

Partial Oxidation of Methane in the Pulsed Compression Reactor: Experiments and Simulation

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Abstract—The Pulsed Compression Reactor promises to be a compact, economical and energy efficient alternative to conventional chemical reactors.

In this article, the production of synthesis gas using the Pulsed Compression Reactor is investigated. This is done experimentally as well as with simulations. The experiments are done by means of a single shot reactor, which replicates a representative, single reciprocation of the Pulsed Compression Reactor with great control over the reactant composition, reactor temperature and pressure and temperature history. Simulations are done with a relatively simple method, which uses different models for the chemistry and thermodynamic properties of the species in the reactor. Simulation results show very good agreement with the experimental data, and give great insight into the reaction processes that occur within the cycle.

Keywords—Chemical reactors, Energy, Pulsed compression reactor, Simulation

I. INTRODUCTION

To cope with the tremendous worldwide energy losses in the chemical industry, the Pulsed Compression Reactor (PCR) is under development. The principles of this reactor were developed over eighty years ago as can be seen from patents by Brutzkus [1] and the book by Kolbanovskii et al. [2]. Further developments have been achieved by Glushenkov [3]. It promises to be a very compact, economical and energy efficient alternative to conventional chemical reactors used for the most energy consuming high temperature processes. The PCR is a free piston impulse compression device. It rapidly compresses the reactants by a free piston. Due to the compression the reactants are heated and react spontaneously. A schematic view of the PCR is shown in Fig. 1. Reactants are injected and products removed, through ports in the side of the reactor, when the piston is near one of its extreme positions.

The functioning of the PCR can be compared to that of an internal combustion engine, with some important differences.

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Where most conventional engines use piston rings, lubrication oil and relatively low operating frequencies and pressures, the PCR uses tight tolerances as sealing, gas lubrication and higher operating frequencies and compression ratios.

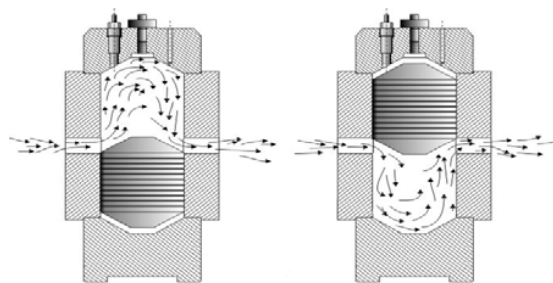


Fig. 1 Schematic view of the PCR

This brings forth some advantages and disadvantages. The PCR does not require lubrication oil, which means that a great versatility of the type of chemical processes that is performed in the reactor is obtained, without the need to develop and apply different types of lubricating fluids for each process as is the case with internal combustion engines. The absence of piston rings means higher compression ratios are obtainable, as well as the possibility to operate at elevated inlet and outlet pressure to significantly increase throughput. Higher operating frequencies mean that a higher throughput per unit of volume of reactor is obtained. Higher pressures both mean a higher throughput, but can also mean shorter reaction times. A more detailed description of the PCR can be found in the work of Roestenberg et al. [4].

The work presented here focuses on the application of the PCR for the partial oxidation of methane, with the emphasis on hydrogen and carbon monoxide (synthesis gas) yield. The work presented is comprised of two parts. The first part consists of experiments in a single shot reactor, aimed at looking at the relation between the composition of reactants to the products in terms of synthesis gas yield and compression ratio and preheat temperature. The second part, the simulations done, aim to give insight into the reaction paths and the interpretation of experimental results as well as creating good predictions about other processes.

The outline of this article is as follows. First the

experimental setup is described, followed by the procedure for doing simulations. Lastly the results, from both experiments and simulations, are presented, discussed and compared to each other.

