

# **CO<sub>2</sub> - Retention Capapility of CH<sub>4</sub>/O<sub>2</sub> - Fired Graz Cycle**

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## **ABSTRACT**

The Graz Cycle, a hydrogen oxygen fired double loop high temperature steam cycle, combining gas turbine philosophy with steam plant praxis, can be adapted for combustion of methane with oxygen. The resulting combustion products carbon dioxide and hydrogen oxide, i.e. high temperature steam, are mixed with cooling steam and expanded to lowest pressure and temperature. By condensing the steam, separation of carbon dioxide in the condenser can be effected, which is then recompressed in an isothermal compressor and is presented at system boundaries at ambient temperature and ambient pressure for storage or further reintegration into a solar hydrogen fuel cycle.

The paper presents the cycle, its thermodynamic and flow conditions, and design deliberations concerning the major components especially the methane oxygen combustion chamber and the high temperature turbine. Methods of cooling the very high temperature blades are studied, the general dimensions of turbomachinery for a typical pilot plant are given.

The development of such a pilot plant would allow the application for carbon dioxide (CO<sub>2</sub>) retention by deep sea storage or by use in chemical industry. Such a pilot plant could demonstrate the feasibility of CO<sub>2</sub> retention, a means of CO<sub>2</sub> emission reduction, an environmental goal to which many governments have devoted themselves.

In the farther future, after the establishment of a world wide solar energy system creating artificial fuels like liquid methane to be transported in the same way as liquid natural gas (LNG) today, such a plant would work as the means of effective reuse of these artificial fuels. CO<sub>2</sub> would be transported back to the solar sites as an essential component in the production of the artificial fuels created there, thus closing the fuel cycle.

## INTRODUCTION

Since the Toronto-conference in 1988 many governments, especially those of the industrialized countries, endeavoured to limit CO<sub>2</sub> emission. The required results could not be achieved in the area of thermal power plants because the measures taken like efficiency improvement of conventional plants, increased use of cogeneration and combined cycle plants were not sufficient [1]. Power consumption in general rose during the last years and so did the overall CO<sub>2</sub> emission. Therefore other ways of mitigating CO<sub>2</sub> emissions in power generation plants have to be deliberated.

Basically, three methods can be mentioned based on the capture of CO<sub>2</sub> from the flue gas:

- CO<sub>2</sub> can be separated from the flue gas (e.g. [2], [3]). But as Boras and Smelser [2] showed the plant capital costs are doubled, whereas the efficiency and power is considerably reduced.
- Rice [4] proposed an open cycle, which uses the Dow process to remove the CO<sub>2</sub> from the stack gases.
- The fossil fuel can be reformed or partially combusted to create a fuel gas of CO and H<sub>2</sub>, by steam reforming a hydrogen fuel gas can be generated which can be burned in any cycle (e.g. [5]).

The first two options can be installed to existing plants although they are very capital extensive and reduce cycle efficiency remarkably, whereas coal gasification and ensuing production of a pure hydrogen fuel is still a matter of intensive development.

Gas turbine cycles using CO<sub>2</sub> as working fluid, fired by fossil fuels and oxygen have been proposed ([6], [7]). Pressurized CO<sub>2</sub> is available from such a cycle and is easy to recover. Mathieu and De Ruyck [7] proposed to burn CO/H<sub>2</sub> with oxygen and to expand a gas mixture of CO<sub>2</sub> and of about 5 % steam. The combustion products CO<sub>2</sub> and steam are to be retrieved after the condenser, the main flow of CO<sub>2</sub> is recompressed and sent to cool the combustion chamber. Using a standard industrial gas turbine this cycle results in net efficiency penalties of about 6 % points for the Brayton cycle to about 10 % points for the combined cycle. Considering the requirement of a significant amount of energy for the production of oxygen by air separation efficiency is decreased by additional 4 % points.

As a further improvement the authors suggest a cycle of highest possible efficiency using a mixture of steam and CO<sub>2</sub> as working fluid [8]. The **Graz Cycle**, a double loop high temperature steam cycle, proposed by H. Jericha ([9], [10]) promises up to 59 % (based on HHV, equivalent to 65 % based on LHV in comparison to air breathing machines) in the hydrogen/oxygen fired version [11]. Its advantages are medium pressures, the possibility to effect the heat input at very high temperatures and to maintain the heat rejection at conventionally low condenser temperature. In both forms, in the hydrogen/oxygen fired version and in the fossil methane/oxygen fired version ([12], [13], [14], [15]), the operation of this Graz Cycle is analogous to a very high temperature internally oxygen fired gas turbine.

