CONFERENCE PROCEEDINGS

Elaboration of Zero Emissions Membrane Piston Engine System (ZEMPES) for Propane Fuelling

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Abstract

Decision makers of the highest rank are committed to hydrogen and electrical options in the world-wide efforts to create a zero-emissions vehicle. Neither option is truly zero emissions due to the carbon dioxide discharged in producing the hydrogen or electricity. In addition, both options require a costly change of existing fuel supply infrastructure.

This paper elaborates on the ZEMPES, introduced at the Second Conference in Alexandria, 2003 and further described in the VAFSEP Conference in Dublin, 2004. Stress is placed on the use of propane as a fuel due to the possibility of storing captured CO2 onboard in the fuel tank, requiring only a sliding baffle to separate it from the fuel. CO2 could be discharged into a central tank at a filling station to create space for the new fuel.

ZEMPES consists of a spark ignition piston engine with a supercharger, an ITMR (ion transport membrane reactor) to separate oxygen from compressed air, an air compressor and depleted air turbine and a CO2 liquefaction system. There is also an optional bottoming Rankine cycle to use the wasted heat.

The crucial new element is the ITMR which has been recently developed by Air Products Co. For 500 kg O2 per day its dimensions are similar to a home breadbox, which is small enough to be used in a car. Air compressed to 7 bar provided to the ITMR delivers pure oxygen to be mixed with recirculated CO2. This mixture is fed with propane and enters the cylinder. After combustion and expansion the CO2 is cooled, compressed and liquefied.

Calculated efficiency at a design point (not optimised) is: without Rankine cycle 37%, with Rankine cycle 44%. The system does not require any change to the propane-fuelled engine or existing fuel supply infrastructure. It might be used for an ordinary gasoline as well after a minor revision. Filling stations should be equipped with a central tank to store liquid CO2 with dissolved contaminants. Then CO2 is to be sequestered. No combustion products are released into the atmosphere.

1. Introduction

This paper continues the ZEMPES line, introduced by Yantovksi and Shokotov (2003) at the Second Annual Conference and developed by Yantovski *et al.* (2004) at the VAFSEP conference in Dublin. It represents an attempt to find a solution to the very important problem of atmosphere protection, which is what a zero emission vehicle really is. After decades of development and billions spent on very popular options like hydrogen or electrical cars, they clearly reveal that they are not zero emissions. Emission of carbon dioxide and some contaminants is unavoidable in both hydrogen production by reforming of hydrocarbons and electricity generation at fuel-fired power plants. Production of hydrogen by electrolysis and electricity generation by solar or wind energy is quite possible, but are unlikely to reach a reasonable cost in the short term future. Dependence on nuclear power is impossible due to known restrictions on its expansion, as demonstrated in all forecasts of the energy supply melange for this century. Even the best engineered hydrogen and electrical cars require a total change of fuel supply infrastructure, which would need tremendous funding and is impossible for many countries.

The real solution could be found if the existing fuel supply system remains and the ordinary piston engine remains with a minor revision, being equipped with some new elements, which form the zero-emissions piston engine system. As the crucial element of such a system is a membrane reactor aimed at producing pure oxygen onboard, the system was named ZEMPES. It converts onboard emissions into effluents by liquefaction of carbon dioxide with dissolved contaminants. This liquid carbon dioxide is released at a filling station into a central tank and is then sequestered.

It should be stressed that the global warming menace is not the only reason a zero emissions car is urgently required. Controversy still surrounds the warnings of global warming and the greenhouse effect and keeps the States out of the Kyoto protocol. But there is no controversy about the danger of vehicle emissions in densely populated urban areas, like New York or Los Angeles.

2. The development of ZEMPES

In order to increase efficiency the schematic becomes increasingly complicated.

The simplest version, with only one turbine, can be seen in Fig.1, which is exactly reproduced from Yantovski *et al*. (2004). The turbine and its compressor are an unavoidable addition to the piston engine as they provide compressed air for oxygen separation in ITM reactor. Here the efficiency is about 28%.

