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EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Pulsed compression reactor

TECHNOLOGY CODE: 3.2.4

AUTHOR: Alexander Kronberg,
Energy Conversion Technologies B.V.

Table of contents

1. Technology

1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Carrying out of gas phase chemical reactions by rapid compression of reactants has been known for more than a century. In this method, known as pulsed or adiabatic compression, a reactive gas mixture in a tube is compressed by a free piston moving with a speed of 5 – 40 m/s. Figure 1 shows one of the set-ups, known as ballistic piston compressor, for adiabatic gas compression.

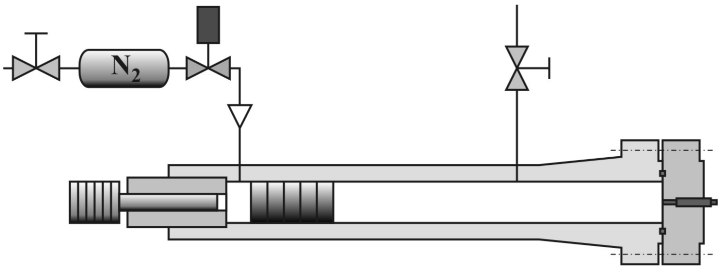

Figure 1. Ballistic piston compressor

The piston is accelerated by a high-pressure driving gas (for example N_2) stored in a start up receiver. The piston executes only one compression stroke expending all its kinetic energy on compressing and heating of the gas. Then the piston is thrown back by the hot compressed gas to the starting position and stopped there by means of a damper. The total cycle duration usually does not exceed 10 ms, the duration of the extreme conditions is about 1 ms. Due to very short duration of the compression-expansion cycle heat losses to the tube wall are negligible. As a result the gas undergoes adiabatic compressive heating followed by adiabatic expansive cooling. Very high temperatures and pressures, up to 12000 K and 10000 bar, which are not attainable otherwise, may be imposed on gas samples with this apparatus (Ryabinin, 1961). An important consequence of the short cycle duration is huge rates of temperature and pressure change, up to 10^7 K/s, 10^7 bar/s.
The achieved pressures and temperatures are ideal for almost instantaneous completion of many industrially important chemical reactions. It was demonstrated that many industrially important products e.g. synthesis gas, ethylene, propylene, acetylene, nitric oxide, silica, etc, can be produced during rapid compression-expansion cycles (Longwell et al., 1958; Kolbanovsky et al., 1982; Morrison, 1989). However single-shot compression machines are definitely not suitable for industrial application. A great deal of effort has already been made to develop a commercial, continuously-operated reactor based on the principle of the pulsed compression. Many researches have attempted to use Internal Combustion (IC) engines or "engine-like" designs as reactors for chemical industry because of their remarkable properties (Kobozev, 1956; Kazarnovskii, 1956; Von Szeszich,1956; Yamomoto, 1963; Karim, 1963, 1990; Matturro et al., US, 5162599, 1992; Kolbanovskii, RU 2072478, 1997; Grunval'd et al., US 6174460 B1, 2001; Sister, et al., 2005).
In spite of the interesting results reported, commercial application of modified IC-engines as chemical reactors is restricted due to several reasons. Some of these are: lubricating oil, high energy losses due to cooling (up to 30%), relatively low inlet/outlet and maximum possible pressures, scaling up problem (sharp decrease of volumetric throughput with the size), impossibility to adjust continuously the compression ratio as the composition of the feed is changed.

Half a century ago Broeze and van Dijck (US, 2814551, 1957) and van Dijck (US, 2814552, 1957) proposed a continuously operating reactor applying the rapid gas compression principle by free piston to carry out chemical reaction at high temperatures and pressures. Later on a lot of effort has been made in the former Soviet Union to develop a commercial reactor based on the same principle (Kolbanovsky et al., 1982). The very energy efficient reactor concepts laid down in the patents have not been realized in practice because of the technical drawbacks of the reactor proposed - neither of the existing patents solved four crucial problems: reactor start-up; stable piston reciprocation; wearless operation and sealing of the piston-cylinder clearance.

A radically new technical solution, which overcomes the problems of the IC-engine based reactors and previous free piston reactors, was given by Glushenkov (RU, 2097121, 1997; RU, 2115467, 1997; RU, 2142844, 1999). The invented free piston pulsed compression reactor 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. In other words theoretically the reactor provides gas heating and compression for free.

The basic operating principle of the reactor is shown in Figure 2. The reactor consists of a double-ended cylinder with inlet and outlet ports for feeding reactants and removing reaction products. A free piston, dividing the cylinder into two compression-reaction chambers, reciprocates as a pendulum between two gas springs with frequencies up to 400 Hz compressing in turn the feed gas in the lower and upper chambers. Rapid, almost reversible compression of the gaseous feed in each chamber results in the heating of the reactants to sufficiently high temperatures (up to 3000 - 4000 K) to drive chemical reactions. The following expansion is accompanied by very rapid quenching (up to 10^7 K/s) of the hot reaction products. The duration of the extreme conditions does not exceed 1 ms preventing a significant heat exchange between the hot, compressed media and relatively cold reactor walls. This provides both the almost isentropic compression-expansion cycle and the feasibility of handling temperatures far beyond the limits determined by heat and corrosion resistances of any materials. The reciprocation is maintained by heat generated in exothermic reactions. For endothermic reactions the reactor design is different, although the operating principle remains the same. An essential feature of the reactor is that gas lubrication (gas bearing) is used to prevent any contact between the piston and the cylinder. The pressure-time and temperature-time conditions imposed upon reactants may be varied within very wide limits by changing parameters such as feed composition, inlet temperature and pressure, reactor dimensions, and piston density.

