ZERO EMISSION FUEL-FIRED POWER PLANT WITH ION TRANSPORT MEMBRANE

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ABSTRACT

Firstly, some points in relation to the history of zero-emissions power cycles are highlighted. Amongst the many schemes, only one which deals with the combustion of a fuel in “artificial air” (i.e. a mixture of oxygen and re-circulated carbon dioxide), is selected.

The paper describes this zero-emissions, gas-fired power plant for electricity generation. In previous papers, the oxygen for combustion was supplied by commercially available cryogenic air separation techniques. In this publication, it is supplied by a new and innovative separation technology - Ion Transport Membrane (ITM) Oxygen. The ITM process uses dense, nonporous, mixed-conducting ceramic membranes to separate oxygen from air when the latter is supplied at a temperature between 800 and 900 °C and at a pressure between 15 and 40 bar. The only atmospheric emission from the plant is oxygen-depleted air, which is harmless. A schematic of the power plant, its description, and the results of a computer simulation are reported here. The cycle T-s diagram at a design point (not optimised) is given.

INTRODUCTION

As usual, the description of the problem of CO_2 mitigation to prevent global warming was initiated by some classic papers from authors such as Joseph Fourier, 1827, and Svante Arrhenius, 1896 followed by books from M.I.Budyko[1-3], 1973-1980. These books are seldom remembered in modern literature.

The history of the earliest attempts of CO_2 mitigation, including the extraction of CO_2 from the atmosphere, is described in the excellent essay by M.Steinberg[4]. It was at the time of nuclear euphoria: …*the early days of nuclear power we thought we could generate large* *quantities of low cost electrical energy using nuclear reactors…It turned out that these developments never materialized because nuclear power turned out to be more expensive than we early predicted and of course the* ***severe safety problems*** *presented by nuclear reactors put a danger for this approach.* (Note, it was stated 9 years before the events of 11th September). In light of the expected fall-off in nuclear power capacity (about 100 GW in the US and a similar figure in Europe), the interest in fossil-fuel-fired **zero emissions power plants** (ZEPP) has greatly increased as these plants could potentially replace old decommissioned power plants, including nuclear ones.

With regard to fossil fuels, we need to be realistic. Fossil fuels are reasonably cheap and plentiful and are a very high-grade energy source. They will certainly dominate the world's fuel energy mix for at least the next half a century. They, in themselves, do not cause pollution – **it is the way in which they are combusted that is the problem.** Many environmentalists wish to ban the use of fossil fuels due to CO_2 emissions and the associated problems of global warming. The authors are very much against this ban. The culprit is not the fossil fuel itself but the wrong use of the fuel. If such fuels are used in ZEPPs, the environment will not suffer.

The development of every new power plant would depend on power cycle selection, schematics and thermodynamic calculations of mass, energy and exergy balances. As it is impossible to violate the mass conservation law, the ZEPP combustion products exist in the same chemical composition as in ordinary power plants. Every atom entering a plant with fuel or oxidizer must leave the plant with emissions, effluents and ash. The only difference is that in the ZEPP, all of the combustion products are in liquid, not gaseous form. In short, **the problem of zero emissions translates into the conversion of emissions to effluents**.

All of the attempts to clean the exhaust gases after combustion by using absorption and/or adsorption methods lead to rather large mass exchangers and **do not** result in zero emissions. These attempts are beyond the scope of the paper. Here, we focus on pre-combustion gas separation, namely schemes which involve fuel combustion in a mixture of O_2/CO_2 followed by CO_2 sequestration.

To our knowledge, the first offer of a zero emissions power unit, the integration of air separation and power generation, with combustion of a gas in O_2/CO_2 mixture, and liquid CO_2 cogeneration, is documented by Degtiarev and Gribovski[5] in 1967. The only "emission" here is the cold nitrogen from air separation. The aim of the unit is cogeneration of electric power and carbon dioxide for industry.

As a measure to prevent global warming, the combustion of fuel in an O_2/CO_2 mixture, followed by CO_2 sequestration in the ocean, was proposed by C.Marchetti[6] in 1979. Here, the mass balance for fuel, oxygen and CO_2 is given.

Some subsequent papers are discussed by Yantovski and Degtiarev[7] in 1993. Here, the hierarchy of cycles is presented diagrammatically. For each of the two possible re-circulating substances (H_2O and CO_2) the external combustion (Rankine cycle) or internal combustion (ZEPP) branches are identified. The latter is divided by many particular cases. The English version of the schematics are also given[5]. The comparison of known data on cycle efficiencies on the graph “efficiency versus temperature” reveals a much higher efficiency using CO_2 re-circulation as opposed to H_2O re-circulation.

The offer by P. Pak[8] et. al. contains a schematic and description of the ZEPP cycle with carbon dioxide re-circulation. In the scheme however, the need to deflect combustion-born water from the cycle is missed.