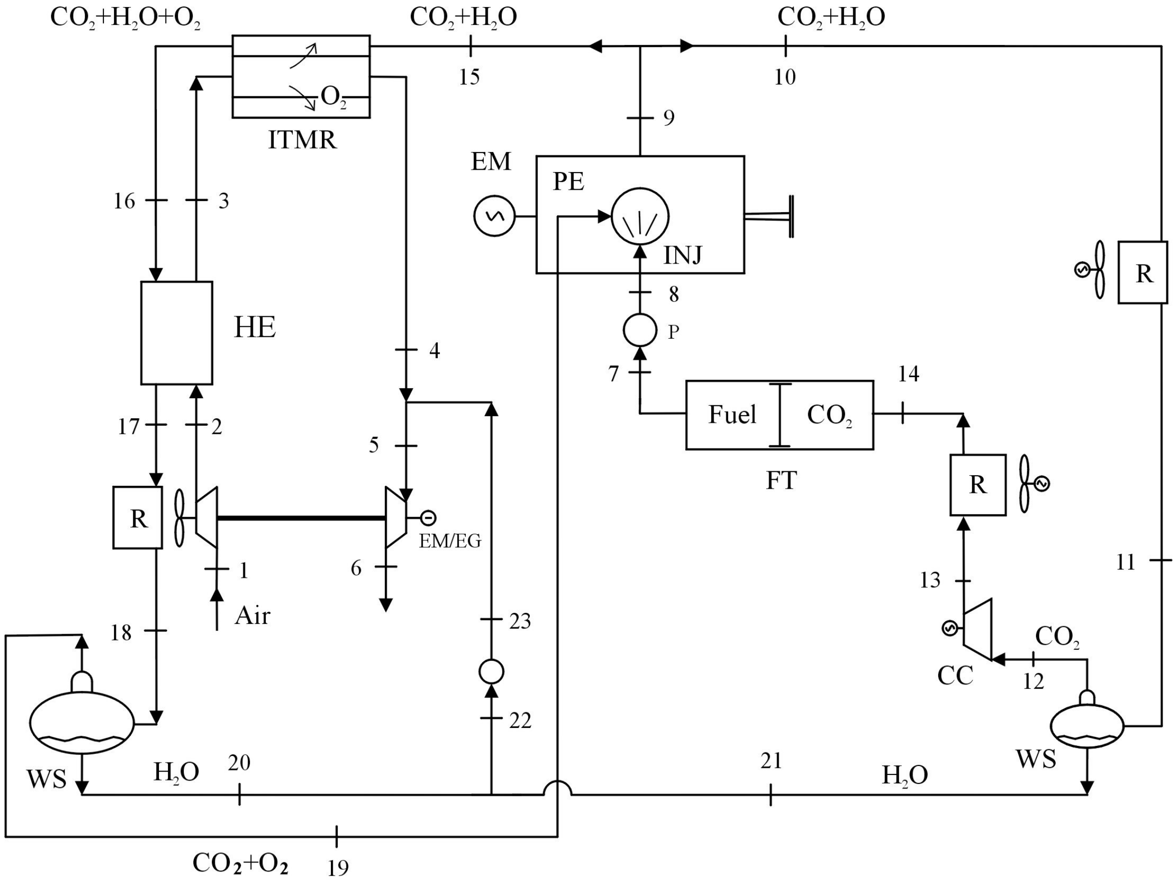

Fig. 1 ZEMPES schematic with one turbine. The simplest case**.**

Legend: CC = CO_2 compressor, EM = Electric Motor (generator or motor for starting), FT = Fuel/CO_2 tank with sliding baffle, HE = Heat Exchanger, INJ = Fuel injection, ITMR = Ion transport membrane reactor, P = Pump, PE = Piston engine, R = Radiator-Cooler, WS = Water separator

The next step is the addition of supercharging with an additional turbine. This two-turbine scheme, presented in Fig.2, has 37% efficiency.