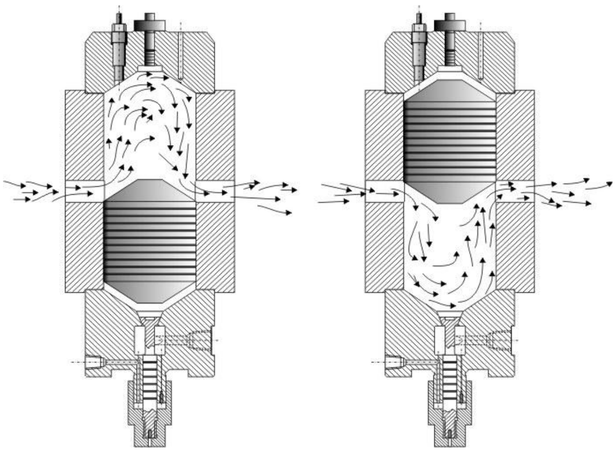

Figure 2. Pulsed compression reactor. Two limiting positions of the reciprocating piston are shown.

1.2 Types and “versions”

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

A number of reactor configurations are known to fit the unique requirements of specific types of reactions and conditions. They differ in the methods of start up, supply of feed, removal of products, and control principles. The only common element of all the reactor designs is the free piston oscillating in between two gas springs (Glushenkov, RU, No 2097121, 1997; RU 2115467, 1997; RU 2142844, 1999).

Basically two types of pulsed compression reactor can be distinguished – double-chamber reactor and single-chamber reactor.

In the double-chamber reactor chemical reactions take place in the both chambers, Figure 2. Only exothermic reactions can be carried out in the reactor shown in Figure 2. The piston reciprocation is maintained at the expense of the reaction heat.

Figure 3 shows the single-chamber reactor. Chemical reactions occur only in one of the chambers. The second chamber is used as a gas spring to control the reactor performance. This mode of operation is intended for highly exothermic reactions. The second chamber can also be used as a part of pneumatic driving system for maintaining the piston reciprocation by supplying of a compressed gas into this chamber. This mode of operation is intended for endothermic reactions.

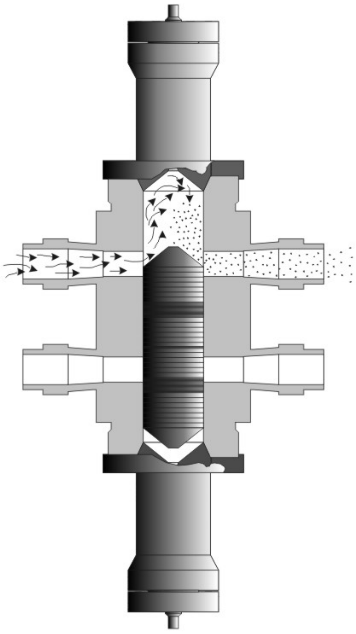

Figure 3. Single-chamber reactor

The reactor in Figure 3 can be operated as a double-chamber reactor. Also a combination of an exothermic reaction in one chamber with an endothermic reaction in another chamber is possible in this reactor. The exothermic reaction heat should be sufficient for the endothermic reaction.

Gaseous (or gas containing fine solid particles) feed is supplied into the reactor as shown in Figures 2 and 3. A liquid or slurry feed can be supplied either to the hot gas inlet lines or directly to the chambers through the reactor covers by a high pressure pump.

Two basic reactor start-up systems are known. With the first system a reactor is started by continuously delivering an actuating, pressurized gas through a throttle into the lower chamber. Under the pressure of the gas the piston moves upward, while the exhaust ports in the lower chamber are closed by the piston, compresses a

gas in the upper chamber and then unblocks the lower chamber's exhaust ports. As a result a fast exhaust of the spent actuation gas from the lower chamber occurs accompanied with sharp pressure drop there. Under the pressure of the gas in the upper chamber the piston is thrown down and then the cycle repeats. Kinetic energy of the piston rises cycle by cycle and, accordingly, the frequency and amplitude of the piston's oscillations rise too. Eventually the reactor attains a periodic steady-state. The gas feed can be supplied into the reactor either before or after the piston reciprocation is established.
With the second start-up system a compressed gas shoves a piston upward once when the reactive gas flows through the reactor.

1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy savings	Depending on the process. Up to 100 % of energy, fuels and chemicals used for heating of feed. Reduction of raw stock consumption by 10-12 % for syngas production.	Significant energy savings result from: • Reversible energy conversion principle eliminating the large energy expenses on heating and compressing of feed. Theoretically the reactor affords heating and cooling for "free". Almost all the energy spent preheating the feed in conventional reactors is saved for processes requiring rapid quenching of the product e.g. pyrolysis processes. • Low energy losses to surrounding due to small reactor size (see below) and relatively low reactor temperature, e.g. 100 – 300 ^{0}C instead of 800 – 1400 ^{0}C for syngas production. • In case of exothermic reactions reaction heat can be utilized in the reactor for heating and/or compressing the reaction products, electricity generation, pumping. • The use of new feedstocks which are cheaper and do not require preprocessing/separation, e.g. natural gas instead of naphta, propane etc. for direct production of olefins or air instead of ammonia and oxygen for production of nitric oxide (nitric acid). The higher the reaction temperature and pressure the larger the benefit is.
Less CO_2 and NO_x emissions	Up to 100 % is expected, e.g. for direct conversion of natural gas to ethylene and acetylene.	Since heating of feed is eliminated no combustion of fuel is needed. Therefore emissions of CO_2 and NO_x due to combustion are eliminated. The process of direct production of ethylene and acetylene from methane can be made ecologically clean by using the hydrogen produced in the process as a fuel to drive the endothermic pyrolysis reactions.
Process intensification	Reaction times can be less than 10^{-4} s	Very rapid chemical transformations result from very high temperatures and the significant increase of the concentrations of the reactants during compression.
Large space velocities	GHSV up to 10^7	GHSV is the ratio of volume throughput at normal conditions to reactor volume. Very large volume throughputs result from very high frequencies of the piston (100 – 400 Hz). For conventional processes GHSV = 10^2 – 10^4. Reactor capacity is determined by the rate of feed supply to the reactor and not by the reaction time.
Compactness	Reactor volume is 10^3 – 10^4 times smaller	Very small dimensions result from very high volume throughput. Because of very small dimensions reactors with super large capacities (e.g. 20000 ton syngas/day) can be skid mounted.