Lorentzen and Pettersen[9] present not only the scheme of ZEPP with gas combustion in an O_2/CO_2 mixture, but also the T-s diagram, which clearly indicates the thermodynamic losses. This offer is based on the great experience of the authors in the use of CO_2 in refrigerators.

P. Pechtl[10] considered the ZEPP cycle with CO_2 re-circulation and gave some figures, confirmed in subsequent papers of other authors. If the efficiencies of an ordinary 500 MW coal-fired power plant and an equivalent ZEPP are compared, the efficiency drops from 38.9 % to 36 %. The liquefaction of CO_2 takes 5.3% of the generated power. Pechtl seems to have been one of the first experimenters to evaluate the demand for CO_2 in world industry to be 1.6 % of the CO_2 released to the atmosphere by power plants. This indicates that if zero-emissions power generation was to be implemented on a global scale, the sequestration of CO_2 would be unavoidable.

Yantovski[11] presents, in some detail, the schematics of ZEPP with combustion of natural or coal-derived gas in an O_2/steam mixture, with triple turbine expansion, CO_2 separation for sequestration and **water re-circulation**. Estimation of the cycle efficiency by means of a T-s diagram, at a temperature of 750 °C before each of the three turbines, gives an efficiency of 37 %. Five years later, exactly the same scheme was patented and used for a large scale project by Clean Energy Systems Inc. They successfully tested the 10 $MW_{thermal}$ combustor of gas in an O_2/steam mixture and are now building a 500 kW demonstration power unit in Antioch.

Bolland and Saether[12] considered ZEPP as a combined cycle: a gas-turbine part with combustion of a fuel in an O_2/CO_2 mixture and a bottoming ordinary Rankine cycle. The reduction of efficiency due to oxygen production and the need for CO_2 compression for transportation, is from 56 % to 41 %. Another scheme in this paper deals with combustion in an O_2/steam mixture and one-stage steam turbine expansion. The maximal efficiency for a steam-cooled turbine at 1550 K is 38.5%. Many useful figures for the equipment costs are also given.

De Ruyck[13] proposed the original scheme of ZEPP with the use of water evaporation in a mixture with CO_2. Extremely high efficiencies of up to 57 % were calculated. These figures, however, were not confirmed in later papers.

Holt and Lindeberg[14] considered an integrated complex comprising a ZEPP with enhanced oil recovery. They concluded that two thirds of the CO_2 produced by combustion in a ZEPP might be returned underground to the same place from where the fuel was extracted.

Van Steenderen[16], in more detail, considered the ZEPP with a combined gas-steam cycle. At 20 bar and 1050 °C at the inlet to the turbine, an efficiency of 44 % is reported.

Yantovski[15] et al. presented the computer simulation of a ZEPP cycle with combustion in an O_2/steam mix, with triple turbine expansion and water re-circulation as was proposed in Ref. 11. At the highest temperature of 1300 °C before the steam turbines, the efficiency does not exceed 40 %. The reason is the very high evaporation heat of water and the inability to recuperate the large enthalpy of condensing steam.

In the series of papers in Ref. 17, a 10 MW ZEPP cycle is presented with liquid CO_2 co-generation, the latter being used to enhance oil recovery. At a temperature of 1000 °C (and 40 bar pressure) at the turbine inlet and 565 °C by 240 bar, with CO_2 production of 1.14 kg/s and steam production of 0.93 kg/s, the efficiency reached 48 %. A similar project is now underway by the Aker Co in Norway, which started about 5 years after Ref. 17.

The detailed description of a highly efficient ZEPP cycle with CO_2 re-circulation and gas combustion in an O_2/CO_2 mixture is given in Ref. 18. It is the COOPERATE cycle, CO_2 Prevented Emission Recuperative Advanced Turbine Energy. At CO_2 pressures of 240/60/15/4 bar and a temperature variation of 950-1350 °C, the efficiency range is between 46.9 % and 55.2 %. Here, a literal citation of a statement given in Ref. 19 by DOE-FETC is given: *4) Innovative cycles will be needed to achieve efficiency goals. Potential cycle modification include intercooling, chemical recuperation, massive moisture injection…and reheat combustor.* As a reply in Ref. 18, one may see the end sentence: *Having looked at the list of statements, p.4) we see that for every reason the COOPERATE cycle should be included into the list.*

The main engineering problem of the COOPERATE cycle was the high temperature and high pressure before the first turbine. Upon consulting with turbine manufacturers, it became apparent that it would be impossible to reach such conditions in the foreseeable future. It led to some sacrificing of the efficiency by eliminating the combustion chamber before the first turbine in the COOPERATE demo cycle[20]. Here the cycle parameters are quite realistic: about 240 bar at 600 °C and 40 bar at 1300 °C, producing an efficiency of about 50 %. This highly efficient realistic cycle consists of two parts: the high pressure Rankine Cycle (on CO_2) and the low pressure Brayton Cycle (on the same CO_2), which is why it was described as "quasicombined". It is described in detail in the book[20] and depicted on the book's front cover. A comprehensive description of almost all such zero-emission cycles can be found in the book by G.Goettlicher[21]. The selected power cycle here belongs to "Process Family II" in the book.