In the present work the capabilities of the Graz Cycle in using methane of fossil or of artificial origin are discussed. Firing methane with oxygen and using steam as a cooling medium results in similar combustion chamber design problems as mentioned in previous articles describing the hydrogen/oxygen fired cycle ([16], [17], [18], [19]). Cooling of burners, combustion chamber liner and high temperature turbine blades is effected by pure steam, a measure which together with the maximum combustion temperature selected, defines the ratio of carbon dioxide and steam in the high temperature cycle loop. So the use of a mixture of about 20 %

carbon dioxide and 80 % steam as the working fluid offers the possibility of regaining CO<sub>2</sub> from this working fluid simply by extracting it after the condenser, so that CO<sub>2</sub> after recompression is available for further use. CO<sub>2</sub> is also regained at atmospheric pressure from the feed water heater, where heat is transferred to the feed water from condensation of the steam part of the expanded gas mixture bled from the low pressure turbine.

The reactivity of carbon and hydrogen towards oxygen being much higher than that to nitrogen will prevent formation of nitrogen oxide even if some nitrogen were present in a fossil natural fuel gas. Due to the absence of nitrogen in the cooling medium and the extraction of the noncondensable gases together with the CO<sub>2</sub> combustion products and due to the closed scheme of the steam-CO<sub>2</sub> mixture cycle there will be no environmental load by toxic and CO<sub>2</sub> emissions and the retained carbon dioxide can be made available for future integrated solar energy systems.

The purpose of this paper is to investigate the possibility of building such a CH<sub>4</sub>/O<sub>2</sub> fired Graz Cycle pilot plant. At first the thermodynamics of the cycle are discussed and the optimised thermodynamic parameters are presented. Also the design of turbomachinery is presented in terms of a feasibility study, which has been discussed with important gas turbine manufacturers. So for a typical pilot plant of 50 MW and 100 MW turbomachinery dimensions are shown. To secure the feasibility of the main components several detailed studies have already been conducted. Important results have been obtained in continuation of the work presented at 1991 CIMAC conference in Florence [17]. A cold flow study of a combustion chamber was undertaken for firing conditions of hydrogen with oxygen with steam cooling, which is now being adapted for the very similar purpose of burning CH<sub>4</sub> and oxygen.

The high temperature turbine uses extensive cooling by high temperature steam in novel configurations as a means to cope with the very high gas temperature of the cycle fluid. These especially effective means of cooling are researched at our institute at the moment and first results are presented here.

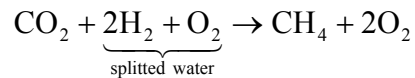
## FUEL SYSTEM

Solar radiation power is most effective in the southern belt of deserts near the equator. Solar power can be gained by thermal plants, by photovoltaic or even by biological systems. Electricity generated could effect the splitting of water by means of electrolyzers or splitting of water could be effected directly by biological systems. So for the solar production of hydrogen the chemical reaction equation reads, regarding the moleculs produced:



These gases could be transported by pipelines or in liquid state. The liquification of hydrogen has the disadvantage that it has to be effected at very low temperatures and the transport is hampered by the fact that liquified hydrogen still has a relatively large specific volume which makes transport tanks bulky and requires extreme thick insulation. So it would be worth-while to deliberate more conventional methods of energy transport. One established procedure is the transport of liquified natural gas which is transported in very large quantities in the pacific area especially supplying Japanese power stations.

So it might be reasonable to deliberate the production of artificial fuels at the sites of solar power stations. By using CO<sub>2</sub> - which could be transported back there from the centers of consumptions - artificial fuels like methanol or artificial methane could be created. The following reaction equation does hold:



The artificial fuel CH<sub>4</sub> thus produced could be transported via pipeline or via overseas transport in liquified state as liquid artificial gas (LAG) to consumers in highly populated areas. Whether it would be economic to transport oxygen as well has still to be investigated, but doing so would relieve the atmosphere completely from taking part in this cycle of reactions. At the centers of consumption the above mentioned Graz Cycle plants could be run, which would operate at an extremely high efficiency compared to conventional plants and which would offer the possibility to retain the carbon dioxide as demonstrated above. After compressing and liquifying the CO<sub>2</sub> combustion product it could be transported back to the sites of solar hydrogen generation and/or ensuing production of artificial fuels, thus closing the transport cycle of such an integrated solar hydrogen energy system.

In that manner thermal power stations could be created which would operate without emitting gases to the atmosphere, without aspiring of air or oxygen and solely with some input and output of water.

In the present situation with the prevalent use of fossil fuels the pilot plant scheme presented would fulfill the task of retaining CO<sub>2</sub>, oxygen would have to be gained by separating air. Assuming a fuel supply of LNG the cold of fuel would greatly facilitate the air separation. In an integrated air separation fuel vaporisation plant a cold source could contribute to cool the compressed air so that only a minimum of power input would be required to produce oxygen. Part of that cold could also be used to liquify carbon dioxide for later return to the solar plants as mentioned above.

