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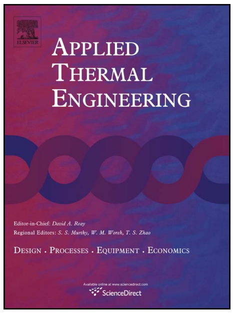

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Renewable energy carriers: hydrogen or liquid air / nitrogen?

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ABSTRACT

The world's energy demand is met mainly by the fossil fuels today. The use of such fuels, however, causes serious environmental issues, including global warming, ozone layer depletion and acid rains. A sustainable solution to the issues is to replace the fossil fuels with renewable ones. Implementing such a solution, however, requires overcoming a number of technological barriers including low energy density, intermittent supply and mobility of the renewable energy sources. A potential approach to overcoming these barriers is to use an appropriate energy carrier, which can store, transport and distribute energy. The work to be reported in this paper aims to assess and compare a chemical energy carrier, hydrogen, with a physical energy carrier, liquid air/nitrogen, and discuss potential applications of the physical carrier. The ocean energy is used as an example of the renewable energy sources in the work. The assessment and comparison are carried out in terms of the overall efficiency, including production, storage/transportation and energy extraction. The environmental impact, waste heat recovery and safety issues are also considered. It is found that the physical energy carrier may be a better alternative to the chemical energy carrier under some circumstances, particularly when there are waste heat sources.

Keywords: Energy carrier, energy storage, liquid air/nitrogen, hydrogen, renewable energy, ocean energy

1. Introduction

Burning of fossil fuels as the main cause of some serious environmental issues such as greenhouse effect, ozone layer depletion and acid rains has long been recognized [1]. An obvious (and also hard) solution is to replace the fossil fuels with renewable ones such as wind, solar, ocean energy etc [2]. Currently, the renewable energy resources account for ~ 5% of global power capacity and 3.4% of global power generation excluding large hydropower (which is about 15 % of the global power generation) [3]. Like a number of other countries, the UK government has set a target for electricity generation from renewable resources to be increased from about 4.6% at present to 20% by 2020, and EU proposed recently an even higher goal of between 30 and 40% [4].,As a consequence, significant efforts have been made in the renewable energy research and these efforts have been mostly focused on solar, wind, biomass and geothermal sources. While these sources are very promising, the world's oceans could emerge as an important source to provide economically viable renewable sources [5]. Ocean winds blow harder and with more reliable consistency than the wind on land, which more than offsets the greater cost of building offshore wind power facilities. Oceans tides also contribute massive amounts of renewable energy that is gravitationally derived through the interplay of the earth and the moon. The energy from ocean waves and tidal streams, along with ocean-based wind energy, make the world's oceans a source of renewable energy that may in the next few decades greatly outstrip solar energy as an economical alternative.

However, renewable energy sources particularly wind and solar are intermittent and they often do not match the actual energy demand. This makes the energy storage and power management increasingly important. There have been reports that the amount of wind energy that could be utilized is seven times greater than the current situation if a stable storage facility is available [6]. Energy storage refers to a process for storing energy produced at times of low demand and low generation cost and releasing at times of high demand and high generation cost or when there is no more generation capacity available. The stored energy can be in the form of either potential energy (e.g. chemical, gravitational or electrical energy) or kinetic energy (e.g. thermal energy or motion).

This paper is concerned about the use of ocean renewable energy resources. A potential issue for the use of the ocean resource is the remote locations [7], which requires high capital, operation and maintenance costs if the conventional electricity transmission and distribution approaches are used. An alternative is to use an energy storage medium, which can be transported by ships. For such an approach to work the energy storage medium is the key. An ideal energy storage medium is the one that has a high energy density and can be detached easily and completely from the generation and release devices so that they can be transportable. In this sense, the energy storage medium can be regarded as an energy carrier, and the conventional methods of large scale energy storage approaches are less useful. For example, the pumped hydroelectric storage (PHS) method stores the gravitational energy of water, which is not suitable for transportation. The compressed air energy storage (CAES) method stores energy in the form of high pressure air, which has a low energy density and is hence too bulky to transport.