Increased yield and selectivity	Depending on process. Yields of ethylene and acetylene from methane can be increased many times.	Increased conversions may result from very high temperatures. A possibility to control the rates of temperature and pressure change in a very broad range up to 10^7 K/s, 10^7 bar/s affords an excellent way of selectivity control. There is an opportunity for "freezing" the high temperature products and delivering better selectivity and yield. Uniform conditions (temperature, pressure, composition) over the reactor chamber and narrow residence time distribution of the reactants in the reaction zone is another factor improving selectivity. In the experiment on hydropyrolysis of methane the methane conversion was 75 %, of which 50% was converted to ethylene and acetylene!
New range of temperatures and pressures	T ~ 3000 K, P ~ 700 bar in oxidation of hydrocarbons	The achieved temperatures and pressures so far are not the limit. The reaction temperature and pressure can easily be increased up to 4000 – 5000 K and 4000 – 5000 bar. The reactor is an extreme machine. No other equipment exist which could handle so high temperatures and pressures.
Capital cost reduction	Instead of the price of large steam reformer the price of locomotive diesel engine	Significant reduction in the reactor cost results from: • Integration of *the entire processing train* in the reactor: heating and compressing of feed, cooling and expansion of products and utilization of released reaction energy occur all together in the reactor. Multiple expensive high temperature heat exchangers and energy recovery units can be eliminated. • Very small dimensions. • Simple reactor designs, piston is the only moving part. • No catalyst is needed. • Relatively low reactor temperature. There is no problem of high temperature corrosion.
Catalyst savings	100 %	For certain processes, especially in small reactors (higher surface to volume ratio) deposition of catalyst on the surfaces of the reactor and the piston may be advantageous for reactions.
Variety of feedstocks		For example, syngas can be produced from associated gas, heavy oil, a residue in crude oil processing, which was considered so far as a waste material that is difficult to dispose of.
Uniform product properties.	No data available	Very uniform conditions in the reactor permit uniform distributions of the product properties.
Increased safety	No data available	In spite of extreme reaction temperatures and pressures the reactor is *inherently safe* due to the very small inventory. In case of super large scale production the reactor is comparable (with respect to the size and safety) with a locomotive diesel engine; the volume of hot, compressed gas in the reactor chamber will be less than 1 liter.
Relative simplicity in scaling up		In view of very large volumetric throughput no large reactors are necessary. Several reactors with inner diameter of 0.3 m could, for example, generate syngas for the largest methanol, ammonia, and GTL plants.
New processes	Potentially – hundreds new processes	The temperature-time and pressure-time conditions in the reactor may be varied within rather wide limits which are not attainable otherwise. A very large pressure - temperature area is becoming accessible now for industrial exploration, e.g. temperatures of plasma chemistry can be attained in combination with pressures of the high pressure technology. Among the possible new process are: direct production of ethylene and acetylene from methane by hydropyrolysis, manufacturing of large number of ultra-fine powders – pigments, fillers for plastics, raw materials for production of advanced ceramics, electronics, magnetic liquids, etc. Now very energy intensive

		processes are used for manufacturing these products. The new technology could be applied to processes, which cannot be carried out in the conventional reactors. For example production of syngas by partial oxidation of heavy sulfur containing feedstock with air is impossible in the conventional reactors because of a very disadvantageous product gas composition. The reason is that catalytic processes are impossible due to the presence of sulfur, whereas the temperatures required for noncatalytic processes (up to 1600^{0}C) can not be achieved.

1.4 Stage of development

A chemical compression reactor, based on the modification of a diesel engine, for production of syngas by partial oxidation of methane with air has been announced by the group of Russian companies Energosyntop (www.energosyntop.com).
The Topchiev Institute of Petrochemical Synthesis and the Institute of Applied Physics, (Russian Academy of Sciences) in cooperation with TK Sibur NN company successfully tested the chemical compression reactor – a modified internal combustion engine with prechamber pilot-flame ignition on the industrial scale for synthesis gas production (Sister et al. 2005).
The free-piston pulsed compression technology is still in the laboratory phase of development. Energy Conversion Technology BV and Twente University have a pilot plant and two reactors (inner diameter 60 mm) for syngas production with capacity of about 100 Nm^3/hour each. The available reactors were designed to demonstrate the feasibility of the novel reactor concept and can be run only for a short periods of time. At the end of 2007 a new reactor for long term operation and a completely new pilot plant for testing of the reactor are expected to be ready.

2. Applications

2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

The technology under consideration is expected to be effective for carrying out of a large number of industrially important chemical reactions. It is comprehensible that the focus in this report is on the most important processes which account for the largest shares of energy use and emissions.

