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Contribution of upcycling surplus hydrogen to design a sustainable supply chain: The case study of Northern Spain

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Abstract

To further advance a world powered by hydrogen, it is essential to take advantage of the environmental benefits of using surplus industrial hydrogen to energy conversion. In this paper, the integration of this renewable source in a hydrogen supply chain has been analysed with the following considerations, (1) the techno-economic modeling is applied over the 2020–2050 period, at a regional scale comprising the north of Spain, covering the main sources of surplus hydrogen in the region, (2) the supply chain feeds fuel cell devices powering stationary and mobile applications and, thereby stablishing the quality standards for the upcycled hydrogen and, (3) a mixed-integer programming model (MILP) is formulated to predict the optimal integration of surplus hydrogen. The advantages of this research are twofold, (i) on the one hand, it provides the methodology for the optimal use of surplus hydrogen gases promoting the shift to a Circular Economy and, (ii) on the other hand, it contributes to the penetration of renewable energies in the form of low cost fuel cell devices to power stationary and mobile applications. The results show that the combination of all the infrastructure elements into the mathematical formulation yields optimal solutions with a plan for the gradual infrastructure investments over time required for the transition towards a sustainable future energy mix that includes hydrogen. Thus, this work contributes to improving the environmental and economic sustainability of hydrogen supply chains of upcycling industrial surplus hydrogen.

Keywords: Hydrogen recovery; Surplus hydrogen; Circular economy; Energy sustainability; MILP optimization model; Hydrogen infrastructure

Nomenclature

MILP

Mixed-Integer Linear Programming

GHG

Greenhouse Gas

PEM

Polymer Electrolyte Membrane

ISO

International Organization for Standardization

HFCV

Hydrogen Fuel Cell Vehicle

HSC

Hydrogen Supply Chains

SMR

Steam Methane Reforming

CCS

Carbon Capture and Storage

NPV

Net Present Value

COG

Coke Oven Gas

BOF

Basic Oxygen Furnace

BTX

Benzene, Toluene and Xylenes

INE

Spanish Statistical Office

PSA

Pressure Swing Adsorption

MEM

Membrane Technology

CH2

Gas Hydrogen

LH2

Liquid Hydrogen

JuMP

Julia for Mathematical Optimization

O&M

1 Introduction

It has been reported that besides its prominent role in hydrogen-to-chemical processes, hydrogen-based energy storage systems could play in the future a key role as a bridge between intermittent electricity provided by alternative sources and the common fossil fuel-based energy system. The versatility and unique properties of hydrogen open the way to accomplish this goal. Hydrogen is an odorless, tasteless and colorless gas that, despite its lower volumetric energy density (0.0108 MJ/L) compared to hydrocarbons, it has the largest energy content by weight (143 MJ/kg) [1–3].

Hydrogen can be obtained from a number of primary or secondary energy sources, depending on regional availability, such us natural gas, coal, wind, solar, biomass, nuclear, and electricity using electrolyzers [4]. Hydrogen production from carbon-lean and carbon-free energy sources could be the long-term aim of the hydrogen utopia [5].

The promotion of sustainable mobility has significantly increased demand for green hydrogen as an attractive alternative to non-renewable energy. In Spain, the transportation sector contributes 25% to the total greenhouse gases emissions, followed by the residential and commercial sectors contributing 15%. With regard to GHG diffuse emissions transportation accounts for 50% [6]. These figures clearly reveal the importance of a shift to a hydrogen economy in both sectors; within this goal, hydrogen technologies must overcome efficiency, cost, and safety challenges [7].

At the same time, hydrogen losses in industrial waste gas streams have been estimated to be 10 billion Nm^3 per year in Europe [8]. Despite this figure being largely based on statistical assumptions, and not on a site-by-site assessment, this surplus hydrogen volume is quite significant. This available “surplus hydrogen” is often recovered as fuel burnt for heat and power production, although cheaper energy sources could be used instead. Within a more sustainable framework, this surplus hydrogen could be recovered as feedstock for the manufacture of commodity chemicals such as ammonia or methanol, or even be used as fuel for both transportation and stationary applications [9].

Polymer Electrolyte Membrane (PEM) fuel cells are electrochemical devices that could be fed with hydrogen to generate clean energy where water and heat are products. In this case, the hydrogen fed must meet a quality standard that requires its purification from multicomponent gas mixtures as per end-users requirements [10–12]. In compliance with the International Standard ISO 14687, hydrogen gas should have a purity of at least 99.97% (minimum mole fraction) for road vehicle PEM fuel cells, and of at least 99.9% for stationary appliances. Furthermore, the maximum mole fraction of total non-hydrogen gases may not exceed 300 µmol/mol for automotive fuel cells and 0.1% for stationary fuel cells.

Industrial waste streams with hydrogen content higher than 50% are considered to be potential promising sources for hydrogen recovery ~~thougth~~though (The word 'though' is not correctly spelled. The complete sentence should be rewritten as follows: *"Industrial waste streams with hydrogen content higher than 50% are considered to be potential promising sources for hydrogen recovery **through** the use of separation techniques."*) the use of separation techniques. It has been estimated that the price of recovered hydrogen could be 1.5~~ to ~~–2 times lower than the price of hydrogen from natural gas reforming [13,14]. These figures highlight the potential and attractiveness of using these hydrogen-rich waste streams as source for hydrogen. However, the final price and opportunity of recovering wasted hydrogen streams is highly dependent on the implementation of cost-effective separation technologies, where membrane separation systems are well positioned [15].