It is well known that hydrogen has been regarded as a popular carrier of renewable energy in remote locations [8; 9; 10]. Using such a chemical energy carrier, the ocean energy generates electricity first, which is then used to electrolyze water to produce hydrogen. Hydrogen is then transported to the end-users for transforming back to electricity or kinetic energy by a fuel cell or other devices. Cryogens normally refer to as liquid media at a temperature below ~ -150℃ and are physical energy carriers [11]. Examples of the cryogens include liquefied natural gas (LNG), liquid air and liquid nitrogen. The use of liquid air/nitrogen as an energy carrier is not commonly known until fairly recently [12; 13; 14; 15]. Energy storage using liquid nitrogen / liquid air involves the production of the cryogen through an air separation and liquefaction process. The cryogen is then transported to end-users where it is heated using the environment heat, waste process heat or heat from renewable resources (e.g. solar) if available and expands to generate electricity using a cryogenic heat engine. As a renewable energy carrier, cryogen can also provide direct cooling and refrigeration, air conditioning units and acts as power source for vehicles and ships.

Fig. 1 illustrates schematically the use of ocean energy with hydrogen and cryogen as the energy carriers. This paper assesses and compares the performance of two energy carriers mainly for the use of ocean renewable energy though the results are expected to be applicable to other renewable energy resources. Liquid air and nitrogen will be used as the model cryogens. The assessment includes production, storage/transportation and energy extraction processes as well as their environmental impacts and safety issues. Note that hydrogen in its liquid form is also a cryogen. For clarity and conciseness, liquid hydrogen will not be referred as a cryogen in this paper.

2. Carrier production

Two main technologies used to produce hydrogen are considered in this work, reforming reaction and water splitting. The most common hydrogen production method in commercial use today is the former, which uses hydrocarbons or other chemical compounds such as coal and biomass as feed stocks. However, as the renewable resources considered here (wind, tides and waves) contain only the mechanical energy of moving masses of air or water, direct chemical path of hydrogen production is to split water using electrical energy generated by the kinetic energy of renewable resources. Therefore, hydrogen production using the ocean resources can be described as follows. The kinetic energy of moving masses (air/seawater) is extracted first by mechanical machines to form the mechanical energy of the machines. The fraction of extractable power depends on the form of energy and extraction processes and devices, and is limited by a theoretical value determined by the thermodynamics. For example the upper bound of the wind energy extraction by an ideal horizontal axis machine is 0.593 (power coefficient) under some rather general assumptions. Then the mechanical energy of the mechanical machines is converted to electricity with a conversion efficiency of about 75-95%. Finally, the electrical energy is employed to produce hydrogen by electrolysis. **Table 1** summarizes the performance of electrolysis technologies, along with their feedstock and efficiencies (defined as the low heating value of hydrogen produced divided by electrical energy consumed in the electrolysis cell) [16; 17; 18]. In the summary table, the high temperature electrolysis efficiency is dependent on the temperature at which the electrolyzer operates and the efficiency of the thermal energy source. If everything is considered, the efficiency of converting mechanical energy to chemical energy (hydrogen) is within a range of 37.5 - 66.5%.

As mentioned above, the cryogen production is done by the air separation/liquefaction process in which cryogenic or Stirling engine coolers liquefy the main components of air through the well-known Joule–Thomson effect, see **Fig. 2**. This is different from the hydrogen production process as discussed above as both the compression and refrigeration processes in the liquefaction process could be directly powered by the mechanical work of the ocean energy. Therefore cryogen production could be more competitive than hydrogen production in terms of the overall efficiency and capital costs as the electricity conversion process is essential in the cryogen production end. However cryogen production is an energy-intensive process. Currently the efficiency of practical air liquefaction plants strongly depends on the plant scales; see **Table 2** for the typical data of cryogenic industry [19]. Note that the efficiency of air separation / liquefaction plants with a capacity of few tons/day of liquid nitrogen are about 50% [20], and there are reports that the efficiency could be further enhanced to 60% and higher [21; 22; 23].

