Pulsed Compression Technology: A Breakthrough in the Production of Hydrogen

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ABSTRACT:

Production of hydrogen by steam reforming or by partial oxidation of hydrocarbons involves rather high temperatures of 800 – 1400 ^{o}C. The required heating of the feed and subsequent recovering of thermal energy of the products entail high capital and operating costs and large sizes of the plants. A fundamentally new chemical reactor concept based on the principle of compressive heating and cooling permits a breakthrough in many chemical processes at high temperatures and pressures in terms of energy efficiency, capital costs and portability. Success of the novel reactor concept is achieved due to reversibility of the heating and cooling processes and integration of all process steps in a single unit. The new pulsed compression reactor suits ideally for production of hydrogen by noncatalytic partial oxidation of hydrocarbons. This paper describes the novel reactor concept, some experimental results obtained and the advantages of the pulsed compression technology.

KEYWORDS : *hydrogen, partial oxidation, pulsed compression, free piston*.

Introduction

Production of hydrogen by steam reforming or by partial oxidation of hydrocarbons involves rather high temperatures: 800 - 1100 ^{o}C in the presence of nickel catalyst or 1350 - 1400 ^{o}C without catalyst. Heating of the reactor inlets (steam, oxygen, methane etc) requires an enormous amount of energy significant part of which is lost. For the steam reforming process, the required high-level heat is generated in a furnace fired by a separate fuel stream that is burned with air. Only about 40 % of the furnace duty is absorbed by the endothermic heat of reaction. Another 25 % of the fired duty is recovered by generating export steam. Of the remaining 35 % of the fired duty, approximately 10% is used in the CO_2 removal section and the final 25 % is lost to the stack gas, cooling water, and heat leaks. With oxygen or autothermal reforming, heat is supplied by burning a portion of the process gas with pure oxygen in the combustion zone of the reactor. About 65 % of the combustion duty is absorbed by the endothermic heat of reaction, about 10 % goes to CO_2, and the remaining 25 % is lost to cooling water and heat leaks [1]. In addition to the problem of high energy losses there are a wide variety of unresolved problems associated with the reliability of materials of construction, like metal-dusting corrosion at high temperatures.

The situation with the hydrogen production by steam reforming or by partial oxidation is typical for other chemical processes at high temperatures and pressures. Generally these processes are accompanied by:

- low thermodynamic efficiency;
- large capital costs;
- problems associated with the reliability of materials of construction.

Half a century ago Ryabinin [2] 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. Later on it was demonstrated that many industrially important products e.g. hydrogen, synthesis gas, nitric oxide, silica, etc, can be produced during rapid compression-expansion cycles [3-5].

Van Dijck [6,7] was the first who proposed a continuously operating reactor applying rapid gas compression by a free piston to carry out chemical reactions at high temperatures and pressures. This very energy efficient reactor principle did not result in development of an industrial reactor due to the technical drawbacks of the reactor design. A great deal of effort has been made later on to develop a commercial reactor based on the principle of the pulsed compression [4, 8-14]. Many researchers attempted to use Internal Combustion (IC) engines or "engine-like" designs as chemical reactors. However, 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.

A fundamentally new technical solution, which overcomes the problems of the previous free piston reactors was given by Glouchenkov [15-17]. The invented free piston pulsed compression reactor, eliminates also the drawbacks of the conventional chemical reactors with respect to energy conversion principles and promises a breakthrough in energy efficiency, capital costs and portability of many energy and capital intensive chemical processes. In particular, the reactor offers temperatures of the plasma chemistry in combination with pressures of the high pressure technology without energy degradation and losses, i.e. theoretically it provides gas heating and compressing for free. The technology suits ideally for production of hydrogen and synthesis gas by noncatalytic partial oxidation of hydrocarbons.

New reactor concept – the free piston pulsed compression reactor

The novel chemical reactor technology is based on the principle of rapid compressive heating and subsequent expansive cooling. The basic operating principle of the reactor is shown in Figure. 1.