Another problem associated with this cycle is the non-condensable gases in the CO_2 condenser. As a radical remedy, it was proposed[22] that CO_2 condensation could be avoided by compressing the CO_2 flow immediately after exiting the cooling tower, without allowing the compression process to cross the saturation line. This version of the COOPERATE cycle was entitled the MATIANT cycle[22]. Recent detailed calculation of many modifications of the MATIANT cycle, made by Ph. Mathieu et al. have indicated a very large efficiency decline due to cryogenic air separation (about 11.5-14.5 percent points). The reader is referred to Mathieu Ph., Dubuisson R., Houyou S. Nihart R. *New concept of CO_2 removal technologies* *in power generation*, www.ulg.ac.be/genienuc/publicat.htm, Fig.4.) Such a penalty does not make the MATIANT cycle competitive. Some new approaches are needed.

Recent advances in the development of dense ceramic membranes for air separation should, in time, replace cryogenic air separation techniques. This will open a new chapter for the development of ZEPPs, which still has no history. Here, oxygen production has a much less detrimental effect on cycle efficiency. It might even be beneficial to the efficiency as an air turbine bottoming cycle.

One example is the AZEP[27] cycle (Advanced Zero Emission Power) which comprises a novel combustor integrated with a ceramic membrane and a heat exchanger. Here, the simplified CO_2 portion of cycle does not allow a high efficiency to be achieved.

The ZEITMOP[28] cycle was developed quite independently of the AZEP cycle and followed the statement by one of the present writers in Ref.25, page 142: ... *"the primary advantage of the membrane reactor approach is…the combination of air separation and chemical reaction in a single high temperature unit*". The simplest version of the cycle is the gas-fired one. With regard to pulverized coal, we hope that measures recommended and tested for an ordinary combined cycle in Ref. 29 will be valid for the ZEITMOP cycle also. The cycle might be employed to use all types of fossil fuels. The authors believe it represents one of the best options for the substitution of decommissioned power plants from the outset of this new millennium.

MEMBRANE SEPARATION PROCESS

In 1899, Walter Hermann Nernst (1864-1941, Nobel prize in 1920 for the 3rd Law of Thermodynamics - the impossibility to reach zero K) investigated the electrical current between metals and solutions. He observed the current of oxygen molecules through dense ceramics, when heated somewhat. The current of oxygen was similar to the current of electrons in metals under an electrical potential difference. The partial pressure of oxygen played the role of electrical potential. Some years later he discussed this with A. Einstein, and this resulted in the Nernst-Einstein formula:

$$j_{O_2} = \frac{\sigma_i RT}{4Ln^2F^2} \ln\left(\frac{P'_{O_2}}{P''_{O_2}}\right)$$

Here j_{O_2} is the oxygen flux, F is Faraday's constant, L is the membrane thickness, n is the charge of the charge carrier (= 2), R is the ideal gas constant, T is the absolute temperature, P'_{O_2} is the oxygen partial pressure at the feed surface of the membrane, P''_{O_2} is the oxygen partial pressure at the permeate surface of the membrane and σ_i represents the material conductivity. This expression clearly identifies the natural logarithm of the oxygen partial pressure ratio as the driving force for the oxygen flux.

Here is a literal citation from Ref.23: *The driving force for overall oxygen transport is the differential oxygen partial pressure applied across the membrane. As the ITM membrane is dense and gas tight, the direct passage of oxygen molecules is blocked. Yet oxygen ions migrate selectively through the membrane. Dissociation and ionization of oxygen occurs at the oxide surface at the high pressure side (feed side) where electrons are picked up from accessible (near-) surface electronic states. The flux of oxygen ions is charge compensated by a simultaneous flux of electronic charge carriers. Upon arrival at the low-pressure side (permeate side), the individual oxygen ions part with their electrons and recombine again to form oxygen molecules, which are released at the permeate side.*

It took about a century to bring this discovery to Energy Engineering. To the authors' knowledge, one of the first papers to describe various schemes for adopting ion transport membranes for oxygen production belongs to Dyer[24] et al. Here, oxygen production using membrane separation technology for gas-steam power production and internal gasifier integration is described. The authors[24] however, have missed the most important opportunity to sweep the oxygen from the permeate side by means of carbon dioxide to increase the driving force for oxygen separation and create the zero emissions power cycle.

When O_2 is separated out from an air stream, the partial pressure of O_2 in the oxygen-depleted air stream decreases. If O_2 on the permeate side of the membrane is not swept away, the O_2 partial pressure increases. This results in a decline in the driving forces for O_2 flux. The solution is either to use a sweeping gas (in our case, CO_2) to sweep away the O_2 on the permeate side, or to bind the oxygen atoms taken from the O_2 molecules, to form molecules of another chemical substance (e.g., using a membrane combustor, where a fossil fuel flows along the permeate side). The question as to which is better, a *separate* membrane reactor to produce "artificial air" and a *separate* combustion chamber, or *combined* air separation and combustion in the permeate side, is still open. This question can only be answered by future tests.

