A Holistic Approach to Promote the Safe Development of Hydrogen As an Energy Vector

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ABSTRACT

If generated using clean technologies (non CO2 emitting technologies), hydrogen may constitute a clean sustainable energy vector usable in the power sector, in the transportation sector, in various industrial sectors and in households. However, the physical and chemical properties of the hydrogen (its leakage, flammability and explosion propensities) call for extreme care for its generalized use, especially at the level of the general public. To make the general public use of hydrogen as safe as electricity will certainly take a long time and will necessitate huge investments. To open the way to the so-called hydrogen society may necessitate a different approach, that we call a holistic approach, meaning that the advent of hydrogen as a generalized energy vector should solve world energy and environmental problems without adding new ones. Among such approaches, the paper discusses the following ones: (i) in situ & on site hydrogen generation to avoid hydrogen transport and storage; (ii) use of renewable hydrogen for captured CO_2 hydrogenation and (iii) hydrogen generation from organic waste streams to contribute to the achievement of circular economy.

KEYWORDS: hydrogen safety, hydrogen generation, CO_2 hydrogenation, organic waste gasification.

INTRODUCTION

The world energy system is undergoing a large mutation today, the pace of which will certainly fasten in the coming decades. Sustainability issues of energy systems and policies are considered more seriously than before. Sustainability goes obviously hand in hand with long term energy sources availability and environmental considerations. Focusing on climate change risks triggered by greenhouse gas emissions, and namely CO2 emissions from burning fossil fuels, clearly shows the complexity of rapidly modifying an already established energy system. This is mainly because energy systems are large scale socio-technical systems impacting all the human activities but also impacted by the social sphere, from economy to geopolitics. Consequently they present an important resistance to any important changes so that energy transitions are usually characterized by long durations.

An energy system is composed of several sub systems, such as resource gathering and transporting (for example mining or building pipelines), resource conversion to useful energy vectors (for example refining or electricity generation), distribution of the energy vectors (for example electricity or gas networks). Changing an element of the energy system, for example the fuel or the useful energy vector, impacts the whole energy system. Each energy sub-system also carries specific hazards and environmental risks [1-3].

Hydrogen is a specific energy vector. If generated using clean technologies (non CO2 emitting technologies), it may constitute a clean sustainable energy vector usable in the power sector, in the transportation sector, in various industrial sectors and in households. However, the physical and

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chemical properties of the hydrogen (its leakage, flammability and explosion propensities) call for extreme care for its generalized use, especially at the level of the general public. To make the general public use of hydrogen as safe as electricity will certainly take a long time and will necessitate huge investments.

To open the way to the so-called hydrogen society may necessitate a different approach, that we call a holistic approach, meaning that it should solve world energy and environmental problems without adding new ones. This paper will discuss some aspects of this approach. In the first section of the paper we outline what we mean by the 'holistic' approach. In the continuing sections, we briefly present three developments within this approach. We finish the paper by some recommendations.

THE HOLISTIC APPROACH

The energy transition strategies should not add new problems but solve simultaneously several existing ones. The transition to a more sustainable energy system needs decarbonized energy resources, de-nuclearized electricity systems, increased renewables based electricity generation and advances in the circular economy.

In this context, hydrogen as an energy vector opens-up several opportunities. Indeed, hydrogen conversion to useful energy by thermo-chemical or electro-chemical processes only generates water and no greenhouse gases. But hydrogen generation should also use clean processes (without emitting GHGs). On the other hand, because of its leakage propensity, including metal fragilization, low density and high reactivity, the transport and storage of hydrogen pose serious threats.

The approach we call 'holistic' aims to use some characteristics of hydrogen and of its use to promote energy transition without introducing new risks or threats. Several strategies to ease the introduction of hydrogen in the energy scenery within the holistic approach can be imagined. In this paper, we develop three of them. They are the following:

- In order to minimize hydrogen leakage, fire and explosion risks in the case of hydrogen use generalization, the most rational strategy is to avoid hydrogen transport and storage, by developing *in situ and on demand* hydrogen generation technologies
- Instead of using hydrogen as a final energy vector, another rational strategy would be to use it as an intermediary one to generate conventional fuels (for which optimized conversion technologies exist such as internal combustion engines, gas turbines, fuel cells) by the hydrogenation of the CO2 emitted from carbon intensive sectors.
- Another rational strategy would be to generate hydrogen from various solid materials including organic waste streams by gasification technologies.