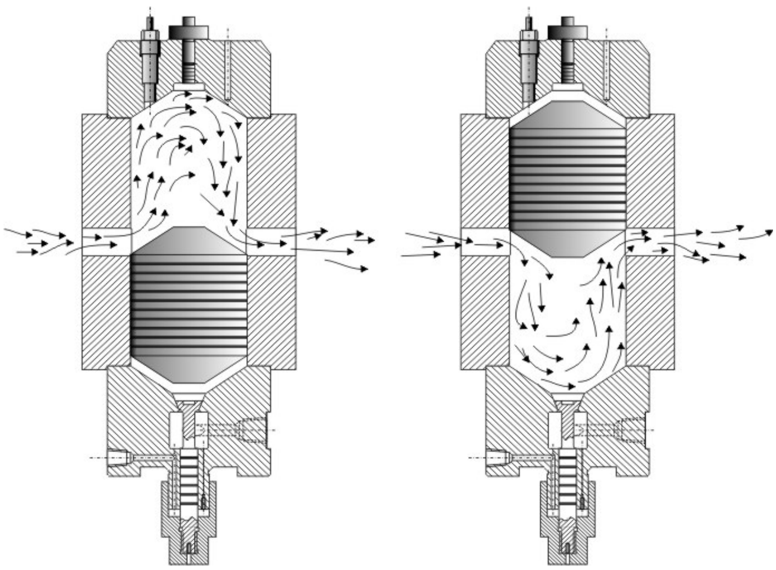

Figure. 1. Pulsed compression reactor. Two limiting positions of the reciprocating piston are shown.

The reactor consists of a double-ended cylinder with inlet and outlet ports in its wall for feeding reactants and removing reaction products and a free piston located inside the cylinder. A feed gas flows across the cylinder in which the free piston, dividing the cylinder into two compression-reaction chambers, reciprocates with a very high frequency (up to 400 Hz) compressing in turn the feed in lower and upper chambers. Rapid, almost reversible compression of the gaseous feed in each chamber results in its heating to sufficiently high temperatures to drive chemical reactions. Reciprocation of the piston is maintained by the reaction itself in case of exothermic reactions. For endothermic reactions the reactor design is slightly different; reciprocation is maintained by an external energy source, e.g. by an actuating gas. The basic idea of the reactor remains the same both for exothermic and endothermic reaction: free piston oscillating between two gas springs.

The new reactor concept is based on two principles: 1) provision of stable self-excited reciprocation (oscillation) of the free piston, and 2) implementation of a combination of contactless, labyrinth sealing of the cylinder-piston clearance and gas lubrication of the piston.

An essential feature of the reactor is that the piston-cylinder assembly has no piston rings - gas lubrication (so-called gas bearing) is used to prevent any contact (i.e. wear) of the piston and cylinder. A significant gas leakage through the annular piston-cylinder clearance is prevented 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. 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 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 [18-20] or by injection of a compressed gas (gas phase feedstock, reaction products or actuation gas) into the annular clearance between cylinder and piston [21-23]. Existing relatively small gas leakage is even desired to provide gas lubrication (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 self centering and self alignment of the piston in the cylinder.
Operation of the reactor resembles that of a two-stroke IC engine. The fundamental difference is that the piston is free: there are no piston rings, lubricants, piston rode, crank gear, valves and other kinematic parts. This permits achieving very high compression ratios (ratios of the initial and final volumes) and frequencies of the piston oscillations. Very short duration of extreme conditions and the absence of piston rings and lubricants permit to achieve extreme temperatures and pressures far beyond those maintainable in conventional chemical reactors and in IC engines. Cooling of the reactor is unnecessary because no piston rings and lubricating oil are used.

