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# Proposal of an innovative, high-efficiency, large-scale hydrogen liquefier

*Gianluca Valenti**, *Ennio Macchi*[1]

*Dipartimento di Energia, Politecnico di Milano, P.zza L. da Vinci, 32, 20133 Milano, Italy*

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ABSTRACT

An innovative, efficient and large hydrogen liquefier is described. Innovations lie in the fact that (i) the feed, $10\,kg\,s^{-1}$, is refrigerated in heat exchangers catalytically promoting the ortho–para conversion (ii) down to the low temperature of 20.5 K and at the high pressure of 60 bar at which it is available and (iii) lastly expanded to the storage conditions of 1.5 bar and 20 K through a liquid-phase turbomachine; (iv) refrigeration is via four helium recuperative Joule–Brayton cycles arranged so that the refrigerant follows the cooling curve of hydrogen and the volume flow rates in compression and expansion processes are typical of axial-flow high-efficiency turbomachines; (v) compression is accomplished in 15 intercooled 8-stage devices derived from gas turbine technology. Heat exchangers require specific surfaces comparable to current state-of-the-art liquefiers. Nevertheless, the predicted work of approximately $18\,MJ\,kg^{-1}$ is half as much as the requirement of those liquefiers and corresponds to a second-law efficiency of almost 48%.



## 1. Introduction

High hydrogen liquefaction work is often emphasized as one of the major barriers for the realization of a hydrogen economy. This criticism orginates from the simple observation or straight extrapolation of the state of the art in the liquefaction technology, as done by Bossel [1]. Currently, though, the world liquefaction capacity is small and liquefiers are a compromise between cost and efficiency. Plants are often relatively simple modifications of the well-known Claude cycle and their second-law efficiencies reach values in the 20–30% interval. However, in the long-term scenario of the use of liquid hydrogen as an energy carrier in the transportation sector, global capacity and liquefier sizes increase by orders of magnitude. Thus, in the last decades a dozen publications have investigated complex modifications of the Claude cycles as well as have proposed innovative schemes with the common scope of maximizing the efficiency. Some of them aim to achieve values above 40% and solely Quack above 50% [2].[2]

The present paper describes an innovative, high-efficiency and large-scale liquefier that is to be coupled with coal integrated gasification combined cycles plants comprising carbon capture and storage technology, as described by Valenti and Macchi at the HYSYDAYS 2007 conference [3,4].

## 2. Plant development and simulation

The liquefier development takes into consideration a number of fundamental design criteria and decisions that are outlined

*Corresponding author. Tel.: +39 02 2399 3845; fax: +39 02 2399 3863.
E-mail addresses: gianluca.valenti@polimi.it (G. Valenti), ennio.macchi@polimi.it (E. Macchi).
[1] Tel.: +39 02 2399 3907.

[2] Quack gives two estimates of the second-law efficiency: 60.7% that reduces to 53.8% if pressure drops are included in the calculations. Moreover, Quack adopts a dead-state temperature of 300 K, whereas the present work assumes one of 288.15 K.

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in the sections following the next paragraph which reports the assumptions made in modeling the plant.

### 2.1. Modeling assumptions

The conceptualized liquefier involves equilibrium-hydrogen and helium as refrigerated and refrigerant fluids, respectively. It is simulated on the computer with the aid of the commercial software Aspen Plus ver. 13.2, developed by Aspen Tech, which includes a wide databank and robust routines for fluid property calculations. However, rather than adopting the built-in correlations and coefficients for hydrogen, a careful calibration of the models for both the ideal gas isobaric heat capacities and the equation of states is accomplished in order to represent more accurately the whole working region. In particular, values of the heat capacity in the ideal gas state for parahydrogen and normal-hydrogen are derived from literature and combined with values of enthalpy of ortho-to-para conversion, taken as well from literature, to yield tabular values of heat capacity for equilibrium-hydrogen. Moreover, the Benedict–Webb–Rubin–Starling equation of state is adopted for all forms of hydrogen along with parameters regressed against volumetric data that are publicly available. Details and references are included in [3]. The developed thermodynamic package for hydrogen is successfully validated against the operating parameters of the existing hydrogen liquefier located in Ingolstadt, Germany, and outlined by Bracha et al. [5]. In contrast, the standard Soave–Redlich–Kwong is utilized for helium. Finally, the other parameters assumed in the simulation can be seen in Table 1 and the conceived scheme in Figs. 1 and 2.

