Design and prototyping of an ionic liquid piston compressor as a new generation of compressors for hydrogen refueling stations



DTU Mechanical Engineering Department of Mechanical Engineering



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PhD Thesis

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Preface

The present thesis is submitted as a partial fulfilment of the requirements for the degree of Philosophiae Doctor (Ph.D.) at the Technical University of Denmark (DTU).

The thesis was completed at the Section of Thermal Energy, Department of Mechanical Engineering. The work was carried out from 1st of December 2012 to 31st of May 2017 (including 1 year maternity leave and 5 month research assistant) under the supervision of Associate Professor Masoud Rokni, and the co-supervision of Associate Professor Brian Elmegarrd.

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The thesis is written in the form of a monograph and includes all the relevant publications produced in the time frame of the present research study.

Copenhagen, May 31st, 2017 Nasrin Arjomand Kermani

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Abstract

The thesis presents design, modeling, and fabrication of a new compressor technology that involves an ionic liquid piston as a replacement for the solid piston in the conventional reciprocating compressors to compress hydrogen in hydrogen refueling stations. The motivation comes from the need to achieve more flexible and efficient compressors with longer life spans in hydrogen stations. This can eventually lead to a lower hydrogen delivery cost and faster penetration of hydrogen fuel cell vehicles into the market.

A thermodynamic model simulating a single-compression stroke is developed to investigate the heat transfer phenomena inside the compression chamber; the system performance is evaluated, followed by the design process. The model is developed based on the mass and energy balance of the hydrogen, and liquid bounded by the wall of the compression chamber. Therefore, at each time step and positional node, the model estimates the pressure and temperature of the hydrogen and liquid, the temperature of the compression chamber wall, and the amount of heat extracted from the hydrogen directly at the interface between the hydrogen and liquid, and through the wall. The results indicate that depending on the heat transfer correlation, the hydrogen temperature reduces slightly between 0.2 and 0.4% compared to the adiabatic case, at 500 bar. The main reasons for the small temperature reduction are the large wall resistance and the small contact area at the interface. Moreover, the results of the sensitivity analysis illustrate that increasing the total heat transfer coefficients at the interface and the wall, as well as compression time, play key roles in reducing the hydrogen temperature. Further optimization and increasing the total heat transfer coefficient at the interface (10000 times) or at the wall (200 times), leads to 22 % or 33% reduction of the hydrogen temperature, compared to the adiabatic case, at 500 bar, during 3.5 seconds compression, respectively.

A suitable ionic liquid is selected as the most reliable replacement for the solid piston in the conventional reciprocating compressors. Ionic liquids are room temperature salts which have very low vapor pressures. The ability to tune the physiochemical properties of ionic liquids by varying the cation-anion combinations is the feature of these liquids that make them as promising candidates to replace the solid piston. However, due to a large number of available combinations for ionic liquids, it is essential to systematically investigate their performance for a particular application and narrow down the final choice. In this regard, certain criteria are determined for our specific application. The roles of the most commonly used cations and anions, as well as the effect of temperature are comprehensively reviewed to identify the most suitable ionic liquids that can fulfill our requirements. Hence, the options are narrowed down to five ionic liquids with triflate and bis(trifluoromethylsulfonyl)imide as the anion choices and three different cation types of imidazolium-, phosphonium-, and ammonium-based as the cation choices. Finally the ionic liquid: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is recommended as the best candidate that can be safely used as a replacement for the solid piston in the conventional reciprocating compressors for compressing hydrogen in the hydrogen refueling stations.

In addition, the corrosion behavior of various commercially available stainless steels and nickelbased alloys as possible construction materials for the components which are in direct contact with the selected ionic liquids is evaluated. The results show a very high corrosion resistance and high stability for all of the alloys tested in any of the five selected ionic liquids. The stainless steel alloy, AISI 316L, with a high corrosion resistance and the lowest cost is selected as a material for all the components in direct contact with the ionic liquid, in the designed ionic liquid hydrogen compressor.

The new compressor consists of three main parts, namely pneumatic, hydraulic, and custom-designed hydraulic to pneumatic transformer, which work together to compress hydrogen. The proposed design addresses the limitations of the current technology and previously designed compressors using the liquid piston concept and ionic liquid, by introducing a custom-designed hydraulic to pneumatic transformer. As proof of concept, a prototype for compression of hydrogen from 100 to 300 bar is built, and a detailed procedure of the design, fabrication, and control of the prototype is described in the presented work.

The new compressor design has high potential to be used as an alternative to the conventional reciprocating compressors in hydrogen refueling stations, as it provides a simpler design with lower manufacturing costs, higher efficiency, much less sliding friction, possibility of internal cooling, higher functional reliability and less maintenance.

Dansk resumé

Denne afhandling præsenterer konstruktion, modellering og fremstilling af en ny kompressor, som til kompression af brint i brintladestationer benytter ionvæskestempel i stedet for en traditionel frem- og tilbagegående kompressor med fast stempel. Motivationen for denne udvikling er behovet for en mere fleksibel og effektiv kompressor med længere levetid. Dette kan til slut føre til billigere brintproduktion og dermed til hurtigere udbredelse af brændselscellekøretøjer på markedet.

En termodynamisk model der simulerer et enkelt kompressionsslag, er blevet udviklet for at undersøge varmeovergangsfænomener i kompressionskammeret. Systemets ydelse er vurderet som udgangspunkt for konstruktionsprocessen. Modellen er udviklet på grundlag af masse- og energibalancer for brint, for væsken og for væggen i kompressionskammeret. For hvert tidsskridt og for hvert positionsknudepunkt estimerer modellen derfor tryk og temperatur af brint og væske, temperaturen af kompressionskammerets væg, varmemængden der udtrækkes direkte ved skillefladen mellem brint og væske, og gennem væggen. Resultaterne viser at, afhængig af den benyttede varmeovergangskorrelationen, reduceres brinttemperaturen ved 500 bar lidt, mellem 0,2% og 0,4%, i forhold til det adiabatiske tilfælde. Hovedårsagen til den lille størrelse af temperaturreduktionen er den store modstand i væggen og det lille skillefladeareal. Desuden resultaterne af en følsomhedsanalyse, at en forøgelse af den illustrerer totale varmeovergangskoefficient ved skilleflade og væg, såvelsom kompressionstiden spiller en afgørende rolle for at reducere brinttemperaturen. Yderligere optimering og forøgelse af den totale varmeovergangskoefficient ved skillefladen (10.000 gange) eller ved væggen (200 gange) fører ved 500 bar og ved 3,5 sekunders kompression til 22% hhv. 33% reduktion af brinttemperaturen i forhold til det adjabatiske tilfælde.