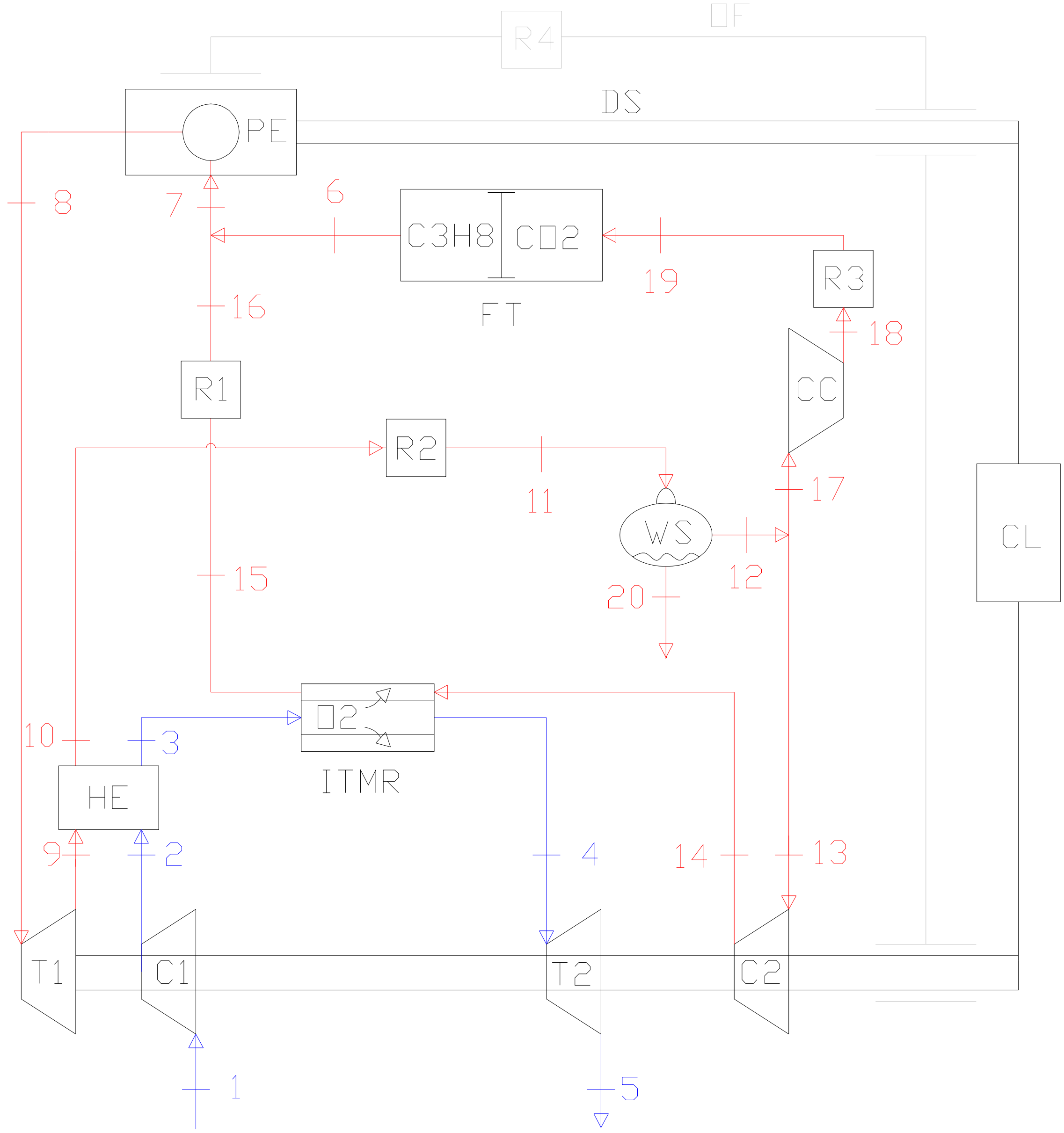

Fig. 2 Extended schematic of the ZEMPES with two turbines

Legend: PE = piston engine, HE = heat exchanger, WS = water separator, CL = one-way clutch, ITMR = ion transport membrane reactor, O2 = oxygen flow through membrane wall, R = radiator for cooling, C = compressor, T = turbine, DS = driveshaft, OF = oil flow in piston engine and turbine shaft.