Although in recent years, the prospects of a shift to a hydrogen economy have created great interest in the scientific community and social stakeholders, the success relies on the availability of the necessary infrastructures [16]. In the specific case of the mobility sector, the main obstacle hindering vehicles manufacturers and consumers from embracing hydrogen fuel cell vehicles (HFCVs) is mostly the lack of a hydrogen infrastructure [17]. A number of works focused on the use of decision-support tools for the design and operation of hydrogen supply chains (HSC), have been reported addressing questions such as the design of the hydrogen fuel infrastructure applied at the country, region and city levels with Almansoori and Shah leading the way [18]. Some studies include the selection of the production technology (primary and secondary energy sources) and hydrogen transport forms (pipeline, truck and on-site schemes) through each node of the supply chain [19]. Also, most of these studies analyze future hydrogen network in terms of capital and operating expenditure of the infrastructure focusing on the transportation sector [20–23]. However, Europe’s future plants expect an increased hydrogen demand in both road vehicle transportation and residential/commercial sectors [24]. Recent evidence suggests that steam methane reforming (SMR) with carbon capture and storage (CCS) is expected to be the most economically and environmentally attractive technology for producing hydrogen while renewable source infrastructures like wind and solar farms continue developing [25–27]. Other studies have been focused on the distribution network for hydrogen describing what is the optimal delivery form inside the chain [17,28,29]. The assessment of environmental, economic and risk aspects by using multi-objective optimization-based approaches has been also reported [16,20,30–37]. This approach is ideal for optimal decisions when two or more conflicting objectives exist. Furthermore, advanced research has been assessed on the environmental impacts of a broad variety in hydrogen production technologies by recent researchers [38–40]. In economic terms, the final decision will define the time when stakeholders shall make their investments in developing the hydrogen infrastructure regarding payback and profit. Finally, economies of scale need to be taken into account to compare the advantages of centralized versus distributed production, as well as the impact in the transportation costs. Interesting studies have been conducted establishing efficient investment strategies over a specific timeframe by using multi-period optimization models. Some optimization models have also considered demand uncertainty by using stochastic modeling approaches [41–45].

The latest studies have included the production of biohydrogen from solid waste streams such as biomass into the hydrogen network showing significant decreases in producing costs and CO_2 emissions [46,47]. Meanwhile, among the list of hydrogen waste gas streams, some studies have concentrated on the management, optimization, and utilization of steel-work off gases in integrated iron and steel plants [48–51]. However, little work has focused on the optimization of various by-product gases in the HSC. To the best of our knowledge, reported optimization models for HSCs do not consider the competitiveness of upcycling hydrogen-rich waste gas sources for its reuse in both transportation and residential sectors.

Hence, the novelty of this study is a methodology for analysing the techno-economic feasibility of a HSC with contribution of upcycled hydrogen-rich waste gas sources to fuel both stationary and road transport applications. We select the northern Spain region with a population of 11,723,776 inhabitants and 4135,4 km^2 of land for the case study to be analyzed. Furthermore, a mixed-integer programming model (MILP) is formulated to determine the optimal investment plan for developing hydrogen recovery and distribution infrastructure, while maximizing the net present value (NPV) over the 2020–2050 period.

2 Methodology

The HSC incorporating industrial waste gas sources has been designed by adapting the procedure reported in Ref. [18]. The design problem addressed in this paper targets the optimal carbon-free HSC infrastructure to satisfy the growing hydrogen demand for stationary and road transport applications, geographically located in the north of Spain and over a 30-year time horizon. The optimization problem embeds the infrastructure elements that are required throughout the future HSC (levels: production, purification, conditioning, delivery and market niches). The goal is to maximize the economic performance across the entire value chain, subject to several constraints. For that purpose, a mathematical model with the objective of maximizing net present value (NPV) is proposed. The NPV considers detailed cash flow with taxation, capital depreciation, transportation and operation costs.

The methodology framework proposed in this work is shown in Fig. 1. The input block consists of all the databases, scenarios, hypothesis and assumptions. Decision-making tools are then used to optimize the design problem as explained in Section 3. Lastly, snapshots and results concerning the objective function and the decision variables are the main outputs as will be explained in more detail in Section 4.

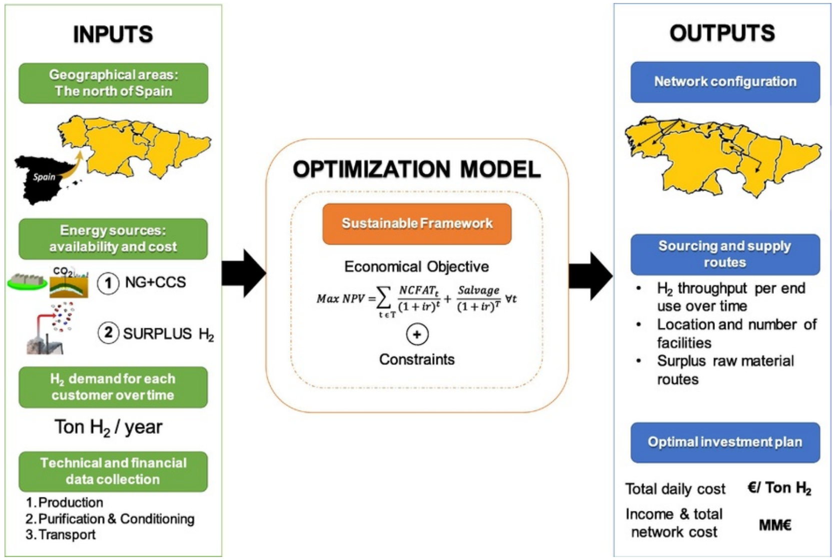

Fig. 1 Methodology framework for the proposed model.

2.1 Study area description

This work is focused in the use of decision-making tools for the techno-economic feasibility of the upcycling of hydrogen-containing multicomponent gas mixtures to feed stationary and portable fuel cells in the north of Spain. At the early stages of design, one of the main goals of this study is to identify and critically analyze the potential of the upcycling of industrial waste gaseous streams to be integrated in a HSC [52].