**Table 1 – Values of main parameters assumed in the simulation of the proposed liquefier**

| Parameter (unit) | Value |
|---|---|
| Liquefaction capacity ($kg\,s^{-1}$) | 10 |
| Temperature (K) | |
| Dead state | 288.15 |
| Helium intercooling | 298.15 |
| Minimum temperature difference (K) | |
| Hydrogen coolers | 2 |
| Helium recuperators | 4 |
| Percentage pressure drop (%) | |
| Coolers and recuperators | 2 |
| Helium intercoolers | 1 |
| Polytropic efficiency (%) | |
| Helium compressors | 92 |
| First helium turbine | 93 |
| Second helium turbine | 92 |
| Third helium turbine | 90 |
| Fourth helium turbine | 88 |
| Hydrogen turbine | 85 |
| Electro-mechanical efficiency (%) | 96.7 |
| Dry tower consumption ($kW_e\,MW_{th}^{-1}$) | |
| Air fans | 3.4 |
| Water–glycol pumps | 2.2 |

In particular, minimum temperature differences are derived from industrial practice and polytropic efficiencies from state-of-the-art turbomachines.

### 2.2. Hydrogen refrigeration and expansion

Hydrogen is assumed to be received from the IGCCs as normal-hydrogen at 99.999% purity, 60 bar, 300 K, and to be delivered to storage tanks as subcooled liquid equilibrium-hydrogen at 1.5 bar and 20 K. Dead state is taken to be 15 °C. The capacity is $10\,kg\,s^{-1}$ of liquid hydrogen corresponding to an output of 1200 MW, with respect to its lower heating value, and exceeding by far that of any built or proposed liquefier. This assumption is in agreement with the scenario of a wide penetration of liquid hydrogen in the transportation sector.

The conversion from the ortho to the para form of hydrogen, which is more and more exothermic with temperature decreasing as documented by McCarty et al. [6], is carried out while refrigerating the feed because this continuous process allows for a lower work requirement compared to the batch-wise process realized by separated reactors. This is achieved technically by packing the hydrogen side of the heat exchangers with an appropriate catalyst [7]. Hydrogen is refrigerated close to the storage temperature, while it is maintained at high pressure, and is expanded thereafter through the single-phase liquid region directly to storage conditions. The expander, indicated by T0 in Fig. 1, replaces the throttling valve commonly employed in built or investigated liquefiers, thus avoiding vapor generation and minimizing entropy production. As a matter of fact, if a throttling valve is used to yield liquid exclusively, the refrigeration process must reach temperatures lower than the storage temperature and requires at least two stages to avoid solidification, increasing complexity and penalizing performance as shown in Fig. 3. In contrast, if the expansion is used from higher temperatures, a portion of the refrigerated fluid flashes to vapor. The vapor may be returned recuperatively to ambient temperature, as frequently opted, adding again complexity and irreversibility though. A number of authors suggest to employ a wet expander instead of the valve; Quack [2] to execute a cold-end re-compression and re-refrigeration of the flashed vapor. These suggestions may mitigate the difficulty related to the hydrogen expansion, but the single-phase expander solves it substantially.

