FREE PISTON PULSED COMPRESSION REACTOR

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A reactor of the free piston type is proposed to carry out chemical reactions at extremely high temperatures and pressures. Operation of the reactor is characterized by both high space velocities and energy efficiency. The reactor comprises the entire processing train and is foreseen to be suitable for conducting of a large variety of chemical reactions. Basic principles of the new reactor concept are explained and experimental data obtained without chemical reaction are reported.

1. INTRODUCTION

High temperatures and high pressures favor many industrially important chemical reactions. Temperatures and pressures used in industry are limited by properties of materials of construction and/or high capital costs and expensive heating and compression of the feed. However, half a century ago Longwel et al. (1958), Ryabinin (1961) and others demonstrated that gas samples can be subjected to transient extremely high pressures (up to 10000 bar) and temperatures (up to 9000 K) using free piston type ballistic compressors. The used equipment consisted essentially of heavy-walled, hollow cylinder, closed from both sides, within which the free piston was located. Gas samples in between the piston and one of the covers were compressed by the piston caused to move at very high speed.

The total cycle did not exceed 10^{-2} s, so that period of the extremely high temperatures and pressures was about 10^{-3} s. This short period prevented the significant heat exchange between the hot, compressed gas and the cylinder and provided a feasibility of attainment of the combination of pressures and temperatures far beyond the conditions attainable in steady state equipment. The achieved pressures and temperatures are ideal for almost instantaneous completion of any chemical reactions. Another consequence of the short cycle duration was high rates of temperature and pressure change (up to 10^7 K/s, 10^7 bar/s) which afford an excellent way of freezing the high temperature products and producing a better yield.

A great deal of efforts has already been made to develop a commercial chemical reactor based on the principle of pulsed compression. Detailed investigations of a number of chemical reactions were performed by many authors (e.g. Longwell et al., 1958; Kolbanovsky et al., 1982; Morrison, 1987, 1989) using free piston single-pulsed set-ups. It was found that a short duration of the extremely high temperatures and pressures was nevertheless quite sufficient for successful carrying out of many industrially important chemical reactions: production of synthesis gas via partial oxidation of methane, synthesis of nitric oxide by direct reaction between nitrogen and oxygen, pyrolysis of hydro- and halocarbons, synthesis of ultrafine powders by means of thermal decomposition of organometallic compounds, etc.

The principle of pulsed compression is also realized in conventional piston internal combustion (IC) engines. Temperature in the combustion near to top dead center of state-of-the-art IC-engines reaches 2700-2900 K, maximum pressure – 160 - 180 bar. None of the commercial chemical reactors is capable of providing such combinations of temperatures and pressures. At speeds of 6000-12000 rpm Gas Hourly Space Velocity (GHSV - ratio of volume throughput to reaction volume) can be up to 700000 h^{-1}. This value is approximately two orders of magnitude higher than, for example, GHSV of the conventional processes for synthesis gas production. Rates of temperature change in high-speed engines reach $1.3 \cdot 10^6$ K/s. Moreover, the quenching is accompanied with delivering useful work rather than waste of useful energy.

