

A jet-stirred reactor for kinetic studies of homogeneous gas-phase reactions at pressures up to ten atmospheres (~ 1 MPa)

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Abstract. An homogeneous stirred reactor designed for kinetic studies of hydrocarbon oxidation in the intermediate temperature range is described. The originality of this reactor lies in its ability to operate under pressure up to 10 atm (~ 1 MPa). The design of the injectors makes it possible to move a thermocouple and a sampling probe throughout a whole diameter of the reactor.

1. Introduction

As a result of the increase in kinetic data available, extensive models have been produced for the combustion of light hydrocarbons (Warnatz 1984). The validation of these models requires experimental data covering a wide range of physical conditions. Different experimental techniques have been used: flames supported by burners, static reactors, plug-flow reactors, single-pulse shock tubes and continuous-flow stirred tank reactors. The last four techniques have the advantage of being free from transport effects, which simplifies the modelling procedure.

Previous data have been obtained on light hydrocarbon oxidation (Cathonnet *et al* 1981, 1984a, b) in a tubular quartz reactor under laminar conditions, for temperatures up to 1200 K, pressures up to 10 atm (~ 1 MPa) and equivalent ratios from 0.25 to 4.0. Provided that the kinetic measurements are limited to a range of moderate temperature gradients, corresponding to low conversion, this apparatus could be approximated to a plug-flow reactor.

Our problem of limitation to low-conversion studies was solved using a continuous-flow stirred tank reactor (CFSTR), first conceived by Matras and Villermaux (1973), for residence times around one second. Such reactors have been built at INPL, Nancy, to study hydrocarbon pyrolysis (Côme 1983, Juste 1981) and low-temperature oxidation (Ferrer *et al* 1983).

In this reactor, the rapid mixing achieves spatial homogeneity inside when it is operated at steady state. The stirring is effected by means of four turbulent jets issuing from the nozzles of the injectors.

The originality of our reactor, built following the guidelines established by David and Matras (1975), lies in its ability to operate under pressures up to 10 atm (~ 1 MPa). Moreover, it is possible to measure gas temperature and to sample in the whole volume of the reactor.

2. Reactor design

The reactor is made from fused silica to prevent wall catalytic reactions. It is a sphere of 40 mm diameter with four nozzles of 1 mm diameter for the admission of the reactants. The four

turbulent jets issuing from the nozzles effect the mixing and recycling of the gases within the reactor. Figure 1 shows the

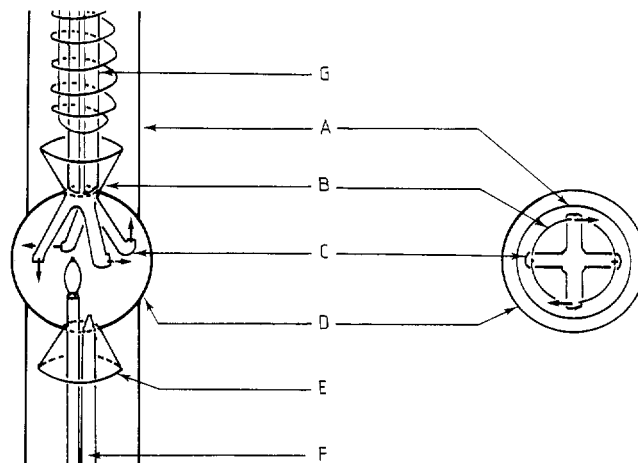


Figure 1. Detail of the reactor: A, external tube; B, convergent cone; C, injectors; D, spherical quartz reactor; E, divergent cone; F, sampling sonic probe and thermocouple probe; G, capillary surrounded by the preheating resistor.