### 2.3. Helium recuperative Joule–Brayton cycles

After analyzing a series of diverse schemes, a cascade of four helium reversed, closed and recuperative Joule–Brayton cycles has been selected. Helium is taken because it has (i) a critical temperature lower than hydrogen and (ii) an excellent heat exchanging capability. As shown later, helium compressors and expanders necessitate an appreciable number of stages, due to its low molar mass, without anyhow penalizing the overall economics as shown in [4]. Given the choice of four cycles, the plant comprises four expanders, indicated by T1–T4 in Fig. 1, four hydrogen coolers, X1–X4, and only three helium recuperators, R2–R4, since the higher temperature cycle does not require recuperation. The cycles are organized such that all share the same maximum pressure but have different minimum ones, an arrangement

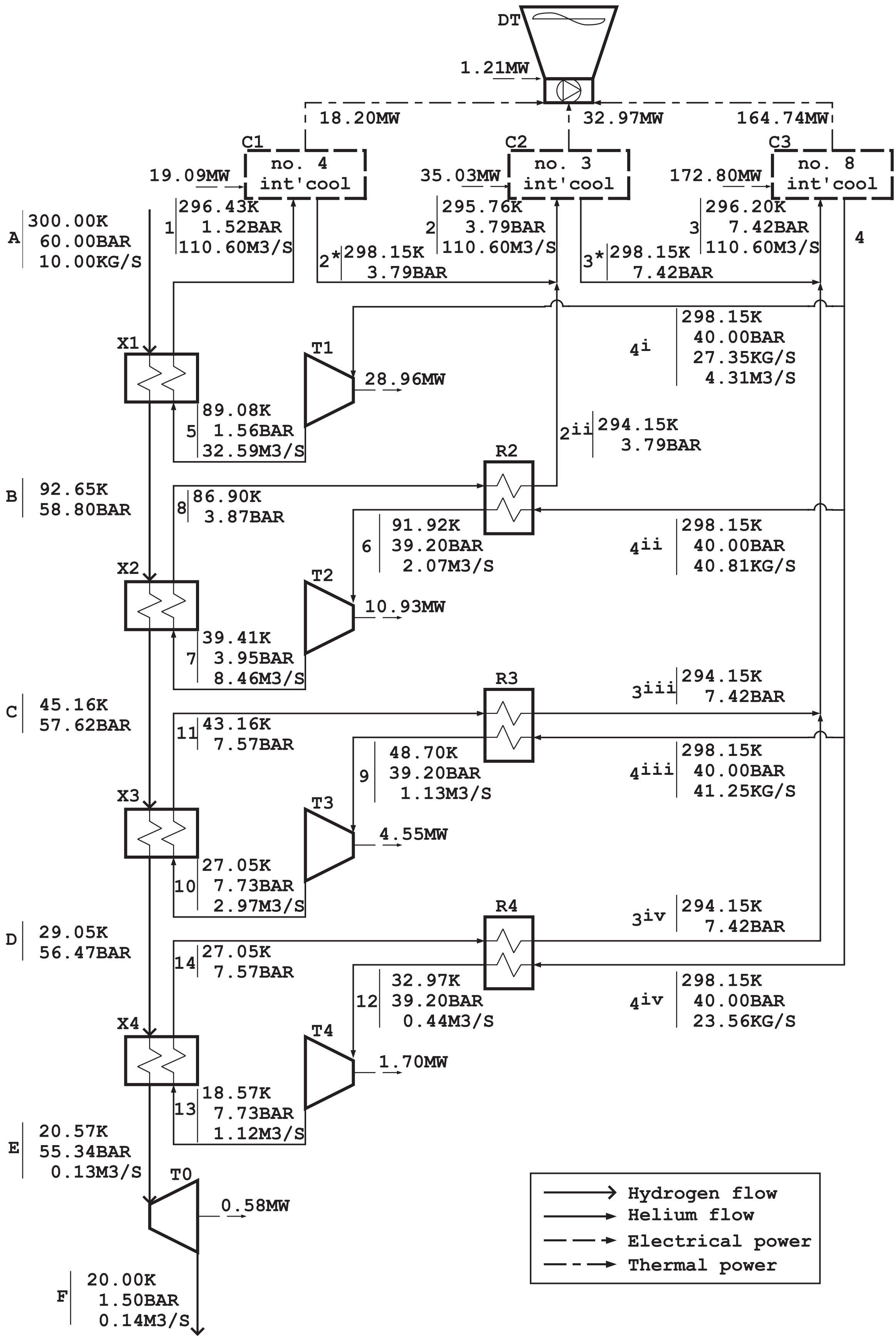


**Fig. 1 – Layout of the plant detailed with results of temperature, pressure and mass flow rate for hydrogen and helium flows; volumetric flow rate and electric power for compressors, expanders and dry cooling towers.**