The main problem associated with the ITM reactor is stability. The stability issue can only be addressed by conducting long experiments on suitable test rigs. "Mechanical tests of the porous perovskite support reveals that these could endure an absolute pressure difference of about 30 bar…application of the supports at temperatures close to 1000 °C will reduce its porosity due to non-negligible sinter activity at these temperatures"[26]. Generally, an ITM reactor will look like a shell-and-tube heat exchanger with the tubes made of alumina substrate combined with a thin layer of membrane material, like perovskites of La, Sr, Co, Fe, and oxygen. Such membrane tubes are presently manufactured by a number of advanced ceramic factories.

CYCLE DESCRIPTION

In the computer simulation presented here an effective algorithm for CO_2 properties is used, based on the Equation of State (EOS) by Span and Wagner. For properties of air, nitrogen, oxygen and the mixture CO_2+H_2O, the modified Peng-Robinson EOS is used. All of the numbers for power and flow rate are given for a fuel flow rate of 1 kg/s. The ZEITMOP cycle presented in Fig. 1 consists of three main loops: circulating CO_2 (components 7, 9, 10, 11 and 12), mixture of CO_2+H_2O (components 3, 6, 7, 10, 12, 13) and air/O_2-depleted air/O_2 branch (components 1, 2, 3, 4, 5, 7) together with the fuel supply system (components 7, 8).

Ambient air enters compressor 1. After compression, it is heated up to around 800 – 900 °C in heat exchanger 3 by the flue gases exiting turbine 6. The hot pressurised air then enters the ITM Oxygen ceramic, 4, which separates the air into an oxygen stream, which penetrates through the membrane, and a relatively high pressure oxygen-depleted air stream. The carbon dioxide after 9 is mixed with oxygen in 4 before being directed to the combustion chamber, 7. The latter is also fed with pressurised natural gas. The hot pressurised oxygen-depleted air stream leaving 4, is expanded in turbine 5 before being discharged to atmosphere. The flue gas mixture of CO_2 and H_2O exiting the combustion chamber (at about 1300 – 1600 °C) is expanded in the low pressure turbine, 6, before being cooled in 3, 10 and 13. At ambient temperature, the water in the flue gas mix is liquid while the CO_2 remains gaseous. The bulk of the water is deflected out of the cycle in 12. Almost pure CO_2 enters the multistaged inter-cooled compressor 11, from where a fraction (some percents) of highly compressed, supercritical or liquid CO_2 is deflected out of the cycle in 14 to be sequestered or used elsewhere. The major portion of the CO_2 is heated in 10 before being expanded in the high pressure turbine, 9, down to about 15 bar. The CO_2 then enters combustor 7 via 4 in a mixture with oxygen.

Numerical results of a computer simulation are presented in Table 2, where mass flow rates, temperature, pressure, enthalpy and entropy at all of the cycle node points are indicated. The T-s diagram for the cycle, including its air and CO_2 parts, is presented in Fig. 2. The CO_2 part of the cycle is simply a quasi-combined one, described in Ref. 20 and depicted on the front cover of the book. The air-part is a simple Brayton cycle. The calculated efficiency 50% might be increased by some cycle improvements, such as injection of combustion-born water to the entrance of air compressor.

EFFICIENCY VERSUS TURBINE INLET TEMPERATURE

The calculation was performed using a real gas model for the analysis of pure gas components and its mixtures. The well-known forms of the thermal EOS and component additivity rules were used. The condensed water from point 12 is injected into the entrance of the air compressor.

Table 1 **Results of ZEITMOP Cycle efficiency calculation**

Element	**Parameter**	**Unit**	**Case study**		
			1	2	3
CGT (CO2-H2O turbine "6")	**Turbine inlet temperature**	^{0}C	**1300**	**1400**	**1500**
	Turbine inlet pressure	**bar**	**17.5**	**17.5**	**17.5**
	Pressure downstream the turbine	**bar**	**1.1**	**1.1**	**1.1**
	Temperature downstream the turbine	^{0}C	**826.6**	**913**	**994.6**
	CO2-H2O exhaust mass flow	**kg/s**	**43.64**	**43.64**	**43.64**
	Relative cooling stream	**%**	**5.7**	**5.7**	**5.7**
	Turbine isentropic efficiency	**%**	**89**	**88.5**	**88**
	Turbine power	**MW**			
	Turbine electric power	**MW**	**15.7**	**16.8**	**18.2**
DAT (Depleted air turbine	**Turbine inlet temperature**	^{0}C	**800**	**885**	**965**

