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Analysis of energy resources - modelling a path towards the hydrogen value

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Analysis of Energy Resources - Modelling a Path towards the Hydrogen Value

A thesis submitted to the University of Limerick in fulfilment
of the requirements of the degree of Masters of Science

By

Emma Sarah Hanley
09006643

Supervisor: Professor Bartek Glowacki

Department of Physics and Energy
And
Bernal Institute
University of Limerick

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Abstract

The world is transitioning to a decarbonised economy, less than 300 years after the emergence of the industrial revolution. There is widespread acceptance for this transition due to accelerating climate change, increasing population and increasing demand for finite resources. A shift towards the use of novel, low carbon alternative fuels and technology is imminent. This Thesis focuses on hydrogen as one such sustainable alternative fuel and cryogen for future energy and resource requirements. Hydrogen's use as an energy carrier is well known; however, it has failed to successfully penetrate energy markets on a large scale. With focus on the transition from conventional energy generation methods and fuels the 'Hydrogen Economy' can now emerge and be a key enabler to securing a sustainable, decarbonised energy future.

In the research presented hydrogen's value in decentralised energy systems is investigated with results indicating hydrogen can play an important role. It is recognised hydrogen technology integrated with other storage technologies will be important in future decentralised systems. Furthermore, hydrogen's synergy with the natural gas industry and the role of liquid hydrogen will be vital for the overall success of the hydrogen economy.

Declaration

I, Emma Sarah Hanley, hereby confirm that the content of this Thesis is a product of my own research. Where use has been made of the work of other people it has been fully acknowledged and referenced in accordance with University regulations. This material has not been previously submitted to any other University or higher education institution for an academic award of any kind.

Signed: ______________________ Date: ____________

Emma Sarah Hanley

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List of Abbreviations

BEV	Battery electric vehicle
CCS	Carbon capture and storage
CF	Capacity factor
CHP	Combined heat and power
CNG	Compressed natural gas
CO	Carbon monoxide
COE	Cost of electricity
CO_2	Carbon dioxide
CRF	Capital recovery factor
CSP	Concentrated solar power
DC	Direct current
DCFC	Direct carbon fuel cell
DECRO	Direct electro-chemical reduction of oxides
DRO	Direct reduction of oxides
EU	European Union
FCEV	Fuel cell electric vehicles
GHG	Greenhouse gas
GHI	Global horizontal irradiance
GHS	Gaseous hydrogen storage
H_2	Hydrogen
HEV	Hybrid electric vehicle
HHV	Higher heating value
ICE	Internal combustion engine

iLH_2	Indirect liquid hydrogen cooling
LCOE	Levelised cost of electricity
LH_2	Liquid hydrogen
LHS	Liquid hydrogen storage
LNG	Liquefied natural gas
MRI	Magnetic resonance imaging
NGV	Natural gas vehicles
NMR	Nuclear magnetic resonance
OCC	Overnight capital costs
O&M	Operation and maintenance
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cell
PHEV	Plug-in hybrid electric vehicle
PV	Photovoltaic
RFB	Redox flow battery
SD	System dynamics
SMES	Superconducting magnetic energy storage
SMR	Steam methane reforming
SOFC	Solid oxide fuel cell
TCM	Thermal cracking of methane
TES	Thermal energy storage
VRFB	Vanadium redox flow battery

List of Units and Symbols

\$	US Dollar
%	Percentage
€	Euro
°C	Degree Celsius
A	Amp
Bcf	Billion cubic feet
c	Centi 10^{-2}
C_{comp}	Cost of a hydrogen compressor
E	Exa 10^{18}
G	Giga 10^{9}
h	Hour
Hz	Hertz
J	Joule
K	Kelvin
k	Kilo 10^{3}
kg	Kilogram
km	Kilometres
kWh_t	Thermal energy in kilowatt hours
kW_p	Peak power in kilowatts
l	Litre
m	Milli 10^{-3}
M	Mega 10^{6}
m^2	Area

m^3	Volume
MMBTU	1 million British thermal units
n	Scaling component for compressors
Nm^3	Normal metre cubed under standard temperature and pressure
Pa	Pascal
T	Tesla
T_{boil}	Boiling temperature
T_{inv}	Inversion Temperature
ton	1 ton = 907 kg
tonne	Metric tonne; 1000 kg = 1 tonne
W	Watt
x	Electrolyser capacity (kg/hr)
y	Electrolyser cost ($)
z	Number of electrolysers

Chapter 1 Introduction

1.1 Background, Motivation and Objectives

Hydrogen is anticipated to be an important sustainable energy carrier and cryogen. The use of hydrogen as an energy carrier is not a new concept; however, with the recent increase of renewable capacity and requirement for storage, increasing concerns for climate change, continued dependence on oil for transport and increasing carbon dioxide emissions (CO_2) focus has turned to the emergence of a hydrogen economy. The term "hydrogen economy" refers to the vision of using hydrogen as a low-carbon energy carrier to replace conventional fossil fuels. The research and development of hydrogen production methods using renewable and non-renewable resources of energy, hydrogen storage and its use in transport, thermal, and electric applications will allow hydrogen to be recognised as a valuable resource for a decarbonised sustainable energy future.

The global energy system needs to transition to low-carbon methods of energy production and generation as energy-related CO_2 emissions in 2050 must be half of the current levels to limit the global temperature increase to 2°C. Future low-carbon energy systems will be characterised by a greater diversity of decentralised technologies and fuels, more renewable energy, and increased complexity across the entire energy system where hydrogen can play a valuable role. A systems approach to energy must be taken to carefully examine the complex relationships existing within energy systems.

Hydrogen is the lightest element on earth and at a standard temperature and pressure hydrogen is a nontoxic, odourless, and highly combustible gas. Currently fossil fuels are used as the main source of hydrogen production as hydrogen is not found in pure form on Earth. The current production of hydrogen is therefore unsustainable; however, with the use of production methods such as renewable electrolysis and microwave plasma processing of natural gas the resulting greenhouse gas emissions (GHG) from hydrogen production can be reduced. Hydrogen's flexibility allows it to be considered as a suitable energy carrier and key enabler of future low-carbon energy systems.

The central research question of this Thesis is what is the value of hydrogen as a sustainable future energy resource and cryogen in integrated systems. System dynamics (SD) is used within the research to allow different factors in relation to hydrogen energy systems to be interrelated and analysed. The use of SD allows complex pathways to be modelled using system stocks and flows combined with causal influences and feedback loops.

The motivation of the Thesis was to analyse the value of hydrogen as an energy carrier and a cryogen. The simplified concept is depicted in Figure 1.1. Figure 1.1 includes the gasification of liquefied natural gas (LNG) as it is anticipated the development of LNG depots will improve energy diversity with the production of hydrogen using microwave plasma processing of natural gas. Alternatively, renewable electrolysis can be used. Overall energy security can be improved and GHG emissions reduced as a result of displacing conventional fossil fuel energy generation. Hydrogen's use in stationary, transport and cryogenic applications are also highlighted in Figure 1.1. From Figure 1.1 three individual aspects of the hydrogen economy were recognised; the use of hydrogen in decentralised energy storage systems (pink shaded region), the synergy between natural gas and the hydrogen economy (green shaded region) and the use of liquid hydrogen for cryogenic applications with focus on hospital systems (blue shaded region).

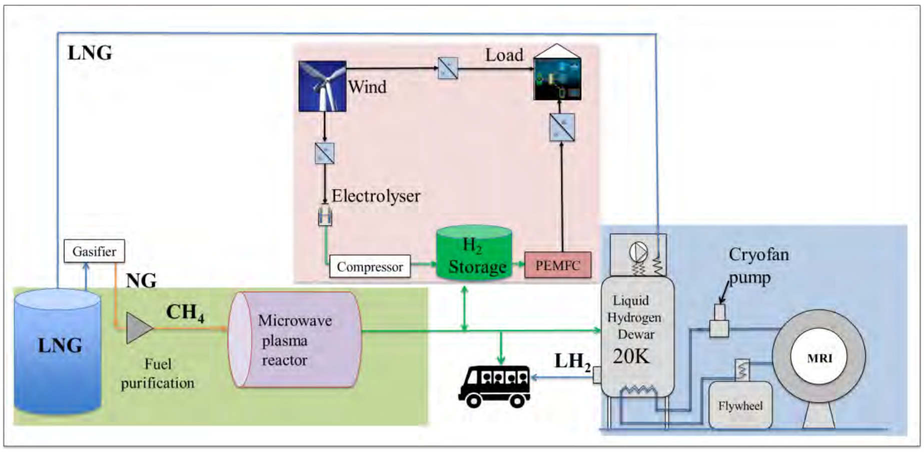


Figure 1.1 Simplified hydrogen economy highlighting the initial concept of the Thesis. Three different individual aspects of the hydrogen economy are highlighted; decentralised hydrogen storage (pink shaded region), synergy with natural gas (green shaded region) and liquid hydrogen as a cryogen for applications within hospitals (blue shaded region).

From the identification of the three individual aspects from the concept in Figure 1.1 the objectives of the Thesis were developed as follows:

- Identify the operation and value of a decentralised hydrogen buffer storage system for supplying electricity to reduce grid energy and CO_2 emissions using SD modelling of various scenarios.
- Compare hydrogen storage with other decentralised storage technology in individual and integrated systems to identify the potential increased value of hydrogen in integrated systems using SD modelling.
- Identify the various synergies between natural gas and the hydrogen economy and conclude on how natural gas can aid in the emergence of the hydrogen economy.
- Research the synergy between liquid hydrogen and the superconducting industry.
- Investigate the impact a decentralised compressed and liquid hydrogen system can have on hospital energy and resource requirements.

The concept shown in Figure 1.1 was extended during the research as new concepts emerged and the complexity of the hydrogen economy was realised. An updated relevant version of Figure 1.1 is included in each research chapter.

1.2 Structure of Thesis

The background, motivation and objectives were presented in the previous section 1.1, Chapter 1. Based on the objectives identified the Thesis was structured as outlined below. The actual conducted research based on the concept in Figure 1.1 is documented in Chapter 4 - Chapter 9.

Chapter 2: A review of literature is presented and includes discussions on different aspects of the hydrogen economy and hydrogen technology. Additional literature is discussed in the individual research chapters.

Chapter 3: SD methodology for analysing complex integrated hydrogen systems is discussed. Different examples of where SD has been used within the energy industry are included.

Chapter 4: The value of the operation of a decentralised hydrogen buffer system using SD modelling is researched.

Chapter 5: A SD comparison of hydrogen with redox flow batteries (RFB) is completed and an analysis of the potential benefits of integrated systems presented.

Chapter 6: The potential value of an integrated molten salt system for energy storage and material production coupled with a hydrogen storage system for securing sustainable energy and material production is investigated.

Chapter 7: The synergy of the natural gas industry with the hydrogen economy and how each industry can benefit from the relationship is researched.

Chapter 8: An introduction to the potential use of liquid hydrogen for cryogenic applications is discussed.

Chapter 9: An investigation with SD analysis looks at the impact the hydrogen economy can have on the development of smart hospital buildings regarding resource and energy consumption.

Chapter 10: Emerging conclusions and potential future research is discussed.

Appendix: A list of peer-reviewed publications, submitted publications and presentations at international conferences is included.

Chapter 2 Literature Review

This chapter introduces literature based on the hydrogen economy, hydrogen technologies and hydrogen applications.

2.1 The Hydrogen Economy

The hydrogen economy has been long anticipated as an energy carrier that can allow the long-term sustainable production and use of energy. The hydrogen economy is now beginning to emerge in different sectors and playing a role in global energy systems; however, it is faced with many challenges and uncertainties [1, 2]. A hydrogen economy can potentially increase energy security and allow for environmental and economic benefits for transport, electric and thermal applications [3]. Research on the hydrogen economy predicts the more widespread use of hydrogen as an energy carrier to mitigate emerging energy challenges in the future. One study predicts the transport sector to be the main market for hydrogen in the energy industry until 2050 due to the importance of reducing the current dependence on oil-derived fuels. In the short-term hydrogen use in passenger transport and buses is expected while in the long-term the use of hydrogen and other alternative fuels in heavy duty transport is expected [4]. Another study predicts hydrogen's use in energy will be an estimated 5.1% of total primary energy demand by 2050 with the majority expected again to be in the transport sector [2, 5]. An additional important role for hydrogen is as an energy carrier for bulk energy storage. This is important for energy security and continued penetration of renewable energy [5]. Although hydrogen has many advantages, competition in the energy sector is a major challenge and as the technology is still being developed some studies predict that hydrogen will not have a significant market share for 10-15 years [1, 3, 6]. The Energy Information Administration predict negligible use of hydrogen by 2030, the Intergovernmental Panel on Climate Change estimate the use of hydrogen within the energy sector will start making an impact in 2050 and Ball M et al. [2] report an estimated several decades before the development of hydrogen infrastructure will allow hydrogen to make a significant contribution to the fuel mix. Furthermore, for the widespread uptake of the hydrogen economy, government support using policy measures are required [2, 6].

Different policy changes and developments in the energy industry can encourage or inhibit the emergence of the hydrogen economy. For example the introduction of CO_2 penalties could encourage a low-carbon hydrogen economy, while lack of incentives coupled with cheap coal and natural gas could be detrimental [7, 8]. Many studies focusing on the emergence of the hydrogen economy have been completed. Moriarty P et al. report that for future energy demand a low energy case (300 EJ) met by a low fossil fuel share (20%) and in which hydrogen will play a role as an energy carrier is the most likely scenario with a high energy demand case (1000 EJ) not probable due to resource limitations and energy costs [1]. Barreto L et al. report hydrogen will contribute in the future energy mix but produced initially by fossil fuels evolving towards renewable production [9]. Barreto L et al. completes a qualitative study; however, also uses a quantitative study that presents a world energy scenario [9]. The scenario consists of a world aiming to achieve sustainable development and it is identified technological change will play an important role for the transition to clean technologies [9]. The study concludes that hydrogen will allow for flexible, decentralised, more secure, efficient, environmental and economic energy systems to emerge in the transport, thermal and electricity sectors [9].

To achieve a sustainable future the use of renewable technologies is required. As previously mentioned hydrogen can be integrated with renewable technology allowing for energy storage and increased renewable penetration [4]. Among different renewable-hydrogen scenarios a solar-hydrogen economy is suggested to play a dominant role [7]. The advantages of such a system include emission free energy, continued development of solar energy and reduction in the use of fossil fuels for energy generation that can be used instead for other applications. Solar energy integrated with hydrogen is a scalable vision and Abbot D reports other renewable industries including wind do not have this potential [7]. However, in this Thesis a wind-hydrogen system is considered as globally solar energy may be dominant but within certain energy systems and countries (Ireland) wind energy can be the dominant renewable energy source available for hydrogen production.

In contrast to the positive studies on the emergence of the hydrogen economy, some studies suggest the time for hydrogen energy systems has passed as a result of developments made in batteries technology and other alternative technologies [5]. Bossel U et al. believe hydrogen cannot compete against electricity as an energy carrier due to efficiencies and reports fuel cells will contribute to a secure energy future but with the use of fossil fuels to displace conventional power plants instead of hydrogen [10]. However, hydrogen can act as a complementary energy carrier to other energy systems for a decarbonised energy future as considered in this Thesis. The widespread introduction of hydrogen as an energy carrier faces major challenges that include developing cost-competitive fuel cell electric vehicles (FCEV) and infrastructure for hydrogen production, distribution and refuelling along with gaining public acceptance and identifying safety considerations (due to limited experience with hydrogen energy systems in consumer environments) [2, 11]. Bossel U et al. state a hydrogen economy can never become a reality due to the cost of hydrogen infrastructure and competition from battery electric vehicles (BEV) [10]. However, the HyWays report states that hydrogen is a cost-effective option for the reduction of CO_2 in the transport sector but as predicted by Bossel U et al. a cash flow analysis shows that high initial investments for hydrogen infrastructure is required [4]. In Chapter 9 the use of hydrogen to compliment BEV will be investigated as hydrogen will be an important alternative energy carrier for complementing other energy carriers such as electricity in the transport sector.

Governments will need to act as the initial market driver to create innovations for the hydrogen economy [12]. Policy drivers for the integration of hydrogen in the European Union (EU) include the ‘20-20-20’ targets that aim to have a 20% reduction in GHG emissions from 1990 levels, to raise the share of EU renewable resources by 20% and improve energy efficiency by 20%. In 2014 national governments agreed that by 2030 a 40% reduction in GHG emissions from 1990 levels, an increase in the share of renewables by 27% and an increase in energy efficiency by 27% would be achieved [12]. Another policy driver is the aim for low carbon transport. Furthermore, the EU clean power for transport directive 2014/94/EU aims to facilitate the development of a single market for alternative fuel within the European transport sector. The Trans-European network for transport programme supports the development of a European network of hydrogen infrastructure. Also the liberalisation electricity systems within countries, (including Ireland with the formation of the single electricity market), is becoming more widespread and this is leading to an increase of the implementation of small generators e.g. fuel cells. Article 14/7 of the Directive of the European Parliament and Council outlines that when planning the development of the distribution network, energy efficiency, demand-side management and decentralised generation should be considered by the distribution system operator [13].

It is envisioned decentralised energy systems will allow for the development of the hydrogen economy. Winter C J et al. considers five milestones for the development of the hydrogen economy in which one is the development of efficient stationary fuel cells for use in decentralised energy systems [14]. Andrews J et al. proposes six principles to guide the role played by hydrogen for sustainable energy in which hydrogen production, storage and distribution centres relying on local renewable energy sources is included [5]. Barreto L et al. states hydrogen will contribute substantially to the transition to a more flexible, cleaner and less vulnerable decentralised electricity generation system [8, 9] while Marban G et al. believes it is clear that beyond 2050 two energy distribution networks of electricity and hydrogen will be operating [15].

It is clear that interest in the emergence of a hydrogen economy continues to grow as the world attempts to transition towards a decarbonised future. With numerous opportunities and uncertainties it is believed hydrogen will have a complimentary role in the energy system for storage, electric, thermal and transport applications and additionally in superconductivity applications supplying an economic cryogen. It is anticipated decentralised energy systems are a key enabler to the emergence of the hydrogen economy.

2.2 Centralised vs. Decentralised Energy

Decentralised energy systems are gaining focus due to energy security and climate change considerations along with the high GHG emissions from centralised fossil fuel plants. Decentralised energy systems can potentially allow for the changes required in the energy sector [13-19]. Advantages include their ability to operate with more than one source of energy and also their potential to be integrated with renewable energy and storage systems [16, 17]. Currently the majority of energy systems consist of centralised power plants. Centralised energy generation benefits from high economies of scale, base load power capacity and reliability (if energy resources are available) [18]. However, it is clear a transition from these conventional fossil fuel power plants is required. Bouffard F et al. states that a fully decentralised energy system is not ideal but a hybrid of centralised and decentralised systems should be considered to benefit from the advantages of both energy supply systems [17]. Challenges of decentralised energy include technical challenges of operating the power plants and reliability of the overall system as if the power plant is relying on non-dispatchable generation the capacity can be affected and require investments in back-up power [16]. Globally, the total share of decentralised power generation has increased to 7.2% in 2004, up from 7% in 2002 [20] so it is clear the advantages of decentralised energy systems are being recognised [16, 21].

The type of decentralised energy system discussed in the Thesis is described by El Khattam W et al. as the use of non-conventional generators that include electrochemical fuel cell devices as a method of decentralised electricity generation [18]. Kaundinya D P et al. divides decentralised energy systems into grid connected where excess energy can be sent to the grid and standalone systems that have no connection to the grid [19], both types of systems are considered in the Thesis. Among the applications of decentralised energy systems El Khattam W et al. includes their applications as a standby energy source for sensitive loads such as hospitals [18]. The use of hydrogen technology within hospital energy systems is presented in Chapter 8 and Chapter 9. Decentralised generation can vary and range from 1 W-300 MW [18], 1 kW-1 MW [16]. A distinction can be made between decentralised micro (< 5 kW), small (5 kW–5 MW), medium (5–50 MW) and large (50–300 MW) generation [22].

The evaluation of different decentralised generation sizes within the energy systems discussed are considered within the Thesis and like Karger C R et al. the technical and economic boundaries of each individual system are embedded within scenarios allowing the response of the systems to be investigated [22]. Decentralised hydrogen production via renewable electrolysis is the main focus of the research; however, the synergies between hydrogen and other energy sources are highlighted throughout with emphasis placed on the synergy between hydrogen and natural gas.

2.3 Hydrogen Production Methods

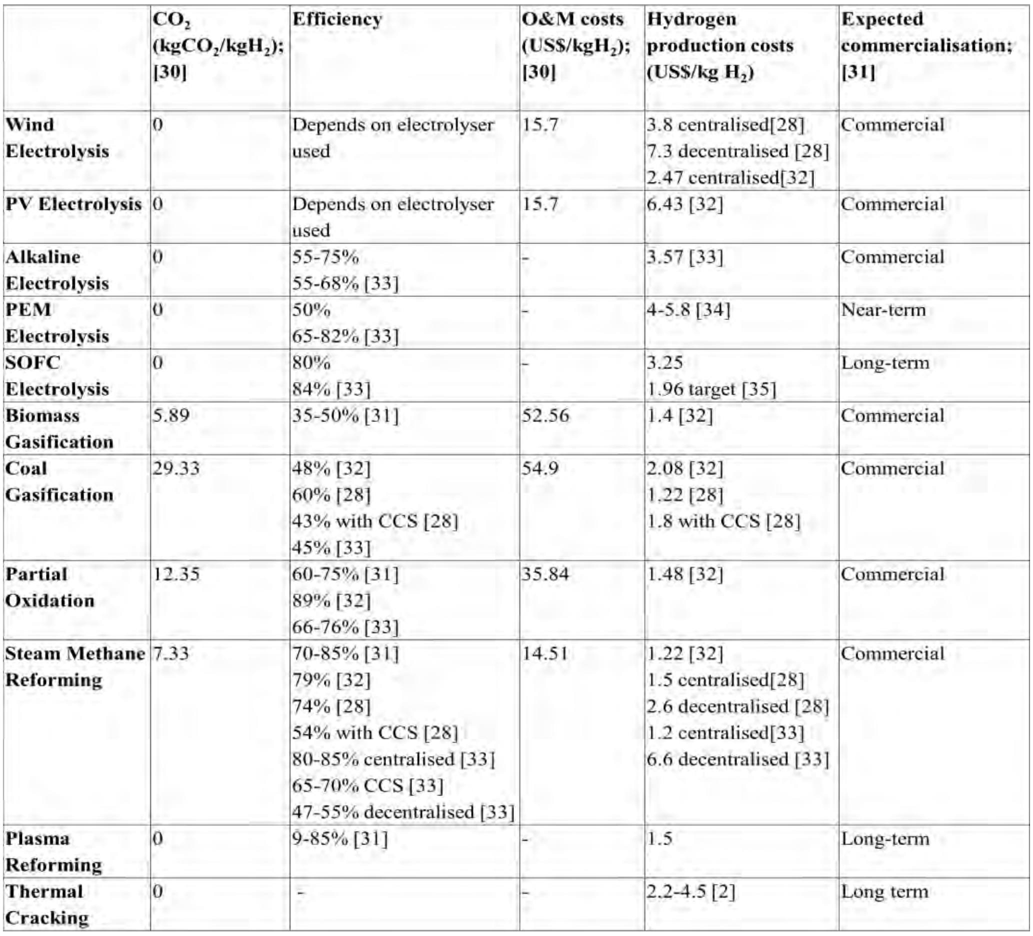
Currently, hydrogen is mainly used in industry as a raw chemical material for ammonia production and oil refineries, with an estimated production of 400-500 billion Nm^3/year. Approximately 97% is captive production with the remainder produced from merchant sources. The centralised production of hydrogen (750,000 kg/day) is anticipated to allow for economies of scale; however, development of widespread hydrogen transport infrastructure would be required, Figure 2.1. Therefore, as discussed a decentralised hydrogen economy is considered in this Thesis [23].

Figure 2.1 Hydrogen pipeline infrastructure currently installed in Europe. A decentralised hydrogen energy system is considered for Ireland due to lack of existing infrastructure [24].

Currently 96% of hydrogen is produced from fossil fuels, 48% produced via steam methane reforming (SMR), 30% from oil reforming and 18% from coal gasification. The remaining 4% of hydrogen is produced from water electrolysis [25, 26]. The use of renewable energy for hydrogen production is limited by cost [25]; however, it can aid in the development of a sustainable future [26]. It is evident it will take time to increase the capacity of clean hydrogen production and reduce costs [27-30].

Hydrogen is generally considered to be a clean fuel and it is important to look at the overall environmental impact of hydrogen production methods [26]. The study by Koroneos C et al. analyses the inputs and outputs from the life cycle of various hydrogen production pathways and report hydrogen production using photovoltaic (PV) energy has low efficiencies and the worst environmental performance due to the manufacturing process. Hydrogen produced by wind, hydropower and solar thermal energy are the most environmentally friendly methods [26]. For the transition to a decarbonised energy system it is anticipated fossil fuels will be important for hydrogen production in the short term and renewable energies will then be used as a substitute for fossil fuel based hydrogen production in the long term [25, 29]. Table 1.1 compares different hydrogen production methods. A further analysis of literature is provided in the sections that follow on SMR, microwave plasma processing of natural gas, thermal cracking of methane (TCM) and electrolysis with a brief discussion on alternative production methods currently at the research stage.

Table 1.1 Comparison of hydrogen production methods.



	CO_2 ($kgCO_2/kgH_2$); [30]	**Efficiency**	**O&M costs (US$/$kgH_2$); [30]**	**Hydrogen production costs (US$/kg H_2)**	**Expected commercialisation; [31]**
Wind Electrolysis	0	Depends on electrolyser used	15.7	3.8 centralised[28] 7.3 decentralised [28] 2.47 centralised[32]	Commercial
PV Electrolysis	0	Depends on electrolyser used	15.7	6.43 [32]	Commercial
Alkaline Electrolysis	0	55-75% 55-68% [33]	-	3.57 [33]	Commercial
PEM Electrolysis	0	50% 65-82% [33]	-	4-5.8 [34]	Near-term
SOFC Electrolysis	0	80% 84% [33]	-	3.25 1.96 target [35]	Long-term
Biomass Gasification	5.89	35-50% [31]	52.56	1.4 [32]	Commercial
Coal Gasification	29.33	48% [32] 60% [28] 43% with CCS [28] 45% [33]	54.9	2.08 [32] 1.22 [28] 1.8 with CCS [28]	Commercial
Partial Oxidation	12.35	60-75% [31] 89% [32] 66-76% [33]	35.84	1.48 [32]	Commercial
Steam Methane Reforming	7.33	70-85% [31] 79% [32] 74% [28] 54% with CCS [28] 80-85% centralised [33] 65-70% CCS [33] 47-55% decentralised [33]	14.51	1.22 [32] 1.5 centralised[28] 2.6 decentralised [28] 1.2 centralised[33] 6.6 decentralised [33]	Commercial
Plasma Reforming	0	9-85% [31]	-	1.5	Long-term
Thermal Cracking	0	-	-	2.2-4.5 [2]	Long term

2.3.1 Steam Methane Reforming

SMR is currently the main method of producing industrial hydrogen. It is a mature production process with high efficiencies and is currently the most economical method for large-scale hydrogen production, Table 1.1.

In the SMR process natural gas and steam are present within the reformer and reacted over nickel-based catalysts that cause the methane present in the natural gas to react with the steam to form hydrogen and carbon monoxide (CO) [36]. The reaction operates at high temperatures, within the range of 900-1200 K and a pressure range of 2-25 bar [37, 38]. This reaction requires heat which is sourced from the combustion of extra natural gas or waste gases produced during the overall process. The syngas that is produced undergoes a water-gas shift phase in a separate reactor, producing syngas composed of CO_2 and hydrogen [38]. The syngas is reacted over iron chrome catalysts that cause H_2O to split and react with the CO to form hydrogen and CO_2 which allows additional hydrogen to be formed [39]. Pressure swing adsorption is widely used for completing the final step to separate the hydrogen from the syngas. The remaining gas after the separation step is used as additional fuel for the reformer.

There are reduced efficiencies in decentralised plants, Table 1.1, and an increased cost of production depending on the amount of hydrogen produced (7 kg/hr) 4.60 \$/kgH_2 and (24 kg/hr) 3.53 \$/kgH_2 [33]. Additionally, the SMR process has associated CO_2 emissions, Table 1.1, and as a result carbon capture and storage (CCS) technologies [36] are being investigated and developed so hydrogen can emerge as a low-carbon fuel from the SMR process [39-4145]. SMR plants with CCS have an overall efficiency reduction of 5-10% as a result of extra energy requirements for CCS [23]. The use of gas absorption in the process is currently a commercially available option [46]. Removal of up to 90% of CO_2 is achievable and it is then compressed and transported through pipelines to a site where the CO_2 can be injected into saline formations [36]. Challenges for CCS technologies include an increased cost per kilogram of hydrogen produced and the requirement of necessary infrastructure along with the suitability of the aforementioned geological formation [47]. As the overall compliance cost associated with future regulatory action on CO_2 emissions becomes likely, CCS systems will appear as a promising option for low-carbon hydrogen production from natural gas. For decentralised production alternative technologies are being considered such as microwave plasma processing of natural gas and the thermal cracking of methane as a result of the CO_2 emissions from SMR and the requirement for transport and storage of CO_2 if CCS methods are used [36].

2.3.2 Microwave Plasma Processing of Natural Gas

Microwave plasma processing of natural gas is an alternative method of hydrogen production using natural gas with no direct CO_2 emissions. The process in addition to hydrogen produces carbon black that can be synthesised into more valuable products. High temperatures >1200°C are required to split the methane. This technology is suitable for small scale decentralised hydrogen production as it is an economically attractive process with high power density and a fast response time, along with high conversion efficiencies [48, 49]. The best results obtained without a heat exchanger were a 95-97% hydrogen yield at a specific energy consumption of 13 MJ/kgH_2 [48]. With a heat exchanger and improved thermal management it is estimated the specific energy consumption can be decreased to 7 MJ/kgH_2 and a higher yield of 97%. The overall thermal efficiency of this system (assuming 80% yield, 40% electrical generating efficiency, 7 MJ/kgH_2 electrical power) is 65%. Cho W et al. carried out an experimental analysis in a microwave plasma-catalytic system. Methane decomposition was carried out with 2.45 GHz microwave plasma and a high conversion and yield of hydrogen and carbon black were obtained [50, 51]. It was found that hydrogen and carbon black were produced at the mole ratio of 2:1. With 3 kW of applied power and 1.0 l/min of flow rate of methane when an input of 1 mole of methane was introduced, 0.6 mole of carbon and 1.62 mole of hydrogen were produced [50]. For 90 kW of electricity to power the microwave plasma reactor, 571 m^3/h of hydrogen can be produced [48]. If the plant has a lifetime of 15 years, then the capital cost is of the order of 150,000 $/year and with an annual hydrogen production of 60,000 MMBTU, the cost of the hydrogen is calculated to be 8.3 $/MMBTU.

The carbon material produced provides another profit stream from the process. Carbon black and synthesised carbon have many applications resulting from the electrical conductivity of carbon. These include use as electrodes in vanadium redox flow batteries (VRFB) [52, 53], all-iron redox flow batteries and use in hydrogen fuel cell membrane assemblies. Furthermore, carbon black is widely used to modify different properties of materials in which they are used [50, 51]. Nano carbon powders, CO_x, C_2H_2, C_2H_4, and HCN are also formed [54]. Microwave plasma processing of natural gas is considered in the research as a promising decentralised hydrogen production technology and included in the SD modelling as it may be a suitable hydrogen production process for Ireland.

2.3.3 Thermal Cracking of Methane

The TCM hydrogen production process uses concentrated solar power (CSP) to generate high temperatures in order to decompose the methane. It is predicted the hydrogen production costs for large scale solar plants will depend on the price of the carbon black produced. An example is given that hydrogen price will be 14 €/GJ for the lowest carbon grade sold at 0.66 €/kg and this decreases to 10 €/GJ for carbon black sold at 0.8 €/kg. A 1 kW laboratory scale test solar reactor is being designed at 1200-1700°C and 1 bar [55]. Abandes S et al. developed a lab-scale high-temperature fluid-wall solar reactor for hydrogen production. The conversion of methane can exceed 97% with a hydrogen yield of 90% [25, 28, 29]. Maag G et al. completed an experimental investigation of the thermal decomposition of methane into carbon and hydrogen using a 5 kW particle-flow solar chemical reactor at temperatures in the range of 1300-1600 K [56]. Methane conversion and hydrogen yield exceeding 95% were obtained with higher hydrogen yields compared to Abandes S et al. There is a large potential for the reduction of CO_2 emissions and it is estimated 14 kg of CO_2 emissions are avoided and 277 MJ/kgH_2 of energy saved compared to hydrogen production via SMR and the processing of carbon black. Methane decomposition using either microwave plasma or thermal cracking is a promising alternative for hydrogen production [25, 57]. As a result of low potential for CSP in Ireland the TCM production method was not included in the research in this Thesis.

2.3.4 Electrolysis

As mentioned hydrogen production from fossil fuels is dominant and electrolysis only makes up 4% of total hydrogen production; however, the main driving force for hydrogen's use as an energy carrier is based on the need for alternative energy systems to diversify resources and move away from fossil fuel energy. Water electrolysis will allow this goal to be achieved [6]. Water electrolysis, including alkaline water electrolysis, high-pressure electrolysis, proton exchange membrane (PEM) water electrolysis and solid oxide steam electrolysis, are promising technologies for use with renewable energy [58]. There is an electrolysis cost target by the US Department of Energy of 3 $/kg; however, costs currently are higher and a disadvantage of electrolysis is due to the cost being directly dependent on electricity cost [59]. Electrolysis can have a large capacity and hydrogen produced from electrolysis is often considered the best method to store energy from renewable and intermittent power sources [60]. Electrolysis is an endothermic reaction and operates by passing an electrical current through the electrolyte. This decomposes the water into hydrogen gas at the cathode and oxygen at the anode.

PEM electrolysers can operate at a current density range of 0.5-2 A/cm^2 and pressures of 0.8-20.7 MPa [61]. This is advantageous and allows for a reduction of the operational costs [62]. Furthermore, PEM electrolyser cells have a fast response to fluctuations in electrical input and are capable of being operated between 0 and 100% of nominal capacity making them suitable for integration with renewable energy [62]. Barriers to PEM electrolysis include relatively high capital costs and as a result of only 4% of hydrogen produced via electrolysis the demand has been low leading to little research on PEM electrolysis being carried out [62]. PEM electrolysis can offer significant potential in improvements and can compete with alkaline technology when cost improvements are achieved. The main difference between alkaline and PEM electrolysis is that alkaline electrolysis is well established and has favourable costs compared to PEM electrolysis [60, 62, 63]. Alkaline electrolysers are currently available in the megawatt range and this allows for the large scale production of hydrogen for bulk energy storage. Operating temperatures are in the range of 70-100°C with pressures of 1-30 bar. Alkaline electrolysers have low current densities of 0.2-0.6 A/cm^2 [61]. One disadvantage of alkaline electrolysers is that they have a lower capability to respond to fluctuations in input electricity which is important for integration with renewable energy.

High-temperature water electrolysis is a more efficient process than the low temperature methods discussed; however, it is faced with challenges that have to be overcome before market application can be considered. Solid oxide electrolysers operate at high temperatures at a current density of 0.25 A/cm^2 in the range of 600-1000°C. The water can be more easily split as a result of the added energy contribution from the heat allowing increased efficiencies; however, it is a novel technology [64]. A maximum system efficiency of 75.9% can be achieved [65].

Electrolysis for hydrogen production would be a suitable solution to Ireland's energy problems integrated with decentralised or centralised wind turbines. Ireland's wind capacity has increased as a result of attempts to meet stricter EU environmental regulations. A feasibility analysis carried out by Goodbody C et al. investigated the available renewable energy options [66]. The net present cost, the cost of energy, and CO_2 emissions of different energy combination were considered to determine the most suitable renewable and non-renewable integrated energy system. From the results wind energy was shown to have the greatest potential for renewable energy generation in Ireland and wind energy was also a component of the optimal hybrid systems. Onshore wind energy is the most competitive form of renewable energy in Ireland, but its intermittent nature is a disadvantage to continued development [67, 68]. González A et al. simulate and optimise a wind-hydrogen system and report even with significant reductions in the cost of electrolysers and low average wind electricity cost, a high hydrogen market price is needed to be economically feasible [67]. However, an integrated wind-hydrogen system can allow an increase in wind penetration in Ireland, GHG emissions reduction, a decrease in curtailment and backup capacity required [67]. A wind-hydrogen system using renewable electrolysis could be piloted in Ireland as a result of the suitable wind speeds and relatively small energy system [68]. Different SD studies and scenarios considering wind-hydrogen decentralised systems are presented in the Thesis as renewable electrolysis is the main method of hydrogen production considered.

2.3.5 Alternative Methods

Alternative methods of hydrogen production with limited negative environmental impact are being developed; however, are not of focus within the Thesis but are included to highlight the extent to which the hydrogen economy is being researched. One such method is hydrogen production from water splitting using photo-semiconductor catalysts [69]. A photo-semiconductor allows the efficient absorbing of solar energy to split hydrogen. Significant advances have been achieved in the design and development of unique photo catalysts; however, the development of new photo catalysts is still a major issue. Roeb M et al. report on the direct thermal splitting of water. Direct water splitting involves the single-step dissociation of water at high temperatures (2200°C) to split water producing hydrogen and oxygen [70]. Estimated hydrogen costs via this process show a high potential in the long-term;

however, market penetration and mass production of materials must be considered along with further research and development [70].

Another alternative energy resource for hydrogen production is the use of biomass [71-73]. Merino V M et al. report that biomass is economically feasible for hydrogen production; however, land availability is a major issue. Bioethanol provides another resource for hydrogen production. Ethanol is a renewable source of hydrogen and has many advantages including availability and high hydrogen content [73]. Biological hydrogen production is still under development and requires further research and development to compete with other hydrogen production methods. The breakthroughs that are being made with hydrogen production are important for the long-term use of hydrogen.

The economic and environmental production of hydrogen will be vital for the widespread use of hydrogen in different applications.

2.4 Applications of Hydrogen as an Energy Carrier and Cryogen

The use of hydrogen in electric, thermal, transport and cryogenic applications is presented along with different methods of hydrogen storage.

2.4.1 Electric and Thermal Applications using Fuel Cells

Fuel cells allow for energy generation with low GHG emissions and are expected to play a role in emerging decentralised and decarbonised energy systems [74-77]. One advantage of hydrogen as an energy carrier is as a result of its flexibility. Stationary applications producing electricity and heat via fuel cells are anticipated to be an important application of hydrogen as an energy carrier.

Stationary fuel cell power plants generating electricity are suitable for varying capacities including; for single houses (10 kW), housing estates (100-300 kW) or on-site generation plants (1000 kW) [78]. The use of stationary applications for electricity and thermal energy are not expected to play as large a role in the hydrogen economy when compared to the transport sector in the short-term, as at an EU level the discussions on hydrogen use is limited to the transport sector. It is generally accepted that the use of hydrogen for stationary power generation will lag behind

[79]. The commercialisation and widespread uptake of hydrogen stationary markets requires identification of niche markets where the system can offer advantages that can justify higher investment costs. These niche markets are identified throughout the Thesis. For example, Chapter 4 investigates the operation of stationary hydrogen storage for supplying a hydrogen buffer allowing increased energy security in decentralised systems. Furthermore, Chapter 5 highlights the increased value of hydrogen for energy storage and generation when integrated with other energy storage systems. Chapter 6 presents an integrated hydrogen and molten salt decentralised system that can target sustainable energy storage and material production. Finally, Chapter 8 and Chapter 9 identify the potential niche market for hydrogen in providing an economical energy carrier and cryogen for hospital systems.

Another potential niche market includes the co-generation of electricity and heat using solid oxide fuel cells (SOFC) as a result of the high operating temperatures [80]. Co-generation increases the efficiency of the overall process and can reach up to 70% for electricity production with an additional 20% as heat recovery in SOFC [81]. This method of combined heat and power (CHP) is suitable for decentralised energy systems [82]. SOFC can also use other fuels such as coal and natural gas, displacing conventional energy generation methods and reducing GHG emissions [80, 82]. The use of fossil fuels in fuel cells will have important consequences for hydrogen use as it will ensure technology is in place that will aid the transition towards sustainable energy systems and the hydrogen economy. Demonstrations of the use of SOFC have proven the benefits of the technology; however, costs are the main barrier [83-85]. Advantages of SOFC include efficiency, modular configuration and they do not contain noble metals so avoiding resource and price issues. System costs of <500 $/kW are expected with power densities of >0.25 W/cm^2 for stationary applications [82].

Siemens have built a 100 kW SOFC for decentralised energy generation and the system has been operated for more than four years in the US, Netherlands, Germany and Italy and there has been no detectable performance degradation. Smaller kilowatt sized CHP units for domestic applications were field tested by Sulzer Hexis of Switzerland (important for identifying required improvements); however, cost and performance degradation was high and stack lifetime low. In Japan, more than 50 prototype systems have been installed in homes and are collecting performance data for commercialisation. Although the systems mentioned operate on natural gas, a transition to hydrogen can be made as a result of the synergies between the hydrogen economy and natural gas as discussed in Chapter 7.

The development of the hydrogen economy is a goal for many countries including the US, Canada and Japan. The number of power-to-gas pilot plants producing hydrogen from renewable energy for electricity generation or for blending into the natural gas distribution system is increasing [85, 86]. Hydrogenics are a company that focus on the manufacturing of fuel cells and hydrogen use for back-up power as one aspect of their business [87]. It is clear that there is a business case for niche hydrogen stationary back-up power plants and it is expected stationary hydrogen fuel cell systems will be integrated within global energy systems for the sustainable production of heat and electricity. The use of hydrogen for storage and stationary applications is considered in the SD models presented in Chapter 4-5 and Chapter 8-9.

2.4.2 Hydrogen as an Energy Carrier for Transport Applications

The transport sector has economic and environmental importance and it is heavily dependent on oil derived fuels. The introduction of alternative fuels such as hydrogen will be key to a sustainable transport sector [88]. Oil derived fuels in the transport sector are expected to remain dominant until at least 2035 to 2050 with other alternatives such as compressed natural gas (CNG), LNG and biofuels penetrating the market. The electrification of the transport sector is important with the widespread use of electric vehicles, including hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV) and pure battery electric vehicles (BEV). Both HEV and PHEV incorporate an internal combustion engine (ICE) whereas the BEV only has an electric engine. FCEV, hydrogen ICE and hybrid hydrogen vehicles should also be considered within the transitioning transport sector. It is anticipated hydrogen and BEV will complement each other in the transport sector. The main challenge for BEV is the limited driving range and long charging times, while the efficiency of the hydrogen pathway is the main disadvantage of the hydrogen energy system. The low efficiency of the hydrogen pathway is highlighted in Figure 2.2. From Figure 2.2 a comparison of FCEV and BEV shows the useful energy resulting from 100 kWh of initial energy for a FCEV is 23 kWh with an overall efficiency of 25% and for a BEV is 69 kWh with an overall efficiency of 69%. The transition to hydrogen FCEV is expected over the next 10-15 years with fossil fuel consumption reduced by the increased penetration of hybrid BEV cars in the near term [86]. Larsson M et al. highlights that the introduction of hydrogen into the transport energy system will create new interactions with the electricity utility sector [89].

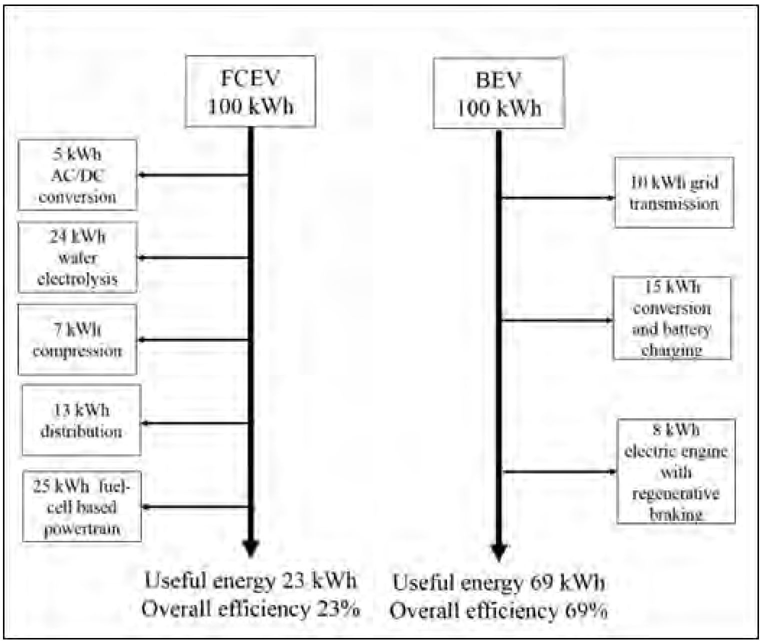


Figure 2.2 Comparison of fuel cell vehicles and battery electric vehicles efficiency [89].

Renewable electrolysis is the most anticipated method of hydrogen production for the transport sector to reduce fossil fuel consumption and GHG emissions [90, 91]. Natural gas and biofuels as mentioned are expected to be important regarding short-term options for reducing GHG emissions and reliance on oil derived fuels with hydrogen and fuel cells expected to have a contribution in the long-term for the transport sector [92].

Martin A J et al. complete a review on advances in fuel cell technologies and report that cost and durability of fuel cells are the main obstacles to be overcome for the widespread introduction of FCEV [93]. Despite the obstacles advances have been made for FCEV in the transport sector. Eight of the world's major car manufacturers signed a memorandum of understanding in 2009 that signalled their intent to commercialise FCEV by 2015. FCEV are currently available through leasing in places such as California or Japan [87]. Government incentives have played a role in early market development in these regions. All FCEV currently use proton exchange membrane fuel cells (PEMFC). Globally, there are around 600 FCEV on the road with ~300 in the USA, ~160 in Europe, ~50 in Japan and ~130 in South Korea. In addition, there are ~100 hydrogen buses in various cities. Fuel cell buses have low pollution and raise public awareness of hydrogen vehicles (e.g. Aberdeen). The Hyundai ix35 third iteration FCEV is expected to be commercialised in 2018. The Hyundai ix35 is the world's first series production hydrogen vehicle and is 2 years ahead of competitors. The fourth generation vehicle has a range of 594 km on a single tank (5.63 kgH_2 at 700 bar) of fuel with zero tailpipe emissions and a refuelling time of three minutes [94]. The Toyota Mirai is a FCEV that is expected to be commercialised by 2020.

