred reactor has often been used to study the gas phase oxidation and the thermal decomposition of fuels. These studies consist in measuring the evolution of the mole fractions of species at the outlet of the reactor as a function of different parameters such as reaction temperature, residence time, pressure and composition of the inlet gas (the fuel concentration and the equivalence ratio in combustion experiments). The reactivity of the fuel and the selectivity of the reaction products can be deduced from these data.

The residence time of the gas in the reactor (Eq. 8.1) is actually a mean residence time (or space time) which is defined as the ratio of the volume of the reactor, V, and of the volume flow rate of the gas flowing through the reactor, Q, which is also the volume flow rate at the outlet of the reactor, Q^o (Fig. 8.1).

To verify that the reactor can be considered as a continuous stirred-tank reactor, one can measure the residence time distribution by doing a short injection of a very small amount of tracer at the inlet and by recording the evolution of the concentration of the tracer at the outlet. The reactor is an ideal continuous stirred-tank reactor if the residence time distribution $E(t)$ can be represented by the expression given by Eq. 8.2.

$$\tau = V/Q \tag{8.1}$$

$$E(t) = \frac{1}{\tau} exp\left(-\frac{t}{\tau}\right) \tag{8.2}$$

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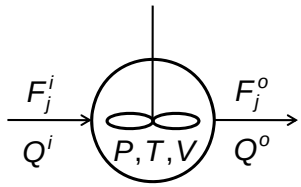

Fig. 8.1 Simplified scheme of a jet-stirred reactor of volume V working at constant temperature T and pressure P. F_j^i and F_j^o are the mole flow rates of the species j at the inlet and at the outlet of the reactor. Q^i and Q^o are the volume flow rates of the gas at the inlet and at the outlet of the reactor (Q^o is defined under the conditions of pressure and temperature inside the reactor)

To our knowledge, glass or fused silica jet-stirred reactors have been used for gas phase kinetic studies by three research teams. It is largely used in Nancy (France) at the Laboratoire Réactions et Génie des Procédés for the study of the oxidation and of the pyrolysis of hydrocarbons and oxygenated fuels at atmospheric pressure (e.g., Marquaire and Côme 1978; Herbinet et al. 2007; Herbinet et al. 2011c; Hakka et al. 2009; Battin-Leclerc et al. 2010). A high pressure jet-stirred reactor is used in Orléans (France) at the Institut de Combustion Aérothermique Réactivité et Environnement for the study of the oxidation of various type of fuels (e.g., Dagaut et al. 1994; Mzé-Ahmed et al. 2010) and for the study of the kinetics of nitrous oxides formation and destruction (e.g., Dayma and Dagaut 2006). It was also used in Leeds (United Kingdom) at the Department of Physical Chemistry and Center for Combustion and Energy to study stationary-state and oscillatory ignition phenomena in fuel oxidation (e.g., Baulch et al. 1988; Griffiths and Inomata 1992). Metallic jet-stirred reactors have been used for the study of the low temperature oxidation of hydrocarbons (e.g., Cavaliere et al. 1993; Ciajolo and D'Anna 1998) and for the study of the cracking kinetics of biomass pyrolysis vapours (Baumlin et al. 2005).

8.2 Jet-Stirred Reactor Construction Rules

The basis for the design of spherical jet-stirred reactors was proposed by the team of Professor Villermaux in Nancy (France) in the seventies (Matras and Villermaux 1973; David and Matras 1975). A little earlier Bush (1969) proposed rules for the construction for cylindrical jet-stirred reactors. Although both designs can be used for gas phase kinetic studies, spherical jet-stirred reactors are preferred to minimize dead volumes. In this chapter we focus on the design of spherical jet-stirred reactors.

The jet-stirred reactor designed by the team of Villermaux is composed of a sphere in which the reaction takes place. The fresh gases enter the reactor through an injection cross located at the center of the sphere and composed of four nozzles providing the jets ensuring the mixing of the gas phase. Fig. 8.2 displays a picture of the jet-stirred reactor which is still in use at the Laboratoire Réactions et Génie des Procédés (Nancy, France) and which was developed from the rules of construction proposed by the team of professor Villermaux.

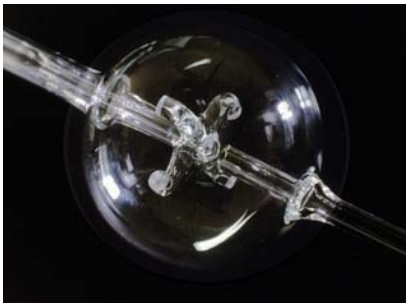

Fig. 8.2 Picture of the jet-stirred reactor used in Nancy (France) and which was developed from the rules of construction proposed by the group of professor Villermaux

The rules of construction of a jet-stirred reactor rely on the theory of the free jet: the jet from a nozzle leads to the motion of the gas phase in which it flows and this motion results in the distribution of the initial kinetic energy in small turbulent pieces of gas phase. It is assumed that a jet provided by a nozzle in the reactor widens in form of a cone which bends along a circumference between two nozzles (Bush, 1969) as shown in (Fig. 8.3).

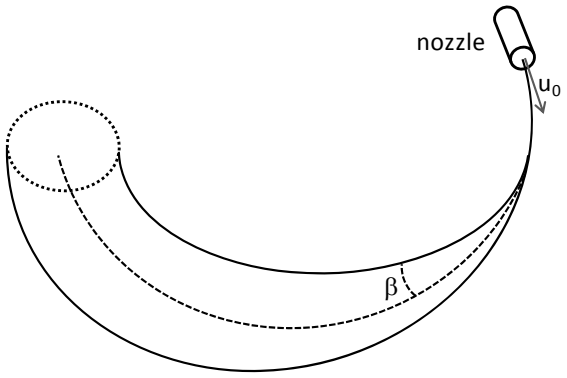

Fig. 8.3 Scheme of the cone of gas from a nozzle in the jet-stirred reactor. u_0 is the velocity of the gas at the outlet of a nozzle. β is the angle at the top of the cone formed by the jet

8.2.1 The Theory of the Free Jet

A jet is assumed to be free if the condition of Liepmann and Laufer (David and Matras 1975) is satisfied (Eq. 8.3). In Eq. 8.3, u_0 is the velocity of the gas at the outlet of a nozzle, R is the radius of the spherical reactor, ρ is the specific weight of the gas, and η is the dynamic viscosity of the gas. The velocity of the gas u_0 (Eq. 8.4) can be expressed as a function of the radius of the reactor R, of the diameter of the nozzle d and of the residence time τ which is given in Eq. 8.1. Replacing u_0 in Eq. 8.3 we obtain the condition given by Eq. 8.5.

$$\frac{u_0\,\pi\,R\,\rho}{2\,\eta} \geq 7.10^4 \qquad (8.3)$$

$$u_0 = \frac{4\,Q}{\pi\,d^2} = \frac{4\,R^3}{3\,\tau\,d^2} \qquad (8.4)$$

$$\frac{2\,\pi}{3}\,\frac{\rho\,R^4}{\tau\,d^2\,\eta} \geq 7.10^4 \qquad (8.5)$$

This condition is always satisfied for reactors with a radius R greater than 1 cm and given the other conditions on the residence time τ and the internal diameter of the nozzles d which are described in the following paragraphs.