	Turbine inlet pressure	**bar**	**18**	**18**	**18**
	Pressure downstream the turbine	**bar**	**1**	**1**	**1**
	Temperature downstream the turbine	**^{0}C**	**301.6**	**355**	**397.4**
	Depleted air mass flow	**kg/s**	**27.4**	**27.4**	**27.4**
	Turbine isentropic efficiency	**%**	**89**	**89**	**89**
	Turbine effective power	**MW**	**15.9**	**17.1**	**18.6**
CDT (CO2 HP turbine "9")	**Turbine inlet temperature**	**^{0}C**	**440**	**470**	**500**
	Turbine inlet pressure	**bar**	**205**	**205**	**205**
	Pressure downstream the turbine	**bar**	**20**	**20**	**20**
	Temperature downstream the turbine	**^{0}C**	**219.6**	**244**	**268.3**
	CO2 mass flow	**kg/s**	**38.4**	**38.4**	**38.4**
	Turbine isentropic efficiency	**%**	**88**	**88**	**88**
	Turbine effective power	**MW**	**8.2**	**8.6**	**8.8**
CDC (CO2 compressor "11")	**Compressor inlet pressure**	**bar**	**1**	**1**	**1**
	Gas inlet temperature	**^{0}C**	**30**	**30**	**30**
	Compressor inter-stage/discharge pressure	**bar**	**I/II/III = 6.2/35.5/210**		
	Gas (CO2) mass flow	**kg/s**	**41.13**	**41.13**	**41.13**
	Compressor isentropic efficiency	**%**	**I/II/III = 87/87/85**		
	Compressor power demand	**MW**	**17**	**17**	**17**
	Inter-stage cooling heat stream	**MW**	**13.1**	**13.1**	**13.1**
ACC (air compressor "1")	**Compressor inlet pressure**	**bar**	**1**	**1**	**1**
	Air inlet temperature	**^{0}C**	**15**	**15**	**15**
	Compressor discharge pressure	**bar**	**21**	**21**	**21**
	Inlet air mass flow	**kg/s**	**31**	**31**	**31**
	Injected water stream	**kg/s**	**1.55**	**1.55**	**1.55**
	Air temperature downstream the compressor	**^{0}C**	**243.7**	**243.7**	**243.7**
	Compressor isentropic efficiency	**%**	**87**	**87**	**87**
	Compressor power demand	**MW**	**11.9**	**11.9**	**11.9**
CHE (CO2 heat exchanger „10")	**Cold stream (CO2) temperature rise**	**^{0}C**	**219.7**	**249.4**	**279**

	Hot stream (CO2-H2O) temperature change	^{0}C	223.6	251.5	279.1
	Pinch point temperature difference	^{0}C	14.8	16.2	17.1
	Cold/hot stream flow ratio	-	0.88	0.88	0.88
	Heat energy flow in the regenerator	MW	11	12.5	14
	Regenerator effectiveness (based on temp.)	%	92.1	93.3	94.1
AHE (air heat exchanger “3”)	Cold stream (CO2) temperature rise	^{0}C	545.1	631.3	709.8
	Hot stream (CO2-H2O) temperature change	^{0}C	377.8	435	487
	Pinch point temperature difference	^{0}C	26.5	28	29.4
	Cold/hot stream flow ratio	-	0.746	0.746	0.746
	Heat energy flow in the regenerator	MW	20.6	24.1	27.4
	Regenerator effectiveness (based on temp.)	%	93.5	94.3	94.4
SEP (H2O separator “13”)	Inlet stream CO2-H2O gas mixture flow	kg/s	43.64	43.64	43.64
	Separated water flow (at 30^{0}C)	m^3/h	8980	8980	8980
	Fluid temperature drop in a separator	^{0}C	197.8	196.8	196
	Heat flow stream	MW	13.4	13.3	13.1
			1	2	3
ICC (coolers in “11”)	CO2 mass flow downstream a compressor unit	kg/s	41.13	41.13	41.13
	Average temperature drop in inter-stage coolers	^{0}C	~160	~160	~160
	Heat power of two inter-stage CO2 coolers	MW	13.1	13.1	13.1
CGG (combustion chamber “7”)	Temperature of oxy-fuel combustion products	^{0}C	1300	1400	1500
	Basic substrate stream mass composition	%	CH4/CO2/O2/H2O=88/2.3/9.1/.6		