The greatest challenge is to reduce fuel cell costs from today's level by at least a factor of 10 [95-97]. HyTrEc for the development of the hydrogen transport economy in the North Sea region formed a joint hydrogen strategy framework. The aim of the undertaking was to improve access to and advance the adoption of hydrogen as an alternative energy carrier across the North Sea region. Seven European counties were involved in the project including Denmark that has a refuelling station at 700 bar and three Hyundai fuel cell ix35 vehicles, the South West of Sweden has a refuelling station in Malmo and three Hyundai ix35 vehicles, Belgium has a refuelling station for 5 buses, another for fuelling material handling equipment and another for fuelling buses and refuse trucks and one Hyundai ix35 vehicle, Gateshead has a petrol/hybrid vehicle and BEV fitted with hydrogen range extenders and Aberdeen has two refuelling stations, fuel cell buses, hydrogen/diesel hybrid vehicles and plug in hybrid fuel cell electric vans. The success of this undertaking allows experience to be gained for the development of the hydrogen economy in the transport sector [96]. Germany, California, Japan, South Korea, Norway and Denmark are recognised as the front runners for the development of hydrogen infrastructure with these countries having 100 refuelling stations with plans to achieve 250 refuelling stations by the end of 2015. Another project called

HyFLEET:CUTE aims to implement 47 hydrogen powered buses across 10 different cities in the US [98].

Raine D et al. suggest hydrogen infrastructure must be built so FCEV can be put immediately into practical use. This means refuelling stations would need to be set up in strategic regions creating transport infrastructure that will encourage the uptake of hydrogen [90]. This approach is suggested in Chapter 9 of this Thesis in relation to the use of hydrogen for ambulances within cities. Another option includes the integration with natural gas vehicles (NGV); however, this option is not a long-term solution as it does not address energy security and fossil fuel depletion concerns. It is clear many issues must be addressed before hydrogen can be a widespread energy carrier for the transport sector. These issues include safety concerns, infrastructure implementation, consumer's acceptance and the competiveness of hydrogen with other alternative fuels [92]. BEV and FCEV are often seen as mutually exclusive options; however in the research presented in Chapter 9 a BEV with a hydrogen range extender is considered as a result of the anticipation that hydrogen and electricity will complement each other in the growth of smart sustainable transport systems. Larsson et al. suggest BEV to be used when possible due to their high energy efficiency and complemented by other vehicles such as FCEV [89].

Verhelst S et al. focus on ICE vehicles and the use of hydrogen blended with fuels for introducing hydrogen as a widespread transport fuel to the marketplace. ICE vehicles can potentially assist with the gradual integration of hydrogen refuelling infrastructure. The much lower cost of a hydrogen-fuelled ICE compared to a FCEV is another advantage. The hydrogen-fuelled ICE has been recognised as a bridging technology to introduce hydrogen as an energy carrier for transportation [99].

Some weaknesses of the hydrogen transport economy include limited number of uniform codes and standards, lack of public knowledge, few commercially produced FCEV along with threats from competition and the lack of a strong incentive to transition towards a hydrogen economy. However, hydrogen can allow for reduced environmental impacts, reduced noise, international competiveness, local production of the energy carrier, security of supply, and sustainable transport. It is in the transport sector that the hydrogen economy is anticipated to play an important role as environmental policies and fuel shortages become dominant.

2.4.3 Potential Methods for Hydrogen Storage Applications

Hydrogen storage is anticipated for the increased penetration of renewable energy and also for providing an additional low-carbon transport fuel into the transport sector. Therefore, suitable methods for bulk energy storage and on-board storage for hydrogen vehicles must be available [100]. It is recognised that hydrogen storage is a critical enabling technology for the successful commercialisation and market acceptance of hydrogen powered vehicles [100]. Storing sufficient hydrogen on-board a wide range of vehicles, while meeting all consumer requirements (driving range, cost, safety, performance, etc.) is a large technical challenge and barrier that must be overcome [100-103]. The US Department of Energy with different automotive industry partners established specific technical targets for on-board hydrogen storage systems [104]. These targets include a gravimetric energy density of 2 kWh/kg, volumetric energy density of 1.5 kWh/1, a hydrogen storage capacity (mass fraction) of 6 wt%, operating temperature range between 30-50°C, refuelling time of less than 5 minutes at a refuelling rate of 1.5 kgH_2/min, a vehicle driving range of greater than 500 km and a system cost target of 5 \$/kWh [100-103]. The fuel cost target set out for hydrogen is 2 \$/kg for 2015.

Four different methods of hydrogen storage are currently being considered; high pressure compressed hydrogen, liquid hydrogen in insulated tanks, solid-state hydride storage and porous solid adsorption of molecular hydrogen [102, 104]. Storage of compressed hydrogen requires high pressures (200-700 bar) and liquid hydrogen requires low temperatures (20.39 K) [101]. Another possibility for storing hydrogen is by the formation of metal hydrides. High volumetric capacities can be reached with metal hydrides, but, energy is required for heating for hydrogen release. Finally, adsorption in porous material is an alternative hydrogen storage method that research has grown significantly.

Carbon fibre-reinforced composite tanks for 350 bar and 700 bar compressed hydrogen are under development and are already used for hydrogen storage for stationary applications and hydrogen powered vehicles. The driving range of FCEV with compressed hydrogen tanks depends on the vehicle type, design and the amount of stored hydrogen. The compression energy penalty must also be considered. The cost of high-pressure compressed hydrogen gas tanks depends on the cost, pressure needed and the amount of the carbon fibre that must be used for structural reinforcement for the storage tanks.

Liquid hydrogen is an alternative hydrogen storage method. A hybrid liquid hydrogen storage and superconducting magnetic energy storage (SMES) system can provide a robust energy system for back-up power. Alternatively it can be considered for storage at refuelling stations for transport [102]. Liquid hydrogen tanks can, in principle, store more hydrogen in a given volume than compressed gas tanks, since the density of liquid hydrogen is 70 kg/m^3 compared to compressed hydrogen that has a density of 39 kg/m^3 at 700 bar, Figure 2.3 [100].

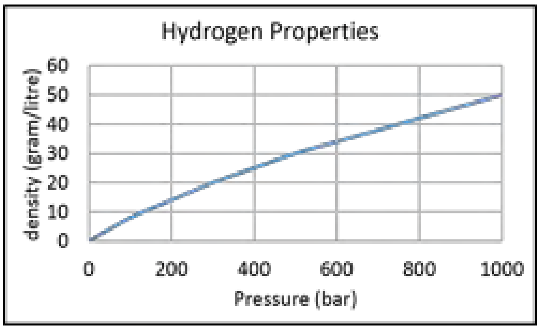


Figure 2.3 Increasing density of hydrogen with pressure for compressed hydrogen storage [100].

Liquid hydrogen is stored in cryogenic tanks at ~20 K at ambient pressure because of the low critical temperature of hydrogen (33 K) [105]. Key issues with liquid hydrogen tanks are hydrogen boil-off estimated at 1 %/day [102], the large amount of energy required for hydrogen liquefaction [102], as well as tank cost [100]. For storage on-board vehicles the driving range excluding the effects of boil-off can be longer than that for compressed hydrogen. Hydrogen boil-off is also considered an issue regarding refuelling frequency, cost, energy efficiency and safety, particularly for vehicles parked in confined spaces.

In addition to compressed gas and liquid hydrogen storage, hydrogen can also be stored in various metal hydrides, in chemical forms such as chemical hydrides or carriers and in high surface area adsorbents. These are mostly of interest for on-board vehicle storage where weight and volume are of concern [106]. In metal hydride stores, hydrogen splits into atoms at the surface of the metal and then enter the metallic lattice in the atomic form, diffuse through the metal and finally forms a hydride phase with an ordered hydrogen sub lattice [102]. The search for a material that is capable of storing hydrogen in the amounts necessary for operation of hydrogen FCEV has become a major objective of materials research [102]. Metal hydride storage has no economies of scale, so it does not compete with the other storage options for long storage times or high hydrogen flows. Metal hydride storage, however, does compete with liquid hydrogen and compressed gas storage at low flow rates and short storage times. Liquid hydrogen storage is not economical at low production rates because of the high capital cost of the liquefier and large energy losses. Compressed gas is more economical for short storage periods; however, with longer storage times, liquid hydrogen is advantageous due to the low capital cost of a liquid hydrogen Dewar compared to a compressed gas pressure tank. Liquid hydrogen storage has the largest energy requirement and for storage times longer than a week the boil-off rate is problematic. For compressed hydrogen the storage cost is eventually limited by the compressor electricity cost. One option for compressed gas storage is to increase the operating pressure of the system. This increases the cost of the pressure vessel and compressor, but the reduction in tank size can result in an overall savings [107]. Compressed and liquid hydrogen storage are the storage methods considered within this Thesis.

2.4.4 Cryogenic Applications

An additional application for liquid hydrogen (20 K) is as a cryogen for superconducting technologies. This application of hydrogen is not usually anticipated; however, as the research indicates in Chapter 8 and Chapter 9 the use of liquid hydrogen will have important implications for the hydrogen economy. Interest has grown in finding a suitable low temperature cryogen as a result of predicted helium shortages and price increases. Applications include the indirect cooling of a closed helium loop for magnetic resonance imaging (MRI), SMES [108-111], data centres, homopolar motors and flywheels are potential applications of liquid hydrogen.

The use of the combination of liquid hydrogen with SMES is a new storage concept [108-111]. A compact liquid hydrogen and SMES storage unit which integrates hydrogen liquefaction, a liquid hydrogen tank and SMES based on Magnesium Diboride cooled by the liquid hydrogen bath is a technology considered in the research [110]. In this system liquid hydrogen has two functions; to be an energy storage medium and cryogen for the SMES technology. SMES is the only storage device that directly stores electrical energy without any electro-chemical or electro-mechanical energy conversion as energy is stored in the magnetic field of a coil. Sander M et al. estimated the key design parameters for a 10-100 MW liquid hydrogen and SMES model plant providing electrical energy storage capacities of 20 GWh in the liquid hydrogen and 12.5 GJ in the SMES [109]. The hybrid energy storage plant is capable of handling fluctuations in renewable energy and therefore can allow for the grid integration of variable renewable energy sources. Makida Y et al. proposed system is similar to Sander M et al.; however, this system is proposed to be built beside a liquid hydrogen storage facility for FCEV [110]. Sander M et al. state liquid hydrogen is a safe method of storing energy and a safe cryogen; however, Makida Y et al. consider liquid hydrogen to have a high-flammability range and suggest special handling methods for storage and transport in order to avoid accidents. Sander M et al. propose the first business case for the integrated system will emerge where the different functionalities of liquid hydrogen and SMES plants can provide different benefits. Hamajima T et al. propose a system that is composed of SMES, a fuel cell hydrogen electrolyser and a liquid hydrogen system to cool the SMES with an installed adjacent liquid hydrogen station for vehicles [111].

The research presented in Chapter 8 discusses the use of liquid hydrogen for the superconducting industry in more detail and Chapter 9 focuses on the use of a liquid hydrogen and SMES storage system as an emergency back-up energy source for a hospital, aiding the development of resource efficient buildings.

2.5 Hydrogen Safety

The introduction of hydrogen as an energy carrier requires significant efforts in the field of safety [112]. Around 55 million tonnes of hydrogen are produced each year for industry and although experience handling hydrogen has been gained from chemical and aerospace industries it cannot be directly transferred as a result of the general public being in contact with hydrogen technologies [113]. Hydrogen is odourless, colourless and tasteless and so a leak cannot be detected easily. In order for hydrogen to combust an adequate concentration of hydrogen is required.

Hydrogen has a wide flammability (4-74% in air); however, an oxidiser must be present in a concentration of at least 10% pure oxygen or 41% air for an explosion to occur. Furthermore there is a low probability of hydrogen exploding in open air as a result of it rising quickly [114, 115]. A goal for hydrogen as an energy carrier is to provide at least the same level of safety and reliability as fossil fuel energy carriers. In the applications discussed hydrogen will require different safety considerations for different applications. HySafe report that to evaluate hydrogen safety the following set of issues should be addressed for each of the applications; hydrogen release, mixing, and distribution, thermal pressure, missile effects from hydrogen fires, and hydrogen air cloud explosions [115]. Hydrogen safety is extremely important in transport applications and a high degree of safety is essential. The Hyundai ix35 has undergone safety tests including a fire test in which it performed better compared to ICE vehicles. Taking into account its high auto-ignition temperature, high specific heat and diffusivity, it has been stated that hydrogen is a safer fuel compared to other vehicle fuels. Experiments carried out on hydrogen leaks in moving vehicles have shown that, because of dispersion, the risk of explosion is minimal. It has also been demonstrated that a hydrogen fire causes less damage to a vehicle than conventional fuels. The hydrogen tank has undergone a Certification Test and hydrogen tanks have passed numerous tests and verifications, including burst tests in pressures higher than working pressure, drop tests in accident scenarios and crash tests involving guns, to be certified as safe for mass production.

Hydrogen safety engineering is key to the success of the hydrogen economy and public acceptance [115-119]. Some of the main barriers for realising the hydrogen economy include lack of infrastructure, costs and public acceptance regarding safety. Addressing hydrogen safety issues is critical for hydrogen penetration as an energy carrier and cryogen for a sustainable future.

The literature discussed presents information about the hydrogen economy and different aspects of production and use. Within the research presented in Chapter 4 - Chapter 9 further literature is discussed regarding additional technologies.

Chapter 3 Methodology of System Dynamic Modelling

In this Thesis the analysis of information with regard to synergies of the hydrogen economy with other energy systems and technologies is discussed. Additionally, further analysis of the energy systems using system dynamics (SD) is completed. This chapter presents a review of literature and includes an explanation of what SD is and where it has been used in the energy sector. Its use within the Thesis is also discussed.

3.1 System Dynamics and its Applications

SD is a system modelling tool first introduced by Jay Forester in the 1960s [120-124]. It uses various control factors and observes how the system and variables behave in response to time-based trends [123, 124]. SD uses the approach of system thinking and numeric simulation to determine the behaviour of non-linear systems as a result of closed loop systems that involve feedback loops [125, 126]. In SD models there are main stock and flow quantities. Stocks represent the status of the system, the quantities that exist at any given moment (e.g. hydrogen storage). Rate variables show the speed of flow in or out of the stocks (e.g. hydrogen production and use) and they serve as the decision making variables in a system. Auxiliaries are variables that can help elaborate the stock and flow connections. Houghton J et al. highlights the necessary steps for the creation of a SD model [123]. A SD model is a system of differential equations. The first step is to clearly identify the purpose for a model and the problem that it addresses. The second step is to build the structure of the model. Formulation of the model with the inclusion of equations is required for the third step and finally the fourth stage is the analysis of results.

Causal loop diagrams can be used when using SD to highlight the feedback loops present within the model. One pertinent example of the use of causal loop diagrams is shown in Figure 3.1. The causal loop diagram represents the analysis of the helium market and allows information about the variable relationships to be highlighted [127]. The positive sign indicates there is a positive relationship between the two variables meaning if one variable increases the other will increase alternatively the negative sign indicates a relationship in which if one variable changes the other will respond in the opposite direction (e.g. as price increases the relative value will decrease and as price decreases the relative value will increase (Figure 3.1)). If the feedback in a closed loop has balancing behaviour it means there is a negative feedback loop and reduces the value of the variable considered while if it has reinforcing behaviour there is positive feedback loop and increases the value of the variable considered. The SD study on helium markets had important findings for policy makers. These included confirmation that venting was a major consideration for the future supply of helium and the growth of high-technology aspects of the global economy was found to play a major role. Furthermore, with assumptions that there would be a growth of high technology helium demand, a plateau in helium production is expected after 2030 along with steadily rising prices [127]. The study on helium markets highlights the insights that can be gained through SD modelling.

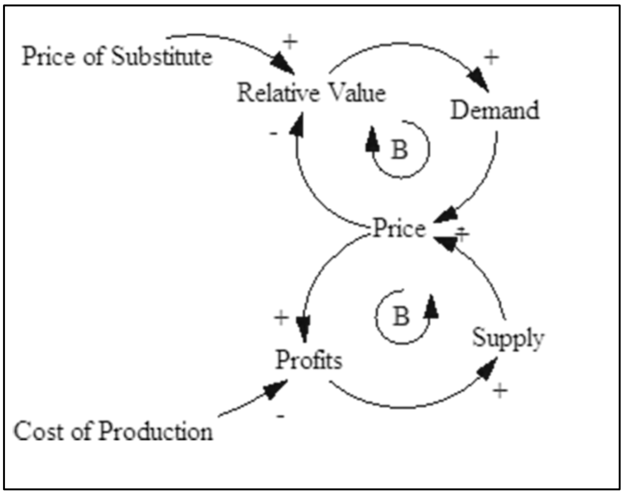


Figure 3.1 Simplified causal loop diagram showing price-cost and supply-demand relationships that are central to the helium market SD model [127].

SD is used to assist in policy design of complex systems. Furthermore, the power engineering sector can make use of SD as it involves many factors including economics, politics and sociology that require a holistic approach [125, 126]. The introduction of new energy systems such as decentralised hydrogen energy systems considered in this Thesis can make use of the SD modelling approach. SD can be used to predict the future of systems in the long-term. However, the SD models considered throughout the research presented in this Thesis are based on the instantaneous analysis of system behaviour of decentralised hydrogen systems in the short term to analyse the response of hydrogen technology and other technologies to various inputs, such as that done by Hollmann M [125, 126]. Hollmann M considered a cogeneration plant with a heat accumulator and a peak load boiler as well as the decentralised energy supply as a new energy system to be modelled with the use of SD. The model can simulate the application of resource scheduling for a decentralised power supply unit in a house on a working day in winter over a 24 hour period. The results are shown in Figure 3.2. One advantage of SD includes the possibility to display and evaluate various parameters in graphical or numerical mode [125]. Hollmann M also considers that the feeding of wind energy can be adjusted for different wind circumstances in decentralised systems. Scenario analysis involving different wind energy inputs is used within the research presented in this Thesis.

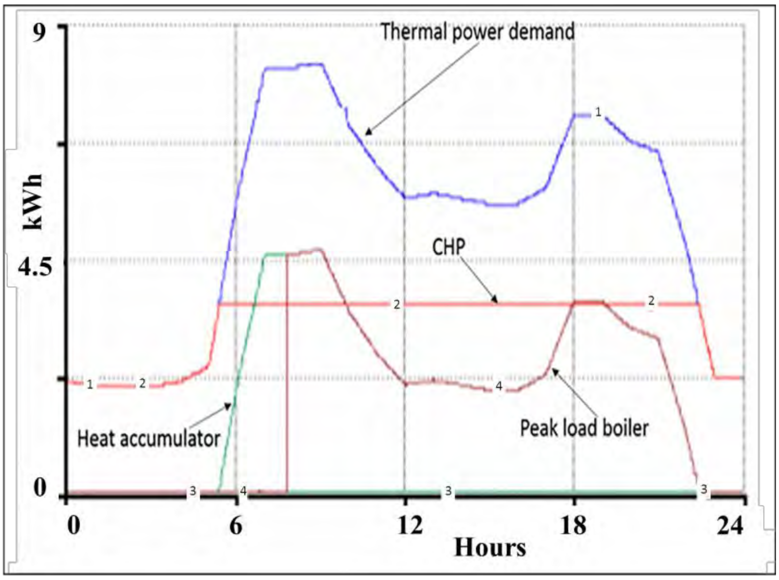


Figure 3.2 Exemplary SD results for the resource scheduling of a decentralised combined heat and power (CHP) plant over 24 hours showing how the thermal demand (1 - blue line) is met by the CHP unit (2 - red line), the heat accumulator (3 - green line) and the peak load boiler (4 - dark red line) [125]. This use of SD for instantaneous analysis depicted is the approach taken for the SD models in this Thesis.

SD was considered for the Thesis as the significance of SD as a modelling concept is that it can be used as a planning instrument for the energy supply industry. SD allows conceptual system research for transition to a new energy supply system such as an integrated, decentralised hydrogen energy system to be analysed. SD has numerous advantages including the use of stock and flow diagrams that provide an easily understood system, all dependencies and relationships are directly visible, all influencing factors are mapped via causal loop diagrams, every process can be scaled and considered individually and influencing relationships can be considered in scenario analysis [125-129].

SD methodology was first published in the energy sector in the ‘Limits to the Growth” [121]. Forrester J W created the first draft of a SD model called ‘WORLD1’, with the refined version called ‘WORLD2’ soon after [121]. The book published used the further updated ‘WORLD3’ model. The ‘WORLD3’ model can simulate the consequence of interactions between Earth and human systems with five variables examined; world population, industrialisation, pollution, food production and resource depletion. Budzik P M created a SD model in 1976 using the methodology developed by Forrester called ‘FOSSIL1’ and investigated the complex interactions between energy prices, financial markets, resource depletion, government regulation, changing technologies, and consumer behaviour to determine future patterns of energy production and consumption. The model was specifically made to allow the user to examine the effects of new energy policy on the behaviour of the US energy system.

More recent SD studies include those by Jeon C et al. that propose a new long-term technology evaluation method for renewable energy technologies that combines SD with Monte Carlo simulation [130]. SD was used in the study for long-term renewable energy technology evaluation as it required the consideration of causalities among various internal and external variables and analysing long-term dynamic uncertainties and their influences. Liu X et al. used SD to forecast the energy consumption, gross CO_2 emissions and CO_2 emission intensity in China from 2013 to 2020 to highlight the effects of different economic growth rates and policy factors on energy consumption. Different scenarios were considered in the model to carry out an analysis that allows different policy changes to be recommended [131]. Chyong C K et al. used SD to model the indigenous natural gas industry in the UK with different scenarios considered. The model allowed numerous conclusions to be drawn [132]. The different factors included in the model were consumption, production, exploration, demand projection and substitution. Many studies identify that the systematic analysis and dynamic modelling of urban energy demand and CO_2 emissions are extremely important to understand and address issues associated with fuel security, energy system planning and management, growth of GHG and investment decisions. SD is a suitable method to describe the inner interactions and identify the desirable and undesirable interactions of the variables [133-136].

Borshchev A et al. compare the three major paradigms in simulation modelling: SD, discrete event and agent based modelling [133]. Agent based modelling can capture more real life phenomena compared to the SD or discrete event modelling approach; however, there are many applications where SD or discrete event modelling can more efficiently solve a problem that agent based modelling would be less efficient or harder to develop. Maidstone R compares the use of SD with discrete event simulation [126]. Discrete event simulation is usually used for systems which naturally involve queues while SD models tend to used more to model systems which naturally form flows or complex systems such as the decentralised hydrogen energy system concept considered in this Thesis. Discrete event simulations are also stochastic or random while SD models are deterministic [126].

From the review of literature, it can be concluded SD is a suitable method for approaching the complex decentralised hydrogen energy system concept, Figure 1.1, considered in this research study.

3.2 System Dynamics used in the Research Analysis

SD was used in this research as SD methodology is suitable for modelling in the energy sector, which is characterised by a large number of interactions between different variables. The professional version of the SD software 'Vensim DSS' was used for the SD models completed in this Thesis. The challenge of moving to sustainable energy systems which provide secure, affordable and low-carbon energy requires the application of methods which recognise the complexity of energy systems in relation to technological, economic and environmental aspects. SD is used in this thesis for identifying the system response of hydrogen and other storage systems in response to varying demand, wind energy and system capacity. Further constraints on the systems in relation to resource scheduling will be identified through different scenario analysis.

As depicted in Figure 1.1 three aspects of the hydrogen economy were identified to be investigated individually; decentralised hydrogen energy storage (Chapter 4-6), hydrogen synergies with natural gas (Chapter 7) and the use of liquid hydrogen as a cryogen (Chapter 8-9).

SD was not used in Chapter 6 as the research investigates the concept of a sustainable functioning hydrogen and molten salt system for energy and material production; however, SD is suggested as being suitable for analysing the complex behaviour in the system. Chapter 7 also does not use SD as it is a qualitative study on the synergies that exist and that may emerge between the natural gas industry and the hydrogen economy. The remaining chapters, Chapter 4-5 and Chapter 8-9 use SD models. Scenario analysis used with SD modelling is a process of analysing possible future events by considering alternative possible outcomes and is used in the research. Therefore, for reference the SD studies and scenarios for the chapters are presented in Table 4.2, Table 5.1 and Table 9.3. The studies and scenarios listed in these tables along with the results will be further discussed in each research chapter.

Chapter 4 Investigation of a Hydrogen Storage Buffer System using Systems Dynamics

This chapter investigates the decentralised aspect of hydrogen identified in Figure 1.1. The use of decentralised hydrogen storage as a buffer system will be considered with analysis of technical and economic aspects of the hydrogen storage operation as well as identification of different advantages and disadvantages using SD analysis.

4.1 Introduction to Low-Emission Hydrogen Production Systems for Storage

Hydrogen, as discussed, can emerge in niche decentralised markets. In this sense, hydrogen could form the basis of a synergistically operating buffer mechanism facilitating the integration of intermittent renewable energy, reducing CO_2 emissions as well as enhancing indigenous energy supply and increasing energy security. A comprehensive SD framework of analysis is used to allow the feasibility of the buffer system to be evaluated and its dynamic response characteristics to be analysed. The conceptualised decentralised energy paradigm, Figure 4.1, may be capable of integrating environmental sustainability with affordable energy as to meet strengthening emission policies electricity generation must become less carbon intensive.

Figure 4.1 has been adapted from Figure 1.1 and highlights the focus area of the present study which is the operation of hydrogen storage to provide flexibility for decentralised energy systems to reduce the need for grid energy. Essential elements of the decentralised hydrogen energy storage system are the electrolyser unit in this study converting wind energy to hydrogen, a compressor, the hydrogen storage system and a hydrogen fuel cell to convert the chemical energy of the hydrogen to electricity. The operation of the hydrogen storage unit as a buffer system is investigated as a hydrogen buffer system can allow the balancing of intermittent wind energy to ensure a constant production level of energy from the wind-hydrogen buffer system or alternatively provide a buffer to supply energy during peak hours.

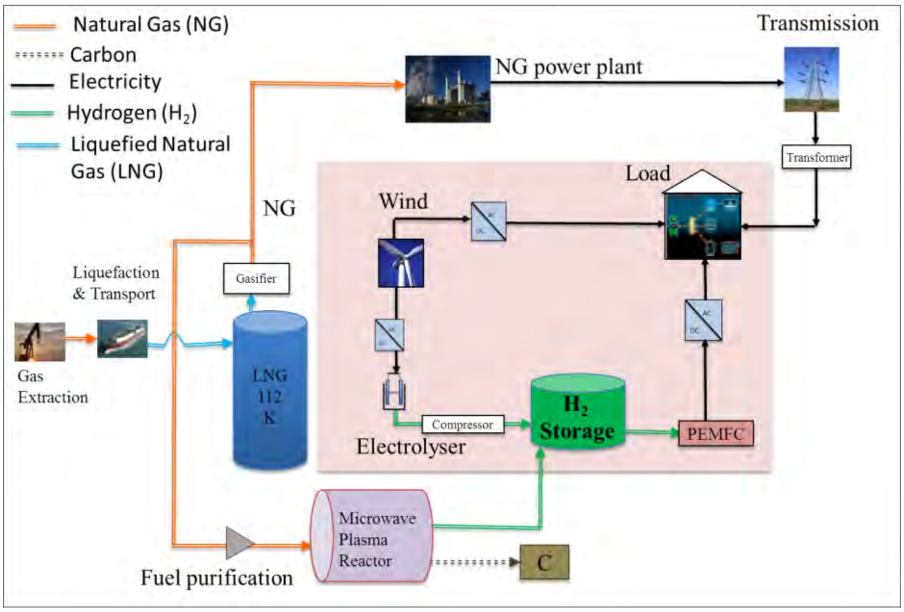


Figure 4.1 Conceptualised decentralised hydrogen buffer system adapted from Figure 1.1. The focus of this study is on the operation of the hydrogen storage unit.

Figure 4.2a shows an example of a hydrogen storage system that over time has a surplus and deficit of renewable energy compared to electrical demand. This allows for hydrogen production when there is a surplus of renewable energy in the system with hydrogen stored being used to meet demand when there is a deficit of renewable energy. However, hydrogen may not be capable of meeting all of the demand, requiring the need for grid energy in the system. Alternatively, Figure 4.2b illustrates hydrogen storage being operated as a hydrogen buffer system which is a more ideal case as the renewable energy supply and hydrogen system is capable of maintaining a stable excess supply of storage energy. However, the case in Figure 4.2b would require a large capacity of renewables to allow this level of security within an energy system. For beneficial operation of the hydrogen storage system, it is necessary to control the use of hydrogen for electricity generation to maximise profit, reduce uncertainties arising from intermittent renewables and reduce dependence on the grid.

For hydrogen to be a sustainable energy carrier near-zero emission hydrogen production processes will be required. Table 4.1 presents a comparison of renewable electrolysis and microwave plasma processing of natural gas. Both processes can produce low-emission hydrogen for the operation of the hydrogen buffer system. The function of the buffer system can be to reduce overall emissions and maximise the use of renewables in the system, to reduce the use of grid energy over the entire demand period or to smooth the grid energy during peak hours.

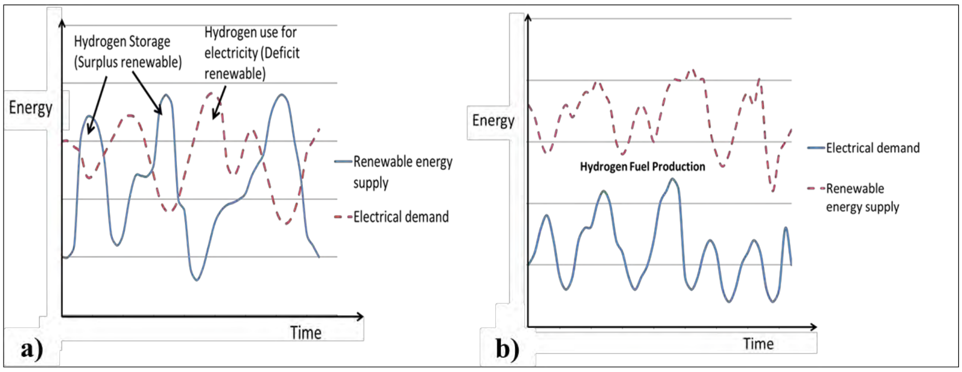


Figure 4.2 Comparison of a) hydrogen storage for meeting demand when required leaving the system vulnerable to a lack of hydrogen energy available in storage, b) hydrogen use as a buffer allowing excess hydrogen to be accessed if required.

Table 4.1 Comparison of renewable electrolysis and microwave plasma processing of natural gas.

Hydrogen Production Type	**Renewable Electrolysis**	**Microwave Plasma processing**
Cost	3.5-7 \$/kg wind electrolysis [137] 28 \$/kg PV electrolysis [137]	1.5 \$/kg [138]
CO_2	0	0 or indirect grid emissions
Advantages	• Wind energy cost estimated to fall ~1% per year [139] • PV cost estimated to fall by over two times current cost [140] • Increases indigenous energy supply	• LNG provides opportunities to diversify natural gas supply source • Production of carbon black a marketable product • Initial use of natural gas can help the transition to a hydrogen economy
Disadvantages	• Intermittent energy • Higher cost than natural gas methods	• Future cost of natural gas unknown • Use of fossil fuels for hydrogen production

For the investigation of the hydrogen buffer operation an unconstrained system using surplus renewable electricity during low demand hours for hydrogen generation and storage is considered; however, hydrogen may not be produced if there is no excess wind. This would mean a lack of energy security within the system. Alternatively, the use of a hydrogen buffer system that constrains the wind energy for hydrogen production instead of demand to provide some security to the system will also be considered. The various advantages and disadvantages of the operation of the hydrogen system will be analysed [141-143].

4.2 Method for the Hydrogen Buffer System Dynamic Model

An SD model looking at the operation of the wind-hydrogen system along with a cost analysis will form the basis of the investigation. Furthermore, such an analytical framework and systems-based approach can explicitly elucidate aspects of the underlying irreducible complexity. Within the proposed SD framework production, storage and use of hydrogen are captured by the main stock and flow quantities. Table 4.2 represents the different studies and corresponding scenarios investigated.

Table 4.2 System dynamic studies and corresponding scenarios. The subject of the SD model is the techno-economic investigation of the operation of hydrogen storage as a buffer system.

Study	Scenario	Scenario Explanation
1	A	Hydrogen storage operated with no hydrogen buffer and with high wind energy curtailment in the system
	B	Hydrogen storage operated with no hydrogen buffer and with low wind energy curtailment in the system
2	A	Hydrogen storage operated with a hydrogen buffer available over entire demand period with high wind energy curtailment
	B	Hydrogen storage operated with a hydrogen buffer available over entire demand period with low wind energy curtailment
3	A	Hydrogen storage operated with a hydrogen buffer available during peak hours only with high wind energy curtailment
	B	Hydrogen storage operated with a hydrogen buffer available during peak hours only with low wind energy curtailment

The capacity requirements and technological operation of a hydrogen buffer storage system are identified by comparing different renewable energy load inputs. The model of the hydrogen buffer system consists of varying subsystems; a technical system of the several energy converters, logic for scheduling the hydrogen buffer system and the cost system calculating the costs of electricity along with environmental savings from the hydrogen buffer system.

The SD model was formulated with the feedback loops identified in Figure 4.3. Reinforcing loop R1 maximises the capacity of the fuel cell which is constrained to 22 kW. If the hydrogen system is capable of meeting more demand but is constrained by the fuel cell capacity then the capacity increases and the electricity generated by the hydrogen system increases accordingly. The reinforcing loop aims to maximise the amount of hydrogen energy that can penetrate the system at a given time if required. The cost of energy (COE) establishes the selling price the hydrogen must be sold at to break even with costs. As the hydrogen used for electricity will increase the capacity factor this in turn will reduce the COE.

Balancing loop C1 acts as a limit to the amount of hydrogen storage available as a result of losses within the system. As the hydrogen in storage increases the losses will decrease the quantity of hydrogen in storage. Balancing loop C2 consists of variables that are reducing the amount of hydrogen in the storage system as a result of electricity generation. As the demand increases the amount of hydrogen required increases to a certain quantity based on the constraints of the system. Balancing loop C3 consists of variables that are reducing the amount of demand in the system by wind. As the demand increases the amount of available wind used for demand increases based on the constraints of the system regarding the amount of wind energy that will be sent to the hydrogen buffer system.

A differential equation is used for the hydrogen storage stock (kg). The hydrogen storage quantity that is constrained by the hydrogen storage capacity is increased by renewable electrolysis in kg/hr based on the capacity of the electrolysis and the wind energy available. The computer simulation model consists of the differential equations and algebraic relations. The time period considered for the simulation is 72 hours. The energy supply from wind and hydrogen in the decentralised set up along with back up energy from the grid can be simulated and the scenarios changed to investigate the characteristic behaviour of the system. Two wind scenarios are considered in the model. In each study, Table 4.2, two wind scenarios are considered. Wind Scenario A is real, high wind speed data over a 72 hour period with wind Scenario B reflecting lower wind speeds. Considering these two different wind speed scenarios differences in system behaviour can be analysed.

Three studies are considered in the model with each wind scenario, Table 4.2: Study 1 has no hydrogen buffer system. The system uses excess wind for hydrogen production with grid energy used to meet the demand that cannot be met by the wind energy and stored hydrogen energy. Operation of the system is highlighted in Figure 4.4.

Study 2 considers the use of wind and hydrogen energy to provide a calculated constant percentage of demand depending on the availability of wind energy. The hydrogen buffer system model calculates the average percentage of demand that should be met by wind energy and the hydrogen buffer system. This reduces grid energy by a certain percentage over the demand period. Any excess wind above the calculated average is used to produce hydrogen.

Study 3 considers the use of grid energy as the base load with wind and hydrogen energy smoothing the energy required from the grid and supplying energy at peak hours only. The hydrogen buffer system model uses a base load of 30 kWh of grid energy with the remainder of demand to be met by the wind-hydrogen buffer system.

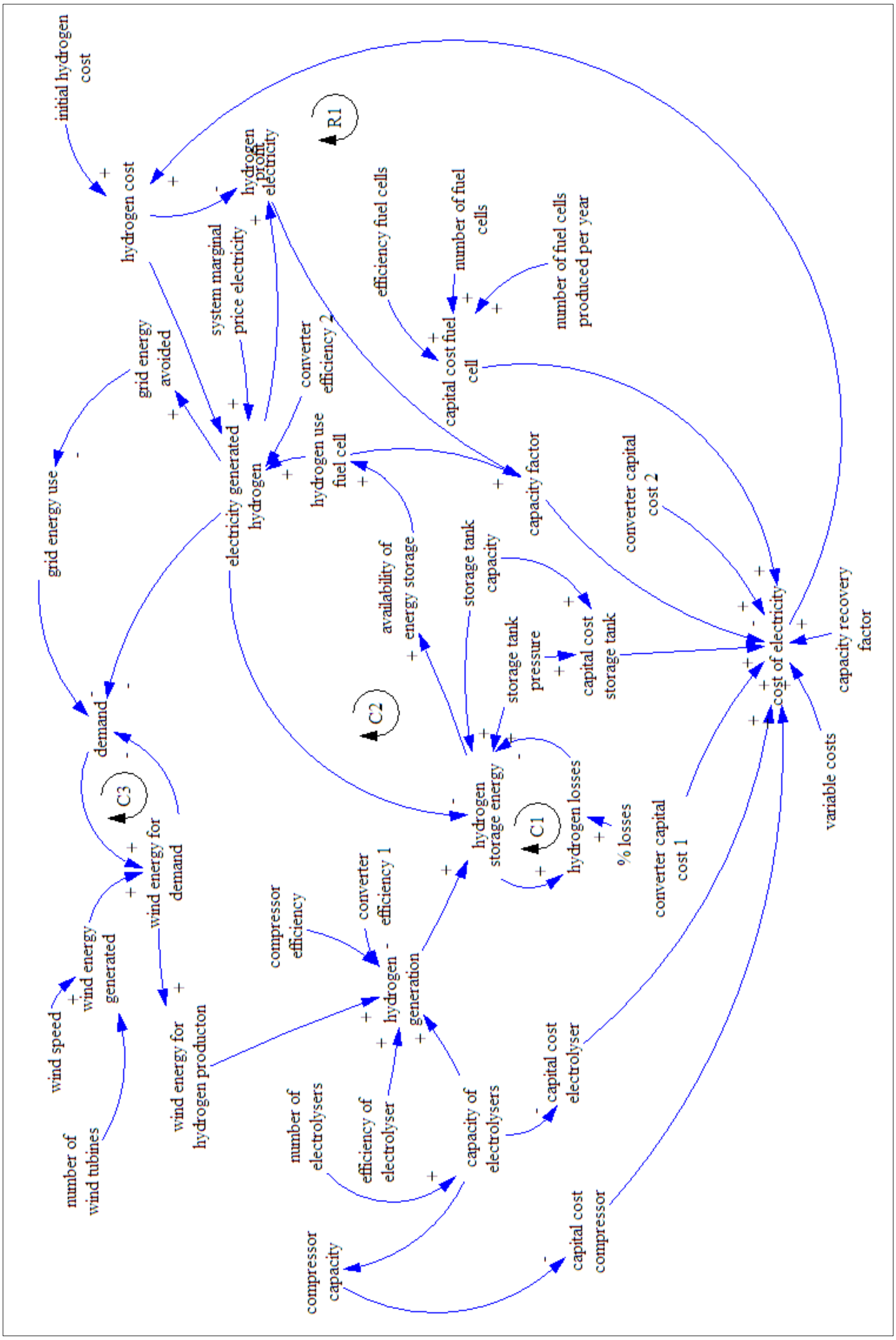


Figure 4.3 Causal loop diagram of the system dynamic model for the hydrogen buffer system.

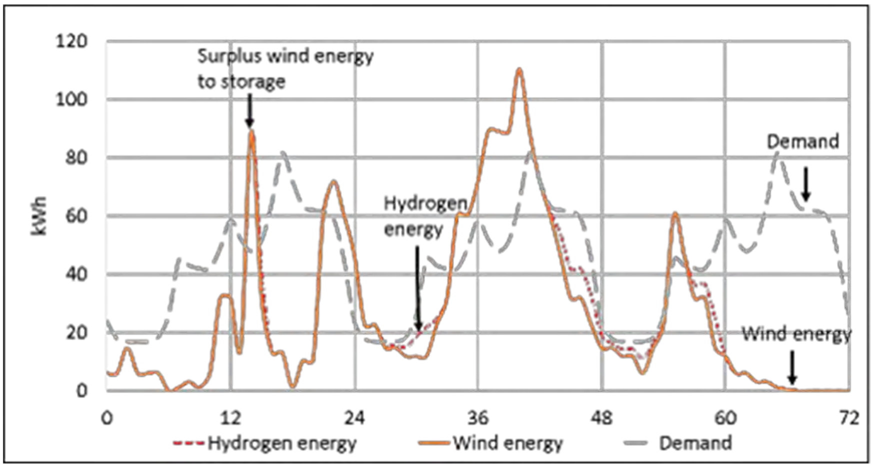


Figure 4.4 Energy versus time diagram for system operation without hydrogen buffer (Study 1). Excess wind energy produces hydrogen for storage, however, not enough hydrogen is available to prevent the requirement of grid energy but reduces curtailment in the system. It is a real representation of Figure 4.2a. The results of Study 1 are presented in Figure 4.6.

The main problem considered is the feasibility of the different operation of the wind-hydrogen systems. As mentioned the hydrogen storage system is composed of many components. For calculating the cost of electricity from the wind-hydrogen systems the capital costs of the main components are considered. Different methods are used with regard to scaling of capital costs of the systems based on different criteria explained below.

The levelised cost of electricity (LCOE) is a long term cost concept and represents a "break-even" cost of electricity [142]. Cost of energy production remains an important factor in determining if an energy technology can reach commercialisation. The cost calculated in the model considers capital costs, O&M (operation and maintenance), and performance but doesn't include financing issues, future replacement or degradation costs which would need to be included for a more complex analysis. The cost of electricity calculated in the model does not represent the LCOE of the system as this would need to be predicted from an expected overall capacity factor rather than over 72 hours (the time period of the SD model). The formula for simple levelised cost of energy is used for calculating the cost of electricity in the model for investigating the economic differences arising between the systems.

The simple LCOE is calculated using the following formula [142]:

$$\text{LCOE} = \frac{\text{OCC} * \text{CRF} + \text{fixed O\&M}}{(8760 * \text{CF})} + (\text{fuel cost} \; * \; \text{heat rate}) \; + \; \text{variable O\&M cost}$$

The overnight capital cost (OCC), is measured in euros per installed kilowatt (€/kW). The capital recovery factor (CRF) is a fraction calculated by considering lifetime and discount rate. A capital recovery factor is the ratio of a constant annuity to the present value of receiving that annuity for a given length of time. The value for the CRF was considered as 0.01 [142]. The fixed O&M costs in euro per kilowatt-year (€/kWyr) are taken as 5% of the capital per year [143]. In the denominator 8760 is the number of hours in a year and capacity factor (CF) is a fraction between 0 and 1 representing the portion of a year that the decentralised hydrogen energy system is generating power and is calculated in the model. Fuel cost is expressed in €/kWh and estimated to be 6 €/kg of hydrogen from wind energy, which equates to 0.18 €/kWh.

The system considered consists of the electrolyser, storage tanks, compressor and fuel cells as the main technologies that make up the capital costs. The electrolyser capital costs are based on the capacity of the electrolyser with regard to the kilograms of hydrogen produced per hour. The formula used for the calculation of the electrolyser costs is $y = 224.29 \cdot x^{0.6156}$ where y is the adjusted capital cost, 0.6156 is the scaling factor calculated as a result of the strong correlation between electrolyser capital cost and costs from literature and are accurate for capacities of 0.1 kg/hr to 100 kg/hr and x is the kg/hr capacity of the electrolyser [143-145]. The compressor capacity required for the electrolyser capacity is calculated within the model. The scaling cost of the compressor is then calculated as $C_{\text{comp}} = \$712 \cdot (z)^n$ where z is the number of electrolysers with an initial capacity of compressors [144]. The scaling exponent for compressors is 0.7. Initial capital cost of a 10 kW compressor is 15000 $ [144]. Hydrogen storage tank capital cost is based on a 200 bar storage pressure. The volumetric energy density of hydrogen compressed to varying pressures and that of liquid hydrogen are shown in Figure 4.5. Stationary fuel cells costs are estimated per unit of electric output that decrease dramatically both with increasing system size and increasing system annual production rate [146-149].

The range of COE for each study are calculated to compare the economic potential of the different operations of a hydrogen buffer system. It is anticipated that the hydrogen economy will emerge as a result of the advantages of decentralised low-carbon hydrogen production, storage and use.

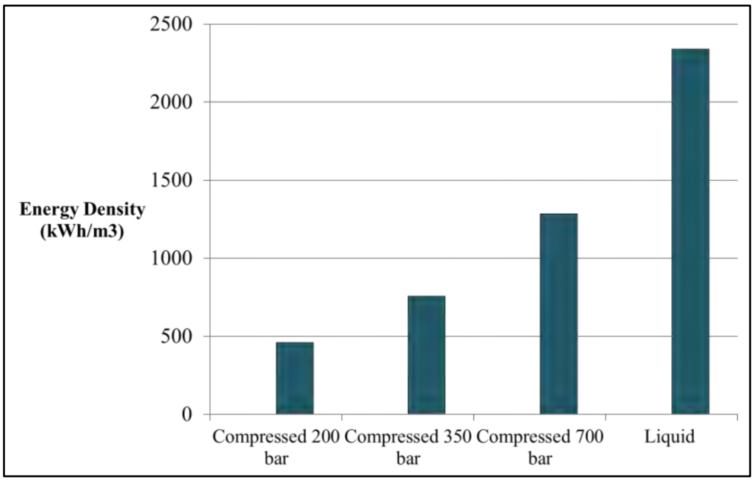


Figure 4.5 Energy density of hydrogen highlighting its use for large scale bulk energy storage or a hydrogen buffer [150].