3. Carrier storage/transportation

As the energy carriers are produced at the offshore power generation facility, they have to be stored and transported to an onshore location for distribution to the end-users. Hydrogen could be delivered to onshore facilities through one of the three forms: gas (compressed), liquid (liquefied), or solid (in a solid hydrogen carrier). In the gaseous form, hydrogen can be compressed and transported to onshore in pressurized containers. Because of its low molecular weight, hydrogen molecules are very small and leakage can be an issue particularly at high pressures. Because of this, the storage pressure of hydrogen is limited to ~ 35 MPa at present. Liquefaction of hydrogen and its transportation in containers are an established technology. However, the liquefaction process is energy-intensive and about 30-40% of the energy content is lost in the liquefaction process [24]. Because of its added complexity and costs for both generation and transportation, the use of liquid hydrogen is not regarded as an attractive option.

Table 3 shows the volumetric capacity of hydrogen under different conditions. The energy density increases linearly with increasing storage pressure, and liquid hydrogen has a higher value. As mentioned above, high-pressure storage of hydrogen gas is limited by the weight of the storage canisters and possible leakage development. This imposes potential safety issues [25]. A promising way to replace the conventional hydrogen fuel storage methods is to use a solid state hydrogen carrier, which refers to any substance that can store and transport hydrogen in either a chemical or a physical state. The advantages of using solid carriers are better safety and reliability in comparison with liquid or compressed gas storage methods. The carrier is charged with hydrogen at the offshore generation site and transported to onshore where hydrogen is stripped off. The carrier needs to be taken back for recharging (two-way carrier) or decomposed at the point of hydrogen use (one-way carrier). Examples of hydrogen carriers include ammonia (one-way) and liquid hydrocarbons and metal hydrides (two-way). It is reported that some of the hydrogen carriers could attain a volumetric capacity as high as liquid hydrogen [26; 27]. However the weight of current hydride substrates and their container is much greater than that of the stored hydrogen, so extra energy is required during both charging and discharging processes. While considerable research has been done on the hydrogen carrier technology, no reports have been found so far on the commercial use of the carriers.

Compared to hydrogen, the delivery of cryogen is much easier. Once produced and stored in insulated containers, cryogen is ready to be delivered. No extra energy required except for the pumping power consumption which is negligible for a liquid. As shown in **Table 3**, the volumetric energy density of cryogen is much lower than liquid hydrogen but at the same order of magnitude with compressed hydrogen. It should be noted that the volume-based energy densities of both cryogen and compressed hydrogen gas (at practicable pressures) are significantly lower than that of traditional fossil fuels.

The only energy loss of cryogen is the heat dissipation of cryogenic tank at the ambient pressure which can be less than 1% per day in an insulated Dewar using conventional insulation technologies.

4. Energy extraction

Upon delivered to end users' side, the energy stored in the energy carriers is extracted. Current technologies converting the chemical energy of hydrogen to mechanical energy or electricity energy use one of the two methods, combustion and electrochemical conversion in e.g. a fuel cell.