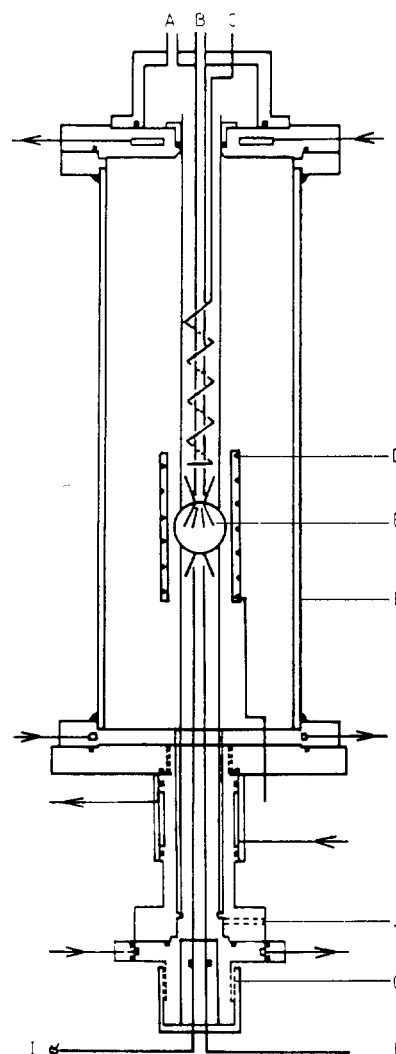


Figure 2. High-pressure apparatus: A, oxygen + nitrogen inlet; B, capillary, hydrocarbon + nitrogen inlet; C, preheating resistor; D, heating resistor; E, spherical quartz reactor; F, pressure-resistant jacket; G, system probe position adjuster; H, sampling sonic probe; I, thermocouple probe; J, gases exhaust; \rightarrow and \leftarrow symbolise water cooling; \blacksquare denotes an O ring.

design of the injectors, the four jets issuing from the nozzles being symbolised by arrows. The nozzle outlets are located in the equatorial plane of the spherical reactor.

The new design of the injectors allows a physical investigation of the whole volume of the reactor; this constitutes a significant improvement on previous designs.

3. High-pressure apparatus

To extend the experimental investigation range to pressures above atmospheric, the quartz reactor is located inside a stainless-steel pressure-resistant jacket (see figure 2). 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 prolongation tube (see figure 3). The gases issuing from the reactor diffuse through the holes into the metallic vessel, thus equilibrating their pressure with the pressure outside the reactor.

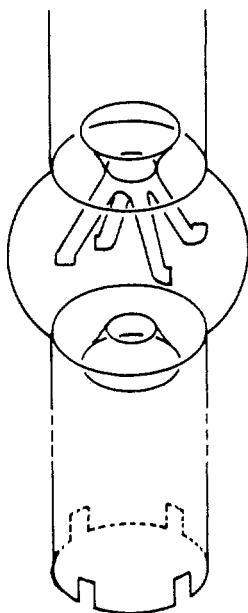


Figure 3. Detail of the reactor and the holes at the bottom of the prolongation tube for pressure balancing.

The flow rates of the hydrocarbon and the oxygen admitted in the reactor are measured and regulated by thermal mass-flow controllers. The flow of the diluent (nitrogen) is measured by means of flow rotameters. The gases are preheated by means of an electrically insulated resistor (Thermocoax) before their admission into the reactor which is also heated using the same type of resistor. The fuel is diluted with nitrogen and introduced into the reactor through a capillary, the mixing point being at the bottom of the convergent cone (see figure 1).

The residence time of the mixture in the injector is more than 300 times lower than the mean residence time (0.01–3 s) in the reactor. Thus the mean residence time is well defined and pyrolysis or oxidation of the fuel inside the injector is prevented. 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. The temperatures of the reactor wall and of the gases upstream are measured by insulated thermocouples (Thermocoax) and regulated by electronic controllers.

4. Physical investigations in the reactor

By means of a system probe position adjuster, we can move both a thermocouple probe and a sampling sonic quartz probe (Lengelle and Verdier 1973) along the vertical axis of the reactor. The thermocouple wires are enclosed in a double-core

alumina tube which is fixed against the sample probe inside a quartz tube. The thermocouple probe is sealed by Araldite glue to prevent leaks.