4.3 Results of the Hydrogen Buffer System Dynamic Model

Figure 4.1 offers a schematic depiction of the system under consideration while Figure 4.2 represents the studies motivating factors, primary objectives and attendant challenges to investigate hydrogen storage system operation. The present study considers three different studies of system operation and these allow key structural components of the overall hydrogen system to be identified and their performance-relevant effects to be analysed with regard to technical and economic data based on the evaluation of hydrogen buffer systems. It is important to note that there will be seasonal variations in the amount of hydrogen that can be supplied to the system, these are reflected in the two wind scenarios used; Scenario A and Scenario B (refer to Table 4.2). The results for the different studies and wind scenarios are presented in Figure 4.6 – Figure 4.8 and represent the percentage of the demand being met at a particular time by either wind, hydrogen storage or grid energy over a 72 hour period.

The results of Study 1 without a hydrogen buffer, following the system operation in Figure 4.2a, are shown in Figure 4.6. For wind scenario A, Figure 4.6a, the system has increased wind energy for meeting demand (73.4%) as it is not constrained by a hydrogen buffer system over time. Only excess wind energy is sent to the hydrogen storage as highlighted in Figure 4.4. The capacity factor is 26% for the hydrogen system (meeting 11% of demand) with the remainder being met by a variable requirement for grid energy (15.6%). The COE from the model is 0.4 €/kWh. Figure 4.6b shows the low wind scenario, the wind energy use is again maximised (49.8%); however, this time there is a reduced capacity factor 7.1% for the hydrogen system (3.5%) as a result of lower wind availability increasing COE to 0.97 €/kWh. There is also an increased requirement for grid energy (46.7%).

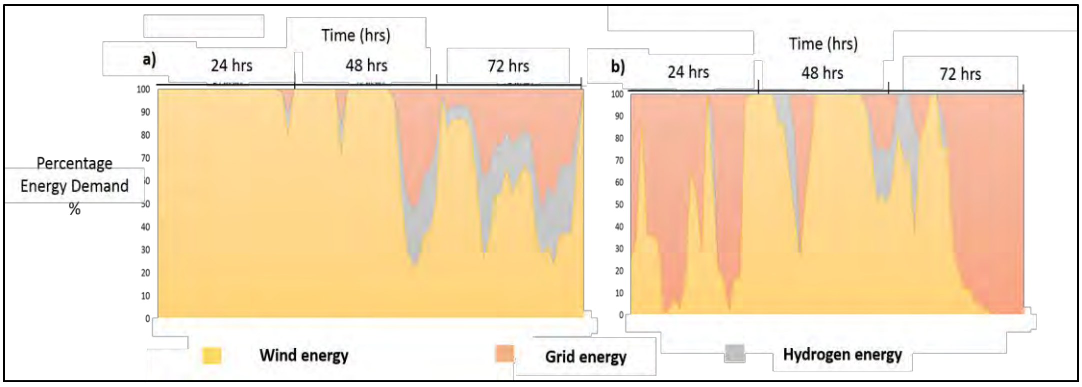


Figure 4.6 Study 1: energy supply with no operational constraints, a) wind scenario A, the majority of demand can be met by wind-hydrogen system, b) wind scenario B, requires increased grid energy. System operation is shown in Figure 4.4.

Study 2 leads to reduced wind energy for meeting demand compared to Study 1 as wind energy above the calculated percentage of demand to be met is used to produce hydrogen for the buffer system. The system operation aims to have a predictable energy level that will allow the hydrogen system to act as a buffer and the wind and hydrogen energy to meet a certain constant percentage of demand over the entire demand period. The system that is described represents the use of a hydrogen buffer system to reduce intermittency and grid energy required to try stabilise the system to ensure 47% (Figure 4.7a) and 22% (Figure 4.7b) of the demand is being met at all times by the wind and hydrogen system. For the high wind scenario wind energy use is 43.4%, with a hydrogen system capacity factor of 8.8% meeting 4.3% of demand and a COE of 0.81 €/kWh. There is a reduced requirement for grid energy (52.3%) in this system over the entire demand period. In the low wind scenario the wind energy for meeting demand is 16.4%, with an increased capacity factor for the hydrogen fuel cell system in this study. This increased capacity factor (10.2%) is as a result of lower wind energy being capable of meeting the required percentage of demand and hydrogen being used (5%). The requirement for grid energy is high (78.6%). The COE is reduced to 0.55 €/kWh compared with the high wind scenario. However, in one instance in the low wind scenario for Study 2 the wind energy and hydrogen buffer system is not able to meet demand as a result of the low wind available at the beginning of the time period. This highlights the vulnerability of the system to a lack of hydrogen production when wind energy is low either before the hydrogen buffer system can store enough hydrogen or over long periods of low wind energy.

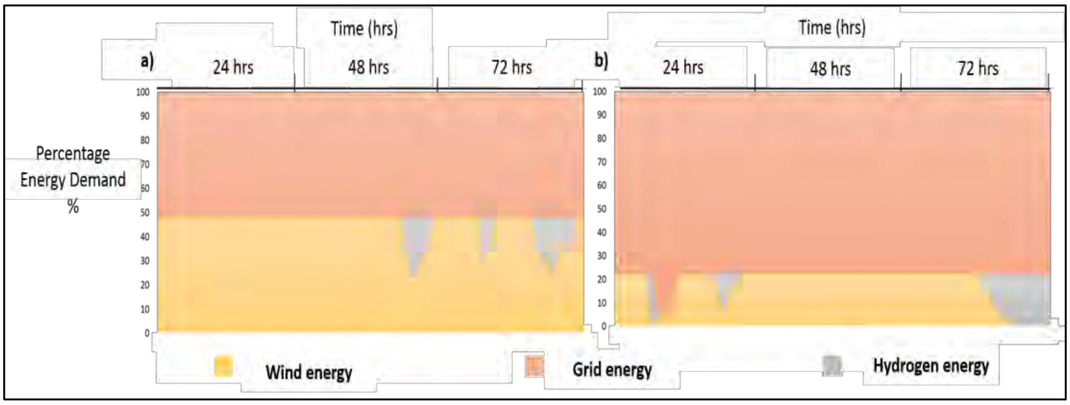


Figure 4.7 Study 2: The average wind energy over the 72 hour period calculated to establish the percentage of demand to be met by the wind hydrogen buffer system, a) wind scenario A, the hydrogen buffer and wind energy is capable of meeting 47 % of demand every hour, b) wind scenario B is capable of meeting 22% of demand every hour except for a period in the first 24 hours.

Study 3 investigates the costs and technical behaviour of the system with grid energy providing base supply of energy when the demand is below 30 kWh. The wind-hydrogen buffer system meets demand above this to smooth the grid energy required. There is therefore reduced wind energy outside peak hours. In the high wind scenario (Figure 4.8a) wind energy provides (34.3%) and hydrogen use is limited to peak hours if wind is unavailable (4.8%). Hydrogen's capacity factor is 10% with a COE of 0.74 €/kWh. Grid energy is increased as a result of it supplying base power (60.9%). In the low wind scenario (Figure 4.8b) the system is vulnerable to a low quantity of hydrogen in the buffer system (23.6%) and an increased requirement for grid energy (72.3%) even during the peak hours is encountered. The system is unsuccessful in smoothing grid energy completely apart from the second day, although still reduces the quantity of grid energy at peak hours significantly. Hydrogen use is 4.1% with a capacity factor of 8.4% and a COE of 0.85 €/kWh.

From the results there are different advantages and disadvantages that emerge from the system, Table 4.3. These include allowing the integration of flexible energy storage systems, maximising the penetration of intermittent renewable energy, enhancing indigenous energy supply by reducing grid energy required, decarbonising the energy supply, smoothing grid demand and allowing a predictable quantity of grid energy to be required.

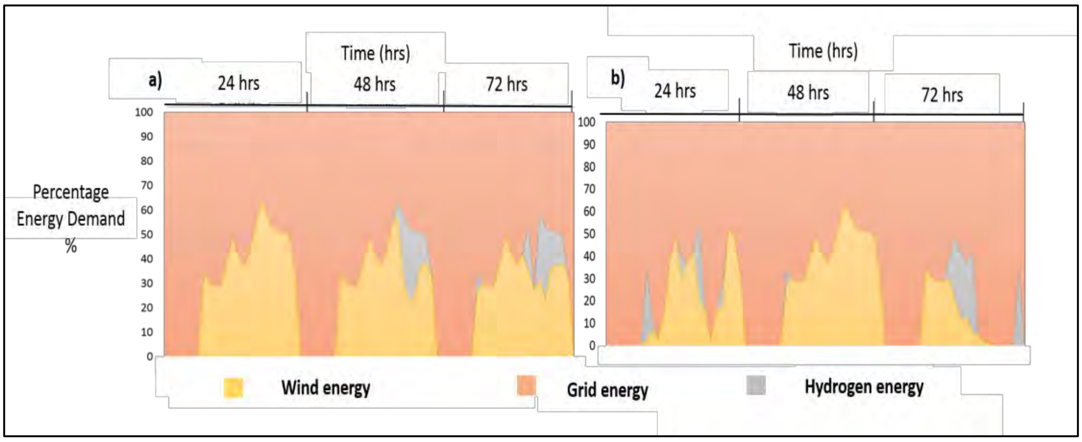


Figure 4.8 Study 3: Wind energy constrained for smoothing demand to allow a predicted amount of grid energy. Grid energy acts as base power and provides 100% of demand when demand is lower than 30 kWh, a) wind scenario A is capable of meeting almost all the required demand, b) wind scenario B due to low energy demand is vulnerable to lack of available hydrogen in the buffer systems.

The COE calculated from the model varies from 0.4-0.97 €/kWh. This large variation occurs within Study 1, the system that is not constrained. Although with optimum cost for the high wind scenario this system is vulnerable to a large increase in the price with low wind energy. The system in Study 2 has a range of 0.55-0.81 €/kWh and Study 3 0.74-0.85 €/kWh. Study 3 shows the lowest range in COE. The estimated COE of hydrogen ranges from 0.28-0.6 €/kWh in literature [149]. The increased COE from the results could be based on assumptions made and also be affected by the low capacity factor of the hydrogen buffer systems. It is evident that hydrogen costs must be reduced for hydrogen to emerge as a competitive sustainable energy carrier.

Table 4.3 Advantages and disadvantages of each wind-hydrogen system operation study.

	Advantages	**Disadvantages**
Study 1: No hydrogen buffer for Scenario A and Scenario B	• High wind scenario A allows maximum renewable and hydrogen use (84.4%). • High wind scenario A achieves maximum decarbonisation of the system with lowest hydrogen cost (0.4 €/kWh). • Reduction of wind curtailment for wind scenario A and B.	• Variable grid energy required as there is no buffer system, requirement for spinning reserves. • Low wind scenario B has lowest hydrogen capacity factor and highest cost of hydrogen (0.97 €/kWh).
Study 2: Hydrogen buffer available over entire demand period for Scenario A and Scenario B	• Predicted percentage of demand met by the wind-hydrogen system for scenario A and B. • Allows the smoothing of intermittent renewable energy.	• Grid energy increased if low wind speed occurs. • In the low wind scenario the buffer system is vulnerable to lack of hydrogen supply. • High wind scenario has higher COE than low wind scenario.
Study 3: Hydrogen buffer available during peak hours only for Scenario A and Scenario B	• Grid energy is smoothed by the wind-hydrogen system providing energy at peak times only, wind scenario A. • Lowest range of COE between high and low wind scenarios A and B.	• If there is low initial wind speed during off peak hours, hydrogen will not be produced for the buffer system. • Increased grid energy in the system. • Low capacity factor for hydrogen increasing price.

As aforementioned the use of zero and low CO_2 emission methods of hydrogen production using natural gas can be considered. The vulnerability of the hydrogen buffer systems in the low wind scenarios are highlighted. The use of microwave plasma processing of natural gas to produce excess hydrogen in the system for providing additional hydrogen for the buffer system would allow a reliable near-zero emissions system to emerge. Furthermore, the production of hydrogen via the microwave plasma processing of natural gas is also more economical than renewable electrolysis. Therefore this production method could be a solution to a stable hydrogen buffer system and to the high costs of generating electricity from renewable hydrogen in the short term.

4.4 Conclusions on the Operation of a Hydrogen Buffer System

The analysis conducted identifies three different operations of wind-hydrogen energy systems. Useful insights into a hydrogen buffer systems role in potentially supporting a hydrogen economy are investigated.

The performance of the hydrogen buffer system for maximising renewable energy penetration and increasing system security are evaluated with opportunities for design rationalisation and performance enhancement identified. Three options of operating the wind-hydrogen energy system were considered in three different studies, Table 4.2. Study 1 with no hydrogen buffer system, study 2 with a hydrogen buffer system with wind and hydrogen meeting a certain percentage of demand over the entire demand period and study 3 with a hydrogen buffer system with wind and hydrogen available during peak hours only.

Policies that support hydrogen as a viable and feasible energy carrier must be present and used to allow the advantages of a hydrogen economy integrated into the energy mix to be realised. The maximum reduction of grid energy is achieved when the system is operated without the buffer system; however, with minimum security within the system. All systems lower CO_2 emissions with some such as the high wind no buffer system (Study 1, Scenario A) being most effective. Stabilising the output from intermittent wind set ups by allowing a certain percentage of demand to be met with quantity of grid energy required is achieved by Study 2 while the smoothing of grid energy is achieved by Study 3. Study 3 has the lowest variability in the cost of hydrogen electricity; however, the hydrogen cost is still high and costs must be reduced in an effort to ensure the hydrogen economy can emerge.

The operation of the system with no buffer is successful in reducing curtailment and decarbonising the energy system; however, with much focus on the negative impacts wind intermittency has on the requirement for variable grid energy the operation of an unconstrained system is not ideal. Although in Study 1 the high wind scenario the system had the lowest COE it also had the highest in the low wind scenario, this again highlights the vulnerability of the system to wind fluctuations and therefore the value of hydrogen storage operation as a buffer. Study 2 operates with a hydrogen buffer system where wind and hydrogen aim to meet a certain percentage of demand. This operation allows for a predictable quantity of grid energy. The system has a lower range of COE than Study 1; however, hydrogen energy can be required during off-peak hours as the system aims to reduce grid energy throughout the 72 hour period. Study 3 also operates with a hydrogen buffer system but this time provides energy during peak hours only smoothing grid energy required. This study has the lowest range in COE reflecting lower price volatility to the intermittency of wind. The type of operation of the hydrogen storage system will depend on the particular function of the system. However, in the low wind scenario the system is vulnerable to a lack of hydrogen in the buffer system. The operation of the system reduces the need for grid energy at peak hours, when grid energy price is at a maximum. It is important to note the potential use of natural gas methods as a back-up for providing hydrogen to ensure the hydrogen buffer can still be capable of supplying clean energy.

The decentralised hydrogen buffer system conceptualised can prove that hydrogen has value as an energy carrier for stationary decentralised set ups that can meet varying system requirements. Chapter 5 further investigates hydrogen storage; however, in the studies conducted hydrogen is compared to other storage technologies in individual and integrated systems.

Chapter 5 Comparison of Decentralised Energy Storage Systems using System Dynamics

From the results of Chapter 4, hydrogen storage is capable of reducing the requirement of grid energy for decentralised energy systems. This chapter further identifies the value of hydrogen storage in decentralised energy systems and compares hydrogen with redox flow batteries in individual and integrated systems using SD models.

5.1 Introduction to the Storage Scenarios Analysed

The requirement for low-cost access to energy storage technologies is increasing with the continued growth of renewable energy. Hydrogen and redox flow batteries (RFB) have promising energy storage characteristics that can allow increased penetration of renewable energy and a reduction in grid energy and CO_2 emissions. The strong synergy between natural gas and hydrogen anticipates that new efficient methods of hydrogen production such as microwave plasma processing of natural gas might have a leading role. Additionally, the improvements in the carbon allotropes properties and their cost are expected to influence the costs and efficiencies of large-scale energy storage systems.

Energy storage systems can be constrained by site, costs and efficiency. Currently, pumped hydroelectric energy storage makes up 98.3% of total global installed grid storage capacity (127 GW) and only less than 10 MW of capacity is from RFB, Figure 5.1 [151, 152]. The use of alternative energy storage technologies to pumped hydro-electric storage can allow the continued successful integration of renewable energy into the grid. The chapter is divided into two studies. The potential mitigation of energy problems using storage applications with a technical comparison of hydrogen and RFB with emphasis on vanadium redox flow batteries (VRFB) is considered in the first study. The second study investigates the techno-economic comparison of hydrogen, VRFB and all-iron RFB as well as the benefits of integrated storage systems. The conceptualised system is depicted in Figure 5.2, further developed from Figure 1.1 with focus on decentralised hydrogen energy systems with integrated RFB.

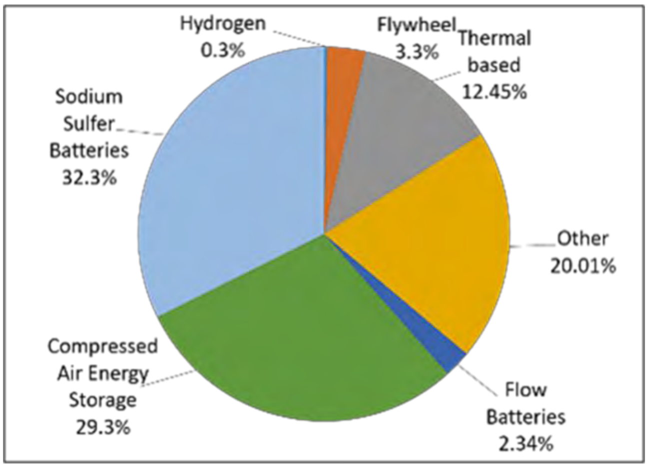


Figure 5.1 Non-pumped hydroelectric storage installed capacity accounting for 1% of worldwide storage capacity, with hydrogen and flow batteries included [151].

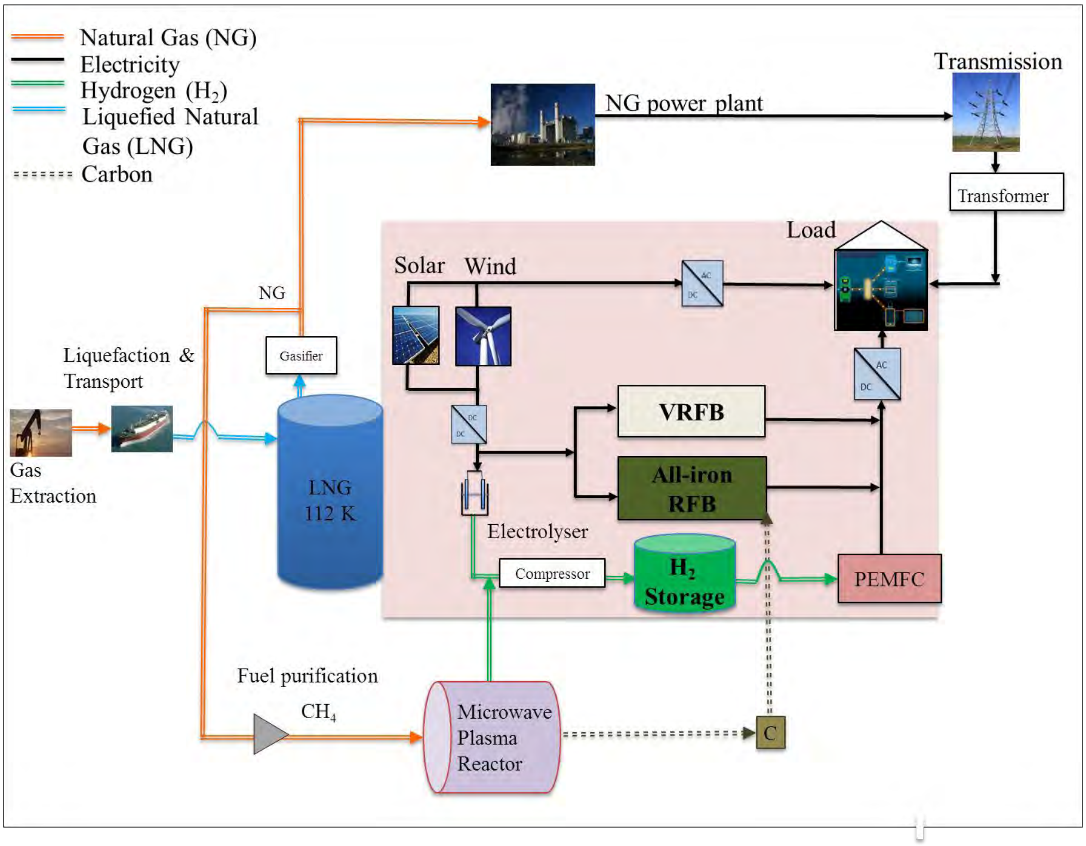


Figure 5.2 Conceptualised, decentralised energy system with alternative energy storage technology including hydrogen, VRFB and all-iron RFB. Furthermore, the use of electrolysis and microwave plasma processing of natural gas is depicted. This figure has been further adapted from Figure 1.1.

SD analysis is used in both studies and the complete system that the models will be based on is shown in Figure 5.3. Table 5.1 lists the different studies considered throughout this chapter with the corresponding scenarios that are used to investigate the technical and economic aspects of storage systems.

Table 5.1 System dynamic studies and corresponding scenarios. The subject of the SD model is the techno-economic comparison of hydrogen with redox flow batteries.

Study	Sub-Study	Scenario	Scenario Explanation
1		A	Equal power and energy capacity of VRFB and hydrogen storage
		B	Equal volume of storage of VRFB and hydrogen storage
2	a	A	Individual testing of VRFB, all-iron RFB and hydrogen storage for high wind energy scenario
		B	Individual testing of VRFB, all-iron RFB and hydrogen storage for low wind energy scenario
2	b	A	Integrated testing of VRFB and hydrogen with curtailment >40% sent to hydrogen storage system
		B	Integrated testing of VRFB and hydrogen with curtailment >60% sent to hydrogen storage system
		C	Integrated testing of VRFB and hydrogen with curtailment >80% sent to hydrogen storage system

For Study 1 the electricity generated by the wind turbine is the input to the energy storage systems and has three potential paths. It can be directly used to meet the demand of a number of houses which can be changed during the simulation. If the wind generated is higher than demand the energy that would be otherwise wasted can be used to store energy in either the RFB or the compressed hydrogen energy storage tank. A comparison is made to determine which energy storage method is the most effective at reducing the energy required from the grid. SD is used to compare important energy storage characteristics of the VRFB and compressed hydrogen storage. These include storage capacity (kWh), power capacity (kW), efficiencies and response time of the storage system. This allows an analysis of the feasibility of the storage systems to be made. As a result of the use of SD scenario analysis in the Thesis, Table 5.1 lists the different studies and summary of each scenario for reference.

Study 2 presents a technical and economic comparison of VRFB and all-iron RFB with hydrogen on an individual and integrated basis. The study also investigates the viability of a zero-emission remote hydrogen production unit from wind and PV electrolysis and microwave plasma processing of natural gas which explores the cost increase in hydrogen production when storage is used for providing energy to the microwave plasma reactor.

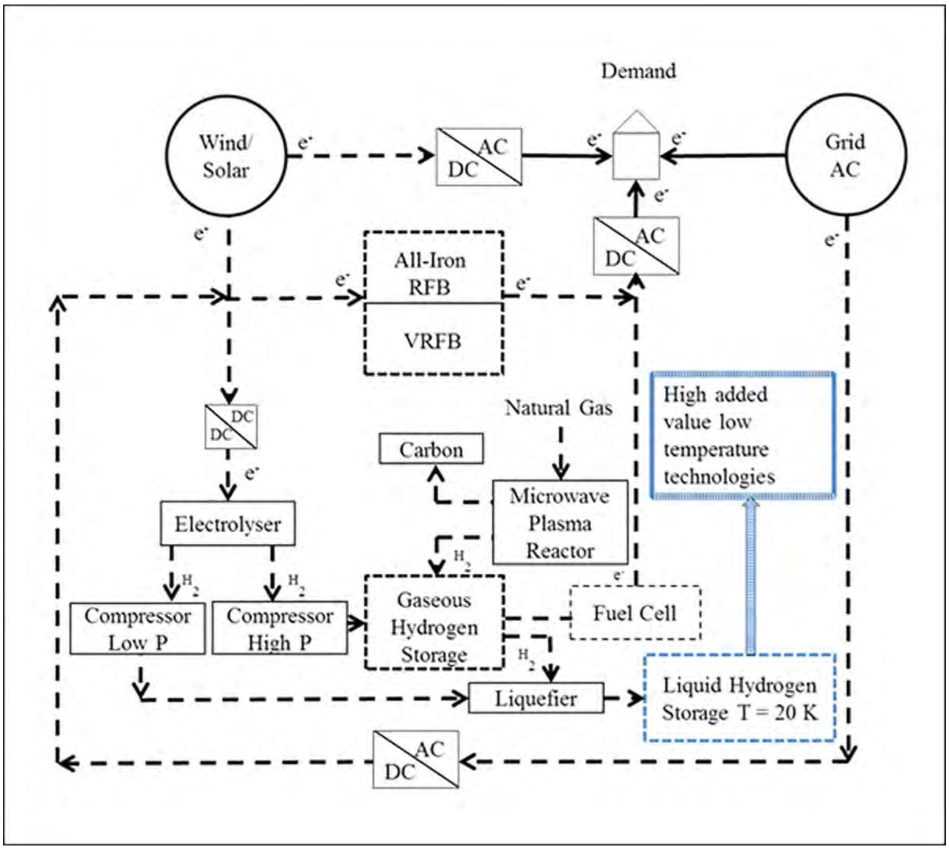


Figure 5.3 Schematic of a system using hydrogen technologies and vanadium (VRFB) and/or all-iron redox flow batteries (RFB) for storage of intermittent wind energy. The role of liquid hydrogen production for use as a high added value cryogen is illustrated as a result of the imminent widespread introduction of superconducting technologies.

5.2 Energy Storage System Technologies

The storage systems considered in the SD analysis which are hydrogen, VRFB and all-iron RFB will be discussed.

5.2.1 Hydrogen Storage System

For decentralised energy systems based on wind and PV energy, hydrogen production either by electrolysis or by microwave plasma processing of natural gas can represent environmental hydrogen production. Large scale electrolysis is possible and it can be implemented for decentralised systems due to the scalability of hydrogen production. The cost of hydrogen from wind electrolysis depends on the wind electricity generation price in a particular region but it can typically vary from 3.58-5.86 \$/kg with other sources estimating higher costs of 6-7 \$/kg [153]. PV electrolysis is more expensive than wind electrolysis with expected current values of 28.19 \$/kg and future values of 6.18 \$/kg due to expected rapid cost decrease of PV energy [153, 154]. Among different processing methods, as mentioned in Chapter 4, microwave plasma processing of natural gas is a ‘low-emission’ production method. The technology has a high efficiency with an estimated hydrogen production cost of 1.5 \$/kg, noticeably lower than the renewable electrolysis process and is dependent on natural gas prices.

The energy density of hydrogen has a lower heating value (LHV) of 120 MJ/kg (33 kWh/kg) and a higher heating value (HHV) of 141.80 MJ/kg (39 kWh/kg). Compression consumes 1.05 kWh/kg of electrical power [155, 156]. The compression, storage and dispensing costs of hydrogen are estimated to range from 2 \$/kg to 2.4 \$/kg [156]. The advantage of compressed hydrogen storage is the high energy density making hydrogen suitable for bulk energy storage [157]. The overall LCOE production from electrolysis is considered. Hydrogenics HyPM^{TM} (the fuel cell considered in the study) have produced a self-contained fuel cell system that is combined with an inverter for AC power and a management system. The system has a capacity of a 1 MW electrical power output. Efficiencies are 49% with a 20 years estimated lifetime. Its consumption of hydrogen is 780 m^3/hr [157]. The estimated mid-range price of PEMFC is 813 \$/kW [158].

5.2.2 Redox Flow Batteries

RFB have promising storage characteristics and, as the power and energy capacity of the battery are independent of each other, the RFB can be optimised to maximise the performance and minimise the cost. RFB are modular and consequently, the installation is flexible [159, 160]. They are rechargeable systems that have the storage medium in the form of electrolyte kept in tanks external to the active cell. The electrochemical reactions and the charging and discharging battery cycles are taking place in the battery stack as the electrolyte flows through the two membrane-separated chambers of the active cell, Figure 5.4 [159, 160]. Once the electrolyte has been discharged it can be recharged allowing the recovery of the spent electrolyte and its reuse. The energy is stored in the separated reactants (electrolytes) while the power is controlled by the stack, Figure 5.4 [159, 160]. In general, RFB share similar flow geometries and the main differences typically occur in the electrolyte that is used [160-162]. The RFB can operate at low temperatures (from -10 to +45°C) as long as the electrolytes remain stable and their precipitation does not occur.

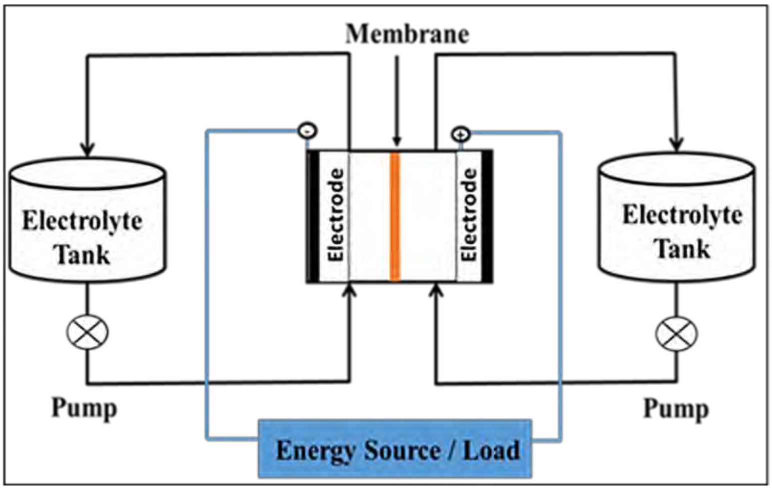


Figure 5.4 Schematic representation of a redox flow battery. The electrolyte is kept in outside tanks and pumped in the two membrane-separated chambers of the active cell.

5.2.2.1 Vanadium Redox Flow Batteries

The VRFB has promising energy storage characteristics (e.g. fast response time, low self-discharge characteristics etc.) and can therefore respond fast to unpredictable changes in wind speed as their response time from shut down is one minute. The VRFB has a high efficiency in the range of 65-80%, but it has a relatively low energy density and this represents one of the main disadvantages [163-165]. The theoretical energy density is 30-47 Wh/l but the practical achievable energy density is lower at 15-25 Wh/l while the specific energy is 20-35 Wh/kg [165]. When storage capacity needs to be increased the low energy density leads to large electrolyte volumes. If the physical area of the site is constrained then the low energy density and relatively high costs of electrolyte, 3.22 $/l of vanadium, will constrain this storage system [162]. The electrolyte is evenly split in VRFB between the positive and negative tanks. The reactions that occur within the cell during charging and discharging cycles are shown in Table 5.2.

Table 5.2 The chemical reactions occurring at the negative and positive side of the VRFB and all-iron RFB.

	VRFB	**All-Iron RFB**
Positive side	$VO^{2+} + H_2O - e^- \rightarrow VO_2^+ + 2\ H^+$	$Fe^{2+} \leftrightarrows Fe^{3+} + e^-$
Negative side	$V^{3+} + e^- \leftrightarrows V^{2+}$	$Fe^{2+} + 2e^- \leftrightarrows Fe^0$

There are several advantages of using VRFB for energy storage applications: long cycle life (>10000 cycles), high reliability, deep discharge capability and high power density. Although the electrodes do not store energy they are important for charging and discharging of the battery, influencing, together with the electrolyte and separation membrane, the life-time of the battery, the energy losses and, consequently, the overall efficiency. It is anticipated that efficiency improvements can be made with regard to the correct selection of electrodes e.g. by using carbon black or its activated composites [52]. Other advantages include the popularity of the battery with regard to research and also the many VRFB installations worldwide. Disadvantages include the high cost of vanadium, the sustainability of the supply and the toxicity of vanadium. Cellcube (the RFB used in the study) is one of the commercial scale VRFB available today [163].

5.2.2.2 All-Iron Redox Flow Batteries

The all-iron RFB like VRFB employs the use of a single chemical element (in this case iron) in several oxidation states on both sides of the active cell, Table 5.2, while the electrolyte is kept outside in the storage tanks. The positive electrode of the all-iron battery is the ferric/ferrous redox couple, and the negative electrode involves iron plating from Fe (II) [161]. An advantage of all-iron RFB is the readily available electrolyte with an estimated low cost of 0.23 $/l [162]. In the traditional all-iron RFB, at the negative side, the ferrous ions are reduced during charge. Their plating as iron metal onto a graphite electrode of the stack occurs leading to a coupling between energy and power. On the positive side of the battery ferrous ions are oxidised to ferric ions during charge remaining in the solution. Reactions are opposite on discharge. Cheap aqueous electrolytes, inexpensive separators and the wide spread availability of iron (~230 billion metric tonnes of iron) give the all-iron RFB the potential of reduced storage system cost, while the plating and, consequently, the coupling between the energy and power represents its main disadvantage [161, 162].

To avoid this disadvantage a slurry electrode containing electrically conductive carbonaceous particles can be made by flowing them in an electrolyte containing the dissolved iron species [161]. Such conductive particles can include carbon black and/or carbon allotropes with different surface areas and enhanced conductivity, carbon micro-flakes, nanofibres, nanotubes etc. Thus, iron is plated onto the carbon particles at the negative side while charging. The carbon particles can then carry the iron metal to be stored in the external tanks allowing for energy storage capacity and power decoupling allowing the economic advantages of scaling inherent to RFB to be recovered [161]. The carbons and their properties influence the electronic conductivity of the slurry electrodes that have to be greater than the ionic conductivity of the electrolyte. This allows for the iron deposition to occur only onto the slurry particles and not on the current collector leading to a better control of the current distribution [161]. The electrode surface area plays an important role in determining the all-iron (hybrid) RFB efficiency and life-time. For slurry all-iron RFB this role becomes secondary. Presently, the slurry all-iron RFB are still in the development stage putting them at a disadvantage to the already commercialised VRFB. Typically, the energy density of the all-iron hybrid battery is 12.7 Wh/l with a specific energy 10.9 Wh/kg. Energy efficiency is 55% with operating temperature $T_0 = 40°C$ [161, 166].

5.3 Study 1 - Technical Investigation of Vanadium Redox Flow Batteries and Hydrogen Storage

The method and results for Study 1 (refer to Table 5.1) are presented in Section 5.3.1 and Section 5.3.2.

5.3.1 Method and Introduction to System Dynamic Scenarios

An SD model was used in this study. The instantaneous output of the model to changing inputs can be tested in SyntheSim mode on Venism. The SD model allows numerical simulations and the interactions between the wind energy, storage system and the demand being met to be analysed to determine the most effective option for energy storage in minimising grid energy. Different flows of energy are represented in the model, Figure 5.5. SD is used to model a complex energy production, storage and use system. In the model the wind energy generated is first used to meet demand from the houses. Any wind that would be otherwise curtailed is then used for the energy storage systems. For the model the curtailed energy is assumed to be available to both energy storage systems so the technical performance of the systems can be compared. The constraint on the amount of electricity that can be stored results from the capacity of the different systems. The problem that is being addressed with this SD model is identifying the suitability of wind energy storage using VRFB and compressed hydrogen storage. The model is a small decentralised production unit and the time boundary for the model is 96 hours with a time step of one hour.

The model considers the efficiencies of the overall VRFB storage system set at 80% [163]. For the hydrogen storage system electrolyser mid-range efficiency of 74.75%, a compressor efficiency of 85% and a polymeric fuel cell efficiency of 53% were considered [167-169]. The compression of hydrogen and subsequent change in volume corresponds with a hydrogen mass/volume lookup table [168]. The converter DC/DC efficiency was set at 85% and the DC/AC efficiency at 65%. The integration of the energy storage systems with a wind turbine that can have an energy output of 225 kW was chosen.

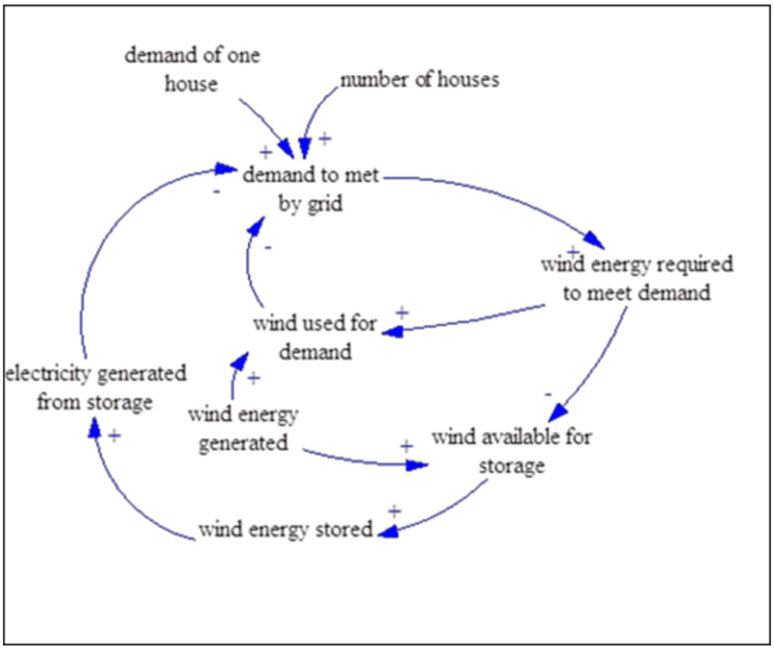


Figure 5.5 Simplified causal loop diagram for the system response to reduce grid energy using wind energy and storage energy from VRFB and Hydrogen.

As SD modelling is used, an outline of a SD model is represented in Figure 5.6, to highlight the complexity of the arising models that are developed from the simple causal loop diagram, Figure 5.5. The use of these complex models are used for the formulation of all the results in this Thesis. The model in Figure 5.6 represents the aspects under consideration highlighted in Figure 5.3.

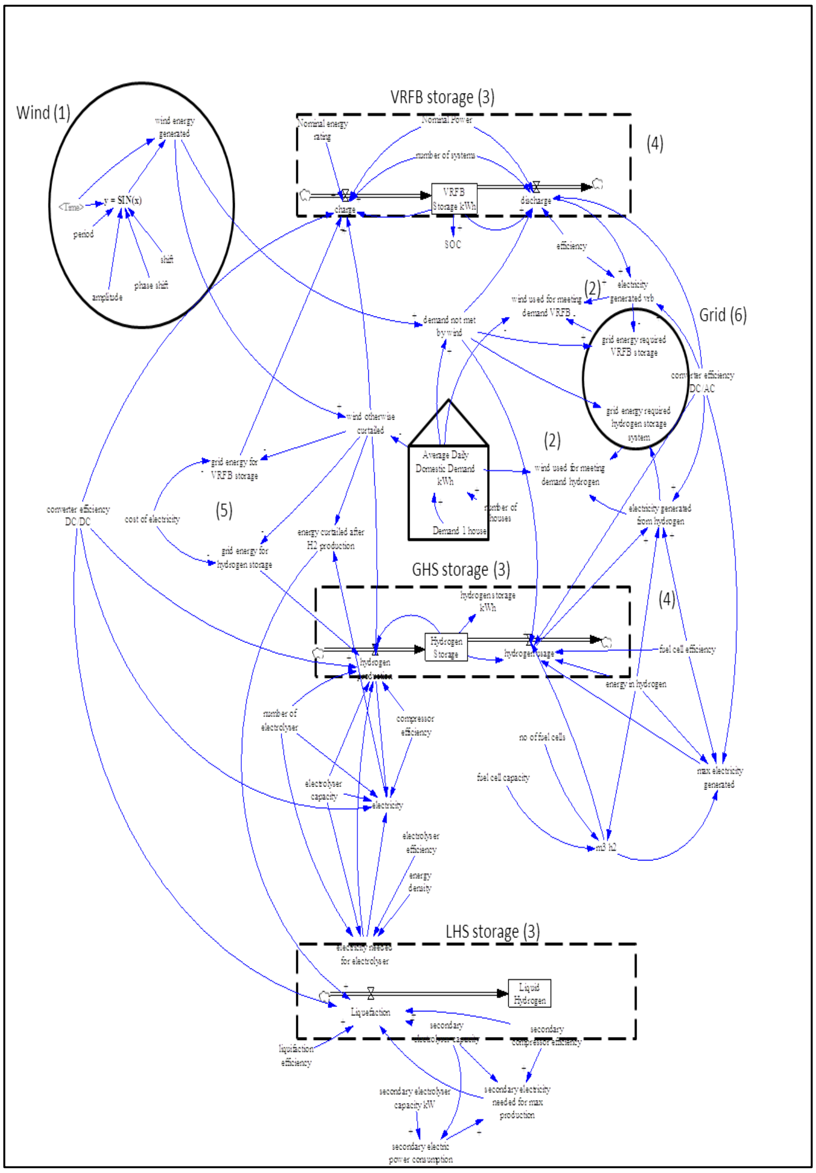


Figure 5.6 SD model developed from the causal loop diagram in Figure 5.5 reflecting the complexity of the system models. (GHS = gaseous hydrogen storage, LHS= liquid hydrogen storage).

The demand for twenty houses was used in the simulation. It was assumed all houses had the same demand trend. Figure 5.7 shows the demand profile used in the simulations. The wind energy trend used to represent fluctuating wind energy per hour used in the model is shown in Figure 5.8. Two scenarios were used to compare the storage systems using this wind trend.

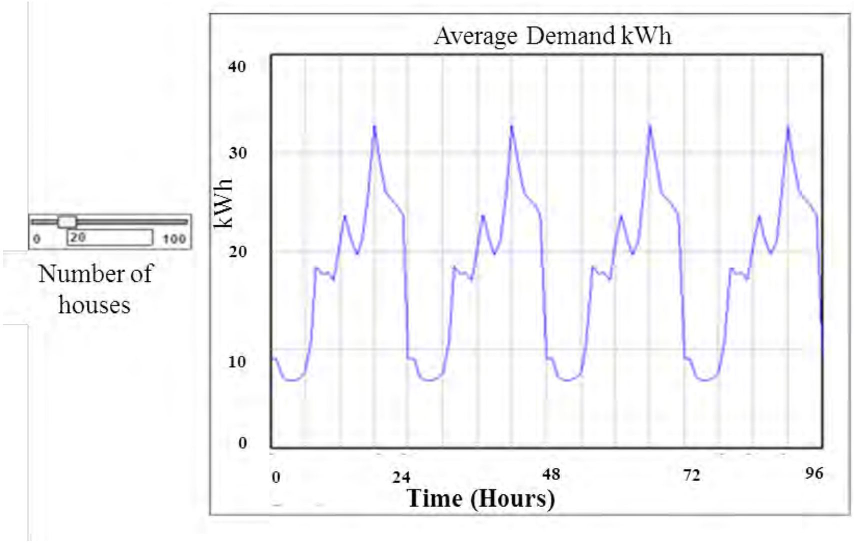


Figure 5.7 Average domestic demand (kWh) for 20 houses of equal demand used in the simulations for Study 1, Scenario A and B.

Equal power and energy capacity represents Scenario A (Study 1) and is used to compare the storage systems that both have a 10 kW charging capacity. The use of a 10 kW/100 kWh VRFB called the Cellcube was used. The Cellcube holds has an overall reported efficiency of 80%. A 10 kW alkaline electrolyser generating 3.33 Nm^3 of hydrogen per hour is stored in a hydrogen storage system having the potential to store 100 kWh, an equal amount of energy capable of being stored in the electrolyte of the VRFB. As compressed hydrogen at 700 bar has a volumetric energy density of 1246 kWh/m^3, a storage capacity of 0.08 m^3 is used. As energy curtailed in the system was large the energy capacity was increased for both systems to 500 kWh by increasing the number of systems in the model.

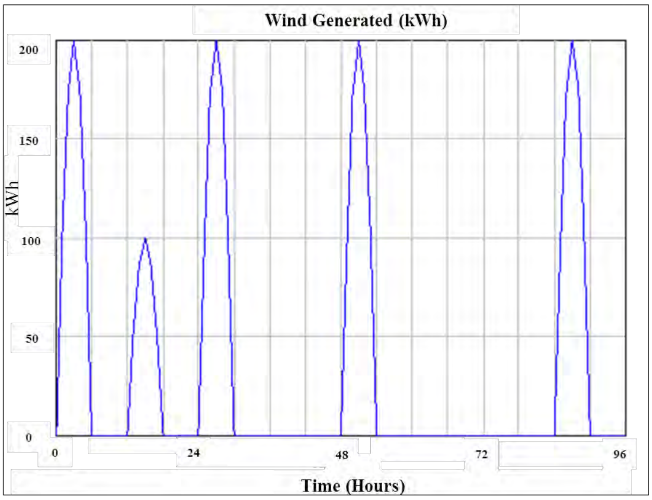


Figure 5.8 Wind energy generated used for Study 1, Scenario A and B.

Equal volumes of storage was used for Scenario B (Study 1). A 100 kWh VRFB was used as the energy storage capacity for the VRFB. For a 100 kWh nominal energy storage capacity, 6 m^3 of electrolyte solution for the VRFB is required. With equal volumes of storage capacity more energy can be stored as compressed hydrogen as a result of the higher energy density for a given volume. The same demand profile and wind energy generated as Scenario A was used. For additional analysis the use of energy stored in this system of equal volume was used only when the price of electricity was high. This explores the potential of using a costing model to identify the optimal amount of energy that should be stored by the systems at times when there is excess wind or when the cost of grid electricity is low.

5.3.2 Results of the Hydrogen and VRFB Comparison

The results for Study 1, Scenario A and Scenario B summarised in Table 5.1 are graphically represented and discussed.

5.3.2.1 Study 1 Scenario A: Equal Power and Energy Capacity

Scenario A results are shown in Figure 5.9 for the system response of the compressed hydrogen storage and Figure 5.10 for the system response of the VRFB. In the comparison of system response to equal power and energy capacity of the systems both storage technologies have the capacity to reduce the amount of wind energy curtailed.