The final step is the addition of a bottoming Rankine cycle to use the wasted heat. The efficiency is increased to 44% and a third turbine appears on the turbine shaft. This latest, most complicated schematic with the three turbines is presented in Fig.3.

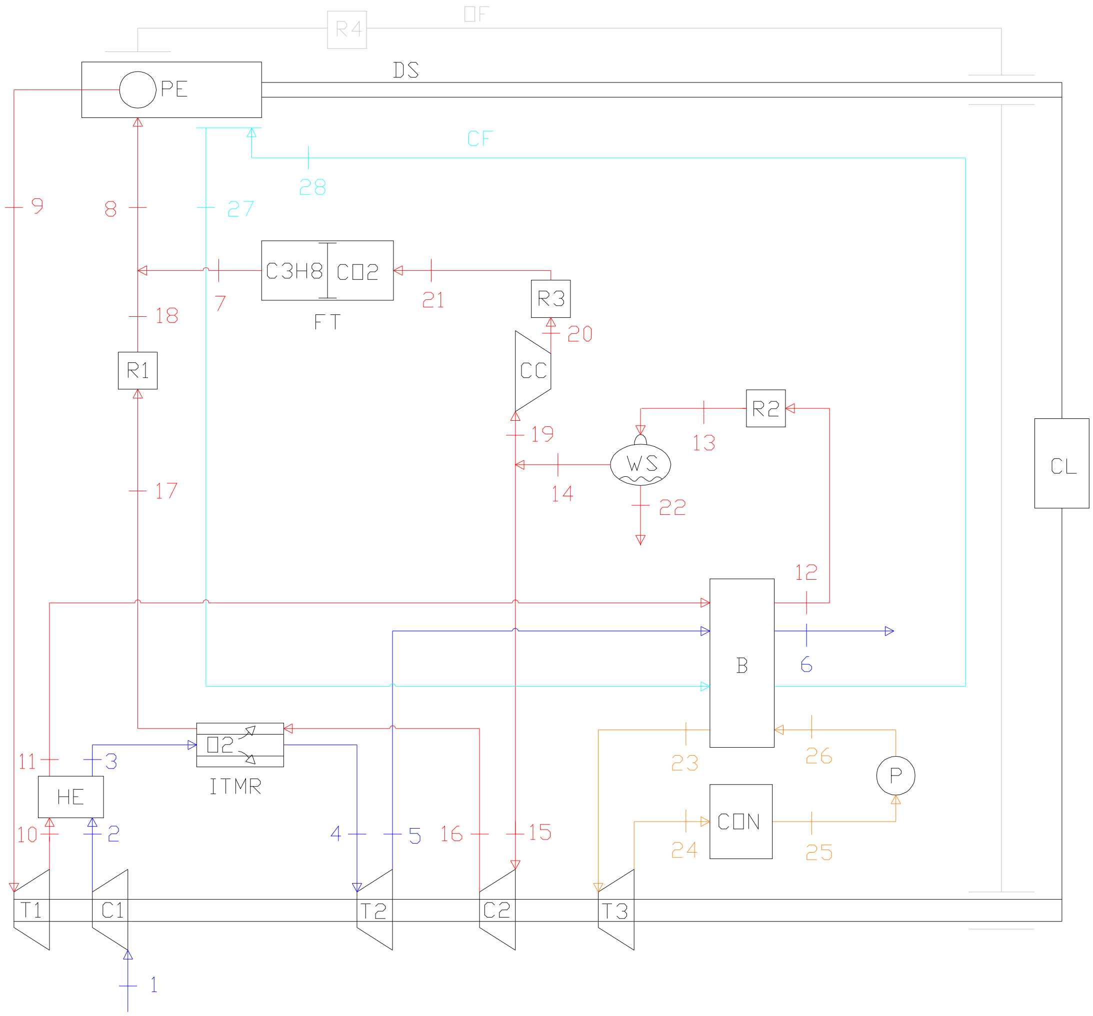

Fig. 3. The full schematic of the ZEMPES with three turbines.