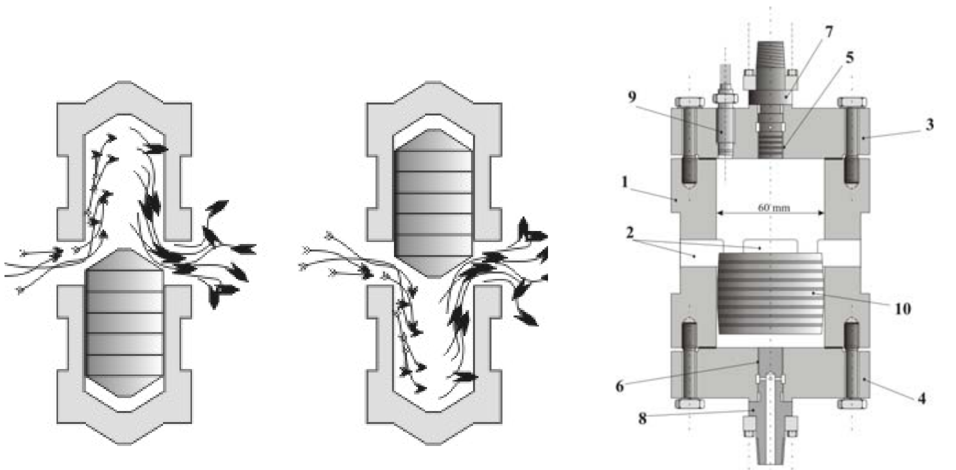
Many researchers attempted to use IC-engines or "engine-like" designs as chemical reactors (von Szeszich, 1956; van Dijk, 1957; Oberdorfer and Winch, 1961; Yamamoto, 1963; Karim, 1963, 1990; Lowther end Bohom, 1990; Kolbanovsky et al., 1982, 1997). However, commercial application of IC-engines as industrial chemical reactors is limited for a variety of reasons: presence of lubricating oil, very high (up to 30%) heat loss in cooling system, sharp drop in speed, GHSV and quenching rates as piston displacement increases, etc. None of the proposed reactor designs could resolve two key problems: 1) to provide the desired combinations of the maximum temperature and pressure and frequency of piston's oscillation independent of the working volume of the cylinder, and 2) to ensure effective, long-life sealing of a cylinder-piston clearance in the absence of lubricants.

2. THE NEW REACTOR CONCEPT

2.1 Reactor concept and design

The basic idea (Glouchenkov, 1997, 1999) of the pulsed compression reactor is schematically shown in Fig. 1a. Fig. 1b shows a drawing of the reactor used in the experiments without chemical reaction. The reactor consists of a hollow cylinder 1, closed at its upper and lower ends by thick-walled covers 3 and 4. The cylinder has inlet and outlet ports 2 in its wall for the admission of the feed and exhaust of the reaction products as well as for the exhaust of the gas actuating the piston. The cylinder encloses a free piston 10 that divides the cylinder into two compression chambers and can freely reciprocate between both the covers. High temperatures and pressures are generated in each chamber as a result of very fast and therefore almost reversible compression of a raw stock charge by the piston reciprocating with very high frequency. The reciprocation is maintained by the reaction itself (exothermic reactions) or by actuating gas (endothermic reaction). The new reactor concept is based on two principles: 1) provision of stable self-excited reciprocation (oscillation) of a free piston, and 2) implementation of a combination of a contactless, labyrinth sealing of the cylinder-piston clearance and gas lubrication of the piston.

A number of reactor configurations have evolved to fit the unique requirements of specific types of reactions and conditions (Glouchenkov, 1997a,b, 1999). They differ in the methods of start up, supply of feed and removal of products. In particular, in the example of Fig. 1a both of the chambers are working chambers. In case of endothermic reactions only one chamber is working, another one is used for maintenance of the piston oscillations.



a *b*

Fig.1: Operation of the reactor (a) and reactor used in the experiments (b).

2.2 Reactor start up and operation

The reactor can be started by delivering an actuating, pressurized gas through a throttle into the lower chamber. The throttle may be a calibrated orifice restrictor, slit, etc. In Fig. 1b the throttle is clearance 6 between the conical hole in the lower cover and the conical sleeve. Under the pressure of the gas the piston moves upward, covers the exhaust ports, compresses a gas in the upper chamber and then communicates the lower chamber with the exhaust ports. As a result, a fast exhaust of the spent actuation gas from the lower chamber and sharp pressure drop occur. Under the pressure of the gas in the upper chamber the piston is thrown down and then the cycle repeats. The kinetic energy of the piston rises cycle by cycle and, accordingly, a frequency and amplitude of the piston's oscillations rise too. Eventually the reactor attains a periodic steady-state. Thereafter supply of the gas feed into the reactor through the inlet ports and exhaust of the reaction products into a product line through the outlet ports begins. The supply of the actuating gas can be stopped now. The subsequent reciprocation of the piston is maintained at the expense of heat release due to the chemical reactions.
Another possible way to start the reactor is to shove a piston once upward by a compressed gas when the reactive gas flows through the reactor. Several mechanical fast acting pressure valves have been developed to that end.