## CYCLE THERMODYNAMICS

The cycle scheme of the Graz Cycle fired with methane and oxygen is represented in fig. 1. The construction of the Graz Cycle as a double loop cycle (see temperature-specific entropy-diagram in fig. 2) is motivated as follows:

By Carnot's law it is necessary for a highly efficient cycle to effect the heat input at highest possible temperature and to reject the heat at lowest possible temperature. Highest temperature is selected in the range of modern gas turbines between 1300° and 1500° C, but for reasons of turbine design according to gas turbine philosophy it is necessary to keep the highest pressure limited. For an industrial machine at these temperatures it does not seem possible at present day technology to run a combustion chamber at pressures much higher than 50 bar. The same holds true for the casing of the following high temperature gas turbine.

An expansion starting at about 1440° C and 50 bar with a gas mixture as mentioned above even down to condenser pressure would result in an extremely high exhaust temperature. The high heat rejection would extremely lower the efficiency and would require extremely large condenser surfaces. Therefore it is absolutely necessary to cool the gases after a sufficient

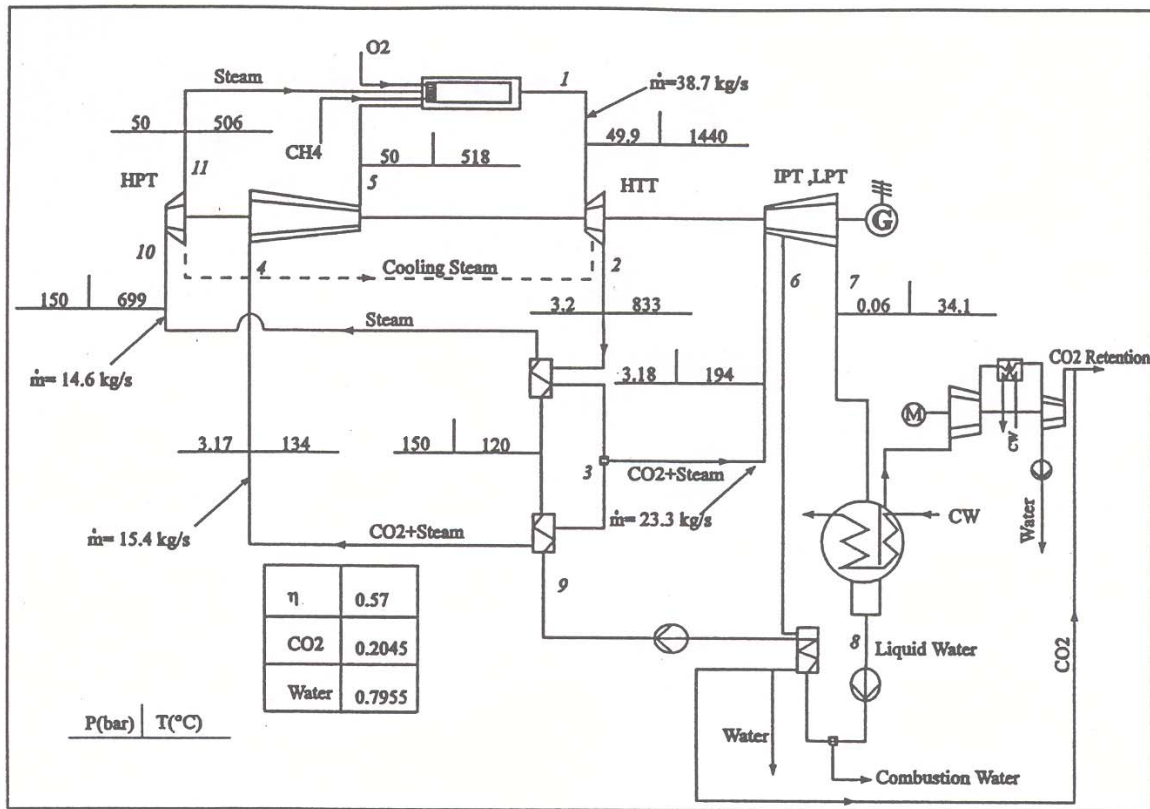


Fig. 1: Cycle Scheme of the CH<sub>4</sub>/O<sub>2</sub> Fired Graz Cycle

pressure ratio of expansion in order to achieve a reasonable condenser temperature. The pressure at which this cooling is done influences the size of the heat exchangers required as well as all turbomachinery bladings. In our proposal we produce high pressure steam by cooling the exhaust steam from the high temperature turbine to the temperature at the inlet of the low pressure turbine or to the temperature at the inlet of the compressor respectively. The larger part of the cycle fluid mass flow is then expanded through the low pressure turbine whereas the smaller part is recompressed, so that ahead of the low pressure turbine a bifurcation of the flow takes place (point 3 in fig. 2). The ratio is determined by the amount of heat rejection and recompression serves to maintain the high mean temperature of heat input in the combustion chamber. So the high temperature loop consists of compressor, combustion chamber and high temperature turbine, whereas the low temperature loop consists of low pressure turbine, condenser, feed heat system, high pressure evaporator, superheater and high pressure turbine. The gas flow after the compressor mixes with the steam flow after the high pressure turbine in the combustion chamber and thus the two loops are connected again (points 5, 11 in T-s-diagram, fig. 2).