En ionvæske er blevet udvalgt som det mest pålidelige valg til erstatning for stemplet i en sædvanlig frem-og tilbagegående kompressor. Ionvæsker er smeltede salte som har forsvindende damptryk og endog smeltepunkt under 0 grad C. Muligheden for at tilpasse ionvæskens fysisk-kemiske egenskaber ved at kombinere kationer og anioner på forskellige måder, er det der gør disse væsker lovende kandidater til at erstatte det faste stempel. På grund af et stort antal mulige kombinationer er det imidlertid væsentligt systematisk at undersøge deres anvendelighed i givne situationer - for at indsnævre de endelige valgmuligheder. Udfra dette hensyn er der opstillet kriterier gældende for en bestemt anvendelse. Med henblik på at finde de ionvæsker der bedst tilfredsstiler de opstillede krav, er der skabt oversigt over de mest almindeligt anvendte kationer og anioner, deres anvendelsesmuligheder og mulige driftstemperaturer. Således blev valgmulighederne begrænset til fem ionvæsker med triflate og bis(trifluormethylsulfonyl)imid som anion-muligheder og tre forskellige kation-muligheder: imidazolium-baseret, phosphonium-baseret og anmonium-baseret. Det endelige valg faldt på 1-ethyl-3-methylimidazolium bis (trifluormethylsulfonyl) imid.

Med udgangspunkt i deres korrosinsegenskaber blev forskellige kommercielle rustfaste stål og nikkel-baserede legeringer vurderet som mulige konstruktionsmaterialer for komponenter der er i direkte kontakt med en af de valgte ionvæsker. Alle de undersøgte legeringer viste høj korrosionsbestandighed overfor de valgte ionvæsker. Valget faldt på det rustfaste stål AISI 316L, som har en høj korrosionsbestandighed og samtidig er det billigste.

Den nye kompressor kommer således til at bestå af tre dele: en pneumatisk del, en hydraulisk del og en specialkonstrueret hydraulisk-pneumatisk transformer. Det foreslåede design er egnet til at overvinde begrænsningerne i såvel traditionel teknologi som i nykonstruerede kompressorer der benytter væskestempel-konceptet og ionvæske. Dette opnås ved at indføre en specialkonstrueret hydraulisk-pneumatisk transformer. For at dokumentere konceptets bæredygtighed blev der fremstillet en prototype til at komprimere brint fra 100 bar til 300 bar. Den detaljerede procedure for konstruktion, fremstilling og afprøvning af prototypen er beskrevet i rapporten.

Den nye kompressorkonstruktion anbefales i stedet for den traditionelle frem-og tilbagegående stempelkompressor i brintladestationer, da den har et enklere design, lavere fremstillingsomkostninger, ingen stempelfriktion, mulighed for intern køling, højere pålidelighed og mindre krav til vedligehold.

List of publication

Journal papers

- 1. Arjomand Kermani N, Rokni M. Heat transfer analysis of liquid piston compressor for hydrogen applications. Int J Hydrogen Energy 2015;40:11522–9. doi:10.1016/j.ijhydene.2015.01.098.
- 2. Arjomand Kermani N, Petrushina I, Nikiforov A, Jensen JO, Rokni M. Corrosion behavior of construction materials for ionic liquid hydrogen compressor. Int J Hydrogen Energy 2016;41:16688–95. doi:10.1016/j.ijhydene.2016.06.221.
- 3. Arjomand Kermani N, Petrushina I, Nikiforov A, Rokni M. Metal alloys for the new generation of compressors at hydrogen stations: Parametric study of corrosion behavior. Renew Energy 2018;116:805–14. doi:10.1016/j.renene.2017.08.066.
- 4. Arjomand Kermani N, Petrushina I, Rokni M. Evaluation of ionic liquids as candidates for replacement of solid piston in conventional hydrogen reciprocating compressors: A Review. Submitted to Renewable & Sustainable Energy Reviews 2017.
- 5. Arjomand Kermani N, Rokni M. Design and fabrication of an ionic liquid piston hydrogen compressor. Submitted to Mechanical Desegin (ASME)-Jurnal 2017.

Peer-review conference papers

1. Arjomand Kermani N, Rokni M. Heat analysis of liquid piston compressor for hydrogen applications. 20 th World Hydrog. Energy Conf. (WHEC 2014), Gwangju Metrop. City, South Korea, Gwangju, South Korea: 2014.

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Nomenclature

Abbreviations

Α	Cross-sectional area, m^2
D	Diameter, m
E_{corr}	Corrosion potential, mV
F	Force, N
f	Factor,-
fr	Frequency, Hz
Н	Enthalpy, J
h	Convective gas or liquid heat transfer coefficient, $W/m^2 K$
<i>i</i> _{corr}	Corrosion current density, mA/cm^2
K	Thermal conductivity, W/mK
L	Length, m
Μ	Total mass, kg
ṁ	Mass flow rate, kg/s
Nu	Nusselt-number, -
n	Number of nodes, -
р	Pressure, Pa or bar
Pr	Prandtl-number, -
Q	Heat, J
Ż	Rate of heat transfer, W
Re	Reynolds-number, -
S(t)	Piston stroke, m
Т	Temperature, K or $^{\circ}C$
t	Time, s

t _w	Wall thickens, m
U	Internal energy, J
UA	Total heat transfer coefficient, W/K
V	Volume, m^3
Vl	Velocity, m/s
<i>v</i>	Volume flow rate, m^3/s
W	Work, J

CSD	Compression, Storage, and Dispensing
DOE	U.S. Department of Energy
DTA	Differential Thermal Analysis
ESM	Electron Scanning Microscopy
NREL	National Renewable Energy Laboratory
TGA	Thermal Gravimetric Analysis
VG	Viscosity Grads
VI	Viscosity Index

Greek Letters

ρ	Density, kg/m^3
μ	Dynamic viscosity, kg/ms or $mPa.s$
V	Kinematic viscosity, m^2/s
η	Efficiency
Δp	Pressure drop across the pump, Pa or bar