II. EXPERIMENTAL SETUP AND PROCEDURE

The experimental setup used consists of a single shot reactor designed to reproduce one compression-expansion cycle of the continuous process. This allows for very good control of the initial mixture in the reaction chamber by avoiding the influence of products remaining in the reactor from previous cycles. It also ensures that other process parameters such as reactor and piston temperature are the same for each experiment. The single shot reactor is shown schematically in Fig. 2. Depicted are, among others, the top cover with pressure sensor and the piston with grooves used for measuring the piston velocity. Some characteristic sizes and the piston mass are shown in Table I.

TABLE I
CHARACTERISTIC PARAMETERS OF THE SINGLE SHOT REACTOR

Bore diameter	60mm
Bore length	325mm
Piston length	165mm
Piston mass	0.854kg

Before the experiment a sample of the reactants in the reactor is taken, after which one compression-expansion cycle is initiated. After this one reciprocation the products are extracted from the reactor and both reactants and products are analyzed using a gas chromatograph.

TABLE II
GC SETTINGS

Variable	MS5	PPQ
Carrier gas	Argon	Helium
Column temperature	70°C	50°C
Injector temperature	80°C	80°C
Injection time	40ms	40ms
Column pressure	150kPa	110kPa with a linear ramp after 60s of 50kPa/min to 200kPa
Sample frequency	100Hz	
Sampling time	180s	
Measuring time	240s	

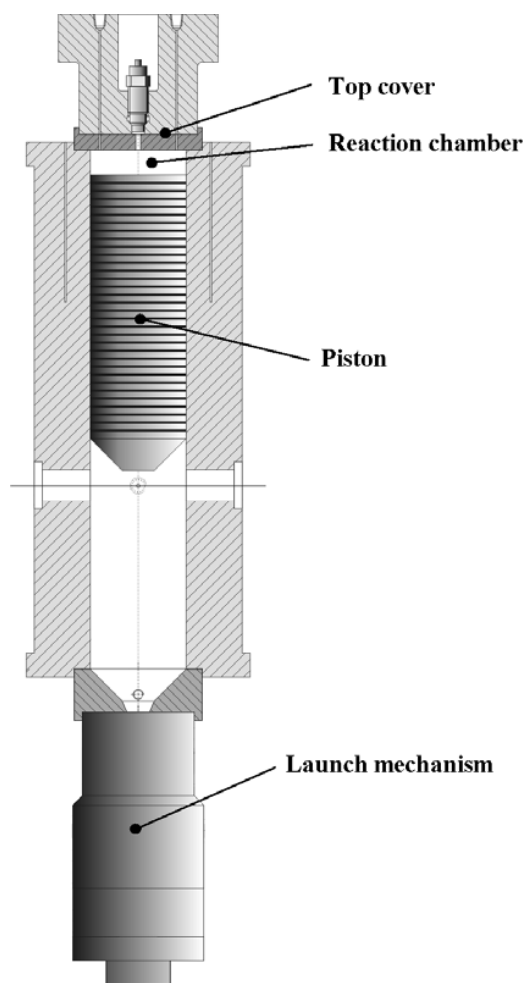


Fig. 2 Schematic view of the single shot reactor

Movement of the piston is initiated by injection of compressed air through the launch mechanism. As the piston moves up, at some point it (if enough energy is supplied), unblocks the outlet ports on the side of the reactor. This allows the launch air to escape. When the piston moves down again under the force of the now compressed gasses above the piston as well as gravity (the latter of which is generally much smaller), the motion of the piston is damped by a small hole in the bottom of the reactor. This reduces the buildup of pressure under the piston, ensuring that the second reciprocation of the piston is significantly damped.

Besides the gas chromatograph (Varian CP-4900 micro-GC equipped with an MS5 and a PPQ column) used to analyze reactants and products, two different sensors are used to monitor important parameters during the experiment. A high speed pressure sensor monitors the pressure in the reactor (Optrand D732A8) for the purpose of estimating the auto ignition moment and viewing the pressure history of the mixture. A fiber optic sensor (Keyence FS-V31M) is used to determine the velocity of the piston. The sensor shines a source of modulated light through a fiber optic wire onto the side of the piston. As the piston moves, a different amount of

light is reflected depending on whether the light hits the flat surface of the piston or a passing groove. From the changing signal in reflected light the moment of passing grooves can be determined and from this the velocity of the piston.