Thus the two loops of the cycle are quite well justified. With respect to temperature the upper cycle loop resembles closely a gas turbine cycle, so that its components can be designed according to gas turbine philosophy. The lower cycle loop represents a steam plant, so that its components, the low pressure turbine, the condenser, the high pressure feed heater, evaporator and superheater and the high pressure steam turbine, can be designed using steam plant technology.

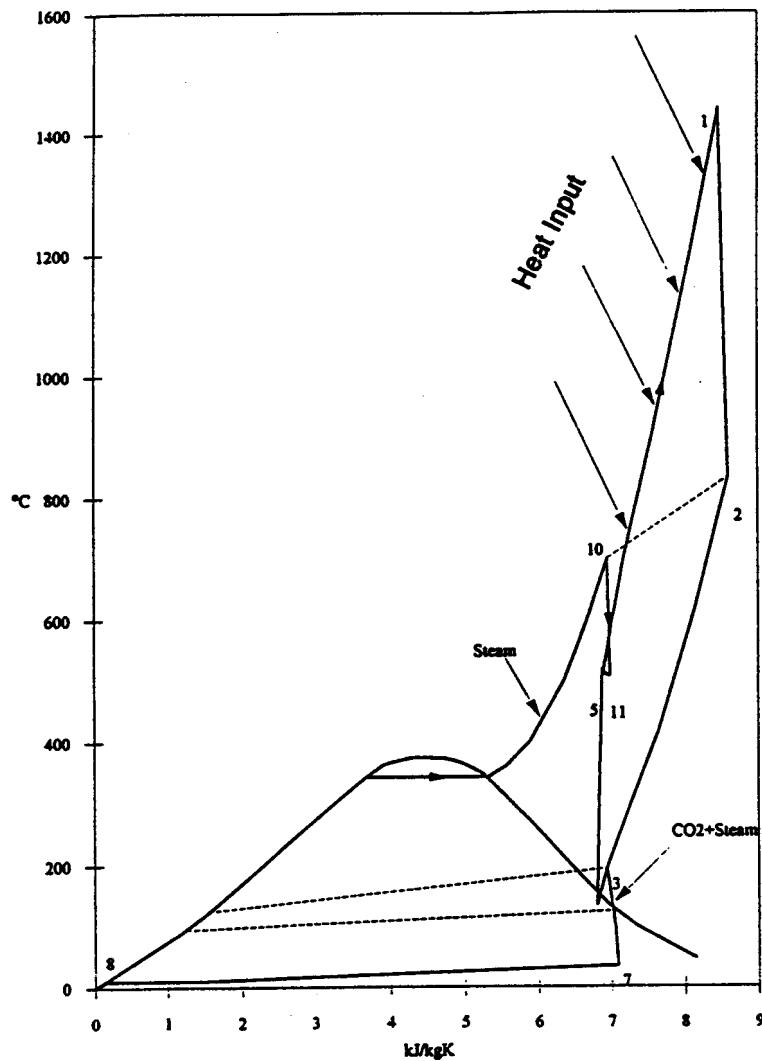


Fig. 2: Temperature - Specific Entropy - Diagram of the CH<sub>4</sub>/O<sub>2</sub> Fired Graz Cycle

indicating a pinch point of 76° C. In the preheater about 60 % of the mass flow are fed to the low pressure turbine of the lower loop of the cycle (point 3 in T-s-diagram, fig. 2).

Expanding the gas flow in the lower loop to a pressure of 0.06 bar the separation of water and carbon dioxide can be effected. The new element of the carbon dioxide separator in form of a condenser with additional counteracting cooling flows is quite near in design to conventional condenser practice. Here we cool the noncondensable gases as much as possible in separated tube arrangements in order to keep the CO<sub>2</sub> compressor power as low as possible. So the recompression of carbon dioxide even from the low pressure of 0.05 to atmosphere (a pressure ratio of 20) needs relatively low compression power in comparison to the overall heat and power balance (see table 1), using several intermediate stages of cooling as is the general practice in isothermal compressors. Some part of the combustion water also goes with the carbon dioxide and is separated continuously in the intercoolers of this carbon dioxide compressor. Part of the gas mixture is extracted from the low pressure turbine to heat the feed water. A pressure of about 1 bar is selected so that after condensation of the water content CO<sub>2</sub> is made available at ambient pressure and is fed to the CO<sub>2</sub> retention line.