The proposed model is focused on two main industrial waste streams, as shown in (There must not be a line break in this paragraph between "***..., as shown in***" and "***Table 1. These streams...***")

Table 1. These streams have been selected for the following reasons: (i) both hydrogen sources are gaseous waste streams with hydrogen content higher than 50% that are currently flared or released; (ii) both industries

develop their activities in stable markets and; (iii) both hydrogen sources are by-product gaseous streams with low market price.

(Rows and columns of *Table 1 Waste hydrogen streams by origin and final use* are not completely well defined. Several rows and/or columns should be merged into one and the text within should be centered. Please, find attached the corrected vision of the table in editable form and as an image.)**Table 1** Waste hydrogen streams by origin and final use.

Raw material	Industry	Waste streams	H_2 flowrate	Burnt off/emitted (%)	Recovered/upcycled (%)
R99	Chlor-alkali industry	Cl_2 production	300 Nm^3 of H_2/ton of Cl2	10	90
		HCl production	6 Nm^3 of H_2/ton of HCl	10	90
		$NaClO_3$ production	668 Nm^3 of H_2/ton of $NaClO_3$	10	90
R50	Steel mills	Coke Oven Gas	209 Nm^3 of H_2/ton of coke	3	97
	Coke plants			60–80	20–40

Table 1 summarizes the estimated volume of “surplus hydrogen” with a pre-set ratio (hydrogen produced per ton of chemical product) that depends on its origin [8,53–55].

The first hydrogen source, R99, corresponds to off gases of the chlor-alkali industry. At a more detailed level, three kinds of hydrogen-rich waste streams have been identified. These are generated in the chlorine, hydrochloric acid and sodium chlorate production, which are manufactured independent of the type of electrolytic process used within the industry. The hydrogen net balance of this type of industrial complexes strongly depends on the generated products and the processes involved. High purity hydrogen streams emitted from chlor-alkali plants in EU countries achieve a share of 9% of total hydrogen generated during their processes, but can vary from 2% to 53% [54,56]. The grade of these off-gases is assumed to be up to 99.9 vol% of H_2 with minor traces of other components such as Cl_2, NO_x, H_2O, O_2 and HCl [57,58]. The resulting gases are usually released to the atmosphere containing hydrogen.

The second most valuable by-product considered in the optimization model, R50, is coke oven gas (COG). The COG is produced at integrated steel mills and coke making enterprises, both located close to coal mines. COG is a by-product of coal carbonization to coke, which is mainly used for the under-firing of coke oven batteries. A large amount of COG is directly flared and discharged to the atmosphere. In the case of steel mills with Basic Oxygen Furnace (BOF) technology, around 3% of the total COG produced is flared [59–61]. Likewise, approximately only 20–40% of the total COG produced in coking plants is recovered in alternative processes [62,63]. Direct flaring of COG generates emissions of toxic pollutants. To avoid these undesirable effects, the first step is to clean the crude COG in order the remove toxic components such as tar, light oil (mainly consisting of BTX (benzene, toluene and xylenes)), sulphur, and ammonia. Although the cleaned COG composition depends on the coking time and coal composition, the average composition is: 36–62 vol% H_2, 16–35% CH_4, 2–10% N_2, 1–5% CO_2, 3–8% CO and small traces of other compounds [61,64].

Taking into account the above-mentioned raw materials for surplus hydrogen, the availability of both hydrogen sources over the whole period, and in the region under study, has been estimated and is summarized in Table 2.

(The text within *Table 2 Availability of surplus hydrogen* should be centered across the columns.)**Table 2** Availability of surplus hydrogen.

	R50 (ton/y)	R99 (ton/y)
Min (2020)	$4.9 \cdot 10^4$	$8.8 \cdot 10^2$
Max (2050)	$5.2 \cdot 10^4$	$1.0 \cdot 10^3$

The geographic distribution of the future hydrogen market, presented in Fig. 2, includes three different kinds of stakeholders [8].

(i) Suppliers: Industrial factory sites that produce hydrogen-rich waste streams as by-product. In the studied region, nine supply industries have been identified: three of them generate the R50 raw material, and the other six suppliers produce R99.

(ii) Merchants: These are the major industrial gas manufacturers and responsible of raw materials transformation into the final hydrogen products. In our case, eleven plant sites and/or filling stations owned by industrial gas companies, such as Air Liquide, Praxair, Abelló Linde, Messer Ibérica and Carburos Metálicos (Air Products Group) have been identified [3]. In addition, we have also considered that surplus hydrogen could also be recovered on-site at the supplier’s plants and could directly be marketed to customers. Therefore, six out of the nine suppliers will be considered as transforming nodes, depending on the throughput managed.

(iii) Customers: Final markets are aggregated into thirty-six urban areas with more than 100.000 inhabitants [65]. The hydrogen is distributed to the final end-users to be used as fuel for both road vehicle transportation and residential/commercial sectors.