Hinze and Hegge Zijnen (1949) experimentally established the expression of the velocity in a free jet with axial symmetry (Eq. 8.6 and Eq. 8.7). $u_a(x)$ is the velocity on the axe of the jet at the distance x from the nozzle and $u_r(x,r)$ is the velocity at the distance r from the axe of the jet and at the distance x from the nozzle (see Figure 8.4). The parameter α in Eq. 8.7 is a dimensionless constant which depends on the nature of the gas and of the thermodynamic conditions ($\alpha^{-1} = 0.016$ for air at 293.15 K).

$$u_a(x) = 6.39\,u_0\,\frac{d}{x+0.6\,d} \qquad \frac{x}{d} > 10 \qquad (8.6)$$

$$u_r(x,r) = \frac{u_a}{\left(1+\alpha\,\frac{r^2}{x^2}\right)^2} \qquad (8.7)$$

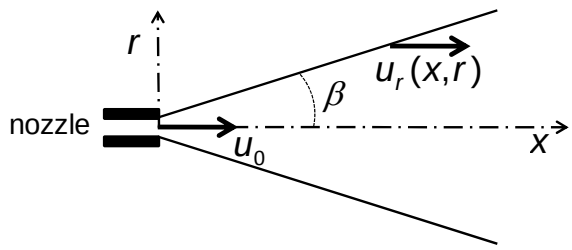

Fig. 8.4 Simplified scheme of the cone of gas from a nozzle in the jet-stirred reactor with the representation of the velocities in the jet. x and r are the axial and the radial positions, respectively. u_0 is the velocity of the gas at the outlet of a nozzle. $u_r(x,r)$ is the velocity at the distance x from the nozzle and at the distance r from the axe of the jet. β is the angle at the top of the cone formed by the jet

Hinze and Hegge Zijnen (1949) experimentally measured u_a and u_r for different values of β which is the angle at the top of the cone as shown in Fig. 8.3 and in Fig. 8.4. It was observed that the velocity u_r is almost zero when β is greater than 11°. The volume flow rate $Q_S(x)$ through the section of the cone at the distance x of the nozzle is obtained from the integration of $u_r(x,r)$ on this section considering β = 11° as limit value for the upper bound of the integration interval. The expression of $Q_S(x)$ is given by Eq. 8.8. Q_0 is the volume flow rate of the gas at the outlet of the nozzle. The parameter A is an adimensionnal constant which is equal to 0.3 in the case of air at 293.15 K and at atmospheric pressure. Matras and Villermaux (1973) showed that the value of the parameter A increases with the temperature, leading to a better mixing of the gas phase ($A = \pi/4$ at 723.15 K and at atmospheric pressure).

$$Q_S(x) = A\, Q_0 \frac{x}{d} \tag{8.8}$$

8.2.2 Criteria of Construction

The homogeneity of the composition of the gas phase in the jet-stirred reactor relies on the three following criteria:

- The jets from the four nozzles must be turbulent; in other words the internal mixing in each of the four jets must be turbulent.
- The four jets must be able to provide a good mixing of the whole gas phase in the reactor; the jets must provide very intense internal recycle streams.
- The velocity of the jets at the outlet of the nozzles must not exceed the speed of sound.

The first and the third criteria fix the range of accessible residence times and the second criterion fixes the geometrical ratio between the internal diameters of the reactor and of the nozzles.

8.2.2.1 Turbulent Jets

The Reynolds number R_e of the jets from the nozzles must be turbulent. The expression of the Reynolds number is given by Eq. 8.9.

$$R_e = \frac{\rho\,(2r)}{\eta}\frac{Q_S(x)}{\pi\, r^2} = \frac{\rho\,\left(4\, Q_S(x)\right)}{2\,\eta\,\pi\, x\, tan(\beta)} \tag{8.9}$$

Using Eq. 8.10, we obtained a new expression of the Reynolds number which does not depend on the distance x (Eq. 8.11).

$$4\, Q_S(x) = 4\, Q_0\, A\, \frac{x}{d} = A\, \frac{x}{d}\, \frac{4}{3}\, \frac{\pi\, R^3}{\tau} \tag{8.10}$$

$$R_e = \frac{4\,\rho\, A\, R^3}{6\,\eta\, d\, \tau\, tan(\beta)} \tag{8.11}$$

Experimentally it is observed that the mixing is not good enough for Reynolds number R_e less than 800. The upper limit for the residence time τ is obtained from Eq. 8.12.

$$\tau \leq \frac{\rho\, A\, R^3}{230\,\eta\, d} \tag{8.12}$$

8.2.2.2 Recycling

The recycling rate R_r is defined as the ratio between the residence time τ and the time t which is needed to carry the whole volume of gas in the reactor from one nozzle to the following one. It is also the ratio between the volume flow rate $Q_S(x)$ at $x = \frac{\pi\, R}{2}$ (distance from one nozzle to the following one) and the volume flow rate Q_0 of the gas at the outlet of a nozzle (Eq. 8.13).

$$R_r = \frac{\tau}{t} = \frac{Q_S\left(\frac{\pi R}{2}\right)}{Q_0} \quad (8.13)$$

Using the geometrical relationship between the two volume flow rates with $x = \frac{\pi R}{2}$ (Eq. 8.14), we obtained for R_r the expression given by Eq. 8.15.

$$Q_S\left(\frac{\pi R}{2}\right) = Q_0 \cdot \frac{\pi A R}{2 d} \quad (8.14)$$

$$R_r = \frac{\pi A R}{2 d} \quad (8.15)$$

Experimentally it was observed that the recycling rate R_r must be larger than 30 to have a good mixing of the gas phase. This leads to the condition given by Eq. 8.16 that fixes the required ratio between the radius of the reactor and the internal diameter of the nozzles.

$$\frac{R}{d} > 64 \quad (8.16)$$

8.2.2.3 Sonic Limit

The velocity u_0 of the gas at the outlet of a nozzle must be lower than the speed of sound $c_{sound}(T, P)$ at the temperature and the pressure of the reaction (Eq. 8.17). The velocity u_0 can be expressed as a function of the radius of the reactor R, the diameter of the nozzle d and the residence time τ (Eq. 8.18), which leads to the lower conditions on the residence time (Eq. 8.19).

$$u_0 \leq c_{sound}(T, P) \quad (8.17)$$

$$u_0 = \frac{4 Q_0}{\pi d^2} = \frac{4}{3} \frac{R^3}{d^2 \tau} \quad (8.18)$$

$$\tau \geq \frac{4}{3} \frac{R^3}{d^2 c_{sound}(T,P)} \quad (8.19)$$

8.2.2.4 Verification of the criteria for Nancy JSR

For the verification of the criteria, it was considered that the gas flowing through the reactor was argon. Calculations were performed at a temperature of 723 K and a pressure of 10^5 Pa. The radius of the reactor, R, and the internal diameter of the nozzle, d, were taken equal to 3.10^{-2} m and 3.10^{-4} m, respectively.

The upper limit for the residence time is given by Eq. 8.12. At 723 K, the specific weight and the dynamic viscosity of argon are equal to 0.71 kg.m^{-3} and $4.23.10^{-5}$ Pa.s, respectively. The value of the parameter A is not known but it is assumed that it does not change significantly from one gas to another. For the calculation, the value of A for air at 723 K was used ($A = \pi/4$). The calculation leads to a maximum residence time of 5.2 s.

The lower limit is given by Eq. 8.19. The speed of sound can be calculated from the equation for an ideal gas (Eq. 8.20).

$$c_{sound} = \sqrt{\gamma R T / M} \quad (8.20)$$

In Eq. 8.20, γ is the adiabatic index, R is the molar gas constant and M the molecular weight of the gas. For argon, at 723 K, c_{sound} is equal to 500 m.s^{-1}. The calculation leads to a minimum residence time of 0.8 s.

The recycling rate is given by Eq. 8.15. The calculation leads to a recycling rate of 123 which is more than the minimum required value of 30.

8.3 Improvements to Jet-Stirred Reactor

The jet-stirred reactor developed by the team of Professor Villermaux was later improved for the study of the oxidation and thermal decomposition of hydrocarbons and oxygenated molecules. One of the major improvements was to preheat the incoming mixture to obtain a more homogeneous temperature in the reactor. New versions of this type of reactor were then developed for studies at high pressure (up to 40 bars) and for studies of hetero-homogenous reactions.

8.3.1 Temperature Homogeneity

The homogeneity of the temperature in the reactor is of importance in gas phase kinetic studies as reaction rates are very sensitive to this parameter. The jet-stirred reactor, the rules of construction of which are presented in the previous part of this chapter, was designed to have a homogeneous composition of the gas phase but little attention was paid to the homogeneity of the temperature.

Azay and Côme (1979) studied the influence of gas preheating on the thermal gradient in a jet-stirred reactor designed according to the rules of David and Matras (1975). Temperature gradients up to 80 K were recorded in the gas phase inside the reactor with no preheating and a significant difference in the mole fractions of methane was observed in the oxidation of *neo*-pentane with and without preheating of the fresh gases.

Following the observations of Azay and Côme (1979), preheating was added to avoid the formation of temperature gradients due to cold fresh gases entering the reactor (Fig. 8.5). The design of the preheater was based on the work of Houzelot and Villermaux (1977). They showed that annular geometries with high surface-volume ratio perform very well for heat transfer as heating rates of 10 $K.s^{-1}$ can be achieved.

The dilution in an inert gas also helps to reduce the formation of temperature gradients in the gas phase due to the strong exothermicity of the reaction in combustion experiments (or due to the endothermicity in pyrolysis studies). Gas phase kinetic studies are usually performed under high dilution conditions using an inert gas such as nitrogen, helium or argon. Fuel inlet mole fractions are typically in the range 10^{-4}-10^{-2}.