For the combustion method, both hydrogen internal combustion engines and hydrogen fuelled gas turbines have been investigated [28; 29; 30; 31]. Because of high burning temperature, hydrogen internal combustion in a conventional engine produces a very high level of nitrogen oxides which cause environmental problems. Although there are a number of ways to decrease nitrogen oxides emissions, this will decrease the efficiency of the engine at the same time. This is serious as currently the low heating value (LHV) efficiency of internal combustion is only 20~35%. Another approach is the use of gas turbines in hydrogen fueled combustion prior to which pure oxygen is generated from an air separation unit to avoid the production of nitrogen oxides. In such a process, liquid water is often used as a mixing fluid to decrease the turbine inlet temperature, see **Fig. 3 (a).** Here water is preheated by the exhaust gas from the gas turbine. Different from the internal combustion, the burning temperature of these cycles is limited by the turbine inlet temperature (TIT) which is currently about 1300℃. In these cycles the exergy loss mainly is caused by preheating and mixing of the three input stream reactants in the combustor and accounts for about 40~50%. This, plus the energy consumed by pure oxygen production, the overall LHV efficiency of this type of cycles is limited to about 50% using current technologies and may increase to about 60% if the turbine inlet temperature is increased to ~2000℃ with future developments in turbine and material technologies [32].

A different approach to the direct combustion of hydrogen is the so-called chemical-looping method for extraction of hydrogen chemical energy as shown in **Fig. 3 (b)**. Such a method uses two successive reactions, metal oxide reduction with hydrogen, and subsequent oxidation of the metal by air, yielding the metal oxide and a high-temperature flue gas. The resulting high temperature gas is then used to power turbines. By adding a chemical-looping process, the exergy loss in the combustion process decreases significantly [33; 34]. It is claimed that the LHV efficiency of hydrogen in such a cycle could be as high as 63% [32; 35].

Another approach for enhancing hydrogen energy extraction efficiency is the use of fuel cells, which could replace internal combustion engines and turbines as a primary way to convert chemical energy to kinetic or electrical energy. Fuel cells work via electrochemical principles, and hence are more efficient than heat engines. **Table 4** [36; 37; 38] lists the technical information of three types of hydrogen fuelled fuel cells including typical efficiencies, operating temperatures, catalysts and other operating parameters, where the efficiency refers the cell efficiency and the system efficiency is generally 10% lower. However, there are still a number of barriers for the industrial take-up of the fuel cell technologies; these include requirements for high purity of hydrogen, high costs to manufacturing, low cell reliability and short service life. For example, the cost of fuel cell technologies is about 4-5 times more expensive than the combustion engines / turbines, while its service life 2-3 times shorter [39].

In contrast to hydrogen, energy extraction from cryogen is much more straightforward and easier. Liquid air/nitrogen is heated and expands to produce power. This is similar to a steam engine but expansion of cryogen does not emit pollutants such as NO_X and particulate matters etc. Heating of the cryogen uses the free environmental heat. However, the exergy efficiency of this approach is limited to about 40% as a considerable portion of the exergy is in the form of cold, which is wasted during the heating process. In order to improve the efficiency, combined cycles are studied to recover the waste cold energy by integrating the direct expansion of cryogen with other cycles, see **Fig. 4** for an example where a direct expansion-Rankine hybrid cycle with propane as the working fluid for the Rankine cycle. The combined methods for cryogenic energy extraction has been discussed in detail by the authors in Ref [40]. It has been concluded that the combined cycle cryogenic heat engines could have an exergy efficiency of 65~78% under ideal conditions [12; 41].

The exergy efficiency of cryogen expansion could be further enhanced if the working fluid is superheated by waste heat or heat from other renewable sources such as solar. At present, only high grade waste heat in gas turbine power cycles could be recovered efficiently by heat recovery steam generator (HRSG) technology while low grade heat is generally vented. The use of a cryogen expansion cycle can be a very effective way to recover such low grade heat as the boiling point of air or nitrogen is much lower than the ambient temperature. Chen et al. [41] claimed that the exergy could be improved from ~78% to 117% if the working fluid were superheated to ~100^oC, and the exergy efficiency could be doubled if the waste heat is as high as 300^oC. Note that here the waste heat is regarded as a free energy source in the calculations by Chen et al. [41].