Olefins

The analysis of energy use and carbon losses in the chemical industry shows that steam cracking to produce olefins (ethylene and its co-products) covers 35% of the energy use in the chemical industry worldwide and in the Netherlands. In the Netherlands olefin production accounts for 5.1 Mt CO_2 (22%). (Neelis et al., Applied Energy, **84**, 853-862, (2007)).
In the cracking process, hydrocarbon feedstocks are preheated in the convection section to 650 ^{0}C (using fuel gas and waste heat), mixed with steam and cracked in the radiant section at temperature of about 850 ^{0}C. The heat is provided to the radiant coils by the burning of an appropriate fuel in a furnace. Subsequently, the gas mixture is rapidly cooled to 400 ^{0}C (or quenched) to stop the reaction, during which high pressure steam is produced. Injection of water further decreases the temperature to about 40-50 ^{0}C and a condensate, rich in aromatics, is formed. Very high energy intensity of this process is partly due to the decoking necessary to maintain cracking furnace tubes.

Feedstocks used in steam cracking are ethane, LPG, naphta, gas oils and sometimes coal-derived feedstocks. The conventional technology is not practical for natural gas (methane) pyrolysis due to the high temperatures involved.

Synthesis gas, hydrogen

Synthesis gas (syngas), a mixture of hydrogen and carbon monoxide, is a present and increasing source of environmentally clean synthetic fuels and many chemicals. Almost all hydrogen gas is manufactured from syngas. Ammonia and methanol are the most important chemicals produced from syngas.

Production of syngas for ammonia and methanol covers about 29% of the energy use in the chemical industry worldwide and 21% in the Netherlands. In the Netherlands ammonia and methanol production account for 6.1 Mt CO_2 (30%) emission (Neelis et al., Applied Energy, **84**, 853-862, (2007)).

Syngas is manufactured from natural gas, coal, petroleum, biomass and even organic wastes. Today, synthesis gas is most commonly produced from the methane component in natural gas. Three processes are commercially practiced. At moderate pressures and high temperatures methane reacts with steam on a catalyst to produce syngas. This process, commonly called steam-methane reforming, is endothermic and the heat transfer limitations place limits on the size of the catalytic reactors used. Methane can also undergo partial oxidation with molecular oxygen to produce syngas. This reaction is exothermic and the heat given off can be used to drive the steam-methane reforming reaction. When the two processes are combined, it is referred to as autothermal reforming.

In these processes syngas is produced at high temperatures (800-1100 ^oC in the presence of a nickel catalyst, to 1350 - 1400 ^oC without catalyst) and moderate pressures (up to 65 bar) within refractory-lined vessels. Heating of the reactor feed (steam, oxygen, methane etc) requires an enormous amount of energy to be obtained at the expense of combustion of a part of the feedstock. This is accompanied with significant energy losses. Even with energy recovery by means of a heat-recovery boiler-steam turbine unit 40 - 60% of energy input is lost.

Acetylene

Acetylene is commonly produced by two commercial processes. The first, batch and bulky process, is based on reaction of calcium carbide with water at normal temperatures. Calcium carbide is produced by highly exothermic reduction of calcium oxide (limestone) by coke in an electric furnace at 1900-2300 °C. The liquid calcium carbide is cooled to normal temperature. The reaction between calcium carbide and water produces a considerable amount of heat which must be removed to prevent the acetylene gas from exploding. The high grade heat used in the process and the heat evolved are not recovered.

The second, more economical process is the thermal cracking of hydrocarbons, also at extremely high temperatures of 1300-2000 °C. There are several versions of this process depending on the feedstock used and the way heat is supplied and removed from the reactor. Some cracking processes use an electric arc to heat the raw materials, while in others the heat required is provided by burning part of the hydrocarbons with oxygen. The reaction products are cooled down rapidly to prevent decomposition of acetylene to carbon and hydrogen. Such a rapid cooling (quenching) prevents effective recovering of high-grade heat of the products.

Nitric oxide

Nitric oxide is produced on a massive scale as an intermediate in the Ostwald process (nitric acid from ammonia). In the first stage of the Ostwald process ammonia is “burned” by heating with oxygen in the presence of a catalyst such as platinum with 10% rhodium, to form nitric oxide and water. Typical conditions for this stage are: pressure between 4 and 10 bar and temperature is about 1173 K.

Various methods of combining nitrogen and oxygen directly to form nitric oxide have been actively investigated, e.g. the electric arc, the Wisconsin process in which atmospheric oxygen and nitrogen are combined in a regenerative furnace operating at about 2000 ^{o}C. However they cannot compete economically with the ammonia oxidation route due to very high-energy consumption and an impossibility to recover effectively the high-grade heat.

Hydrogen cyanide

The most important process for the production of hydrogen cyanide is the Andrussov oxidation in which methane and ammonia react in the presence of oxygen at about 1200 °C over a platinum catalyst.

Nanoparticles

Nanoparticles can be produced by different methods such as flame aerosol synthesis, plasma processes or sol-gel. Today the most cost-effective process for production of ultra-fine particles is flame aerosol synthesis. It is employed widely for the manufacture of carbon black, fumed silica, titanium dioxide etc.

Production of many pure oxygen- or carbon-free metallic and ceramic particles is impossible in flames because the feed has to be flammable i.e. to contain a fuel and oxygen. Other known methods can only be used for producing research quantities. Plasma-based synthesis, for instance, requires huge amount of energy for heating reagents and carrier gas to the reaction temperature and therefore is not practicable in case of large production volumes (e.g. 3 millions tones of titanium dioxide worldwide). Nonuniform size of the particles produced is another disadvantage of the available technologies - the required separation of the particles is very costly.