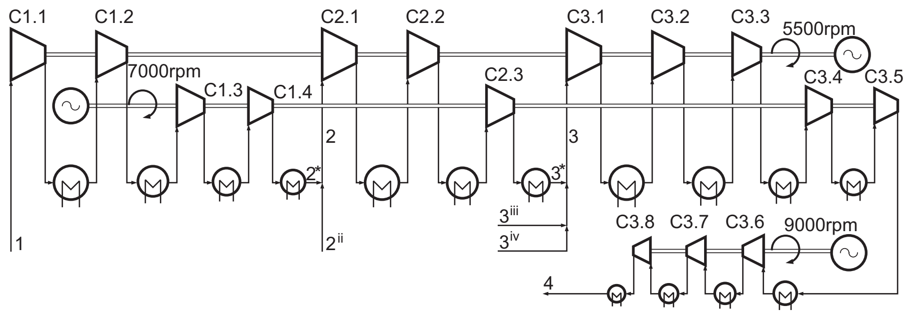


**Fig. 2 – Layout of the 15 intercooled compressors showing the adopted three-shaft arrangement and the chosen rotation speeds.**

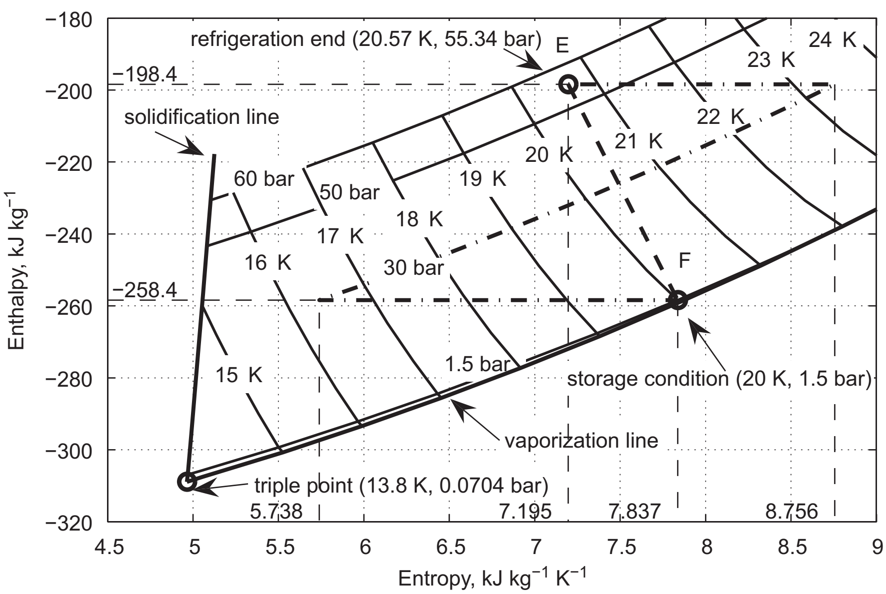


**Fig. 3 – Comparison between expansion in the single-phase liquid region executed with an expander, direct path EF, and two valves, indirect path EE′F′F. At least two valves are necessary to avoid solidification. In the expander process shaft work is generated, whereas in the valves process refrigeration work is required, segment E′F′. Enthalpy difference in the direct path is 60.00 kJ kg$^{-1}$, exergy difference in the indirect is 809.6 kJ kg$^{-1}$. Assuming a second-law efficiency equal to that of the plant, about 48%, in the indirect path 1687 kJ kg$^{-1}$ of mechanical work is required. If 10 kg s$^{-1}$ of hydrogen is liquefied, 0.60 MW is produced with the expander while 17 MW is required with the valves, which proves the advantage of the single-phase expander over the valves.**