The paper argues that rational uses of hydrogen such as these three strategies suggest may accelerate the generalized use of hydrogen with minimal risks and contribute to the development of a low carbon circular economy. The following sections briefly develop these strategies, based on the worldwide knowledge accumulation in the concerned areas, including the authors' own work.

IN SITU AND ON DEMAND HYDROGEN GENERATION

In order to diminish the leakage, fire and explosion risks of a generalized use of hydrogen, one rational approach is to shorten the duration and the distance between its generation and energy conversion steps and locations. This also means generating hydrogen and using it without storing, which is a "in situ & on demand" hydrogen generation approach. A promising way within this approach is using low temperature reactions between water and Aluminum for water splitting. Several studies exist in this domain, including at ICARE-CNRS [4, 5].

Metal particles such as Ni, Fe, V, Mn, Ti, Ag, Ca, Zn, Zr, Al, and their corresponding alloys can be potentially used to produce hydrogen through catalyst (water-soluble inorganic salts) assisted reactions in water. For example, some theoretical hydrogen production rates are: 1 g of sodium borohydride gives 2.4 l of hydrogen; 1 g of aluminum gives 1.244 l with bayerite/boehmite formation; 1 g of magnesium gives 0.95 l, and Al and Mg hydrides give respectively 2.24 l and 1.88 l of hydrogen. Compared to other systems, aluminum has several favorable features, such as cost-effectiveness, non-reactivity at normal conditions, easy storability, safety during transportation, and non-toxicity.

As aluminum is covered by its natural oxide, several researchers have investigated various aluminum activation processes, such as treatment with iodine vapor, reaction at supercritical conditions, treatment of the metal surface with NaOH or KOH solutions, surface contact with activator metals (mercury, gallium, indium) and metal-alloys (gallium-indium eutectics). For example, Kravchenko et al. [6] investigated the reaction of water with aluminum-based metal composites doped with gallium (Ga), indium (In), zinc (Zn), or tin (Sn). Parmuzina and Kravchenko [7] demonstrated the method of aluminum activation by liquid eutectics Ga–In (70:30) and Ga–In–Sn–Zn (60:25:10:5) (galinstan) leading to reactions with water and hydrogen production. Activator metals remove the alumina layer and generate fractures on the aluminum core which is a potential way to enhance the reactivity of the aluminum. For safety and environmental reasons, the gallium-indium eutectics seem to be the best choice to activate aluminum particle reactions with water.

At ICARE we have chosen the galinstan (Ga–In–Sn–Zn -60:25:10:5) eutectic, which gives optimized performances over Ga-In eutectics [4] and we have addressed some of the associated problems in this aluminum activation method, and mainly the dependency of hydrogen production rate and yield on aluminum particle sizes, aluminum and galinstan eutectic content, and reaction temperature. In addition we have examined the effects of Al particles specific surface area and galinstan eutectic content on hydrogen production rate and yield. We have examined three compositions of mixtures: 85% Al -15% galinstan eutectics, 90% Al-10% galinstan eutectics and 95% Al – 5% galinstan eutectics by mass. The galinstan eutectic composition is fixed as Ga-In-Sn-Zn (60:25:10:5). Figure 1 shows cracks initiation and propagation under the effect of the galinstan eutectics. Figure 2 displays the hydrogen evolution rate for various aluminum particle sizes and water temperatures, showing the effects of both parameters.