Development of the reactor(s), experiments and results

Eight reactors of different design and dimensions and many pistons of various materials, dimensions and shapes were studied without chemical reactions in order to develop effective methods to start up the reactors and to determine conditions that provide smooth, wearless reciprocation of the pistons without gas losses through the piston-cylinder clearance. Two types of start-up systems were developed and tested using these reactors.
Based on the results obtained a number of reactor configurations have evolved to fit the unique requirements of specific types of reactions and conditions. They differ in the methods of start up, supply of feed and removal of products. In particular, in the example of Figure 1 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. Two reactors for carrying out chemical reactions – one with a single working chamber and a second with two working chambers, as shown in Figure 1, were designed and manufactured to demonstrate the technical feasibility of the new reactor concept for synthesis gas production and to study the reactor performance with chemical reactions. The inner diameter of the both reactors was 60 mm. Figure 2 shows a photograph of the reactor with two working chambers. Also a powerful pilot plant, (maximum inlet gas flow rate of about 2000 Nl/min) for testing these reactors was designed and built.

Figure 2. Double-chamber reactor placed inside massive frame.

The experiments with compressed air showed 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 was proven that high-precision manufacturing of the piston-cylinder pairs ensures perfect gas lubrication of the piston, i.e. the piston reciprocates without friction and wear. The reactors driven by compressed air demonstrated unique performance in terms of the achieved combinations of compression, frequency, temperature and pressure which cannot be achieved in other known piston-compression machines e.g.: compression ratio - 45, piston frequency - 200 Hz; piston speed - 30 m/s; piston acceleration - 10^4g; maximum pressure - 200 bar; maximum temperature - 1360 K [24].
Experiments with reactive mixtures were performed using different hydrocarbon (gaseous and liquid) - air mixtures in a very broad concentration range – within and even far beyond the inflammability range at normal outlet pressure. Most of the experiments were conducted with propane/air mixtures. Concentration of propane in the feed gas varied from 0.8 to 20 vol % (fuel/air equivalence ratio, ϕ = 0.2 – 6.0). The measurements of the pressure change during reactions showed unique for chemical engineering temperatures, pressures and reaction rates.
At first, the conditions required for the reactions were studied in experiments without gas flow through the reactors. The occurrence of the reactions manifested through a significant increase of the maximum pressures (20 – 200 bar) compared to that at similar conditions but only with air. Figure 3 shows the influence of propane on the pressure change. Extremely short reaction times (~ 10 μs) and huge rates of pressure change can be seen. In this particular experiment, at first air at ambient conditions in the upper chamber of the single-chamber reactor was subjected to the rapid compression by the piston. Then 2.6 vol % of propane was added to the air and the experiment was repeated.

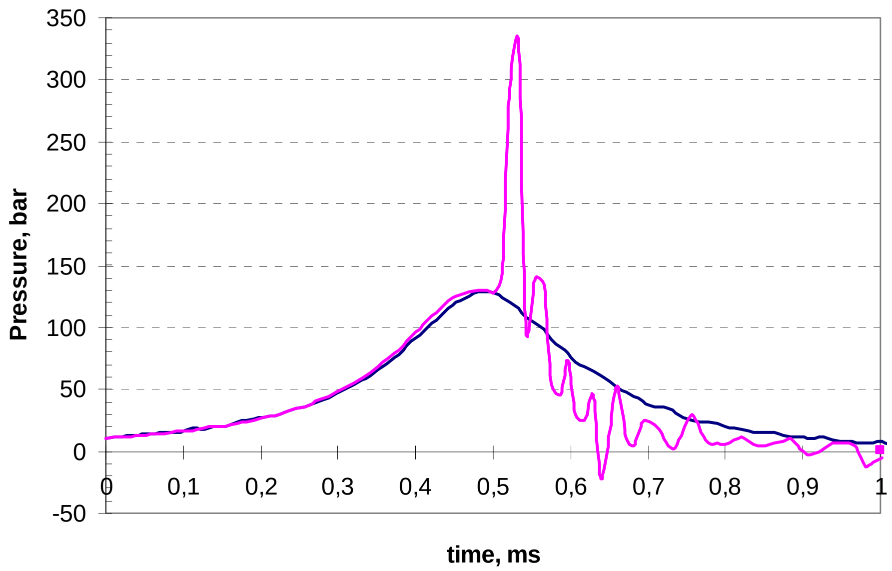

Figure 3. Influence of propane on the pressure change in the reactor; dark blue line – without propane, purple line – with propane (ϕ = 0.63).

