Thermal Solar Plant for Methane/Hydrogen Mixtures Production

Giampaolo Caputo, Irena Balog, Domenico Mazzei
Energy Technologies Department
Italian National Agency for New Technologies, Energy and Sustainable Economic Development
Via Anguillarese, 301 – 00123 Rome, ITALY

Abstract

The massive use of hydrogen as an energy vector would be the last step towards the energy decarbonisation process, solving the greenhouse gases and pollutantemissions in our industrial and civil systems. On the other hand, technological development of the production processes, storage, distribution and use of hydrogen is still quite far from a real competitiveness compared to traditional fossil fuels. Up to now, there is no market for hydrogen as an energy carrier. In near future, hydrogen economy could replace fossil fuels, even if the environmental and societal issues related to energy production are perceived as urgent where solutions are absolutely required. Enriched methane could be an intermediate step able to introduce hydrogen in our energy systems, using the consolidated natural gas infrastructures at competitive costs and leading to a significant reduction of the pollution immediately applicable and without high structural costs: the new blend is a necessary step towards the "dream of hydrogen". An innovative hybrid plant, composed by a solar section for heating up a molten salt stream through a Concentrating Solar Power (CSP) plant, a chemical section for the production of mixture Hydrogen/Methane, and an electrical section for the electricity production by a Rankine Cycle unit is presented. The core of the process is the CSP plant. The molten salt stream is heated up to 550 °C by the CSP plant, then it supplies the reforming process heat duty and generates electricity.

Key-Words: -*Solar energy, Methane/Hydrogen, Thermal Storage, Automotive, Fuel*

I. INTRODUCTION

The use of methane as an automotive fuel has the theoretical potential to reduce the CO_2 tailpipe emissions of 29% compared to gasoline. In real conditions, engine efficiencies on different test cycles will be different and vehicles using Compressed Natural Gas (CNG) cylinders normally have a slight weight penalty compared to similar gasoline powered vehicles. State-of-the-art Natural Gas Vehicles (NGV) achieve a 25% CO_2benefit compared to similar gasoline powered vehicles [1-3].One of the main drawbacks associated to NGVsis the limited kilometric range associated to the low density of methane and to the low gravimetric and volumetric energy density of high pressure automotive storage systems. Hydrogen is considered one of the most promising future energy carriers and transportation fuels but, because of a distribution infrastructure lack, a widespread introduction of vehicles powered by pure hydrogen is not probable in the near future. Blending hydrogen with methane could be one solution to pave the way for hydrogen economy [4-5]. Only minor adjustments in spark regulations and injection duration are necessary to tune and calibrate a vehicle engine in order to operate and run on pure methane or hydrogen/methane blends. An effective way to produce hydrogen/methane blends is to perform a low temperature steam reforming reaction of natural gas and to convert partially methane to hydrogen. The obtained gas stream is then purified to reach the required specifications. The steam reforming reaction is highly endothermic wherean environmental and economic feasible approach is to use Concentrated Solar Power (CSP) to supply the required heat in process. A CSP plant is an energy conversion system that makes use of solar radiation as main or exclusive source of energy instead of conventional fossil fuels [6-9]. CSP plants use optical systems, "concentrators", to collect and focus the electromagnetic radiation on a specific component, "receiver", which has the scope to transfer the energy to a thermal fluid. In this way the solar heat is stored and is used to produce electrical energyand heat to perform selected chemicalreactions. CSP plants use only the direct component of the solar radiation DNI (Direct Normal Irradiance). The areas where DNI reaches high medium values during the year (>400 W/m2) are the potentially good location to install the CSP plant. In case of lower DNI the integration with an external fossil or, better, renewable energy source is necessary.

This work describes the CSP technology developed by Italian National Agency for New Technology, Energy and Sustainable Economic Development (ENEA), which makes use of linear parabolic solar concentrators and of a mixture of sodium and potassium nitrates (60/40 %w/w) as heat transfer and thermal storage fluid. In standard applications the heat is used to power a steam production plant coupled with a Rankine cycle for the production of electric energy. In this study a part of theheat produced by the CSP plant was used to feed a steam reforming reactor converting natural gas in hydrogen/methane blends for automotive applications [10-11].