Subscripts

0	Property at the inlet condition
amb	Ambient
axial	Axial distance inside compression chamber
comp-ch	Compression chamber
comp	Compression
el	Electromotor
gas	Gas
IL	Ionic liquid
in	Inlet
int	Interface between gas and liquid
int erface	Interface between gas and liquid
liq	Liquid
oil	Hydraulic oil
out	Outlet
ритр	Pump
sur	Surrounding
w	Wall

1. Introduction

1.1 Motivation

Many environmental analyses show a strong connection between carbon dioxide (CO_2) emissions, due to fossil fuel consumption, and global warming [1]. Therefore, over the last several decades, attention has been given worldwide towards sustainable solutions that can reduce CO_2 emissions. Currently, more than 95% of all global energy in the transport sector is supplied by fossil fuels. This sector is responsible for over 23% of all energy-related CO_2 emissions [2,3]. In this context, fuel cell vehicles have gained attention as a long-term solution that would enable the use of renewable energy for transportation with zero carbon and particle emission [4]. It is expected that with a 25% share of fuel cell electric vehicles on the roads by 2050, the cumulative transport-related carbon emissions will be reduced by up to 10% [5].

To establish a solid ground for the significant market penetration of fuel cell vehicles, challenges such as fast refueling, long driving range and high energy efficiency must be overcome. To produce fuel cell vehicles with a driving range that is comparable with the current technologies based on fossil fuels, on-board high-pressure hydrogen storage seems to be a promising option. The high-pressure storage of hydrogen in tanks requires the compression of hydrogen to more than 700 bar at refueling stations and the cooling of hydrogen to approximately -40 °C before refueling [6].

Compressors are costly components in hydrogen refueling stations. Current compressor designs have low efficiencies and high capital and operating costs [7–9]. On an average, compression processes consume 11.3% of the energy contained in hydrogen fuel [7]. The National Renewable Energy Laboratory of the U.S. (NREL) reported that based on data from 2005 to 2011 provided by the U.S. Department of Energy (DOE), the hydrogen compressor is the second component causing most of the problems in refueling stations with 18% of the events, after system control and safety with 22% of the maintenance events [7]. Furthermore, it has been reported that hydrogen compressors are the leading causes of unscheduled maintenance labor hours with 28% of the total, and are responsible for 28% of safety near-miss events and 25% of hydrogen leaks [7]. A non-functioning hydrogen compressor leads to incomplete fills, slow fills, or station unavailability, and consequently, a significant increase in hydrogen compression, storage, and dispensing costs in hydrogen delivery pipelines and production [8].

There are three overall categories of compressors for compressing hydrogen in hydrogen refueling stations. Each category contains several different types of compressors. The list below briefly describes the main categories and the corresponding subdivisions.

Positive displacement Compressors:

Positive displacement compressors work by reducing a closed volume of hydrogen inside the compression chamber in order to compress it. Different types of compressors in this category are

Reciprocating compressors

The reciprocating compressors use a moving piston inside the compression chamber to compress hydrogen. They are adoptable to any type of hydrogen supply and are applicable for all kinds of hydrogen refueling stations [10]. This type of compressors is often used for indirect refueling over high pressure buffer storages or booster refueling [10]. However, there is also possibility of using them for direct refueling. The only disadvantage of direct refueling is a requirement for huge compressor with high loads [10]. An example of a reciprocating compressor for compressing hydrogen to high pressures can be seen in [11].

Diaphragm compressors

The diaphragm compressors use a flexing diaphragm with hydrogen on one side and hydraulic oil on the other side. The hydraulic side includes a motor-driven crankshaft that reciprocates a solid piston in the hydraulic oil. The piston pulses the hydraulic oil against the lower side of the diaphragm, hence pushing the diaphragm towards the hydrogen side and pressurizing hydrogen. This type of compressor is used for applications with high gas purity requirements, both for indirect refueling and as a booster compressor in 350 and 700 bar hydrogen refueling stations [10]. However, the low delivery rate per unit of compressor brings up a requirement for several diaphragm compressors in the refueling stations with a large hydrogen demand [10]. An example of a diaphragm compressor for compressing hydrogen to high pressures can be seen in [12,13].

Ionic liquid compressor (Presented by Linde)

The ionic liquid compressor works the same as reciprocating compressors. The main difference is substituting the solid piston of the reciprocating compressor with an ionic liquid in the ionic liquid compressor. Ionic liquids are room temperature salts with very low vapor pressures that can act the same as a solid piston for compressing hydrogen inside the compression chamber. The development of this technology has been started in 2002 by Linde [14]. This type of compressors is used for indirect or booster refueling in 350 and 700 bar hydrogen refueling stations [10]. The Linde ionic liquid compressor installations can be seen in [14].

Cryogenic pumps

The cryogenic pumps combine the advantages of liquid hydrogen pumps and gaseous hydrogen compressors. They use liquid hydrogen at very low temperatures which turns to high pressure cold hydrogen gas during the pressurization process. This type of pump is used for both indirect refueling over high pressure and direct refueling in hydrogen refueling stations [10].

Dynamic compressors:

Dynamic compressors use a set of rotating blades to accelerate the flowing gas into a high velocity, which eventually resulting as the rise in the pressure. Centrifugal compressor is a type of dynamic compressor which is used for compression of hydrogen in hydrogen refueling stations up to medium pressure, 500 bar [15]. In this type of compressor the transferred energy to the flowing gas for rising up the pressure comes from a change in the centrifugal forces acting on the gas.

Thermal and electrochemical compressors:

Electrochemical compressors

The electrochemical compressors use electricity to separate hydrogen into protons and electrons, and transport protons across a membrane before merging with the negative loaded hydrogen atoms at high pressures. An example of a small scale electrochemical compressor, developed in a DOE hydrogen research program, can be seen in [16].

Metal hydride compressors

The metal hydride compressors absorb hydrogen at low temperatures and pressures, later thermally heated, and release hydrogen at higher pressures. This type of compressor has a low pressure ratio within a reasonable operating temperature and cycle production which requires a multistage compression correspondingly both "low-temperature "and "high-temperature" metal hydrides for the heat management applications [17–19]. An example of a metal hydride compressor can be seen in [20].