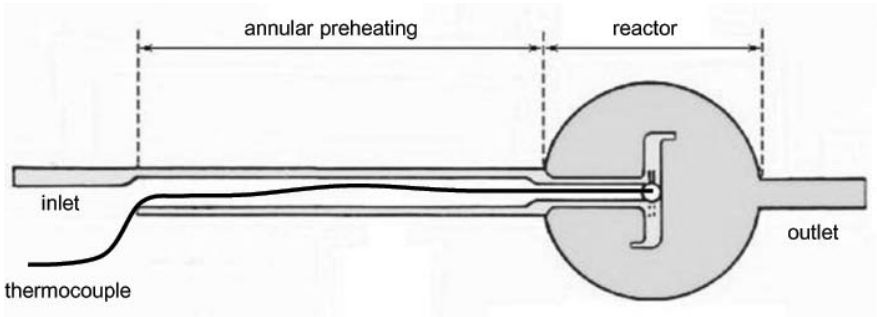

Fig. 8.5 Scheme of the jet-stirred reactor and of the annular preheating used in Nancy at the Laboratoire Réactions et Génie des Procédés for oxidation and thermal decomposition gas phase studies

The heating can be performed using either an oven or heating wires. The advantages of using heating wires are that there is very little thermal inertia and that it is possible to coil them directly around the different parts of the reactor and to heat the zones at different temperatures (Azay et al. 1981). Thus the preheating can be divided in several zones (typically two) to obtain progressive heating of the fresh gases before they enter the reactor. The measure of the reaction temperature is performed thanks a thermocouple which is slipped in the intra-annular part of the preheater with the extremity of the thermocouple located in the center of the sphere as shown in Fig. 8.5.

8.3.2 High-Pressure Gas Phase Kinetic Studies

In order to investigate the pressure effect on the reactivity and the homogeneity of the mixture some other improvements were made at the Institut de Combustion Aérothermique Réactivité et Environnement (Orléans, France). To extend the experimental investigation range to pressures above atmospheric, the quartz reactor is lo-

cated inside a stainless-steel pressure-resistant jacket (Dagaut et al. 1986). Working under high pressure is made possible by means of pressure balancing inside and outside the reactor. This was achieved by drilling four holes at the bottom of the propagation tube as shown in Figure 8.6. The pressure is kept constant in time in the apparatus by means of a pressure regulator on the exhaust line. A safety valve prevents any accidental pressure rise in the system.

Fig. 8.6 Detail of the reactor developed in Orléans. The holes at the bottom of the prolongation tube are for pressure balancing

Although built following the guidelines established by the team of Professor Villermaux, the design of the reactor was revisited. The reactor is still a sphere made of fused silica to prevent wall catalytic reactions, but the injectors were shifted towards the upper part of this sphere instead of being located in the equatorial plane. Nevertheless, the four nozzle outlets are still located in the equatorial plane of the spherical reactor so that the shape of the streams recommended by Matras et al. to ensure a perfect mixing is respected. This new design of the injectors allows a physical investigation of the whole volume of the reactor. By means of a system probe position adjuster, a thermocouple probe and a sampling sonic quartz probe can be moved along the vertical axis of the reactor. The thermocouple wires are enclosed in a thin-wall fused silica tube which is fixed against the sample probe. A residence-time distribution study was performed at 10 atm (~1MPa) by pulsed injection of argon at the inlet of this reactor at room temperature: this led to the same conclusions as Matras et al. with their own design. Thus, this reactor is perfectly stirred for mean residence times varying from 0.01 to several seconds in the pressure range of 1 to 10 atm. Moreover, the reactor's homogeneity can be checked during experiments by measuring the temperature of the gases by means of a chromel-alumel thermocouple probe and by analyzing by gas chromatography the gases sampled with the sonic probe at different locations inside the reactor.

8.3.3 Study of Hetero-homogeneous Reactions

A special version of the jet-stirred reactor was developed at the Laboratoire Réactions et Génie des Procédés (Nancy, France) in the nineties for the study of the coupling of hetero-homogeneous reactions (Côme et al. 1996). The spherical jet-stirred reactor was modified to make it possible to add pellets of catalyst or matrix (for the study of the fabrication of composite materials) inside the reactor (Fig. 8.7): the upper part of the reacting zone is hemispherical (as in the original jet-stirred reactor) whereas the lower part is cylindrical with a removable piston. The catalyst is deposited on the surface of the piston.

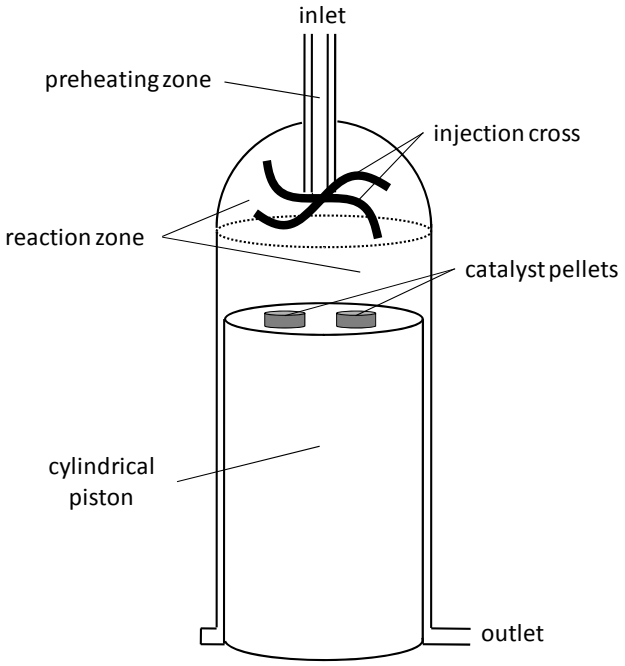

Fig. 8.7 Scheme of the special version of the jet-stirred reactor developed in Nancy for the study of the coupling of hetero-homogeneous reactions

This type of reactor was mainly used for the study of the catalytic partial oxidation of methane (Côme et al. 1996; Fleys et al. 2006) and for the study of surface reactions in chemical vapour infiltration of pyrocarbon (Ziegler et al. 2005).

8.4 Sampling Methods

The sampling of the species in the gas phase is of importance for the accuracy of the analysis. One major difficulty is to avoid any change in the composition of the gas between the outlet of the reactor and the analysis. Two types of methods can be used for the sampling: online and offline sampling.

The offline sampling consists in collecting the species in a vessel connected to the outlet of the reactor and to inject the content of the vessel in a gas chromatograph. The species can be kept in the gas phase with collection and storage in a low pressure (50 mbar) Pyrex bulb to avoid condensation of water and species with low vapor pressure (Dagaut et al. 1986) or can be condensed in the solid phase at liquid nitrogen temperature and afterward reheated with addition of a solvent such as acetone (Herbinet et al. 2007; Hakka et al. 2009). This second option (use of a solvent) can be problematic as there is a risk of reaction between unstable species (e.g., species with hydroperoxide functions) and the solvent.

The online sampling consists in sending the gas exiting from the reactor directly through the loop of the injection valve of a gas chromatograph. The tube used for connecting the outlet of the reactor to the injection system must be heated to avoid condensation of the species and it is better to use a tube the wall of which has been rendered inert to avoid adsorption phenomena and reactions at the wall (Herbinet et al. 2011a).

The sampling with species remaining in the gas phase is definitely the best manners to limit changes in the composition of the gas exiting from the reactor. Nevertheless it was observed that unstable species such as hydroperoxides still decompose before the analysis as they are very reactive and that there is still a risk that some species with low vapor pressures, such as polycyclic aromatic hydrocarbons, condense in the transfer line. For these heavy species it is better to use offline sampling for a more accurate quantification (Hakka et al. 2009; Bax et al. 2010).

The online sampling can be performed in the gas flowing in the outlet of the reactor or in the gas phase inside the reactor using a sonic probe. The second method is used when the reactor and the analytical apparatuses are working at different pressures (for example in the high-pressure oxidation studies or when the analytical device works at very low pressure). The use of a sonic probe, with a very small orifice, helps to maintain the difference of pressure between the reactor and the analytical device. The pressure drop through the orifice also leads to the

freezing of the reaction thanks the concomitant decrease of temperature and of the partial pressures. Fig. 8.8 displays a picture of a sonic probe and of a glass finger with a thermocouple inside used to sample species and measure the reaction temperature in the high pressure jet-stirred reactor used in Orléans (Dagaut et al. 1986).