	Combustion products composition (per vol.)	%	CO_2/H_2O=87/13		
	Fuel (CH_4) / oxygen mass ratio	kg/kg	1 : 3.99		
ITM (oxygen separator “4”)	ITM feed air mass flow	kg/s	32.55	32.55	32.55
	Feed air composition (per mole)	%	$N_2/O_2/H_2O$=73.3/19.3/7.4		
	Feed air inlet temperature	^{0}C	800	885	965
	Feed air pressure at ITM inlet	bar	20.5	20.5	20.5
	Desired O_2 production in ITM separator	kg/s	4	4	4
	O_2 partial pressure inside ITM reactor	bar	1.745	1.745	1.745
	O_2 partial pressure on permeate side (assumed)	bar	0.1	0.1	0.1
	O_2 depletion inside reactor part	%	55.9	55.9	55.9
	O_2 molar flux per unit area on permeate side	mole/m^{2}s	5.7E-3	6.2E-3	6.6E-3
	Surface area of ITM (σ_i=1 S/m, L=30μm, n=2)	m^2	2.2E+4	2E+4	1.9E+4
	The same surface by O_2 lower pressure due to its sweeping by CO_2, p = 10^{-9} bar,		1.6E+3	1.5E+3	1.4E+3
	Net power output in the cycle	MW	23	25.5	28.3
	Thermal cycle efficiency	%	46	50.9	56.5
	Relative CO_2 deflection for sequestering	kg/MWh	429	387	349
	Disposed heat output	MW	26.6	26.4	26.3

One of the most sensitive figures in the table relates to the attainable oxygen flux. This oxygen flux will have a direct bearing on the surface area requirement of the ITM separator, 4. Further experiments of flux density measurements might be conducted on one tube only, which should be relatively inexpensive. If the sweeping effect on the flux density is to be as expected above, the size of ITM separator would be reasonable. The relevant calculations of oxygen fluxes compared with experiments on a small disk-shaped membrane of 1 mm thickness can be seen in Ref. 25, Figs.3.2 and 3.4.

ECONOMICAL GUESS

The guess is based on the two figures from membrane manufacturers:

- the oxygen flux at 900 °C and sufficient partial pressure difference: $j = 1\ gO_2/m^2s$
- the specific cost of the membrane tubes: $c = 1500\ US\$/m^2$

The chemical equation for the combustion of methane in pure oxygen can be written as: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. If $H_{methane}$ = 50 MJ/kg, $M_{methane}$ = 16 kg/kmol and M_{oxygen} = 32 kg/kmol, then the rate of thermal energy flux is given by:

$$H_{methane} \times \frac{(1 \times M_{methane})}{(2 \times M_{oxygen})} \times j = 50 \times \frac{(1 \times 16)}{(2 \times 32)} \times 0.001 = 12.5\ kW/m^2$$

Here, $H_{methane}$ represents the heating value of methane, and $M_{methane}$ and M_{oxygen} represent the molecular masses of methane and oxygen respectively.

Assuming a thermal efficiency of 50 %, the generated power density is 12.5 × 0.5 = 6.25 kW/m^2.

The specific capital investment in membranes is $\frac{1500}{6.25}$ = 240 US$/kW, which is about half of today's cost per kW of a gas-fired power plant or a quarter of the cost of a coal-fired one. It seems reasonable.

CONCLUSION

The results of the calculation are encouraging. At the highest cycle temperatures of 1300-1500 °C a cycle efficiency of 46-56 % is attainable. There are a number of ways to increase the cycle efficiency. Further development of the cycle includes its use for zero-emissions transportation engines (turbine and piston), co-generation, decentralised energy supply and a zero-emissions Rankine cycle.

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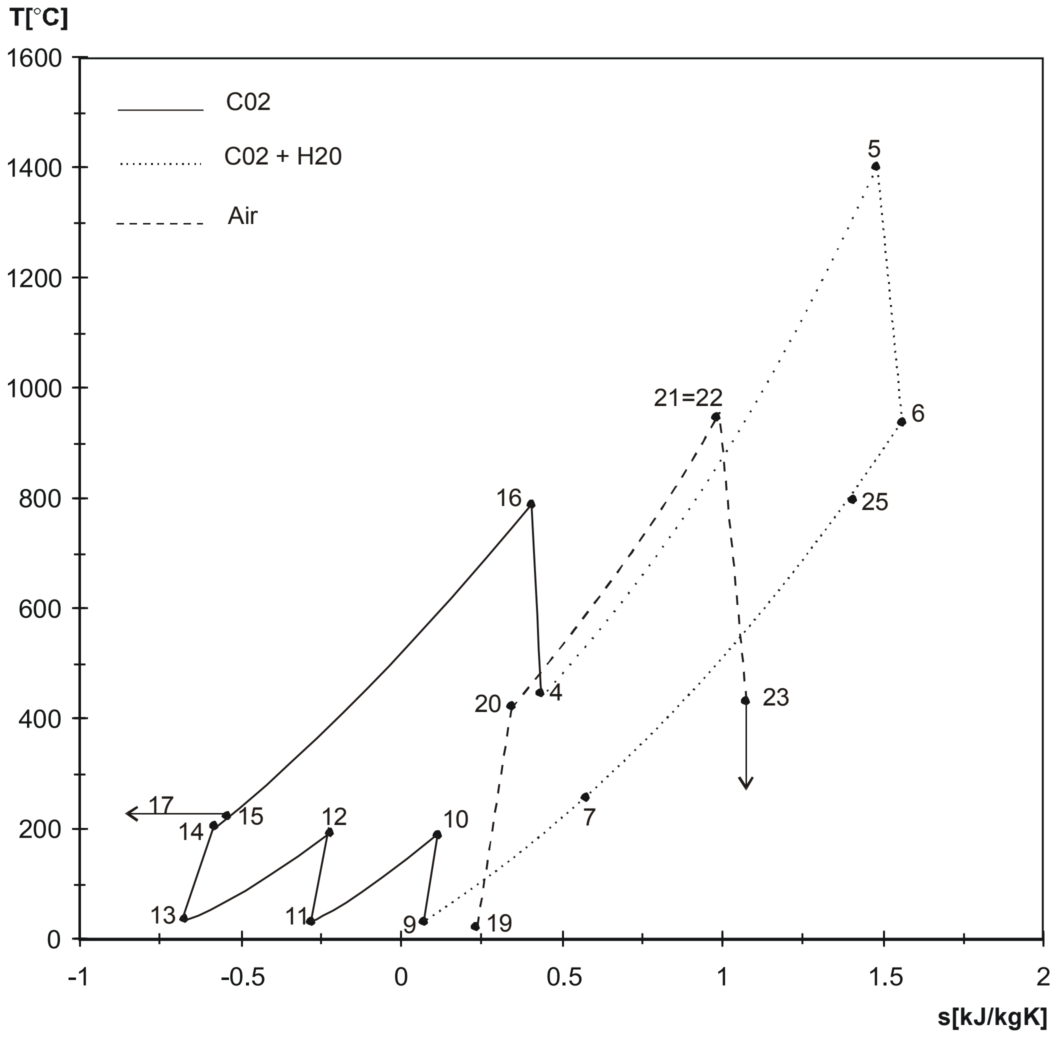