that permits a favorable condition for the compression of the refrigerant as motivated later on. The analysis of the heat transfer between hydrogen and helium shows that the optimal expansion ratio of the cycles decreases from high to low temperature. For technical considerations on the compression process, the third and fourth cycles are taken to have the same ratio. Consequently, the plant includes three compression sections placed in series, denoted by C1–C3, so that C1 processes helium from the sole first cycle, C2 from the second cycle mixed with C1 outlet and C3 from the last two cycles mixed with C2 outlet, as shown in Figs. 1 and 2. Minimum pressures, mass flow rates and hot side outlet temperatures of heat exchangers are tuned simultaneously to optimize heat transfer curves of all exchangers and to achieve identical volumetric flow rates entering the three compression sections, as detailed in [3]. Maximum pressure is instead a free parameter that affects this unique value of the three volumetric flow rates. In particular, the choice of a maximum pressure of 40 bar results in flow rates entering C1–C3 of about 110 m$^3$ s$^{-1}$, which is typical of large aeroderivative compressors. Within each section, compression is accomplished in an intercooled fashion. The number of intercoolers for each section is determined as the one that returns the optimum condition between the two opposite phenomena of reducing the compression work and increasing the total pressure drop. The analysis of the simulations shows that the optimum number of intercoolers is four for the first compression section, three for the second and eight for the last.

## 3. Plant component preliminary design

The liquefier efficiency is strongly affected by the quality of all its components: turbocompressors, turboexpanders and heat exchangers. A preliminary design of them is provided next in order to prove that high-performance operational units can be manufactured.

### 3.1. Compressors and expanders

Volume flow rates and specific work of all compressors are typical of medium-sized axial-flow machines. The approach of employing gas turbine technology has been positively applied in the past to the investigation of helium turbomachinery of nuclear power plants [8]. A mid-stage of the low-pressure compressor of the intercooled LMS100 gas turbine manufactured by General Electric is taken as reference in the preliminary design of the compressors through the theory of similitude. Technical information on the gas turbine is provided by Reale and by Ramachandran and Conway [9,10]. The first stage of all compressors is taken to be in similitude with the reference stage. Subsequent stages are designed at constant mean diameter. All compressors are assumed to be mounted alternatively on three different shafts, which are illustrated in Fig. 2, allowing for an almost optimal combination of specific speed and specific diameter for all their stages. As a result, all compressors have eight stages each, an almost constant profile in the meridian plane, an inlet diameter falling in the 1.43–0.85 m interval and a rotation speed in the 5500–9000 rpm. In its turn, intercooler technology can be derived directly from the experience of the LMS100.

Given the flow rates and the enthalpy drops involved, also hydrogen and helium expanders can be designed of the axial-flow type with the aid of an in-house software based on the one-dimensional analysis and the empirical correlations described by Macchi and Perdichizzi [11]. As a result, the hydrogen (T0) and the two coldest helium turboexpanders (T3 and T4) are single-stage machines rotating at optimal speeds of about 105,000, 31,000 and 38,000 rpm and achieving predicted stage efficiencies of 85.6%, 90.5% and 88.5%, respectively.[3] The two warmest expanders (T1 and T2) are seven- and two-stage single-shaft devices rotating at approximately 12,500 and 25,000 rpm and achieving predicted stage efficiencies in the 92.1–93.4% range. T1 is characterized by speed and power typical of mid-size steam turbine and thus can acquire their technology of reducer gear box and electrical generator. T2–T4 have instead modest power outputs and may be mounted in a geared arrangement with a single electrical generator. Finally, T0 recalls closely a gas microturbine generator, with which it can share the inverter technology.