Fig. 8.8 Picture of a sonic probe (in the left) and of a glass finger with a thermocouple inside (in the right) used to sample species and measure the reaction temperature in the high pressure jet-stirred reactor used in Orléans (Dagaut et al. 1986)

8.5 Analytical Devices

One of the advantages of the jet-stirred reactor is the possibility of easy coupling with several types of analytical devices. Gas chromatography is the most used technique for the quantification and the identification of species. This technique is well adapted to the analysis of most stable molecules such as hydrocarbons or permanent gases. However it is not well adapted to the quantification of some species (e.g., water and formaldehyde for which Fourier transform infrared spectroscopy is more suitable), of unstable molecules (such as hydroperoxides which are common intermediates in the low temperature oxidation of hydrocarbons), and of radicals. Thus tentatives of coupling of the jet-stirred reactor with new analytical techniques (e.g., mass spectrometry with direct sampling in the reactor and spectroscopic techniques) have been carried out to quantify an enlarged range of types of species.

8.5.1 Gas Chromatographic Analyses

Gas chromatography is a very common analytical technique that is widely used for the identification and the quantification of species in gas phase kinetic studies. This technique is mainly coupled to the following detectors: flame ionization detectors (FID) for the quantification of species containing carbon atoms, thermal conductivity detector (TCD) for the quantification of permanent gases and mass spectrometer which can be used for both the identification and the quantification of species. Fig 8.9 displays mole fraction profiles obtained in the experimental study of the oxidation of methyl decanoate using gas chromatographic analysis (Glaude et al. 2010).

The identification of the reaction products is most of the time performed using a gas chromatograph coupled to a mass spectrometer with electron impact ionization at 70 eV. The identification work becomes sometimes difficult in gas phase studies as the mass spectra of the species are not always in the databases and as the mass spectra of isomers are very similar. The deciphering of experimental mass spectra can be carried out when they are not available in the databases. For example, this is often the case for cyclic ethers which are very common and important intermediates formed by the propagation steps involved in the low temperature oxidation of hydrocarbons (Herbinet et al. 2011b).

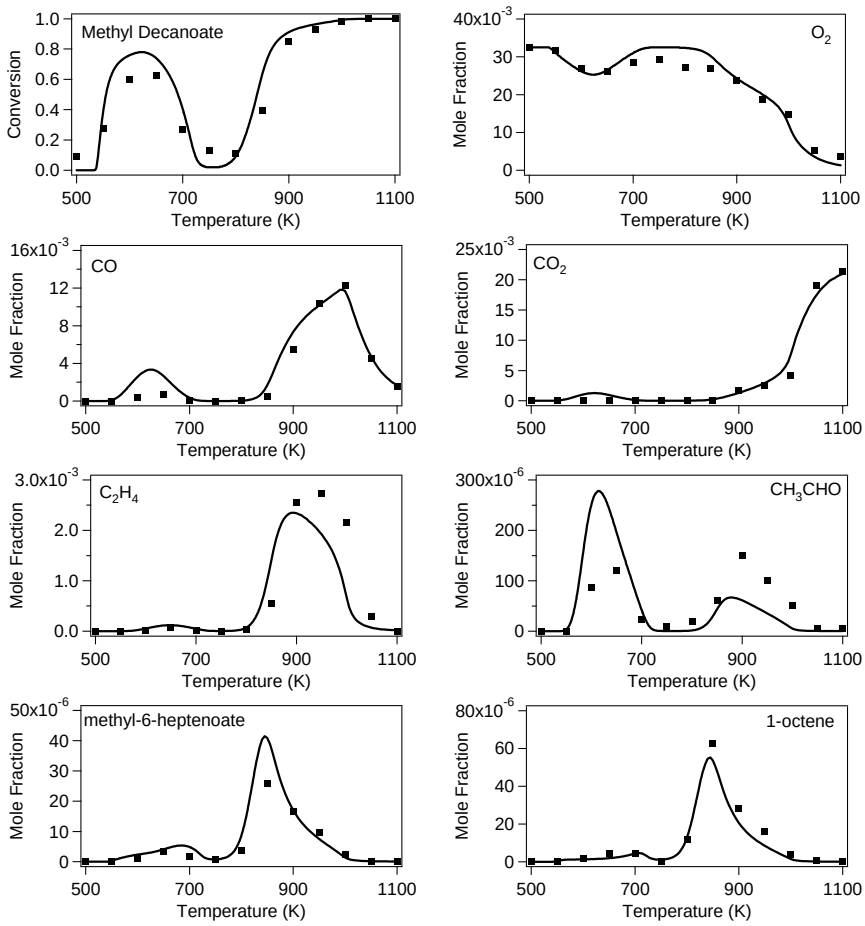

Fig. 8.9 Mole fraction profiles of reactants and of some reaction products obtained using gas chromatography during the experimental study of the oxidation of methyl decanoate in a jet-stirred reactor. Symbols are experimental data and lines are data computed with a model (Glaude et al. 2010)

8.5.2 Infrared Spectroscopy

Fourier transform infrared spectroscopy is a technique used to obtain the infrared spectrum (IR) of a molecule and since, in principle, each IR spectrum is unique it therefore aids identification. In addition the technique can be used quantitatively provided that standards are available whose spectrum can be obtained under the same set of conditions as the analytes themselves. This is because the structure of the spectra is sensitive to concentration, as well as pressure and temperature. Hence, the pressure and the temperature of the analysis cell are controlled and the cell is connected to the sampling probe of the reactor by means of heated line to avoid condensation. The cell is filled of the reacting mixture at the pressure and the temperature at which the standards of species targeted were performed. Finally, a software is able to deconvolute each experimental spectrum and recover the individual spectra and to quantify**.**

Fig 8.10 displays mole fraction profiles of CO, CO_2, H_2O, NO, NO_2 and CH_2O obtained in the experimental study of the oxidation of a blend of *n*-heptane and toluene (80-20 mol%) in a jet-stirred reactor using Fourier transform infrared spectroscopy (Dubreuil et al. 2007).

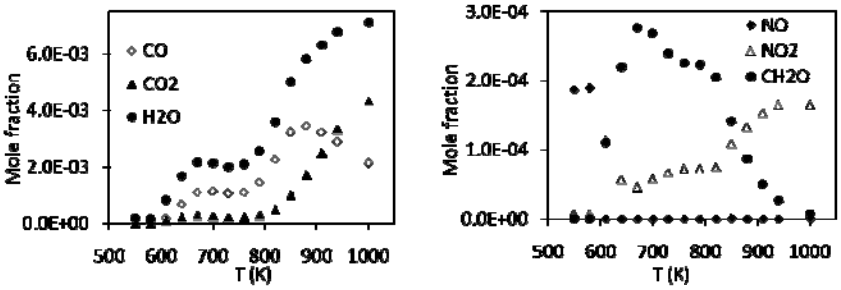

Fig. 8.10 Mole fraction profiles of CO, CO_2, H_2O, NO, NO_2 and CH_2O using Fourier transformed infrared spectroscopy during the experimental study of the oxidation of a blend of *n*-heptane and toluene in a jet-stirred reactor (Dubreuil et al. 2007). Experiments were performed in a jet-stirred reactor at a pressure of 10 atm, a residence time of 0.5 s, fuel and NO inlet concentrations of 800 and 50 ppmv, respectively, and equivalence ratio of 2

8.5.3 SVUV Photo-ionization Mass Spectrometry

A coupling of a jet-stirred reactor and a reflectron time-of-flight mass spectrometer (RTOF-MS) with tunable synchrotron vacuum ultra violet (SVUV) photo-ionization was achieved using a molecular beam sampling system (Battin-Leclerc et al. 2010; Herbinet et al. 2011a). The coupling was made through a cone-like nozzle which was pierced with a very small orifice (the diameter of which was about 50 μm) and which was inserted in the lateral wall of a spherical jet-stirred reactor (Fig 8.11). Fig 8.12 is a picture of the jet-stirred reactor connected to the mass spectrometer at the National Synchrotron Radiation Laboratory (Hefei, China).