Fig. 2 T-s diagram of ZEITMOP Cycle

Table 2 **Basic parameters of ZEITMOP cycle at node points**

Stream:	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Components:	CH_4	CH_4	O_2	CO_2	CO_2/H_2O	CO_2/H_2O	CO_2/H_2O	CO_2/H_2O	CO_2	CO_2	CO_2	CO_2
m, [kg/s]	1	1	3,99	38,4	43,4	43,4	43,4	43,4	41,14	41,14	41,14	41,14
T, [^{o}C]	15	267,3	920	420	1400	936,7	256	30	30	186,2	30	192,5
p, [bar]	1	16	5 $^{\&}$	15,2	14	1,03	1,01	1	1	6,16	5,85	35
h, [kJ/kg]	586,6	1237,7	921	494,4	1580,7	937,7	99,6	-222,1	103,3	246,6	98,9	240,3
s, [kJ/kgK]	11,566	11,742	0,693	0,385	1,483	1,565	0,574	-0,272	0,072	0,200	-0,262	-0,218

Table 1 (cont.)

13	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
CO_2	CO_2	CO_2	CO_2	CO_2 *	H_2O *	Air	Air	Air	Depl. Air	Depl. Air	CO_2/O_2	CO_2/H_2O
41,14	41,14	38,4	38,4	2,75	2,25	19,1	19,1	19,1	15,11	15,11	42,4	43,4
30	209,8	209,8	730	209,8	30	15	411,1	920	920	389,1	468,8	747,2
34	210	210	208	210	1	1	16	15,8	13,7	1	14	1,02
68,5	196,5	196,5	861,4	196,5	125,8	10,7	429,7	996,5	996,4	394,7	549,4	687,5
-0,667	-0,624	-0,624	0,318	0,624	0,450	0,223	0,312	0,990	0,991	1,116	0,488	1,345

Comments: * - extracted streams of CO_2 and H_2O from the cycle.

$^{\&}$ - assumed pressure of compressed oxygen after ITM separation.

Basic data for ZEITMOP cycle - Calculation of energy balances for turbine and compressor units:

$N_9 = N_{HPT} = m_4 (h_{16} – h_4) = 14.08$ MW - CO_2 high-pressure turbine (element “9” on the cycle schematic),

$N_5 = N_{AirT} = m_{23} (h_{22} – h_{23}) = 9.10$ MW - Depleted Air (Dair) turbine (element “5” on the cycle schematic),

$N_6 = N_{GasT} = m_6 (h_5 – h_6) = 27.91$ MW - CO_2+H_2O (Gas) turbine (element “6” on the cycle schematic),

$N_{11} = N_{CO2} = m_9 [(h_9 – h_{10}) + (h_{11} – h_{12}) + (h_{13} – h_{14})] = 16.98$ MW - CO_2 compressors unit (element “11” on the cycle schematic),

$N_1 = N_{Air} = m_{19} (h_{19} – h_{20}) = 8.0$ MW - Air compressor (element “1” on the cycle schematic),

$N_8 = N_{Fuel} = m_1 (h_1 – h_2) = 0.65$ MW- Fuel (CH_4) compressor (element “8” on the cycle schematic).