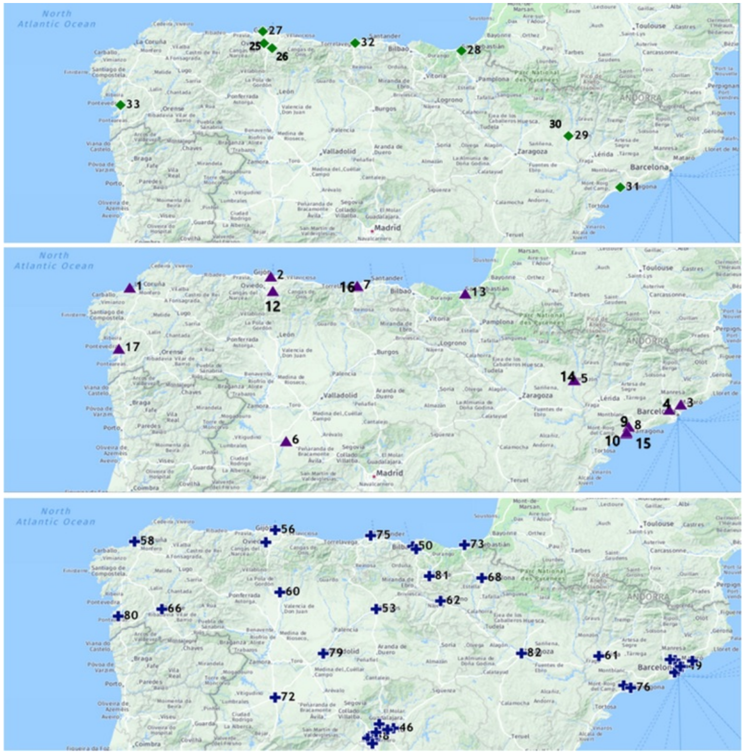

Fig. 2 Geographic breakdown studied ◆ Supplier Company i ∈ I; ▲ Merchant company j ∈ J; ✚ Customer area k ∈ K.

2.2 Problem statement

The overall network that integrates surplus hydrogen in the supply chain is shown in Fig. 3. Within the network presented, the proposed optimization model integrates the following items, (i) technology selection and operation, (ii) hydrogen demand forecast, (iii) geographical information, (iv) capital investment models, and (v) economic models. Some parameters have been collected from recent publications, INE [66] and Eurostat [67], industrial reports, and data provided by companies. The corresponding problem is stated as follows. Given:

- the potential sources for hydrogen recovery composition and their quality;
- a set of suppliers with their corresponding time-dependent maximum supply;
- locations of the key stakeholders in the target region: suppliers, merchants, and customers;
- a set of allowed routes between the three stakeholders, the transportation mode between them, the delivery distance between both routes; supplier-to-merchant and merchant-to-customer;
- hydrogen demand forecast by customer for both transport and residential sectors;
- raw material and product prices;
- a set of production, purification and conditioning technologies, and their yields to upgrade raw materials to hydrogen product, as well as their capacity at different scales;
- investment and operating costs of each intermediate technology, transportation mode, depreciation, and the residual values at the end of the time horizon;
- financial data (such as interest and tax rates).

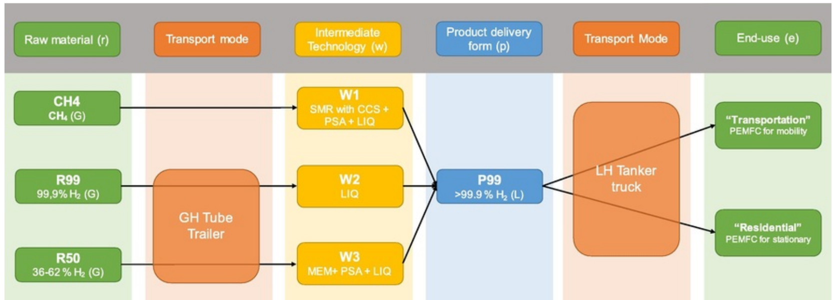

Fig. 3 Structure of the waste gaseous streams-based HSC.

The goal of the proposed multi-period mixed-integer linear programming model is to assess the techno-economic impact of integrating upcycled surplus hydrogen in a HSC that will satisfy the demand of stationary and road transport applications in the north of Spain considering the 2020–2050 period. The outputs provided by the model are:

- optimal investment plan for all the merchants considered and related logistics;
- location (single- or multiplant), type, scale, and number of intermediate technologies, as well as production rates;
- sourcing and supply routes for the raw materials and product considered;
- connections between the stakeholders, and hydrogen flows through the network.

2.3 Data collection

2.3.1 Estimation of the hydrogen demand

In this study, two scenarios concerning two levels of demand for road vehicle transportation and residential/commercial sectors have been considered (see Table 3).

(Rows and columns of *Table 3. Demand scenarios of hydrogen market penetration by end users and timeframe* are not completely well defined. Several rows and/or columns should be merged into one and the text within should be centered. Please, find attached the corrected vision of the table in editable form and as an image.) **Table 3** Demand scenarios of hydrogen market penetration by end users and timeframe.

Scenario (S)	End-use (e)	2020	2030	2040	2050
S1	e1: Transport sector	0.0	2.1	13.9	34.2
	e2: Residential/Service sector	0.0	0.9	3.0	6.5
S2	e1: Transport sector	1.5	12.6	34.8	68.1
	e2: Residential/Service sector	1.9	6.4	10.2	13.5
Total S1 (100 tons H_2 per year)		89	1200	2700	4600
Total S2 (100 tons H_2 per year)		400	3400	6300	9200

The hydrogen market penetration for the above mentioned end-users has been collected from report [24]. The potential demand of hydrogen in two demand scenarios is computed as in Ref. [68] according to Eq. (1):

$$Demand_{kset} = \frac{Pop_k \cdot \mathrm{FE} \cdot sf_{ke}}{LHV} \cdot dsat_{set} \quad \textbf{(1)}$$

where the total demand for each customer ($Demand_{kset}$) results from the population in location (Pop_k), the final energy consumption per capita in Spain (FE), the share of final energy consumption in location per end use (sf_{ke}), the hydrogen lower heating value (LHV), and the market penetration ratio per scenario, end use and timeframe ($dsat_{set}$) [24,65,66,69] (see Appendix A. Model Parameters). The demand has also been estimated according to the methods described in Refs.[4,18,25,30] to support the reliability of these calculations.

2.3.2 Techno-economic data

The characteristics of the final value-added product have been defined in compliance with the International Standard ISO 14687, which defines quality specifications for hydrogen. According to this regulation, pure liquefied hydrogen could be used to meet hydrogen demand for both transportation and residential sectors using PEM fuel cells [70]. Moreover, the final product named P99 is manufactured applying different sequences of intermediate technologies, which have been considered in this study (see Table 4).