II. MATERIAL AND METHODS

A. Site features

The meteoclimatic characteristics of the chosen site are one of the fundamental importances how to select the location of the renewable source power plant. Meteorological phenomena are largely irregular and unpredictable. Technical and economic analysis of chosen location requires all knowledge of the trends over time of the meteorological magnitude. In the case of CSP, the meteorological magnitude involved is DNI. In order to fully characterize the location for CSP plant, it is necessary to collect a series of weather data covering a period of a severalyears and to determine a Typical Meteorological Year (TMY). The best option in evaluation of CSP plant location is to obtain the measurements of the meteorological values through the use of appropriate meteo-radiation stations installed in the chosen location or in the immediate vicinity, with adequate acquisition frequency and for a sufficient period (minimum of 2 years). Alternative methods to estimatethe solar radiation have been developed, where the using appropriate simulation tools are used or by processing available satellite images cover of a clouds for selected location.

B. Analysis of solar radiationfor location PrioloGargallo

In this work, the site of PrioloGargallo (Italy) was examined, where the hourly curve of DNIare acquired from the weather station installed on the site of the Archimede plant. The observations period of meteorological parameters in this location is from 2002 to 2006. The total annual value of the DNI is 1936 kWh/(m^2 year), with the hourly distribution shown in Fig. 1. The maximum value is 1042 W/m^2 with an average value over the year of 220 W/m^2.

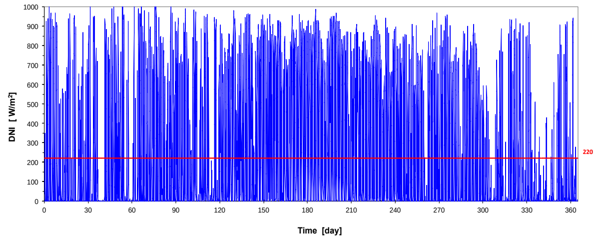

Fig. 1: Hourly distribution of direct solar radiation, where in red is presented an average value

Fig. 2 shows the monthly distribution of the average daily value; the average daily energy is higher in the summer months, with a maximum value of 8.25 kWh/(m^2 day) in July and a minimum of 1.65 kWh/(m^2 day) in December.

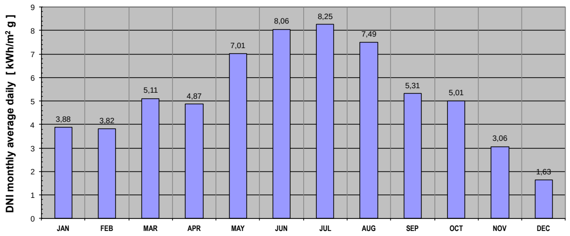

Fig. 2: Monthly distribution of the average daily value of direct solar radiation

Fig. 3 shows the distribution of solar radiation. The radiation is present for about 4000 h/y, for 2100 h it is higher than 500 W/m^2, while only for 856 h it is higher than 800W/m^2.

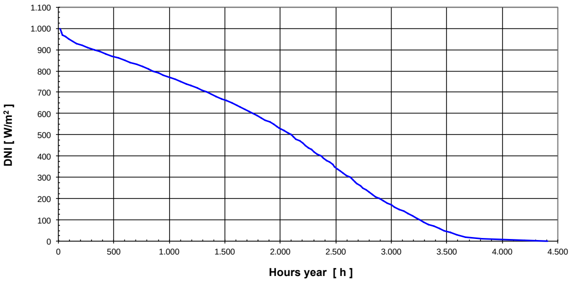

Fig. 3: Distribution of direct solar radiation

In this study theParabolic Trough Collectors (PTC), Fig. 4, are considered as the solar concentration system.

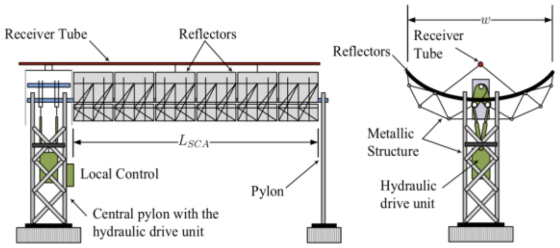

Fig. 4: Parts of a Solar Collector Assembly [12]

PTCs are composed of parabolic trough-shaped mirrors, which reflect the incident radiation from the sun on the solar receiver tube. The receiver tube is located at the focus of a parabola in whose sides the mirrors are located. A solar field consists of hundreds of Solar Collector Assemblies (SCA), which are independently tracking assemblies of parabolic trough solar collectors. Each SCA has the following components: metallic support structure, mirrors, solar receiver, and collector balance of the system. In order to reach the operational conditions, the solar collector assemblies are arranged in a series configuration normally known as a loop. The length of the loop depends on the PTC performance, where most common has a U shape to minimize the pressure drop through the pipe header as shown in Figure 8. Usually the PTCs are oriented in North-South to track the sun fromeast to west, but this also depends on the land constraints. The tracking of solar radiation takes place only on one axis. To calculate the solar radiation that affects the opening of the collector it is necessary to take into account the effect of the cosine of the angle of incidence, angle between the solar radiation and the normal at the surface of the collector. There are other factors, which depend on the angle of incidence, and which further reduce the effective radiation on the manifold opening and which can therefore be concentrated on the receiver and transferred to the heat transfer fluid:

$$\mathrm{ANI} = \mathrm{DNI} \times \cos(\theta) \cdot \mathrm{IAM} \cdot \mathrm{RS} \cdot \mathrm{EL} \qquad (1)$$