Legend: PE = piston engine, HE = heat exchanger, WS = water separator, CL = one-way clutch, ITMR = ion transport membrane reactor, O2 = oxygen flow through membrane wall, R = radiator for cooling, C = compressor, T = turbine, DS = driveshaft, OF = oil flow in piston engine and turbine shaft, CF = coolant flow.

Parameters in the node points are presented in Table 2.

There are four distinct flow streams: air and depleted air (1,2,3,4,5,6), fuel, oxidizer and combustion products (7,8,9,10,13,14,15,16,17,18, 19, 20, 21), steam and water in the optional Rankine cycle (23, 24, 25, 26), and engine coolant (27, 28). The oil flow, carrying mechanical losses from both the turbo-compressor shaft and the driveshaft, is cooled in a radiator.

4. ZEMPES cycle with bottoming Rankine cycle (Fig. 3)

Ambient air (1), is compressed in C1 (2), then heated in HE (3) and loses some oxygen in ITMR (4). This hot oxygen depleted air expands in T2 (5), is cooled in boiler B and discharged harmlessly to the atmosphere (6).

Fuel (7) is mixed with oxidiser (8) and burns in the piston engine PE, which releases combustion products CO_2+H_2O (9) to the supercharger turbine T1. After expansion (10) these gases are cooled in HE (11), then in the boiler B (12), then in radiator R4 (13). Water is condensed in separator WS and deflected from the cycle (22). Alternatively water could be used as in Fig.1; being injected before air turbine T2. The dry CO_2 (14) is split: the smaller part is deflected out of the cycle (19) to be compressed (20) and cooled (21) for liquefaction and storage onboard, whereas the major part (15) is compressed in C2 (16), oxidised in ITMR (17), cooled (18) and returns as oxidizer to the engine PE.

The optional Rankine cycle, consisting of boiler B, condenser CON, turbine T3 and feed pump P, is quite ordinary. Water is boiled in the boiler; the steam (23) is expanded in turbine T3 (24), and condensed to water (25), before being pumped back to the boiler (26).

Hot engine coolant (27) is cooled in boiler B (28) and returns to the engine.

5. Storage of liquid carbon dioxide

One possibility for storing CO_2 onboard is a dedicated tank. However, a different and more attractive possibility for ZEMPES is the storage of liquid CO_2 in the fuel tank. The more fuel consumed, the more empty volume remains for CO_2. The volume flowrate of propane is very little less than the flowrate of liquid or supercritical CO_2 (pressure 74 bar). This eliminates the need for two heavy high-pressure storage tanks onboard. Fuel tanks for compressed methane, already widely used, are designed for pressures up to 250 bar, so development of a tank for nearly critical CO_2 at 70- 80 bar is a mild problem. A cylindrical tank is equipped with a sliding baffle, which moves slowly inside the tank as fuel is gradually consumed, allowing CO_2 to occupy the volume. Pressure on both sides of the baffle is nearly equal. A small leak of either substance through a gap between the baffle and cylinder wall is not dangerous due to the lack of reaction between the substances.

At a filling station the stored onboard CO_2 can be discharged into a central tank to be sequestered while new fuel enters the same tank. This central tank could also be used for joint fuel and CO_2 storage. Such a situation, where CO_2 is returned when fuel is purchased, would integrate well with economic incentives for carbon sequestration, as the price of the CO_2 could be deducted from the price of the fuel, allowing users to see the benefit of carbon sequestration in their own pockets. Such a situation would occur if carbon dioxide has a positive market value, which could happen in a number of situations e.g. in a carbon tax situation, a situation in which a significant amount of CO_2 is required by industry, or a situation in which companies have a carbon emissions quota, which can be increased by sequestering external carbon dioxide.

6. Numerical results of calculations

Here are the dimensions of the selected piston engine for a numerical example and some key numbers for ZEMPES:

Table 1.