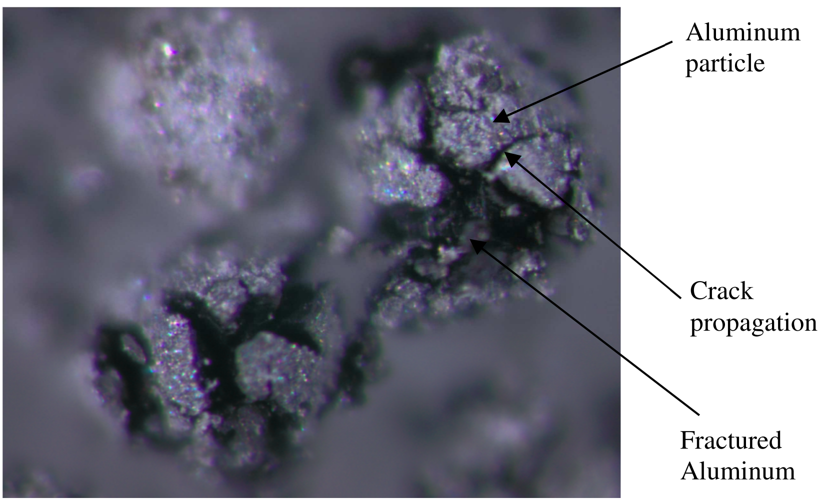

Fig. 1. Crack formation on the activated aluminum particles at ~30 °C.

These preliminary studies indicate that low temperature reactions between water and aluminum constitute a promising way for water splitting and in situ and on site hydrogen generation. Once optimized this approach may considerably reduce the hydrogen storage necessity and the associated risks for on-board and portable systems applications using fuel cells.

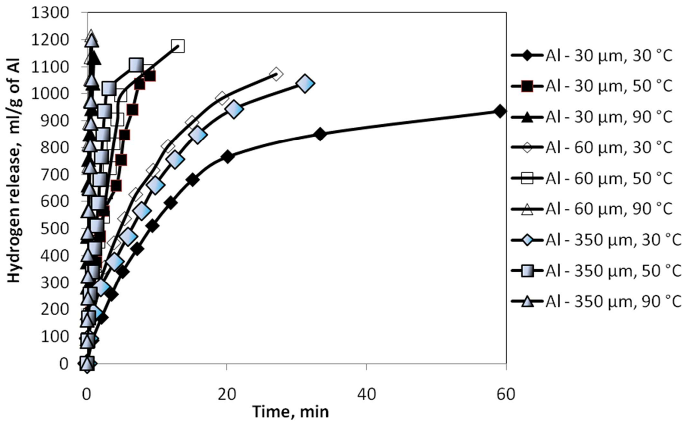

Fig. 2. Hydrogen evolution rate of the activated aluminum mixtures with water, Al-85% and Galinstan eutectics 15% by mass (Ga-In-Sn-Zn = 60-25-10-5).

HYDROGEN GENERATION USING RENEWABLE ELECTRICITY AND CO_2 HYDROGENERATION TO GASEOUS AND LIQUID FUELS

Wind energy and solar power are clean, sustainable but intermittent electricity generation technologies. Given the difficulties to store electricity, hydrogen generation by water electrolysis using renewable electricity is a way of storing PV electricity during day time and the excess wind electricity during lower electricity consumption periods such as nights. The generated renewable electricity can be used to electrolyze water for hydrogen generation and for CO_2 hydrogenation to gaseous (methane) or liquid (methanol, DME) fuels. This approach may permit to continue to use well optimized energy conversion technologies such as gas turbines and internal combustion engines, but also fuel cells. It might then provide a nice solution for the valorization of captured CO_2 especially from CO_2 intensive industries such as cement, glass, steel and refineries by creating a carbon circulation or transfer process between sectors [8-11].

Carbon dioxide is one of the major greenhouse gases. The need to control the emission of CO_2 into the atmosphere has encouraged its capture from flue gases generated by power plants and carbon intensive industrial processes. Several methods for capturing CO_2 in the atmosphere have been investigated. Separation techniques are today mature and can be implemented on a large scale. CO_2 capture using membranes is a less energy consuming capture technology especially suited for CO_2 concentrations nearing 15 % and higher. This is for example appropriate for calcination kilns in the cement industry where CO_2 concentrations are high. For power plants CO_2 concentrations in the flue gases can be increased using combustion in oxygen enriched air. Figure 3 shows the efficiency of this technology for a swirling turbulent methane – oxygen enriched air flame [12].