Where IAM is Incident Angle Modification, RS is RowShadow, losses due to the effect of shading between the different rows of collectors, EL stands forEndLoss, terminal losses, when part of the receiver tubes are not affected by solar radiation. Considering listedeffects, the effective solar radiation for the location PrioloGargallois 1543 kWh/(m^2 year), with an average value of 176 W/m^2 and a maximum value of 967 W/m^2, fig. 5.

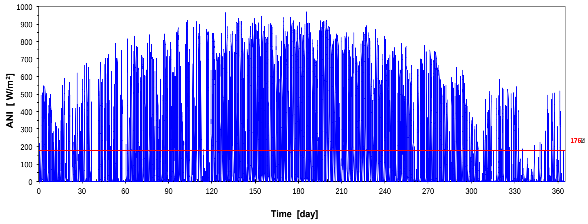

Fig. 5: Time trend of ANI for N-S orientation, where in red is presented an average value

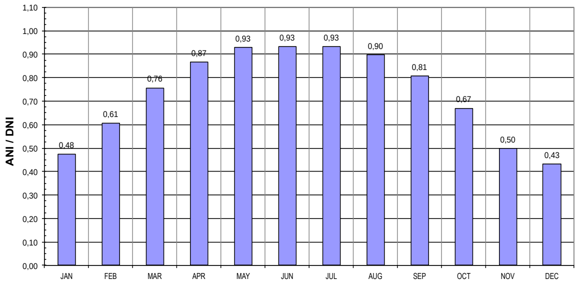

Fig. 6: Relationship between ANI and DNI

Fig. 7 shows the comparison with the DNI regarding the monthly average daily radiation and the distribution of solar radiation.

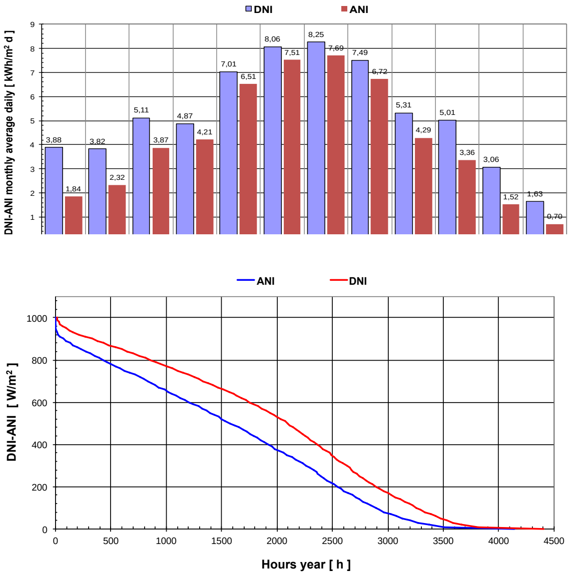

Fig. 7: Comparison between the distributions of solar radiation

C. Solar plant

In this study we consider 100 m solar collectors with loop length of 600 m; the loop is 6 collectors connected in series, Fig. 8. In each collector there are 24 receiver tubes (4.06 meter) for a total number of 144 tubes per loop. The performance evaluation of the whole string was simulated considering not only the solar collectors but also all the internal components: valves, hoses and pipes.

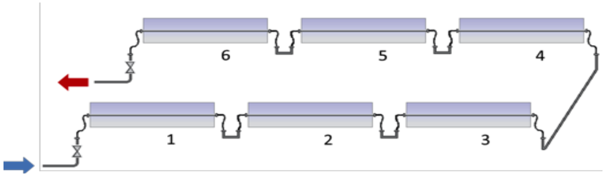

Fig. 8: Loop SCA

The efficiency of the loop (thermal and overall) and the mass flow rate of the fluid as a function of solar radiation are presented in Fig. 9.