2.3 Sealing and gas lubrication of the free piston

Prevention of the gas leakage through the annular piston-cylinder clearance is achieved by using contactless (labyrinth) seals. High efficiency of these seals under fast compression-expansion cycle conditions has been repeatedly demonstrated in a number of different types of single-pulsed experimental set ups. Although labyrinth seals cannot entirely prevent leakage, their sealing ability increases sharply as the frequency of the piston reciprocation rises. At frequencies of about few hundreds Hz the sealing ability of the labyrinth seals is highly competitive with that of the conventional oil lubricated piston ring seals. However, unlike piston rings, the combination of labyrinth seals and gas lubrication (so called gas bearing) serves at very high temperatures, pressures and speeds of the piston and eliminates the wear problem of the cylinder-piston pair without using lubricating oil. The gas feed and reaction products itself can be used as lubricant. Gas lubrication can be implemented in several ways, e.g. by shaping of the surface of the piston and/or the cylinder wall (Doll, 1964; Mourelatos, 1988; Etsion, 1995) or by injection of a compressed gas (gas phase feedstock, reaction products or actuation gas) into the annular clearance between cylinder and piston (Constantinescu, 1962; Gross, 1962; Majundar, 1980).

2.4 Advantages and application of the new reactor concept

The free piston pulsed reactor can be viewed as a continuously operating ballistic compressor. Therefore it exhibits all the advantages of the previous pulsed compression equipment and reveals a number of advantages over the reactors utilizing the principle of IC-engines: no sealing rings and lubricants; high gas compression ratio and piston frequency; low heat losses because cooling is not necessary; the piston is the only moving part (no piston rod, crank gear, mechanical valves and no electronic control of the valves); gas compression can be adjusted depending on desired conditions and not determined by the piston rings; simple reactor design.
The free piston in operation is a pendulum swinging between two gas springs. Only compensation of the inevitable energy losses due to heat exchange and gas leakage is required in order to maintain oscillation. These energy losses are much smaller than the losses in the conventional processes. Undoubtedly, operation of the free piston pulsed compression reactor is optimal in terms of energy efficiency.
The reactor combines the functions of a compressor, a heater, the reactor as such, a cooler, a heat-recovery boiler-steam turbine unit and a gas-expansion machine. Thus the reactor comprises the entire or almost entire processing train and it can be assumed that significant reduction of capital and operating costs of the production plant is possible. The pulsed reactor is anticipated to be suitable for conducting of a great variety of industrially important gas phase, gas-liquid and gas-solid chemical reactions.

3. EXPERIMENTS

Up till now experiments have been performed without chemical reaction. Two reactors of 105 mm and 70 mm height both with inside diameter of 60 mm have been studied using two different start up systems and many pistons of different materials, dimensions and shape. The reactors differ also in configuration and size of inlet and outlet ports.
The drawing of the long (105 mm) reactor is given in Fig. 1b. Both of the covers in Fig. 1b accommodate throttles which are annular clearances 5 and 6 of 20 – 500 μm formed between calibrated bores in the covers and tailored calibrated sleeves. The lower throttle was used for the reactor start up and operation whereas the upper one only for controlling purposes. Starting of the reactor with the developed fast acting pressure valves was also studied using special lower covers integrated with the valves. The pressure change in the upper chambers was measured by means of a quick change pressure sensor 9 (Entran).
Essential features of the reactor are rather simple but care in design is necessary. After the interior surface of the cylinder was bored and honed, a variation in inside diameter was less than 5 μm. The same requirement was set to the diameter of the pistons.
Pistons were made of hard bearing steel, bronze and aluminum alloy (Alumec). For the long cylinder the used pistons were 30, 40 and 45 mm in height. For the short cylinder

the heights of the pistons were 20 and 24 mm. The diametral clearances (difference in diameters of the cylinders and pistons) were 20, 50 and 100 μm. The pistons were straight cylinders or barrel-like in shape (taper 1:10 - 1:500) with smooth surface or with several annular grooves at their side surface.