Firing the Graz Cycle with methane and oxygen and optimizing its parameters, the conditions as shown in the cycle scheme (fig. 1) result. Entering the high temperature turbine with a temperature of about 1440° C a mixture of about 80 % H<sub>2</sub>O and 20 % CO<sub>2</sub> flows in the upper loop. In order to obtain a cold casing internal insulation design has to be used and the blades of several stages have to be effectively cooled. All this can be done by the steam supplied by the high pressure turbine in the range of 500° C.

The high temperature turbine expands to a pressure of about 3.2 bar, which results in reasonable dimensions and heat exchange surfaces of the high pressure steam evaporator and superheater. The heat flow-temperature-diagram (fig. 3) shows the conditions of heat transfer in cooling the exhausted gas mixture from the high temperature turbine and evaporating and superheating the high pressure steam,

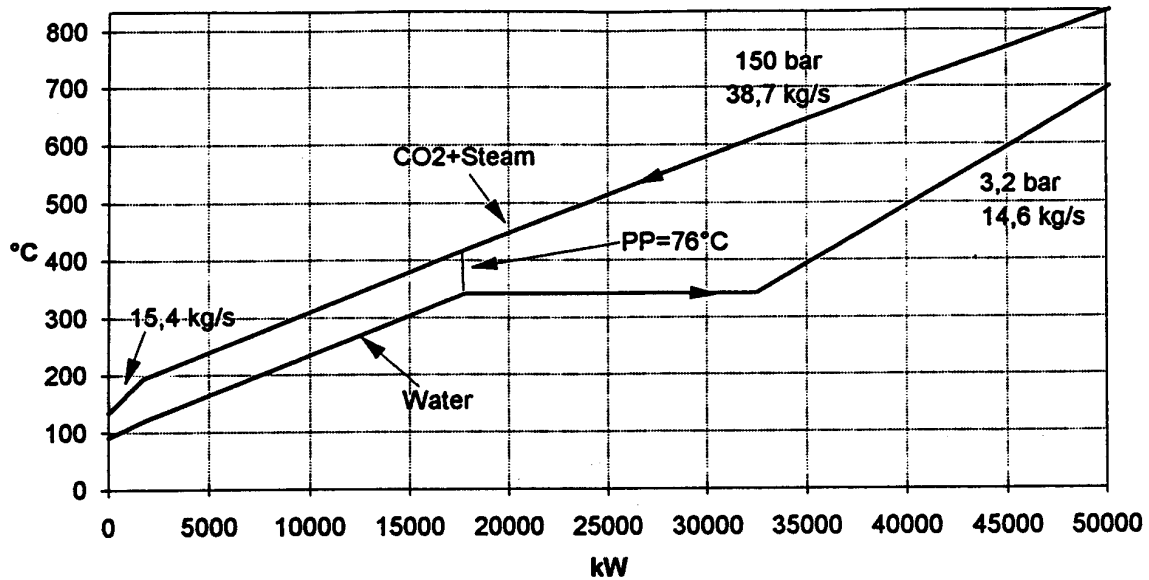


Fig.3: Heat Flow - Temperature - Diagram of the CH<sub>4</sub>/O<sub>2</sub> Fired Graz Cycle

Table 1: Power Balance of the CH<sub>4</sub>/O<sub>2</sub> Fired Graz Cycle

<b>Turbomachinery</b>	<b>Power [kW]</b>
High Temperature Turbine HTT	51016
High Pressure Turbine HPT	5470
Low Pressure Turbine LPT	10589
Compressor	-10425
<b>Power Output</b>	<b>56650</b>
Electrical Power Output	55635
-CO <sub>2</sub> Compressor	-931
-Feed Pump	-341
<b>Net Electrical Power Output</b>	<b>54363</b>
Heat Input (HHV)	95662
<b>Thermal Efficiency (HHV)</b>	<b>56.8 %</b>
<b>evaluated to LHV</b>	<b>63.1 %</b>

So the mass of carbon dioxide of the condenser and of the preheater are equal to the carbon dioxide of the combustion and are then presented at atmospheric pressure and ambient temperature for further use (e.g. for deep sea storage as proposed by [20]). The excess water of the combustion is retrieved from the cycle partly after the preheater, partly in the isothermal compressor and the rest after recompression after the condenser. So the mass flow of the

lower loop is determined by the mass of combustion carbon dioxide which has to be completely separated.