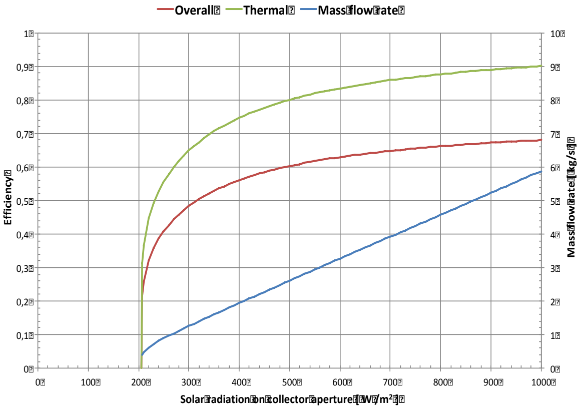

Fig. 9: Efficiencyand mass flow rate of the loop

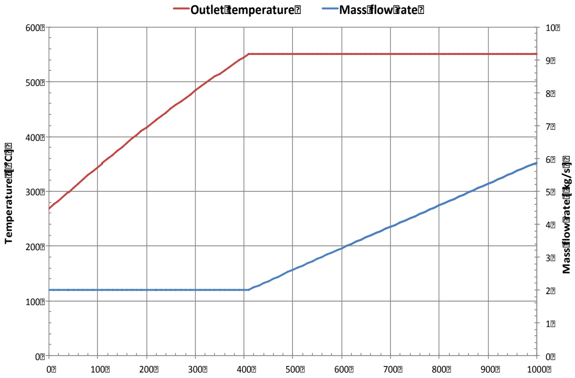

Fig. 10: Flow rate and temperature with limit on minimum mass flow rate

The inlet temperature of the molten saltsis 290 °C whilethe outlet temperature is 550 °C. The flow rate of the molten salts must be adjusted according to the intensity of the solar radiation to keep the outlet temperature constant. A minimum value of 2 kg/s is set with a fluid velocity of0.35 m/s which corresponds to a transit time of 30 minutes of corresponding power plant. In this case it is possible to keep the temperature of the outlet fluid constant below a certain value of solar radiation, 400 W/m^2.

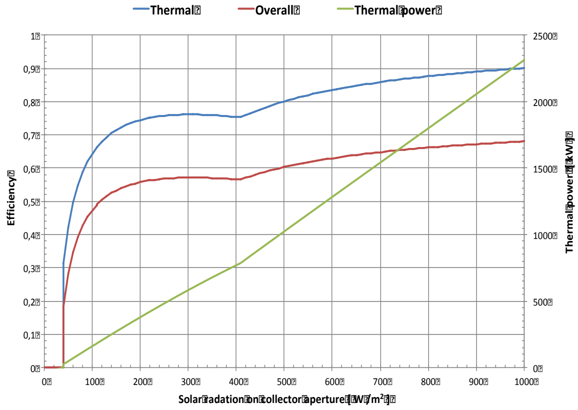

Fig. 11: Efficiency and loop power with minimum mass flow rate limit

The total efficiency of the loop, in the operating range at nominal temperature, is in range between 0.57 and 0.68, with a thermal power transferred to the fluid between 780 and 2300 kW, while the flow rate of the fluid is adjusted between 2 and 5.9 kg/s. At the maximum solar radiation value for the site location, the maximum thermal power that can be transferred to the fluid is 2220 kW with a yield of 0.678 and a fluid flow rate of 5.66 kg/s, whilean average yearly value is estimated to 800 W/m^2. The thermal power transferred to the fluid with mentioned site characteristics is 1800 kW with a yield of 0.662 and a flow rate of 4.57 kg/s.The distribution of solar radiation together with the operation of the loop is considered and the preliminary analysis of the annual working efficiency of thesolar plant loop can be made, Fig. 12.

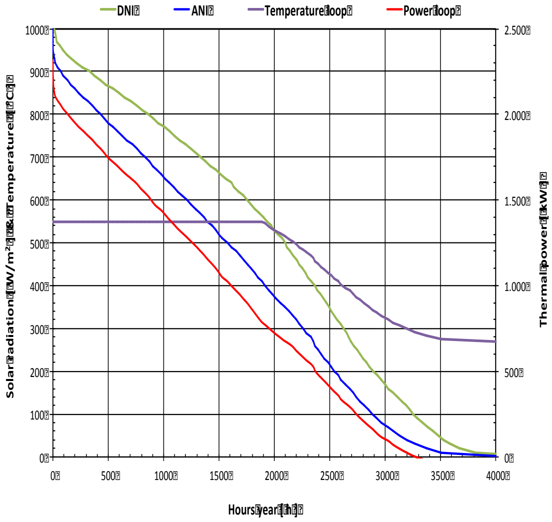

Fig. 12: Annual operation of the loop

From the Fig. 12, it is possible to get information that maintain of the power plant outlet temperature at the projected value of 550 ° C is operational for about 1900 h/year (~22%), while the energy conversion results in 3200 h/year (~ 37%). The thermal energy collected annually by the presented loop is 3140 MWh, and 2800 MWh at the nominal temperature of 550 ° C. Energy at a temperature lower than 550 °C, (340 MWh/year), is stored in thecold storage tank and used tocompensatethe thermal losses in periods of absence of solar radiation.