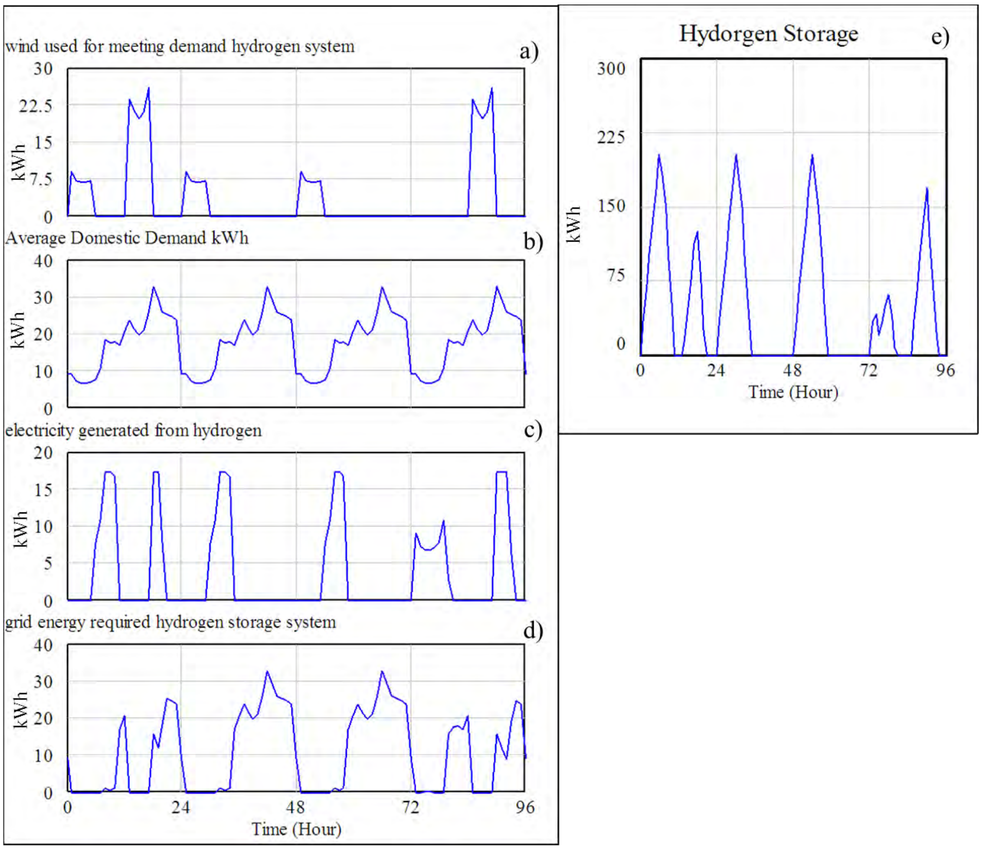


Figure 5.9 Hydrogen storage system response over 96 hours with equal energy storage capacities of 500 kWh (Study 1, Scenario A). a) wind energy used for meeting demand, b) demand needed to be met, c) electricity generated from the hydrogen storage system to meet demand, d) grid energy required to meet demand when wind and hydrogen cannot meet it, (e) quantity of energy stored.

Figure 5.9a and Figure 5.10a shows the total wind used to meet demand. It is same in both systems as the wind energy is first used to meet demand. Figure 5.11 shows that 19.5% of the overall demand indicated in Figure 5.9b and Figure 5.10b is met by wind energy. This means 80.5% of demand must be met by the storage systems or grid energy. Figure 5.9c and Figure 5.9d illustrates how this demand is met by the electricity generated by hydrogen and grid energy respectively. Figure 5.9e shows that hydrogen storage never reaches full energy storage capacity of 500 kWh indicating the system is constrained by the capacity of the electrolyser. The storage system reaches zero over the 96 hour period and so increasing the power and energy capacity would benefit the storage system by allowing more wind energy to be used to produce hydrogen for storage.

From Figure 5.10c it is found that more electricity is generated from the VRFB storage system than the hydrogen storage system. The VRFB storage system generates 41.2% of energy needed to meet demand. This is almost double the energy of the hydrogen system indicating that due to the higher efficiency of the VRFB storage system when the two storage systems are compared the VRFB is more effective at reducing the grid energy required in the system, Figure 5.10d. Figure 5.10e shows more energy is stored in the VRFB system again indicating the higher efficiencies achieved by the system. Figure 5.11 shows a breakdown of the percentage of total demand being met by wind energy, grid energy and the storage systems with a storage capacity of 500 kWh.

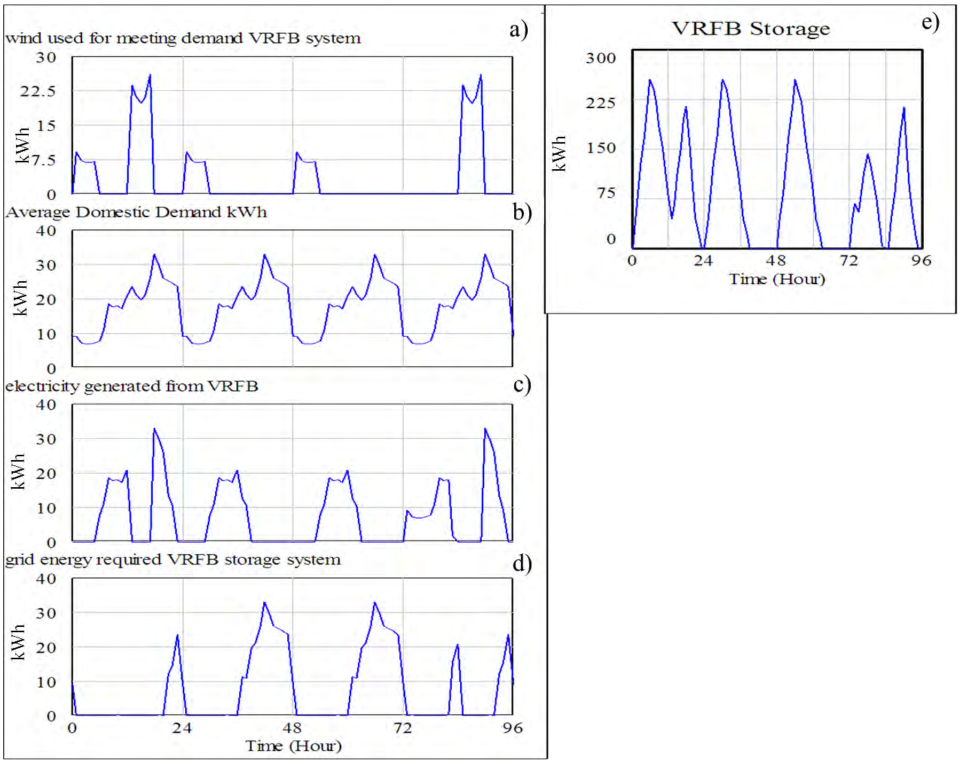


Figure 5.10 VRFB storage system response over 96 hours with equal energy storage capacities of 500 kWh. (Study 1, Scenario A). a) wind energy used for meeting demand, b) average demand needed to be met, c) electricity generated from the VRFB storage system to meet demand, d) grid energy required to meet demand when wind and the VRFB cannot meet it, e) quantity of energy stored.

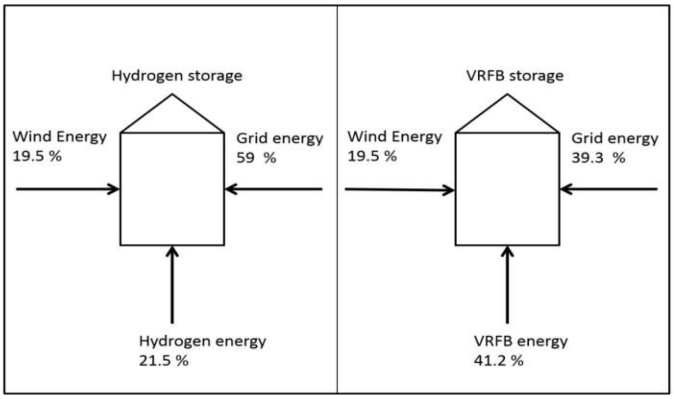


Figure 5.11 Comparison of total demand being met by wind energy, grid energy and the storage systems for Scenario A, Study 1, with a total energy storage capacity of 500 kWh. The storage system has five electrolysers and five fuel cells with a 10 kW capacity and five 10 kW/100 kWh VRFB.

The VRFB is capable of reducing curtailment in the system and the amount of grid energy required in meeting total demand more effectively than the hydrogen storage system in the equal power and energy capacity scenario.

5.3.2.2 Study 1 Scenario B: Equal Volume of Storage

Scenario B uses equal volumes of storage. The hydrogen system is capable of storing more energy as a result of higher volumetric energy densities. As there is no constraint on the power capacity, the electrolyser and fuel cell capacity were increased to make a more realistic model that allows the extra storage capacity to be used. The nominal capacity of the VRFB can be changed but the nominal energy capacity remaining at 100 kWh. With 6 m^3 of electrolyte storage medium, an equal volume of hydrogen compressed at 70 MPa with 1246 kWh/m^3 would allow 7500 kWh to be stored. This property of hydrogen is important for bulk energy storage as identified in Chapter 4. The power capacity of the VRFB, the electrolyser and fuel cell can be changed during the simulations to give optimum performance. Due to hydrogen's large volumetric energy density at high pressures when the volume of the storage system is not constrained it is more effective at reducing grid energy that the VRFB.

With equal volumes of storage the maximum amount of energy stored in the hydrogen system reaches almost 600 kWh, Figure 5.12, while the VRFB can only have a maximum energy capacity of 100 kWh with a total volume of 6 m^3 of storage medium. The hydrogen fuel cell output was set equal to the VRFB output to ensure a realistic comparison could be made.

Management of when the energy is used could benefit the storage systems to ensure there is stored energy available at peak times in the system to maximise profit. From Figure 5.13c the electricity from the VRFB system is generated for shorter time intervals compared to the hydrogen system and so more grid energy is needed in the system, Figure 5.13d. The shorter generation intervals of the VRFB system is due to the storage system containing less stored energy in the system, Figure 5.13e.

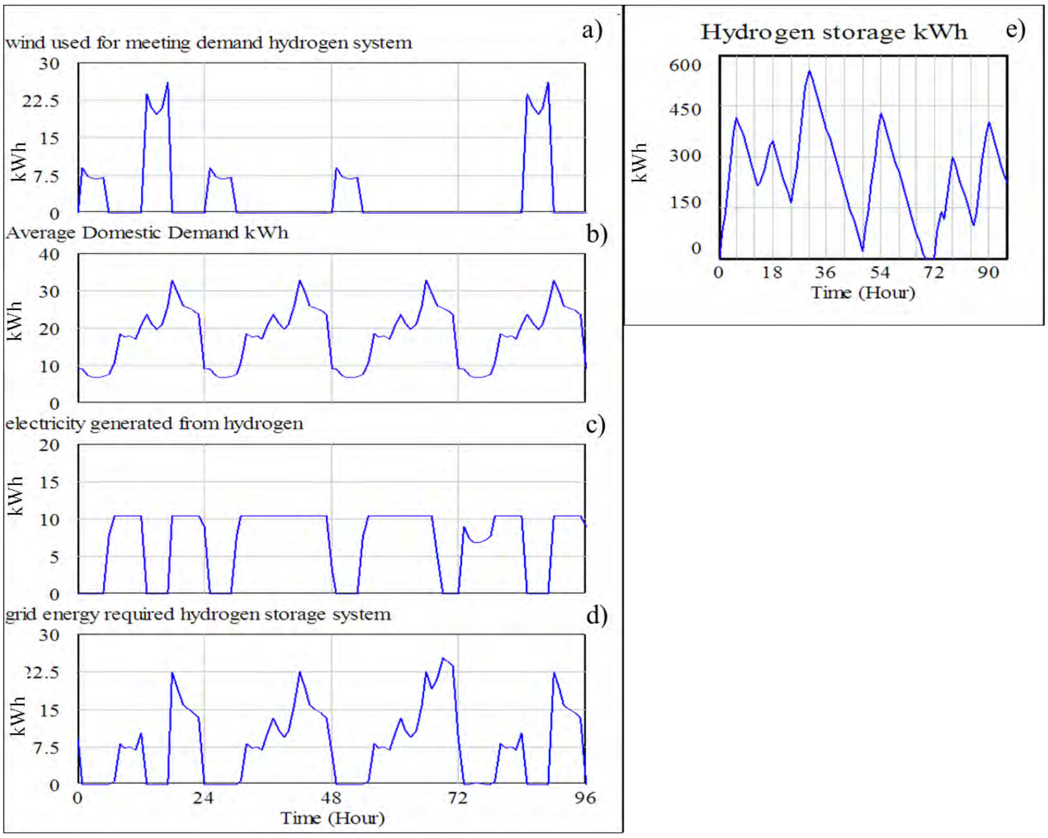


Figure 5.12 Hydrogen storage system response for equal volume of storage 6 m^3. (Study 1, Scenario B). a) wind energy used for meeting demand, b) average demand needed to be met, c) electricity generated from the hydrogen storage system to meet demand, d) grid energy required to meet demand when wind and hydrogen cannot meet it, e) quantity of energy stored.

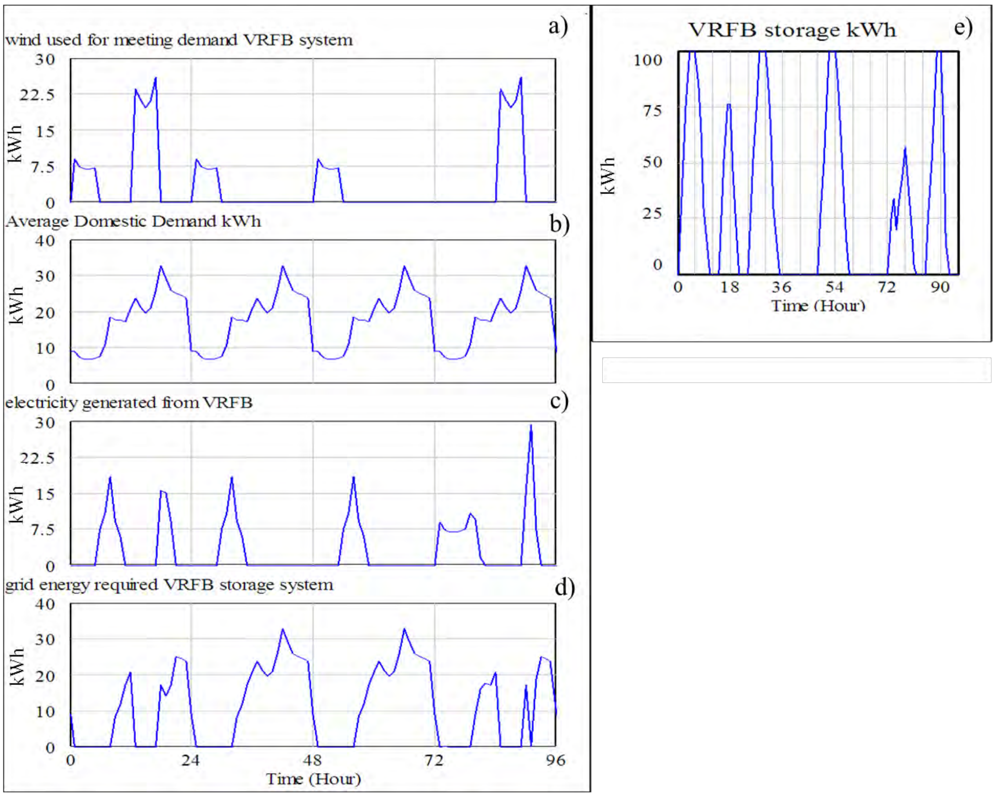


Figure 5.13 VRFB storage system response for equal volume of storage 6 m^3. (Study 1, Scenario B). a) wind energy used for meeting demand, b) average demand needed to be met, c) electricity generated from the VRFB storage system to meet demand, d) grid energy required to meet demand when wind and the VRFB cannot meet it, e) showing the quantity of energy stored.

Figure 5.14 shows the percentage breakdown of how wind energy, grid energy and the storage systems meet the demand. It indicates that hydrogen is more effective with the same wind and demand input for an equal volume of energy storage medium.

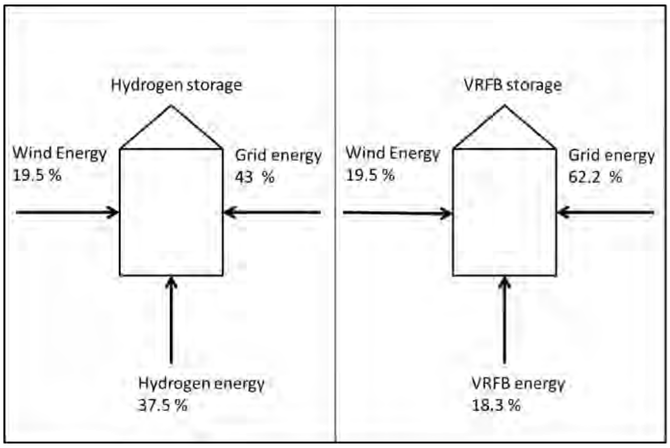


Figure 5.14 Comparison of how total demand is met by wind energy, grid energy and the storage systems for Scenario B with an equal volume of 6 m^3 storage. The hydrogen storage system has a 40 Nm^3 electrolyser and fuel cell capacity of 30 kW. The VRFB storage system has a 30 kW charge/discharge.

5.4 Study 2 - Towards Decentralised Hydrogen and Redox Flow Battery Integrated Storage.

The method and results for Study 2 (refer to Table 5.1) are presented in Section 5.4.1 and Section 5.4.2.

5.4.1 Method and Introduction to System Dynamic Scenarios

The previous demand in Study 1 had a low system demand that could be used for a small decentralised village; however, depending on the system sizing and overall load, the decentralised wind-hydrogen storage system can support towns by meeting the domestic demand and/or they can be used to supply commercial or industrial buildings as well as potentially being a viable option for remote production of hydrogen integrated with renewable energy. This study (Study 2) considers a larger system.

Scenario analysis (refer to Table 5.1) is used by employing different energy inputs, Figure 5.15. The input parameters of the model are set and the output delivers the valuable characteristic quantities for the characterisation and assessment of the system. This framework enables the identification of opportunities for the design rationalisation of the integrated energy storage system. The charging and discharging of the energy storage systems form the basis for stocks and flows within the model and the response of the storage system assessed.

The wind energy generated from a 0.5 MW wind turbine for two wind scenarios over a 72 hour period is considered for demand and renewable electrolysis, Figure 5.15a. Solar output is presented in Figure 5.15b. Figure 5.15 outlines the vulnerability of a decentralised system to both wind and PV intermittency indicating the requirement for storage.

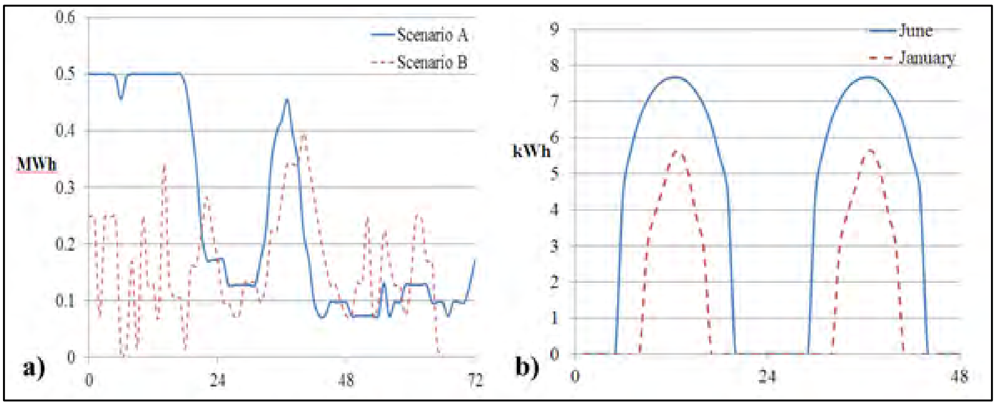


Figure 5.15 a) Wind-speed energy generated over a 72 hour period showing the response of the wind turbine based on the power curve of one 0.5 MW wind turbine. Scenario A (Study 2) has periods of very high wind energy and Scenario B (Study 2) has typical moderate wind energy used for determining the system response, b) Solar energy generated in a 40 kW solar PV system taken from data in January and June [170].

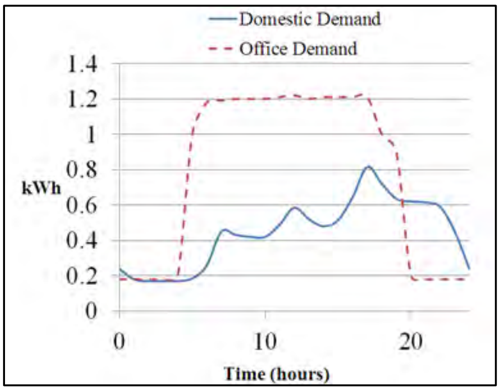


Figure 5.16 Trend patterns of the domestic and office electrical demands. A decentralised integrated energy storage system with wind energy can provide decarbonised electrons to supply the demand, while the grid is maintained as a backup source of electricity [171, 172].

As mentioned a larger demand is considered in Study 2. A town with both domestic and office demand is considered (Figure 5.16). Study 2 is divided into two areas of focus; an individual analysis (2a) and an integrated analysis (2b). In Study 2a, the individual study, the response of a decentralised renewable-storage system, as depicted in Figure 5.17, is tested. The investigation of the technical and environmental potential of the individual decentralised energy storage systems is the primary objective.

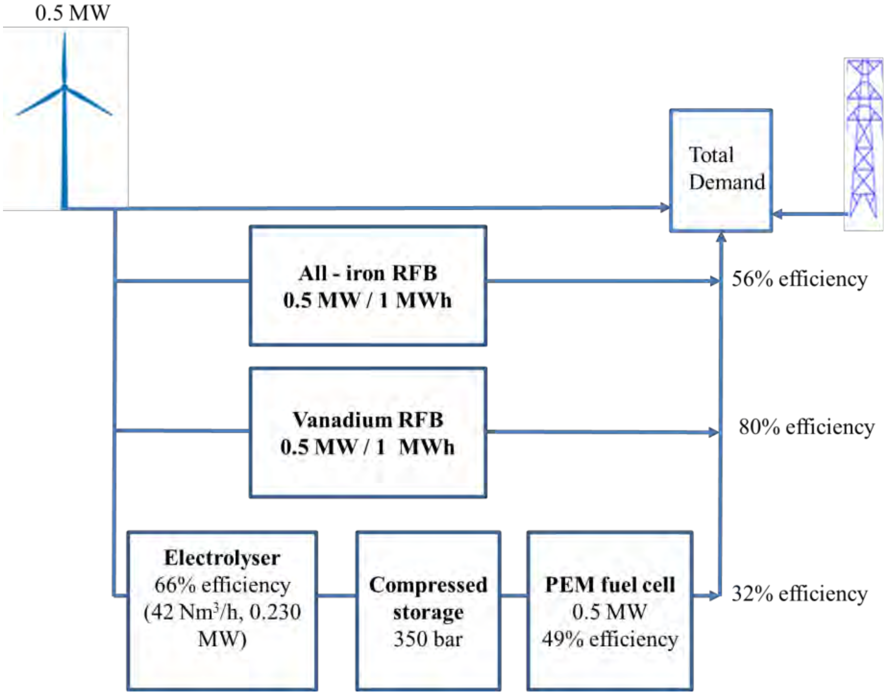


Figure 5.17 Decentralised wind and individual energy storage systems used in the model. A 0.5 MW wind turbine is integrated with 0.5 MW energy storage technologies for Study 2.

In Study 2b for the integrated study the combination of hydrogen and VRFB storage, is considered to investigate the potential benefits and outcomes of integrated systems, Figure 5.17. The SD model causal loop diagram is depicted in Figure 5.18, highlighting the variable interactions within the integrated system. Furthermore, a remote hydrogen production system with microwave plasma processing of natural gas and electrolysis is considered in Study 2b, Figure 5.19. Integrated solar and wind energy are used to meet the electrical demand of the production systems. Additionally carbon black/allotropes are produced from the microwave plasma processing of natural gas. The advantages of low-cost carbon allotropes on energy storage technology will be discussed.

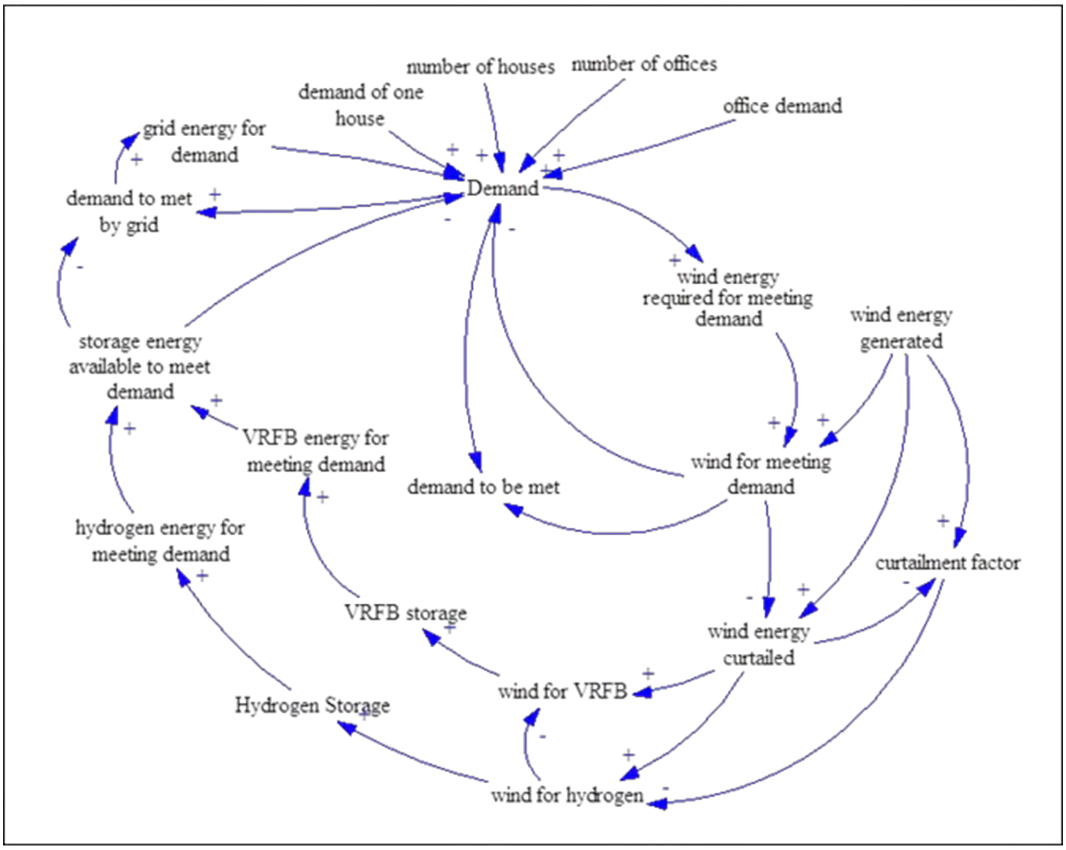


Figure 5.18 Causal loop diagram for the integrated VRFB and hydrogen storage systems (Study 2b).

Hydrogen storage can be advantageous to wind energy systems as it was reported that adding hydrogen storage to a wind energy system can reduce the total LCOE if the storage system can reduce the curtailment by greater than 5%; this is as a result of hydrogen's ability to act as a bulk energy storage medium and to increase the capacity factor of the system [33].

As previously mentioned carbon materials have the potential to enhance the efficiencies of some storage technologies. The PEMFC already are reliant on platinum as a material that increases its price. Therefore, platinum replacement with cheaper (carbon) composites would increase the commercial viability of fuel cells and, consequently, of hydrogen as an energy carrier. Carbon allotropes, nanofibres or nanotubes exhibit physical and chemical potential characteristics that could improve the batteries, making them an ideal material for VRFB solid electrodes [165, 166]. This can result in widening the operating potential range and a higher chemical stability. Also, all-iron RFB can become an economically viable energy storage technology as a result of the relatively low cost of the electrolyte required.

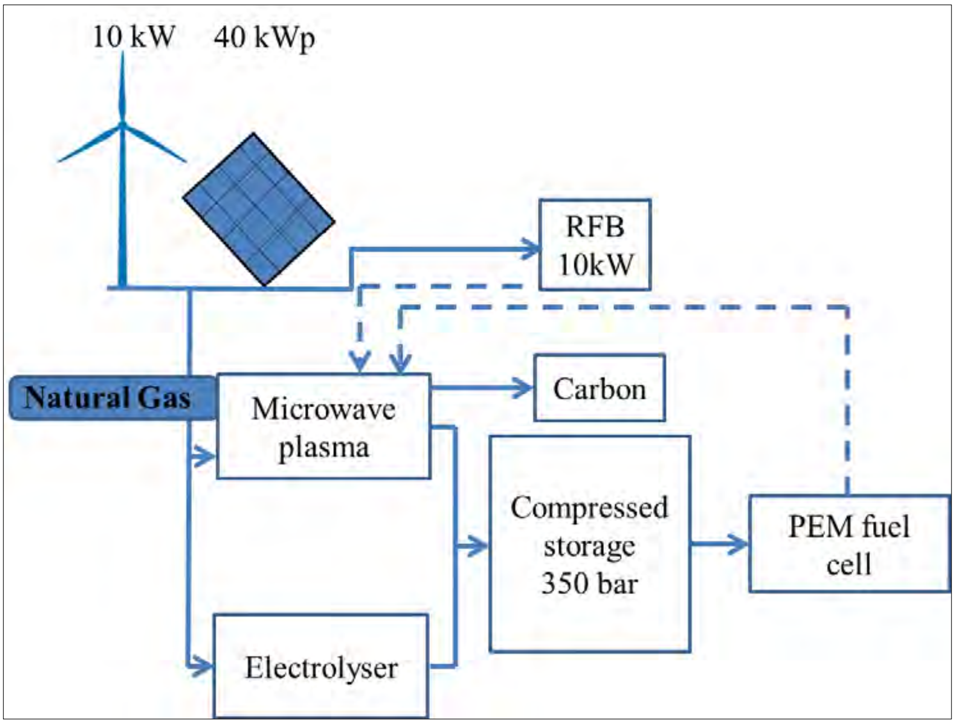


Figure 5.19 Decentralised remote wind and solar energy integrated with a hydrogen production system as the demand centre. A direct carbon fuel cell (DCFC) and proton exchange membrane fuel cell (PEMFC) are presented indicating the potential for electricity generation from fuel cells within the integrated system.

The improvements on the system efficiency offered by the slurry electrodes are making these batteries more attractive [166]. Carbon felt is another typical electrode material with a wide operating electrode potential range and stability, a high surface area, and is economic but it possesses poor electrochemical activity. Consequently, much attention has been provided to electrode modification to enhance their electrochemical properties.

The main components where carbon, in its different forms, can affect the RFB economic costs are detailed in Figure 5.20 (patterned segments [165, 166]). These costs are emphasised for 1 MW/4 MWh systems. In VRFB systems the carbons can be used to modify and improve the properties of the membrane electrode assembly (i.e. felt, membrane and bipolar plates), Figure 5.20a, and the impact can be up to 34% of the component's cost. In all-iron RFB the carbon impact can be radical (up to 67%), Figure 5.20b, especially when carbon slurries are employed.

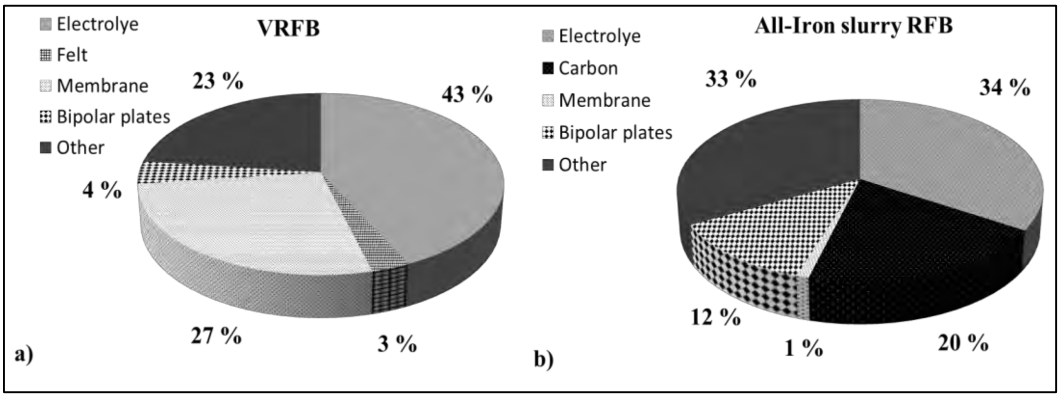


Figure 5.20 Percentage of economic costs associated with 1 MW/4 MWh systems using a) VRFB (where other represents the cost for: tanks: 2%, pumps: 5%, poly-vinyl chloride frames: 2%, power conditioning systems: 11% and other materials for battery construction: 3%), b) all-iron slurry RFB (where other represents the cost for: tanks: 8%, pumps: 8%, poly-vinyl chloride frames: 4%, flow frames: 5% and other materials for battery construction: 8%). The patterned segments represent the areas in which carbon price can affect the economic costs of the system when introduced into the battery.

The total cost of the cell for an all-iron RFB will decrease with increased efficiency. The use of carbon slurry is expected to increase the efficiency of the all-iron RFB. However, it is important to note that the cost decreases sharply with increasing current density below 150 mA/cm^2, and then tends to level off at 200 mA/cm^2 with further increases in current density [166]. This important observation implies that there is no economic incentive to increase the current density of the battery over 200 mA/cm^2 as the balance between costs and current density is already achieved [166]. The costs of the flow frames and for the carbon particles used to form the slurry are both highly uncertain and these are two of the largest costs considered. The cost of carbon is in a range of 700-2500 \$/ton. For a current density of 200 mA/cm^2 with a round trip efficiency of 75% and a parasitic loss to pumping the slurry of 0.6% and with the current cost of other cell components the cost of the slurry particles must be kept under 1.1 \$/kg to meet the economic goal of 200 \$/kW [166].

5.4.2 Results of the Individual and Integrated System Response

The objective of the individual technology system model (Study 2a) was to complete the testing of the technologies using different wind scenarios (Scenario A and Scenario B) explained in section 5.4.1. For this study a tornado graph was included *to describe how the quantitative analysis responds to reasonable variations in the parameters. The objective of the integrated technology system model (Study 2b) was to identify potential advantages of hydrogen and RFB technology integration and additionally investigate the integration of wind and solar energy with a remote hydrogen production plant.*

5.4.2.1 Study 2a - Techno-Economic Investigation of Individual RFB and Hydrogen

The total demand that resulted from the real domestic and office demand was 10.27 MWh. The demand needed to be met by a 0.5 MW wind turbine, a storage system and the grid as back-up over the 72 hour period in two different wind scenarios, Figure 5.15 [171, 172]. To reduce the curtailment the system load can be increased; however, during the night curtailment can still remain high. The extent to which each storage system can respond in the system as well as costs are considered. The model calculates the average use of the wind for different storage systems and the grid energy for both wind scenarios.

The techno-economic results for wind Scenario A which has a high curtailment of wind energy (Study 2a) are presented in Table 5.3 and Table 5.4. The results indicate hydrogen's suitability for bulk energy storage. Hydrogen was produced from the renewable electrolyser system. After compression hydrogen is used by the fuel cells employed, Figure 5.17. The high curtailment within the system during certain periods can be seen in Figure 5.21 (represented by 'wind to storage'). The hydrogen system acts as a buffer for the wind energy for a long period of time and represents 18.2% of the demand over the 72 hours period, Figure 5.21a. The two RFB systems have similar response to each other with a better performance from VRFB (here depicted in Figure 5.21b) due to higher efficiencies. Both the RFB responses are lower than hydrogen as a result of the energy storage being constrained by the lower energy densities.

Table 5.4 shows the calculated cost of the storage energy and the grid energy over the time period. It can be observed that hydrogen has higher production costs per MWh (469 €/MWh) compared to VRFB (276 €/MWh). As they are still under development the levelised cost of all-iron RFB are not currently available but it can be anticipated that the use of carbon slurries within the all-iron RFB will allow for a lower levelised cost compared to VRFB. This will put the all-iron RFB as a strong candidate for energy storage systems. In the present scenario the levelised cost of all-iron RFB was estimated based on the levelised cost of the electrolyte in the iron-chromium RFB as this technology benefits from the low cost of iron as an electrolyte (230 €/MWh). The cost of hydrogen production is larger than RFB; however it is able to meet more demand in this scenario. This result is one motivation behind the application of an integrated hydrogen and RFB storage system.

Table 5.3 Average percentage of demand met by wind, grid and storage energy for a 72 hour period, wind Scenario A in Study 2a, Figure 5.21.

	All- Iron RFB	**VRFB**	**Hydrogen**
Direct wind	81.8%	81.8%	81.8%
Direct grid	11.3%	11.1%	0%
Storage system	6.9%	7.1%	18.2%

Table 5.4 Calculated costs for the direct grid generated and storage energy using wind Scenario A in Study 2a in Figure 5.21 (€0.92= $1).

	All-Iron RFB	**VRFB**	**Hydrogen**
Direct grid cost based on system marginal price	€83.44	€82.71	€0
Storage system cost - *All-iron RFB estimated from iron-chromium battery*	0.71 MWh * 230 €/MWh = **€163**	0.73 MWh * 276 €/MWh = **€202**	1.87 MWh *469 €/MWh = **€877**

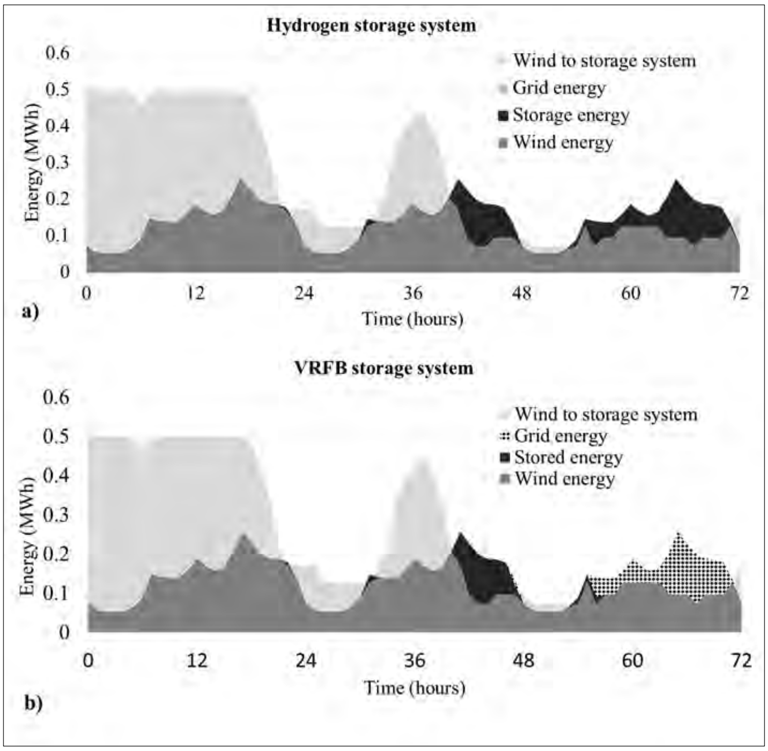


Figure 5.21 The response of the decentralised a) hydrogen and b) VRFB storage system for Scenario A. Grid energy, stored energy and wind energy are used for meeting demand. Wind otherwise curtailed is used for the a) production of hydrogen and b) charging of VRFB and is indicated as "wind to storage system" in the graph. Grid energy is used as a back-up of the system for when the storage system cannot meet demand.

Table 5.5 represents the results from wind Scenario B with a low curtailment of wind (Study 2a). This shows that the RFB can meet more of the demand compared to the hydrogen system, Figure 5.22, as a result of higher round-trip efficiencies.

Table 5.5 Average percentage of demand met by wind, grid and storage energy for a 72 hour period, wind Scenario B in Study 2a, Figure 5.22.

	All-Iron RFB	**VRFB**	**Hydrogen**
Direct Wind	71.8%	71.8%	71.8%
Direct Grid	19.7%	18.6%	20.7%
Storage system	8.5%	9.6%	7.5%

From the results, the value of hydrogen as a storage system is not realised when there is low curtailment within the system as a result of lower efficiencies. Consequently, it cannot take advantage of its bulk energy capability, Table 5.5. Table 5.6 shows the costs resulting from the system highlighting hydrogen's lower energy supplied and higher costs. For the RFB costs, the all-iron RFB cost of electricity generation is estimated to be lower by ~27% compared to the VRFB. Furthermore, their ability to meet similar demand allows the all-iron RFB to become a suitable replacement for VRFB if further developments will be implemented to the present technologies.

Table 5.6 Calculated costs for the direct grid generated and storage energy using wind Scenario B in Study 2a, Figure 5.22 (€0.92= $1).

	All-Iron RFB	**VRFB**	**Hydrogen**
Direct Grid cost based on system marginal price	€155	€144	€163.3
Storage system *All-iron RFB estimated from iron-chromium battery*	0.87 MWh * 230 €/MWh = **€200**	0.985 MWh * 276 €/MWh = **€272**	0.76 MWh * 469 €/MWh = **€356**

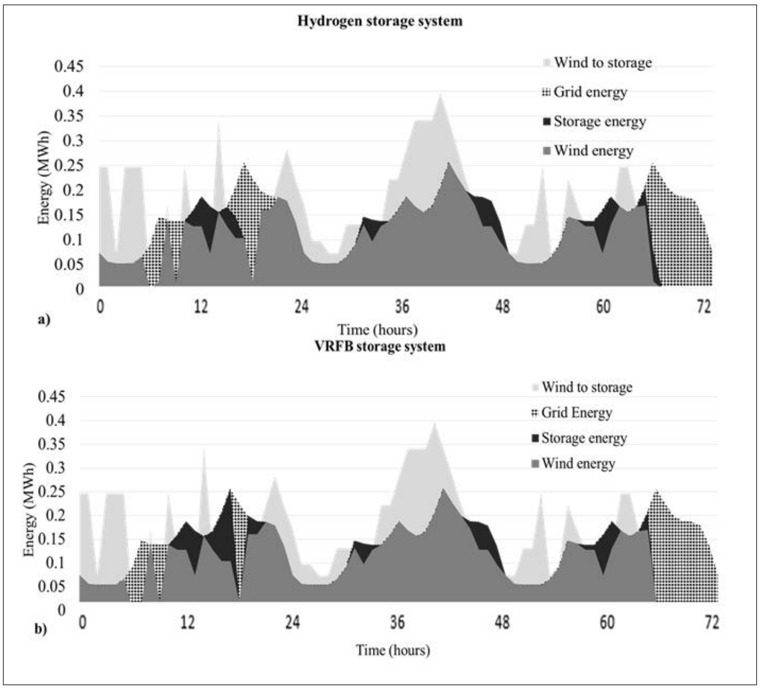


Figure 5.22 The response of the decentralised integrated a) hydrogen and b) VRFB storage system with wind Scenario B (Study 2a). Grid energy, stored energy and wind energy are used for meeting demand. Wind otherwise curtailed is used for the a) production of hydrogen and b) charging of VRFB and is indicated as "wind to storage" system in the graph.

For Study 2a, Figure 5.23 and Figure 5.24 represent tornado charts for hydrogen, VRFB and all-iron RFB technologies for Scenario A and B respectively. They compare the uncertainties that contribute to the percentage of storage energy used for meeting demand. A sensitivity of 10% was used for total demand, wind energy generated and wind energy curtailed in the system. In Figure 5.23a it can be seen the hydrogen system has a reduction in the amount of energy when wind curtailment is reduced. No change was observed when the curtailed wind increased. The lack of change is a direct outcome of hydrogen already providing the maximum energy to the system. The hydrogen reduction with the increase in wind generated energy arises from the fact that wind is used to meet the demand and not for hydrogen production. The increase and decrease of demand leads to a reduction of hydrogen present in storage. Lower demand results in a reduced hydrogen requirement. Higher demand results in an increase of hydrogen required by the system. It can be seen that hydrogen is more sensitive to curtailment in Scenario A than the RFB. The RFB, Figure 5.23b and Figure 5.23c, show similar trends to each other.

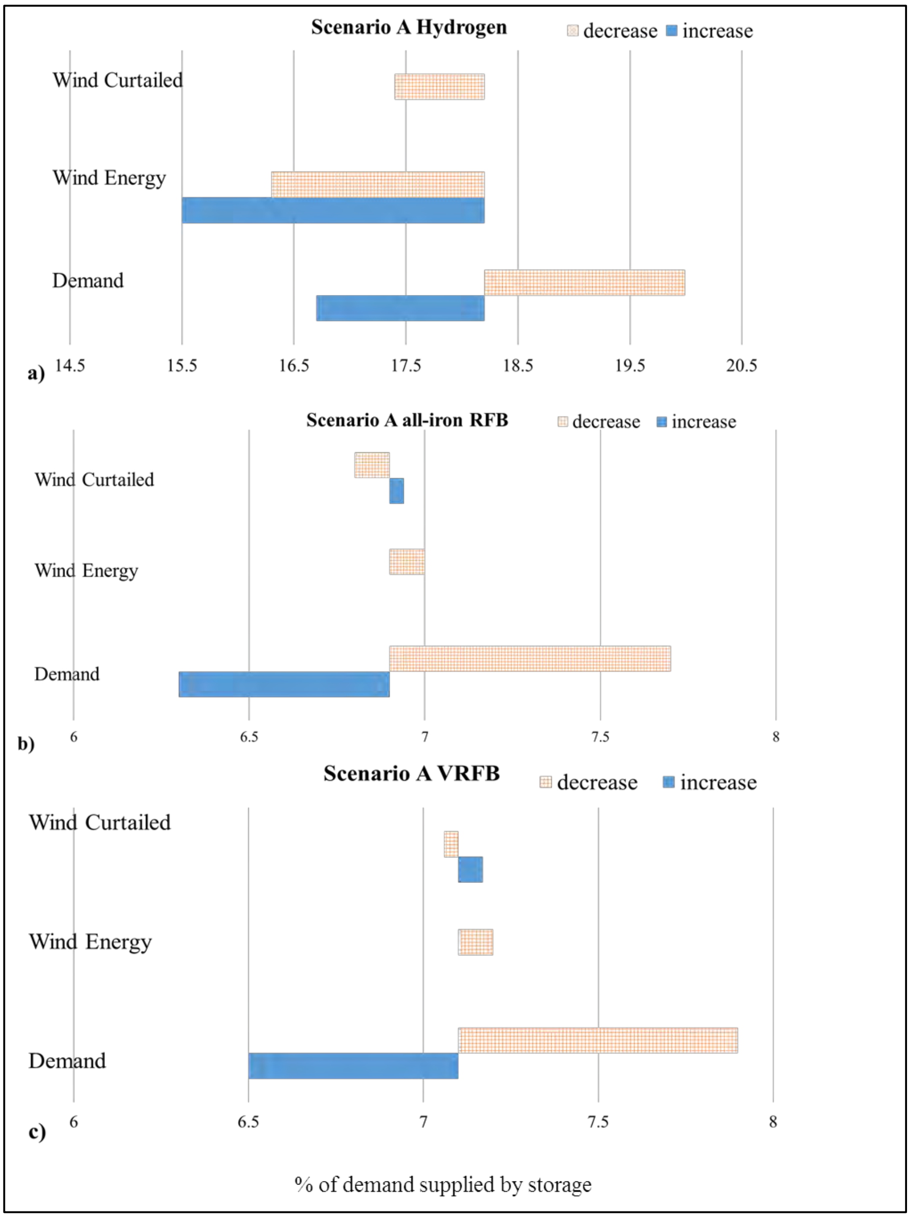


Figure 5.23 Tornado graph representing the uncertainties in the percentage of a) hydrogen, b) all-iron RFB c) VRFB energy storage used for meeting demand with a sensitivity of 10% in the values of wind curtailed, wind energy generated and demand in wind Scenario A (Study 2a).

