Pulsed Compression Reactor

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1. Introduction

High temperatures and pressures are favorable for many industrially important chemical reactions, whereas temperatures and pressures used in industry are limited mainly due to properties of materials of construction and/or restrictions imposed by high capital costs and expensive heating and compression of a feed. In most industrial chemical processes temperature and pressure do not exceed 1000 K and 300 bar respectively.

However, half a century ago Ryabinin (1961) 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 drivers, also called free piston ballistic compressors. The compression of gases was conducted within a heavy-walled, hollow cylinder by a free piston moving at very high speed. The piston expended all its kinetic energy to the gas compression and then was thrown back by the hot, compressed gas to the starting position and stopped there by means of a damper.

The total cycle duration did not exceed 10 ms, the duration of the extreme conditions was about 1 ms. It prevented a significant heat exchange between the hot, compressed gas and the cylinder and made it possible to attain combinations of pressures and temperatures far beyond the maintainable in steady state equipment. The achieved pressures and temperatures were ideal for almost instantaneous completion of many industrially important chemical reactions as has been proven later on by many researchers. Another consequence of the short cycle duration was huge rates of temperature and pressure change (up to 10^7 K/s, 10^7 bar/s). Such the rates afford an excellent way of freezing the high temperature products and producing a better yield i.e. reaction products that exist at extreme conditions have no time for chemical transformations during the cooling stage. Mostly pressure-volume-temperature relationships or products formed in chemical reactions were investigated by this method. It was demonstrated that many industrially important products e.g. synthesis gas, nitric oxide etc, can be produced during rapid compression-expansion cycles (Longwell et al., 1958; Ryabinin 1961; Kolbanovsky et al., 1982; Morrison, 1987, 1989).

Figure 1 shows approximately the pressure-temperature scopes of different chemical technologies. Very large *P-T* area can be covered by the pulsed compression technology which uses the principle of ballistic compressors. However single-pulsed compression machines are very unsuitable for industrial application.

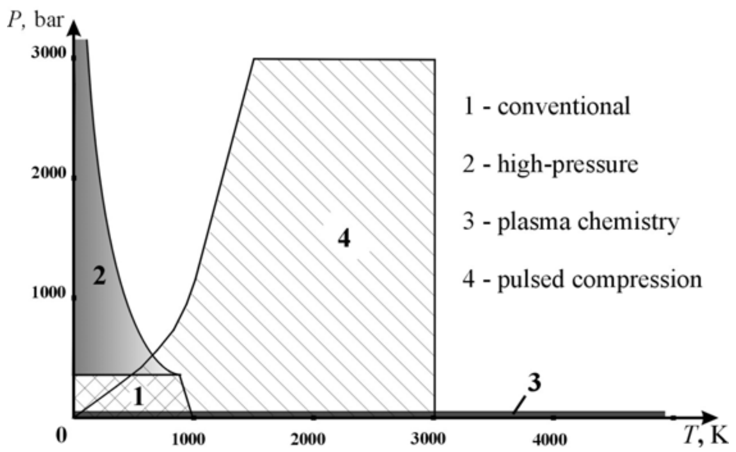


Figure 1. Pressure-temperature scopes covered by different process technologies.

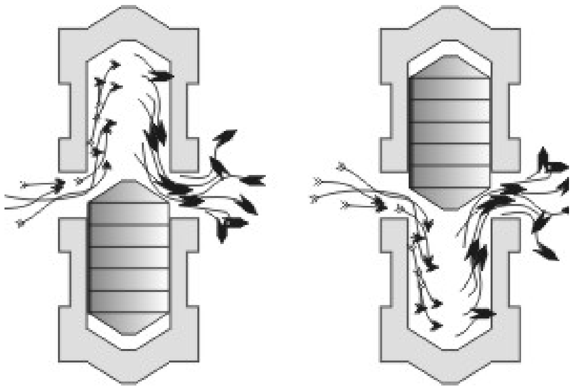
A great deal of efforts has already been made to develop a commercial reactor based on the principle of pulsed compression reactors (von Szeszich, 1956; Broeze and van Dijck, 1957; van Dijck, 1957; Oberdorfer and Winch, 1961; Yamamoto, 1963; Karim, 1963, 1990; Lowther end Bohom, 1990; Kolbanovsky et al., 1982, 1997). Many researchers attempted to use internal combustion (IC) engines or "engine-like" designs as chemical reactors. However, a commercial application of the IC-reactors is limited for a variety of reasons:

- oil lubricated piston rings require cooling that results in high energy loss (up to 30%); presence of the oil is also not desirable or harmful for many chemical reactions
- pressure can not be higher than 200 - 220 bar because the piston rings and bearings can not withstand overloads caused by so high pressures
- if the working volume of an engine increases, its speed sharply drops down due to very high dynamic loads on movable parts of the engine (crank gear, bearings).

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 (i.e. the reactor throughput) 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. New reactor concept – the free piston pulsed compression reactor

To avoid the problems typical of engine-like reactors a new type of pulsed compression reactor has been suggested (Glouchenkov, 1997, 1999). The basic idea of the reactor is schematically shown in Figure 2. A feed gas flows across a double-ended cylinder in which free piston reciprocates with a very high frequency compressing in turn the feed in lower and upper chambers. The cylinder has inlet



and outlet ports in its wall for the injection of the feed and exhaust of the reaction products respectively. The reciprocation is maintained by the reaction itself in case of exothermic reactions. For endothermic reactions the reactor design is slightly different. But the basic idea remains the same: free piston oscillating between two gas springs.