Piston engine data		**Propane properties:**	
Bore [m]	0.092	Lower heating value [kJ/kg]	46360
Stroke [m]	0.092	Boiling temperature at 1 bar [°C]	- 42
Number of cylinders	6	Pressure at 27-58 °C [bar]	10-20
Shaft speed [rpm]	3800	Propane fuel mass flow rate [kg/h]	58.7
Supercharging pressure [MPa]	0.258		
Inlet temperature [°C]	80		

Inlet mixture contents, mol %: $C_3H_8 = 4.01$, $CO_2 = 75.92$, $O_2 = 20.07$

Cylinder outlet contents, mol %: $CO_2 = 84.57$, $H_2O = 15.43$

Table 2.

Flow parameters at node points of the schematic in Fig.3

No	P [Pa]	T [K]	M [mole/s]	$\dot{H}$ [kW]	Substance
1	101325	293	14.886	123.46	Air
2	709275	545.3	14.886	234.33	Air
3	707775	1060	14.886	474.71	Air
4	707775	1060	13.036	414.67	Depleted air
5	102825	700.4	13.036	266.86	Depleted air
6	101325	450.0	13.036	167.12	Depleted air
7	-	293.0	0.37	5.802	C_3H_8
8	258000	353.0	9.22	132.49	C_3H_8+CO_2+O_2
9	309600	1247.0	9.59	549.76	CO_2+H_2O
10	107000	1080.0	9.59	467.21	CO_2+H_2O
11	105000	560.3	9.59	228.02	CO_2+H_2O
12	103500	450.0	9.59	180.68	CO_2+H_2O
14	103500	313	8.111	108.4	CO_2’’+CO_2’’’
15	103500	313	7.0	93.54	CO_2’’’
16	259500	383.4	7.0	115.57	CO_2’’’
17	259500	486.7	8.85	174.42	CO_2’’’+O_2
19	101325	313.0	1.11	14.83	CO_2’’
22	101325	313.0	1.48	34.94	Water
23	2000000	673	6.116	278.13	H_2O
24	101325	373	6.116	221.78	H_2O
25	101325	373	6.116	35.89	Water
26	2000000	373	6.116	36.06	Water
27	250000	403.0	252.43	7672.36	Water
28	250000	398.0	252.43	7577.17	Water

CO_2’’= combustion born flow deflected from the cycle into the tank onboard
CO_2’’’= recirculated flow.

Table 3.

Parameters in the engine cylinder

Compression ratio		13	16
Pressure after compression	MPa	5.647	7.216
Temperature after compression	K	679.6	701.5
Maximum pressure	MPa	18.06	22.5
Maximum temperature	K	2094	2106
Thermal power	kW	756.28	756.28
Indicated power	kW	254.1	270.1
Indicated efficiency		0.336	0.357
CO_2’’ flowrate	kg/h	175.82	175.82

In all calculations stoichiometric combustion was assumed according to the equation:
$C_3H_8 + 5O_2 \Rightarrow 3CO_2 + 4H_2O + 2.044$ MJ/mol
Or by molecular mass:
44 + 160 = 132 + 72

Table 4

Power balance for fuel energy flow 756.28 kW

	kW		% of fuel energy
Indicated power	270.11		35.71
Friction losses	14.29		1.89
Exhaust and intake in piston engine	20.0		2.645
Contribution of T1	55.67		7.3
Contribution of T2 – C1	28.2		3.73
Contribution of T3 – C2	53.21		7.03
Radiator fans power	20.7		2.737
CO_2 liquefaction compressor	20.0		2.645
Effective power of ZEMPES	332.17	Efficiency:	43.93

In the case of the simplified scheme without the bottoming Rankine cycle (Fig.2) the effective efficiency would be about 7 percentage points less.

7. Ion Transport Membrane Reactor

7.1 History of ITM development

The foundation of the ZEMPES concept is based on recent achievements in membrane reactor development. The background is somewhat similar to fuel cell development. The effect of voltage in chemical reactions was first observed by Grove in 1839, but the applications of this were not explored in depth until the sixties of the last century, when the first real O_2/H_2 fuel cells for space ships were developed in the States and the Soviet Union.