Once, the solar radiation curve on the collector, the solar field configuration and its efficiency are known, the solar system can be dimensioned. The plant specifications, in particular regarding the solar field and the storage system, are defined on the basis of the thermal power required through an energy balance between the various systems: solar field, thermal storage and production. It is necessary to determine the thermal power that must be supplied through the solar radiation collection efficiency and then the surface of the solar field can be calculated with corresponding numbers of collectors and their arrangement. The surface of the solar field could be oversized in order to have an excess thermal power that can be stored and then used in periods of scarce or lack of solar radiation.Theentire study, involves the construction of a solar plant able to supply thermal energy to a steam system for the production of electricity and to a chemical plant for the production of methane / hydrogen (hydromethane) mixtures, to be used for the automotive in natural gas powered vehicles. The simplified scheme of the solar plant is shown in Fig. 13.

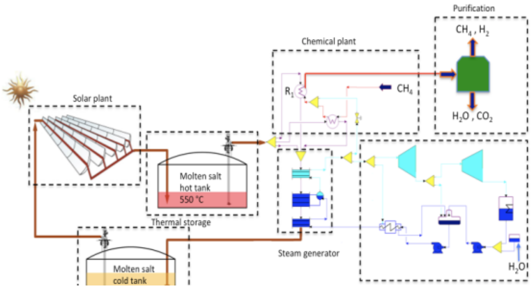

Fig. 13: Scheme of theplant

III. RESULT

A part of the high temperature of the molten salts accumulated in the hot tank are sent to a series of heat exchangers of the chemical plant for steam reforming of natural gasfor the production of methane/hydrogen mixtures.The mentioned process also requires steam for electrical production and for the chemical reaction.The adiabatic fixed-bed reactor has been sized to produce 350 kg/h of hydromethane (600 Nm^3/h) with a CH_4/H_2 equal to 3:1 or 25% molar and 4% in mass (42 buses and 150 cars consumption per day). The natural gas to be sent to the reforming reactor is 160 kg/h while the steam flow rate, considering a "steam to carbon" ratio of 3, is 480 kg/h [13-16]. The reactant mixture enters in the reactor at the temperature of 510 °C and at the pressure of 15 bar.The electric consumption of the filling stations and the variousaccessories are considered and the steam cycle is sized for a net electricity production of 700 kWe. The study of this complex system, especiallyregarding thermal loads and electrical production, was carried out with the GateCycle program.

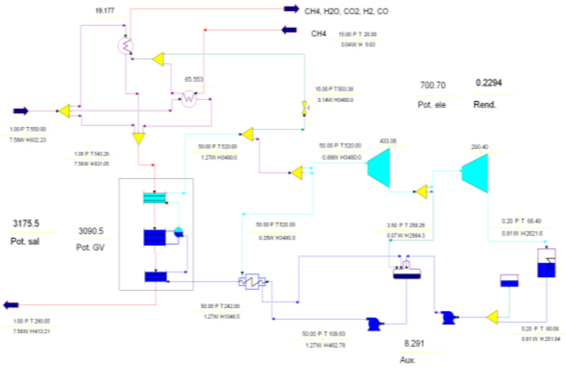

Fig. 14: Simulation for an electric power of 700 kWe

The thermal power supplied with molten salts is 3175 kWt. A solar field is designed to be required with 2 collector loops.Moreover, if apart of the collected thermal energy has to be stored to be used during the periods of low insolation, then it isnecessary to increase the number of collector loops into solar field. The analysis therefore envisages the usage of asolar field consisting of 3 loops of collectors as shown in Fig. 15.