Figure 5.24 highlights the sensitivities for Scenario B. The wind energy and wind curtailed results highlight the sensitivity of the storage technologies to wind in the system. Unlike RFB, hydrogen has an increased generation of energy when wind energy is increased. This is a result of low hydrogen production in this scenario and any additional wind available for storage will ultimately increase hydrogen production.

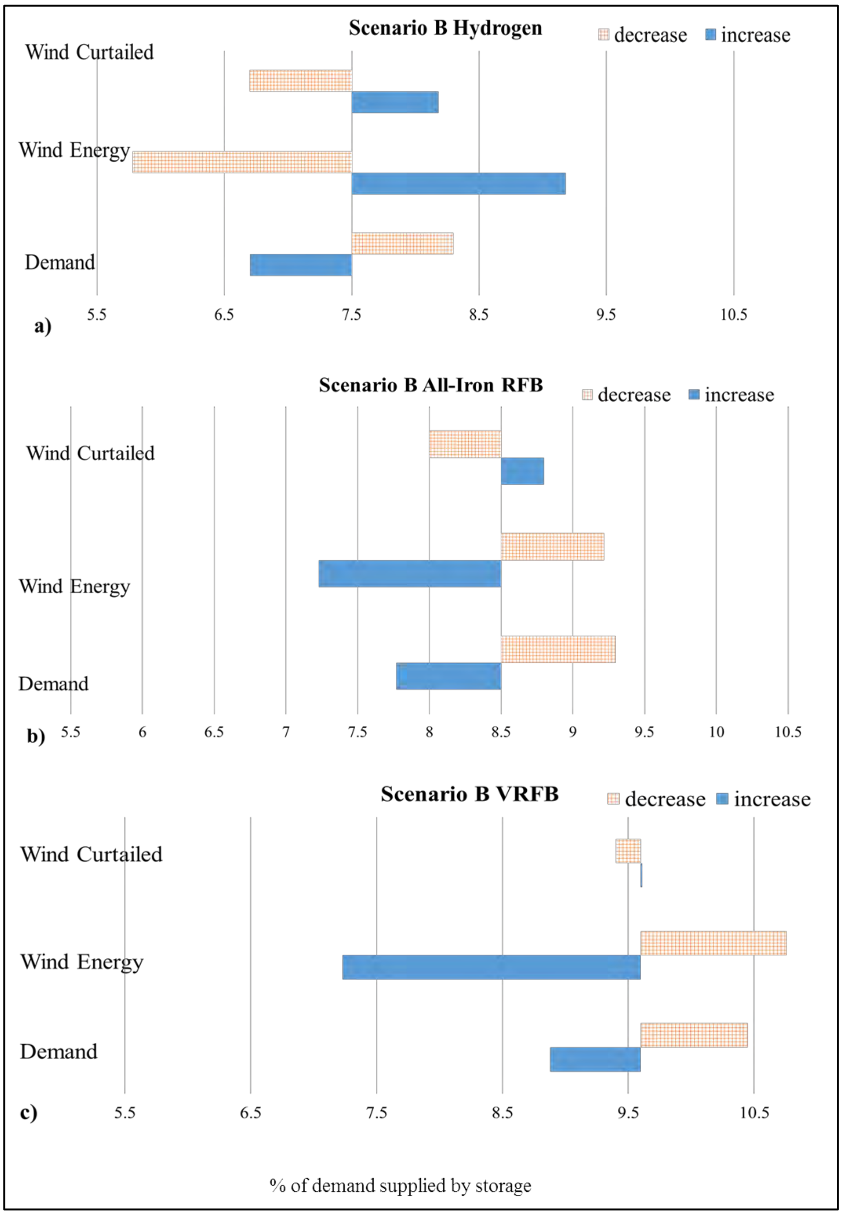


Figure 5.24 Tornado graph representing the uncertainties in the percentage of a) hydrogen, b) all-iron RFB, c) VRFB energy storage used for meeting demand with a sensitivity of 10% in the values of wind curtailed, wind energy generated and demand in wind Scenario B (Study 2a).

A system with PV instead of wind was also considered in this study; however as a result of the solar output matching the demand trend there was no excess energy meaning that no energy was available for storage. Therefore, integrated wind and solar energy systems could be considered. Such decentralised systems as discussed can help increase energy security and decarbonisation of the electricity system while addressing the intermittency of renewables. The results indicate the use of integrated storage systems can potentially allow one storage system to counteract the problems of another.

5.4.2.2 Study 2b - Techno-Economic Investigation of Integrated Systems

Individual storage systems hold many advantages; however, the use of integrated systems can potentially allow a higher mitigation of grid energy and CO_2 emissions. From Figure 5.23 and Figure 5.24 the varying sensitivity to wind curtailment can be identified. To compare the integrated system, the wind from Figure 5.15 was combined to create a model with a time boundary of 144 hours. As hydrogen's value is obtained when excess wind is high, the model for Study 2b considers three different scenarios of varying levels of wind being sent to the hydrogen storage. The scenarios are summarised in Table 5.1. These scenarios are when the system encountered greater than 40% (Scenario A), 60% (Scenario B) and 80% (Scenario C) of curtailment; excess wind was sent to the hydrogen system with the remaining wind then sent to the VRFB. The percentage of the demand that can be met by the integrated storage systems with the different curtailment function and their comparison to the individual systems is shown in Table 5.7. The results indicate reduced grid energy use in all three integrated cases compared to the individual systems. It is also interesting to note that the operation of the individual hydrogen system over the 144 hours is able to reduce overall grid energy by 12.8% while the VRFB system only reduces it by 8.3%; however, from the cost comparison presented in Table 5.8 the overall cost of electricity generation from the individual hydrogen system is estimated to be ~50% higher than the VRFB system. The integrated system in Scenario A is the most expensive case regarding electricity generation as a result of hydrogen being used more than the VRFB as more wind energy was sent to the hydrogen system.

Table 5.7 Comparison of individual VRFB and hydrogen storage with integrated VRFB and hydrogen storage (if curtailment of >40%, >60% and >80% is sent to the hydrogen system).

	VRFB	**Hydrogen**	**Integrated Hydrogen and VRFB-Scenario A** (Curtailment >40% to hydrogen)	**Integrated Hydrogen and VRFB-Scenario B** (Curtailment >60% to hydrogen)	**Integrated Hydrogen and VRFB-Scenario C** (Curtailment >80% to hydrogen)
Wind	76.8%	76.8%	76.8%	76.8%	76.8%
Grid	14.9%	10.4%	8.4%	6.8%	9.2%
Storage	8.3%	12.8%	14.8%	16.4%	14%

Table 5.8 Comparison of individual VRFB and hydrogen storage costs with integrated VRFB and hydrogen storage (if curtailment of >40%, >60% and >80% is sent to the hydrogen system).

	VRFB	**Hydrogen**	**Integrated Hydrogen and VRFB-Scenario A** Curtailment >40% to hydrogen	**Integrated Hydrogen and VRFB-Scenario B** Curtailment >60% to hydrogen	**Integrated Hydrogen and VRFB-Scenario B** Curtailment >80% to hydrogen
Direct Grid Cost Based on System Marginal Price	€227	€163.3	€144	€113	€151
Storage System Cost	€474	€1231	€1309	€1240	€916

From the results shown in Table 5.7 and Table 5.8 the advantages of the integrated VRFB and hydrogen system can be identified. In all three scenarios of Study 2b the integrated system has a reduced grid energy requirement compared to the individual systems. It can be seen that there is an optimum percentage when curtailment is higher to be sent to the hydrogen energy storage. This is identified as when a curtailment of >60% (Scenario B) is sent to the hydrogen storage the mitigation of grid energy is greater than the other two curtailment scenarios; however, costs in Scenario C are lower. From the results it can be identified a trade-off must be made between mitigation of grid energy and costs.

In addition the potential of a remote hydrogen production plant using a renewable electrolysis system and a microwave plasma reactor can be considered, Figure 5.19, with no connection to the grid. With wind intermittency highlighted in the previous study, a wind and PV integrated renewable system is considered as they can complement each other. Almost 75% of all small wind turbines are used for generation in remote applications as a result of lower cost. Therefore, in this Study 2b a 10 kW wind turbine with 40 kWp PV energy is used.

The estimated cost of microwave plasma processing of natural gas is 1.5 $/kg (1.38 €/kg) compared to an estimated 3-7 $/kg from electrolysis. The varying inputs costs of the microwave plasma reactor were calculated per kilogram of hydrogen produced. These costs depend on the energy source used. The wind levelised cost can vary from 0.04-0.11 €/kWh and for PV from 0.1-0.14 €/kWh. If no renewable energy is available for hydrogen production energy from storage must be used with the use of a hydrogen fuel cell and RFB considered. Natural gas prices vary but are considered as 2.53 €/MMBTU in this study.

Considering variable input costs, for the microwave plasma processing of natural gas the cost of hydrogen production resulting from the model was 1.51-2.22 €/kg (when highest levelised cost for wind and solar are considered). This highlights the economic viability of hydrogen production through microwave plasma processing of natural gas. If a constant demand of 5 kW is placed on the system the hydrogen production cost with microwave plasma increases to 1.55-2.3 €/kg. This highlights the vulnerability of system to rely on back-up storage. Ideally, the back-up would be supplied by relatively cheaper sources of electricity; however, in a remote location a trade-off must be made for the availability of energy.

A potential solution considered is the deployment of a RFB as back-up storage for the hydrogen production plant due to the anticipated lower costs of electricity production. This can lead to costs in the range of 1.51-1.81 €/kg; however, additional energy is required in the first three hours of the simulation as a result of low available renewable energy (no energy being present in storage). A fossil-fuel powered back-up generator could be considered if the RFB is to be deployed for a stable system. When energy shortages occur in the system over a longer period of time hydrogen's capability for bulk energy storage is an advantage.

It is evident that integrated systems will play an important role in future decentralised systems as a result of higher flexibility.

5.5 Conclusions on Hydrogen and RFB Energy Storage

Many conclusions can be drawn from the scenario analysis arising from Study 1 and Study 2a and Study 2b. In Study 1 the storage systems are directly compared to analyse the response of the systems. This direct comparison of the decentralised model indicates the VRFB is effective as a result of high efficiencies when hydrogen production is limited by production and storage capacity. Decentralised generation of electricity using renewable sources is becoming more realistic as technology advances with the capability of effective energy management and control. With high roundtrip efficiencies and lower costs than compressed hydrogen storage VRFB will be one solution to small decentralised wind generation. Hydrogen is also suitable for decentralised storage of energy and with ability for bulk energy storage is also suitable for centralised wind generation storage. Hydrogen has the potential of increasing the energy security of a country as a result of the capability of bulk energy storage; however, at a small decentralised plant a large amount of energy may not be available for hydrogen to be used to its full potential. The main findings from Study 1 show the VRFB with higher efficiencies can compete against the hydrogen storage system when compared with equal power and energy capacity (Scenario A) but as compressed hydrogen has a higher volumetric energy density it can compete against the VRFB when the volume of the storage systems are equal (Scenario B). This indicates that VRFB are suitable for smaller scale storage while hydrogen is suitable for bulk energy storage.

Energy management of storage systems is important for optimal use of the stored energy. Minimal energy management ensures no constraint is on the storage system for when it is used. The costs of storage systems are high and the use of energy management is realistic in order to reduce the length of the payback period by maximising profits. The amount of energy stored needs to be identified to ensure at times of high demand the storage system can respond effectively. As a further investigation into the benefits of energy management the storage systems in Study 1, Scenario B were constrained. Figure 5.25 shows the results of the simulation. The energy stored was only used during the peak hours of the day when grid price was at a maximum. This simulation was done to prove the benefit of energy management and the results for this VRFB storage system are shown in Figure 5.26. The use of the stored energy was constrained to times when the price of grid energy was high which occurred between 09:00-11:00 and 16:00-19:00. Figure 5.26 compares the constrained use with unconstrained use during these times. With energy management the use of grid energy during peak times is reduced by 24% indicating the importance of energy management of storage systems.

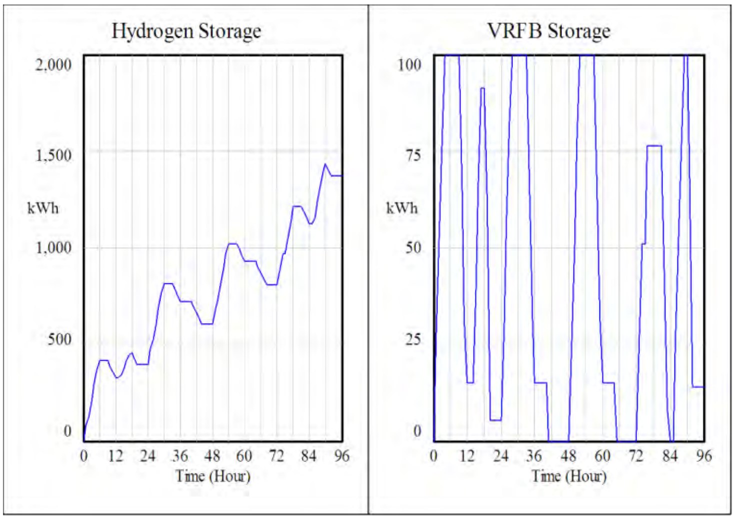


Figure 5.25 Storage system response with storage volumes of 6 m^3 to supply energy only at times when grid energy price is high, occurring at seven peak hours during the day.

With increased renewable technologies being used to supply the grid and used for decentralised electricity distribution the use of storage systems will be important in allowing intermittent technologies to increase their supply of energy. If the barrier of costs can be overcome the deployment of these energy storage systems will increase.

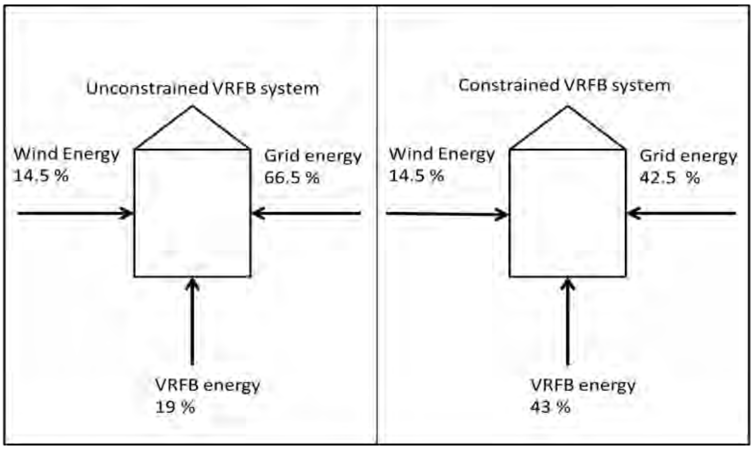


Figure 5.26 Comparison of how demand is met by the VRFB during peak demand times only from 9:00-11:00 and 16:00-19:00 with unconstrained energy usage of stored energy.

The overall results from Study 2 provide information that decentralised renewable energy benefit from an integrated approach. The results suggest that hydrogen storage systems benefit from increased value regarding technical and economic factors when integrated with complementary RFB energy storage technology.

From the research of the independent systems in Scenario A (Study 2a), it was identified as a result of higher available wind energy for storage, the hydrogen system is able to provide more energy to the system due to its capability as a bulk energy storage medium. In contrast the RFB are capable of providing more energy to the system in Scenario B, with reduced availability of energy for storage, as a result of higher efficiencies. Therefore, VRFB or all-iron RFB are more efficient energy storage at times when there are no high periods of curtailment. Furthermore, carbon allotropes produced from microwave plasma processing of natural gas can lead to higher efficiencies in RFB. The most important impact on costs is predicted for all-iron RFB as a result of the use of carbon slurry in the all-iron electrolyte. For VRFB the impact is predicted to be lower as the electrolyte (which is the most expensive component in the system) cost cannot be reduced by carbon.

Study 2b considers the integration of a hydrogen and VRFB storage system over a 144 hour period to investigate the extent to which the energy storage system can benefit from an integrated approach. In this case the capability of hydrogen for bulk energy storage and VRFB with higher efficiencies is complementary. Furthermore, it was found that the effect of the integrated systems depends on the level of excess wind sent to either the hydrogen or VRFB storage system. In independent systems all the excess wind is sent to each individual storage technology; however, with an integrated approach the excess wind must be split between the two storage systems. As hydrogen's value is obtained when excess wind is high, three different levels of wind to hydrogen storage were considered. These were when the system encountered greater than 40% (Scenario A), 60% (Scenario B) and 80% (Scenario C) of curtailment; excess wind was sent to the hydrogen system with the remaining wind then sent to the VRFB. Scenario B has the best response (compared to both Scenario A and Scenario C) increasing the amount of storage energy used within the system and therefore mitigating grid energy. There is an optimum percentage when curtailment is higher to be sent to the hydrogen storage. The findings emphasise the requirement of the integration of energy storage systems with optimisation to ensure the most effective response from the system.

Additionally, a remote location for a zero emission hydrogen production facility was considered in order to investigate its viability and stability. An integrated system with small wind turbines, PV and hydrogen storage can provide a viable remote solution for an energy demand centre. The costs of hydrogen production from microwave plasma processing is 1.51-2.22 €/kg (when highest levelised cost for wind and solar are considered). When the deployment of a RFB was considered to provide the back-up storage for the hydrogen production plant the costs were in the range of 1.51-1.81 €/kg; however, the system was vulnerable at the beginning of the simulation to the lack of energy within the storage system.

The results suggest that storage systems benefit from increased value regarding technical and economic factors when integrated with other complementary energy storage technology.

Chapter 6 further investigates the value of decentralised energy storage systems with an integrated hydrogen and molten salt storage system concept considered. This system has added value due to use of molten salt assisted material production.

Chapter 6 Study of Synergies and Value of a Decentralised Molten Salt and Hydrogen System

This Chapter investigates the added value of a decentralised hydrogen storage system integrated with a molten salt energy storage and material production unit.

6.1 Introduction to the Motivation of an Integrated Molten Salt and Hydrogen System

From Chapter 4 and 5 it can be concluded decentralised hydrogen energy storage systems will aid in the transition towards sustainable functioning of energy systems. Along with a secure supply of energy the EU must have a secure supply of material resources. Regarding GHG emissions from energy generation and material production, the effects of climate change are becoming more apparent with 14 of the last 15 warmest years recorded occurring since 2000, indicating the urgency of transitioning towards a low carbon economy [173]. Table 6.1 highlights the vulnerability of the EU to gas and electricity price increases. The price changes between 2005 and 2012 in the EU are alarming and it is clear efforts must be made to change current trends. One of the most important economic benefits of renewable and storage technology such as (hydrogen, RFB and molten salt) is the reduction in exposure to fuel price volatility.

Table 6.1 Price changes 2005-2012, EU and USA comparison.

Type	**EU**	**USA**
Gas industry	+35%	-66%
Gas household	+45%	+3%
Electricity industry	+38%	+4%
Electricity household	+22%	+8%

The growth of renewable energy within the EU is coming at a time when material security is of growing concern [174]. It is essential the EU identifies the most effective methods to transition from a fossil-fuel and material dependent economy to a sustainable economy integrated with low carbon material production and a renewable energy system with energy storage. The concept of the decentralised integration of hydrogen and molten salt is considered as hydrogen and molten salt are capable of bulk energy storage for increasing energy security while molten salt is also a key enabler for the procurement of the sustainable supply of materials, Figure 6.1. Molten salt thermal energy storage (TES) is a method already integrated with CSP for large scale energy storage. This study will further look at the added value of molten salt assisted production, recycling and refining of materials to address the EU’s additional problem of having a high import dependence on raw materials. The concept of the integration of hydrogen storage technology within the high temperature molten salt storage and material production system is considered for mitigating arising global problems. The proposed integrated system will form a sustainable, high temperature and low carbon method of material and energy procurement and can help develop a resource efficient economy with the sustainable supply of materials within the EU.

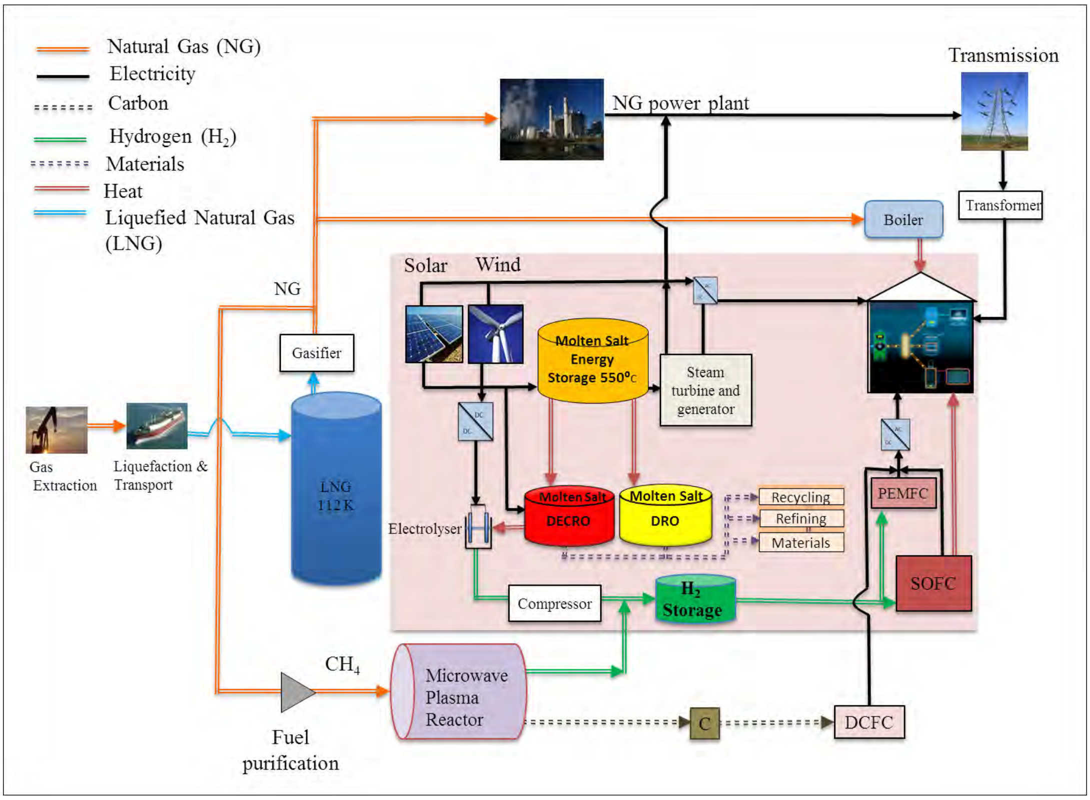


Figure 6.1 Complex integrated energy system using high temperature technologies including direct carbon fuel cells (DCFC), solid oxide fuel cells (SOFC), high temperature electrolysis, molten salt storage and microwave plasma processing of natural gas. This figure has been further developed from Figure 1.1.

Unlike hydrogen, molten salt stores the electricity in the form of thermal energy for reconversion to electricity. This concept however, proposes wind energy to be integrated with molten salt as an alternative to solar power for countries that do not have adequate solar resources. The added value of the integrated hydrogen and molten salt system is due to raw materials being essential for the sustainable functioning of modern countries and economies. The EU is highly dependent on the import of metallic minerals and domestic production is limited to 3% of global production [174]. These materials are crucial for a strong industrial base as they are an essential building block of growth and competitiveness, Figure 6.2. From all electronic waste that is generated in the EU, only 19% is recycled and the rest sent to landfill, incineration or other countries for disposal [175].

Furthermore, the concentrated supply of rare earth elements, with greater than 95% of metal currently sourced from China has resulted in a supply chain for European end-users that is not robust when considering high capital investments in modern technologies [174]. Over the last seven years, China has reduced the amount of rare earth elements available for export by approximately 40%, by the application of quotas. Export tariffs have increased the cost of rare earth elements to non-Chinese consumers to encourage raw rare earth materials to be downstream processed within Chinese borders. European countries risk supply constraints for some highly sought rare earth elements vital for green technologies. Failure to secure alternative long-term sources would affect the role Europe can play in the manufacture and development of low-carbon, energy efficient and modern energy technologies [174].

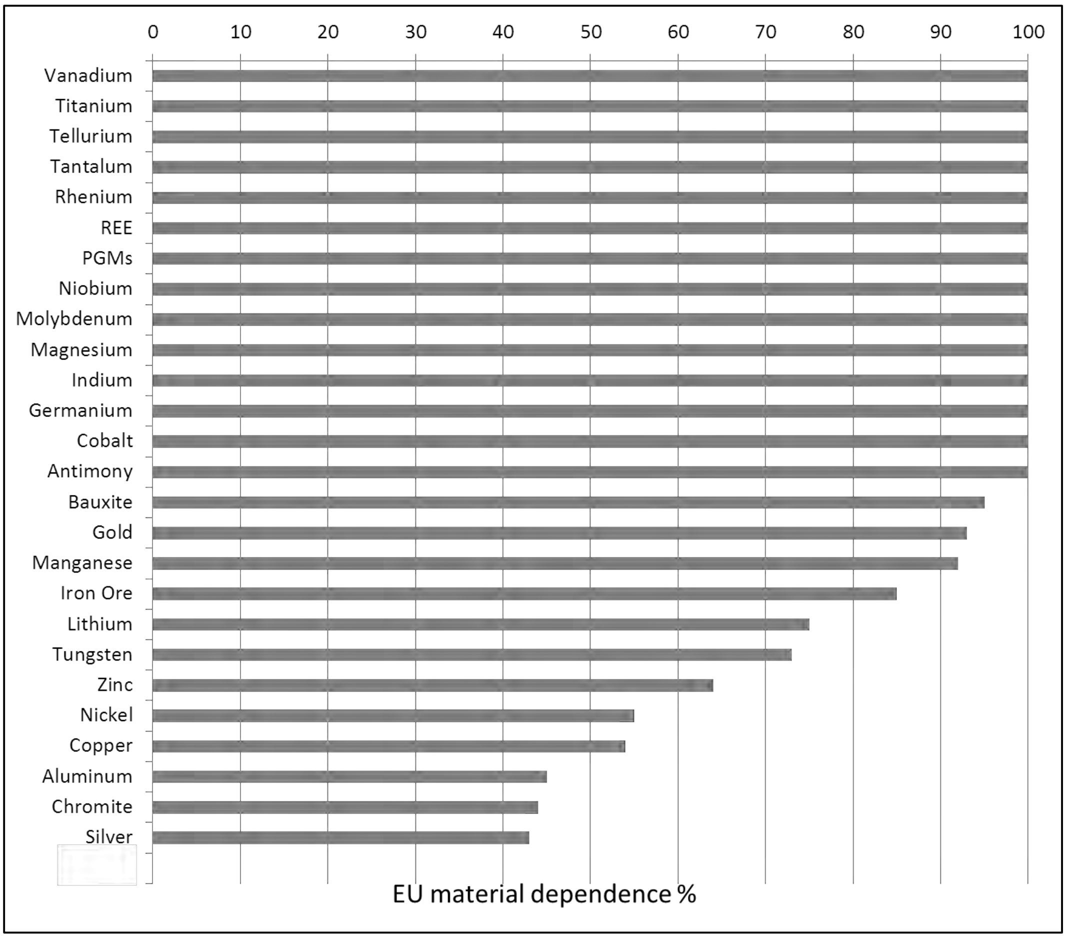


Figure 6.2 Import dependence (%) of EU countries on raw materials (2006) [176].

It is clear the need for indigenous material production in the EU is critical as seen in Figure 6.2 with 100% dependency on 14 out of the 26 materials shown.

The system proposed is a new integrated sustainable processing material and energy concept with high technical, economic, energy and environmental performance and flexibility. Additionally, molten salt can be used to sequester CO_2, thus the entire system can be used to offset any additional CO_2 generation nearby. The concept will be researched further considering the potential impact it can have on EU countries. It is now that material and energy security in the EU must be addressed and this study will look at addressing both issues directly with a discussion on the decentralised integrated sustainable molten salt and hydrogen solution.

6.2 Growth of Renewable Energy and Need for Storage

Table 6.2 represents a comparison of population, energy import dependency along with installed wind and CSP capacity for a selection of countries in the EU; Ireland, Italy, the UK, Macedonia and France. It highlights the growth of renewable energy and need for storage systems to improve energy security of countries.

Table 6.2 Comparison of Ireland, Italy, UK, Macedonia and France energy and population.

Country	**Energy Import Dependency 2011**	**Population (million)**	**Installed Wind (2014)**	**Installed CSP**
Ireland	88.9%	4.595	2263 MW	0 MW
Italy	81.3%	59.83	11895 MW	5.35 MW , 313 MW planned
UK	36%	64.1	8445 MW	0 MW
Macedonia	47.9%	2.107	37 MW	0 MW
France	48.9%	65.34	7564 MW	9 MW

Due to the lack of solar resources available in Ireland and the UK, Figure 6.3a, an alternative to CSP is required for molten salt TES, resulting in the consideration of wind energy. Global horizontal irradiation (GHI) is the most important parameter for the evaluation of solar energy potential of a particular region. Ireland has a GHI of 1000-1200 kWh/m^2 and the UK has a GHI of 900-1200 kWh/m^2 while Italy and Macedonia have a GHI of 1300-1800 kWh/m^2 [177]. Abundant wind energy in Ireland and the UK, Figure 6.3b, make the molten salt system integrated with wind energy a viable solution.

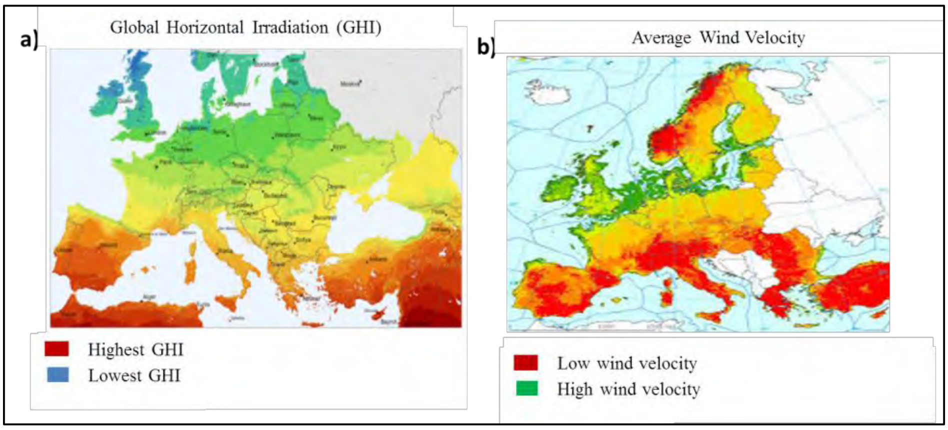


Figure 6.3 a) Global horizontal irradiation (GHI) in Europe showing Italy and Macedonia with high potential for solar power, France with medium potential and the UK and Ireland with low GHI [177], b) average above ground level wind speed map of Europe [178].

6.2.1 Wind Energy

Wind energy capacity in the EU has increased by 93.1 GW from 2000 to 2012 [179] as shown in Figure 6.4; however, there are many issues with the integration of wind power into the power system as a result of intermittency that can be reduced with the use of storage systems.

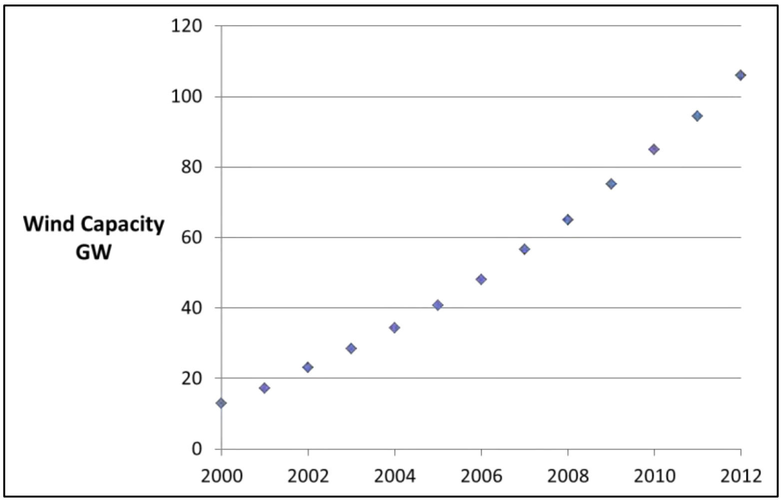


Figure 6.4 Cumulative installed wind power in the EU between 2000 and 2012.

Currently, the most common commercial wind turbines installed in Ireland are between 1.5 and 2 MW [180]. However, in central Europe the steady progression of wind turbine size and capacity has been increasing as shown in Figure 6.5 [181]. Many developments to wind turbine technology continue including the development of homopolar wind generators [182] and safe and silent urban wind turbines [183] that can potentially, in addition to storage, allow the continued expansion of wind energy.

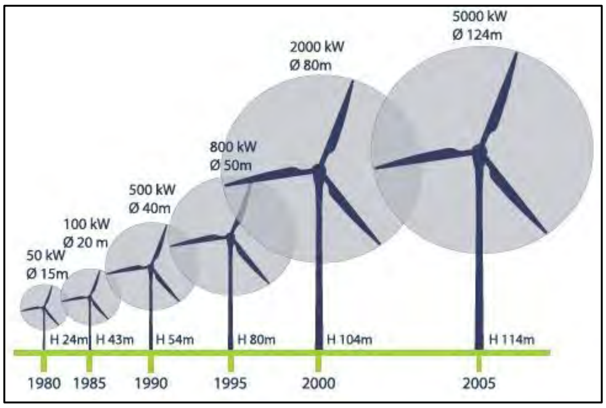


Figure 6.5 Evolution of wind turbine size and rated capacity [181].

According to a study from the Environmental Protection Agency in Ireland wind generated in Ireland could contribute to 2.5% of the EUs' electricity demand by 2050 allowing Ireland to potentially play a major role in Europe's transition to a low carbon and sustainable economy. Ireland has enough renewable energy resources to supply all the energy demand required. Ireland needs to utilise its renewable energy resources more effectively. In 2012, 14.5% of overall national energy demand was met by wind and this was increased to 16.4% of demand in 2013 [184]. Ireland had a capacity factor of 31.6% in 2011 [185]. UK's wind capacity is similar to Irelands at 29% [186]. This is in comparison to Italy's capacity factor of only 19%, highlighting the potential unsuitability of a wind and molten salt system in Italy.

As discussed in Chapter 4 and Chapter 5 wind-hydrogen storage systems can increase the penetration of renewable energy. Alternatively, it is envisioned that wind energy coupled with resistive heating in molten salt can be another viable solution for the reduction of import dependence and CO_2 emissions.

6.2.2 Concentrated Solar Power and Molten Salt

CSP captures and concentrates the sun's energy to provide the heat required to generate electricity and can be equipped with a heat storage system to increase the capacity factor, Figure 6.6. The efficiency of CSP power plants is about 14-16% and the capacity factor is on the order of 25-30%, depending on the location. Unlike wind energy, CSP plants are already integrated with molten salt TES systems and can have storage capacities of between 6-15 hours, which increase the plant capacity factors to over 40% and 70%, respectively [187, 188].

Molten salt is solid at standard temperature and pressure and enters the liquid phase due to elevated temperatures. The key features and physical properties of molten salt for thermal energy storage include being a non-flammable, nontoxic fluid, low cost fluid with good heat transport properties as a result of a high coefficient of heat transfer. It has a freezing temperature of 238°C, and a melting temperature of 221°C with a heat capacity at 300°C of 1400 J/kg.°C [189]. The molten salt used at the Archimede plant is 60% $NaNO_3$ and 40% KNO_3 that is available at low costs at an estimated 0.49 \$/kg and a storage cost of 5.8 \$/kWh_t [190].

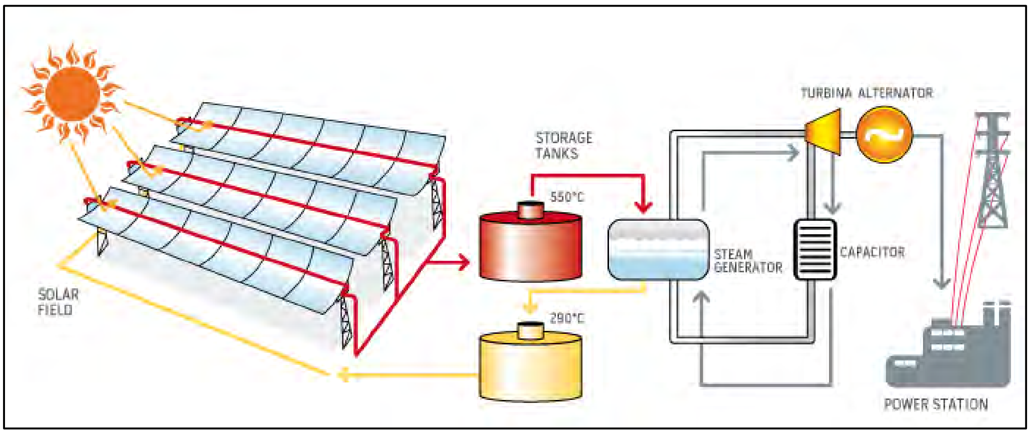


Figure 6.6 **C**oncentrated solar power system integrated with molten salt [189].

Cost competitiveness is a key barrier for CSP as the cost of producing electricity from CSP was approximately twice as high as electricity produced from fossil fuels in 2007 [191]. CSP solar power plants integrated with molten salt can be an interesting case to use molten salt for material processing to improve the economics of the system and provide not only a sustainable supply of energy but a secure supply of materials.

6.2.3 Decentralised Integrated High-Temperature Molten Salt and Hydrogen System

The Archimede project inspired the main concept of this study for an Irish or UK outlook where the use of the abundant wind energy can be considered instead of CSP which can be further developed in Italy and Macedonia, providing for molten salt assisted production, recycling and refining of materials along with a suitable thermal energy store that can be integrated with high temperature renewable electrolysis. Therefore, molten salt and hydrogen can be a key enabler of a sustainable pathway to the low carbon production of materials and energy that the EU requires.

Figure 6.1 represents the overall integrated molten salt and hydrogen energy system concept for a resource efficient economy. Figure 6.7 highlights the molten salt system in more detail for energy storage and material production as the hydrogen system has been discussed in Chapter 4 and Chapter 5. The concept presented can bridge sustainable energy and material supply and will allow for the innovative and integrated sustainable low carbon supply of materials and energy, Figure 6.8. The proposed system will help European competiveness with regard to supply of raw materials and energy in an environmental and economic resilient and sustainable manner. The investigation into sustainable processing, recycling and refining will allow the protection and management of the environment.

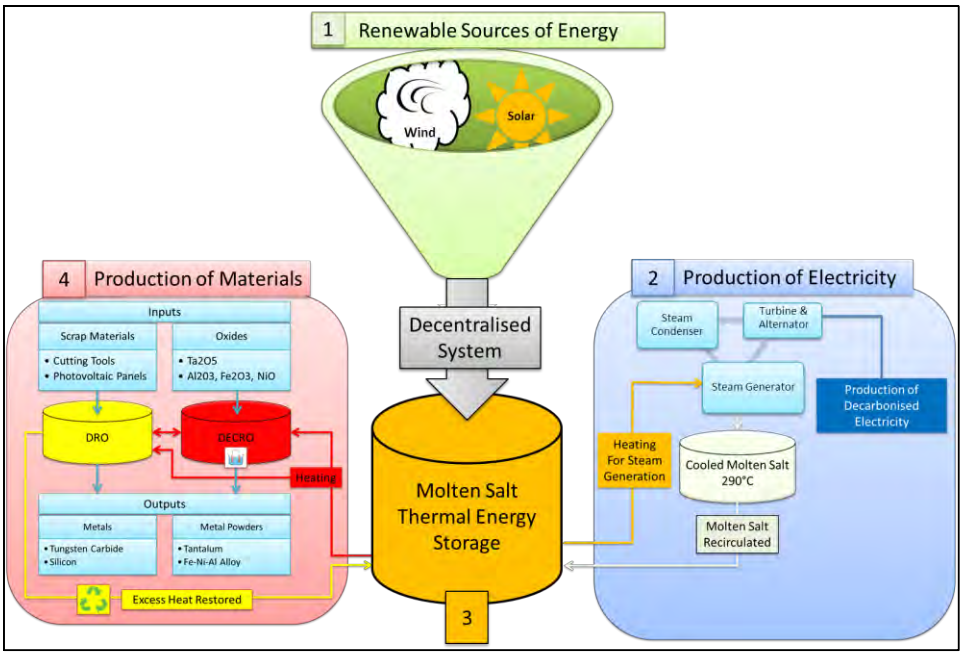


Figure 6.7 Theorised decentralised hybrid schematic of an integrated molten salt energy and material processing system for a low carbon, resource efficient economy, part of the overall hydrogen integrated decentralised system, Figure 6.1. The different components of this system include 1) the supply of renewable energy, 2) the production of electricity from storage, 3) the storage system and 4) the production of materials.

Molten salt TES and molten salt for material production operates at high temperatures. Therefore, an integrated system that combines high temperature hydrogen production including high temperature electrolysis and the microwave plasma processing of natural gas can be considered. Figure 6.9 depicts the operating temperatures of the various technologies and energy systems.

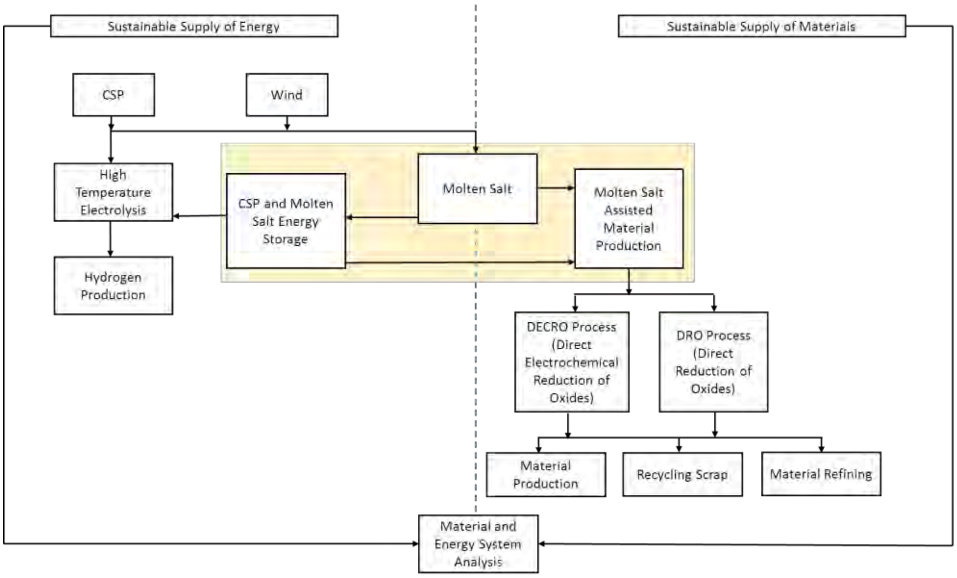


Figure 6.8 Areas of focus reflecting key requirements of the conceptualised hydrogen-molten salt integrated complex system highlighting the link that is required between sustainable energy and material supply.

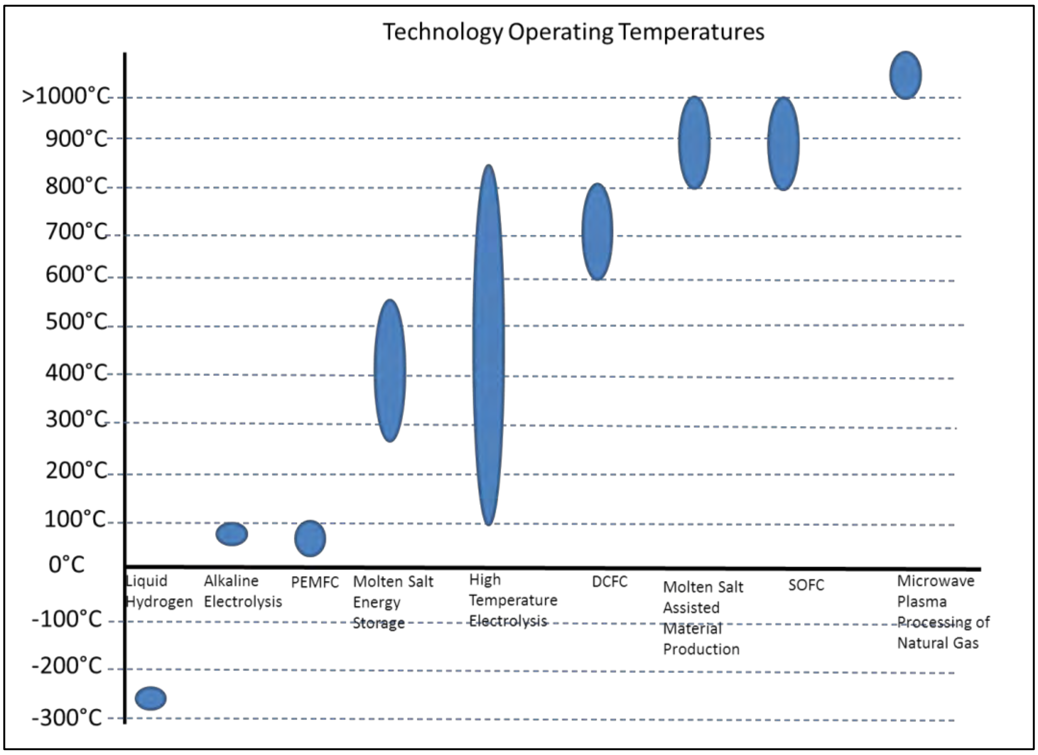


Figure 6.9 Operating temperatures of technologies depicted in Figure 6.1.