Table 1.1 shows the general characteristics of different types of compressors for compressing hydrogen over 700 bar.

	Reciprocating Diaphragm Ionic liquid Metal hydride Electr					
	compressors	compressors	compressor	compressors	compressors	
Delivery rate	Medium [10]	Low [10]	Medium [10] (Linde claimed at 60 g/s at 900 bar [21])	Low to medium (Depends on a phase diagram of hydrogen –metal system and varies significantly from alloy to alloy [17])	Very low (As an example: 453 g/day [16])	
Maximum pressure	High [11]	High [12,13]	High (Linde claimed at maximum operating pressure = 1000 bar [21])	Medium to high [17,18,22]	Medium to high [16]	
Specific energy consumption	High [7,10]	High [7,10]	Claimed to be low [10,23]	Claimed to be low [18] (In the case of available waste heat, the energy consumption is almost zero [22])	Claimed to be low [24]	

Table 1.1 - General characteristics of different types of compressors

Volumetric efficiency	Not specifically mentioned (Generally, low efficiency has been reported for this type of compressors [7–9])	Low to high (Claimed to be 87 to 94% [25] in designs made by PDCmachines [13])	Claimed to be high (Linde claimed at 100% volumetric efficiency [26])	Claimed to be high [27]	Claimed to be high (Hydrogen recovery efficiency > 95% [16])
Capital cost	Medium to high[7–10]	Medium to high [7–10]	Claimed to be low [10,23]	Can be high (Mass production can affect the price [17])	Not specifically mentioned (Depends on the number and cost of the cells [16])
Maintenance and operating cost	High[7–10]	Medium to high [7–10]	Low [23,28]	Claimed to be low [18]	Not specifically mentioned
Status	Well known technology (>50 years)	Well known technology (>50 years)	Ongoing development (Monopoly of one supplier ,Linde [14])	Ongoing development	Ongoing development
Design aspects*	 Complicated design Numerous moving parts Complicated sealing system High sliding friction Risk of hydrogen contamination No possibility of internal cooling 	 Complicated design Numerous moving parts Medium sliding friction Risk of hydrogen contamination No possibility of internal cooling 	 + Simple design ± Low number of moving parts ± Very low sliding friction + High purity of hydrogen delivery + Possibility of internal cooling 	 + Simple design + No moving part + No sliding friction + High purity of hydrogen delivery + compactness - Sensitive to hydrogen impurities - Performance depends on the metal hydride material and thermodynamic of metal – hydrogen systems [17] 	+Simple design +No moving part + No sliding friction + High purity of hydrogen delivery + an easy scalable technology - Performance depends on the nature of reactions

*The points illustrate with "-" present the negative design aspects of the compressor types, the point illustrate with "+" present the positive design aspects of the compressor types, and the points illustrate with "±" present the positive design aspects of the ionic liquid compressor compared to the reciprocating and diaphragm compressors and the negative design aspects of the ionic liquid compressor compared to the metal hydride and electrochemical compressors.

The reciprocating compressor is one of the most commonly used type of compressors in hydrogen stations [9]. Conventional reciprocating compressors can cause a lot of problems because of the following: complicated design due to numerous moving parts; complicated sealing system and problems related to hydrogen contamination/leakages resulting in lack of product purity, low durability of piston sealing in dry-running compressors, reduction of volumetric efficiency, and explosion issues; high sliding friction; high manufacturing costs; high maintenance hours, and short life spans; and finally, there is no possibility of internal cooling during the compression process, leading to a reduction in the overall efficiency, requirement for high-strength metallic materials that are compatible with hydrogen at high temperatures, and requirement for pre-cooling of hydrogen before refueling.

Therefore, innovative compression technologies with better performance, higher efficiency, higher hydrogen quality (oil-free designs), and longer life spans are crucial for reducing the total cost of hydrogen and achieving a significant market penetration of hydrogen fuel cell vehicles [7–9].

Liquid piston compressor is a reliable approach in this regard. Substituting the solid piston with liquid can address many of the restrictions faced by most conventional reciprocating compressors. A significant improvement in efficiency and a 50% reduction in cost compared to a conventional hydrogen compressor with the same flow rate and compression ratio has been reported for a single prototype unit that uses hydraulic oil to compress hydrogen [29]. Nevertheless, selecting the appropriate liquid is a fundamental choice in this regard. Some liquids may decompose at elevated temperature, as reported previously for hydraulic oils [29]. Also the ionic liquid compressor presented by Linde [16] seems a promising compressor. Linde claimed at volumetric efficiency of 100% [26]. However, so far, this technology has been limited to the monopoly of a single supplier (Linde [16]), and although the type of ionic liquid and the detailed design of mechanical components have significant effect on the performance of the compressor, they have never been specifically described by Linde.

1.2 Thesis statement

The overall aim of this study is to propose a novel compression technology that can overcome the limitations of the existing technologies. To this end, the project investigates the performance of the liquid piston compressor technology, for compression of hydrogen in hydrogen refueling stations with respect to:

- Heat transfer phenomena inside the compression chamber and the possibility of internal cooling and reduction of the hydrogen outlet temperature
- Selection of the most appropriate and reliable liquid as a replacement for the solid piston
- Design and fabrication of a prototype as proof of concept

1.3 Thesis outline

The thesis contains 5 chapters and 2 appendixes:

Chapter 1 is the introduction containing the motivation for the study, the thesis statement, and the thesis outline.

Chapter 2 presents a detailed thermodynamic model built to investigate the heat transfer phenomena inside the compression chamber. The model includes a sensitivity analysis to find the critical parameters that could maximize the amount of heat which can be extracted from the compressed gas. The obtained results in this chapter are used to evaluate the system behavior, followed by the design process and selection of the components.

Chapter 3 covers a comprehensive review on the roles of ionic liquid cations and anions, as well as the effect of temperature, in order to identify the best ionic liquid candidate as a replacement for the solid piston that can fulfill the requirements.

Chapter 4 presents the corrosion study of several commercially available stainless steels and nickelbased alloys at 23 and 80 °C, as possible construction materials in the five ionic liquids which have been selected in chapter 3. The roles of ionic liquid cations and anions, viscosity and water absorption on the corrosion resistance of the alloys in contact with the selected ionic liquids are discussed.