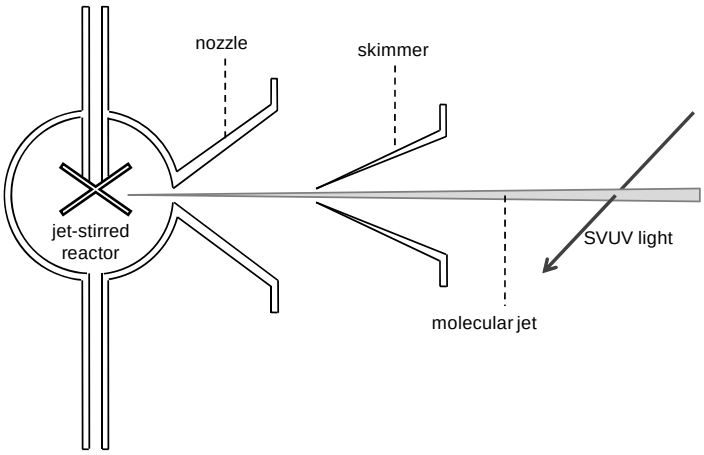

Fig. 8.11 Simplified scheme of the coupling of a jet-stirred reactor and a reflectron time-of-flight mass spectrometer with tunable synchrotron vacuum ultra violet photo-ionization using a molecular beam sampling system

This arrangement alleviates the problem of changes in the composition of the gas between the outlet of the reactor and the analytical apparatus. SVUV photo-ionization mass spectrometry is a very powerful method for the identification of molecules (especially unstable molecular intermediates) and radicals in gas phase kinetic studies (Hansen et al. 2009; Li and Qi 2010; Qi 2013). This analytical technique was already used to study the oxidation of hydrocarbons and allowed the identification of enols in flame experiments (Taatjes et al. 2005). Two major difficulties in this technique are the separation of isomers which are identified using their photo-ionization energies (which are sometimes very close) and the quantification of species which requires the knowledge of the cross sections of the species as a function of the photon energy.

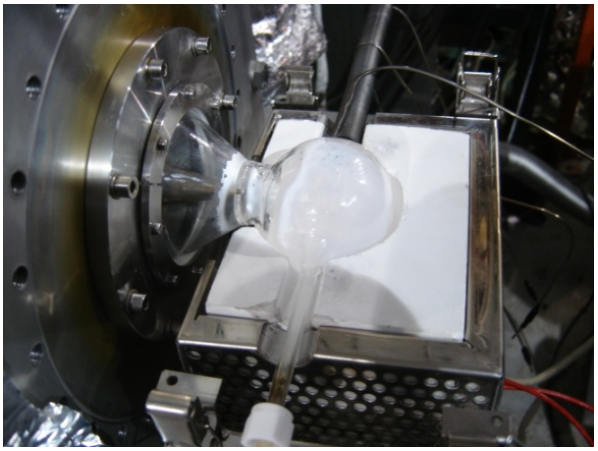

Fig. 8.12 Photograph of the jet-stirred reactor coupled to the reflectron time-of-flight mass spectrometer at the National Synchrotron Radiation Laboratory (Hefei, China)

The study of the low-temperature oxidation of n-butane was performed using a jet-stirred reactor coupled to the RTOF-MS (Herbinet et al. 2011a). No radical species were observed during this study due to the very low concentration of this type of species in a jet-stirred reactor (as an example, orders of magnitude of the concentrations of hydroperoxyl and hydroxyl radicals are 1 and 0.01 ppm, respectively). But this technique allowed the identification of an important class of molecules involved in the low temperature oxidation chemistry of hydrocarbons: hydroperoxides and ketohydroperoxides. Fig 8.13 displays the mole fraction profiles of hydroperoxides and ketohydroperoxides detected in the study of the low-temperature oxidation of *n*-butane (experiments performed at 106 kPa, a residence time of 6 s, fuel and oxygen inlet mole fractions of 0.04 and 0.26, respectively).

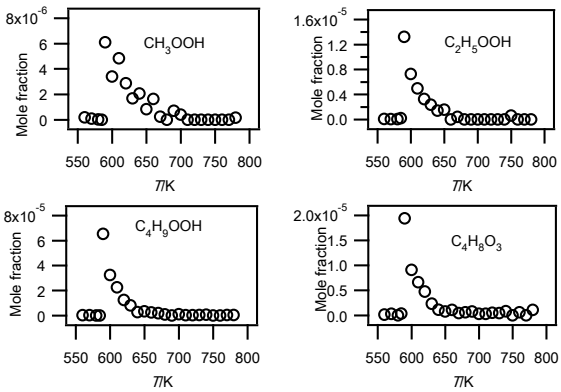

Fig. 8.13 Experimental mole fractions of hydroperoxides and ketohydroperoxides formed in the low temperature oxidation of n-butane. Experiments were performed in a jet-stirred reactor and using SVUV photo-ionization mass spectrometry (Herbinet et al. 2011a)

8.5.4 Cavity Ringdown Spectroscopy

A jet-stirred reactor has been coupled to a cavity where continuous wave cavity ring-down spectroscopy (cw-CRDS) can be performed at the Laboratoire Réactions et Génie des Procédés (Nancy, France) in collaboration with the laboratory PhysicoChimie des Processus de Combustion et de l'Atmosphère (Lille, France). cw-CRDS is a technique which has already been used to measure the concentrations of OH and HO_2 radicals in the photolysis of hydrogen peroxide (Parker et al. 2011). The coupling of the jet-stirred reactor and of the spectroscopic cell was achieved using a sonic probe as in flame experiments (Fig. 8.14). The use of a sonic probe instead of a molecular beam allowed the sampling of species in the gas phase in the reactor and the maintenance of a high enough pressure in the spectroscopic cell.

Studies of the oxidation of methane and *n*-butane were recently performed using this apparatus (Bahrini et al. 2012a and 2012b). The high sensitivity of this absorption technique allowed the quantification of some stable species in the oxidation of methane: water, methane and formaldehyde (Fig. 8.15), whose IR spectra around 1506 nm are well structured and well known, particularly for methane and formaldehyde. Hydrogen peroxide, which was not detected in the methane oxidation study because its concentration was too low, could be quantified in the *n*-butane study. The corresponding mole fraction profile is displayed in Fig. 8.16.

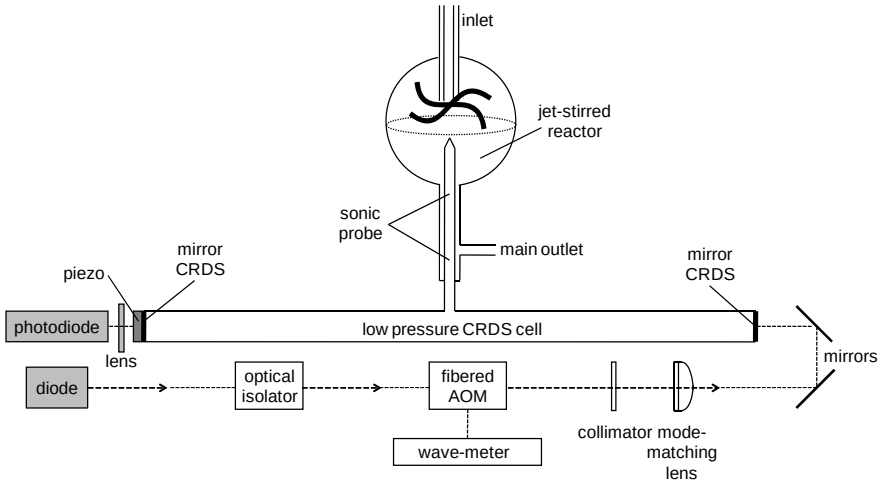

Fig. 8.14 Scheme of a jet-stirred reactor coupled to a cavity cw-CRDS (Bahrini et al., 2012)

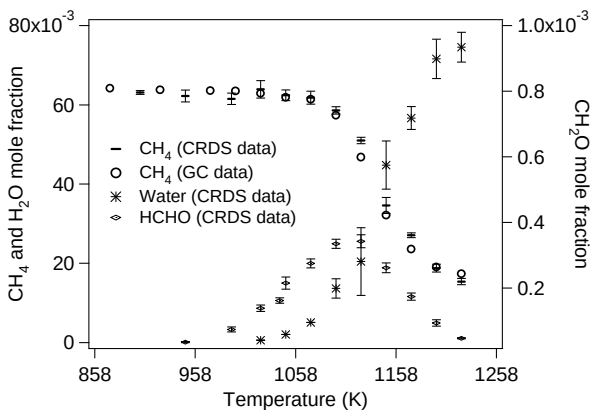

Fig. 8.15 Mole fraction profiles of methane, water and formaldehyde obtained in the study of the oxidation of methane in a jet-stirred reactor using cw-CRDS and gas chromatography (GC) analyses (Bahrini et al. 2012a). Experiments were performed in a jet-stirred reactor at a pressure of 106 kPa, a residence time of 2 s, fuel and oxygen inlet mole fractions of 0.0625