The bridging of energy and material production is the solution required for establishing a sustainable energy and material production pathway required for the emergence of a resource efficient economy.

6.3 Sustainable Energy Storage with Added Value of Material Production

6.3.1 Hydrogen and Molten Salt Storage

From Figure 6.1 wind can be stored with the use of resistive heating for molten salt TES or for high temperature electrolysis and can be a solution to demand and supply mismatch.

Hydrogen production from high temperature electrolysis can then be integrated with a high temperature molten salt system and potentially provide a portion of thermal requirements. Additionally, the use of direct carbon fuel cells (DCFC) can operate with coal. DCFC have the potential to almost double electrical efficiency (i.e. to 65-70%) and halve GHG emissions compared with conventional coal-based power plants. DCFC operate by consuming solid high-carbon fuel to produce electrical power [192]. Molten salt can play a further role as a valuable material as an electrode in the DCFC. There are three types of DCFC depending on the electrolyte; the use of molten Salt (KOH, NaOH) operating at 500-600°C, molten carbonate (Li, Na, K) operating temperature of 750-800°C and oxygen ion conducting ceramic operating 800-1000°C [193]. The DCFC technology is at an early stage of development with considerable effort required to take it to the pre-commercialisation stage.

Additionally the use of microwave plasma processing of natural gas produces carbon and hydrogen streams, Figure 6.10, and can be considered in the system [194]. The carbon can then be potentially fed to a molten carbonate DCFC to produce electrical power, part of which can be fed back to power the hydrogen plasma displacing the use of coal. The hydrogen produced can be used in a SOFC for power generation. This method enables the conversion of fossil fuels to electricity at higher efficiencies compared to conventional methods. The use of molten salt as electrodes in DCFC further highlights the importance of molten salt as a key enabler for efficient energy systems.

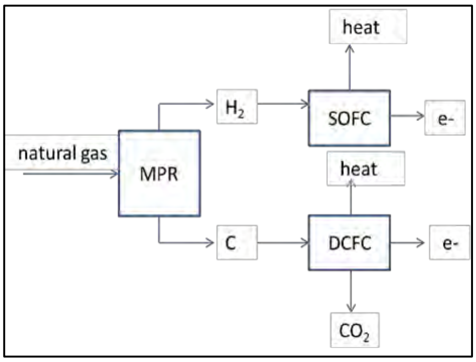


Figure 6.10 Use of microwave plasma processing of natural gas producing carbon and hydrogen for use in solid oxide fuel cells (SOFC) and direct carbon fuel cells (DCFC) that can use molten salt material as electrodes.

Molten salt can be integrated within the systems mentioned; however, different compositions are required for different functions, Table 6.3, with the different costs shown in Table 6.4. A DCFC uses a 32% Li_2CO_3 and a 68% K_2CO_3 melt as the electrolyte and Archimede TES uses a 60% $NaNO_3$ and a 40% KNO_3 molten salt mix.

Table 6.3 Molten salt compositions for different uses [195, 196].

Direct Carbon Molten Salt Fuel Cells	**Solar Salt**	**Material Production**
Li_2CO_3/K_2CO_3 (750 °C)	$NaNO_3/KNO_3$ (freezing point 221°C)	$CaCl_2$ (> 800°C))
Li_2CO_3/Na_2CO_3 (750 °C)	$NaNO_3/KNO_3/NaNO_2$ (freezing point 141°C)	LiCl (650°C)
	$LiNO_3/CaNO_3/KNO_3$ (freezing point 120°C)	

Table 6.4 Molten salt prices.

Media	**Cost $/kg**	**Cost $/kWh**
$NaNO_3$	0.2	3.6
KNO_3	0.3	4.1
Na_2CO_3	0.2	2.6
K_2CO_3	0.6	9.1

As a hybrid system is proposed with the capability for storing and generating electricity and for material production the system can be analysed using system techno-economic analysis. Important feasibility results can emerge from the analysis of the integrated approach of materials and electricity production.

6.3.2 Sustainable Supply of Raw Materials from Molten Salt

Aside from its ability to store energy at elevated temperatures for an extended period of time, molten salt as mentioned has other applications including its function as an electrolytic medium in which the electrochemical reduction of metal oxides to their corresponding metals occurs [197].

The direct electro-chemical reduction of oxides (DECRO) via the FFC process was patented globally in 1998. Although originally developed for titanium, the process economics indicate that other metal powders, including chromium, tantalum, silicon, cobalt, molybdenum, vanadium, tungsten, and niobium can be produced at a fraction of the current cost [198]. During the process a molten salt acts as the electrolyte for the electrochemical reduction of a metal oxide to metal. The metal oxide powder is contained in the cathode and is directly converted into metal by electro-deoxidation [198]. Oxygen ions carry the current across the cell and gas is evolved at the anode, leaving pure metal at the cathode. The FFC process has demonstrated its ability to produce tantalum and titanium from their corresponding oxides with the other metals and alloys of these metals capable of being produced highlighted in Figure 6.11. The use of this process integrated with renewable energy to produce materials could reduce import dependence of materials. The process can currently produce seven of the materials that the EU is 100% dependent on for imports, Figure 6.11. This system will inevitably have positive implications on Europe's material security.

Table 6.5 highlights additional materials that can be produced via DECRO with the corresponding import quantity to Ireland, Italy, UK, Macedonia and France.

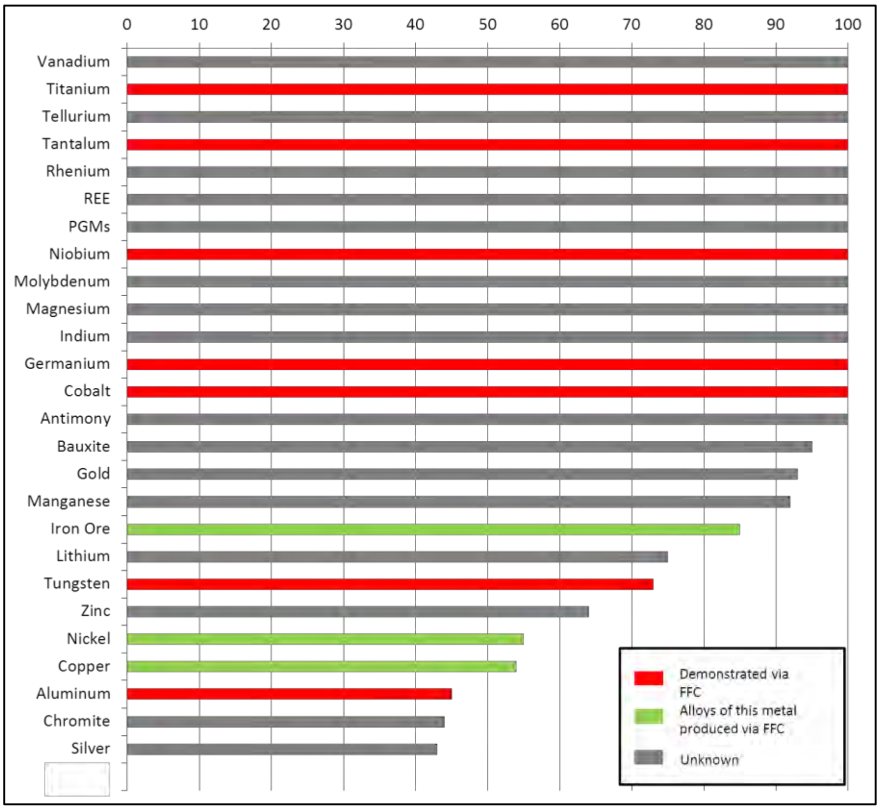


Figure 6.11 Materials and corresponding import dependence for the EU. Red highlights the materials that can be produced by the FFC process, green highlights materials representing the ability of the FFC process to produce alloys of this metal and grey represents unknown ability to produce these metals.

Table 6.5 Import dependence of materials that can be produced by the direct electro-chemical reduction of oxides of Ireland, UK, Italy, Macedonia and France [199].

Material	Type	**Ireland import (tonne)**	**UK import (tonne)**	**Italy import (tonne)**	**Macedonia import (tonne)**	**France import (tonne)**
Tantalum and Niobium	Metal	1	274	-	-	39
Titanium	Metal	432	33943	7367	-	13169
	Oxides	3924	63058	137976	455	129659
	Minerals	-	117860	4132	-	91304
Chromium	Metal	40	9124	1598	-	837
	Ores and concentrates	-	1603	30547	324	10639
Iron	Pig iron	1182	55845	1106558	1075	187416
	Sponge and powder	1216	176638	551034	-	72852
	Ferro-chrome	100	65219	416091	-	121183
	Other ferro alloys	139	147567	525548	3251	11741
	Ingots, blooms, billets	4952	835691	3169000	100791	1696098
	Scrap	6565	284086	5271612	157401	2377000
Nickel	Unwrought	568	11521	33635	-	16608
	Ores and concentrates	-	-	-	1518156	252
	Unwrought alloys	-	4771	2626	-	4943
	Scrap	-	9237	899	-	3063
	Mattes and sinters	-	57108	-	-	19053
Zirconium	Metal	146	482	135	-	26688
	concentrates	-	8928	40897		363
Cobalt	Metal	743	6197	609	-	1533
	Oxides	-	164	679	-	650
	Ore	-	125		-	-

6.3.2.1 Production of Materials by Direct Electrochemical Reduction

The use of the decentralised molten salt system would be an important step for Europe in increasing supply of raw materials. The materials produced, recycled or refined can open new production routes for the supply of materials within Europe. These metals are described with regard to potential applications below.

Tantalum is amenable to reduction over a wide range of temperatures. Metalysis have reduced Ta_2O_5 between 650°C and 950°C. The price of Ta_2O_5 varies considerably depending on purity. Ore concentrate may be less than 100 €/kg. Prices of €1000-2000 are attained for high purity tantalum metal [198]. The most common use of tantalum is for capacitors, super alloys, chemicals and carbides. The scale at which the process is viable depends on the value of the product and at the bottom end of the viability scale, it is assumed that 500 kg of molten salt producing 3 kg of tantalum per day or equivalent is the smallest economically viable system [198]. Since 1982, the dramatic increase in demand for tantalum has been at a rate of 10% per year by the electronics industry. This makes tantalum a high value product but it is characterised by a low natural abundance with few known deposits.

Titanium has many applications in the fields of pyrotechnics and aerospace. Revenues from titanium are expected to increase by 70% over the next five years as manufacturers of next-generation jet engines look to titanium solutions for engine structural components. The electrochemical reduction of TiO_2 into titanium metal in a molten salt medium has also been demonstrated by Metalysis. TiO_2 prices are approximately 3 €/kg with titanium powder selling for approximately 236 €/kg [200]. The energy consumption in making titanium using the FFC process is estimated to be below 20 kWh/kg whereas the energy consumption for the production of titanium using the Kroll process for producing titanium is over 50 kWh/kg.

Nb and niobium alloys and intermetallics can be formed from the electrochemical reduction of Nb_2O_5-SnO_2 [201]. Nb_3Sn has been utilised for the central solenoid and toroidal field superconducting magnets for the planned experimental fusion reactor. If successful, this could revolutionise the production rate of superconducting materials, and in turn, change the landscape of large-scale electrical transformers and hospital MRIs.

Fe-Ni-Al material is as strong and light as titanium, but estimated to be lower in cost [202]. The manipulated structure of the iron-aluminium alloy creates a new material for many applications. Trials for the use of the material at industrial scale are underway as an alternative for titanium. Metalysis have yet to demonstrate the production of this alloy, although it is predicted that this material can be produced by this process.

Ce-Co_5 could potentially be produced on a large scale by the FFC process in the near future. If the theorised hybrid system is developed up to an industrial scale, Ce-Co_5 may soon become the material of choice for applications such as electric watches, magnetic coupling and microphones.

Co-Cr has similar process parameters to that of Ce-Co_5 regarding the FFC manufacturing process so too can be considered for production. Co-Cr is predominantly used in the medical industry [203].

Crofer 22 H is a high-temperature stainless steel especially developed for application in SOFC [204]. The relatively new material can be used to produce lightweight fuel cell stacks. Crofer 22 H is a lower-cost alloy with superior properties to steel. Its chemical composition mainly consists of Cr-Fe. SOFC as mentioned have many advantages over other fuel cells, which include fuel flexibility, high efficiency, long-term stability, low emissions, and relatively low cost and will allow a decentralised, low carbon and sustainable hydrogen economy to emerge. For this reason, the production of Crofer 22 H via the FFC process as part of the energy efficient molten salt hybrid system could lead to improved hydrogen technologies.

Erbium and Praseodymium alloy is said to exhibit better regenerator properties than that of lead and can be fabricated into fibres [205]. Using these properties of Er-Pr, Sunpower Inc. has produced a single stage high frequency cryocooler capable of reaching very low temperatures. The CryoTel LT, a hand-held single stage cryocooling product developed by Sunpower Inc. is said to have a cooling capacity of 0.5 W at 20 K. It may potentially be used in hydrogen refuelling stations of the future as a handheld cooling device for the safe transfer of hydrogen fuel from tank to vehicle.

Aluminium is another material that can be produced by the FFC process; however, currently the most widely used non-ferrous material it is usually formed using electrolysis via the Hall Heroult process taking an average 15 kWh/kg to produce aluminium. The worldwide average production was 41.4 million tonnes in 2010 equating to 621 billion kWh using approximately 3% of total worldwide electricity demand. Aluminium is a low density metal that can form strong alloys (alloying with relatively small percentages of Cu, Mn, Si, Mg or Zn, has high thermal and electrical conductivity is non-magnetic and highly ductile. Aluminium and its alloys can be cast, rolled, extruded, forged, drawn, and machined. The production of recycled aluminium in the EU was 4.1 million tonnes in 2012; however, the import dependece of the EU aluminium industry has increased from 35% to 50% in 2012 with 5.4 million tonnes imported in 2012 [206].

The FFC process utilising the direct reduction of oxides can potentially allow the growth of a low carbon, resource efficient economy with the sustainable supply of raw materials to be actualised.

6.3.2.2 Recycling of Scrap Materials

The recovery of metals from scrap materials with the use of molten salt is another process that can be used. Molten salts are used commercially to strip metal clean of impurities. This simple process utilizes the high temperature and catalytic and oxidative properties of sodium nitrite/nitrate ($NaNO_2/NaNO_3$) salts. For example, Whirlpool [207] uses a molten salt bath of sodium nitrite/nitrate salts to clean the paint off of its appliances that fail quality control checks. The molten salt cleans the metal of all paints by thermally decomposing and oxidising the paint into CO_2 and water vapours. The stripped metal appliance can then be repainted and reused.

It has been theorised that the recovery of Tungsten-Carbide, a very strong and valuable alloy, from cutting and drilling tools is possible in a similar dissolution process.

Silicon is another material that can be recycled from whole PV panels in a molten salt medium. At certain temperatures and concentrations, molten salt has the ability to dissolve polymers and glasses to leave the valuable silicon cells for retrieval and reuse, this is typically conducted at 500°C. In Europe, the emergence of end-of-life modules was estimated to be 290 tons in 2010 and 33500 tons in 2040 representing the increasing need for recovering and recycling methods for silicon. Silicon is currently traded for 18 $/kg but is expected to increase. The recycling of technologies will increase the competitiveness of Europe's PV industry. With a useful life of around 20 years, most solar panels installed in the early 1990s will require disposal soon and the potential environmental, financial and social impact of this issue, if addressed directly, could make solar a sustainable process [208-211].

To achieve a sustainable economy a systemic change in the use and recovery of resources are required for effective waste management. Recycling will help secure future materials and reduce import dependence and the loss of material through the export of old scrap.

6.3.2.3 Direct Electrochemical Reduction of Oxides and Direct Reduction of Oxides

The DECRO process, as mentioned, currently allows the economic production of titanium and tantalum metals. Alternatively, the direct reduction of oxides (DRO) reduces the quantity of electricity required. There are advantages and disadvantages to the two processes which are highlighted in Figure 6.12. Both processes can be used for material production, recycling of scrap and for refining. DECRO has the ability to produce more materials and capable of refining; however, the electricity required and resulting CO_2 emissions can be large. The DRO process has a higher ability to process scrap than the production of materials and refining and it uses low amounts of electricity and also has no resulting CO_2 emissions if renewable energy is the source of electricity.

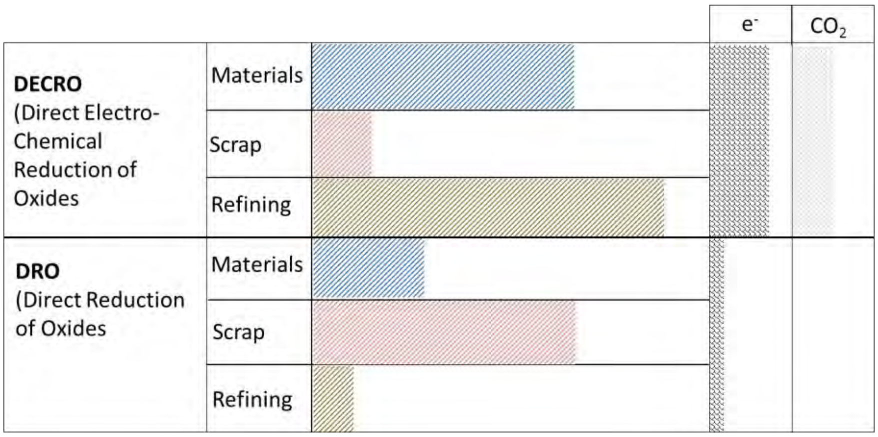


Figure 6.12 Direct electro-chemical reduction of oxides (DECRO) and direct reduction of oxides (DRO) process that both have the ability to produce materials, process scrap and refine materials with different capacities shown as a guideline. The amount of energy required for the process and resulting CO_2 emissions are also depicted.

6.4 Analysis of the Integrated Decentralised Hydrogen and Molten Salt System

As discussed the hybrid system will have two valuable resources, energy and materials; therefore two profit streams. Energy storage will play an important role in the system as it can supply the energy required for material production or recycling making it a sustainable, green process, but can also supply decarbonised electricity when integrated with renewable energy. A system analysis is required for optimising the size and operation of the integrated system and also for comparing the various advantages and disadvantages of the DECRO and DRO processes. SD is an approach that is proposed for system analysis as the system will have various inputs including costs of metal oxides for the material production, scrap for recycling, the price of electricity and the quantity of molten salt used by the system. The production of materials and hydrogen along with energy stored in the molten salt and hydrogen system will also have to be considered. The capacity requirements, material processes and technological operation of an integrated hydrogen and molten salt storage and material production system will need to be identified comparing different renewable energy and load inputs that are necessary for the emergence of a viable system. By combining SD with real option models, the dynamic complex interactions among investors, consumers, and policymakers, as well as future uncertainties of key energy, economic, and environmental factors can be captured.

Different scenarios such as those depicted in Figure 6.13 can be analysed to find the optimum way to operate the integrated decentralised system to maximise profits and minimise environmental impact by limiting carbonised electrons. Energy is required for heating the molten salt for TES and electrolysis for providing an energy buffer and for the production of materials, recycling or refining. In the first scenario, as a result of the intermittency of renewables a grid connection could act as back-up and add security to the system; however, this would introduce carbonised electrons and carbon emissions into the process, Figure 6.13a. There will be an optimum relationship between the input power and the mass of molten salt used by the decentralised system and research that investigates the characterisation of this optimum correlation will be required. To establish if grid energy is a necessity the second scenario could be considered without a connection to the grid with only the use of renewable energy and energy from the molten salt TES and hydrogen storage, Figure 6.13b. To realistically comprehend the importance of the molten salt TES and hydrogen storage, when combined with a renewable source of energy, in order to provide the energy required for material processing the third scenario could be considered. It would investigate the use of renewable energy integrated with material production without the use of a TES, Figure 6.13c. The need for an intermediate storage facility is required to buffer the material production process as a result of the intermittency of renewable energy.

Futhermore, market demand for products is uncertain and forecasts will be needed to determine when to use stored electricity for meeting electric demand or for the electric demand arising from the material production, recycling and refining processes.

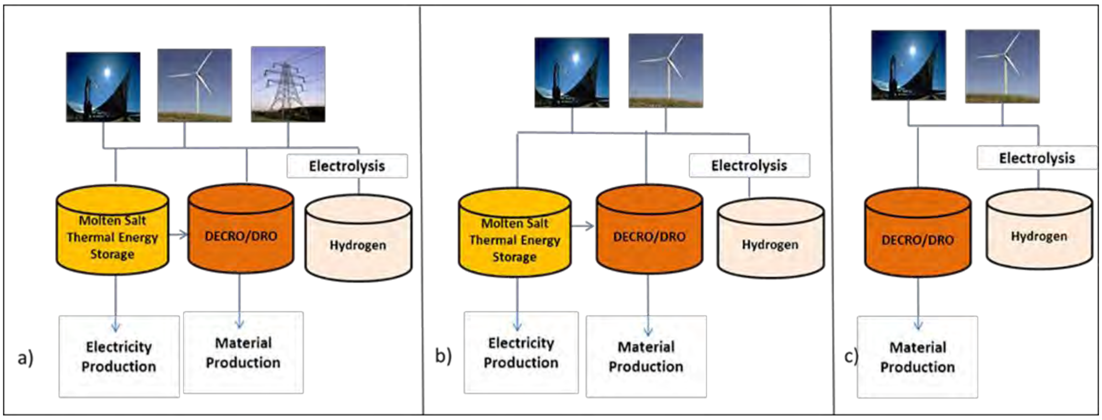


Figure 6.13 Schematics depicting potential scenarios, a) grid and renewable energy with a molten salt energy store for electricity and material production and hydrogen production and storage, b) renewable energy with a hydrogen and molten salt energy store for electricity and material production, c) renewable energy for hydrogen and material production only.

6.5 Conclusions on the Potential of Integrated Molten Salt and Hydrogen Systems

The decentralised hybrid system has the ability to store excess renewable energy improving energy security and can be integrated with hydrogen technology and fuel cells to provide additional storage and energy pathways. The decentralised hybrid molten salt system also has the potential to decarbonise the energy required for the production of valuable metals and metal alloys allowing an increase in Europe's material security. Molten salt is a key enabler for improving energy and material security. SD is proposed to allow the complex behaviour of the system to be analysed along with the completion of an economic analysis. The theorised decentralised integrated hydrogen and molten salt storage and material production system concept has the ability to grow a low carbon, resource efficient energy system while providing a sustainable supply of resources for Europe.

The synergies between hydrogen and other energy technologies and energy resources can increase the value of the hydrogen system as discussed for an integrated hydrogen and molten salt system. In Chapter 7 the key synergies between the natural gas industry and the hydrogen economy will be discussed.

Chapter 7 Investigation of Natural Gas Synergies with Hydrogen

As concluded in Chapter 6 hydrogen can have synergies with other energy technologies that can increase the value of the system. This chapter provides comprehensive research into the identification of potential synergies between hydrogen and the changing natural gas industry within the context of an operationally reliable, economically viable and environmentally compliant global energy system (the second aspect of the hydrogen economy identified from Figure 1.1).

7.1 Introduction to Potential Synergies

The efficient production and use of alternative fuels along with the development of infrastructure is fundamental for low-carbon, well-functioning energy systems. Hydrogen as discussed is an alternative fuel that is expected to play a significant role in future energy systems and is currently inextricably linked to natural gas. Natural gas synergies with hydrogen can cause further changes to the already changing natural gas industry. Within such a context, natural gas-hydrogen synergies and assorted technology options in a carbon-constrained future are of central importance. An important synergy is the potential role natural gas and hydrogen integrated with renewable and low-emission generation will have in securing a low-carbon future. The main synergies are outlined in Figure 7.1 with natural gas-based hydrogen production technology options identified, including the traditional option realised through the conventional SMR and advanced technology options of SMR integrated with CCS along with microwave plasma processing of natural gas and TCM. Furthermore, the cryogenic link between LNG and liquid hydrogen will be discussed. Figure 7.1 further highlights the aspect of natural gas and the hydrogen economy as first identified in Figure 1.1.

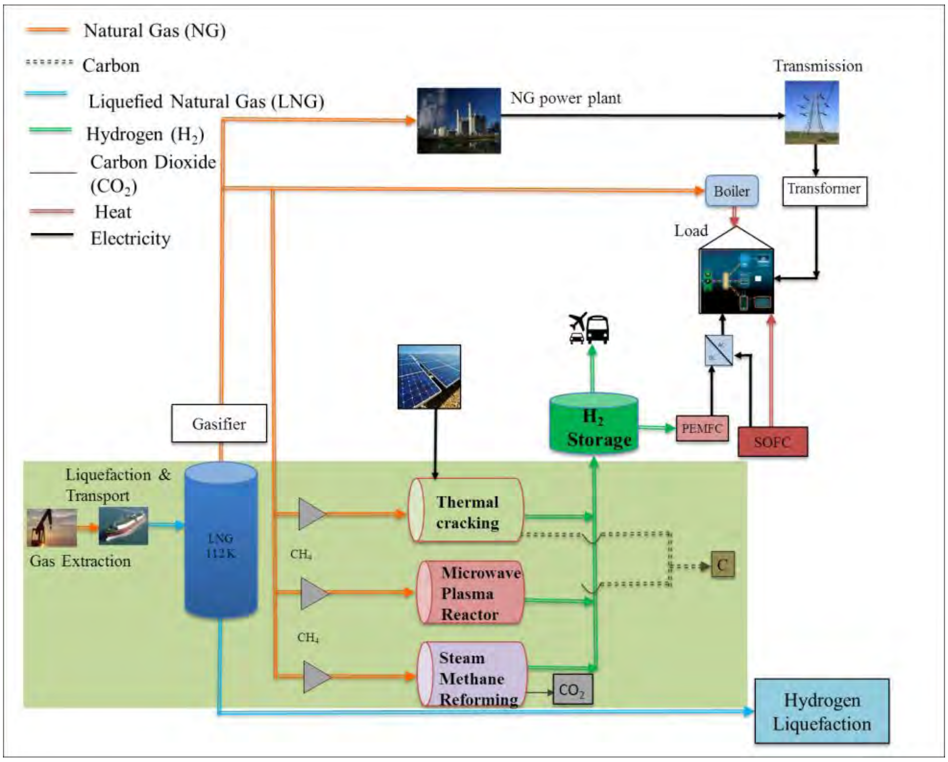


Figure 7.1 Hydrogen-natural gas system, indicating the current synergies and potential future synergies between natural gas and hydrogen production adapted from Figure 1.1.

7.2 Changing Natural Gas Industry

Natural gas is a moderately clean energy source that is vital for global energy systems. Global demand for natural gas is increasing and in 2012 it increased by 2% from the 2011 demand level [212-214]. The current transformation of the natural gas industry due to the extraction of shale gas deposits and the recognition of LNG as an economical method of transportation could prove vital for the future development of the hydrogen economy. Figure 7.2 illustrates the increase of natural gas production in the US from 1949-2011 reflecting the growing demand of the fuel [215]. The availability of economical shale gas is contributing to the increase of natural gas production in recent years. Natural gas deposits stored in shale formations had previously been uneconomical to extract but with technological advancements (a combination of horizontal drilling and hydraulic fracturing) these unconventional resources have now become economic [216].

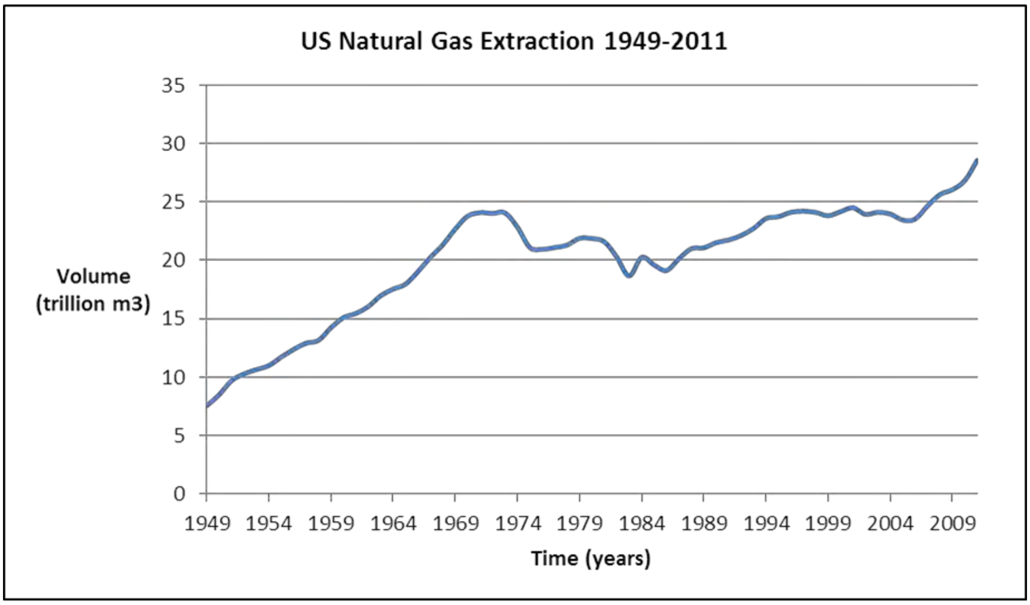


Figure 7.2 US natural gas extraction 1949-2011, indicating the increased quantity of natural gas extracted in the US [215].

The increased production of natural gas has caused a reduction in its price in North America and led to a decrease in the consumption of coal. Increases in coal consumption in Europe are identified, Figure 7.3, resulting from direct exports of the plentiful, now surplus, cheap North American coal. The production of shale gas is also affecting the electricity market with the effects on consumption of natural gas and coal for electricity showing similar trends Figure 7.4, comparative to overall energy consumption, Figure 7.3, in both North America and Europe [216]. The displacement of coal aided the reduction of US CO_2 emissions by 7.7% from 2006-2011, a positive environmental gain of increased natural gas use [217]. The impact of increased coal consumption on European CO_2 emissions are a cause for concern and efforts will have to be made in Europe to mitigate emissions [218]. The development of the shale gas industry can facilitate the emergence and development of the hydrogen economy due to competitive feedstock prices. With the declining role of natural gas in Europe for electricity generation as indicated in Figure 7.4, it should be noted it still has important implications and in 2012 provided 22% of global electricity demand [212].

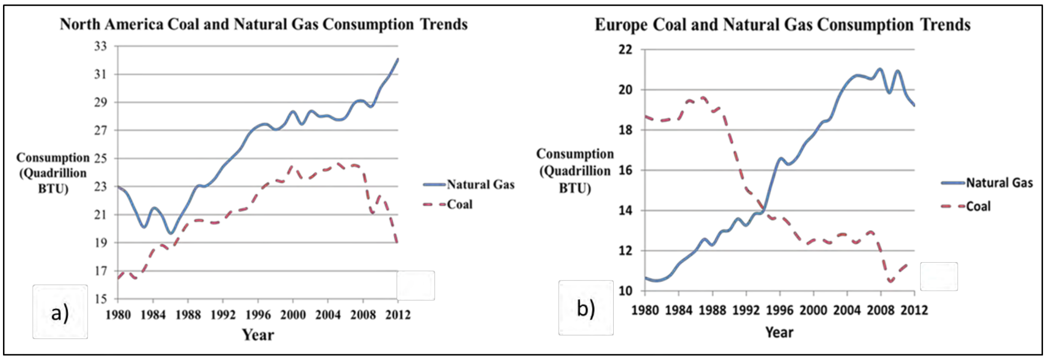


Figure 7.3 Coal and natural gas consumption trends in a) North America showing a large consumption of gas, b) Europe showing a reduction in natural gas consumption. These market trends are partly caused by the increasing production of shale gas in North America [213].

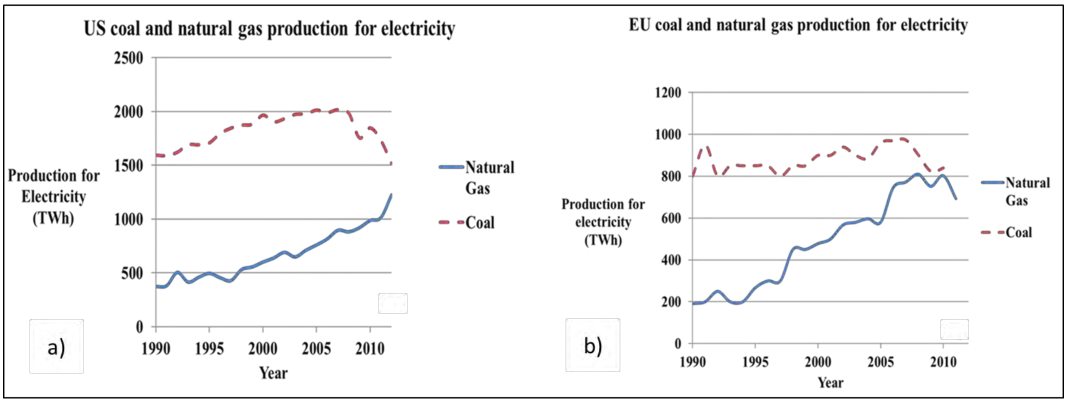


Figure 7.4 Changes in the use of natural gas and coal for electricity generation in a) the US [217, 219] and b) Europe [220]**.**

In addition to shale gas, LNG is also changing the natural gas industry and is growing in importance allowing larger volumes of energy to be transported and stored under standard conditions for meeting greater demand [214]. The global LNG outlook is somewhat complicated due to the supply, demand and associated market pricing dynamics with the price of LNG being critically linked to the supply destination region. LNG markets in Asia have higher profitability margins given the robustness of demand growth [221] and LNG consumption levels of 70%, Figure 7.5 [222]. The corresponding dynamic complexities arise from supply-demand imbalances and regulatory uncertainties. It is predicted that LNG supply could be constrained by the availability of the requisite infrastructure [223].

Although LNG consumption fell by 0.4% in 2013 from 2012 levels, various forecasts converge to the view that LNG consumption will increase in the near future. Forecasts suggest that by 2030 the capacity of natural gas transported by LNG will increase dramatically when compared to transportation via pipeline networks. This highlights the forecasted continuing role LNG will play in the natural gas industry [224].

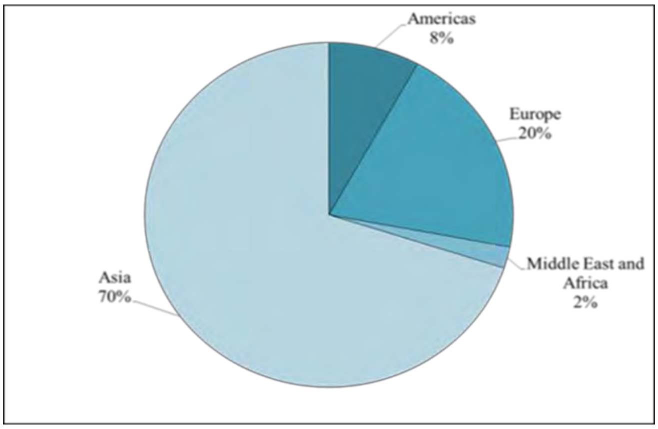


Figure 7.5 Liquefied natural gas (LNG) consumption by region 2012, showing the main consumption is in Asia due to the requirement of LNG to meet domestic gas and energy needs [221]. It should be noted the importance of Japan as an importer of LNG increased as a result of the nuclear disaster at Fukushima Daiichi, Japan, 2011 [225].

Through the development of LNG and hydrogen infrastructure integrated with renewable energy technologies; energy diversification can be realised. This can be achieved by an integrated, diversified and reliable portfolio of energy resources development, supply as well as storage options. Within such a context, hydrogen could potentially assume an indispensable role. A creatively structured hydrogen production pathway network involving various technology options could potentially play a significant security enhancing role. LNG is also a cryogen and as liquid hydrogen's role as a cryogen is expected to have an important impact on the superconducting industry the future synergy between these cryogens may have important future implications. It is evident that natural gas and hydrogen energy resources produced via natural gas are linked. The current trend towards lower natural gas prices and expected future prices will ultimately influence competitive economic aspects of hydrogen.

It is important to note in recent years US, European and Japanese prices for natural gas have approximately been in the ratio 1:2:4 [226]. Furthermore, the German price of natural gas has reduced in 2013 suggesting that natural gas can play an important role in the development of the hydrogen economy in Europe as well as the US. The prospect of US LNG exports can equalise those prices reducing European prices. There is growing interest for hydrogen energy due to the need for diversification of fuels and decarbonisation of the economy [227]. Fourteen European Member States already have hydrogen networks. It is anticipated that even with higher prices for natural gas compared to the US renewable low-emission hydrogen production via natural gas will still emerge. Also in Europe much natural gas is sold under secretive bilateral long-term contracts indexed against the oil price. The rise of LNG has not yet, but could still erode the reality [228]. In any case oil-indexed gas is becoming cheaper as the oil price falls. With regard to oil-indexed long-term contracts dominating natural gas trading in Europe there are efforts to re-negotiate the assorted prices in the above contracts given pressures from the real prospect of substantial LNG-export growth in the US.

The synergy with natural gas could prove to be problematic due to potential supply disruptions and cost escalations; however, the maturation of the hydrogen economy could make other production techniques such as those relying on renewable-based technologies appealing. Furthermore, synergies between natural gas and hydrogen can cause further changes to an already changing natural gas industry.

7.3 Hydrogen and Natural Gas System Synergies

The 'Golden age of Gas' currently being experienced will provide the hydrogen economy with opportunities to develop [213]. Key complex links emerging from the natural gas and hydrogen synergies are depicted in Figure 7.1. The hydrogen produced by natural gas methods shown and alternatively from renewable energy-based electrolysis can be compressed and used for transportation and storage purposes; integrated into fuel cell systems to generate distributed heat and electricity; or finally be liquefied and stored for use in transportation or cryogenic applications.

It should be noted extra added value products are produced as a result of hydrogen production via microwave plasma processing and TCM processes due to the production of carbon black as a by-product. This adds extra value to the hydrogen production chain as carbon is electrically conductive and used in different applications such as conductive plastics, ultra-capacitors and many other applications. Therefore, this synergy between hydrogen production via microwave plasma processing and TCM creates the potential for the carbon industry to grow in parallel with the hydrogen economy. Figure 7.1 identifies a preliminary conceptual map of potential synergies between natural gas and hydrogen adapted from Figure 1.1 to focus on natural gas and hydrogen synergies.

Another synergy between natural gas and hydrogen is linked to the potential of energy storage. LNG can be used as an energy storage medium and each year 35-68 Bcf ($9.9\ x10^8$-$1.9{\cdot}x10^9$ m^3) of LNG is stored during summer and used under peak load conditions in winter in the US [229]. With the development of the requisite LNG infrastructure for energy storage purposes in the above context along with the appropriate functional hydrogen infrastructure, both LNG and renewably produced hydrogen could provide energy storage capabilities. This stored LNG and hydrogen can be then used within natural gas-hydrogen synergistic applications.

The use of LNG transportation to hydrogen production facilities coupled with its use as a pre-coolant in the liquefaction of hydrogen, Figure 7.1, suggests that LNG represents the basis of an important synergy between natural gas and hydrogen industries [230, 231]. The large scale liquefaction of hydrogen with the integration of an LNG-based pre-cooling system is a promising technology option currently at the conceptual plant design stage which is expected to display hydrogen liquefaction efficiencies of 40-50% [231]. This method of liquefying hydrogen would be of course constrained, as it could only be done at plants where the natural gas from LNG is used to produce hydrogen.

In light of the above remarks, growing interest in hydrogen production from natural gas along with other methods and the different application of hydrogen will be discussed.

7.4 Hydrogen production from Natural Gas

Hydrogen production from natural gas constitutes the current dominant synergistic link that exists between natural gas and hydrogen. Figure 7.6a demonstrates the importance of natural gas as a feedstock to the hydrogen industry [232]. With the focus placed on the decarbonisation of the economy, hydrogen production methods need to transition towards cleaner technology options. Renewable electrolysis currently contributes only a small proportion to overall hydrogen production; Figure 7.6a. If grid electrolysis is considered electrolysis is only economical if electricity prices are low and this would lead to resulting grid emissions for hydrogen production. Alternatively, with focus on decarbonised electrons the use of renewable electrolysis is growing in interest; however, with the intermittent nature of renewable energy it can provide unstable hydrogen production and requires a backup energy supply or the operation of a hydrogen buffer system as discussed in Chapter 4. It is anticipated advanced electrolysis with increased efficiency has a role to play in providing a sustainable energy future with the production of hydrogen [233].

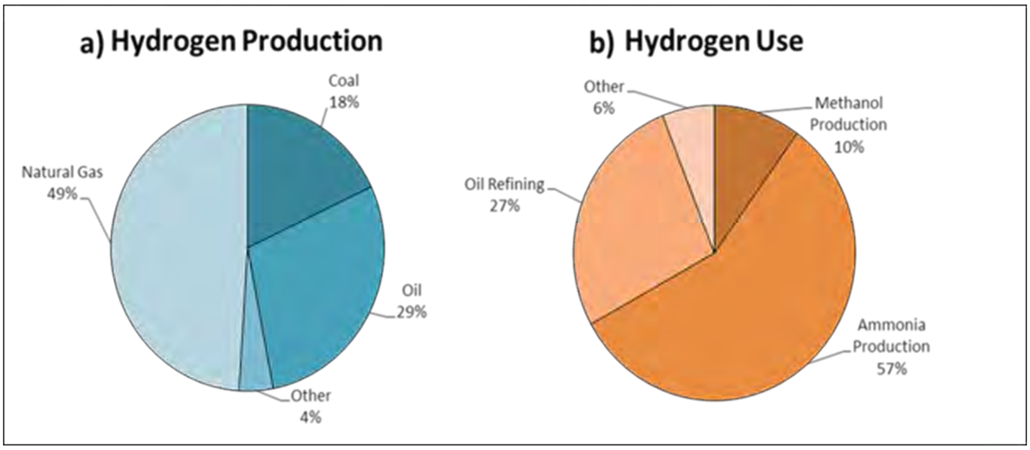


Figure 7.6 a) Fuels used for the production of hydrogen, b) hydrogen use, industry is 94% of overall use [232].

The choice of fuel for hydrogen production depends on developments in the pertinent markets and the assorted price signals, the evolving state of the regulatory landscape, technology risks (when new advanced technology options are considered versus the well-tested mature conventional ones) as well as the existing infrastructure. All the above factors introduce irreducible uncertainty, and as these uncertainty sources are progressively resolved fuel switches can be triggered. Currently, the dominant fuel choice for hydrogen production, despite the price differential and in the absence of a global well-functioning natural gas market, remains methane in both the US and Europe. Legislative action in the US aiming at lifting current restrictions on natural gas exports coupled with the impact of difficult to predict geopolitical events may induce changes. This could also raise the level of complexity in the valuation of hydrogen production projects in both continents. With this uncertainty in mind it is also important to note the importance of hydrogen and anticipation of its role in low carbon energy futures. Three different production methods of hydrogen using natural gas as a feedstock are discussed in Chapter 2 due to their potentially major contribution to the hydrogen economy if feedstock prices can remain competitive. The three methods are depicted in Figure 7.1, SMR, microwave plasma processing of natural gas and the thermal cracking of methane.

7.5 Hydrogen Synergistic Applications with Natural Gas

Currently hydrogen is mainly used in industrial processes such as ammonia production. As shown in Figure 7.6b only 6% of the demand pertains to other applications (metal works, transport fuel, in semiconductor manufacturing, food preparation, cryogenics, storage medium and as an energy carrier) [234]. It is therefore anticipated that future demand growth will be more robust given hydrogen’s expected advanced role as an energy carrier in both transportation and electricity sectors as well as for heat generation and cryogenic applications. In the following sections the synergy between natural gas and hydrogen use in different applications will be discussed.

7.5.1 Hydrogen and Natural Gas Use in Synergistic Applications

One important application of hydrogen is the potential to replace oil-derived fuels in the transport sector which is a major contributor of GHG emissions and air pollution [235]. The commercialisation path of hydrogen vehicles and their penetration of the corresponding markets will be certainly fraught with challenges due to competition from oil-derived fuels that currently having significant market power. Hydrogen fuel for vehicles could provide a beneficial diversification of the energy resources used in the transportation sector. However, uncertainty surrounds the widespread development of hydrogen as a transport fuel as infrastructure must be readily available before people start seriously considering investments in hydrogen vehicles. Hydrogen can be used in FCEV and hydrogen ICE both of which rely on the development of a robust reliable hydrogen infrastructure involving production, transportation, storage and refuelling capabilities. Hydrogen engine efficiencies are competitive, Figure 7.7, but infrastructure requirements and cost-competitive production currently represent significant barriers to widespread utilization and this is why its synergy with the potential to be integrated within NGV is important.

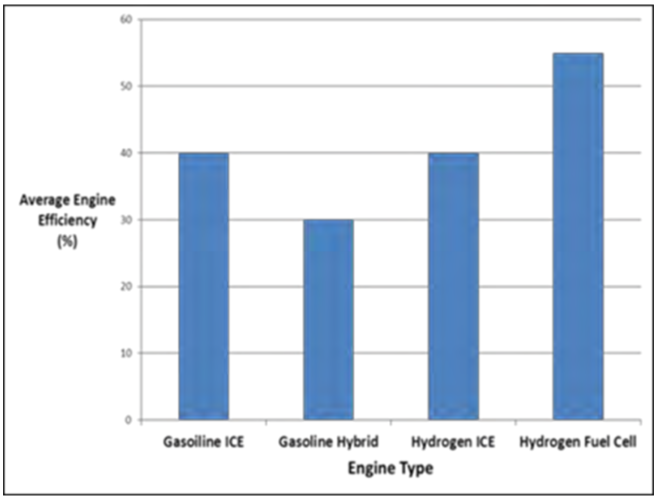


Figure 7.7 Comparison of the average efficiency that can be achieved for different gas and hydrogen vehicles engine types [236].