After the condenser the working fluid is pure water, which is compressed to 150 bar by the feed water pump. After heating, evaporation and superheating according to fig. 3, steam is expanded in the high pressure turbine to a pressure of 50 bar. This steam is mixed together with the gas mixture delivered by the compressor in the combustion chamber, thus cooling the combustion chamber liner and burners.

The cycle function can be better demonstrated by using a temperature-entropy (specific entropy times mass flow) -diagram (fig. 4). The reader is asked to observe the high temperature gas turbine loop and the low temperature steam plant loop, the heat transfer in the generation of high pressure steam, and also the mass transfer connections in the formation of the double loop cycle. Please note that entropy increases with heat transfer over finite temperature differences and the entropy span increases accordingly. In comparison the heat transfer is shown in a heat flow-temperature-diagram (fig. 3) which clearly shows the temperature differences and the pinch point as a function of heat flow. Ample temperature differences are provided which serve to keep the required heat exchangers surfaces within economic limits.

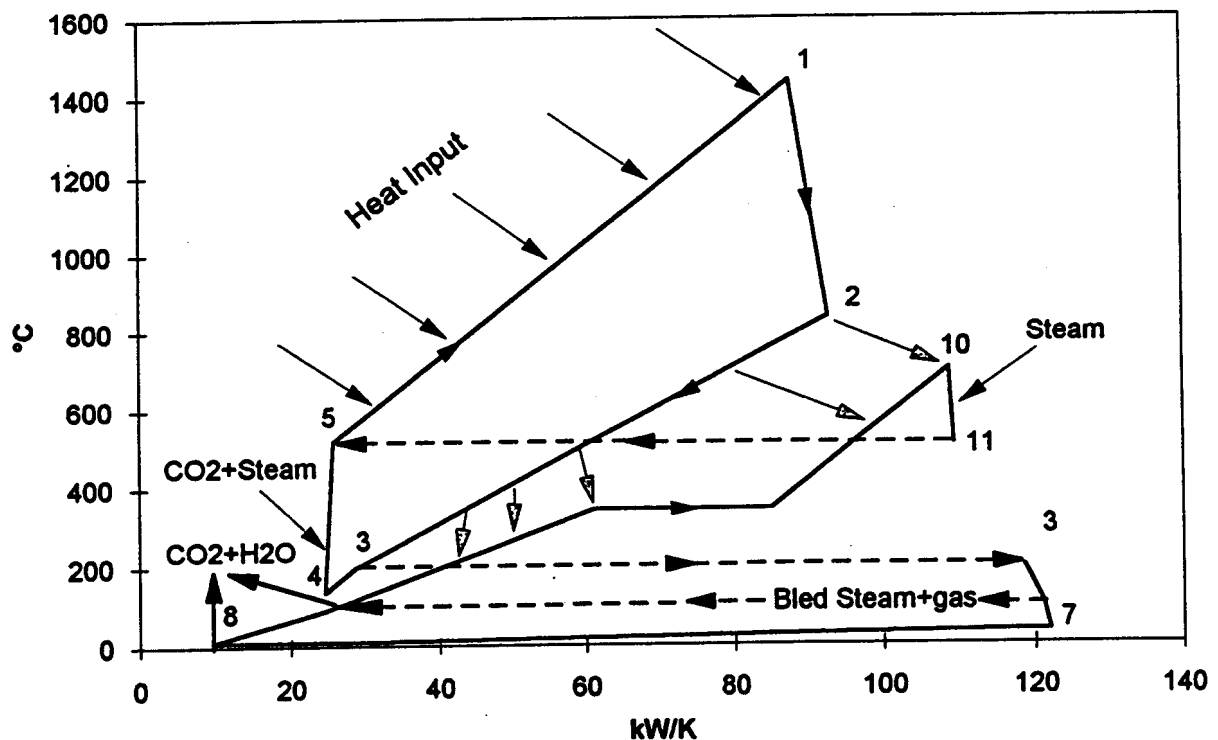


Fig. 4: Temperature - Entropy - Diagram of the  $\text{CH}_4/\text{O}_2$  Fired Graz Cycle

It can be said therefore, that the cycle proposed makes definite use of established engineering practice in gas turbine and steam turbine design, tries to minimize the necessary heat exchanger surfaces and effects the separation of carbon dioxide and water in an effective manner also by well proven isothermal compressor design. According to the heat power balance (table 1) the efficiency of the cycle is about 56.8 % based on HHV (equivalent to 63.1 % based on LHV in comparison to an air breathing machine), making it a most efficient and promising means of retaining  $\text{CO}_2$  from the atmosphere.