(Rows and columns of *Table 4 Raw materials, products and corresponding technologies under study* are not completely well defined. Several rows and/or columns should be merged into one and the text within should be centered. Please, find attached the corrected vision of the table in editable form and as an image.) **Table 4** Raw materials, products and corresponding technologies under study.

Raw materials (r)	Technology description (w)	Product yield (p)
CH4 → CH_4 (G)	W1 → SMR with CCS + PSA + LIQ	P99 → 99.9% H_2 (L)
R99 → 99,9% H_2 (G)	W2 → LIQ	
R50 → 36–62% H_2 (G)	W3 → MEM. + PSA + LIQ	

Steam methane reforming (SMR) with carbon capture and storage (CCS) has been considered as the benchmark technology in order to satisfy the expected demand for hydrogen [19]. The reaction between natural gas, mainly methane, and steam in a catalytic converter strips away the hydrogen atoms, while carbon dioxide (CO_2) is generated as byproduct. According to this process, the capital and operating costs of SMR with post-combustion capture and storage have been considered, including water gas shift reaction and physical separation process through solid adsorbents [71]. In this study, methane is considered an inlimited source where transportation methane costs are included in the raw material price for merchants. With regard to the upcycling of surplus hydrogen, we have selected a combination of two of the most mature technologies for hydrogen purification: membrane technology (MEM) followed by pressure swing adsorption (PSA) [72,73]. Recently, Alqaheem et al. (2017) compare current purification technologies for hydrogen recovery, and state that purification technologies are limited by among other reasons, the hydrogen feed composition. Consequently, industrial gaseous waste streams are pre-enriched via hydrogen-selective membrane separation and further upgraded to the required quality by PSA [74,75]. The final product requires a liquefaction stage. Each plant type incurs in fixed capital and unit production costs, as a function of its capacity. Each of these technologies can be designed at five different production scales [41]. For larger plant capacities, fixed capital investments increase while unit operating costs decrease (see Appendix A. Model Parameters).

2.3.3 Conditioning and transportation

The transportation costs depend on the selected mode and distance [29]. The selection of the transportation mode depends on the transported flow. Specifically for small and intermitent demands, liquid delivery is cheaper than using pipelines. For lower demands, and short distance delivering compressed gas cylinders is a good alternative [76,17]. We considered that raw materials are transported as compressed gaseous hydrogen (CH_2) by tube trailer, and the final hydrogen products are shipped as liquid hydrogen (LH_2) by truck (see Appendix A. Model Parameters). We have considered the corresponding unit transportation cost for each type of hydrogen delivery mode [41,77]. The transportation costs have been estimated according to the method described in Ref. [18]. In this paper, we considered straight-line distances between two geographical coordinates for each stakeholder: supplier-to-merchant and merchant-to-customer, as illustrated in Fig. 4.

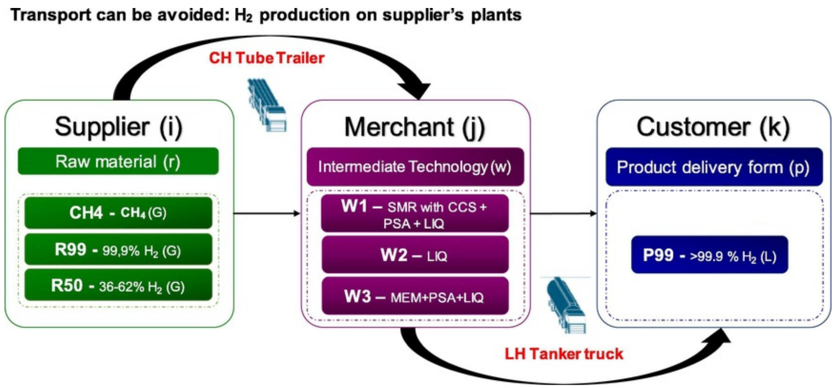

Fig. 4 Waste gaseous streams-based HSC studied for the north of Spain ◆ Supplier Company i ∈ I; ▲ Merchant company j ∈ J; ✚ Customer area k ∈ K.

2.4 Assumptions

The study is based on the following assumptions:

- the amount of raw materials emitted or flared, is based on statistical assumptions and not on a site-by-site assessment.
- the growth rate of chlor-alkali and steel markets are assumed constant.
- the model is prepared to design a network capable of satisfying a given hydrogen demand forecast over time.
- all intermediate technologies will be located at merchant companies where the investors own 100% equity.
- no existing plants are considered at the beginning of the planning horizon.
- in order to account for the economies of scale of technologies, the six-tenths-factor rule has been used to estimate the capital cost based upon the investment cost of a reference case [78].
- no reduction in costs due to learning or technology improvements is considered,
- the facility costs accrue from the moment it is put on service.
- the selling price for P99 is the same as the retail price for hydrogen in the transportation sector (99.99% LH_2).
- the unit transportation cost of raw materials R99 and R50 is identical, and considered on a mass basis.
- due to the complexity involved, our study case has not included the following costs and facilities: storage units, compression units for hydrogen-compressed transportation, refueling stations, and CO_2 transportation to reservoirs.

3 Mathematical model

An optimization modeling approach based on a multi-scenario multi-period mixed-integer linear programming (MILP) has been developed. The planning horizon considered is 30 years (2020–2050). The mathematical model was implemented in JuMP (Julia for Mathematical Programming) and the experiments were conducted in the Intel (R) Core (TM) i7-7700 (3.60 GHz) computer, and 32 GB of RAM. The optimization solver used was Gurobi 7.0.2. In the proposed formulation, the next sequence has been followed: the raw material (r) that comes from supplier (i) is delivered to merchant company (j). Inside these factory sites, hydrogen product form (p) is produced from technologies (w) including different technological processes. Then, it is distributed to customers (k) according to the final use (e). Fig. 5 shows a graphical representation of the connection between the decision variables.