Chapter 5 describes the design procedure consisting of three main parts, namely pneumatic, hydraulic and custom-designed hydraulic to pneumatic transformer. The advantages of the ionic liquid compared to the hydraulic oil and water as replacement for the solid piston are discussed. The type of components selected for each system and the corresponding drawings and pictures are presented. Finally the procedure related to control of the system is explained.

Chapter 6 summarizes the most important findings in the thesis and gives suggestions for further work within the field.

<u>Appendix A</u> contains further information on the corrosion study of the alloys in contact with the selected ionic liquids, explained in chapter 4.

Appendix B contains one of the EES Codes for the thermodynamic model explained in chapter 2

2. Heat transfer analysis of the liquid piston compression process

2.1 Introduction

Novel ideas are required to improve the functionality of conventional reciprocating compressors and make them more feasible from energy and cost point of view. Liquid piston compressor is a unique approach that can be applied to explore such prospects. As indicated by its name, in this approach the solid piston used in the conventional reciprocating compressors is replaced by a liquid piston.

The liquid piston concept was applied for the first time in an internal combustion engine known as Humphrey pump in 1906 [30]. However, to our knowledge, very few studies have investigated the heat transfer phenomena inside the compression chamber of the liquid piston compressors.

A liquid piston compression was proposed as a concept to improve the behavior and efficiency of the gas compression and expansion [31]. In this study, the compression chamber was divided into several small bores to improve the surface area to volume ratio in the working chamber [31]. Similar methodology as [31] has been used in [32], for developing a numerical method (using finite difference method), to investigate the theoretical efficiency of the liquid piston and recognize the optimal system characteristics.

Moreover, a thermodynamic model for a two stage liquid piston compressor, applied in the compressed air energy storage systems has been developed previously [33]. However, none of these studies considered the real properties of the operating gas and liquid, the heat transfer at the interface between gas and liquid, and the role of the compressor wall resistance [31,33].

Several other studies have investigated the trajectories of the compressor/expander that lead to optimal tradeoff between efficiency and power in the compressed air energy storage systems [34–37]. Although, the heat transfer model plays an important role in finding the optimal trajectory, a detailed heat transfer model has never been used in any of the mentioned studies.

The main objective of this chapter is to develop a detailed heat transfer model which covers most of the shortcomings which have not been covered in the previous studies mentioned above. The model investigates the heat transfer phenomena inside the compression chamber of the liquid piston compressor and points out the critical parameters that could maximize the amount of heat which can be extracted from the compressed gas for further optimization. The developed model is followed by the design process and selection of components explained in the next chapters.

2.2 Methodology

A single-compression stroke of a reciprocating liquid piston gas compressor is simulated to predict the heat transfer to the liquid, wall, and surrounding, and accordingly estimate the system pressure and temperature. Figure 2.1 presents the cross-sectional view of a compression chamber and outlines its components and schematic heat transfer mechanisms among those. As illustrated in figure 2.1, it is assumed that at each time step, the properties of liquid and gas are distributed uniformly, whereas the wall is discretized into n positional nodes. A node system can be defined with "i" as the subscript identifying a node at which the heat transfer occurs. At each time step the number of nodes in contact with liquid and gas is determined; consequently the wall temperature at each positional node is estimated. The model is built based on the properties of hydrogen, considering it as a real gas, and water, using EES Software [38]. All the properties of water and hydrogen are calculated at each time step for the estimated temperature and pressure.

The application of this analysis is a single stage compressor to compress hydrogen for the hydrogen refueling stations. The compressor is intake hydrogen at 100 bar and 303 K and compresses it with a pressure ratio of 5:1 to 500 bar when running at a compression frequency of 2.5 Hz. The compression chamber is a cylinder made of stainless steel (AISI 316) with the wall thickness of 0.022 m. Inside diameter, and the stroke length of the piston are 0.08 m and 0.2 m, respectively. The total displaced piston volume is 0.9 L, considering the point that 10% of the volume is occupied by water from the beginning to avoid the penetration of hydrogen into the hydraulic system. The speed of the compressor is controlled by adjusting the rotating speed of the hydraulic pump.

The equations which are used in the thermodynamic model to analyze the heat transfer inside the compression chamber are explained in the following section.



Figure 2.1 - Cross-sectional view of a compression chamber and the schematic heat transfer mechanisms between the gas (white), liquid (green) and wall.

2.2.1 Mass and energy balance

Since the compression will start after the inlet valve is closed, the total amount of hydrogen trapped in the compression chamber is constant during the compression procedure. Hence, the energy conservation of the gas is determined from the first law of thermodynamics for a closed system as following:

$$\frac{dU_{gas}}{dt} = \frac{\delta Q}{\delta t} - \frac{\delta W}{\delta t} \to M_{gas} \frac{du_{gas}}{dt} = \dot{Q}_{gas} + P \frac{dV}{dt}$$
(2.1)

where M_{gas} is the total hydrogen mass inside the compression chamber, du_{gas}/dt is the change in the internal energy of hydrogen, \dot{Q}_{gas} is the total rate of heat transfer between the hydrogen and wall, and the hydrogen and water, and PdV/dt is the rate of work which is done by the water on the gas side to compress hydrogen. The energy equation for the liquid has the following form

$$\frac{dU_{liq}}{dt} = \frac{\delta Q}{\delta t} - \frac{\delta W}{\delta t} - \frac{dH_{in}}{dt} \rightarrow \frac{d}{dt} \left(M_{liq} u_{liq} \right) = \dot{Q}_{liq} - P \frac{dV}{dt} + \frac{d}{dt} \sum \left(\dot{m}_{liq} h_{in} \right)$$
(2.2)

Since water is pumped into the compression chamber, the energy equation for an open system is employed, where dH_{in}/dt is the enthalpy flow of water entering the compression chamber. The specific enthalpy of water enters the compression chamber (h_{in}) is estimated based on the isentropic efficiency of the pump and assuming the inlet conditions of 298 K and 1.013 bar for the water. The isentropic efficiency of 0.7 is assumed for the pump. Moreover, \dot{Q}_{liq} is the total rate of heat transfer between the water and wall, and the water and hydrogen, and M_{liq} is the water mass which can be calculated based on a constant mass flow rate as following

$$\frac{dM_{liq}}{dt} = \sum \dot{m}_{liq} \rightarrow M_{liq} - M_{liq0} = \int_0^t \dot{m}_{liq} dt$$
(2.3)

where M_{lia0} is the initial water mass inside the compression chamber at time t = 0 second.