A residence-time distribution study has been performed on a similar reactor by Matras and Villiermaux (1973), showing that good macromixing is obtained at atmospheric pressure. The same study was performed at 10 atm (~ 1 MPa) by pulsed injection of a tracer (argon) at the inlet of our reactor at room temperature; this led to the same conclusions. Thus our CFSTR is perfectly stirred for mean residence times varying from 0.01 to several seconds in the pressure range of 1 to 10 atm (see figure 4). The reactor's homogeneity was checked during

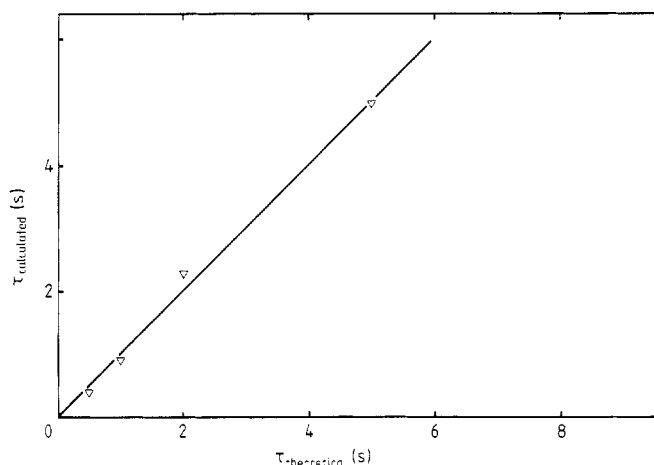


Figure 4. Residence-time distribution study. This figure shows results obtained under a pressure of 10 atm (~ 1 MPa). The macromixing is good when the ratio (mean residence time calculated) \div (mean residence time theoretical) = 1.

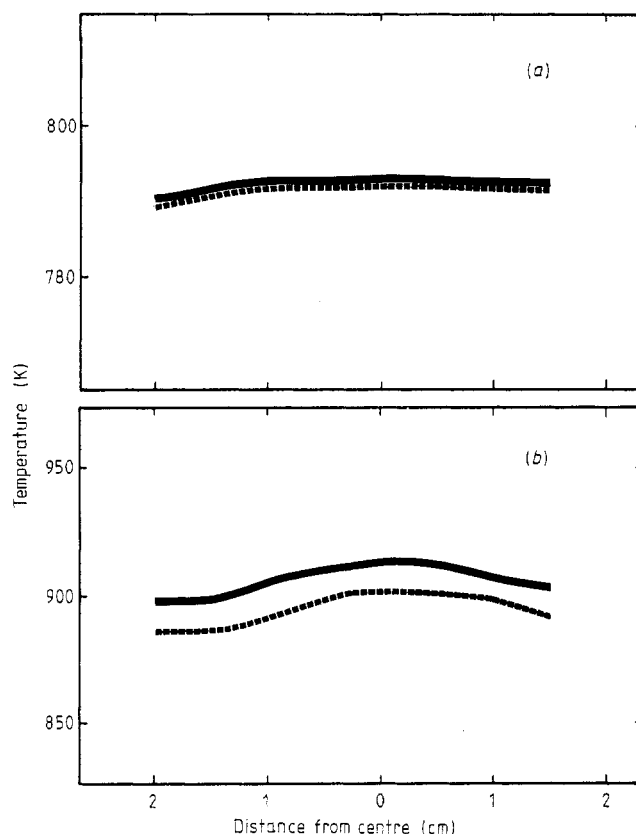


Figure 5. Two examples of temperature profiles in the reactor: ----, without reaction; —, in presence of 0.15% of propene. (a) $P = 1$ atm (~ 0.1 MPa); $\phi = 0.15$; $\tau = 0.05$ s. (b) $P = 5$ atm (~ 0.5 MPa); $\phi = 2.00$; $\tau = 1.20$ s. (Equivalent ratio, ϕ ; mean residence time, τ).

experiments by measuring the temperature of the gases by means of a chromel–alumel thermocouple probe and by analysing by GPC the gases sampled with the sonic probe. Figure 5 shows an example of these verifications.

5. Applications

The apparatus described above was used to study the kinetics of oxidation of light hydrocarbons, namely ethylene, propane and propene. Experiments were carried out under the following conditions:

pressure range: up to 10 atm (~ 1 MPa)
temperature: 900–1200 K
equivalence ratio: 0.15–4.0
mean residence time: 0.01–3 s
initial percentage of hydrocarbon: 0.15–0.5 (in volume)
carrier gas: nitrogen.

Experimental results have been presented for propane oxidation (Cathonnet *et al* 1984a, b). A detailed chemical kinetics reaction mechanism was used to model experimental data obtained with ethylene (Dagaut *et al* 1985). The experimental and modelling study of propane and propene oxidation up to 10 atm is in progress.

Acknowledgment

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