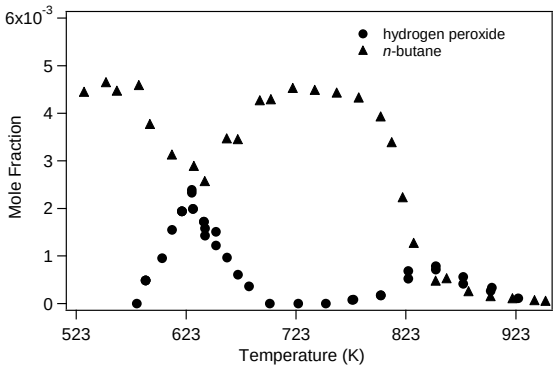

Fig. 8.16 Mole fraction profiles of hydrogen peroxide (cw-CRDS analyses) and *n*-butane (gas chromatography; mole fraction /5) obtained in the study of the oxidation of *n*-butane in a jet-stirred reactor (Bahrini et al. 2012b). Experiments were performed in a jet-stirred reactor at a pressure of 106 kPa, a residence time of 6 s, fuel and oxygen inlet mole fractions of 0.023 and 0.149, respectively

8.6 Effect of Wall Reactions

It has long been known that the coating of the wall of a reactor can have an influence on the kinetics of combustion phenomena (Pollard 1977; Griffiths and Scott 1987). As an example, wall reactions can affect the reactivity of a fuel and can change the boundaries between the different oxidation phenomena (slow oxidation, cool flames, auto-ignition) that can occur in a batch reactor (Konnov et al. 2005). Brocard and Baronnet (1983), who studied the oxidation of methyl tert-butyl ether in different closed vessels (packed and unpacked, coated and uncoated) also observed large difference of reactivities that were attributed to wall effects. A catalytic effect was also observed in the oxidation of methyl and ethyl tert-butyl ethers in a jet stirred reactor (Glaude et al. 2000)

The effect of wall reactions in a jet-stirred reactor was numerically investigated by adding wall reactions involving the HO_2 radical in a detailed kinetic model for the oxidation of methane (Fig. 8.17). These wall reactions were taken from the work of Porter et al. (2008). The first reaction is the adsorption of the HO_2 radical at the wall and the second reaction is the reaction of adsorbed HO_2 radicals yielding water and oxygen. It can be seen in Fig. 8.17 that these wall reactions have a slight inhibiting effect on the reactivity.

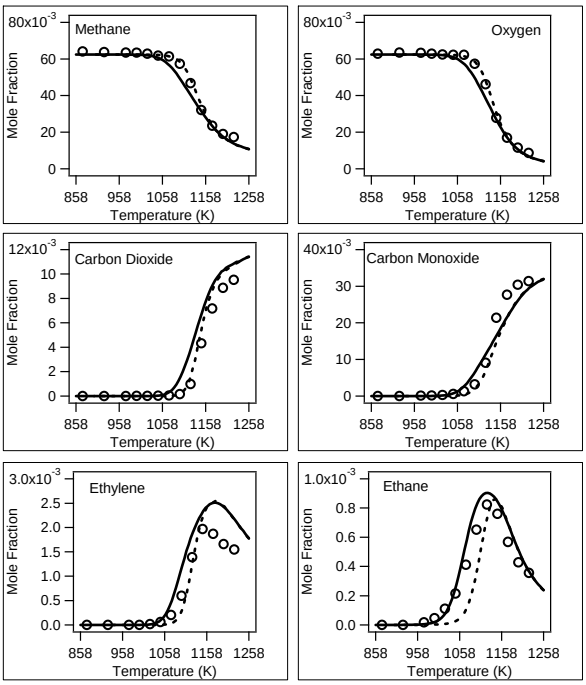

Fig. 8.17 Influence of the addition of wall reactions in a detailed kinetic model of the oxidation of methane. Symbols: experimental data obtained using gas chromatography; Full line: model without wall reactions; Dashed line: model with wall reactions. Experiments were performed in a jet-stirred reactor at a pressure of 106 kPa, a residence time of 2 s, fuel and oxygen inlet mole fractions of 0.0625

8.7 Modeling and Simulation

One advantage of the jet-stirred reactor relies on the relatively easy modeling which simplifies a lot the simulations with detailed kinetic models (Scacchi et al. 1996). This type of reactor is modeled by two types of equations: the mass equation and the conservation of energy (Villermaux 1995).

The mass equation is given by Eq. 8.21. In this equation, F_j^i and F_j^o are the mole flow rates of the species j at the inlet and at the outlet of the reactor, respectively, V is the volume of the reactor, r_i is the rate of the reaction i, and $\upsilon_{i,j}$ is the stoichiometric coefficient of the species j in the reaction i ($\upsilon_{i,j}$ is positive if the species j is formed in the reaction i, and negative if it is consumed).

$$F_j^o = F_j^i + \sum_i \upsilon_{i,j} r_i V \qquad (8.21)$$

For the special case of a unimolecular reaction A → P, the expression of the concentration C_A^o of the species A at the outlet of the reactor (Eq. 8.22) can be easily deduced from the mass equation given by Eq. 8.21. In Eq. 8.22, C_A^i is the concentration of the species A at the inlet of the reactor, k is the kinetic constant of the reaction A → P, and τ is the residence time.

$$C_A^o = C_A^i/(1 + k\tau) \qquad (8.22)$$

The conservation of energy is given by Eq. 8.22. In this equation, h_j^i and h_j^o are the mole enthalpies of formation of the species j at the inlet and at the outlet of the reactor, and W is the reactor heat loss. Note that jet-stirred reactors are most of the time operated at constant temperature. In this case the heat loss term W in Eq. 8.23 disappears.

$$\sum_j F_j^o h_j^o + W = \sum_j F_j^i h_j^i \qquad (8.23)$$

A system composed of $j + 1$ algebraic equations is obtained. This system can be solved using a Newton algorithm. PSR program included in Chemkin II (Glarborg et al. 1986) is largely used to performed jet-stirred reactor simulations. This program solves the system of algebraic equations using the damped modified Newton algorithm. This algorithm needs a starting estimate of the solution to begin the iteration. A difficulty is to provide a reasonable starting estimate. If no good starting estimate is available the software uses the equilibrium composition at an estimated temperature as starting estimates. For very difficult problems, it is recommended to start the calculation with a long residence time and a high temperature and then to use the continuation feature to shorten the residence time and decrease the temperature progressively. Sometimes the Newton method does not converge and a transient computation with integration of a system of ordinary differential equations using the backward-Euler method is performed before returning to the Newton algorithm.

8.8 Experimental Studies of Oxygenated Fuels

Jet-stirred reactors have been used for the studies of the oxidation and pyrolysis of numerous hydrocarbons and oxygenated compounds (Tran et al. 2012). Experimental studies of the oxidation and the pyrolysis of oxygenated compounds in a jet-stirred reactor are displayed in Table 1.1. It can be seen that many studies of the oxidation of alcohols and esters have been carried out. There is much less studies on ethers and particularly on cyclic ethers which can be derived from ligno-cellulosic biomass. Note that almost no jet-stirred experimental data study about the oxidation of aldehydes and ketones was reported while these species are important intermediates formed in the combustion of hydrocarbons and oxygenated species (Piperel et al. 2009).