### 3.2. Heat exchangers

In cryogenic applications heat exchangers are typically of the plate–fin kind. Here, they are investigated implementing the method given in the Engineering Sciences Data Unit manual [12]. Adopting the minimum temperature differences indicated in Table 1, logarithmic mean temperature differences and thermal loads for the hydrogen coolers turn to be in the intervals from 2.30 K to 3.15 K and from 1.10 MW to 29.5 MW, corresponding to efficiencies from 80.9%–98.3%, for the helium recuperators from 4.35 K to 4.50 K and from 32.8 MW to 53.9 MW, corresponding to efficiencies of about 97.8%. For the sake of comparison between the heat transfer requirement in both the Ingolstadt and the proposed liquefiers, the parameter $ua$ is defined as follows:

$$ua \doteq \frac{1}{m_{\mathrm{LH_2}}} \sum_{\text{all heat exchangers}} \frac{Q_j}{\mathrm{LMTD}_j}$$

where the sum is extended to all heat exchangers present in one plant, $m_{\mathrm{LH_2}}$ is the liquefaction capacity, $Q_j$ and $\mathrm{LMTD}_j$ the thermal load and mean log temperature difference for the $j$-th heat exchanger. The $ua$ for the Ingolstadt liquefier is computed to be $4275\,\mathrm{kJ\,kg_{LH_2}^{-1}\,K^{-1}}$, that for the proposed liquefier $4490\,\mathrm{kJ\,kg_{LH_2}^{-1}\,K^{-1}}$ proving that the latter plant does not impose greater heat transfer requirements although it performs much better. Finally, the intercooler refrigeration load is met by dry coolers promptly taken from the refrigeration industry.

## 4. Results and discussion

The detailed prediction of mass and energy flows is indicated in Fig. 1. The computed overall electrical liquefaction work is $18.14\,\mathrm{MJ\,kg_{LH_2}^{-1}}$ that, compared to the computed ideal work of $8.659\,\mathrm{MJ\,kg_{LH_2}^{-1}}$, yields a second-law efficiency of 47.73%. The second-law analysis returns the breakdown of entropy generation as shown in Fig. 4. As expected, the most critical processes are helium compression, including compressors and intercoolers, and heat transfer in all heat exchangers accounting globally for 22.97% and 20.99%, respectively. Fluid dynamic irreversibilities in turbomachines add up totally to 18.31% while pressure drop irreversibilities in heat exchangers to 7.29%. Interestingly, intercooling heat transfer is the largest irreversibility (9.48%) among all despite the high number of intercoolers considered. A slightly lower loss occurs in helium compression (8.92%) thanks to the employment of high-efficiency turbomachines. The same consideration holds for helium and hydrogen expansion (9.39%). Heat transfer irreversibility is important in helium recuperators (7.49%) and, to a lesser extent, in hydrogen coolers (4.02%). Also appreciable is the contribution to losses due to electromechanical conversion in gears, generators and motors (5.01%). Pressure drops are quite affective in intercoolers (4.57%) but less in helium recuperators (1.40%) and hydrogen coolers (1.32%). Dry tower losses are almost negligible (0.67%).

Obtained results are among the best predictions found in literature and second only to Quack [2], who conducted a preliminary design with the intention to set a benchmark for all subsequent investigations.

## 5. Conclusions

An innovative scheme for liquefying the massive rate of $10\,\mathrm{kg\,s^{-1}}$ of hydrogen is described here. The coupling with

[3] With regard to single-stage turbines and to the last stage of multi-stage turbines, the stage efficiency accounts for the partial recovery of exit kinetic energy via a well-designed flow diffuser. With regard to all other stages, the stage efficiency is equal to the total-to-total efficiency.