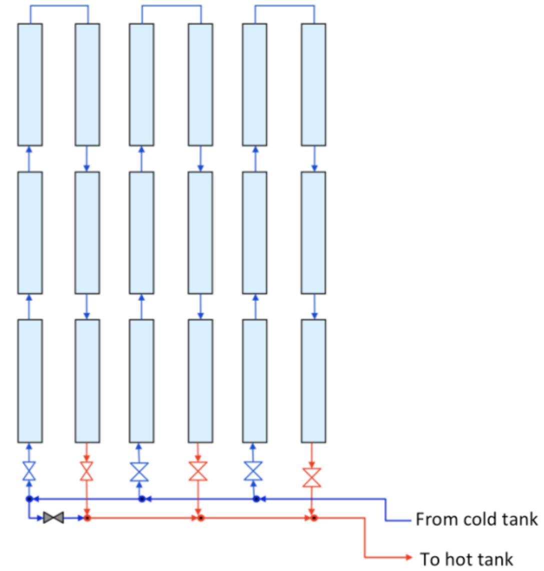

Fig. 15: Solar field configuration

In total, in the solar plant, there are 18 solar collectors with an area of 10200 m^2. The thermal power collected by the solar field, with an average radiation of 800 W/m^2 per year, is 5400 kWt, where 60% of thermal power is used by the production system, while the remaining 40% is accumulated to extend production to the periods of insufficient solar radiation. It is necessary to consider, during periods of low solar radiation, the integration ofthe solarplant from the outside for the requiredthermalpower (Back-up) as shown in the functional scheme in Fig. 16.

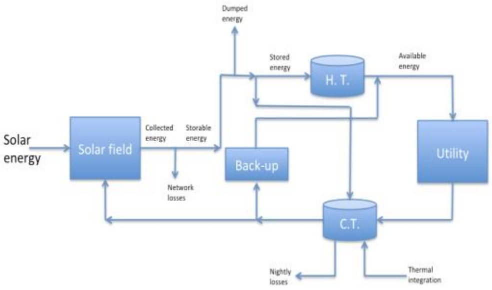

Fig. 16: Functional scheme of the system

The molten salt from the cold tank(C.T.), is sent to the solar field where is heated up to 550 °C and is accumulated in the hot tank(H.T.). The flow rate of molten saltin the solar field is regulatedand depends on the intensity of the solar radiation.Calculated flow is maintain to the outlet temperature atthe design value of 550 °C, where flow rate is set between a minimum value of 6 kg/s and 17 kg/s in correspondence to the maximum radiation value. If the solar field temperature is lower than a pre-set value (between 450-500 °C), then the molten salt is recirculated in the C.T. The salt from theH.T. is sent to the production plant,where the nominal heat output has to be supplied by constant and equal values of 3175 kWt (between 550 °C and 290 °C), correspond to a flow rate of 8 kg/s. If the heat output available in the storage system is lower than the nominal value, then the difference is integrated via an integration boiler(Back-up). The maximum thermal energy that can be collected in the solar field and also the maximum accumulable energy depend on the capacity of the storage system. In cases whenthe storage system is lower than the maximum possible value, then it will be necessary to discard a part of the available solar thermal energy, by defocusing the collectors of solar field.

D. Storage system

To determine the maximum capacity of the storage system it is necessary to make the energy balance between the various systems (solar field, storage and production), according to the scheme of Figure 16, regarding the best day of the year. Analyzing the solar radiation curve of the site location, first case scenario with the maximum solar radiation was observed in July 8(2006) with hourly distribution of the radiation showed in Fig. 17.

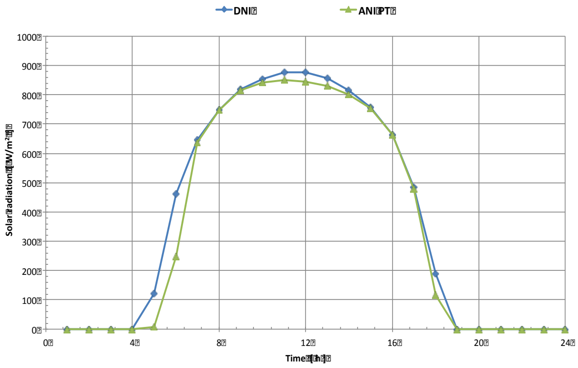

Fig. 17: DNI and ANI for July 8 2006

The initial hypothesis basis that all the molten salt is first stored in the cold tank at 290 °C (the storage system is discharged), the plant operates continuously with constant heat output of the users at 3175 kWt. With the hourly curve of the solar radiation of 8 July, the hourly distribution of the collected, accumulated and integrated thermal powers is shown in Figure 18. Up to 6 o'clock, the thermal power is supplied exclusively by the integration boiler (Back-up), as the solar radiation increase, the heat load is supplied by the energy collected in the solar field. The excess of energy compared to the demandof the users is stored in the H.T. and it is used when the intensity of solar radiation is reduced. The maximum storage energy is estimated for 20453 kWht, 35.5% of solar energy collected, corresponding to approximately 6.5 hours of plant operation at nominal power without the direct solar radiation. Before the sunset 4260 kWhtisaccumulated as sensible heat in molten salts, allows the operation of the system for another 1.4 hours. To calculate the required mass of molten salt, it is necessary to consider the temperature operating range of the storage system, limited between 550°C (high temperature storage) and 290°C (vessel collecting the thermal fluid arriving from the steam generator). The specific heat capacity of the fluid in solar plant, takinginto account a temperature variation of 260°C, is 190.4 kWh/m^3, referred to the required mass of molten salts of 188616 kg. The dimensions of the two tanks (hot and cold) are 7.5 m in diameter, 4 m in absolute high.The energy demanded for a daily plant operation is 76224 kWhtwhere 49% of energy is supplied by the solar plant and 26% by the back-up heater. The storage system is 25% of the total energy, where the total energy by solar plant is 74%.