All of the experimental results presented are from three series of experiments, using the same mixture for each experiment: 8.8 vol% CH₄, 4.9 vol% O₂, 19 vol% N₂ and 67.3 vol% Ar. This mix is chosen for two reasons. Firstly, the methane/oxygen ratio is close to the stoichiometric ratio for the formation of only hydrogen and carbon monoxide. Secondly the added argon increases the adiabatic temperature of the mixture during compression. The settings of the GC used to analyze the results are shown in Table II.

Initial pressures for all experiments were 1 bar; initial temperatures were varied from 295 to 543 K.

III. PROCESS SIMULATION

Simulation of the process as it occurs in the PCR is done, in the case of the results discussed in this article, by means of a relatively simple code programmed in Cantera [5]. It is capable of using several reaction mechanisms for the reaction kinetics and thermodynamic properties of the species in the reactor: the GRI 3.0 reaction mechanism [6], the Leeds mechanism [7], the Konnov mechanism [8], the C3 mechanism [9] and the C5 mechanism [10]. In Cantera it is possible to create ideally stirred tank reactors. These reactors can have multiple inlets and outlets, exchange heat with the surrounding or other reactors and the volume can be variable. A network of reactors can be created to simulate and model all kinds of chemical and thermodynamic problems. This makes it perfectly able to simulate the PCR without losses.

The simulation created for the PCR consists of an ideally stirred reactor with a certain initial volume and composition, which is compressed by a wall with a certain mass and area. The movement of the wall is determined by the pressure difference between the reaction chamber on one side of the wall and the pressure in the lower chamber on the other side of the wall. As results will show, this is a very robust and accurate way of simulating the processes as they occur in the PCR.

IV. RESULTS

In the following paragraph the results of the experiments are compared to the results of the simulations done. In order to make the results comparable the yields of products are plotted as a function of the maximum piston velocity. The reason for this is that this best describes the "input" into the system: the piston velocity is a measure for its kinetic energy. So, if experiment and simulation have comparable energy input, their output in terms of yield can be compared. In Fig. 3 the pressure traces of four experiments are shown. The experiments were performed in a preheated reactor at 423K. It can be seen that for the lowest energy input in this series (maximum piston velocity 17.6 m/s) no ignition of the mixture in the reactor takes place.

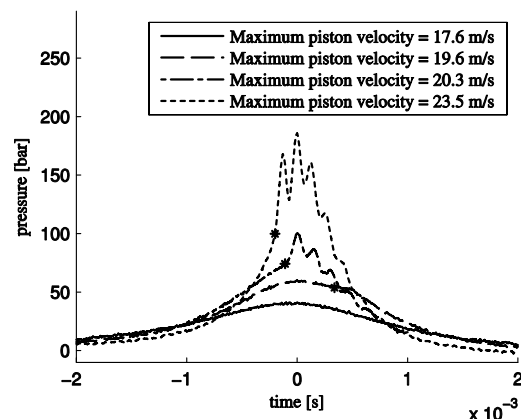


Fig. 3 Pressure traces of four experiments with different maximum piston velocities

The pressure curve simply shows a smooth compression expansion cycle, without any humps caused by ignition. As the energy input is increased, the measurement with the maximum piston velocity of 19.6 m/s shows ignition just after the piston reached top dead centre (TDC). This moment is marked in the graph. As the energy input is increased stepwise again and again, the ignition moment moves forward relative to the cycle, igniting around and even before the TDC. The oscillating pressure signal after the initial ignition moment can most likely be attributed to the characteristics of the pressure sensor and its mounting method and the reaction kinetics, but this is still under investigation and will not further be discussed in this article.