General comments

Out of 3.73 quadrillion Btu of fuel and electricity delivered “to the fence” of chemical industry facilities in 2001, a conservative estimate claims that 37 % was lost in combustion, distribution, and energy conversion activities. At fuel prices of about $7 per MMBtu, those losses equate to over $26 billion.

The technologies with which these losses are associated have reached a stage of maturity. Improvements in yield, product selectivity and energy efficiency are becoming increasingly difficult. For example, for the conventional steam cracking process, ethylene yields are improved by raising the cracking temperature and reducing residence time, i.e., increasing the cracking severity. These severe conditions, however, are constrained by the metallurgy of the cracking tubes and rapid coking tendency in the cracking coils. Improvements in the high temperature processes could be achieved via new materials capable of withstanding higher temperatures. This scenario is, however, hardly feasible in the foreseeable future. Even if such materials will be developed the operating cost will increase due to the higher temperatures.

Therefore one of the chemical industry’s biggest challenges is developing of radically new technologies.

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

No commercial applications of the pulsed compression technology/reactor have been reported.

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity /Plant size	Year of application	Reported effects

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
Large volume chemicals	Topchiev Institute of Petrochemical Synthesis, Institute of Applied Physics, (Russian Academy of Sciences) and TK Sibur NN company. Syngas production by partial oxidation of methane with air	Modified six-cylinder gas engine with prechamber pilot-flame ignition. Displacement volume 45.8 liter, compression ratio 11.8, rotational speed 500 rpm, air excess ratio 0.42	before 2006	Syngas production capacity 3120 Nm^3/hour. CH_4 conv. – 86%. Product composition (vol %): H_2 (16.6), CO (11.2), CO_2 (2.5), CH_4 (3.2)
Large volume chemicals	Group of Russian companies Energosyntop. Syngas production by partial oxidation of methane with air and subsequent production of methanol.	Modified diesel engine	2007	Syngas production capacity 12500 Nm^3/hour. Product composition (vol %): H_2 (26.5), CO (14.5), CO_2 (2.8), CH_4 (0.6), O_2 (<0.5). Simultaneous electricity generation.

The feasibility of the free piston pulsed compression reactor for syngas production from gaseous and liquid hydrocarbons by partial oxidation with air was demonstrated in the project:
“*Development of the free piston pulsed compression reactor for synthesis gas production from hydrocarbons*” Energiebesparing door innovatie BSE-programma, project nummer EDI01123, see
Glouchenkov, M. et al. Final report, Twente University, Enschede, June 2005. Available at SenterNovem.

For the time being Shell, Energy Conversion Technology BV and Twente University are developing the pulsed compression reactor for production of synthesis gas by partial oxidation of methane:
"Pulsed compression technology: a breakthrough in high temperature processes. SenterNovem", EOS-LT, project number EOSLT04025.
See, Monitor, February 2007, p.11.

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

Figure 4 shows approximately the pressure-temperature scopes of different process technologies. Very large pressure - temperature area is becoming accessible now for industrial exploration.
The reactor 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 by the use of the available pulsed compression reactors, the single-shot compression apparatuses, and the modified internal combustion engines.

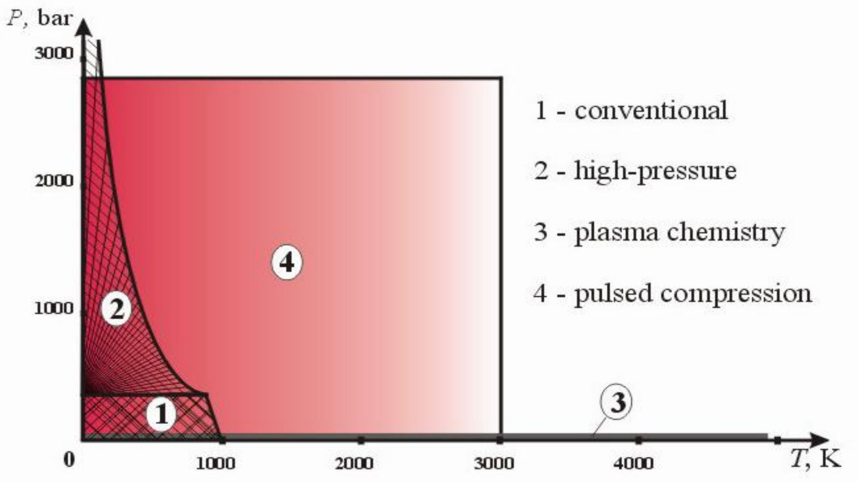

Figure 4. Pressure-temperature scopes covered by different process technologies.

The most important applications are:

- Poduction of synthesis gas from various gaseous, liquid and solid hydrocarbons.
- Direct conversion of natural gas (methane) to ethylene, acetylene, hydrogen, carbon black by (hydro/oxy-) pyrolysis of methane and other hydrocarbons.
- Olefin production by dehydrogenation of paraffins.
- Direct synthesis of nitric oxide from nitrogen and oxygen, and hydrogen cyanide from nitrogen and hydrocarbons.
- Controlled generation of monodisperse ceramic, metallic, and amorphous nanoparticles by thermal decomposition of appropriate precursors (carbonyl- and organometallic compounds, salts, etc.).
- Thermal destruction of impurities that are discharged in industrial process exhausts (air cleaning) and toxic compounds.

The range of temperatures and pressures attainable in the reactor is far beyond the capabilities of the conventional chemical reactors and other known devices. Therefore unique chemical transformations at very high temperatures and pressures, which have not been possible so far in the process industries, become feasible.