 \dot{Q}_{gas} and \dot{Q}_{lia} are calculated based on

$$\dot{Q}_{gas\liq} = \sum_{i=m}^{i=n} \pm \dot{Q}_{w,i} \pm \dot{Q}_{interface}$$
(2.4)

where $\dot{Q}_{w,i}$ is the rate of heat transfer between the hydrogen or water and the wall, which is estimated based on the convection mechanism, and $\dot{Q}_{interface}$ is the rate of heat transfer between the water and hydrogen, which is estimated based on the conduction mechanism, at each time step. In order to estimate \dot{Q}_{liq} in equation 2.4, m is equal to 1 and n corresponds to the last node at which

water is in a direct contact with the wall. However, for \dot{Q}_{gas} , m is equal to the first node at which hydrogen is in a direct contact with the water and n corresponds to the total number of discretization.

2.2.2 Heat transfer analysis

The hydrogen temperature increases during the compression procedure. Due to the direct contact between hydrogen and water, the heat will directly transfer from the hydrogen to the water based on newton's law of cooling:

$$\hat{Q}_{\text{interface}} = UA_{\text{interface}}(T_{liq} - T_{gas})$$
(2.5)

where $UA_{interface}$ is the total heat transfer coefficient and can be calculated based on the conduction mechanism between the water and hydrogen as

$$UA_{\text{interface}} = \frac{1}{\sum R_{\text{total}}}$$
(2.6)

where

$$\sum R_{total} = \frac{L_{liq}}{K_{liq}A} + \frac{L_{gas}}{K_{gas}A}$$
(2.7)

where $L_{liq \setminus gas}$ and $K_{liq \setminus gas}$ are the axial thickness and thermal conductivity of the water and hydrogen at each time step, and A is the cross-sectional area of the compression chamber.

Moreover, due to the temperature difference between the hydrogen and compressor wall, heat begins to flow into the vessel wall, through convection; in which part of the heat will be absorbed by the water and the rest will be transferred to the surrounding. Depending on the distance from the bottom of the chamber, the heat transfer coefficient of the gas, the wall resistance, and the total amount of external cooling, water may absorb heat from the wall or transfer heat toward the wall. The amount of heat transfer from the liquid or gas through the wall can be calculated as

$$\dot{Q}_{w,i} = UA_{w,i}(T_{w,i} - T_{gas \setminus liq})$$
(2.8)

where $T_{w,i}$ is the wall temperature at node i, and $UA_{w,i}$ is the total heat transfer coefficient which can be calculated based on the total resistance of the gas or liquid side and the wall

$$UA_{w,i} = \frac{1}{\sum R_{totalw,i}}$$
(2.9)

$$\sum R_{totalw,i} = \frac{1}{h_i(\pi D L_i)} + \frac{\ln\left(\frac{D}{2} + \frac{t_w}{2}\right)}{2\pi L_i K_w}$$
(2.10)

where $L_i = L/n$ and L is equal to the total length of the piston, t_w is the wall thickness, n is the total number of nodes, D is the piston diameter, K_w and h_i are the thermal conductivity of the wall and convective gas or liquid heat transfer coefficient, respectively.

The following energy balance in the wall is used to estimate the wall temperature, and the amount of heat which will transfer from the gas side toward the water or to the surrounding at each positional node and time step.

$$-\dot{Q}_{w,i+1} + \dot{Q}_{axial,i+1} - \dot{Q}_{axial,i} + \dot{Q}_{sur,i+1} = 0$$

$$i = 2, ..., n - 1$$
(2.11)

where $\dot{Q}_{axial,i}$ and $\dot{Q}_{sur,i}$ stands for the axial conduction heat rate, and the radial convection heat rate transfer inside the wall and toward the surrounding respectively, and it can be calculated as

$$\dot{Q}_{axial,i} = K_w A_w (T_{w,i+1} - T_{w,i}) / L_i$$
(2.12)

$$\dot{Q}_{sur,i} = UA_{air}(T_{amb} - T_{w,i}) \tag{2.13}$$

In equation 2.12 and 2.13 A_w is the cross-sectional area of the wall, T_{amb} and UA_{air} are the ambient temperature and total heat transfer coefficient between the outlet flow and wall. UA_{air} can be calculated from

$$UA_{air} = \frac{1}{\sum R_{t,i}}$$
(2.14)

$$\sum R_{t,i} = \frac{1}{h_{sur}\pi(D+2t_w)L_i} + \frac{\ln\left(\frac{\frac{D}{2}+t_w}{\frac{D}{2}+\frac{t_w}{2}}\right)}{2\pi L_i K_w}$$
(2.15)

where h_{sur} is the convective heat transfer coefficient to the surrounding. In the present study, it is assumed that the wall will be cooled down by an external air flow with a constant convective heat transfer coefficient equal to $100W/m^2K$.

The first step in estimation of the heat transfer coefficient of both water and hydrogen is to determine the flow regime, defined by the Reynolds-number (Re), equation 2.16. Since a constant volume flow rate is assumed for the pump, the velocity of the liquid column (Vl) is calculated based on the constant rate of piston travel as

$$\operatorname{Re} = \frac{\rho_{liq\backslash gas} VID}{\mu_{liq\backslash gas}} \quad \text{where} \quad VI = \frac{\dot{v}}{A}$$
(2.16)

where $\rho_{liq \setminus gas}$ and $\mu_{liq \setminus gas}$ are the density and viscosity of water or hydrogen respectively.

It is assumed that the hydrogen has the same velocity as the water all over the piston. This can be a good estimation for predicting the bulk motion of the gas. However, in reality this motion will decay throughout the end of the stroke. A fair amount of work has been done on estimation of the convective coefficient of the working gas such as [39][40][41][42][43][44][45][46]. Table 2.1 lists the widely used empirical heat transfer correlations available in the literature. All the equations follow the general from of

$$Nu = A \operatorname{Re}^{a} \operatorname{Pr}^{b} \left(\frac{\mu}{\mu_{0}}\right)^{c} \text{ where } h = \frac{Nuk}{D}$$
 (2.17)

where Nu, Pr, k and μ are respectively Nusselt-number, Prandtl-number, thermal conductivity, and viscosity of the fluid. μ_0 is the viscosity of the fluid at the inlet condition.