Table 8.1 Experimental studies of the oxidation and the pyrolysis of oxygenated compounds performed in a jet-stirred reactor

Species	Experimental conditions T (K)	P (kPa)	Φ	τ (s)	x_{fuel}	Reference
Alcohols						
ethanol	1000-1200	101	0.2-2	0.04-0.24	0.003	Aboussi 1991
	890-1250	101	0.25-2	0.07-0.7	0.002	Leplat et al. 2011
n-butanol	800-1250	101-1010	0.25-2	0.07-0.7	0.001-0.012	Dagaut et al. 2009 ; Sarathy et al. 2009
2-butanol	770−1250	1013	0.275-4	0.7	0.001-0.0015	Togbé et al. 2010a
iso-butanol	770−1250	1013	0.275-4	0.7	0.001-0.0015	Togbé et al. 2010a
n-pentanol	770-1220	1013	0.35-4	0.7	0.001-0.0015	Togbé et al. 2011a
iso-pentanol	530-1220	1013	0.35-4	0.7	0.001-0.0015	Dayma et al. 2011
n-hexanol	560-1220	1013	0.5-3.5	0.7	0.001-0.0015	Togbé et al. 2010b
Ethers						
dimethyl ether	550-1275	101-1013	0.2-2.5	1	0.001-0.002	Dagaut et al. 1996 ; 1998a
methyl tert-butyl ether ; ethyl tert-butyl ether ; tert-amyl methyl ester ; dipropyl ether	800-1150	1013	0.5-2.0	0.5	0.001	Goldaniga et al. 1998
dimethoxymethane	800-1200	507	0.444-1.778	0.25	0.0015	Daly et al. 2001
tetrahydrofuran	800-1100	101-1013	0.5-1.0	0.1-0.5	0.001	Dagaut et al. 1998b
Aldehydes						
propanal	800-1100	1013	0.3-2.0	0.7	0.0015	Veloo et al. 2013
Esters						
methyl-butanoate *methyl-2-butenoate*	850-1400	101	0.375, 0.75 & 1.13	0.07	0.00075	Gaïl et al. 2008
methyl pentanoate	530-1220	1013	0.5, 1 & 2	0.7	0.001	Karsenty et al. 2012
methyl hexanoate	500-1000	1013	0.5-1.5	1.5	0.001	Dayma et al. 2008
methyl heptanoate	550-1150	1013	0.6-2	0.7	0.001	Dayma et al. 2009
methyl decanoate	500-1100	106	1	1.5	0.0021	Glaude et al. 2010
	773-1123	106	1-4	pyrolysis	0.0218	Herbinet et al. 2011c
methyl palmitate / n-decane	550–1100	106	1.0	1.5	0.00052/ 0.00148	Hakka et al. 2009
methyl oleate / n-decane	550–1100	106	1.0	1.5	0.00052/ 0.00148	Bax et al. 2010
rapeseed oil methyl esters	800-1400	101-1013	0.25-1.5	0.07-1	0.0005	Dagaut et al. 2007

As shown in Table 1.1 there is a lack of JSR data for some types of molecules. Future studies could focus on large methyl esters that are present in biodiesel fuels (methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate) in order to study the influence of double bonds in the oxidation chemistry. Another interesting field of investigation is the study of the oxidation of the numerous molecules derived from the decomposition of ligno-cellulosic biomass (C_2-C_3 hydroxy-carbonyl species such as hydroxyl-acetone, anhydrosugars such as levoglucosan, furans such as furfural and aromatics such as guaiacol). In addition, the study of aldehydes, ketones and cyclic ethers will be valuable for the understanding of the oxidation chemistry of petrol based fuels.

8.9 Nomenclature

Latin symbols:

A: adimensionnal constant which is equal to 0.3 in the case of air at 20°C and at atmospheric pressure
c_{sound}: speed of sound
C_A^o: concentration of a species A at the outlet of the JSR
C_A^i: concentration of a species A at the inlet of the JSR
d: diameter of a nozzle in the JSR
F_j^o: mole flow rate of the species j at the outlet of the JSR
F_j^i: mole flow rate of the species j at the inlet of the JSR
h_j^o: mole enthalpy of formation of the species j at the outlet of the JSR
h_j^i: mole enthalpy of formation of the species j at the inlet of the JSR
i: index for reaction
j: index for species
P: pressure of the gas in the JSR
Q: volume flow rate in the JSR
$Q_S(x)$: volume flow rate of the gas at the distance x from the outlet of a nozzle in the JSR
Q_0: volume flow rate of the gas at the outlet of a nozzle in the JSR
r: radial distance from the axe of a jet from a nozzle in the JSR
r_i: rate of the reaction i
R: radius of the JSR
R_e: Reynolds number
R_r: recycling rate in the JSR
t: time needed to carry the whole volume of gas in the JSR from one nozzle to the following one
T: temperature of the gas in the JSR
u_a: axial velocity of a jet from a nozzle in the JSR
u_0: velocity of the gas at the outlet of a nozzle in the JSR
u_r: radial velocity of a jet from a nozzle in the JSR
V: volume of the JSR
W: JSR heat loss
x: axial distance from a nozzle in the JSR
x_{fuel}: mole fraction of a fuel

Greek symbols:

α: adimensional constant in the expression of the radial velocity of a jet from a nozzle in the JSR
β: angle at the top of the cone formed by a jet from a nozzle in the JSR
η: dynamic viscosity of the gas
Φ: equivalence ratio
$\upsilon_{i,j}$: algebraic stoechiometric coefficient
ρ: specific weight of the gas
τ: residence time of the gas in the JSR

References

Aboussi B. PhD Dissertation, University of Orleans, France, 1991

Azay P, Côme GM (1979) Temperature gradients in a continuous flow stirred tank reactor. Ind Eng Chem Process Des Dev 18:754–756

Azay P, Marquaire PM, Pommier P et al (1981) A versatile oven with very little thermal inertia. J Chem Educ 58:441

Bahrini C, Herbinet O, Glaude PA et al (2012a) Detection of some stable species during the oxidation of methane by coupling a jet-stirred reactor (JSR) to cw-CRDS. Chem Phys Lett 534:1–7

Bahrini C, Herbinet O, Glaude PA et al (2012b) Quantification of hydrogen peroxide during the low-temperature oxidation of alkanes. J Am Chem Soc 134:11944–11947

Battin-Leclerc F, Herbinet O, Glaude PA et al (2010) Experimental confirmation of the low-temperature oxidation scheme of alkanes. Angew Chem 122:3237–3240

Baulch DL, Griffiths JF, Pappin AJ et al (1988) Stationary-state and oscillatory combustion of hydrogen in a well-stirred flow reactor. Combust Flame 73:163–185

Baumlin S, Broust F, Ferrer M et al (2005) The continuous self stirred tank reactor: Measurement of the cracking kinetics of biomass pyrolysis vapours. Chem Eng Sci 60:41–55

Bax S, Hakka MH, Glaude PA et al (2010) Experimental study of the oxidation of methyl oleate in a jet-stirred reactor. Combust Flame157:1220–1229

Brocard JC, Baronnet F (1983) Chemical kinetics of the oxidation of methyl tert-butyl ether (MTBE). Combust Flame 52:25–35

Bush SF (1969) The design and operation of single-phase jet-stirred reactors for chemical kinetic studies. Trans. Inst. Chem. Eng. 47:59–72

Cavaliere A, Ciajolo A, D'Anna A et al (1993) Autoignition of n-heptane and n-tetradecane in engine-like conditions. Combust Flame 93:279–286

Ciajolo A, D'Anna A (1998) Controlling steps in the low-temperature oxidation of n-heptane and iso-octane. Combust Flame 112:617–622

Côme GM, Li Y, Barbé P, Gueritey N et al (1996) Competition between the gas and surface reactions for the oxidative coupling of methane: 2. Isothermal experiments in a catalytic jet-stirred gas phase reactor. Catal Today 30:215–222

Dagaut P, Reuillon M, Boettner JC et al (1994) Kerosene combustion at pressures up to 40 atm: Experimental study and detailed chemical kinetic modeling. Symp (Int) Combust 25:919–926

Dagaut P, Cathonnet M, Rouan JP et al (1986) A jet-stirred reactor for kinetic studies of homogeneous gas-phase reactions at pressures up to ten atmospheres (~1 MPa). J. Phys. E: Sci. Instrum. 19:207–209

Dagaut P, Boettner JC, Cathonnet M (1996) Chemical kinetic study of dimethylether oxidation in a jet stirred reactor from 1 to 10 ATM: Experiments and kinetic modeling. Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 26:627–32

Dagaut P, Daly C, Simmie JM et al (1998a) Oxidation and ignition of dimethylether from low to high temperature (500-1600 K): Experiments and kinetic modeling. Twenty-Seventh Symposium (International) on Combustion; The Combustion Institute: Pittsburgh, PA, 27:361–69

Dagaut P, McGuinness M, Simmie JM et al (1998b) The ignition and oxidation of tetrahydrofuran: Experiments and kinetic modeling. Combust Sci Tech 135:3–29

Dagaut P, Gaïl S, Sahasrabudhe M (2007) Rapeseed oil methyl ester oxidation over extended ranges of pressure, temperature, and equivalence ratio: Experimental and modeling kinetic study. Proc Combust Inst 31:2955–2961

Dagaut P, Sarathy SM, Thomson MJ (2009) A chemical kinetic study of n-butanol oxidation at elevated pressure in a jet stirred reactor. Proc Combust Inst 32:229–237