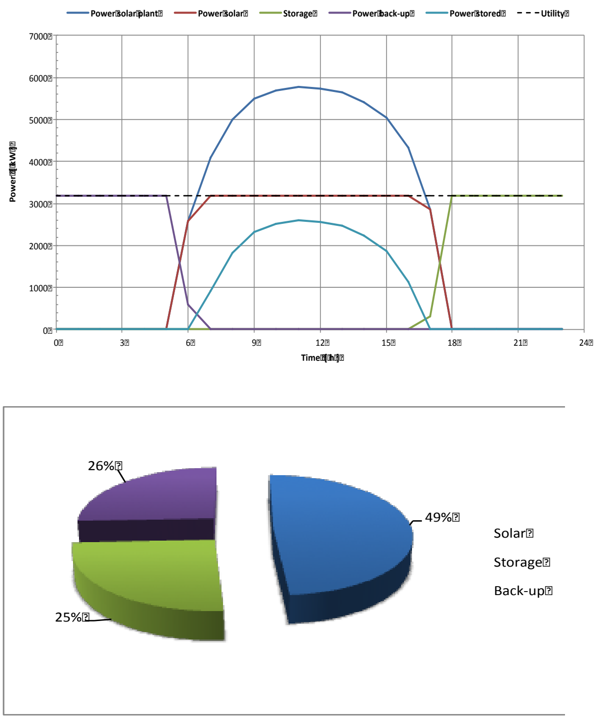

Fig. 18: Distribution of thermal power

E. Example in minimum solar radiation

The second case scenario, when solar radiation is insufficient for optimal function of solar plant, is the case of February 1(2006). The hourly distribution ofDNI and ANIfor this case is showed in Fig. 19.

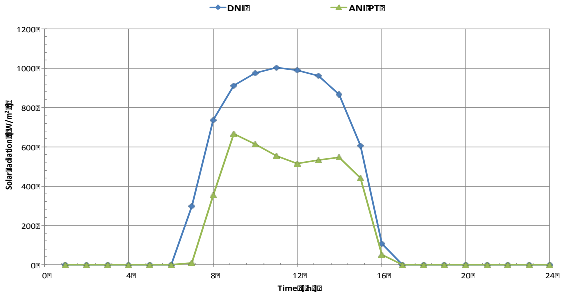

Fig. 19: DNI and ANI for February 12006

The hourly distribution of the collected, accumulated and integrated thermal powers for this day is shown in Fig. 20.

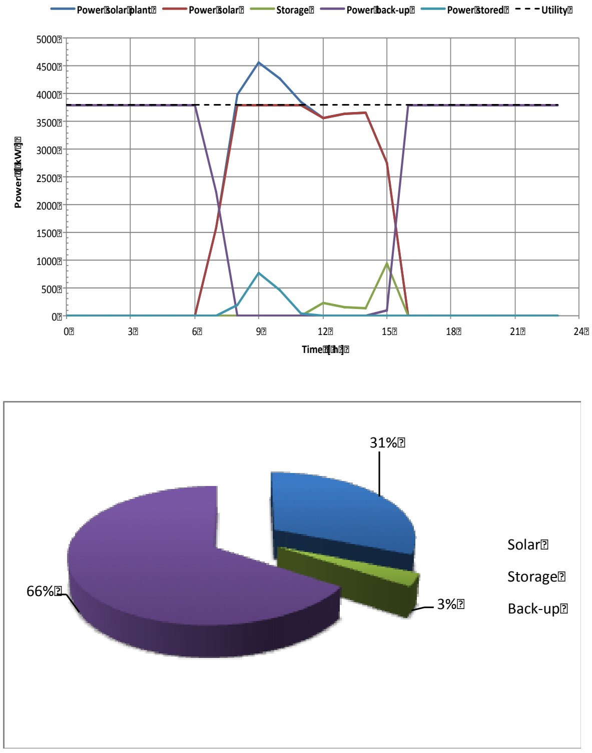

Fig. 20: Distribution of thermal power, February 1 2006

The total energy is 31% by solar plant and 66% by back-up heater. The storage system is about 3% of the total energy. The total energy by solar plant is 34%.