Name	Date	Α	а	b	С	Equation
Dittus & Boelter [39][40]	1930	0.03	0.8	0.3	0.0	$0.03 \mathrm{Re}^{0.8} \mathrm{Pr}^{0.3}$
Sieder & Tate [41]	1936	0.03	0.8	0.3	0.1	$0.03 \mathrm{Re}^{0.8}\mathrm{Pr}^{0.3} \left(\frac{\mu}{\mu_0}\right)^{0.1}$
Annand [42][47]	1963	0.70	0.7	0.7	0.0	$0.7 \mathrm{Re}^{0.7} \mathrm{Pr}^{0.7}$
Adair et al. [43]	1972	0.05	0.8	0.6	0.0	$0.05 \mathrm{Re}^{0.8} \mathrm{Pr}^{0.6}$
Hamilton [44][47]	1974	0.02	0.8	0.6	0.0	$0.02 \mathrm{Re}^{0.8} \mathrm{Pr}^{0.6}$
Liu & Zhou [45]	1984	0.75	0.8	0.6	0.0	$0.75 \mathrm{Re}^{0.8} \mathrm{Pr}^{0.6}$
Hsieh et al. [46]	1996	0.16	1.1	0.0	0.1	$0.16 \operatorname{Re}^{1.1} \left(\frac{\mu}{\mu_0}\right)^{0.1}$

Table 2.1 - Seven widely used empirical heat transfer correlations

The first correlation in table 2.1 is Dittus & Boelter correlation which estimates the fully developed turbulent heat transfer coefficient in circular tubes, with the smooth surfaces and moderate temperature difference between the wall and fluid mean temperature. For flows characterized by large property variations, Sieder & Tate recommended an extended Dittus & Boelter correlation which also taking into account the wall effect when the wall temperature differs significantly from the fluid mean temperature. Similarly, Hamilton proposed an alternative correlation to Dittus & Boelter correlation. However, in general, using Dittus & Boelter correlation is only valid for a fully developed flow where L/D > 60 [48]. Since, this condition is not satisfied in most of the conventional compressor chambers, especially as the stroke moves toward the top dead center of the position, researchers like Annand, Adair et al., Liu & Zhou, and Hsieh et al. proposed other correlations extracted from experimental data.

Annand proposed a correlation for the internal combustion engines, whereas neglecting the combustion terms and replacing Re-number by Peclet-number ($\text{Re} \times \text{Pr}$). Annand correlation can be used for the compressors with a good accuracy [47]. In addition, Adair et al., Liu & Zhou, and Hsieh et al. found other constants for equation 2.17 (shown in table 2.1) which have been extracted from the experimental results obtained originally for the reciprocating compressors.

In order to find the best fit with the experimental data, Adair et al. and Liu & Zhou used an alternative equation for calculating Reynolds-number which is based on the time varying equivalent diameter and swirl velocity rather than the chamber diameter and averaged piston speed, as

$$\operatorname{Re}^{*} = \frac{\rho_{gas} \mathcal{M}_{s} D_{e}}{\mu_{gas}}$$
(2.18)

and

$$D_{e} = \frac{6volume}{Area} = \frac{6\pi (\frac{D}{2})^{2} s(t)}{\pi D s(t) + 2\pi \frac{D^{2}}{2}}$$
(2.19)

where Vl_s is the swirl velocity, and s(t) is the piston stroke. Since in the present work, water enters into the compression chamber with a constant volume flow rate, the swirl velocity is estimated to be twice as the frequency of compression (fr) [33], as

$$Vl_s = \frac{D_e}{2} fr$$
(2.20)

It should be mentioned that for calculating the convective coefficient of the liquid, Dittus & Boelter equation (shown in table 2.1) is used. Furthermore, for a longer compression period in which the gas or liquid regime changes from turbulent to laminar condition equation 2.17 with A= 0.664, a= 0.5, b= 0.3,c=0 coefficients ($Nu = 0.664 \text{ Re}^{0.5} \text{ Pr}^{0.3}$) is used [49].

After defining all the parameters, equations 2.1, 2.2, and 2.3 can be solved simultaneously by using forward differencing numerical integration and updating the properties of the system at every time step for the estimated temperature and pressure.

2.3 Results and discussion

The results obtained for the heat analysis of the reciprocating liquid piston compressor is presented in this section. Figure 2.2 shows the instantaneous Nusselt-number (Nu) derived from different correlations as a function of Reynolds-number (Re). The results show a significant difference between different correlations. It can be observed that the estimated Nu-numbers based on the three correlations suggested by Hamilton, Dittus & Boelter, and Sieder & Tate are very small. However, the Nu-numbers estimated by Adair et al., Annand, and Liu & Zhou correlations are approximately 2, 11, and 30 times larger than the one derived by Hamilton correlation. Moreover, the correlation suggested by Hsieh et al. estimated the largest Nu-number which is about 120 to 190 times larger than Hamilton. Figure 2.2 also illustrates that the Re-numbers which are calculated based on the swirl velocity in Adair et al. and Liu & Zhou correlations, vary within the smaller range compared to the other correlations, and the Nu-numbers start to decrease from the Re-number larger than about 2.1×10^4 . Such trend can be explained by decreasing the swirl movement of the gas as the piston moves toward the top dead center.



Figure 2.2 – Nusselt-number as a function of Reynolds-number, calculated based on seven different correlations

As the hydrogen is compressed from 100 to 500 bar, the hydrogen temperature will rise from 300 K to about 477 K in the adiabatic case. When the hydrogen temperature exceeds the temperature of the cylinder wall, all the previously described correlations will predict heat transfer into the wall. Figure 2.3 shows the hydrogen temperature during the compression procedure, considering heat transfer at the interface and through the walls based on the seven heat transfer correlations mentioned above, and compares them with the adiabatic case, for one set of operating conditions. The results show a slight deviation of the hydrogen temperature based on Hamilton, Dittues & Boelter, and Sieder & Tate correlations compared to the adiabatic case. Since these correlations estimate very small convective gas heat transfer coefficients, the total heat amount transfers toward the wall, calculated based on any of these equations, is very small. However, larger deviations of the hydrogen temperature based on the other correlations.