Net turbine power: $N_{net} = [(N_9 + N_5 + N_6) – (N_{11} + N_1 + N_8)]\, \eta_m = 25.2$ MW, (at the mechanical efficiency: $\eta_m = 0.99$).

Thermal efficiency of principal ZEITMOP cycle: $\eta_{th} = N_{net} / (m_1 Q_d) = 0.5038 = 50.38\%$, (at Lower Heating Value for CH_4 : $Q_d = 50$ MJ/kg).

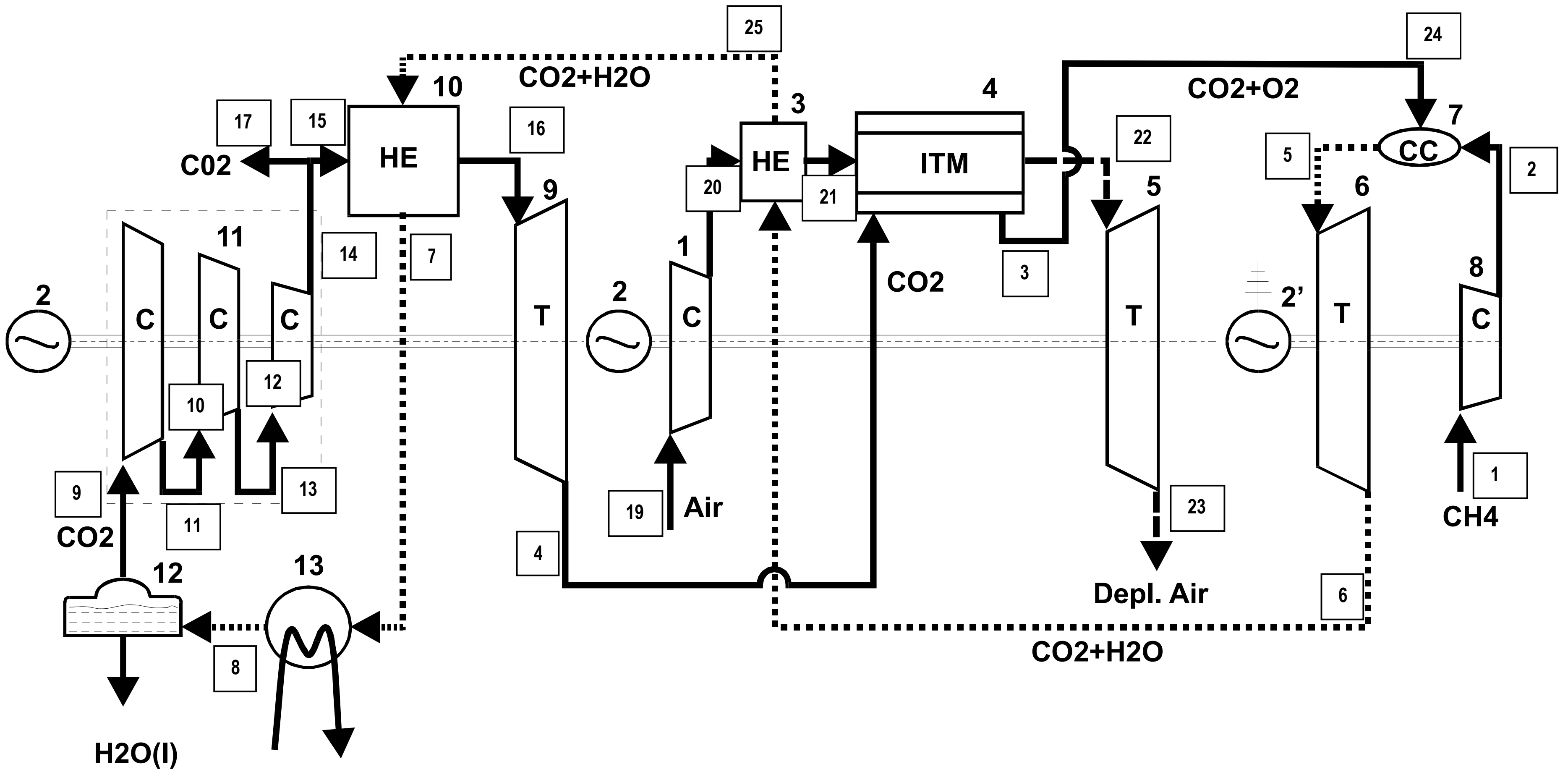

Fig. 1 ZEITMOP Power Cycle with separate Combustion and ITM reactor. Legend: 1-air compressor, 2-synchronous electrical machine, 2-electric generator, 3-heat exchanger (recuperator), 4-ITM reactor, 5-depleted air turbine, 6-CO2+H2O turbine, 7-combustor, 8-fuel gas compressor, 9-CO2 turbine, 10-recuperator, 11-CO2 compressor, 12-water separator, 13-cooling tower. Symbols: 1 - 25 are showing the node points of the cycle.