NGV will perhaps emerge in competition with hydrogen fuelled cars. Although natural gas is also expected to enable the integration of hydrogen ICE into the transportation sector, so the importance of compressed natural gas (CNG) vehicles should not be overlooked as their use is growing worldwide. It is clear that an overhaul of the fossil fuel-dominated global transportation sector is necessary given the 93% dependence on oil, Figure 7.8.

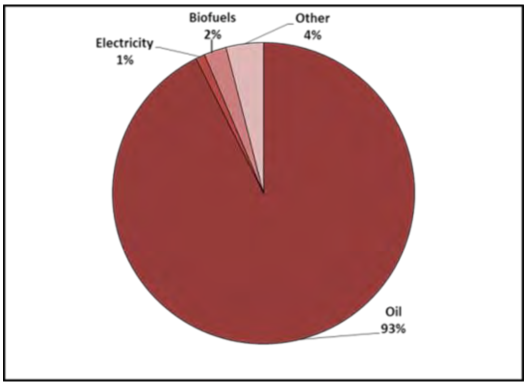


Figure 7.8 Global transport sector energy consumption by fuel type 2011, 2% of other contributed to use of compressed natural gas.

The use of CNG vehicles reduces direct fuel CO_2 emissions by approximately 35% and 60% when compared to diesel and petrol fuel respectively [237]. Home fuelling devices are being considered such as Phill technology that are developing a safe certified home natural gas refuelling appliance; however, this technology is still at a nascent stage [238]. General Electric Co. is also developing a home refuelling system that is aiming to reduce the refuelling time and costs [239].

As an additional note LNG can also be used in transportation and is especially suited for long distance travel. NGV are thus allowing the transition from oil-derived transportation fuels to lower emission vehicles. In addition, the successful penetration of these reduced-emission vehicles into the market will potentially improve emissions arising from the transport sector. It is important to note that the integration of hydrogen fuelled vehicles into the transport sector has started to take place, demonstrating its future prospect as a transport fuel.

Hydrogen FCEV are one option for hydrogen based transport and a discussion on hydrogen FCEV is presented in Chapter 2. Furthermore, hydrogen ICE can be considered that provide an alternative option for hydrogen in the transportation sector. A potential synergistic link between natural gas and hydrogen can be identified as the use of NGV becomes important to the transition to and development of hydrogen ICE technologies. NGV can use blended gas with up to 20% hydrogen gas without the need to alter the original engine beyond the ignition timings and allows the NGV to realise the benefit of lower emissions. A company, Hythane, are developing NGV with the use of hydrogen. If a hydrogen blend is used in the above context it reduces NO_x pollutants by 50% and GHG emissions by 7% and the use of natural gas as for the Hythane patent it uses 80% natural gas blended with 20% hydrogen with regard to volume [240].

In light of potential synergies between natural gas and hydrogen in the transportation sector it is evident that natural gas, along with renewable energy could facilitate the transition from oil-derived to cleaner transportation fuels. Given the above developments, a hydrogen-accommodating transportation sector allowing the introduction of an initial fleet of hydrogen vehicles and the development of decentralised infrastructure emerges as a pragmatic vision in the near term.

The stationary applications of hydrogen for generating electricity are promising for the reduction of carbon emissions in the electricity sector by displacing traditional combustion methods and also for the supply of heat if high temperature fuel cells are used. High temperature range fuel cells, e.g. SOFC, benefit from higher efficiencies as the heat can be harnessed [82, 241, 242]. The use of fuel cells to generate heat and electricity would be an option for decentralised generation.

Membrane technology embedded into integrated gasification or natural gas combined cycle power plants represents a new advanced technology option for the co-production of electricity and hydrogen that enhances environmental and economic performance in the presence of future regulatory action of CO_2 emissions. The tri-generation of electricity, heat and hydrogen is another process option that is being investigated and it is estimated that heat is produced with expected efficiency of 45%, hydrogen with 18.55% and electricity with 28.25% [243-245]. Another potential synergistic link is the use of hydrogen in existing natural gas transmission and distribution pipelines. Introducing low-emission produced hydrogen into natural gas pipelines would be advantageous to natural gas users which could benefit from reduced reported CO_2 emissions. It is estimated that blends between 5% and 15% depending on the resulting calorific value of the natural gas would be suitable for natural gas pipelines that would not have to be altered [246].

The opportunities that exist in this sector would also facilitate the formation of a robust hydrogen economy as it would be contributing to the enhancement of cost-effectiveness in the use of existing infrastructure and the reduction of CO_2 emissions. Fuel cells are in operation in many places for storage and electricity back up generation; however, technological advancements are required for these systems to improve efficiency and costs of the process for hydrogen's use to become widespread.

7.5.2 Liquid Hydrogen as a Cryogen

Hydrogen's use in cryogenic applications is often not considered when contemplating hydrogen's future with the main focus placed on its potential in the transportation sector and for stationary applications [247, 248]. Liquid hydrogen must be stored in cryogenic Dewars that are thermally insulated to minimise boil-off. One important aspect to further minimise losses is the completion of ortho-para conversion. Hydrogen can exist as both para-hydrogen and ortho-hydrogen depending on the spin of the nuclei. Almost all hydrogen molecules are para-hydrogen at equilibrium at liquid temperature (20.3 K), while the ortho-hydrogen fraction becomes 75% at room temperature. As the liquid hydrogen warms up in the cryogenic storage vessel the liquid hydrogen is converted from para-hydrogen to ortho-hydrogen and absorbs energy causing evaporation [248]. Therefore the ortho-para conversion of hydrogen is required to reduce losses [249]. The liquefaction process is energy intensive and uses a minimum of 30% of the hydrogen's HHV depending on the quantity of hydrogen produced as shown in Figure 7.9 [10]. LNG (112 K) can act as a pre-coolant for hydrogen liquefaction potentially reducing the energy penalty.

Therefore, potentially rich synergies arise as hydrogen represents a versatile energy carrier and cryogenic medium that will be important in mitigating some challenging energy and resource problems that is an added value to the production of liquid hydrogen. The synergy between liquid hydrogen and the superconducting industry is discussed further in Chapter 8 and Chapter 9. Furthermore, as mentioned LNG is a cryogen and can have important implications for the liquefaction of hydrogen.

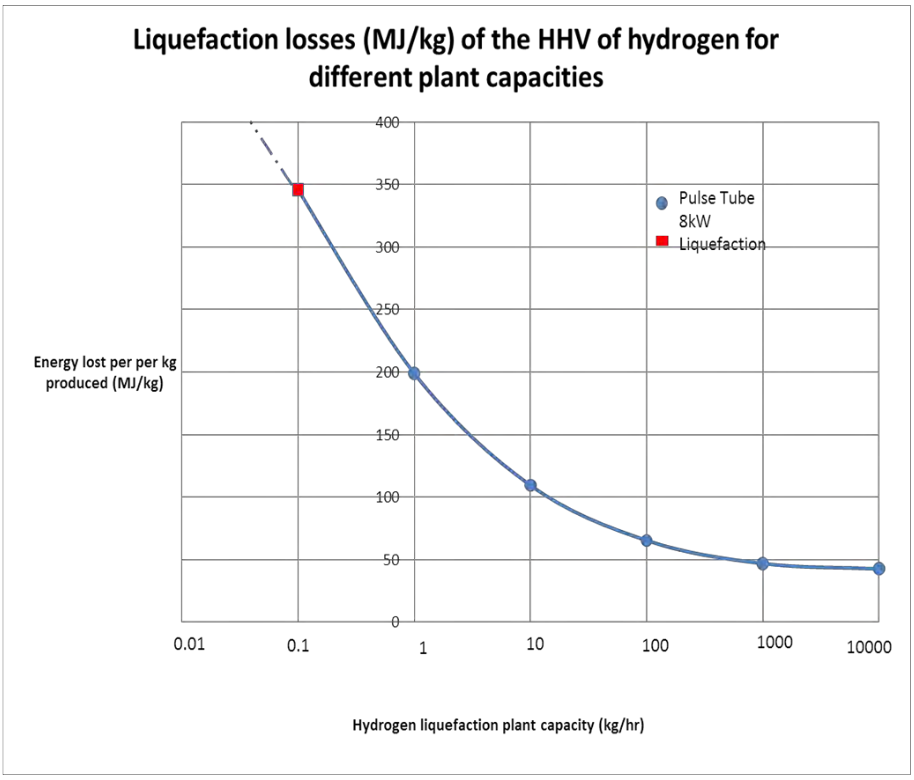


Figure 7.9 Higher heating value (HHV) loss as a result of hydrogen liquefaction [10].

7.6 Conclusions on Natural Gas and Hydrogen Synergies

The study identified preliminary potential synergies between the natural gas and hydrogen industries. This synergy was identified as one important aspect of the hydrogen economy. Developments in the hydrogen economy will almost surely induce changes in the natural gas industry and vice versa. These complex interdependencies could further evolve in light of the recent surge in shale gas production and the transportation and storage appeal of LNG. With regard to natural gas-based hydrogen production there is the traditional option realised through the conventional SMR pathway and advanced technology options considering the integration of CCS methods. Other promising advanced technology options for decentralised production being developed include microwave plasma processing of natural gas and TCM which also produce valuable carbon increasing the value of the hydrogen production chain.

Moreover, the use of natural gas blended with hydrogen in transport and natural gas pipeline networks is certainly advantageous to the hydrogen industry. It allows the potential of hydrogen to be recognised and advantageous to the natural gas industry, as it could reduce energy company associated emissions. The synergies will also allow hydrogen to be recognised as an important cryogen to reduce the dependency on helium which is being affected by resource problems and increasing prices.

A creatively structured hydrogen production pathway network involving various technology options for hydrogen fuel can improve energy security. This can be realised through an ideally integrated, diversified and reliable portfolio of energy resources development, supply as well as storage options. Within such a context, hydrogen could potentially assume an indispensable role.

Hydrogen-accommodating infrastructure for transport and stationary applications must be developed and financed by managing uncertainties, exploring opportunities and minimising risks in such a challenging environment. Natural gas, low-emission and renewably produced hydrogen along with renewable energy will be the future of a low-carbon economy. It is evident the links between natural gas and hydrogen are very long-standing but are likely to grow and not diminish.

As discussed, liquid hydrogen's application as a cryogen will have important implications for the hydrogen economy. Therefore, liquid hydrogen's synergy with the superconducting industry will be further researched in Chapter 8 and Chapter 9.

Chapter 8 Synergy between Liquid Hydrogen and Superconductivity

This chapter will provide a comprehensive background and present the use of liquid hydrogen applications in decentralised systems as a cryogen for superconductivity as introduced in Chapter 7. The interaction of compressed hydrogen and liquid hydrogen systems will also be briefly discussed.

8.1 Introduction to Liquid Hydrogen Applications

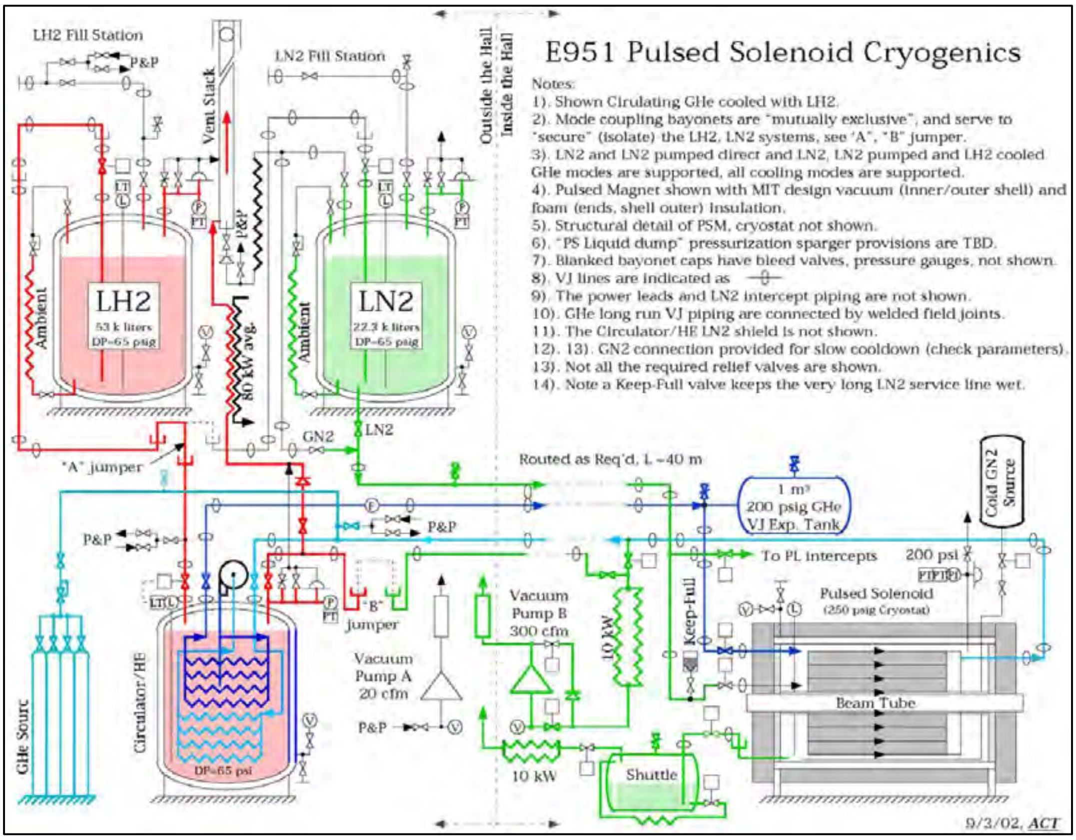
Superconductivity interlocked with the hydrogen economy can be the solution to decentralised energy and resource supply problems [250-252]. In addition to compressed hydrogen as discussed in Chapter 4 and Chapter 5, hydrogen can be stored as liquid at temperatures ranging from 14-33 K. An important application of liquid hydrogen is as a cryogenic coolant that can be used for almost all technical superconductors. As the quantity of hydrogen liquefied is increased, less energy is wasted and the more efficient and cost-effective the process. The liquefaction process can occur by the Joule-Thomson expansion cycle. The hydrogen is compressed at ambient pressure and passed through a heat exchanger in which the temperature is reduced. As a result of hydrogen cooling on expansion, the temperature should be below the inversion temperature T_{inv} = 200 K. A nitrogen precooling step is introduced before the hydrogen is passed to the expansion valve. The energy required for the compressor and expansion valves reduces the overall efficiency of the process. As liquid hydrogen is a cryogen with a low boiling temperature of T_{boil} = 20 K (under normal pressure), it must be stored in insulated cryogenic containers which are designed with double walls and an insulating space between the two walls to reduce heat transfer to the liquid. Heat transfer causes the liquid to evaporate and form gas a process called boil off. Heat also arises from the ortho-para conversion of hydrogen. To minimise boil off of the hydrogen for longer storage, an ortho-para conversion must be completed before liquefaction. The use of catalysts facilitate the ortho-para conversion of hydrogen [253].

There is a predicted and well-documented incoming shortage of helium for superconducting applications [247, 250] and hydrogen as a cryogenic coolant has been envisaged as a viable and more economically justified cooling option for superconducting devices [247]. There are many novel engineering designs that can be made possible by using medium-temperature MgB_2 superconducting wires, as developed originally in Cambridge [254], that include the following; a self-contained fully electric superconducting ship, DC fault current limiters, high DC current homopolar motors, cheaper superconducting MgB_2 magnets for fusion [255], SMES [108-110] and MRI systems. Development of liquid hydrogen indirectly cooled MgB_2 superconducting high voltage DC cables especially for computer data centres present ideal candidates for early implementation. Hydrogen's use as a coolant, as well as an energy carrier, will spin off new research and developments in superconducting materials and efficient energy use.

8.2 Indirect Liquid Hydrogen Cooling

Considering liquid hydrogen safety, direct cooling can only be handled by highly specialised organisations and companies, but indirect liquid hydrogen cooling, (iLH_2), can be a viable option for a decentralised economy. In iLH_2 installations, a helium gas exchanger can be used, transferring cooling power of the hydrogen bath at ~20 K to the desired cryomagnetic installation [255]. A pertinent example of indirect cooling by liquid nitrogen is given by McDonald et al. that designed a cooling system for a 15 T pulsed copper solenoid magnet to a desired temperature of 30 K in order to reduce the resistance of the Cu and thereby reducing the power requirements of the system [255]. The design as proposed cooled the magnet via a closed helium loop circulated through a heat exchanger filled with liquid hydrogen from a storage Dewar. The piping and instrumentation diagram is shown in Figure 8.1.

Helium is chosen as the circulating gas due to the danger of hydrogen in operating circumstances as there is a chance of ignition through internal shorting of magnets. Development of efficient and cost-effective helium gas cryopumps is a paramount task for the implementation of iLH_2 technology to the market and making the synergy between superconducting applications and liquid hydrogen a reality.



Notes:
1). Shown Cirulating GHe cooled with LH2.
2). Mode coupling bayonets are "mutually exclusive", and serve to "secure" (isolate) the LH2, LN2 systems, see 'A", "B" jumper.
3). LN2 and LN2 pumped direct and LN2, LN2 pumped and LH2 cooled GHe modes are supported, all cooling modes are supported.
4). Pulsed Magnet shown with MIT design vacuum (inner/outer shell) and foam (ends, shell outer) insulation.
5). Structural detail of PSM, cryostat not shown.
6). "PS Liquid dump" pressurization sparger provisions are TBD.
7). Blanked bayonet caps have bleed valves, pressure gauges, not shown.
8). VJ lines are indicated as —0—
9). The power leads and LN2 intercept piping are not shown.
10). GHe long run VJ piping are connected by welded field joints.
11). The Circulator/HE LN2 shield is not shown.
12). 13). GN2 connection provided for slow cooldown (check parameters).
13). Not all the required relief valves are shown.
14). Note a Keep-Full valve keeps the very long LN2 service line wet.

Figure 8.1 Piping and instrumentation schematic for 15 T Cu indirect cooling system. The design utilises two stages of cooling. The first preliminary stage of cooling is provided by LN_2 to 77 K and the second stage of cooling is provided by LH_2. The location of the compressed helium gas circulator is located above the bottom LH_2 tank. This pump circulates helium through the closed loop between the heat exchanger that is immersed in the LH_2 Dewar and magnetic coil [255].

Currently, the hydrogen cryogenic gas circulator (e.g. Cryo-pump and CryoFan designs) industry is not well developed and only one product is readily available, the CryoZone CryoFan range, Figure 8.2 [256]. Ongoing research aims to develop the concept of a magnetically coupled motor/impellor "CryoMagFan" which maintains a complete, uninterrupted vacuum envelope to reduce heat loss, prevent helium leakage and also allow for a higher operating pressure. The successful and efficient liquefaction of hydrogen can allow liquid hydrogen to have an important role in the hydrogen economy [257].

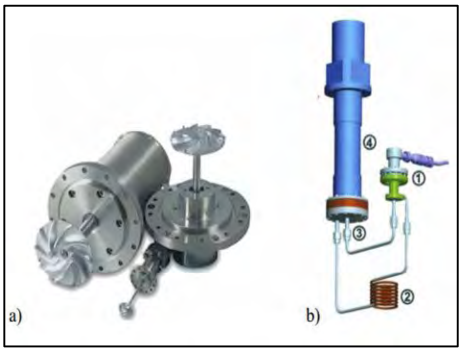


Figure 8.2 a) A range of Cryozone cryofans [256]; b) 1 Schematic helium gas cooling system of Noordenwind CryoFan by Cryozone, 2 superconducting application such as electromagnet, bearing, 3 helium heat exchanger, 4 closed cycle cryocooler head or LH_2 cryostat.

8.3 Liquid Hydrogen's role in the Emergence of the Hydrogen Economy

Considering the use of indirect cooling of superconductors with liquid hydrogen in conjunction with a compressed closed helium gas loop, one hospital-related system that is generic for the decentralised hydrogen economy will be discussed, where synergy between hydrogen generation, liquefaction, storage and use can have a well justified place. The concept will be further developed in Chapter 9.

Figure 8.3 highlights the use of hydrogen for hospital cryogenic applications. Hydrogen is delivered to the hydrogen cell from renewable or zero-CO_2 emitting sources where it is liquefied outside the building, and from the storage reservoir it can then be pumped to provide indirect cooling via a helium closed loop to both MRI magnets and to the superconducting bearings of a flywheel energy storage system. Figure 8.4 shows a decentralised scenario for the use of hydrogen in meeting future energy storage, energy demand and cryogenic requirements in conjunction with a hospital environment, first introduced in Figure 1.1 where the use of liquid hydrogen was identified as an important concept for the hydrogen economy. The importance of the hydrogen industry in enabling other industries can be identified with the production of carbon for the carbon industry as a product of microwave plasma processing and the production of liquid hydrogen providing 20 K for cryogenic applications enabling the superconducting industry. Additional cryogenic applications for liquid hydrogen can be identified from Figure 8.4 including SMES, homopolar wind turbines and DC cables for datacentres. From Figure 8.4, liquid hydrogen is also suitable for transport applications for use in cars, e.g. BMW and buses. The decentralised production of hydrogen can be used for domestic, transport and industrial applications, making it a cryogen that can be used both as an energy carrier and a cryogenic medium.

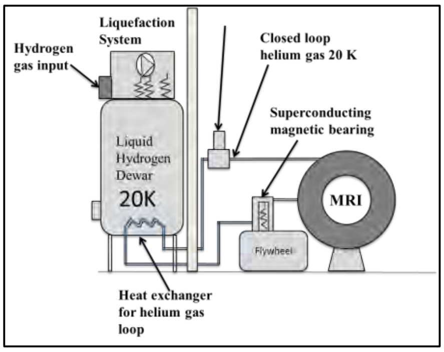


Figure 8.3 Building infrastructure for the iLH$_2$ concept of MRI and flywheel energy storage from Figure 8.4. The superconducting bearing is cooled indirectly by LH$_2$ using a closed-loop helium circuit. The LH$_2$ storage Dewar is located externally to the hospital. Helium gas is pumped around a closed loop with one end cooled to 20 K via a heat exchanger connected to a liquid hydrogen Dewar. This setup will be part of a liquid hydrogen laboratory in the new Department of Materials Science and Metallurgy building, University of Cambridge.

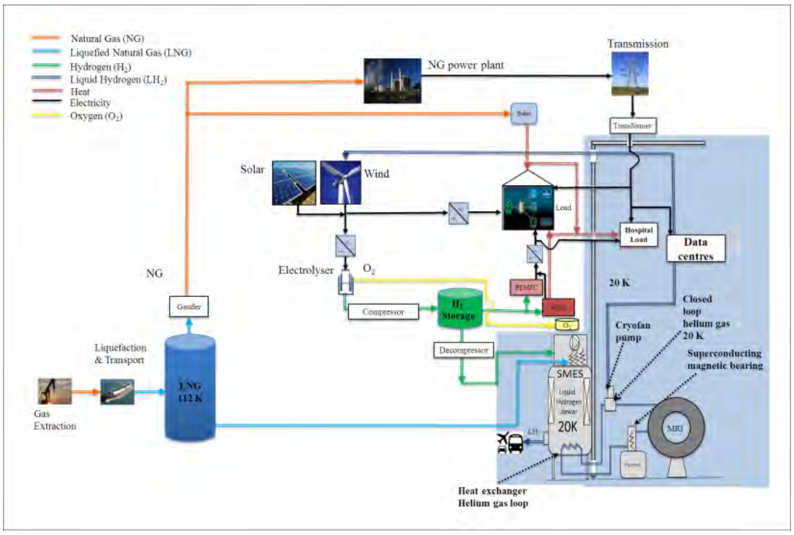


Figure 8.4 Decentralised production of hydrogen via near zero-CO$_2$ emission processes and use as an energy carrier, energy storage medium and cooling cryogenic medium. The superconducting devices to benefit from the synergy with iLH$_2$ are SMES, flywheel, MRI, DC cables for datacentres and homopolar wind generators. Also included is the potential of LNG to be used for hydrogen liquefaction.

From Figure 8.4, a preliminary SD model simulating liquid hydrogen production as well as compressed hydrogen production for providing energy to a hospital will be considered. The concept will be further investigated in Chapter 9.

8.4 System Dynamics Simulation of a Hospital Scenario

Following the successful study on helium availability from natural resources using SD as discussed in Chapter 3 [127], SD is used to research the synergy between hydrogen and superconducting applications. The formulation of a preliminary SD model is based on the schematic depicted in Figure 8.5 with wind energy being used to meet demand and also to supply excess energy to the energy storage systems, which also supplies energy to meet demand. Grid energy is used to meet any demand not met by the renewable technologies and storage systems.

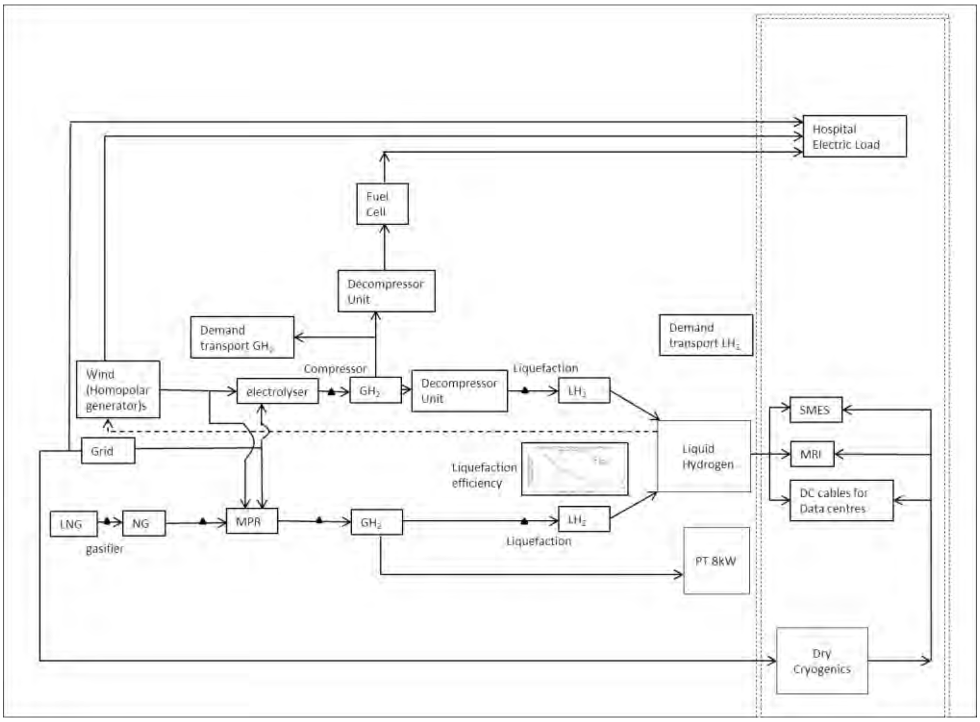


Figure 8.5 Schematic showing the potential paths of wind energy, the potential electricity sources in meeting the electrical load and the potential methods for cryogenic applications. The graph shown in the figure indicates the relationship used to model the cost and efficiency change of liquefaction that occurs depending on demand.

The model looks at two different aspects of hydrogen production and use. It looks at the use of hydrogen as a storage medium and energy carrier for electricity and also at the liquefaction efficiencies and the use of liquid hydrogen to meet demand. As mentioned in Chapter 7, a large energy penalty is encountered when liquefying hydrogen, Figure 8.6. This means that for the efficient production of hydrogen, large amounts of hydrogen must be available for liquefaction. Using natural gas for hydrogen production results in the use of a fossil fuel, making this source of hydrogen unsustainable and not a long-term solution to global energy needs. It is clear that even if hydrogen production and its applications are proven to be cost-effective, the success of the hydrogen economy both gaseous and liquid depends on the support from government policies. For the SD modelling it is assumed that liquid hydrogen is only produced if the demand is present, the demand is constant per hour throughout the day and the overall demand can be changed. As a result of the energy penalties that are present when liquefying hydrogen, extra hydrogen is produced to account for the overall energy loss. Compressed hydrogen use is also considered as a store for a decentralised wind energy system for a hospital. The result of hydrogen storage to displace grid energy is depicted in Figure 8.7. The preliminary results highlight that there is a potential for an integrated compressed and liquid hydrogen system to improve energy security of both energy and resources for a hospital building.

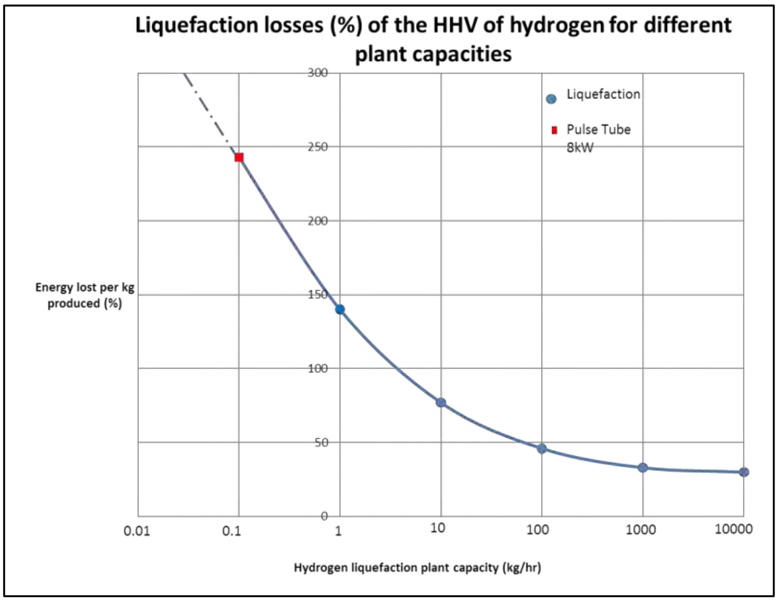


Figure 8.6 Percentage of the HHV of hydrogen lost during the liquefaction process for different plant capacities. The efficiency of a pulse tube cryorefrigerator condenser-like liquefier is shown as a reference point

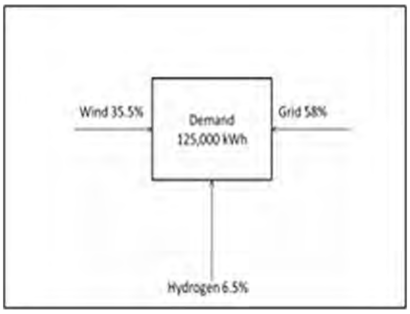


Figure 8.7 Exemplary hospital sub-unit demand being met by wind energy, stored energy and grid energy. Hospital Demand is for one building representing 20% of overall demand over a 72 hour period of Addenbrookes Hospital in Cambridge

8.5 Conclusions of Liquid Hydrogen Potential in Hospitals

In the presented case, the use of indirect cooling is necessitated by safety concerns over storage of hydrogen within the building envelope. However, fundamental concerns over the cost and availability of helium which are already hampering progress for direct cooling dictate that superconducting cooling will be increasingly catered for via indirect closed loop systems in order to conserve helium and reduce operating costs. The development of effective low-loss and high efficiency helium gas CryoMagFans is of paramount importance for the safe use of cryogens. The decentralised production of hydrogen via electrolysis for a hospital has the potential to supply the hospital with an energy store, electricity and liquid hydrogen for cryogenic applications. With regard to energy storage and supply, the demand from hospitals is large, and so a large decentralised system would have to be built, maybe in combination with a biomass CHP to reduce overall emissions and become independent from grid energy. If a building with an approximate demand of 41,600 kWh/day was powered by the wind-hydrogen system, then the grid dependency of the building over a 72 hour period will be 58 %, with 35.5 % from wind and 6.5 % from hydrogen storage using actual wind data. As hospitals are often composed of different buildings, it could be assumed that a decentralised system would aid one building in reducing grid dependency. In can be concluded that the larger the role of LH_2 generation in the hospital environment, the less important is the cost of the cryogenic coolant for superconducting applications.

The further development of the integration of hydrogen within hospital infrastructure is presented in Chapter 9.

Chapter 9 Integration of the Hydrogen Economy for Hospital System Solutions

This Chapter further investigates the role liquid hydrogen has in the emergence of the hydrogen economy and analyses the impact liquid hydrogen systems integrated with compressed hydrogen can have on the development of resource efficient sustainable hospital energy systems.

9.1 Introduction to the Hydrogen Economy for Sustainable Cities and Resource Efficient Buildings

Cities have a high consumption of global resources (75%) [258] and currently generate 80% of global GHG emissions [259]. Furthermore, there is a continued urban population growth (54% of the total global population in 2014) [260] indicating a continued increase of energy demand within cities. Therefore, sustainable cities are anticipated to emerge in an attempt to reduce resource demand and environmental impact.

The emergence of sustainable cities that focus on the effective management of resources will continue due to threats posed by population growth, climate change and energy security. Resource efficient buildings will play an important role in the emergence of sustainable cities as large buildings are essential in the existing energy system of cities and are responsible for ~40% of the entire energy consumption [261]. It is anticipated a decentralised wind-hydrogen system can be integrated within building energy infrastructure to complement other strategies for enabling sustainable cities. An investigation into hospital buildings will be completed as they have an important role in emerging sustainable cities due to their diverse energy and resource requirements as highlighted in Chapter 8. Hospitals need an uninterrupted energy supply, a sustainable energy carrier for transport demand and specialist resources such as cryogens. In this context compressed and liquid hydrogen can provide a sustainable solution. The hydrogen economy can have a complex and direct role in emerging sustainable cities with focus on the use of energy and natural resources in hospitals, Figure 9.1.

From Figure 9.1, in the context of hospital's energy and resource use, compressed hydrogen can be integrated within the hospital's transport infrastructure to reduce dependence on oil and reduce GHG emissions. Liquid hydrogen's use as a cryogen can be a solution to the problems of helium price increases and supply shortages for cryogenic hospital applications. Additionally, liquid hydrogen's use as an energy storage medium can provide a back-up energy supply for a hospital building [250].

Figure 9.1 represents the use of hydrogen infrastructure in sustainable cities. Additionally, the microwave plasma processing of natural gas and thermal cracking of methane are near-zero emission hydrogen production methods that produce valuable carbon allotropes that can facilitate the growth of the carbon industry important for emerging smart technologies [50].

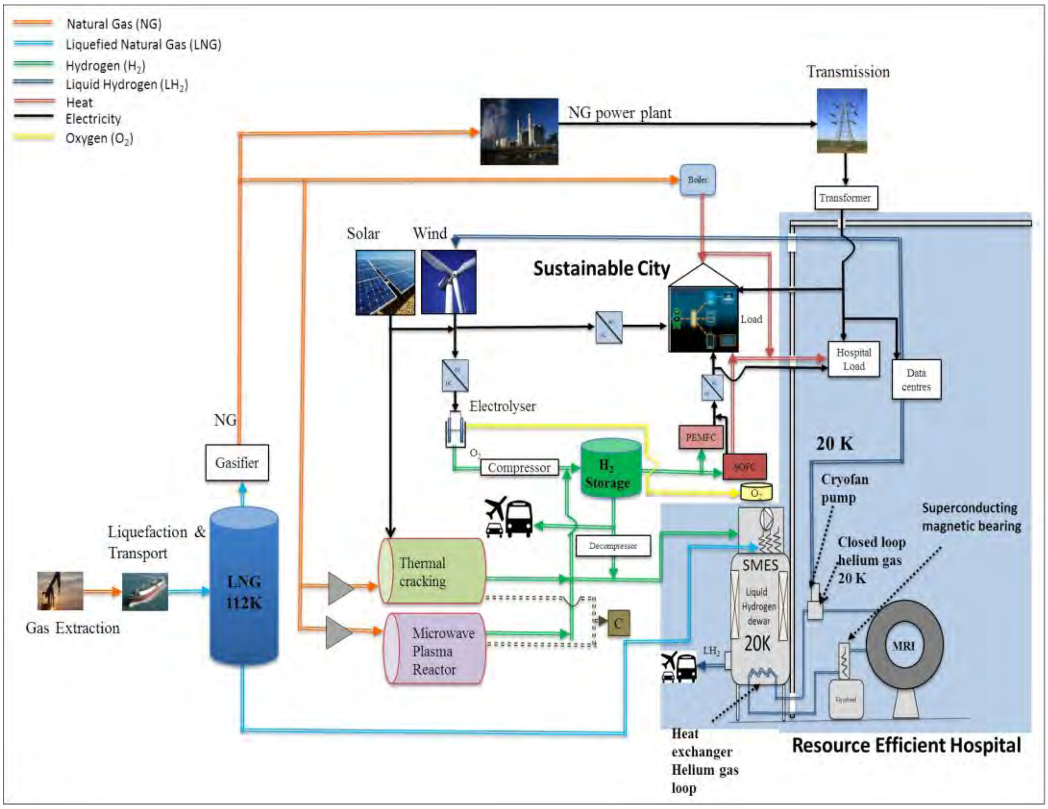


Figure 9.1 Decentralised production of hydrogen via near zero-CO_2 emission processes and hydrogen use as an energy carrier, energy storage medium and cryogen for the development of resource efficient hospitals in sustainable cities. The production of carbon can facilitate the development of smart technologies.

The motivation of the choice of hydrogen as a suitable energy carrier and cryogen for hospital infrastructure is further discussed in section 9.1.1 and section 9.1.2. The impact of an integrated compressed and liquid hydrogen system for the development of a robust, secure and environmentally friendly energy and resource system will be investigated.

9.2 Hydrogen for Hospital System Solutions

Hydrogen's use as an energy carrier for transport, as a cryogen and as an energy storage medium will be presented.

9.2.1 Hydrogen for Transport in the Health Sector

The transport sector currently consumes 25% of global energy demand and is 93% dependent on oil which raises both energy security and GHG emission issues [262]. Currently, the transport sector is only 4% dependent on alternative fuels which include hydrogen. It is expected health-care facilities can cut their transportation emissions by using high-efficiency or alternative fuel vehicles

Table 9.1 introduces the properties and characteristics of hydrogen as a vehicle fuel compared to other fuels. It highlights the suitability of hydrogen for transport in relation to CO_2 emissions and cost. As uncompressed hydrogen has a low volumetric energy density (0.0096 MJ/l) it must be compressed to increase this energy density. From Table 9.1 it can be seen hydrogen has a relatively low cost per litre of fuel. Fuel cell vehicles have no tailpipe CO_2 emissions and have a higher efficiency than gasoline ICE vehicles with a longer fuel range. This highlights the advantages of hydrogen as an alternative fuel within cities. However, cost of infrastructure and technologies remains a major barrier for the widespread introduction of hydrogen.

Table 9.1 Hydrogen as an energy carrier compared to other vehicle fuels.

Transport Fuel	Volumetric energy density; [264]	Cost per litre; [265, 266]	Tailpipe CO_2 emissions; [267]
Units	MJ/l	€/l	gCO_2/km
H_2 350 bar	2.8	0.2	0
H_2 700 bar	4.9	0.27	0
Diesel	35.8	1.29	132
Petrol	31.2	1.44	120
CNG 200 bar	8	0.70	113

Decentralised refuelling stations can avoid excessive capital costs of hydrogen pipelines. The installation of a refuelling station in a city could be used by vehicles such as ambulances that do not require a large refuelling network. This could be considered in countries that have no plans for the development of a hydrogen transport network as a method to introduce hydrogen as a vehicle fuel.

Due to the flexibility of hydrogen it can be used as an energy carrier in different types of vehicles. These include FCEV, hybrid ICE using diesel/natural gas and hydrogen blends, ICE hydrogen vehicles or BEV with a hydrogen fuel cell range extender [267]. Passenger cars usually require a pressure of 750 bar while other larger vehicles including ambulances and buses can be operated at lower pressures (350 bar) as a result of the capability of storing larger quantities on board.

An ambulance that is a BEV with an installed hydrogen range extender is considered in the study. The use of these vehicles can facilitate the emergence of the hydrogen economy [268]. An electric vehicle without the fitted hydrogen range extender has a range of 160 km (12.5 kWh/100 km); however, with the range extender the vehicle can travel a further 160 km with hydrogen (0.5 kg H_2/100 km) leading to a reduced requirement for charging and refuelling along with reduced CO_2 emissions, an important consideration for sustainable transport within cities [267]. The integration of these vehicles can allow the health sector to play an essential role in mitigating the effects of climate change. Furthermore, hospitals can play an important role in accelerating the transition to hydrogen and alternative fuels within the transport sector.

9.2.2 Liquid Hydrogen as a Cryogen and Energy Store for Hospitals

Helium is currently the cryogen of choice for superconducting applications; however, helium shortages are continuing to challenge the superconducting industry. Hospitals use helium for MRI applications but must monitor cryogen levels closely as MRI manufacturers are raising questions about guaranteed supply of helium for medical purposes. While the contract price of liquid helium is ~8-9 €/l, shortages have led to a rise in the spot price of liquid helium to ~20 €/l [269]. The delay between a rise in the price of helium and the resulting decrease in demand are central to the dynamics of the hydrogen market [270]. The current global use of helium for cryogenic applications including superconductivity is estimated to be 29% from which 75% is used by MRI/nuclear magnetic resonance (NMR). It is evident a sustainable, secure and economic cryogen is required for the continued functioning of the superconducting industry.

Liquid hydrogen's use as a cryogen is a less established scenario for future applications of hydrogen; however, iLH_2 of a closed loop helium gas system as discussed in Chapter 8 can be a viable option for a decentralised economy. Some potential applications of indirect cooling using liquid hydrogen as mentioned include in MRI technology [271, 272], SMES [110], flywheel energy storage [273, 274], DC cables for datacentres [275-277], homopolar wind turbine generators [182] and the magnetic heating of billets [278].

Table 9.2 highlights the feasibility of hydrogen as a cryogen. Liquid hydrogen generated from centralised production has a cooling cost ~200 times lower than helium. Even with price increases as a result of decentralised production, liquid hydrogen cost still remains ~45 times lower than helium, Table 9.2.

Table 9.2 Hydrogen as a cryogen compared to other cryogens [255, 278, 280].

Cryogens	T_{boil}	Latent heat of vaporisation	Density	Cost per litre	Cost per kJ latent heat of vaporisation
Units	K	kJ/kg	kg/m^3	€/l	€/kJ
LH_2 (centralised)	20.3	446	70.8	0.57	0.018
LH_2 (decentralised)	20.3	446	70.8	2.5	0.079
LHe	4.2	20.3	124.9	9.00	3.57
LNe	27.1	85.8	1207	111	1.07

The use of liquid hydrogen as an energy storage medium is also considered in this study. If hospitals are integrated with renewable energy, in an effort to reduce carbon emissions, energy storage technology will be required as a result of the arising intermittency of renewables. The use of SMES with a liquid hydrogen store to provide back-up energy supply to a hospital will be further investigated.

SMES with a MgB_2 superconducting magnetic energy storage coil and a liquid hydrogen storage Dewar, Figure 9.2a, combined with a fuel cell enables continuous power supply in case of an emergency, Figure 9.2b [110].

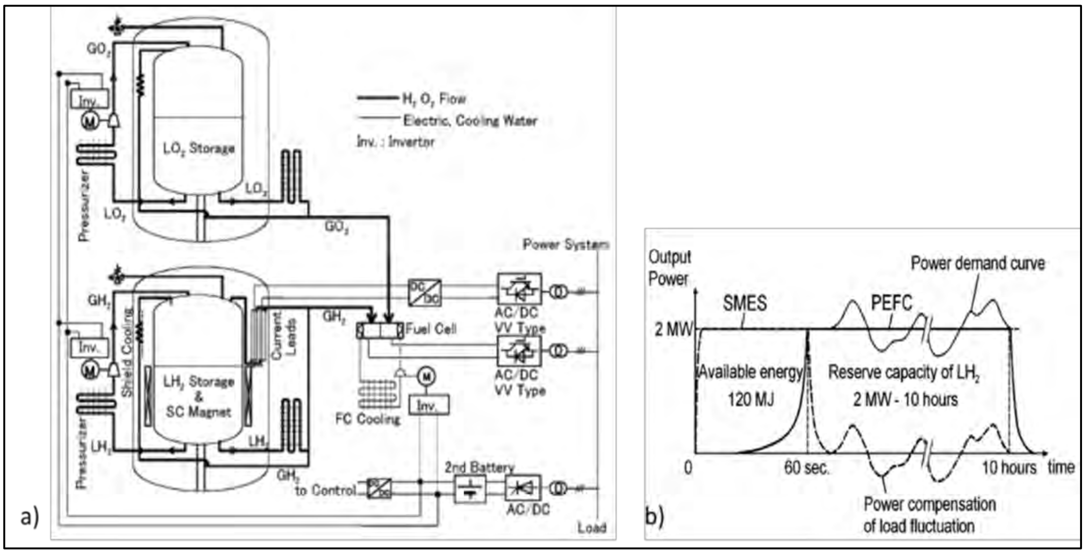


Figure 9.2 a) Whole system configuration of liquid hydrogen cooled SMES and fuel cell generation for 2 MW emergency power supply, b) Schematic diagram of the output power sharing between the proton exchange membrane fuel cell (PEMFC) and SMES [110].

Decentralised renewable energy generation and storage can ensure a reliable and resilient system, improving energy security. Additionally, the health sector can play an important role in improving the economies of scale of hydrogen systems and making alternative energy more economically viable [281].

The use of liquid hydrogen as a cryogen in SMES integrated with liquid hydrogen storage as described will be important for resource efficient hospitals for moving towards a sustainable future.

9.3 Method for Modelling Hydrogen's Impact on Hospital Systems

A holistic SD methodological framework is proposed, as a means to investigate the operation of a hospital system integrated with hydrogen for energy and resource requirements. SD is an appropriate method to analyse and comprehend resource use within hospitals systems. Table 9.3 lists the different scenarios considered in the SD study.

Table 9.3 System dynamic study and corresponding scenarios for Chapter 9. The subject area of the SD model is the impact the integration of hydrogen in hospital energy infrastructure can have for the development of resource efficient buildings.