The utilization of the captured carbon dioxide has an economic value as a waste is converted into useful, added value products. The availability of large amounts of recovered CO_2 may sustain the development of new synthetic fuel technologies based on its hydrogenation. The free energy of formation of CO_2 (ΔG = -96.5 kcal/mol) suggests that its conversion may require a large energy input.

The conversion processes such as

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ ($\Delta H = -49.5$ KJ/mol),

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ ($\Delta H = -164.9$ KJ/mol),

are likely to be a catalytic or thermal treatment processes. In both processes, the fundamental mechanism involves creation and stabilization of active species, which initiate the necessary reactions under kinetic and thermodynamic limitations. Incorporation of catalysts to this conversion process is already studied extensively to promote these conversions. One of the elementary mechanisms is to produce the reactive species which helps dissociating the molecules. Once the species are generated, it should have enough energy to propagate the desired reactions. One of the approach to generate the reactive environment is by means of gas discharges.

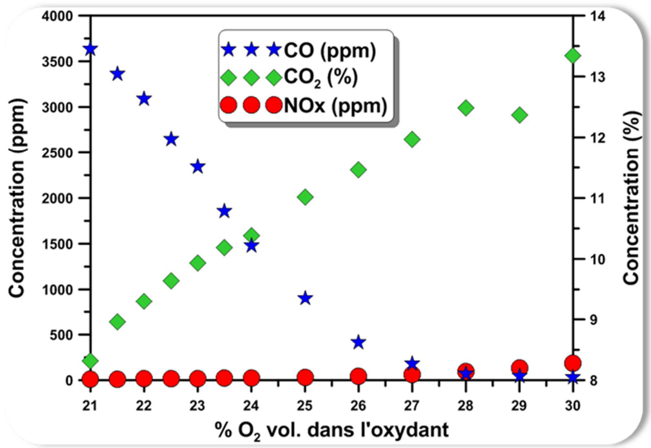

Fig. 3. Effect of the oxygen enrichment rate on the CO2 concentration in the burnt gases of a swirled turbulent methane – air flame.

Atmospheric non-thermal plasmas (ANTPs) or atmospheric pressure gas discharges have received a great deal of attention in the recent years [13,14]. ANTPs are generated by a diversity of electrical discharges such as corona discharges, dielectric barrier discharges (DBD), atmospheric pressure plasma jet (APPJ) and micro hollow cathode discharges (MHCD), all having their own characteristic properties and applications. The important characteristics of non-thermal plasmas is their high electron temperature (~10^5 K) while the bulk gas temperature remains as low as room temperature and its generation of high energy electrons (6 ~10eV) which dissociates the molecules and hence creates the necessary reactive environment. Therefore, this conversion process can be performed independently of the gas temperature, an inherent advantage being to perform the chemical conversion at low temperatures as demonstrated by bench scale investigations involving batch experiments and column reactors.

Once optimized, the integration of hydrogen generation from renewable electricity through water electrolysis and of the captured CO_2 hydrogenation to liquid or gaseous fuels will become a viable sustainable CO_2 valorization technology. The rationale behind this approach is to circulate the carbon between various sectors without using additional carbon containing fuels, for example using the CO_2 generated in the process industry as a carbon containing fuel source for the transport sector.