5. Concluding remarks and outlook

This paper assesses and compares two energy carriers, hydrogen and cryogen, for exploitation of ocean energy sources. The assessment and comparison are based on the overall efficiency including production, storage/transportation and energy extraction. The environmental impact, waste heat recovery and safety issues are also touched upon. The following observations are drawn:

- The production efficiencies of hydrogen and cryogen are similar at 40 ~ 65% based on the current technologies. However, cryogen may be more competitive than hydrogen as an energy carrier in terms of capital costs because there is no electricity conversion at the cryogen production end.
- As an energy-intensive process which consumes up to ~ 40% of the chemical energy, pretreatment is required for the storage and transportation of hydrogen regardless of the form of the carrier being compressed gas, liquefied hydrogen or solid hydrogen carrier. In addition, the hydrogen carrier transportation may be two-way if the two-way carrier is adopted. In contrast, transportation of cryogen requires neither pretreatment nor other carriers but insulated containers. However it should be noted that hydrogen has a higher volumetric energy density than cryogen regardless of storage forms.
- The energy extraction efficiency of hydrogen depends significantly on the conversion methods. Currently, gas turbine and fuel cell methods have better performances than conventional internal combustion engines though significant developments are needed in order for the fuel cell technologies to be competitive. Cryogen engines, if cold recovery technology is employed, may have an even higher efficiency than the fuel cell technologies.
- Waste heat especially low grade heat could be recovered efficiently by the use of cryogen engines.
- Although hydrogen is regarded as a clean fuel, nitrogen oxides can be produced if air is used as an oxidant. Cryogen is much more environmentally friendly as the processes of production (using the ocean energy) and extraction are both physical involving no chemical transformation. Even the transportation of the cryogen can be cryogen-based.

Overall, hydrogen is viable as an ocean energy carrier only if a practical method to store and carry hydrogen is introduced and fuel cells become cheap, more tolerant to impurities of hydrogen, and with their service life much improved. Before these are achieved, cryogen appears to be a more attractive energy carrier as there are few technical difficulties to overcome. Moreover, the overall efficiency of the use of cryogen can be greatly increased if low grade heat is used in the process of cryogen energy extraction. The low grade heat can be obtained from either traditional heavy industrials like power plants or directly from the abundant renewable solar energy. As mentioned before, the electricity conversion efficiency of solar energy is limited; it is much easier to use solar thermal energy in countries blessed with good sunshine (e.g. India with a mean daily solar radiation of 5-7kW/m^2[42]) via e.g. a cascading way. Solar energy, along with the thermal energy storage technology using e.g. phase change materials, has been extensively studied and used for heating, cooking and even electricity production [42; 43; 44; 45]. Therefore, a solar-cryogen hybrid energy storage system appears to be a promising way for both transportation system and electricity production. In such a system, solar energy is stored in the form of heat in e.g. phase change materials and other renewable energy like ocean energy is stored in cryogen. After transported to end users, the two energy sources are combined to produce kinetic power or electricity, using the cryogen as the working fluid. As both the heat and cold sources are generated by renewable energy sources and there are no chemical reactions involved, the system can be very environmental friendly and sustainable.

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List of Tables:

Table 1
Efficiencies of the different electrolysis technologies

Electrolysis Technology	Feed stock	Efficiency	Maturity
Alkaline Electrolyzer	water + electricity	50 ~ 60%	Commercial
PEM Electrolyzer	water + electricity	55 ~ 70%	Near term
Solid Oxide Electrolysis Cells	water + electricity + heat	40 ~ 60%	Med. Term

Table 2
Real world efficiency for liquid air/nitrogen production in typical cryogenic industry

Plant Scale (Litres/hour)	100	1000	5000	10000
Efficiency of liquid air production	~0.11	~0.31	~0.37	0.4 ~ 0.5
Efficiency of liquid nitrogen production	~0.11	~0.25	~0.30	0.35 ~ 0.4