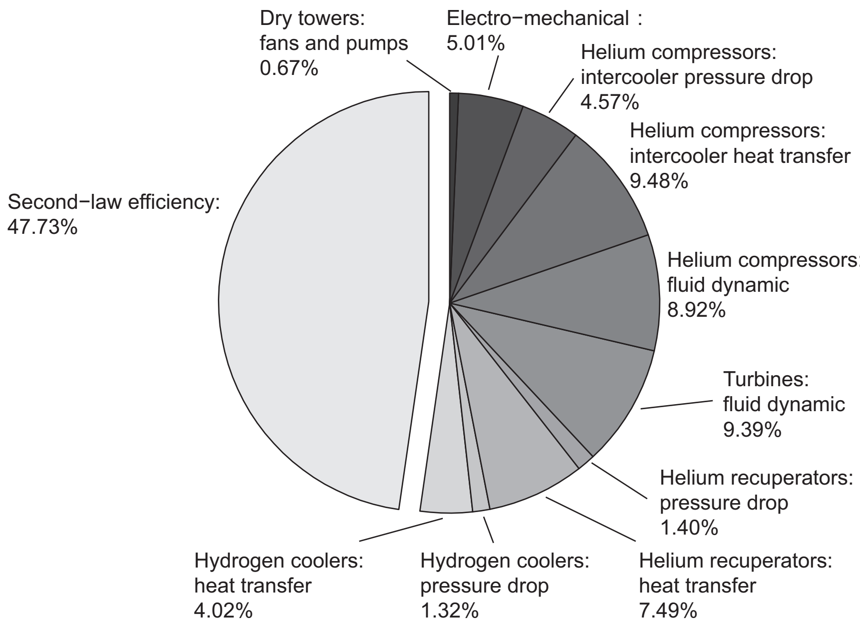


**Fig. 4 – Breakdown of the irreversibilities divided by category.**

high-pressure IGCCs, the optimization of plant parameters and the adoption of components from the best available technology allow for a work requirement as low as about 18 MJ $kg^{-1}$, which corresponds to a second-law efficiency of almost 48% given the inlet condition of normal-hydrogen at 60 bar and 300 K while the outlet of equilibrium-hydrogen at 1.5 bar and 20 K. This work reduction is a fundamental contribution to the rationale of liquid hydrogen in the transportation sector.

## REFERENCES

[1] Bossel U. Does a hydrogen economy make sense? Proc IEEE 2006;94(10):1826–37.
[2] Quack H. Conceptual design of a high efficiency large capacity hydrogen liquefier. Adv Cryog Eng 2001;47:255–63.
[3] Valenti G, Macchi E. Liquid hydrogen: from clean coal to filling station. Part A: proposal of an innovative, highly-efficient, large-scale liquefier. In: HYSYDAYS—2nd world congress of young scientists on hydrogen energy systems 2007, 2007.
[4] Valenti G, Macchi E. Liquid hydrogen: from clean coal to filling station. Part B: analysis of an advanced, highly-integrated, IGCC-liquefier infrastructure. In: HYSYDAYS—2nd world congress of young scientists on hydrogen energy systems 2007, 2007.
[5] Bracha M, Lorenz G, Patzelt A, Wanner M. Large-scale hydrogen liquefaction in Germany. Int J Hydrogen Energy 1994;19(1):53–9.
[6] McCarty R, Hord J, Roder H. Selected properties of hydrogen 1012 (engineering design data). Technical Report Monograph 168, US National 1013 Bureau of Standards (now NIST); 1981.
[7] Lipman MS, Cheung H, Roberts OP. Continuous conversion hydrogen liquefaction. Chem Eng Prog 1963;59(8):49–54.
[8] McDonald CF, Orlando RJ, Cotzas GM. Helium turbomachine design for GT-MHR power plant. In: ASME joint international power generation conference, 1994 [94-JPGC-NE-12].
[9] Reale MJ. New high efficiency simple cycle gas turbine—GE's LMS100. Technical Report GER-4222A, General Electric Company; 2004.
[10] Ramachandran J, Conway MC. MS6001FA—an advanced-technology 70-MW class 50/60 Hz gas turbine. Technical Report GER-3765B, General Electric Company; 1996.
[11] Macchi E, Perdichizzi A. Efficiency prediction for axial-flow turbines operating with nonconventional fluids. J Eng Power Trans ASME 1981;103(4):718–24.
[12] Engineering Sciences Data Unit (ESDU). Item 97006. Selection and costing of heat exchangers—plate–fin type, 1997.