Figure 4 shows an example of the pressure change in the single-chamber reactor during synthesis gas production by partial oxidation of propane with air. It explains some of the remarkable capabilities of the reactor. The maximum pressure in this particular experiment was about 400 bar at temperature of about 3000 K. Any other reactor would instantly melt or break down at such conditions whereas both the reaction temperature and pressure can significantly be increased in the pulsed compression reactor. This is possible because the average pressure and temperature in the chamber are much smaller than the maximum values.

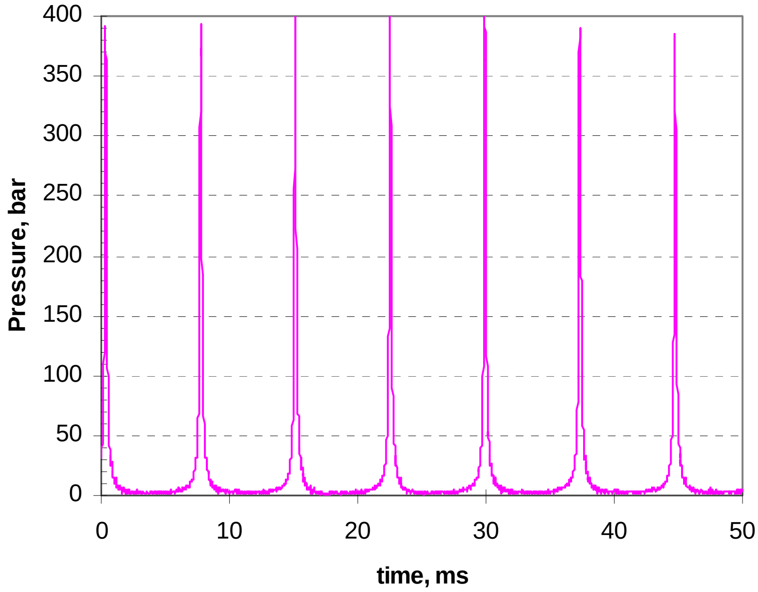

Figure 4. Pressure change in the reactor during continuous production of syngas (ϕ =3.6).

The analysis of the product composition revealed significant conversion of hydrocarbons and oxygen to hydrogen and carbon monoxide. The experiments showed also that the reactor permits reacting of very reach and very lean hydrocarbon - air mixtures. In particular, stable operation of the reactors was observed during combustion of propane with air at concentration of propane less than 0.5 vol %.
The available two reactors were not designed for long-term operation, therefore only short runs of about 60 s were performed.

Advantages of the novel reactor concept

Many advantages of the new reactor concept stem from the reversibility of heating and cooling processes in the reactor and the fact that chemical conversions occur at very high temperatures and pressures whereas the reactor body, feed and products remain at ambient or mild temperature and pressure. These advantages of the novel technology over conventional ones are shortly discussed below.

Energy efficiency.
Energy consumption in gas phase chemical reactors is determined to a large extent by heating and compressing of the reactants to the reaction temperature and pressure and by the heat effects of the reactions. Utilization of the heat of hot products in the conventional reactors is inevitably accompanied with losses of energy and exergy which increase substantially with the process temperature. The process in the pulsed compression reactor is fundamentally different. Adiabatic compression-expansion process in the reactor provides reversible heating and cooling i.e. without energy and exergy degradation. In other words, in theory, the reactor permits heating up to several thousands degrees and subsequent cooling “for free”. The higher the required reaction temperature and pressure the more advantageous the reactor is from the point of view of energy efficiency compared to the conventional reactors.
Although chemical and physical conversions in the reactor occur at very high temperatures, the reactor body remains relatively cold, e.g. 300 – 500 ^{o}C in contrast with 800 – 1500 ^{o}C within the conventional reactors. Therefore energy losses to surroundings are reduced significantly.
Noticeable deviations from the ideal performance may only occur due the gas leakage though the piston-cylinder clearance and heat transfer to surroundings. However they are very much smaller than the total losses in several process units (reactor, heat exchangers, furnaces, compressors, heat recovery boiler-steam turbine) in the conventional processes. The energy input to the reactor is only necessary to compensate heat effects of endothermic reactions.
Rough estimates of the expected energy savings show that the use of the free piston pulsed compression reactor for synthesis gas production will enable to improve the thermodynamic efficiency from 80-85 % to 92-95 %, i.e. to reduce the raw stock consumption by 10-12 %, and to reduce oxygen consumption from 0.60 –