Table 3
Volumetric capacity of energy carriers under different conditions

Energy Carrier	Liquid Air	Liquid Nitrogen	Compressed Hydrogen				Liquid Hydrogen
Pressure (bar)	1	1	50	150	250	350	1
Volumetric capacity (kWh/m^3)	177	171	133	377	593	785	2360

Table 4
Efficiency of hydrogen fuel cells

Fuel cell type	Operating temperature (°C)	Electrolyte	Catalyst, anode	Electrical efficiency (%)	Qualified power (kW)
Alkaline (AFC)	70 ~ 100	KOH (aqueous solution)	Ni	60 ~ 70	10 ~ 100
Proton exchange membrane (PEM)	50 ~ 100	polymer membrane	Pt	50 ~ 70	0.1 ~ 500
Phosphoric acid (PAFC)	150 ~ 220	Phosphoric acid (immobilized liquid)	Pt	40 ~ 55	5 ~ 10000

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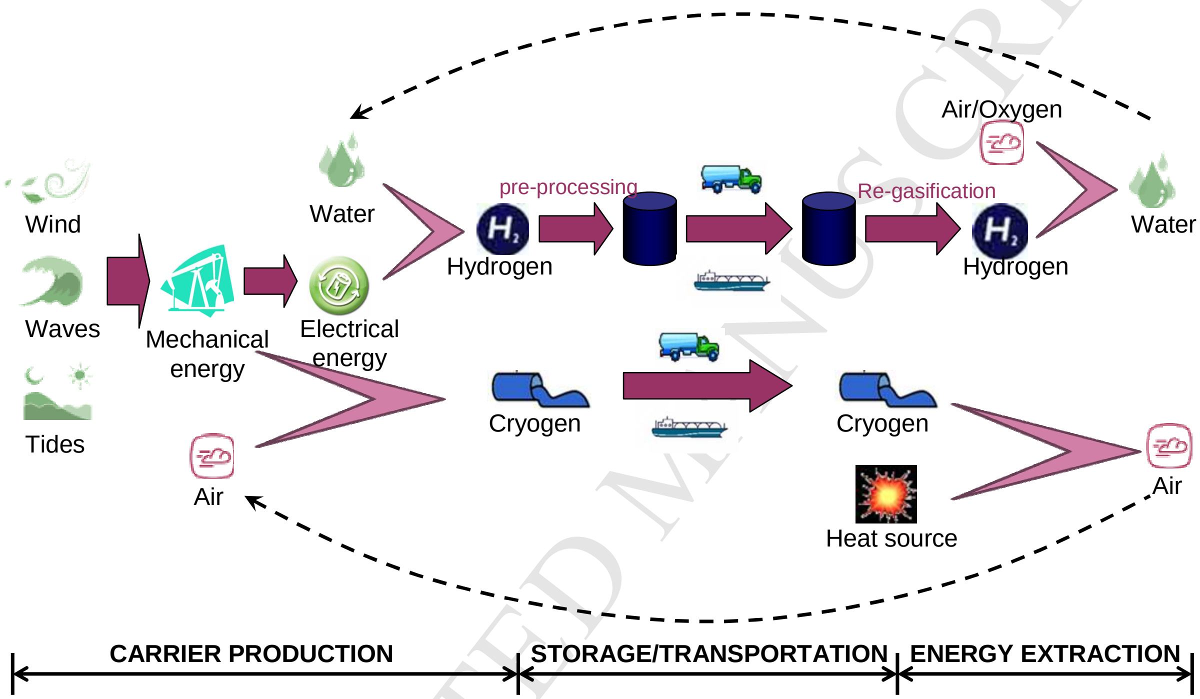