4. RESULTS OF INVESTIGATION

The experiments have shown that the reactors can easily be started using the both start up systems and operate smoothly. Based on the obtained data a reactor for carrying out chemical reactions has been designed.

It has been proven that high-precision manufacturing of the piston-cylinder pairs ensures perfect gas lubrication of the piston. The frequency of the piston oscillations was as high as 60 – 100 Hz. Fig. 2 shows examples of pressure change in the upper chamber after the reactor start up with the throttle and fast acting pressure valve. The observed in this experiments compression corresponds to the temperature of 1200 K at maximum compression.

A simplified analysis of the piston motion has been performed assuming that the gas behaves ideally and gas compression and expansion is an adiabatic process.

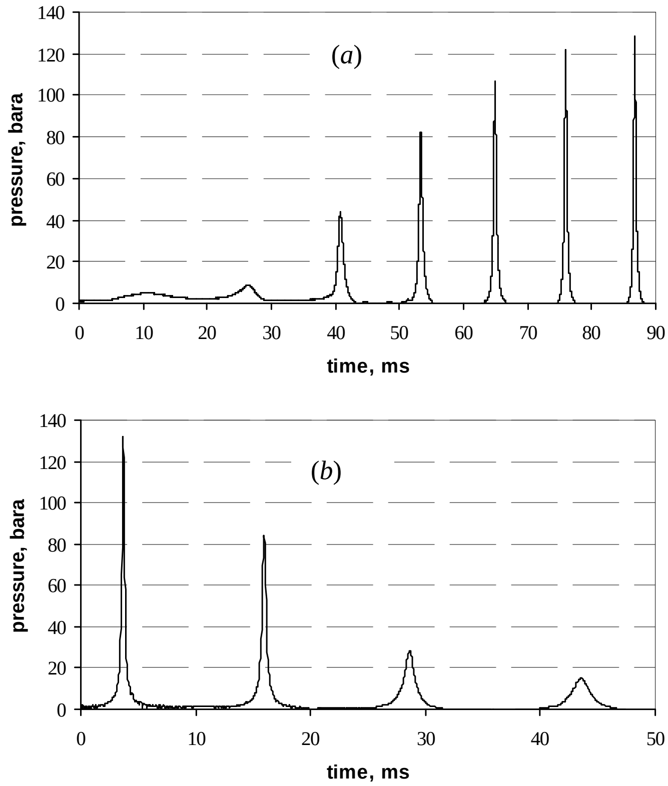


Fig. 2: Pressure change in the upper chamber during the reactor start-up, H = 105 mm, h = 45 mm, diametric clearance 20 μm: (a) - with the throttle, clearance 500 μm, actuating pressure 60 barg; (b) - with fast acting pressure valve, pressure 140 barg

The obtained relation between the maximum volumetric compression ε and the frequency of piston oscillations ν is:

$$\nu(\varepsilon)=\left[\frac{2P_0\beta^{\gamma}}{\rho h\left(H-h\right)}\right]^{0.5}\left[2\int_{-1+\beta/\varepsilon}^{1-\beta/\varepsilon}\frac{1}{\sqrt{2\left(U\left(1-\beta/\varepsilon\right)-U\left(x\right)\right)}}dx\right]^{-1}$$

where

$$\beta=\frac{H-w}{H-h},\qquad U(x)=U_0(x)+U_0(-x)$$

$$U_0(x)=\frac{\left(1-x\right)^{1-\gamma}}{\gamma-1}\quad if\quad x>-s=-\frac{h-w}{H-h},\quad U_0(x)=\frac{x+s}{\beta^{\gamma}}+\frac{\left(1+s\right)^{1-\gamma}}{\gamma-1}\quad if\quad x<-s$$

and w is the height of the inlet and outlet ports.
The derived equation shows the parameters determining the piston frequency from which the inlet pressure P_0, density of the piston ρ, height of the reactor H and piston h and adiabatic constant γ are the most important. The predicted frequencies agree very well with the measured values. For example, the frequency of the piston in the experiment presented in Fig. 2a at the periodic steady state is 89.4 Hz whereas the equation gives 92.7 Hz for the observed compression ε of 30.5 and $\gamma = 1.4$.

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