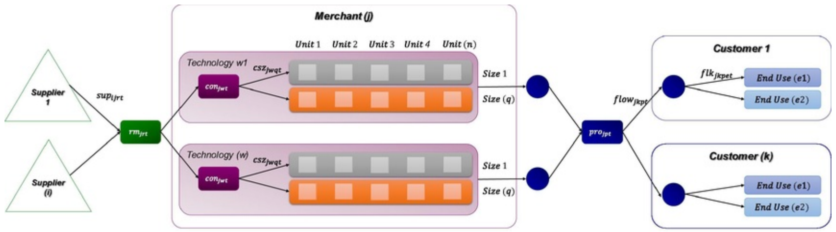

Fig. 5 Superstructure of connections for the waste gaseous streams-based HSC.

The objective of the MILP model is maximizing the net present value (NPV) over 30 years (planning time horizon) of the more environmentally sustainable HSC that integrates upcycled surplus hydrogen. Furthermore, the operational planning model regarding plant capacity, production transportation, and mass balance relationships is considered together with the constraints of these activities. The corresponding constraints and relationships are grouped into four classes: mass balances, demand satisfaction, technology capacity, and decision constraints. The NPV and constraints are fully explained in Appendix B. Mathematical Formulation.

Because of the complexity of the proposed model, a two-stage hierarchical approach has been used in order to solve the MILP model in reasonable computational time, achieving near-optimal solutions (5% optimality gap) in less than 2 h [25,68,79,80]. The first step consists of the solution of a relaxed single-period problem to determine the location of production plants at the end of the horizon. From this initial assessment, merchant companies that are not selected in the first step are eliminated. Next, in the second step, the 30-year horizon problem is solved with a reduced set of merchants. The optimality gaps have been set to 2% and 5% for the first and second step, respectively. The size of the MILP problem is summarized in Table 5, where S1 corresponds to a low demand scenario and the S2 is an optimistic one.

(Rows and columns of *Table 5 Computational outputs solved with the two-step hierarchical procedure* are not completely well defined. Several rows and/or columns should be merged into one and the text within should be centered. Please, find attached the corrected vision of the table in editable form and as an image.) **Table 5** Computational outputs solved with the two-step hierarchical procedure.

Scenario (S)	Step	Number of variables		No. of constraints	GAP (%)	CPU time (s)
		Integer	Continuous			
S1	Step 1	10,200	5542	10,020	2.00	200.87
	Step 2	45,360	30,318	74,958	5.00	616.60
S2	Step 1	31,875	5542	27,340	2.00	423.15
	Step 2	165,375	35,371	176,390	5.00	5305.97

4 Results and discussion

This section describes the main results obtained by application of the proposed model. The optimal solution provides information about the most economical pathways for northern Spain to achieve its 2050 transportation and residential decarbonizing targets. To understand the sensitivity of the techno-economic impact of integrating upcycled surplus hydrogen in a HSC, as well as the strategic and operational decisions, a group of case studies has been set up for analysis. The case studies were built to understand the influence of the hydrogen demand scenarios: pessimistic (S1) and optimistic (S2). They are described as follows:

- Case S1 deals with modeling and optimization of the network infrastructure for the fulfilment of low hydrogen demand (S1). The model will determine: i) the volume of upcycled hydrogen (R50 and R99) that will be converted into liquefied hydrogen at the supplier's plants, and ii) the optimum SMR-CCS plant site locations.
- Case S2. The optimization problem set in S1 is modified for the fulfillment of high hydrogen demand (S2), so that the NPV is maximized.

A brief discussion of the most interesting results is presented below (for more detailed input data, refer to Appendix A. Model Parameters):

Investment Network: Case S1 yields a solution with NPV of 941 MM€, where the revenue derived from hydrogen sales (3370 MM€) is able to absorb the costs (2030 MM€). Although investment costs are significantly high as a consequence of building more plants over the time period, the revenue of opening plants closer to the potential customers compensates the investment, operational and logistics costs. Fig. 6 indicates that integration of surplus hydrogen SC needs 14 years to recover the original investment when the net cash flow equals zero.

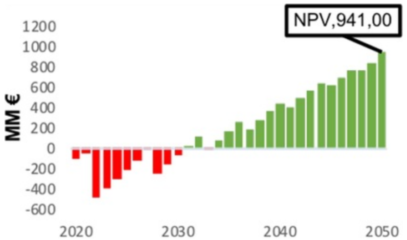

Fig. 6 Cumulative yearly net cash-flows for the entire network for Case S1.

Regarding the production costs over the entire period, methane costs correspond to the most significant share with 49.4% of the total cost. The impact of the surplus hydrogen upcycling costs on the overall operating and maintenance (O&M) costs are not substantial. On the other extreme, transportation costs represent a small contribution (3.1%). Furthermore, no single hydrogen production method is profitable for producing the hydrogen volume to fulfil the expected demand on its own. The optimal solution that integrates surplus hydrogen in the SC leads to the installation of ten units of different technologies until 2050 in northern Spain: W1 (7 units), W2 (2 units) and W3 (1 unit), as depicted in Fig. 7.

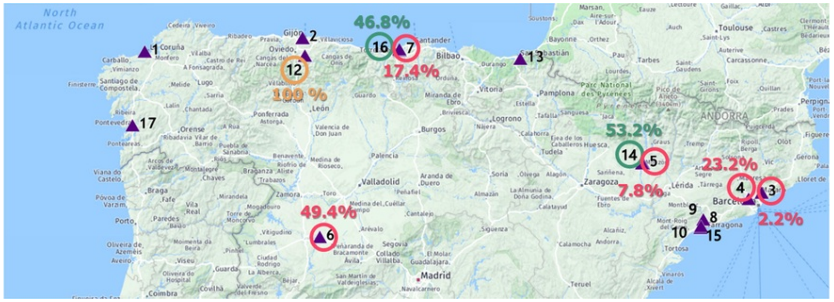

Fig. 7 Network structure in 2050 by ▲ Merchant company j ∈ J and technology w ∈ W; ■ w1 → SMR with CCS + PSA + LIQ.; ■ w2 → LIQ.; ■ w3 → MEM + PSA + LIQ.