Fig. 1 Diagram of Ocean Energy Utilization

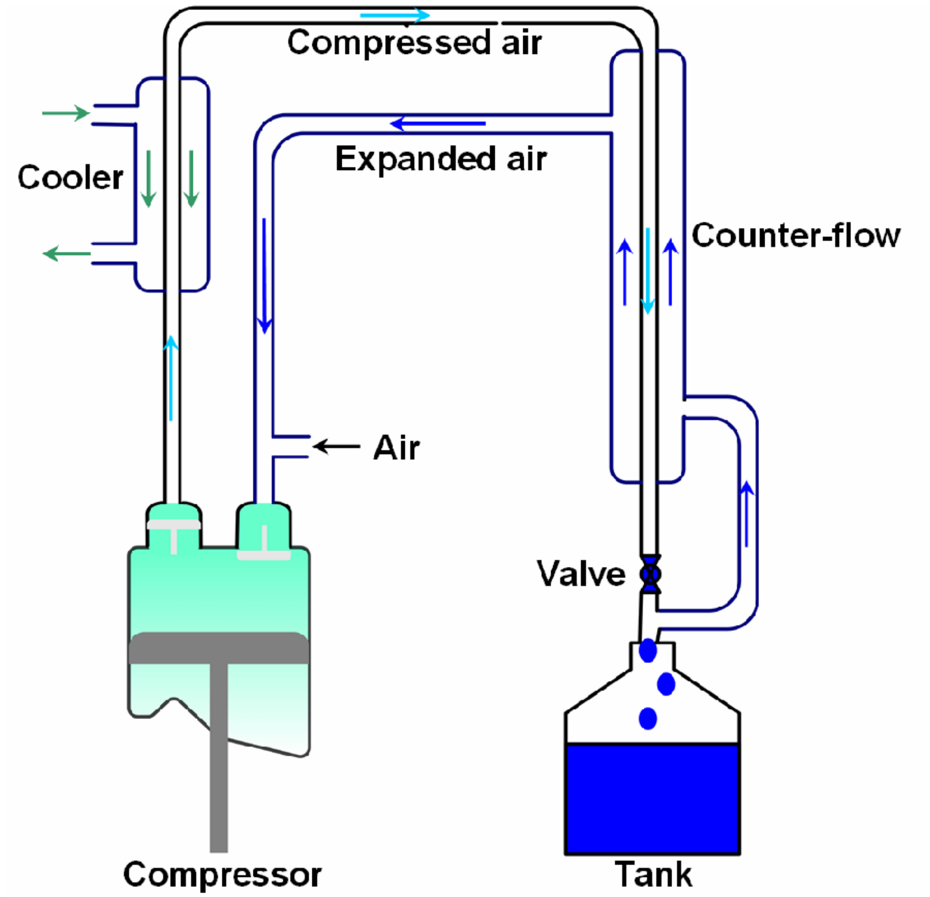

Fig. 2 Simple process of air liquefaction

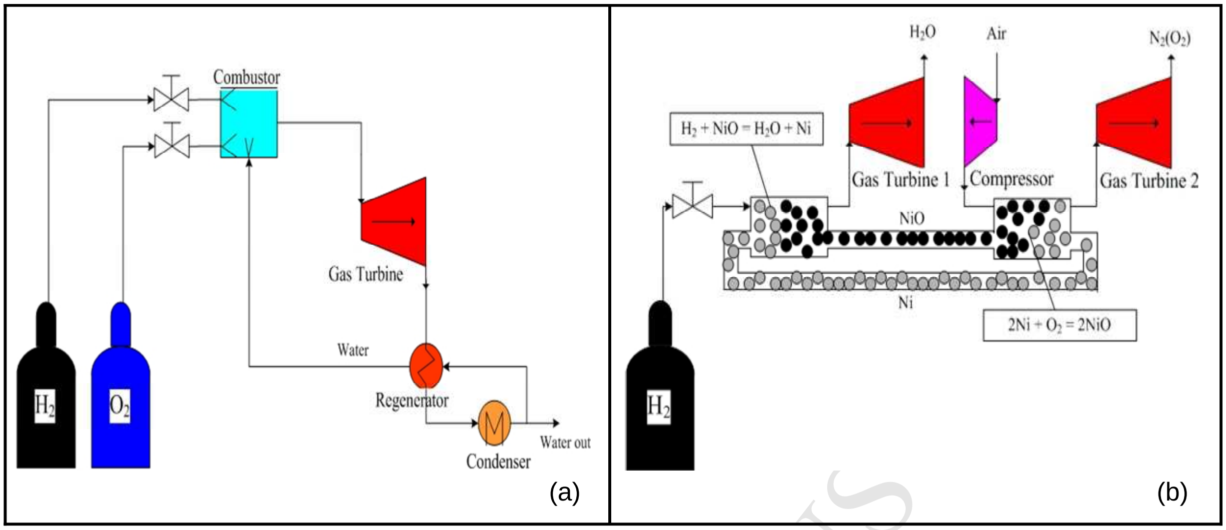