Daly CA, Simmie JM, Dagaut P et al (2001) Oxidation of dimethoxymethane in a jet-stirred reactor. Combust Flame125:1106–1117

David R, Matras D (1975) Rules for the construction and extrapolation of reactors self-stirred by gas jets. Can J Chem Eng 53:297–300

Dayma G, Dagaut P (2006) Effects of air contamination on the combustion of hydrogen-effect of NO and NO_2 addition on hydrogen ignition and oxidation kinetics. Combust Sci Tech 178:1999–2024

Dayma G, Gaïl S, Dagaut P (2008) Experimental and Kinetic Modeling Study of the Oxidation of Methyl Hexanoate. Energ Fuel 22:1469–1479

Dayma G, Togbé C, Dagaut P (2009) Detailed kinetic mechanism for the oxidation of vegetable oil methyl esters: New evidence from methyl heptanoate. Energ Fuel 23:4254–4268

Dayma G, Togbé C, Dagaut P (2011) Experimental and Detailed Kinetic Modeling Study of Isoamyl Alcohol (Isopentanol) Oxidation in a Jet-Stirred Reactor at Elevated Pressure. Energ Fuel 25:4986–4998

Dubreuil A, Foucher F, Mounaïm-Rousselle C et al (2007) HCCI combustion : effect of NO in EGR. Proc. Combust. Inst. 31(2):2879–2886

Fleys M, Simon Y, Swierczynski D et al (2006) Investigation of the reaction of partial oxidation of methane over Ni/La_2O_3. Energ Fules 20:2321–2329

Gaïl S, Sarathy SM, Thomson MJ et al (2008) Experimental and chemical kinetic modeling study of small methyl esters oxidation: Methyl (E)-2-butenoate and methyl butanoate. Combust Flame 155:635–650

Glarborg P, Kee RJ, Grcar JF et al (1986) PSR : a Fortran program for modeling well-stirred reactor. Sandia Report 86-8209

Glaude PA, Battin-Leclerc F, Judenherc B et al (2000) Experimental and modeling study of the gas-phase oxidation of methyl and ethyl tertiary butyl ethers. Combust Flame 121:345–355

Glaude PA, Herbinet O, Bax S et al (2010) Modeling of the oxidation of methyl esters–validation for methyl hexanoate, methyl heptanoate, and methyl decanoate in a jet-stirred reactor. Combust Flame 157:2035–2050

Goldaniga A, Faravelli T, Ranzi E et al (1998) Oxidation of oxygenated octane improvers: MTBE, ETBE, DIPE, and TAME. Twenty-Seventh Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 26:353–60

Griffiths JF, Scott S (1987) Thermokinetic interactions: Fundamentals of spontaneous ignition and cool flames. Prog Energ Combust Sci 13:161–197

Griffiths JF, Inomata T (1992) Oscillatory cool flames in the combustion of diethyl ether. J Chem Soc Faraday T 88:3153–3158
Hakka MH, Glaude PA, Herbinet O et al (2009) Experimental study of the oxidation of large surrogates for diesel and biodiesel fuels. Combust Flame 156:2129–2144
Hansen N, Cool TA, Westmoreland PR et al (2009) Recent contributions of flame-sampling molecular-beam mass spectrometry to a fundamental understanding of combustion chemistry. Prog Energy Combust Sci 35:168–191
Herbinet O, Marquaire PM, Battin-Leclerc F et al (2007) Thermal decomposition of n-dodecane: Experiments and kinetic modeling. J Anal Appl Pyrol 78:419–429
Herbinet O, Battin-Leclerc F, Bax S et al (2011a) Detailed product analysis during the low temperature oxidation of n-butane. Phys Chem Chem Phys 13:296–308
Herbinet O, Bax S, Glaude PA et al (2011b) Mass spectra of cyclic ethers formed in the low-temperature oxidation of a series of n-alkanes. Fuel 90:528–535
Herbinet O, Glaude PA, Warth V et al (2011c) Experimental and modeling study of the thermal decomposition of methyl decanoate. Combust Flame 158:1288–1300
Hinze JO, Hegge Zijnen BG (1949) Transfer of heart and matter in the turbulent mixing zone of an axially symmetrical jet. Appl. Sci. Res. 1:435-461
Houzelot JL, Villermaux J (1977) Mass transfer in annular cylindrical reactors in laminar flow. Chem Eng Sci 32:1465–1470
Karsenty F, Sarathy SM, Togbé C et al (2012) Experimental and Kinetic Modeling Study of 3-Methylheptane in a Jet-Stirred Reactor. Energ Fuel 26:4680–4689
Konnov AA, Zhu JN, Bromley JH et al (2005) The effect of NO and NO2 on the partial oxidation of methane: experiments and modeling. Proc Combust Inst 30:1093–1100
Leplat N, Dagaut P, Togbé C et al (2011) Numerical and experimental study of ethanol combustion and oxidation in laminar premixed flames and in jet-stirred reactor. Combust Flame 158:705–725
Li Y, Qi F (2010) Recent applications of synchrotron VUV photoionization mass spectrometry: Insight into Combustion Chemistry. Acc Chem Rev 43:68–78
Matras D, Villermaux J (1973) Un réacteur continu parfaitement agité par jets gazeux pour l'étude cinétique de reactions chimiques rapides. Chem Eng Sci 28:129–137
Marquaire PM, Côme GM (1978) Non quasi-stationnary state pyrolysis. Induction period of *neo*-pentane pyrolysis. React Kinet Catal Lett 9 :165–169
Parker AE, Jain C, Schoemaecker C et al (2011) Simultaneous, time-resolved measurements of OH and HO_2 radicals by coupling of high repetition rate LIF and cw-CRDS techniques to a laser photolysis reactor and its application to the photolysis of H_2O_2. Appl Phys B 103(3):725–733
Piperel A, Dagaut P, Montagne X (2009) Impact of acetaldehyde and NO addition on the 1-octene oxidation under simulated HCCI conditions 32:2861–2868
Pollard RT (1977) Gas phase combustion. In Comprehensive Chemical Kinetic, Bamford, C. H.; Tipper, C. F. H., Eds.; Elsevier: Amsterdam 17:249–368
Porter R, Glaude PA, Buda F et al (2008) A tentative modeling study of the effect of wall reactions on oxidation phenomena. Energ Fuel 22:3736–3743
Qi F (2013) Combustion chemistry probed by synchrotron VUV photoionizatio mass spectrometry. Proc Combust Inst 34:33-63
Mzé-Ahmed A, Hadj-Ali K, Diévart P et al (2010) Kinetics of oxidation of a synthetic jet fuel in a jet-stirred reactor: Experimental and modeling study. Energ Fuel 24:4904–4911
Sarathy SM, Thomson MJ, Togbé C et al (2009) An experimental and kinetic modeling study of n-butanol combustion. Combust Flame 156:852–64
Scacchi G, Bouchy M, Foucaut JF et al (1996) Cinétique et catalyse. Tec & Doc - Lavoisier, Paris
Taatjes CA, Hansen N, McIlroy A et al (2005) Chemistry: Enols are common intermediates in hydrocarbon oxidation. Science 3008:1887–1889
Togbé C, Mzé-Ahmed A, Dagaut P (2010a) Kinetics of Oxidation of 2-Butanol and Isobutanol in a Jet-Stirred Reactor: Experimental Study and Modeling Investigation. Energ Fuel 24:5244–5256
Togbé C, Dagaut P, Mzé-Ahmed A et al (2010b) Experimental and Detailed Kinetic Modeling Study of 1-Hexanol Oxidation in a Pressurized Jet-Stirred Reactor and a Combustion Bomb. Energy Fuels 24:5859–5875
Togbé C, Halter F, Foucher F, Mounaim-Rousselle C et al (2011) Experimental and detailed kinetic modeling study of 1-pentanol oxidation in a JSR and combustion in a bomb. Proc Combust Inst 33:367–74
Tran LS, Sirjean B, Glaude PA et al (2012) Progress in detailed kinetic modeling of the combustion of oxygenated components of biofuels, Energy 43:4–18
Veloo PS, Dagaut P, Togbe C et al (2013) Jet-stirred reactor and flame studies of propanal oxidation, Proc Combust Inst 34:599–606
Villermaux J (1995) Génie de la reaction chimique : Conception et fonctionnement des réacteurs. Tec & Doc – Lavoisier, Paris
Ziegler I, Fournet R, Marquaire PM (2005) Influence of surface on chemical kinetic of pyrocarbon deposition obtained by propane pyrolysis. J Anal Applied Pyrol 73:107–115