IV. CONCLUSION

This work is a preliminary analysis of a thermal solar plant, with linear parabolic collectors that uses a mixture of molten salts as heat-transfer fluid and also as thermal storage fluid. Thermal solar plant provides the production of electrical and thermal energy for the production of methane/hydrogen mixtures. Followed by the basis and hypothesis of the methane/hydrogen production and the plant accessories of electrical consumption for the filling station, the thermal power of the solar plant has been defined.The size and the configuration of the solar field have been defined, based not only on the heat output but also on the capacity tostorage system. The solar field is made with18 collectors arranged in three U loops of 6 collectorswhile the thermal storage system is sized for a capacity of 6.5 h without sun radiation (nominal power operation in the absence of solar radiation). The energy balances of the solar plant were calculated according to a reference site of PrioloGargallo (Italy) where are available the hourly curve of DNI. The detailed analysis was carried out and it was found that the storage capacity of 6.5 h, the maximum solar fraction (share of the thermal energy that is supplied by the solar plant), is74%. Therefore, for a continuous operation of the plant, as hypothesized, it is necessary to integrate part of the energy required with an external source, from 100 to 26%, depending on the solar radiation. The calculation was made for July 8 2006(the day with the highest solar radiation). The difference between July 8 2006and February 1 2006 was presented. To obtain the annual average values of the solar fraction, the energy balance was extended for the whole year with a maximum time interval of one hour.

REFERENCES

[1] Saad, A., Wan Mohd, F., Shahrir, A., Yusoff, A. (2014), Comparison of Performance and Emission of a Gasoline Engine Fuelled by Gasoline and CNG Under Various Throttle Positions, Journal of Applied Sciences 14, 386-390;

[2] How, H. G., Taib, I. M., Shahrir, A., Yusoff, A., Azhari, S., Elvis, A. (2009), Experimental Investigation of Performance and Emission of a Sequential Port Injection Natural Gas Engine, European Journal of Scientific Research 30, 204-214;

[3] Munde, G. G., Dalu, R. S. (2012), Compressed Natural Gas as an Alternative Fuel for Spark Ignition Engine: A Review, International Journal of Engineering and Innovative Technology 2, 92-96;

[4] Nitnaware. P. T., Suryawanshi J. G. (2014), Investigation on multi-cylinder S.I engine using blends of hydrogen and CNG, International Journal of Research in Engineering and Technology 03, 976-981;

[5] Akansu, S. O., Dulger, Z., Veziroğlu T. N. (2004), Internal combustion engines fueled by natural gas hydrogen mixtures, International Journal of Hydrogen Energy 29, 1527–1539;

[6] Lovegrove, K., Stein, W. (2012), Concentrating Solar Power Technology Principles, Developments and Applications, IT Power Group, UK;

[7] Giaconia, A., De Falco, M., Caputo, G., Grena, R., Tarquini, P., Marrelli, L. (2008), Solar steam reforming of natural gas for hydrogen production using molten salt heat carriers. AIChE Journal54, 1932–1944;

[8] M. De Falco, M., Giaconia A., Marrelli L., Tarquini P., Grena, R., Caputo, G. (2009), Enriched methane production using solar energy: an assessment of plant performance. International Journal of Hydrogen Energy 34, 98-109;

[9] De Falco M, Piemonte V (2011) Solar enriched methane production by steam reforming process: reactor design. International Journal of Hydrogen Energy 36:7759–7762;

[10] ENEA Report Solar Thermal Energy Production 2001 ENEA/TME/PRES;

[11] Herman et al., Two-tank molten salt storage for parabolic trough solar power plant; Energy 2004; 29:883;

[12] Goswami, D., and Kreith, F., 2008. Energy conversion. CRC;

[13] Berlier, G. Low Temperature Steam Reforming Catalysts for Enriched Methane Production; Enriched Methane The First Step Towards the Hydrogen Economy 2016; 53-74;

[14] Gopalakrishnana S. et al.; Unravelling the structure and reactivity of supported Ni particles in $NiCeZrO_2$ catalysts, Applied Catalysis B:Environmental; 138-139, 17, (2013), 353-361;

[15] Augelletti, R. Purification of Hydrogen-Methane Mixtures Using PSA Technology; Enriched Methane The First Step Towards the Hydrogen Economy 2016; 129-146;

[16] Ortenzi F, Chiesa M, Scarcelli R, Pede G (2008) Experimental tests of blends of hydrogen and natural gas in light-duty vehicles. International Journal of Hydrogen Energy 33:3225–3229.