## PLANT CONFIGURATION

The following fig. 5 and table 2 show the dimensions for the turbomachinery of the pilot plant in question, one for 50 MW output, the other for over 100 MW output. For such a pilot plant the limitations of gears have to be considered which are assumed to be of a maximum transfer power of 50 MW. So a 100 MW pilot plant could be built with high speed turbines according to fig 5. For very large power stations the gears could be replaced by direct drive or some part of the high temperature expansion could be effected at generator speed, other parts as the high temperature recompression and the high pressure turbine could also be effected at higher speeds, balancing power consuming and power producing turbomachinery on each shaft.

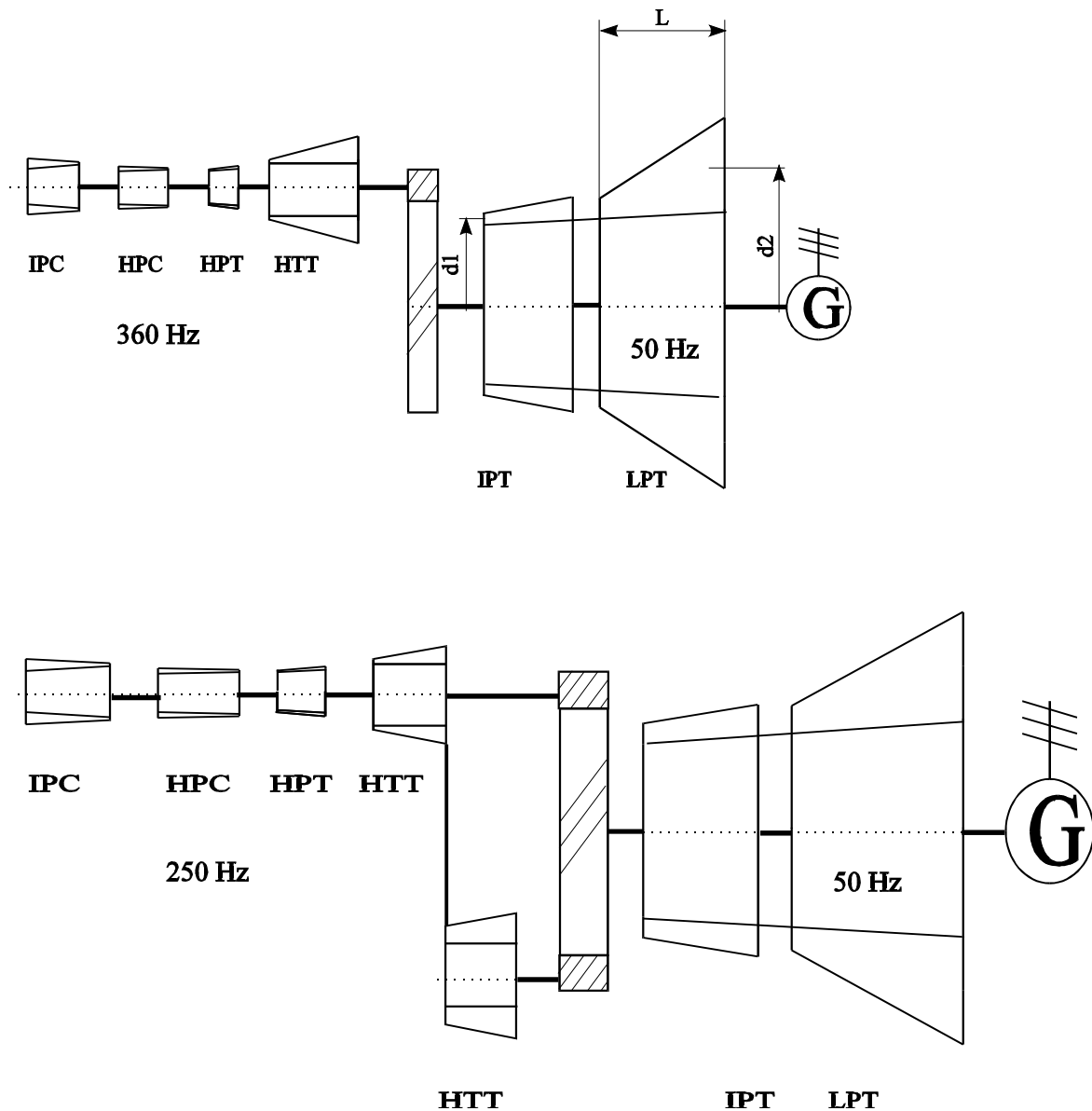


Fig. 5: Turbomachinery Dimensions for a Pilot Plant of 50 MW and 100 MW

Table 2: Turbomachinery Dimensions for a Pilot Plant of 50 MW and 100 MW

50 MW pilot plant

	d1[m]	d2[m]	l1 [m]	l2 [m]	L [m]	Z st	f [Hz]
LPT	1.06	1.567	0.121	0.52	0.7	8	50
IPT	0.94	1.08	0.094	0.135	0.52	7	50
HTT	0.32	0.454	0.021	0.154	0.5	6	360
HPT	0.19	0.222	0.011	0.019	0.17	6	360
HPC	0.211	0.211	0.027	0.010	0.28	15	360
IPC	0.257	0.257	0.058	0.018	0.29	9	360