0.68 m^3 O_2 per m^3 CH_4 (conventional processes) to approximately 0.5 m^3/m^3, i.e. by 17-25 % because of reduction of energy required for direct feed heating.

Process intensification.
Extreme pressures and temperatures from several hundreds to several thousands of bars and up to several thousands of K are ideal for instantaneous completion of many chemical reactions. The considerable increase in the reaction rates occurs not only due to the high temperature but also owing to the significant increasing of the concentrations of reagents during compression.

Space velocity.
Very high reaction rates and high frequencies of the piston oscillation (100 – 400 Hz) allow very high space velocities - GHSV~ 10^7, i.e. three-four orders of magnitude as high as that in the conventional chemical reactors.

Selectivity and yield.
Very large rates of temperature and pressure change (up to 10^7 K/s, 10^7 bar/s) afford an excellent way of "freezing" the high temperature products and producing a better selectivity and yield.

Compactness.
Reactor volume will be 10^3 – 10^4 times smaller than that of the conventional reactors.

Investment.
Several factors determine significant reduction in the capital cost:

- the reactor comprises the entire processing train: gas compression, heating of the reactants, reaction itself, cooling of products and utilization of the released reaction energy all together occur in the single unit. Expansive heat exchangers, furnaces, compressors, heat recovery boilers and turbines can be eliminated or replaced by relatively inexpensive low temperature units;
- very small dimensions;
- very simple reactor designs, piston is the only moving part;
- no catalyst is needed and sulfur compounds present in the feed may remain in the reactor.

Safety.
In spite of extreme reaction temperatures and pressures the reactor is inherently safe due to the very small inventory – 10^3 – 10^4 times smaller than that of the conventional reactors.

Environmental issues.
Since heating of the feed is eliminated no combustion of fuel is necessary. This cuts significantly CO_2 emission and eliminates NO_x. The temperatures and pressures attainable in the reactor permit to use waste, difficult to dispose materials (which are now combusted) as a feedstock for chemical industry, e.g. for production of hydrogen and synthesis gas.

Other applications.
The new reactor permits exploration of temperature-pressure range that is not covered with the available manufacturing technologies. The new technology is anticipated to be superior for conducting of many industrially important gas phase, gas-liquid and gas-solid chemical reactions as has been proven experimentally with single-shot compression machines, e.g. for manufacturing acetylene, ethylene and propylene by pyrolysis of methane and other hydrocarbons. It was also found that the basic reactor principle can be adapted to many technical applications outside the chemical industry. In particular, the reactor principle has already been implemented to develop a novel engine-generator for micro Combined Heat and Power (micro - CHP) systems.

Conclusions

The main conclusion of the performed research and development is that the free piston pulsed compression reactor is feasible for production of hydrogen. No other reactors operate at so energy efficient heating and cooling mode, integrate so many functions and allow so high pressures and temperatures, so high quenching rates and so high space velocities. The novel technology is superior over the existing ones in energy efficiency, process intensification, compactness, investment, safety and environmental friendliness.
Due to its extraordinary properties the pulsed compression reactor is anticipated to be superior over the existing technologies for conducting many other industrially important reactions, e.g. for manufacturing acetylene, ethylene and propylene by pyrolysis of methane and other hydrocarbons.

The new technology permits exploration of temperature-pressure range that is not covered with the available manufacturing technologies. Therefore unique processes at very high temperatures and pressures, which have not been possible so far in the process industries, become feasible.

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