Fig. 3 Diagrams for hydrogen fuelled gas turbine cycles

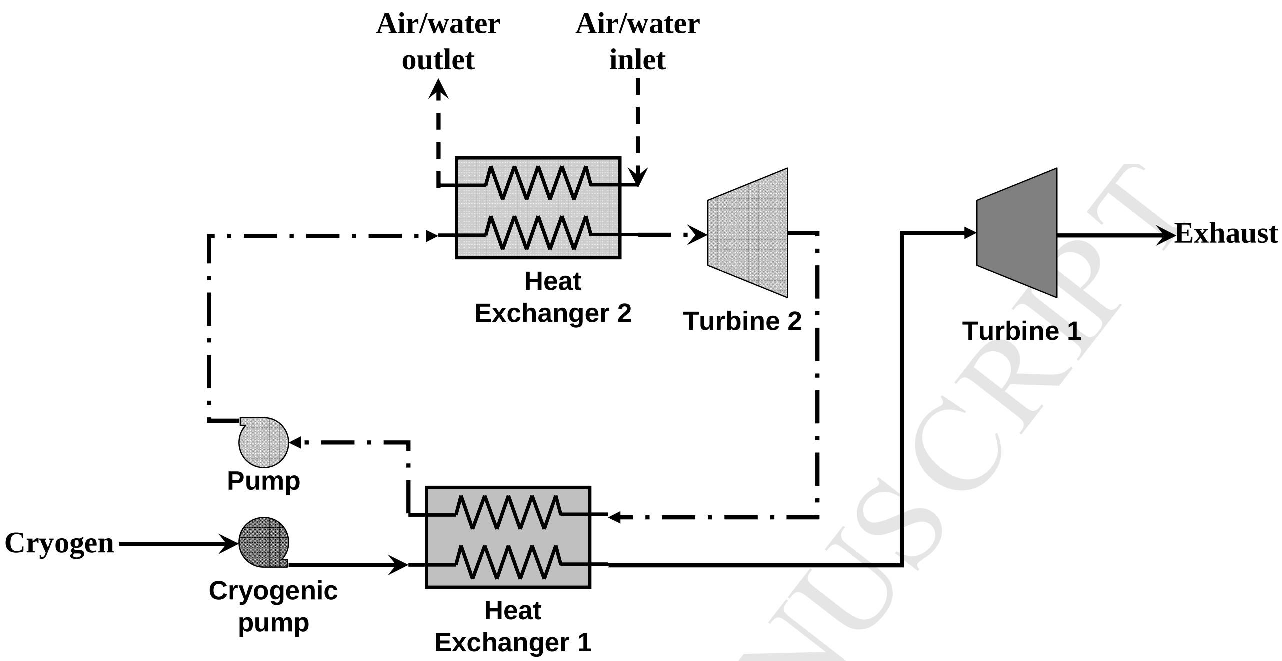

Fig. 4 Schematic diagram of a direct expansion-Rankine hybrid cycle