HYDROGEN GENERATION BY GASIFICATION OF SOLID FUELS INCLUDING ORGANIC WASTE

An important environmental and sustainability issue of today's societies is the waste management problem. Humanity is generating on a daily basis huge amounts of various kinds of organic waste streams which pose disposal and resource management problems. Good examples are end-of-life tires, organic fractions of municipal waste, sewage sludge from water purification facilities, agriculture and food industry waste. Gasification technologies are appropriate ways to produce a synthetic gas (composed mainly of H_2 and CO) from such organic waste. Depending on the moisture content of the waste material, conventional thermal gasification (for example for scrap tires) or hydrothermal gasification (for example for sewage sludge) technologies can be mobilized. In addition, several countries do not possess natural gas or oil reserves but have large reserves of lignite type coal. The generation of synthetic gas by gasification from lignite is a viable technology for natural gas import substitution in such countries. The produced gas can be used as a natural gas substitute for various uses, can be further processed to produce various chemicals and liquid fuels or for pure H_2 generation after a water gas shift process. H_2 can be used to enrich natural gas and the separated CO_2 may enter the carbon circulation approach as outlined above. Several studies are conducted worldwide and also at ICARE-CNRS to optimize syngas generation technologies from solid fuels and to solve both the organic waste disposal and natural gas import substitution problems [15-18].

Figure 4 shows the 1 MW circulating fluidized bed solid fuel gasification facility developed during the FP7 OPTIMASH project (2011-2016) in order to optimize the gasification of high ash content lignites from India and Turkey. The gasification cold gas efficiencies of 70% were obtained with this facility and the design of upscaled versions of the facility in under progress to approach commercial scales [17].

Fig. 4. 1 MW circulating fluidized bed gasification facility developed within the EU OPTIMASH project.

Based on the knowledge gained on circulating fluidized bed gasification technologies, a scrap tire granules gasification facility has been designed. In order to feed this design, scrap tires gasification kinetics has been first determined at ICARE-CNRS using a high heating rate thermogravimetric analysis apparatus coupled to a mass-spectrometer and to a gas chromatography [15]. Figure 5 displays typical mass loss curves showing that scrap tires can be efficiently gasified.

Based both on the basic knowledge on scrap tire gasification kinetics and on the technological expertise gained on circulating fluidized bed gasification technologies a 5 MW electricity generation facility has been designed [19]. The main features of this facility are shown on Fig. 6.

For very humid organic waste such as sewage sludge or several other agricultural and food industry waste streams, conventional thermo-chemical gasification techniques are not appropriate as the waste needs to undergo a pre-drying process. This of course considerably diminishes the waste to energy potential. Instead, hydrothermal processes can be used. Figure 7 shows a major result from ICARE-CNRS on the hydrothermal carbonization of olive pomace, a 70 % humid waste issuing from olive oil industry. It is observed that once optimized hydrothermal carbonization process is able to generate a solid fuel having chemical composition and thermo-physical properties very close to a lignite type coal [20]. This solid fuel can be therefore readily gasified or co-gasified to generate a syngas.

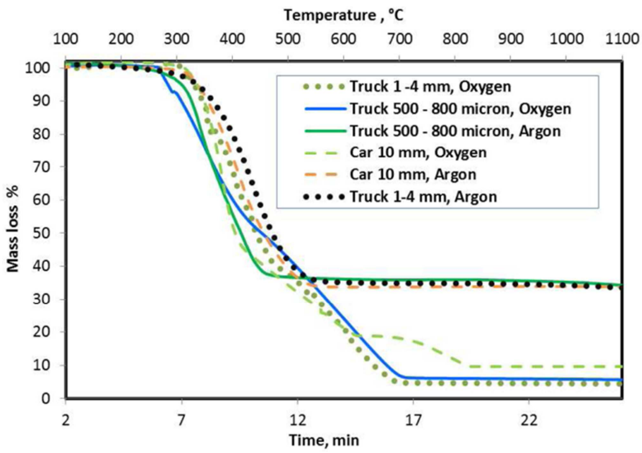

Fig. 5. TGA studies of scrap tires.