A. Hydrogen Yield

In Fig. 4 the hydrogen yield as a function of maximum piston velocity is shown for the three different initial temperatures used. The yield is expressed as a fraction of the theoretical maximum yield (so a yield value of 1 means all the hydrogen atoms present are in the form of hydrogen, a yield value of 0 means all the hydrogen atoms are bound in other compounds than hydrogen). When looking at the data the trend that was observed in the different pressure traces in Fig. 3 is visible in the hydrogen yield also. For low velocities (what constitutes low is different for the different initial temperatures), no significant reaction takes place, and no hydrogen is produced. Then, as the energy input is increased, at a well defined threshold value of the velocity the hydrogen yield suddenly goes up, as ignition events become possible. Higher energy inputs does cause the hydrogen yield to climb further still, to a maximum for piston velocities around 7-8 m/s beyond the threshold. The hydrogen yield just beyond the threshold is about 50%, while the maximum yield recorded is 83%.

When comparing results for the different initial temperatures, it is visible that an initial temperature change merely shifts the entire hydrogen yield graph along the piston velocity axis, without having much effect on the shape of the

graph. The threshold energy input for significant reactions to take place becomes lower, as initial temperature is increased. For the mixture used in these experiments, the threshold energy input for significant reactions to occur with an initial temperature of 295K corresponds to a maximum piston velocity of about 25 m/s. The threshold energy input for significant reactions to occur with an initial temperature of 543K corresponds to a maximum piston velocity of about 15 m/s.

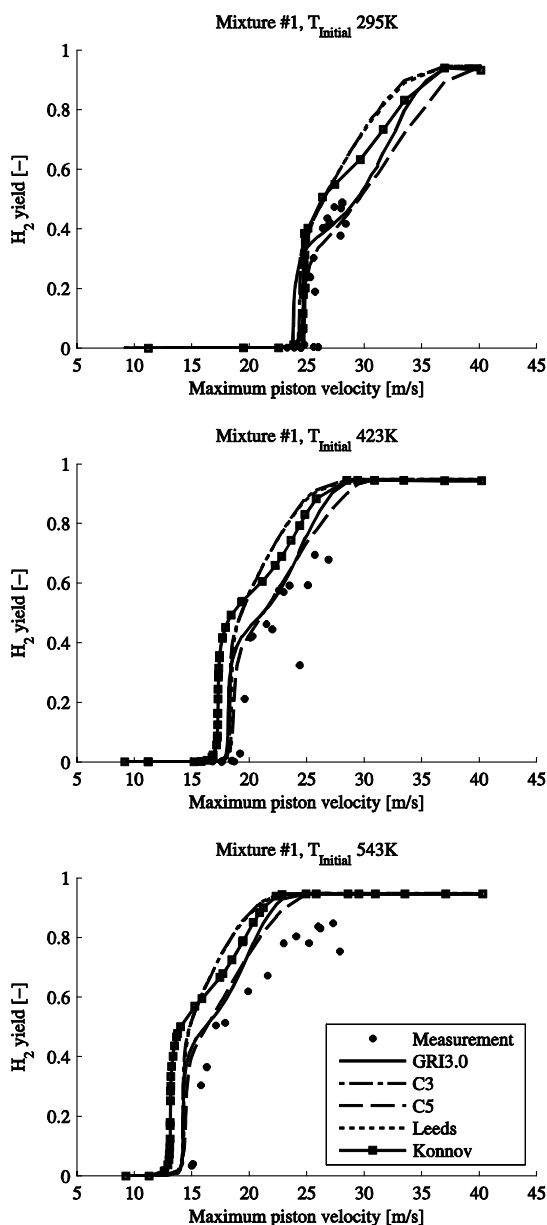


Fig. 4 Hydrogen yield of experiments with different initial temperatures, compared to simulations

When comparing the experimental results to the simulations done with the various models, a good correspondence between results is visible. However, especially for the higher temperature experiments, all models predict the threshold

energy input to be slightly lower than is observed experimentally. Also, the observed yield in the experiments, for energy inputs well beyond the threshold energy, is lower than the predicted yield. The different models used give very similar results in terms of yield and threshold energy, no clear “best” model is visible (at least not in terms of predicting the hydrogen yield).