Study	Scenario	Scenario Explanation
1	A	Hospital system carbon emissions without an integrated compressed and liquid hydrogen system
	B	Hospital system carbon emissions reduction, liquid hydrogen production and system response to an integrated compressed and liquid hydrogen SMES system without occurrence of a black-out
	C	Hospital system carbon emissions reduction, liquid hydrogen production and system response to an integrated compressed and liquid hydrogen SMES system with the occurrence of two black-outs

Across Europe energy consumption in hospitals is increasing and it is estimated ~50% of energy demand for hospitals is from electricity. Hospitals have a large electricity demand as a result of the 24 hour operation of hospital buildings. An approximate hospital electricity trend (the demand used in the SD model) is shown in Figure 9.3. It can be seen that there are two demand peaks throughout the day and this high energy demand leaves the system vulnerable if there is an occurrence of a black-out.

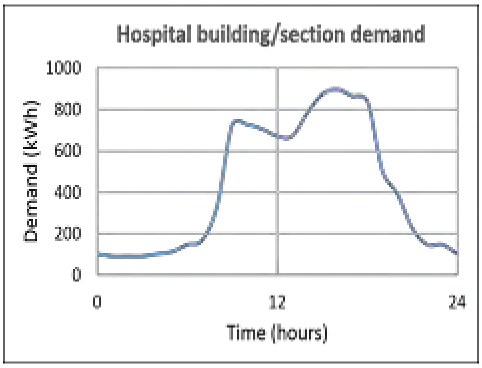


Figure 9.3 Hospital energy demand trend (non-transport) [282].

As a result of the high energy demand of hospitals, it was anticipated that a small hospital building would be supplied by the decentralised wind turbine as well as the SMES and liquid hydrogen for back-up energy supply. The hospital building was assumed to have 40 beds. The hospital section therefore has a total demand of ~10.4

MWh based on the average European electricity consumption of 261 kWh per bed each day [283].

A liquid hydrogen requirement of 40 kg per day was considered that is used to meet the cryogenic requirements of SMES and liquid hydrogen energy storage requirements. Although an economical cryogen, Table 9.2, there is a large energy penalty encountered when liquefying hydrogen. The larger the quantity of hydrogen produced the more efficient the process; however, this poses problems for the production of liquid hydrogen via intermittent wind energy. This is as a result of an unpredictable and potentially low quantity of energy being available for hydrogen production. Therefore, a back-up energy source for hydrogen production is required in the system. In the SD model presented, the use of grid electrolysis is considered as a back-up for hydrogen production. The decentralised production of liquid hydrogen also incurs additional costs as seen from Table 9.2; however, the use of liquid hydrogen could potentially be a key enabler of the hydrogen economy.

Figure 9.4 depicts an overall decentralised hydrogen economy integrated within a city with focus on the use of hydrogen for hospital energy and resource requirements. The areas of focus are highlighted (shaded regions). These include the use of renewable electrolysis and grid electrolysis for hydrogen production and hydrogen use for transport, storage and cryogenic applications.

Figure 9.5 represents the causal loop diagram for the SD model. It highlights the interaction between the different variables. There are seven balancing feedback loops within the model. These include B1, B2 and B4 reducing the hospital energy demand with use of wind energy, grid energy and SMES and liquid hydrogen energy respectively while B3 includes the interaction between the use of grid energy for demand and its dependence on the quantity of wind energy generated. The balancing loop B5 relates to the reduction of hydrogen available for use due to liquefaction with B6 relating to the reduction of overall liquid hydrogen demand due to liquefaction. B7 is an important feedback loop as it determines the quantity of hydrogen available for the transport sector. The availability of hydrogen is directly linked to liquid hydrogen demand within a particular hour. Different scenarios are considered to highlight the impact the hydrogen economy can have on hospital resource consumption and CO_2 emissions, Table 9.3.

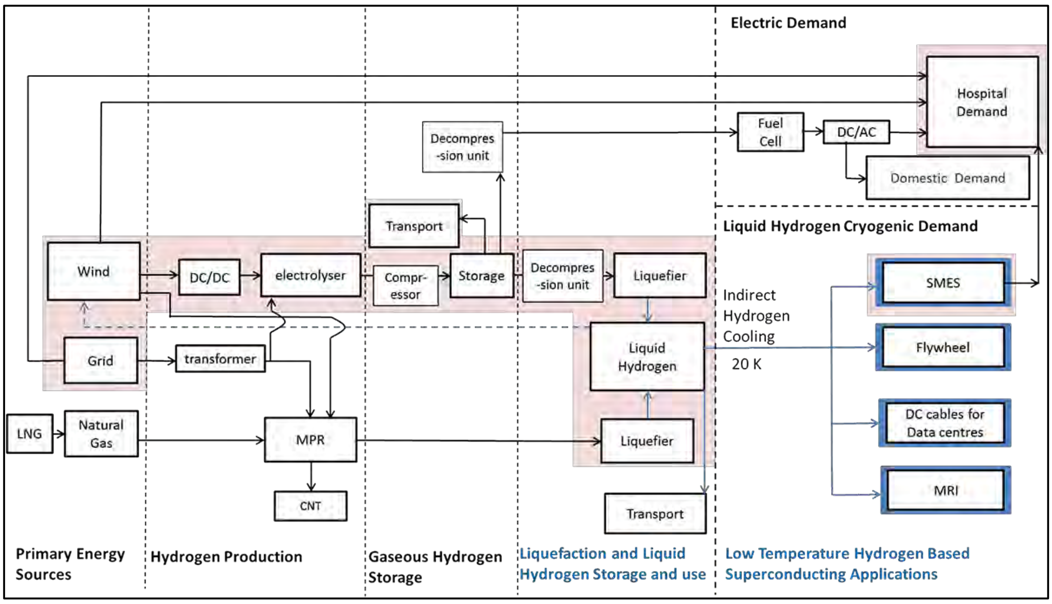


Figure 9.4 Schematic of hydrogen pathways showing the potential for the integration of the hydrogen economy within hospital and transport infrastructure for the development of sustainable cities.

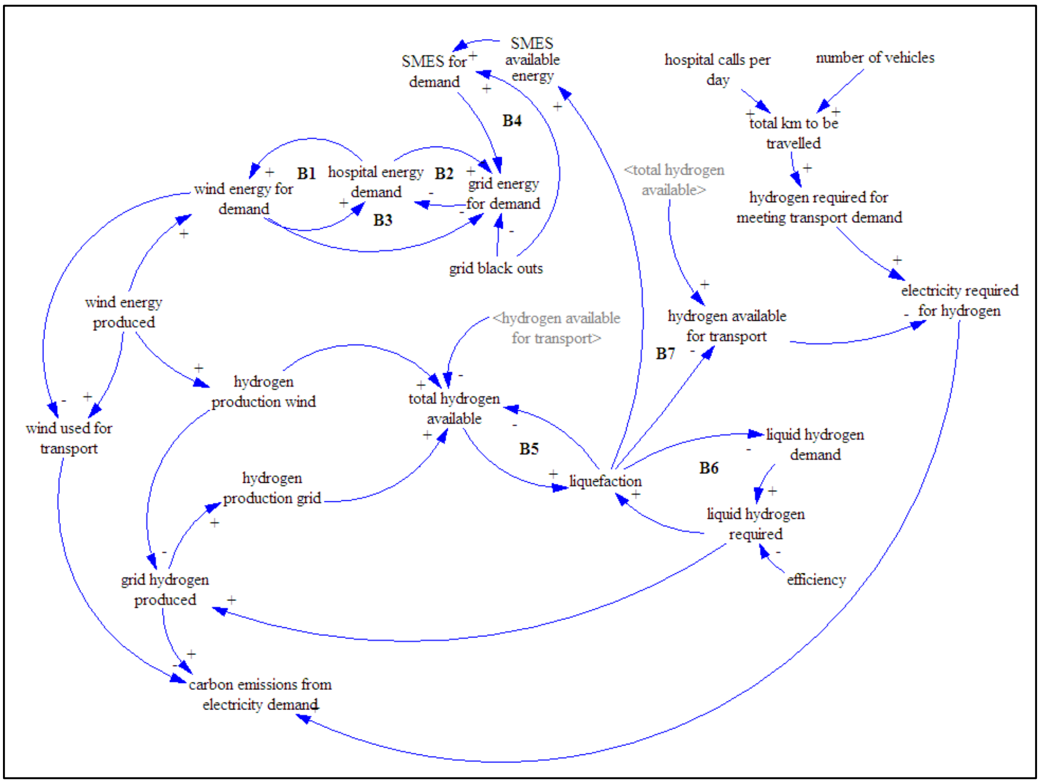


Figure 9.5 Causal loop diagram for the hospital system that highlights the interactions between the different variables in the model reflecting the actual system presented in Figure 9.4.

A decentralised 500 kW turbine generates electricity for the hospital with excess energy going to storage. An additional 500 kW wind turbine is installed for renewable electrolysis producing emission-free hydrogen for the range extender vehicles and liquid hydrogen for the SMES technology and liquid hydrogen store.

If there is no hydrogen available for transport, grid energy is not considered for hydrogen production. This is due to the more efficient process of using the grid energy directly for charging the electric vehicle. Therefore, within the system there is a potential trade-off for the use of hydrogen or electricity for the ambulance fleet vehicles. Grid energy is only used to produce hydrogen if wind cannot meet liquid hydrogen demand. For SMES electricity is stored in magnetic fields of a coil comprised of superconducting wire with near zero loss of energy. Time sharing of output power of SMES and a fuel cell is complementary. When a blackout occurs SMES can supply electric power for the first minute, and the fuel cell can supply it for the remaining energy storage capacity, Figure 9.2b. The SMES and liquid hydrogen storage system considered in the SD model has 36 GJ available at full capacity and can supply a system in emergencies with 1 MW over 10 hours [110]. With fuel cell efficiencies of 50% considered 606 kg of hydrogen is required to ensure 36 GJ of energy is available as back-up in the storage system.

The SD model investigates different system scenarios; Scenario A investigates hospital consumption and CO_2 emissions without the integration of the hydrogen economy in a ‘business-as-usual’ case, Scenario B models the availability of hydrogen in a given hour for liquid hydrogen and transport and then calculates the reduced CO_2 emissions. Liquid hydrogen is produced for back-up energy but SMES technology is not required as no black-outs occur, Scenario C investigates the ability of SMES and liquid hydrogen storage to respond to black-outs.

9.4 Results of the Impact of the Hydrogen Economy on Hospitals

From the SD model and three scenarios the impact of hydrogen in the context of the hospital environment where it is used as an energy carrier for transport, an energy storage medium and a coolant for superconducting devices within the hospital, Figure 9.4, will be emphasised.

In a ‘business-as-usual’ centralised case where grid electricity is used for charging BEV, ~9 $kgCO_2$ per ambulance fleet per day (166 km travelled) is emitted. Furthermore, without the integration of decentralised wind and hydrogen technologies for electricity generation over the 72 hour period an average of 4 tonnes of CO_2 per day is emitted.

For Scenario B and Scenario C the use of an integrated wind-hydrogen system was investigated. The use of a BEV with a hydrogen range extender allows the advantages of both transport technologies to be realised. These include the benefit of longer driving ranges and shorter refuelling times for the hydrogen system and higher efficiency for the electric system. Furthermore, liquid hydrogen can enable a sustainable back-up energy supply system.

In Scenario B the model considers an integrated 500 kW system for hydrogen production and use for BEV and a 500 kW turbine for providing energy to the hospital system. Additionally, the system has a liquid hydrogen demand. The liquid hydrogen store has an initial value of 300 kg of LH_2. At full capacity, 606 kg, it is capable of providing 1 MW to the hospital system for 10 hours Figure 9.6, highlights the electrical demand of the hospital, met by wind energy and the remainder met by grid energy when no blackout occurs. From Figure 9.6 the integration of decentralised wind energy can impact the CO_2 emissions of a hospital by the reduction of grid energy as shown. The area under the wind energy graph is the quantity of grid energy displaced.

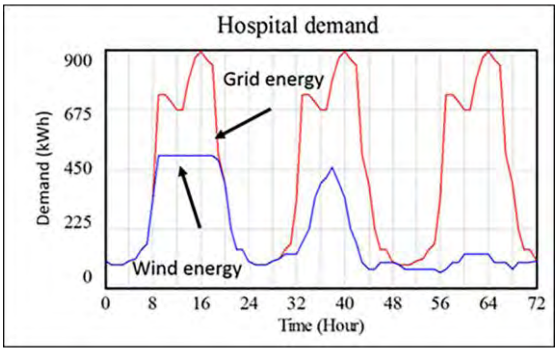


Figure 9.6 Effect of the integration of a 500 kW decentralised wind turbine on hospital grid requirement.

The use of the decentralised wind turbine can displace an average of 2 tonnes CO_2 from the electrical demand and is capable of meeting all the vehicle demand. A liquid hydrogen demand of 40 kg/day of liquid hydrogen was met, 58% from wind energy and 42% from grid energy. Therefore, there is a CO_2 penalty associated with the production of liquid hydrogen.

Scenario C investigates the response of the SMES as a back-up emergency supply for when a blackout occurs with the results shown in Figure 9.7. When grid energy was unavailable the SMES and liquid hydrogen system was capable of meeting the demand not met by wind energy.

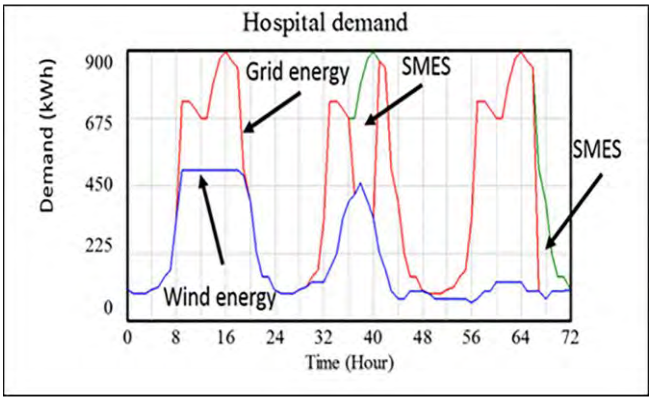


Figure 9.7 SMES and liquid hydrogen's ability as a back-up energy source for the hospital.

From the results the advantages of integrating the hydrogen economy into smart cities for hospital infrastructure is highlighted. The decentralised wind-hydrogen energy system allows for the successful supply of electricity, back-up energy and transport fuel. The SMES and liquid hydrogen storage system allows a sustainable back-up energy source to be available for hospitals when two black-out periods over the 72 hours were experienced. Furthermore, a decentralised wind turbine reduces the overall energy required from the grid.

9.5 Conclusions on the Potential of Hydrogen for Hospital System Solutions

The hydrogen economy is the vision of using hydrogen as a low carbon energy source to replace conventional fuels. This can help the development of sustainable cities that aim to integrate transport and energy to reduce air pollution, energy costs, and resource use to allow for a clean urban environment. In moving towards sustainable cities it is anticipated the development of resource efficient buildings will play a dominant role.

The results indicate that a decentralised wind-hydrogen system can effectively address both transport and emergency back-up electricity for hospitals in a sustainable manner.

The use of hydrogen in a decentralised hospital scenario as an energy carrier, storage medium and cryogen is an important way for hospitals to reduce vulnerability to power shortages (SMES) and price volatility of resources (helium and oil). Additionally, a large system integrated with fuel cells can also reduce grid energy dependency.

As the dominant role of hydrogen is expected to be as an energy carrier it can be concluded that the integration of liquefaction will emerge as an important aspect of the hydrogen economy. The decentralised production of hydrogen pathways for cities will play an important role in achieving a secure and sustainable energy future.

The synergies of hydrogen and the superconducting industry will allow for a reduced cost of system operation and reduce the risk surrounding helium supply shortages.

Chapter 10 Conclusions and Future Research

The research studies presented throughout the Thesis in Chapter 4 - Chapter 9, all focus and investigate hydrogen's potential and value in decentralised energy systems for stationary, transport and cryogenic applications as well as potential synergies that can arise between hydrogen and other technologies and energy sources that can increase hydrogen's overall value.

The objectives of the Thesis included looking at different aspects of the hydrogen economy individually in more detail to investigate hydrogen's value in energy systems. The different areas of focus were developed throughout the research, first identified in Chapter 1 from Figure 1.1 (also Figure 10.1).

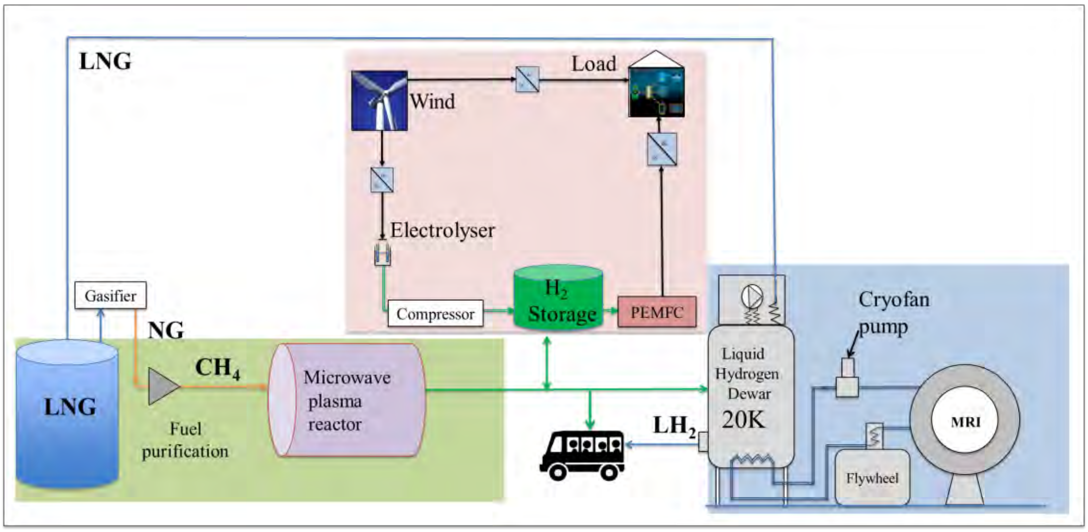


Figure 10.1 Simplified hydrogen economy highlighting the initial concept of the Thesis (as previously presented in Figure 1.1). The three highlighted areas represent three different individual aspects of the hydrogen economy, decentralised hydrogen production and use (pink shaded region), synergy with natural gas (green shaded region) and liquid hydrogen as a cryogen for applications within hospitals (blue shaded region). (This figure was repeated intentionally from Chapter 1 to achieve better overall clarity of the conclusions).

Each aspect was researched and discussed in more detail throughout the Thesis with adapted versions of Figure 10.1 presented in each research chapter. The final concept of an integrated complex hydrogen economy identified through the research is depicted in Figure 10.2.

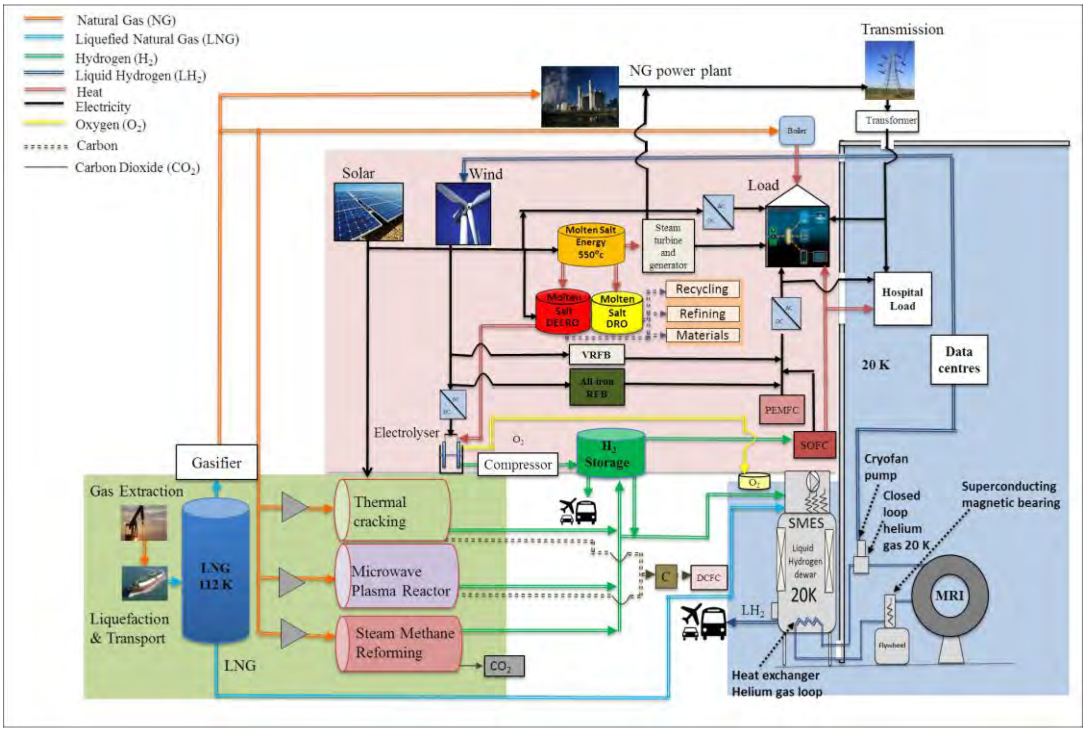


Figure 10.2 Final conceptualised decentralised hydrogen energy system that were considered individually throughout the research study. The pink shaded region indicates the potential of a decentralised hydrogen system integrated with other energy sources and technologies (Chapter 4-6). The green shaded region highlights the area of research on natural gas and hydrogen (Chapter 7) and the blue shaded region represents hydrogen's use in cryogenic applications (Chapter 8-9).

The analysis of energy resources by modelling a path toward the hydrogen value was divided into three areas of individual focus highlighted in Figure 10.2. From the literature a decentralised hydrogen economy is anticipated (pink shaded region represented in Figure 10.2). A decentralised hydrogen energy storage system was investigated in further detail and compared to other energy storage technologies on an individual and integrated basis, (Chapter 4 and Chapter 5). A study on the concept of an integrated molten salt and hydrogen system for the secure and sustainable supply of energy and materials was included (Chapter 6). From the study of hydrogen's value in decentralised energy systems, hydrogen's value can benefit from an integrated approach with other storage technologies. RFB were considered and technical, environmental and economic benefits arise from integrated systems. Hydrogen's value as an energy storage is identified when operated as a buffer energy storage system. Furthermore, molten salt is a key enabler to the sustainable and secure supply of energy and materials and this system can be integrated with high temperature electrolysis and microwave plasma processing of natural gas creating a sustainable high temperature decentralised energy system with added material production. These research studies fulfilled the initial objectives of identifying the operation of a decentralised hydrogen storage system and value for supplying electricity to reduce grid energy and CO_2 emissions using SD modelling of various scenarios. The comparison of hydrogen storage with other storage technologies in individual and integrated systems to identify the potential value of integrated systems using SD modelling was also completed.

The second aspect, represented by the green shaded region in Figure 10.2, looked at the synergies that exist between natural gas and hydrogen (Chapter 7). Natural gas is the main feedstock for hydrogen production and it is anticipated natural gas and LNG will play an important role in the hydrogen economy. Both energy sources can benefit from the existing synergies. Natural gas benefits from lower CO_2 emissions when blended with hydrogen and hydrogen benefits from the use of natural gas methods of hydrogen production and technologies for aiding in the transition to the hydrogen economy. This study completed the objective to identify the various synergies between natural gas and the hydrogen economy and conclude on how natural gas can aid the emergence of the hydrogen economy.

Finally, the third aspect considered and researched is shaded blue in Figure 10.2 and represents liquid hydrogen and its use for cryogenic applications. Chapter 8 introduces the synergy between liquid hydrogen and the superconducting industry and Chapter 9 further explores this synergy in relation to integration with hospital energy systems for resource efficient buildings in sustainable cities. From the studies it is evident liquid hydrogen has an important role in the hydrogen economy and highlights the benefits of liquid hydrogen for sustainable cities and the superconducting industry. Chapter 8 and Chapter 9 fulfil the objective to investigate the synergy between liquid hydrogen and the superconducting industry and the impact a decentralised compressed and liquid hydrogen system can have on hospital energy and resource requirements.

A renewable decentralised hydrogen energy system integrated with liquefaction along with other complementary storage technology such as VRFB and molten salt,

Figure 10.2, is envisioned as a system that will allow the hydrogen economy to emerge. The concept in Figure 10.2 highlights hydrogen's value as an energy carrier and cryogen for a sustainable future.

The objectives formulated in Chapter 1 have been successfully researched and elaborated providing a base for the future intensive work on the emerging decentralised hydrogen economy.

Further Research

The study on various individual aspects of the hydrogen economy presented requires a more detailed analysis of each section to further understand the impact the hydrogen economy will have on global energy systems. Economic analysis is required to calculate expected costs of such integrated systems. Furthermore a complex system dynamic model including the integrated final conceptualised system in Figure 10.2 is required to detail the underlying interdependencies of each of the variables of the hydrogen economy.

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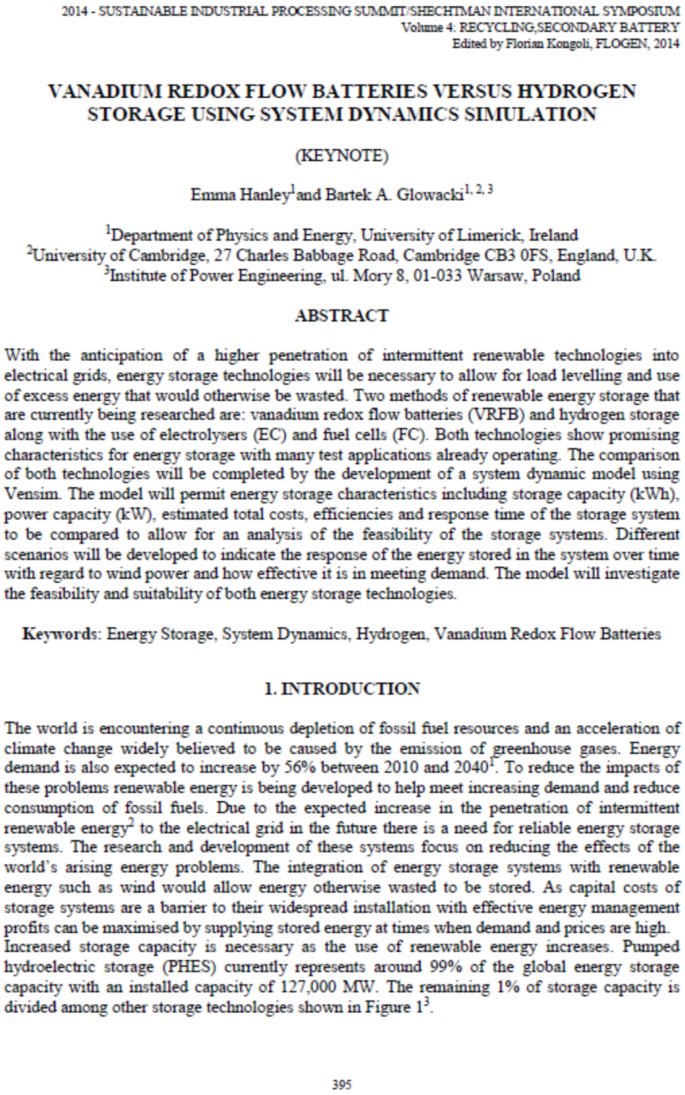
Appendix

i) Published Research Results in International Scientific Journals

[1] Emma S. Hanley, Bartek A. Glowacki, Vanadium redox flow batteries versus hydrogen storage using system dynamics simulation, Keynote paper for Shechtman International Symposium 2014 and published for the Volume 4, Recycling Secondary Batteries. Edited by Florian Kongoli, FLOGEN 2014. ISBN 978-0-9879974-9-4.



2014 - SUSTAINABLE INDUSTRIAL PROCESSING SUMMIT/SHECHTMAN INTERNATIONAL SYMPOSIUM
Volume 4: RECYCLING,SECONDARY BATTERY
Edited by Florian Kongoli, FLOGEN, 2014

VANADIUM REDOX FLOW BATTERIES VERSUS HYDROGEN STORAGE USING SYSTEM DYNAMICS SIMULATION

(KEYNOTE)

Emma Hanley[1] and Bartek A. Glowacki[1, 2, 3]

[1]Department of Physics and Energy, University of Limerick, Ireland
[2]University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, England, U.K.
[3]Institute of Power Engineering, ul. Mory 8, 01-033 Warsaw, Poland

ABSTRACT

With the anticipation of a higher penetration of intermittent renewable technologies into electrical grids, energy storage technologies will be necessary to allow for load levelling and use of excess energy that would otherwise be wasted. Two methods of renewable energy storage that are currently being researched are: vanadium redox flow batteries (VRFB) and hydrogen storage along with the use of electrolysers (EC) and fuel cells (FC). Both technologies show promising characteristics for energy storage with many test applications already operating. The comparison of both technologies will be completed by the development of a system dynamic model using Vensim. The model will permit energy storage characteristics including storage capacity (kWh), power capacity (kW), estimated total costs, efficiencies and response time of the storage system to be compared to allow for an analysis of the feasibility of the storage systems. Different scenarios will be developed to indicate the response of the energy stored in the system over time with regard to wind power and how effective it is in meeting demand. The model will investigate the feasibility and suitability of both energy storage technologies.

Keywords: Energy Storage, System Dynamics, Hydrogen, Vanadium Redox Flow Batteries

1. INTRODUCTION

The world is encountering a continuous depletion of fossil fuel resources and an acceleration of climate change widely believed to be caused by the emission of greenhouse gases. Energy demand is also expected to increase by 56% between 2010 and 2040[1]. To reduce the impacts of these problems renewable energy is being developed to help meet increasing demand and reduce consumption of fossil fuels. Due to the expected increase in the penetration of intermittent renewable energy[2] to the electrical grid in the future there is a need for reliable energy storage systems. The research and development of these systems focus on reducing the effects of the world's arising energy problems. The integration of energy storage systems with renewable energy such as wind would allow energy otherwise wasted to be stored. As capital costs of storage systems are a barrier to their widespread installation with effective energy management profits can be maximised by supplying stored energy at times when demand and prices are high.
Increased storage capacity is necessary as the use of renewable energy increases. Pumped hydroelectric storage (PHES) currently represents around 99% of the global energy storage capacity with an installed capacity of 127,000 MW. The remaining 1% of storage capacity is divided among other storage technologies shown in Figure 1[3].

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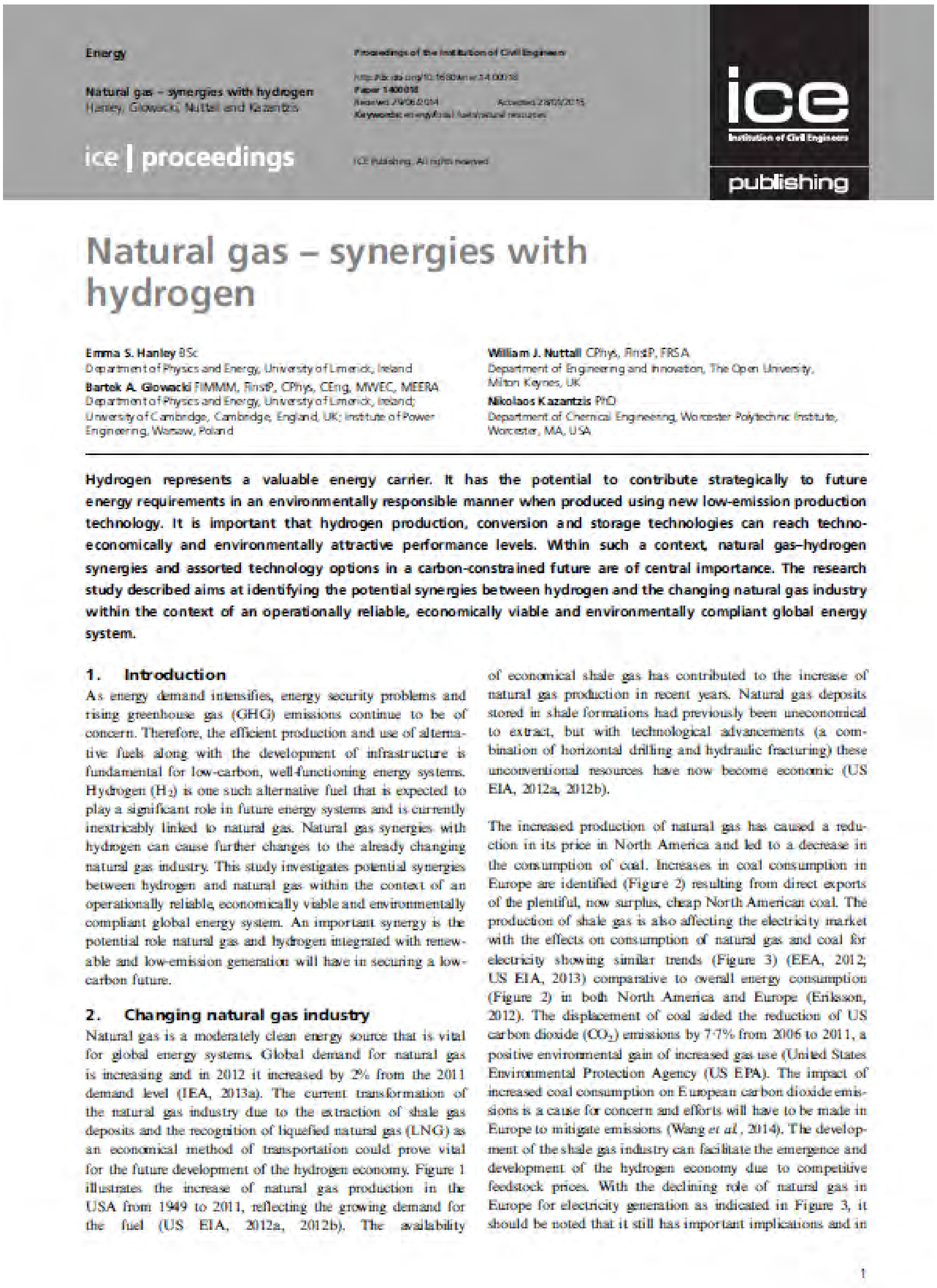

Energy

Natural gas – synergies with hydrogen
Hanley, Glowacki, Nuttall and Kazantzis

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Natural gas – synergies with hydrogen

Emma S. Hanley BSc
Department of Physics and Energy, University of Limerick, Ireland
Bartek A. Glowacki FIMMM, FInstP, CPhys, CEng, MWEC, MEERA
Department of Physics and Energy, University of Limerick, Ireland; University of Cambridge, Cambridge, England, UK; Institute of Power Engineering, Warsaw, Poland

William J. Nuttall CPhys, FInstP, FRSA
Department of Engineering and Innovation, The Open University, Milton Keynes, UK
Nikolaos Kazantzis PhD
Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA, USA

Hydrogen represents a valuable energy carrier. It has the potential to contribute strategically to future energy requirements in an environmentally responsible manner when produced using new low-emission production technology. It is important that hydrogen production, conversion and storage technologies can reach techno-economically and environmentally attractive performance levels. Within such a context, natural gas–hydrogen synergies and assorted technology options in a carbon-constrained future are of central importance. The research study described aims at identifying the potential synergies between hydrogen and the changing natural gas industry within the context of an operationally reliable, economically viable and environmentally compliant global energy system.

1. Introduction

As energy demand intensifies, energy security problems and rising greenhouse gas (GHG) emissions continue to be of concern. Therefore, the efficient production and use of alternative fuels along with the development of infrastructure is fundamental for low-carbon, well-functioning energy systems. Hydrogen (H_2) is one such alternative fuel that is expected to play a significant role in future energy systems and is currently inextricably linked to natural gas. Natural gas synergies with hydrogen can cause further changes to the already changing natural gas industry. This study investigates potential synergies between hydrogen and natural gas within the context of an operationally reliable, economically viable and environmentally compliant global energy system. An important synergy is the potential role natural gas and hydrogen integrated with renewable and low-emission generation will have in securing a low-carbon future.

2. Changing natural gas industry

Natural gas is a moderately clean energy source that is vital for global energy systems. Global demand for natural gas is increasing and in 2012 it increased by 2% from the 2011 demand level (IEA, 2013a). The current transformation of the natural gas industry due to the extraction of shale gas deposits and the recognition of liquefied natural gas (LNG) as an economical method of transportation could prove vital for the future development of the hydrogen economy. Figure 1 illustrates the increase of natural gas production in the USA from 1949 to 2011, reflecting the growing demand for the fuel (US EIA, 2012a, 2012b). The availability of economical shale gas has contributed to the increase of natural gas production in recent years. Natural gas deposits stored in shale formations had previously been uneconomical to extract, but with technological advancements (a combination of horizontal drilling and hydraulic fracturing) these unconventional resources have now become economic (US EIA, 2012a, 2012b).

The increased production of natural gas has caused a reduction in its price in North America and led to a decrease in the consumption of coal. Increases in coal consumption in Europe are identified (Figure 2) resulting from direct exports of the plentiful, now surplus, cheap North American coal. The production of shale gas is also affecting the electricity market with the effects on consumption of natural gas and coal for electricity showing similar trends (Figure 3) (EEA, 2012; US EIA, 2013) comparative to overall energy consumption (Figure 2) in both North America and Europe (Eriksson, 2012). The displacement of coal aided the reduction of US carbon dioxide (CO_2) emissions by 7·7% from 2006 to 2011, a positive environmental gain of increased gas use (United States Environmental Protection Agency (US EPA). The impact of increased coal consumption on European carbon dioxide emissions is a cause for concern and efforts will have to be made in Europe to mitigate emissions (Wang *et al.*, 2014). The development of the shale gas industry can facilitate the emergence and development of the hydrogen economy due to competitive feedstock prices. With the declining role of natural gas in Europe for electricity generation as indicated in Figure 3, it should be noted that it still has important implications and in

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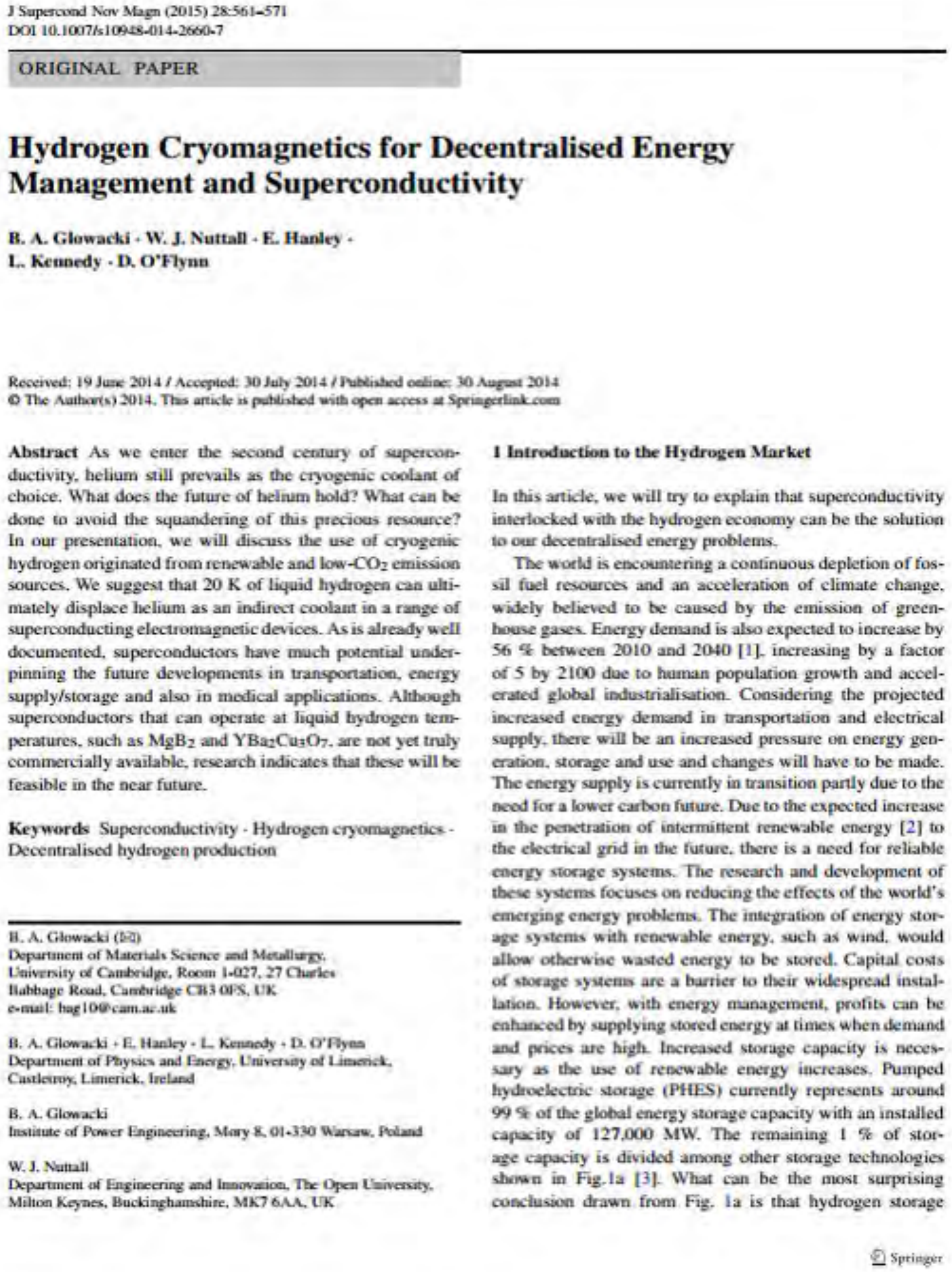

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ORIGINAL PAPER

Hydrogen Cryomagnetics for Decentralised Energy Management and Superconductivity

B. A. Glowacki · W. J. Nuttall · E. Hanley ·
L. Kennedy · D. O'Flynn

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Abstract As we enter the second century of superconductivity, helium still prevails as the cryogenic coolant of choice. What does the future of helium hold? What can be done to avoid the squandering of this precious resource? In our presentation, we will discuss the use of cryogenic hydrogen originated from renewable and low-CO_2 emission sources. We suggest that 20 K of liquid hydrogen can ultimately displace helium as an indirect coolant in a range of superconducting electromagnetic devices. As is already well documented, superconductors have much potential underpinning the future developments in transportation, energy supply/storage and also in medical applications. Although superconductors that can operate at liquid hydrogen temperatures, such as MgB_2 and $YBa_2Cu_3O_7$, are not yet truly commercially available, research indicates that these will be feasible in the near future.

Keywords Superconductivity · Hydrogen cryomagnetics · Decentralised hydrogen production

1 Introduction to the Hydrogen Market

In this article, we will try to explain that superconductivity interlocked with the hydrogen economy can be the solution to our decentralised energy problems.

The world is encountering a continuous depletion of fossil fuel resources and an acceleration of climate change, widely believed to be caused by the emission of greenhouse gases. Energy demand is also expected to increase by 56 % between 2010 and 2040 [1], increasing by a factor of 5 by 2100 due to human population growth and accelerated global industrialisation. Considering the projected increased energy demand in transportation and electrical supply, there will be an increased pressure on energy generation, storage and use and changes will have to be made. The energy supply is currently in transition partly due to the need for a lower carbon future. Due to the expected increase in the penetration of intermittent renewable energy [2] to the electrical grid in the future, there is a need for reliable energy storage systems. The research and development of these systems focuses on reducing the effects of the world's emerging energy problems. The integration of energy storage systems with renewable energy, such as wind, would allow otherwise wasted energy to be stored. Capital costs of storage systems are a barrier to their widespread installation. However, with energy management, profits can be enhanced by supplying stored energy at times when demand and prices are high. Increased storage capacity is necessary as the use of renewable energy increases. Pumped hydroelectric storage (PHES) currently represents around 99 % of the global energy storage capacity with an installed capacity of 127,000 MW. The remaining 1 % of storage capacity is divided among other storage technologies shown in Fig.1a [3]. What can be the most surprising conclusion drawn from Fig. 1a is that hydrogen storage

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B. A. Glowacki (✉)
Department of Materials Science and Metallurgy,
University of Cambridge, Room 1-027, 27 Charles
Babbage Road, Cambridge CB3 0FS, UK
e-mail: bag10@cam.ac.uk

B. A. Glowacki · E. Hanley · L. Kennedy · D. O'Flynn
Department of Physics and Energy, University of Limerick,
Castletroy, Limerick, Ireland

B. A. Glowacki
Institute of Power Engineering, Mory 8, 01-330 Warsaw, Poland

W. J. Nuttall
Department of Engineering and Innovation, The Open University,
Milton Keynes, Buckinghamshire, MK7 6AA, UK

ii) Research Results Submitted for Publication

1. Emma S. Hanley, Bartek A. Glowacki, William J. Nuttall, Nikolas Kazantzis, A systems-based approach to hydrogen production methods and the emergence of the hydrogen economy. Special Issue for the International Journal of Hydrogen Energy.

2. Emma S. Hanley, George Amarandei, Bartek A. Glowacki, The potential of redox flow batteries and hydrogen as integrated storage for decentralised energy systems. ACS Energy and Fuels.

3. Emma S Hanley, James Codd, Nigel Reams, Jake, Bracken, R Vasant Kumar, Greg Doughty, Luca Turchetti, A Grozdanov, A Dimitrov, Baretk A Glowacki, Study of decentralised resource efficient system with a sustainable supply of materials and energy using molten salt. Journal of Resources, Conservation and Recycling.

iii) Research Results Presented at International Conferences

1. Emma S. Hanley, Bartek A. Glowacki, Stage 1 - System dynamic comparison of decentralised wind energy storage; compressed hydrogen vs vanadium redox flow batteries. Poster presentation at the 32nd International Conference of the System Dynamics Society 20-24 July 2014.

2. Emma S. Hanley, William J. Nuttall, Bartek A. Glowacki, Integration of the hydrogen economy in smart cities - transport and hospital system solutions. Presented at the 15th International Conference on Technology, Policy and Innovation, Milton Keynes, UK, 17-19 June 2015.

3. Emma S. Hanley, Bartek A. Glowacki, William J. Nuttall, Nikolas Kazantzis, A systems-based approach to hydrogen production methods and the emergence of the hydrogen economy. Presented at the 1st International conference on Hydrogen, Aveiro, Portugal, 20-22 July 2015.