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to “boundary” issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
1. Engineering & design reactor concepts for large scale production.	The available reactors were designed to demonstrate the feasibility of the novel concept. They have relatively low production capacity and were run for shorts periods at near ambient inlet/outlet pressures. The following main issues should be addressed. 1. Thermal control/stabilization necessary for long-term operation. 2. Effective start-up methods. 3. Gas exchange in the chambers (geometry of the chambers, position, size and shape of inlet and outlet ports). 4. Materials for pistons and cylinders. 5. Effective gas lubrication, providing stable, wearless reciprocation of the piston and labyrinth sealing preventing gas leakage through the gap between the piston and the cylinder.	R&D projects on the thermal and gas dynamics processes, tribology, and material science carried out at universities and research institutes, also in collaboration with reactor developers and end users. Participation of research teams having experience in internal combustion engines and free-piston devices could be very helpful.
2. Modeling and optimization	All the reactors made so far were designed based on the available data in the fields of internal combustion engines, free piston devices, rough balance estimates, and the results obtained with the previous reactors. A systematic reactor modeling which could replace expensive and time consuming experiments is needed.	R&D projects carried out at universities and research institutes, also in collaboration with reactor developers and end users.
3. Chemical transformations at extreme conditions.	The reactor provides temperatures and pressures for which no kinetic and even thermodynamic data are available. Systematic study is necessary both for the known reactive mixtures and new ones.	R&D projects carried out at universities and research institutes. Experimental facilities such as Rapid Compression Machines (RCM) used in the combustion research for IC-engines could be used for investigation of many chemical reactions.
4. Reactor control	Proper control of the exothermic chemical reactions is crucial for the energy efficiency, yield and selectivity. No problems are foreseen in case of endothermic reactions.	R&D projects carried out at universities and research institutes. The issue closely relates to the modeling and optimization and the research on the chemical transformations (pos. 2, 3 this table).

5. Noise and pressure drop reduction	By designing of the inlet and outlet lines preventing pressure oscillations and by using of silencers, Helmholz resonators, fluidic elements.	R&D projects on the gas dynamics, carried out at universities and research institutes.
6. Suppression and practical use of vibrations	Appropriate dynamic vibration absorbers are to be developed.	R&D projects on the vibrations carried out at universities and research institutes,

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	**Description**	**How and by whom should the challenge be addressed?**
Simultaneous power production	In case of exothermic reactions the energy released can in principal be converted to electricity. There are different concepts to approach this problem, e.g. by coupling of the reactor body with linear alternators.	This challenge should be addressed in the R&D projects on engineering & design reactor concepts, reactor control and suppression and practical use of vibrations (pos.1, 4 and 6 in Table 4).
Compression of the reaction product	In the existing reactors the products are removed from the reactors at the end of the expansion stroke at pressure lower than the inlet pressure. In case of exothermic reactions a part of the reaction products can be removed from the reactor before or during expansion stroke at pressure significantly higher than the inlet pressure. In that case the reactor would perform an additional function – feed compressing – which could be very valuable for some processes from energy point of view.	This challenge should be addressed in the R&D projects on engineering & design reactor concepts (pos.1 in Table 4).
Combination of endothermic and exothermic reactions in a reactor.	In the currently available reactors endothermic reactions occur in one of the reactor chambers, whereas the second one is used for driving the piston by a compressed gas. From technological and energy efficiency points of view it could be economical to drive the piston by combusting a fuel in the second chambers or to carry out simultaneously exothermic and endothermic reactions, both resulting in valuable products.	This challenge should be addressed in the R&D projects on engineering & design reactor concepts (pos.1 in Table 4).
New materials for the reactor body and the piston.	Application of new advanced ceramics and composites.	This challenge should be addressed in the R&D projects on engineering & design reactor concepts (pos.1 in Table 4).
Useful utilization of pressure oscillations in the inlet and outlet lines.	Appropriate shape and size of the inlet and outlet lines and application of special techniques, such as fluid diodes, and Helmholz resonators could be beneficial for reduction and, possibly complete elimination of the pressure drop over the reactor.	This challenge should be addressed in the R&D projects on noise and pressure drop reduction (pos.5 in Table 4).

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Glouchenkov, M., A. Kronberg, and H. Veringa, Free piston pulsed compression reactor, *Chemical Engineering Transactions*, Vol. 2, 983-988, 2002. 4th Int Symp on High Pressure Process Technology and Chemical Engineering, September, 22-25, 2002, Venice, Italy.	Research paper	First experimental data on the reactor performance without chemical reactions.
Glouchenkov, M., and A. Kronberg, Pulsed compression reactor, *Proceedings of the 3rd International Symposium on Multifunctional Reactors*, 246-249, 2003. August 27-29, 2003, University of Bath, U.K.	Research paper	Experiments on combustion of lean mixtures in single-shot reactor
Maxim Glouchenkov, Alexander Kronberg, Pulsed compression technology: a breakthrough in production of hydrogen. *16th World Hydrogen Energy Conference (WHEC16)*, June 13 – 16 2006, Lyon, France. Paper S06-385.	Research paper	Production of syngas from reach hydrocarbon-air mixtures.
Maxim Glouchenkov, Alexander Kronberg, Pulsed compression: advanced technology for synthesis gas production. 8th Natural Gas Conversion Symposium (NGCS 8) May 27 – 37, 2007, Natal, Brazil. Book of Abstract, p. 213 - 214.	Extended abstract	
Longwell, P. A., et al., Ballistic piston for investigation gas phase reactions, Ind. Eng. Chem., **50**, No 4, 603 – 610 (1958).	Research paper	Contains experim. data on direct synthesis of NO from N_2 and O_2. Quenching rate of 7 10^{-6} K/s was already sufficient for significant yield of NO.
Karim, G. A., The production of synthesis gas and power in a compression ignition engine; Journal of the Institute of Fuel, March, 98-105 (1963).	Research paper	Production of syngas from methane and oxygen-enriched air with ignition provided by the injection of a small quantity of diesel fuel.
Karim, G. A., Production of synthesis gas and power in reciprocating internal combustion engines, British Chemical Engineering, **8**, No.6, 392-396 (1963).	Review and research paper	
Karim, G. A., and N.P.W. Moore, The Production of Hydrogen by the Partial Oxidation of Methane in a Dual Fuel Engine; SAE Techn. Pap. Ser, No. 901501 (1990).	Research paper	