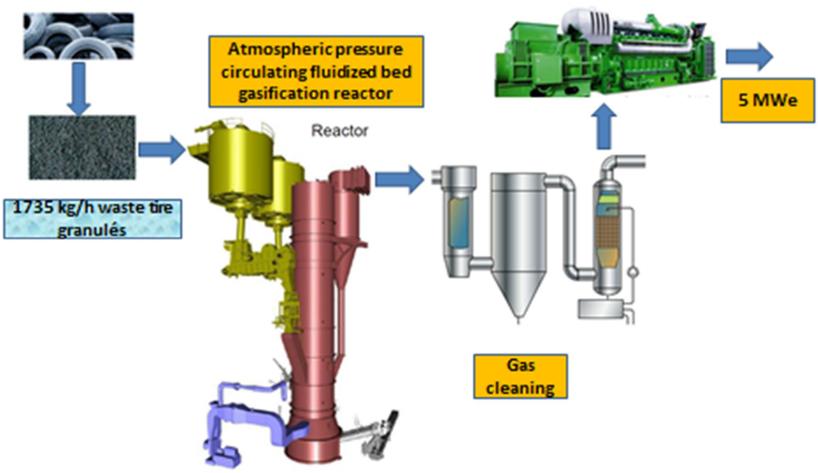

Fig. 6. Gasification of used tire granules: a project for 5 MW electricity generation.

CONCLUSIONS

This paper argued that in order to generalize the use of hydrogen as an important element in the energy transition, a holistic approach is necessary. The approach we call 'holistic' aims to use some characteristics of the hydrogen and of its use to facilitate energy transition without introducing new risks or threats. In this paper, we briefly developed three technological paths that may contribute to this approach. They are the following.

- In order to minimize hydrogen leakage, fire and explosion risks in the case of hydrogen use generalization, it is proposed to avoid hydrogen transport and storage, by developing *in situ and on demand* hydrogen generation technologies.
- Instead of using hydrogen as a final energy vector, it is proposed to use it as an intermediary one to synthetize conventional gaseous or liquid fuels (for which optimized conversion technologies exist such as internal combustion engines, gas turbines, fuel cells) by the hydrogenation of the CO_2 emitted from carbon intensive sectors. For this purpose it is proposed to generate hydrogen by water electrolysis using renewable electricity.
- Finally, it is proposed to develop hydrogen or syngas generation technologies from various solid fuels including organic waste streams by optimized gasification technologies

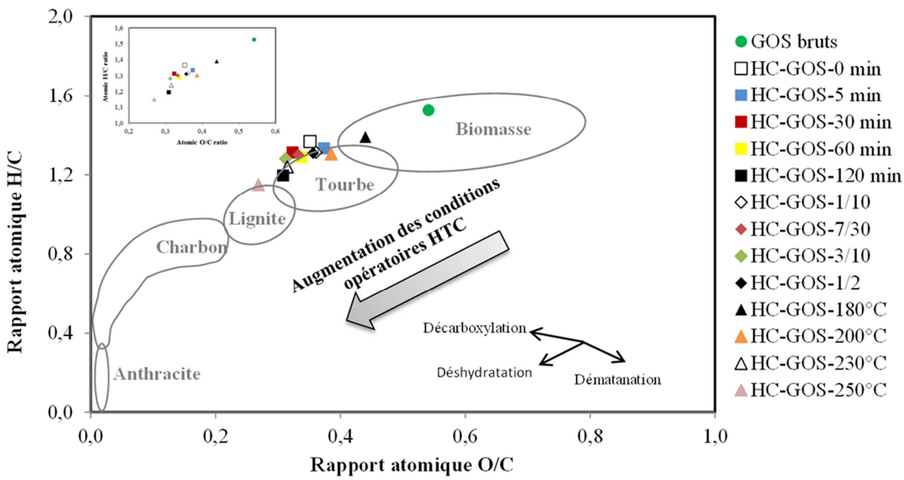

Fig. 7. Van Krevelen diagram for olive pomace.

The main argument of the paper is that hydrogen related technologies here outlined may help developing sustainable energy policies to accelerate the generalization of hydrogen use by reducing the associated risks, and at the same time, constitute solutions for renewable electricity storage, captured CO2 valorization, organic waste management, natural gas import substitution for some countries and therefore facilitate the transition to a low carbon circular economy.

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