The effect of oxygen ion conductivity in heated ceramics was first investigated by Walter Nernst in 1899, but dense ceramic membrane engineering research only truly began in 1985, when Teraoka et al. discovered exceptionally high oxygen flux through perovskite ceramics.

The roles of H. Bowmeester, J. ten Elshof and M. van der Haar of Twente University in the Netherlands in scientific research on dense ceramic membrane properties were shown by Yantovski *et al*. (2003, 2004).

7.2 Commercial ITM technology

Many commercial ITMs are now available, but only three are shown here. CSIRO Manufacturing & Infrastructure Technology (2003) advertised available ceramic tubes in their Internet-magazine under the headline “Oxygen When, Where and How you want it. Ceramic Membrane Oxygen separation technology”. Shockling *et al.* tested some tubular reactors which deliver oxygen to the afterburner of a fuel-cell unit for the complete oxidation of reaction products. Many records of measured oxygen flux versus time during 500 hours test were given, however no graphs are provided with a scale, so the value of the flux achieved remains unclear. The most advanced seems to be Armstrong *et al.* (2003), working with the US company Air Products & Chemicals. These are not tubular but flat (wafer-type) ITM reactors. The tests demonstrated stability for 200 days at an air temperature of 875 °C and pressure of about 10-15 bar, producing pure oxygen. The history of the flux increase in recent years was reported, but only in relative numbers. The value of flux achieved is not indicated either. A photograph shows a wafer-reactor similar in size to a domestic bread-box, offering 500 kg O_2 / day (= 0.1808 mol/s). 11 of these size reactors would be required for the ZEMPES system described in this paper. This is a reasonable size for a commercial vehicle.

7.3 ITMR calculations based on published academic work

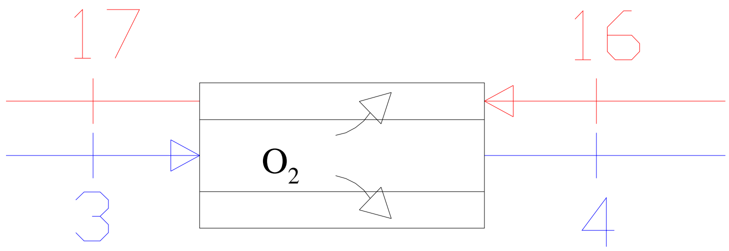

Fig. 4 ITMR

Academics are also making great advances in ITM technology. The ITMR required for the ZEMPES system in Fig. 3 must provide 1.85 mol/s oxygen from 15 mol/s air at 7 atm and 787°C, to 7 mol/s CO_2 at 2.56 atm and 110°C. The working temperature of the ITM could be taken to be 787°C. The air enters with an oxygen partial pressure of 1.47 atm, and leaves with an oxygen partial pressure of 0.69 atm. The average feed side oxygen partial pressure (P_1) is therefore 1.08 atm. The carbon dioxide flow enters with an oxygen partial pressure of 0 atm and leaves with an oxygen partial pressure of 0.54 atm. The average permeate side oxygen partial pressure (P_2) is therefore 0.27 atm. Wang *et al.* (2002) presented results for the oxygen flux through a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane as a function of $\ln(P_1/P_2)$. Assuming a temperature of 787°C and a thickness of 0.17 mm, the flux is estimated as 6.05 µmol/(cm^2 s). For 1.85 mol/s, ~ 300 000 cm^2 would be required. Assuming tubes 7 mm in diameter, the overall size of the ITMR required can be estimated at 53 cm x 53 cm x 50 cm. This is large, but acceptable for a commercial vehicle.

5. Conclusions

Calculations show it is possible to create a zero-emissions vehicle, using propane as fuel and with a minor revision to a piston engine. The attainable efficiency is 37% and with a bottoming Rankine cycle reaches 44%. The only element significantly different to a modern Internal Combustion Engine is an Ion Transport Membrane reactor to produce oxygen onboard. Such systems are already commercially available.

The next step should be a prototype ZEMPES vehicle. Automobile manufacturers are invited to investigate ZEMPES as a development option.

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