Kobozev, N.I. et al. The explosive conversion of methane, Part 1, and Kazarnovskii Ja.S. et al., The explosive conversion of methane Part 2. Published by Akad. Nauk S.S.R. Moscow, 1956 (Trudy Vses. Sovesch po KompleksnoiKhim Perer. Neft. Gasov.) pp. 133 – 152.	Research paper	The first recorded research into the use if IC engine for the reforming of methane to syngas, performed in 1937
Kolbanovskii, Y. A., et al. Impulsnoe sgatie gasov v chimii i technologii./ Moskva, Nauka)). 1982. 240 c. (Pulsed compression of gases in chemistry and technology, Moskow, Nauka, 1982, 240 p) (in Russian).	Book	Comprehensive overview of the technology
Von Szeszich, L., Herstellung von Synthesegas im Otto-Motor bei gleichzeitiger Arbeitsgewinnung, Chemie-Ing-Techn., **28**, (3), 190-195 (1956).	Research paper	
Kolbanovskii, Yu.A., and N.V. Plate, Power units in chemical engineering, Petroleum Chemistry, **40**, No. 5, 323-333 (2000).	Review	Among others applications of CCRs (modified IC-engines) for syngas production, pyrolysis of hydrocarbon gases and destruction of toxic compounds are discussed
Morrison, Jr., P. W. and J.A. Reimer, Silane pyrolysis in a piston reactor, AlChE Journal, **35**, No. 5, 793-802 (1989).	Research paper	Experimental proof of applicability of the technology for silane pyrolysis.
Mikalsen, R., and A.P. Roskilly, A review of free-piston engine history and applications, Applied Thermal Engineering, 27, 14-15, October 2007, pp. 2339-2352.	Review	Overview of free-piston engines
Ryabinin, Y. N. Gases at High Densities and Temperatures; Pergamon Press, Inc., N. Y. 1961.	Book	The only book on rapid gas compression techniques.
Zubov V. A. et al., Structure and properties of the silicone carbide based inorganic polymer from high-temperature gas phase, J. Inorganic Chemistry, **39**, 11, 1784-1787 (1994).	Research paper	Synthesis of SiC nanoparticles by the rapid compression of tetrametilsilane in argon-hydrogen mixtures.
Yamamoto, T. et al. Production of Synthesis Gas by an Internal Combustion Engine. Sixth World Petroleum Conference; Frankfurt Main, 19-26 June 1963, Section IV: paper 12, (1963).	Conference paper	

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
Brutzkus, M. Apparatus for chemical production and research, US 1586508, 1926.		Probably the first patent on application of the compression-expansion principle for carrying out chemical reactions. The author argues for his piston compressor can be used for carrying out practically all chemical reactions. Among them production of nitrogen-oxygen compounds and other inorganic substances and formation, dissociation or conversion of organic substances and their synthesis from their elements and from inorganic compounds, e.g. cracking of various hydrocarbons for the obtaining of less complicated hydrocarbons.
Pescara, R.P. Motor compressor apparatus, US 1657641, 1928.		The original Pescara patent describes a single piston spark ignited air compressor but the patent seeks to protect a large number of applications utilizing the free-piston principle. The model GS-34 free piston gas generator (SIGMA in France) was based on further Pescara's patents. It was used for large scale applications such as marine and industrial powerplants.
Odel, W.W. Process of making oxidation products, US 1939018, 1933.		The use of an IC-engine for manufacturing of oxidation products (methanol, formaldehyde, carbon monoxide, etc.) by the control, (usually

		incomplete) combustion of the oxidizable matter.
Broeze J.J. and W. J. D. Van Dijk, Method and reciprocating compression-reactor for short period, high temperature and high pressure chemical reactions. US 2814551, 1957.	Shell Development Company	The first free piston reciprocating compression reactor which may be used to perform chemical reactions, such as cracking of hydrocarbons, synthesis reactions, etc.
Van Dijk, W. J. D., Reciprocating compression-reactor for short period, high temperature and high pressure chemical reactions. US 2814552, 1957.	Shell Development Company	An improvement over US 2814551.
Lowther, F. E., and W. M., Bohom, Integrated product generation and catalytic product synthesis in an engine-reactor. US 4965052, 1990.	Atlantic Richfield Company	A two-chamber engine-reactor wherein an initial product, e.g. syngas, is generated within the first chamber. This product is contacted with a catalyst in the second chamber to synthesize an end product, e.g., methanol.
Matturro, M.G. et al., Rapid thermal pyrolysis of gaseous feeds containing hydrocarbon molecules mixed with an inert working gas. Pat USA, No 5162599, 1992.	Exxon Research and Engineering Co.	A process for the rapid conversion of methane, under high temperature and pressure conditions, to unsaturated gaseous hydrocarbons, especially olefins, and hydrogen.
Glouchenkov M. Y. Apparatus for pulsed gas compression. RU, 2097121, 1997	D. A. Paraschuk	Various applications in the chemical industry, power engineering and engines, including, e.g. production of syngas, ammonia, ultra-disperse powders.
Glouchenkov M. Y. Apparatus for pulsed gas compression. RU, 2115467, 1997	M. Y. Glouchenkov, D. A. Paraschuk	For large variety of chemical high temperature processes, e.g. production of syngas, hydrogen, nitrogen fixation, carbon, sulfur, ultra-disperse ceramic and metallic powders, thermal disposal of toxic compounds, etc.
Glouchenkov M. Y. Apparatus for pulsed gas compression. RU, 2142844, 1999	M. Y. Glouchenkov, D. A. Paraschuk	For carrying out various chemical transformations.