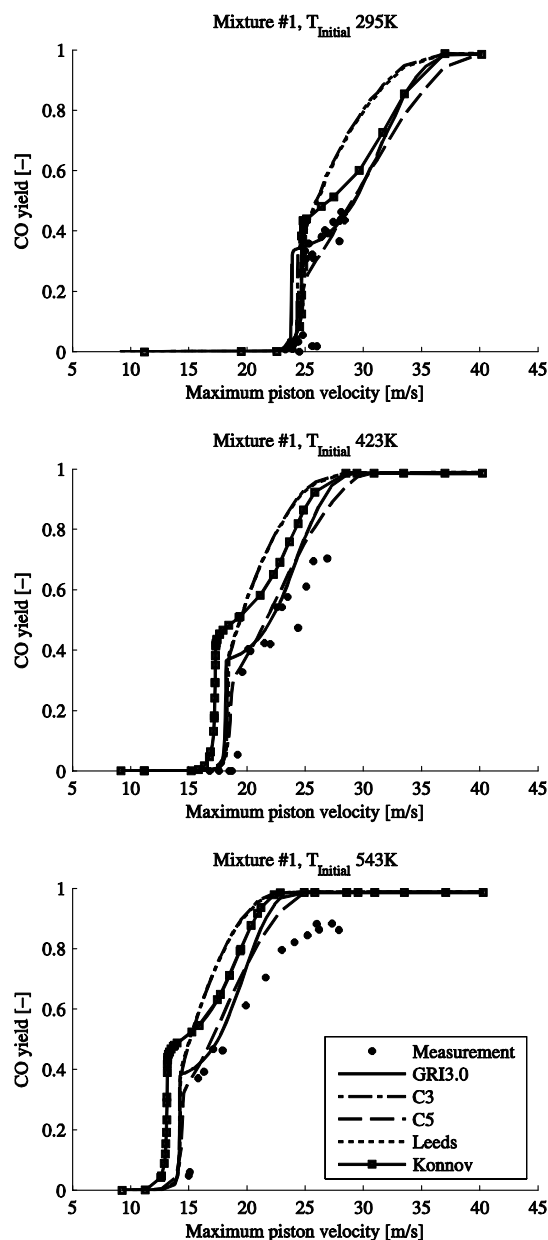


Fig. 5 Carbon-monoxide yield of experiments with different initial temperatures, compared to simulations

B. Carbon-monoxide Yield

In Fig. 5 the yield of carbon-monoxide as a function of the maximum piston velocity is plotted. The yield is defined the same way as the previously discussed hydrogen yield. When looking at the results, a striking resemblance is seen to the

hydrogen yield results. Clearly, both hydrogen and carbon-monoxide are produced at the same moment. The same as with the hydrogen results, the carbon-monoxide yield just beyond the threshold is relatively low, only about 40%. The carbon-monoxide production increases as piston velocities are increased further beyond the threshold, to a maximum recorded yield of 87%.

When comparing the carbon-monoxide experimental results to the simulations again a good agreement is observed. While the threshold is again predicted slightly lower, trends are predicted well. The jump to about 50% yield at the threshold is predicted well, as well as the gradual increase after this jump.

C. Simulation During The Cycle

The simulations can also be used to get an idea of what happens during the compression-expansion process. In Fig. 6 the evolution of the major species simulated by the GRI3.0 mechanism are shown, for the situation where the maximum piston velocity is 28.5 m/s and the initial temperature 543 K.

The evolution of the major species as found by the simulation show that the reaction progress can be divided in two steps. The first step is a combustion step. In this step, which is very short (in the order of 30 μ s), all of the oxygen present is consumed with the bulk of the methane, and converted to hydrogen, water and carbon-monoxide. In the second step, which is much slower, some of the water produced in the first step reforms the remaining methane to hydrogen and carbon-monoxide.