Investment in technology W1 is profitable for high capacity plants and in the proximity of customers in order to minimize logistics costs. Most of the methane is transformed close to the biggest urban areas where economic activities and population densities are higher. For instance, in this integrated approach the demand of urban areas at the Autonomous Community of Madrid, where the municipality of Madrid accounts for about 32% of the total hydrogen demand will be satisfied by the methane transformed in Salamanca, where half of the total methane volume is transformed to hydrogen. Thus, hydrogen centralized productions are ideal routes to the future global hydrogen-incorporated economy in highly populated areas at low market penetration.

As mentioned above, the combination of three merchant's plant sites was identified as the key hotspot to obtain on-site liquefied hydrogen from industrial waste streams based upon technologies W2 and W3. Initially, surplus industrial hydrogen is transformed on-site and localized production technologies such as PSA and membrane systems play a pivotal role in introducing hydrogen for early market penetration.

Because suppliers of R99 are spread over the entire target region, a combination of two optimal merchants close to the markets was identified. The optimal capacity installed of technology W2 at both factory sites reaches 1000 ton/year with an investment per plant site of 8 MM€ in 2020 and a payback period of six years. The main sources of R99 come from chlor-alkali industries with larger capacity, the largest volume of surplus streams is reused in the hydrogen network. Owing to the fact that suppliers of R50 are concentrated in the northern part of the studied region, almost the totality of this raw material is purified in a single-facility of 50,000 tons/year of capacity. The overall investment is 116.3 MM€ in 2020 with a maximum payback period of three years. The main sources of surplus hydrogen are coking plants instead of integrated steel mills where the volume of available R50 is slightly lower. Thus, in order to satisfy the low hydrogen demand scenario decentralized on-site hydrogen production by the upcycling of industrial surplus hydrogen is the best choice, as it reduces from the economic and environmental points of view for market uptake and for avoiding costly distribution infrastructure until the demand increases.

In contrast, the number of installations built up in Case S2 is higher than in Case S1, as shown in Table 6. Furthermore, the case study based upon optimistic hydrogen demand scenario (S2) leads to an optimal solution where the revenue (78,900 MM€) absorbs the costs (49,600 MM€) with a payback period of 14 years.

(Rows and columns of *Table 6 Results of the proposed mathematical model by hydrogen demand scenario s ∈ S* are not completely well defined. Several rows and/or columns should be merged into one and the text within should be centered. Please, find attached the corrected vision of the table in editable form and as an image.) **Table 6** Results of the proposed mathematical model by hydrogen demand scenario s ∈ S.

		Scenario (S1)	Scenario (S2)
NPV maximization (MM€)	941.0	2366.0	
Number of facilities by technology w ∈ W	W1	7	16
	W2	2	3
	W3	1	2
Location of merchant company j ∈ J	3,4,5,6,7,12,14,16	4,6,8,12,14,16	

Surplus hydrogen flowrates: As summarized in Table 7, in Case S1, the full amount of R99 is utilized with an inflow of 293,400 tons over the next 30 years due to the model constraints. On the other hand, the model determines that the optimal amount of R50 converted into liquefied hydrogen is 96.9% of the total amount available in northern Spain over the entire period, which is 1,497,000 tons of R50. This conversion is achieved primarily due to the fact that the maximum capacity of the technology W3 used to transform R50 is reached in the year 2038, and building more facilities is not economically feasible due to the fixed capital investment costs.

(Rows and columns of *Table 7 Total surplus hydrogen flowrates for the entire period* are not completely well defined. Several rows and/or columns should be merged into one and the text within should be centered. Please, find attached the corrected vision of the table in editable form and as an image.) **Table 7** Total surplus hydrogen flowrates for the entire period.

Raw material	Smax (100 tons of raw material)	Used (100 tons of raw material)	Produced (100 tons of H_2)	Demand (100 tons of H_2)
R99	2934	2934	2928	63,990
R50	15,460	14,970	6439	

Moreover, R99 is able to meet 0.5% of the total hydrogen demand in the north of Spain for the entire time period, whereas the amount of liquefied hydrogen produced from R50 is able to cover a much larger hydrogen demand accounting for 10.1% of the total hydrogen demand. As expected, the purification of R50 stands out as the most profitable solution on account of the large available volume of this industrial waste stream. Consequently, the rest of the hydrogen produced to fulfill demand is obtained from CH_4 using SMR with CCS as benchmark technology while producing the least CO_2 emissions compared to the rest of the commercially available technologies.

However, the use of inexpensive surplus hydrogen sources may have a central role in the early phase of hydrogen infrastructure build up in the north of Spain. In the case of low hydrogen demand scenario (S1), hydrogen is already beginning to be incorporated into the road vehicle sector from the year 2020, clean hydrogen that feeds stationary fuel cells for residential and commercial sectors starts to be used from the year 2024. As illustrated in Fig. 8, in Case S1, surplus hydrogen (R50 and R99) would be sufficient to cover the hydrogen demand for transportation applications between the years 2020 and 2022 in the target study region. In Case S2, although the share of surplus hydrogen contribution to cover hydrogen demand is slightly lower than in the other case study, more than half of the hydrogen demand would be fulfilled by upcycling industrial hydrogen-rich waste gas streams.