Grunval'd, V.R. et al. Method for producing synthesis gas, US 6174460 B1, 2001	Experimentalny Komplex "Novye Energeticheskie Teknologii" (EK "Net") Obiedinennogo Instituta Vysokikh Temperatur Rossiiskoi Akademii Nauk; Institut Neftekhimicheskogo Sinteza Rossiiskoi Akademii Nauk, both Moscow (RU)	An improved method for producing syngas from gaseous hydrocarbons in a modified internal combustion engine.
Dolinskii, Yu.I. et al. A process for manufacturing technical carbon (variants thereof), RU 2096433, 1997	Experimentalny Komplex "Novye Energeticheskie Teknologii" (EK "Net") Obiedinennogo Instituta Vysokikh Temperatur Rossiiskoi Akademii Nauk; Institut Neftekhimicheskogo Sinteza Rossiiskoi Akademii Nauk, both Moscow (RU)	Application of chemical compression reactors for production of carbon.
Kolbanovskii, Yu.A. A process for disposal of toxic compounds, RU 2072478, 1997.	Institut Neftekhimicheskogo Sinteza Rossiiskoi Akademii Nauk, Moscow (RU)	Application of chemical compression reactors for destruction of toxic compounds.
Van Blarigan, P. Free-piston engine. US 6199519, 2001.	Sandia Corporation	The engine employs homogeneous charge compression ignition (HCCI and is aimed tp operate on a variety of hydrogen-containing fuels.

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

Development of pulsed compression technology for various applications is core business of Energy Conversion Technology B.V. The company together with Shell and Twente University is developing a free-piston pulsed compression reactor for syngas production. No other institutes or companies are known to work specifically on the development of this technology.

Several Russian research institutes and companies are developing Chemical Compression Reactors based on internal combustion engines for different applications, see Table 8.

Free-piston internal combustion engines, from the air compressors and gas generators through to recent free-piston hydraulic engines and linear electric generators are under investigation by a number of research groups world-wide. Some of them are listed in Table 8.

Many research institutes and companies all around the world are doing research on internal combustion engines. Their experience and the experimental facilities could be very useful for the development of the free-piston pulsed compression reactors.

Table 8. Institutes and companies working on the technology

Institute/Company	**Country**	**Remarks**
Toyohashi University	Japan	Research in the field of hydraulic free-piston engines

Technische Universitätr Drezden	Germany	Research in the field of hydraulic free-piston engines
Tampere University	Finland	Dual piston hydraulic free-piston engines
West Virginia University	USA	Spark ignited dual piston engine generator
Sandia National Laboratories	USA	Dual piston free-piston engine generators
Innas BV	The Netherlands	The company is among the research leaders within free-piston technology.
Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences	Russia	Reactors based on modified IC engines – chemical compression reactors (CCRs)
Institute of Applied Physics, Russian Academy of Sciences	Russia	Reactors based on modified IC engines – chemical compression reactors (CCRs)
TK Sibur NN	Russia	Chemical Compression Reactors for syngas production
Group of companies Energosyntop	Russia	Chemical Compression Reactors for syngas production

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

No suppliers of commercial pulsed compression reactors are known. Manufactures of reactors which are currently used for the research and developers and producers of large IC-engines can be seen as potential manufactures of commercial reactors and stakeholders. These manufactures are listed in Table 9.

Table 9. Supplier and developers

Institute/Company	**Country**	**Remarks**
ECN	The Netherlands	Two reactors and many spare parts (e.g. pistons, reactor covers, etc) were manufactured at ECN Engineering and Services department. A new reactor is currently under construction there.
Vossebelt precisiebewerking B.V.	The Netherlands	One reactor and many spare parts were manufactured at the company.
Kluin Wijhe B.V.	The Netherlands	Potential manufacturer of commercial reactors
MAN Diesel	Germany	The world's leading provider of large-bore diesel engines for marine and power plant applications.
ABC	Belgium	Development, construction and commercialization of internal combustion engines, mainly diesel engines, but also gas engines and dual fuel engines.

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Potential group of end users includes energy companies producing fuels and chemical companies producing olefins, ammonia, methanol, nitric acid, hydrogen cyanide, carbon black, silicon powders, ceramic and metallic nanoparticles.

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

The pulsed compression technology promises a breakthrough in energy efficiency, capital costs and portability of a large number of energy and capital intensive processes in the chemical industry. No other chemical reactors can compete with the pulsed compression reactor in terms of the attainable combinations of the pressures, temperatures and the rates of their change. Therefore new chemical processes which were not possible so far in the process industries become feasible.

The technology is in an early stage of development and an interdisciplinary R&D effort is needed to develop commercial reactors for large number of applications. Industrial reactors could be developed and implemented within next 5-10 years.