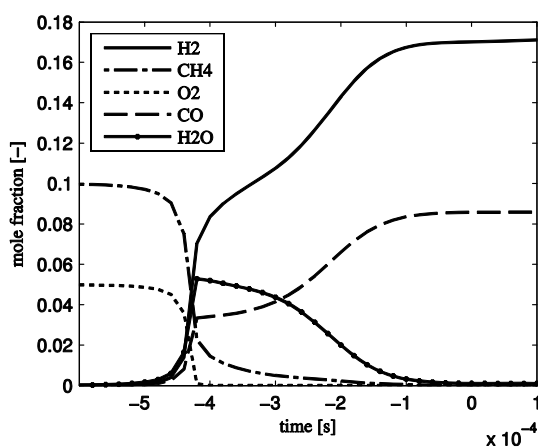


Fig. 6 Major species during compression-expansion cycle as simulated by the GRI3.0 mechanism.

The understanding of these two consecutive steps also explains the experimental results. When little energy is supplied, a piston velocity just over the threshold, only the first combustion step occurs. As more energy is supplied, the total cycle length becomes shorter, while at the same time, peak temperatures are higher. The higher temperatures speed up the chemistry, so in fact, while the cycle length is shorter, higher reaction rates mean that the second step will be able to proceed further. This mechanism is confirmed by the

experimental results, where there is a base production of hydrogen and carbon-monoxide when the threshold velocity is exceeded, followed by a more gradual increase in yield as the piston velocity is increased further.

V. CONCLUSIONS

From the results obtained, several conclusions can be drawn. The experimental results show that synthesis gas production by PCR, at least in the single shot setup, is feasible. The concentrations of hydrogen and carbon-monoxide are high, especially for high compressions. It was demonstrated that for reactions to occur a certain threshold compression is required, depending on the initial temperature of the mixture. The model used shows good agreement with the experimental results, deviating mainly in the prediction of the threshold energy and product yield for very high energy inputs. Different models used do not show very large differences, at least not so large that one specific model can be named as best suitable to simulate this process.

The model also allows one to look "inside" the process. When doing so, it is observed that the reactions occur through two steps. The first one being a fast combustion step, the latter a slower steam reforming step. Since the simulation results show a good agreement with the experimental data, it can be concluded that this simulation method can be used to predict the products from other, but similar, processes, initial temperatures and maximum piston velocities.

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REFERENCES

- [1] Brutzkus, M., Apparatus for chemical production and research, US Patent 1586508, 1926
- [2] Kolbanovskii, Y. A., et al., *Impulsnoe sgiatie gasov v khimii i tekhnologii*, Moskva, Nauka, 1982. (Pulsed compression of gases in chemistry and technology, Moscow, Nauka, 1982.)
- [3] Glushenkov M. Y., Russian Pat., No 2097121, 29.01.1997; No 2115467, 02.12.1997; No 2142844, 05.04.1999.
- [4] Roestenber, T., et al. Heat transfer study of the pulsed compression reactor, Chemical Engineering Science, 2009
- [5] Open source code downloaded from: <http://code.google.com/p/cantera/> Cantera website is under construction <http://www.cantera.org> (accessed Jan 2010)
- [6] Smith, Gregory P., et al., http://www.me.berkeley.edu/gri_mech/
- [7] Hughes, K. J. et al. Development and testing of a comprehensive chemical mechanism for the oxidation of methane. International Journal of Chemical Kinetics, 33:513-538, 2001
- [8] Konnov, A. A., Detailed reaction mechanism for small hydrocarbons combustion. Release 0.5. <http://homepages.vub.ac.be/~akonnov/>. (accessed Dec 2009)
- [9] Petersen, E. L., et al., Methane/propane oxidation at high pressures: Experimental and detailed chemical kinetic modelling. Proceedings of the combustion institute, 31:447-454, 2007.
- [10] Bourque, G., et al. Ignition and flame speed kinetics of two natural gas blends with high levels of heavier hydrocarbons. Proceedings of the ASME Turbo Expo, 3:1051-1066, 2008