100 MW pilot plant

	d1[m]	d2[m]	l1 [m]	l2 [m]	L [m]	Z st	f [Hz]
LPT	1.49	2.216	0.171	0.735	0.99	8	50
IPT	1.33	1.53	0.133	0.191	0.74	7	50
HTT	0.45	0.642	0.030	0.218	0.5	6	250
HPT	0.269	0.314	0.161	0.028	0.24	6	250
HPC	0.298	0.298	0.037	0.015	0.39	15	250
IPC	0.363	0.363	0.082	0.025	0.41	9	250

## COMBUSTION CHAMBER

One of the most critical parts in the design of such a high temperature cycle is the combustion chamber burning  $\text{CH}_4$  and oxygen. A cold flow study of a combustion chamber was done using air, helium and nitrogen to match Reynolds number and flow conditions according to the high temperature combustion chamber. The flow scheme for such a combustion chamber was presented recently ([17]) using additional cooling flows introduced by axial jets supplying the liner with cold steam near the wall. Four different liners had been tested and the flow conditions visualized. Swirler flow, return flow and cooling flow had been studied under varying velocities, mass flows and injection angles [21]. These experimental investigations indicated that flow conditions in combustion chambers for such high temperature cycles follow standard design principles but special care has to be taken in the design of the recirculation area and the axial cooling jets. This is topic of ongoing investigations.

## HIGH TEMPERATURE TURBINE COOLING

It has to be born in mind that a mixture of 20 % carbon dioxide and 80 % steam has a distinctly higher specific heat in comparison to a mixture of air and combustion gases as they are expanded in a conventional gas turbine. Since the temperature limits are about the same the expansion in the proposed turbine takes place at the higher heat drop and therefore requires a higher number of stages. The same is true for the number of stages to be cooled. As can be seen from the plant configuration (table 2), the high temperature turbine requires about six stages, where at least four stages have to be cooled. This means cooling has to be supplied

for about 8 blade rows additional to the combustion chamber and transition piece cooling requirements. On the other hand due to the high density of the gas expanded the flow areas are relatively low and the same is true for blade span and blade length. The authors therefore have deliberated new and very intensive methods of cooling by means of steam into a gas turbine expanding a gas-steam mixture. Designing the high pressure turbine for extraction and using steam at a very high pressure for blade injection cooling enables supercritical conditions at the slot exit. In this area supersonic effects take place thus bending the injected cooling steam towards the blade surface even at areas of higher blade curvature. Experiments performed recently ([22]) indicate a high dynamic range of possible pressure ratios (up to 4:1 were observed) for the input of the cooling steam (see fig. 6) in continuous close contact to the blade surface.

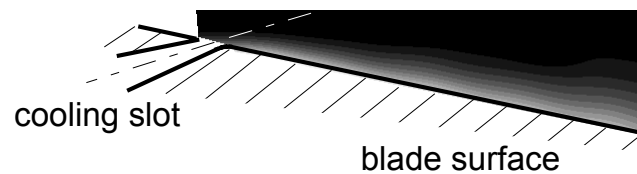


Fig. 6: Result of an interferometric investigation of cooling air films on turbine blades using supersonic film cooling . Light gray indicates higher air density corresponding to lower temperature air film on blade surface.

## CONCLUSION

CH<sub>4</sub>/O<sub>2</sub> firing of the Graz Cycle has been proposed. The feasibility study concerning the components of a pilot plant in the range of 50 to 100 MW has been presented. Using newly developed designs for burners, combustion chamber cooling and blade cooling within the frame of gas turbine design philosophy the feasibility of such a plant can be secured. Such a pilot plant would have the advantage to be used under present conditions for CO<sub>2</sub> retention, thus contributing greatly to the goal of CO<sub>2</sub> emission reduction to which all governments of industrial states submitted themselves. Otherwise it could be used without any alterations as part of an international world-wide solar energy system as proposed by the Japanese government in its WE-NET Research program [23]: Artificial fuels should be produced by solar plants, transported into the centers of consumption and the CO<sub>2</sub> retained in the power plants supplied back to these solar plants. Our plant proposed would guarantee an extremely high efficiency of use of hydrogen, artificial methane or methanol without exhausting any gases to the atmosphere and being able to close the cycle of energy production and energy consumption in a most effective manner.

## ACKNOWLEDGEMENTS

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