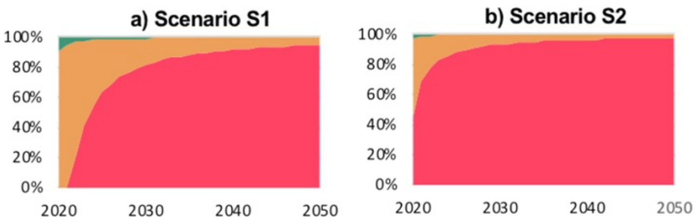

Fig. 8 Pure hydrogen produced from raw material r ∈ R; ■ CH4; ■ R99; ■ R50 by hydrogen demand scenario s ∈ S.

Therefore, industrialized hydrogen also plays an important role in initiating the transition to a hydrogen economy with localized plants of SMR with CCS; this will support the demand before expanding to less populous areas forming a more decentralized green hydrogen production. Analyzing the surplus hydrogen flowrates by customer it can be observed that although R50 is partially marketed to all final end-users, it has a pivotal contribution when the production of the final product is closer to the customers. The key hotspot demand markets where surplus hydrogen has a central role are displayed in Fig. 9.

Fig. 9 Total hydrogen produced at ▲ Merchant company j ∈ J from raw material r ∈ R; ■ R99, ■ R50 by ✚ the key hotspots demand markets.

Additionally, our study confirms that the price of upcycled hydrogen is in the range of 1.5~~to~~-2 times lower than the price of hydrogen obtained by steam conversion of natural gas with CCS, as summarized in Table 8.

(The text within *Table 8 Average levelized cost of hydrogen by technology w ∈ W* should be centered across the columns.) **Table 8** Average levelized cost of hydrogen by technology w ∈ W.

Technology	Production Cost (€/year)	Hydrogen Produced (kg H_2/year)	Levelized Cost (€/kg H_2)
W1	1.56E+08	9.75E+07	3.28
W2	1.68E+05	5.02E+05	0.35

W3	2.27E+07	2.08E+07	1.09

5 Conclusions

In this paper, we have addressed the design of the optimal hydrogen supply chain network for the northern Spain region that integrates hydrogen-rich waste gas sources and converts them into liquefied hydrogen, by maximizing the net present value as the objective function. This research has a twofold objective: (i) on the one hand, it provides the methodology to assess the techno-economic feasibility of reusing surplus hydrogen gases promoting the shift to the Circular Economy and, (ii) on the other hand, it contributes to the penetration of renewable energies expressed as low cost fuel cell devices to power stationary and mobile applications.

Optimal decisions are provided by using a mathematical modeling approach regarding the technology selection, facility location and sizing, and yearly production planning. The proposed problem was based on 3 possible raw materials, 8 possible suppliers, 17 merchants, 3 available conversion technologies, 36 customers and 1 unique product, liquefied hydrogen. The analysis has been performed over a number of case studies leading to the following conclusions,

- Within a more sustainable framework, new features to accommodate industrial hydrogen-rich waste streams in a hydrogen supply chain HSC have been developed to determine how and when stakeholders shall invest in developing the hydrogen infrastructure.
- For both scenarios of hydrogen demand (S1 and S2), all generated case studies lead to a solution with positive net present values NPVs, where the revenue is able to absorb the costs. This means that the more sustainable HSC that integrates upcycling of surplus hydrogen is economically feasible.
- The results reinforce the fact that the use of inexpensive surplus hydrogen sources, such as raw materials named R50 and R99, offer an economic solution to cover hydrogen demand in the very early stage of transition to the future global hydrogen-incorporated economy.
- Industrialized hydrogen has a pivotal contribution when its generation is closer to the demand markets. Moreover, hydrogen production via purification systems stands out as the most profitable solution, which strongly depends on the available volume of the industrial waste streams.

In conclusion, the environmentally advantageous waste-to-energy route based on the use of industrial hydrogen-rich gas sources has been evaluated from the techno-economic perspective. The optimization modeling approach based on multi-scenario multi-period mixed-integer linear programming has been applied to the northern Spain region, 4135,4 km^2 and 11,723,776 inhabitants, having identified a pull of 8 suppliers, 17 merchants and 36 customers leading to the optimum HSC over a 30-year period. The obtained results, that for the first time analyze the economic advantages of integrating upcycled industrial hydrogen in HSCs, could support future decision-making policies and the methodology could be extended to different spatial regions and timeframes.

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Appendix A. Supplementary material (The section heading Appendix A. Supplementary Material should be rewritten to Appendix. Supplementary material. Inside, the document is divided into two Appendix: Appendix A: Model Parameters and Appendix B: Mathematical Formulation.)

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apenergy.2018.09.047. These data include Google maps of the most important areas described in this article.

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Appendix A. Supplementary material **(The section heading Appendix A. Supplementary Material should be rewritten to *Appendix. Supplementary material*. Inside, the document is divided into two Appendix: Appendix A: Model Parameters and Appendix B: Mathematical Formulation.)**

The following are the Supplementary data to this article:

Multimedia Component 1

Supplementary Data 1

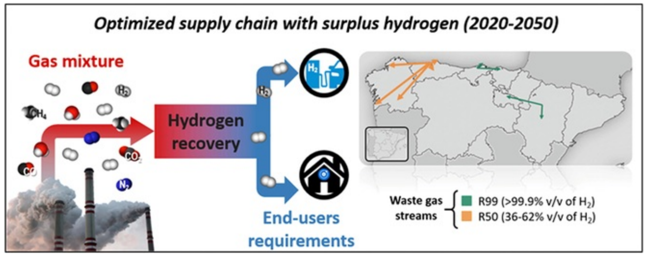
GoogleMap

The following KMZ file contain the Google maps of the most important areas described in this article.

Multimedia Component 2

Map

Graphical abstract



Highlights

- Upcycling of surplus hydrogen streams.
- Integration of recovered hydrogen into a hydrogen supply chain.
- Techno-economic feasibility of hydrogen upcycling using optimization-modelling.
- Surplus hydrogen has a pivotal role in initiating the shift to a hydrogen economy.

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