To put the free piston pulsed compression reactor into practice two types of systems for starting up the reactor have been developed. With the first system a compressed gas is continuously injected into the lower chamber under the piston and exits the chamber through the outlet ports when the piston goes up under the pressure of the gas. The gas injection is arranged so that a frequency and amplitude of the piston's oscillations rise regularly until attaining a periodic steady state. With the second system the reactor is started by pushing the piston once upward by a portion of a compressed gas. Several pure mechanical fast acting valves have been developed to that end.

An essential feature of the reactor is that the piston-cylinder assembly has no rings. A significant gas leakage through the annular piston-cylinder clearance is prevented by using contactless, labyrinth seals. Their sealing ability increases sharply as the frequency of the piston reciprocation rises. Existing relatively small gas leakage is even desired to provide gas lubrication (also called gas bearings) i.e. to prevent any contact of the piston with the cylinder wall during the reciprocating motion of the piston by means of centering of the piston in the cylinder. Unlike piston rings, the labyrinth seals serve at very high temperatures, pressures and speeds of the piston.

3. 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; as a consequence:
  - higher gas compression and piston frequency can be achieved
  - lower heat losses because cooling is not necessary
- piston is the only moving part - no piston rod, crank gear, mechanical valves and no electronic control of the valves; as a consequence:
  - simpler reactor design
- gas compression can be adjusted depending on desired conditions and not determined by the design of an engine
- no wear of the piston-cylinder pair due to contactless operation

Therefore the application area could significantly be expanded. The advantages of the pulsed compression reactor over conventional chemical reactors are:

- unique combinations of extreme pressures and temperatures. These conditions are ideal for almost instantaneous completion of many chemical reactions and without catalyst
- very high space velocities, i.e. ratio of volume throughput to reactor volume (millions per hour), and therefore a compact reactor design and safe operation; compactness of the reactor makes it possible to place gas-to-liquid (synthetic fuels) plants in immediate vicinity of oil and gas fields, on sea gas platforms, special ships, barges etc.
- extremely fast compression cycle and, as a consequence, extremely high quenching rates ($\sim 10^6$ - 10^7 K/s) makes it possible to influence the mechanism and selectivity of chemical reactions; therefore new processes could thus be anticipated
- the free piston reciprocates between two gas springs; only compensation of the inevitable energy losses due to gas friction, gas leakage and heat losses is required in order to maintain oscillation; these energy losses are incomparably smaller than the losses in the conventional processes; therefore, operation of the pulsed reactor is optimal in terms of energy efficiency
- very fast and simple reactor start up and shut down
- the same reactor can be applied for very different reaction systems without any changes.

The salient feature of the new concept is that the reactor comprises the entire or almost entire processing train: feed compression, heating, reaction itself, cooling of products and utilization of released reaction energy all together occur in the reactor. Thus it can be assumed that significant reduction of capital expenditures and operating costs of the production plant is possible.
The pulsed reactor is anticipated to be superior for conducting of a great variety of industrially important gas phase, gas-liquid and gas-solid chemical reactions as has been proven experimentally with single-pulsed compression machines, for example:

- production of synthesis gas via steam-oxygen/air conversion of various hydrocarbon containing feedstocks e.g. natural gas, crude oil, low-value refinery residues, oil-water emulsions, coal (in the form of powder or coal-water slurry), tars, pyrolysis oil.
- pyrolysis of hydro- and halocarbons aiming at manufacturing acetylene, ethylene, propylene, black etc.
- nitrogen fixation (e.g. direct synthesis of nitric oxide by reaction between oxygen and nitrogen)
- manufacturing of ultrafine ceramic and metallic powders by means of thermal decomposition of appropriate precursors (salts, carbonyl- and organometallic compounds etc.)
- thermal destruction of volatile organic compounds that are discharged in industrial process exhausts.

The new apparatus is particularly useful for vapor-phase reactions, but it may also be adapted to gas-liquid and gas-solid reactions and for many technical applications.

4. Experimental study

Two reactors of 105 mm and 70 mm height both with inside diameter of 60 mm have been studied without chemical reaction using the two different start-up systems and many pistons of different density, dimensions and shape. The diametric clearance - the difference in diameters of the cylinders and pistons - was 20 - 100 μm.
The experiments have shown that the reactors can easily be started using the both start up systems and operate smoothly without wear - the pistons reciprocate with no contact with inner surface of the cylinders. It has been proven that high-precision manufacturing of the piston-cylinder pairs ensures perfect gas lubrication of the piston. Some results of the performed experiments have been reported by Glouchenkov et al. (2002). The process parameters that were used and measured in the experiments are:

Compression ratio	5 – 45
Pressure	4 – 200 bar
Temperature	560 – 1360 K
Frequency of piston reciprocation	50 – 200 Hz
Maximum piston speed	5 – 30 m/s
Piston acceleration	$(1 – 12)\times10^3$ g

The obtained combinations of compression, frequency, temperature and pressure can not be achieved in the state of the art IC-engines, whereas the values of these parameters can easily be increased several times in the available reactors. Severe conditions were not studied because of the restrictions imposed by the used dynamic pressure sensor (max pressure – 200 bar).
Based on the obtained experimental data two reactors for carrying out chemical reactions have been designed and built. One of these reactors operates as shown in Figure 1. In the second reactor chemical reactions take place only in the upper chamber; the lower one is used for reactor control purposes. The inside diameter of the both reactors is 60 mm. Combustion of methane and partial oxidation of methane with air are carried out in the reactors. The first process is used as a means to study the performance of the reactors and as a prototype of a reactor for combustion of volatile organics that is discharged in industrial process exhausts. The later process is of a great practical significance as a route for synthesis gas production.
The results of the experiments will be reported at the symposium.

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