Fagotti et al. has previously compared the experimental results obtained for the conventional reciprocating compressors with the results of heat transfer models in which Annand, Adair et al., Hamilton, and Liu & Zhou correlations were used. They concluded that the Annand correlation showed the best fit [47]. additionally, It has been pointed out that the correlation suggested by Hamilton, resulted in almost no heat transfer [47], similar trend is observed in the present study.

As expected, the largest deviation from the adiabatic case is obtained from Hsieh et al. correlation, in which the estimated heat transfer coefficient of the gas is about 120 to 190 times larger than Hamilton correlation. However, even in this best case ($T_{hydrogen, Hsieh et al.} = 475.4$ K), only 0.4% reduction in the hydrogen temperature is observed compared to the adiabatic case ($T_{hydrogen, Adiabatic} = 477.1$ K) at 500 bar. Therefore, it can be concluded that the sensitivity of the model to different correlations is quite low. The main reason of that can be the large wall resistance which practically will avoid transferring a considerable amount of heat (more conductive walls can play an important role in decreasing the gas temperature). Furthermore, the large wall resistance will also avoid the linear increasing of the total heat transfer coefficient with the convective heat transfer coefficient of the gas, consequently reducing the amount of heat that can transfer to the wall (see second term of equation 2.10).

Unlike the developed model in the present study, in the previous studies which have used the first law of thermodynamic and heat transfer correlations for the prediction of gas temperature inside the compressor, wall temperature equal to ambient temperature is assumed [31][33]. Such models did not take into account the wall resistance, which is essential for estimation of the gas temperature inside the compressor.

Additionally, it can be observed in figure 2.3 that the heat transfer at the interface does not play an important role in cooling the hydrogen temperature. It should also be mentioned that the current study only considers the conduction mechanism between the liquid and gas. In a real condition, the heat transfer behavior may become more complicated than a single conduction mechanism, which can correspondingly affect the results.



Figure 2.3 - Hydrogen temperature as a function of piston travel, calculated for seven different heat transfer correlations, as well as the adiabatic case

Figure 2.4 shows the temperature distribution along the compressor wall, at the end of the compression process. As expected, the wall temperature at the top side of the compression chamber is closer to the temperature of the compressed hydrogen from the correlations that estimate larger heat transfer coefficients for the gas. Nevertheless, for the correlations like Adair et al., Sieder & Tate, Dittus & Boelter, and Hamilton, the temperature obtained at 19 cm from the bottom of the vessel deviates about 14, 16, 16, and 16% from the hydrogen temperature ($T_{hydrogen, Adiar et al.} = 476$ K, $T_{hydrogen, Sieder & Tate} = 476.2$ K, $T_{hydrogen, Dittus & Boelter} = 476.2$ K, and $T_{hydrogen, Hamilton} = 476.23$ K at 500 bar), respectively.

Wall temperature distribution shows that for the nodes which are in direct contact with the hydrogen the temperature is above 370 K, whereas it decreases considerably toward the bottom side of the compression chamber. The bottom side of the compression chamber wall has almost the same temperature as water during the compression.



Figure 2.4 - Temperature distribution in cylinder wall, the colors inside the chamber represent the space inside the compression chamber which occupied by the liquid (green) and gas (red), at the end of the compression process

Equations 2.5, 2.8, and 2.14 show that increasing the total heat transfer coefficients, both at the interface and wall, will increase the amount of heat flux and consequently reduce the hydrogen temperature.

Table 2.2 shows the role of three parameters of the total heat transfer coefficient at the interface, at the wall, and the compression time, in reduction of the hydrogen temperature compared to the adiabatic case.

	$f \times UA_{int}$ (a	a)		$f imes UA_{air}$, w	' (b)
	T _{hydrogen} (K) at 500 bar		T _{hydrogen} (K	() at 500 bar
f	$t_{comp} = 0.4 s$	$t_{comp} = 3.5 s$	f	$t_{comp} = 0.4 s$	$t_{comp} = 3.5 s$
1000	472.9	452.2	50	434.1	362.3
4000	465.1	413.1	100	408.2	340.2
8000	455.3	381.7	150	391.2	330.6
10000	450.8	371.4	200	379.3	319.0

Table 2.2 - Role of increasing (a) total heat transfer coefficient at the interface by a factor of f(b) atthe wall by a factor of f, and time on reduction of hydrogen temperature

It can be seen that increasing the total heat transfer coefficient by a factor of f and the compression time, will increase the deviation of hydrogen temperature compared to the adiabatic case ($T_{adiabatic}$ at 500 bar = 477.1 K).

Figure 2.5 shows the changes of pressure and temperature during 0.4 and 3.5 seconds of compression, considering that the total heat transfer coefficient is 10000 times larger than what is estimated by equation 2.6 and using Annand correlation for calculating the convective coefficient of the gas.

Figure 2.5-a shows lower pressures compared to the adiabatic case for the above mentioned scenarios. The main reason of such behavior can be explained by a significant reduction of temperature due to a considerable increase of heat flux at the interface. As observed in figure 2.5-b, the temperature reduction of 5-6 and 22% are obtained during the 0.4 and 3.5 seconds compression compared to the adiabatic case, at 500 bar corresponds to 69% of piston travelling. Increasing the compression time will provide the possibility of transferring more heat from the gas to the liquid, consequently larger reduction of the gas temperature.

Increasing the total heat transfer coefficient up to 10000 times larger than what is estimated, requires increasing the heat transfer area by the same amount. This is practically not possible by increasing the diameter versus the length of the cylinder. Spraying liquid into the compression chamber can considerably increase the contact area between the liquid and gas. However, still a detailed model is required to estimate the total amount of heat that can be extracted from the gas by spraying the liquid.



Figure 2.5 - Studying the role of total heat transfer coefficient at the interface, and compression time on reduction of (a) hydrogen pressure and (b) hydrogen temperature compared to the adiabatic case

Furthermore, increasing the total heat transfer coefficient between gas to wall, liquid to wall, and wall to air can also play an important role in decreasing the hydrogen temperature. As shown in figure 2.6, hydrogen pressure during the compression decreases compared to the adiabatic case, mainly due to the significant reduction of temperature. It can be seen in figure 2.6 that if the total heat transfer coefficient in both equations 2.8 and 2.14 increases up to 200 times more than what is estimated by the model developed here, the hydrogen temperature will decrease up to 20 and 33% according to Annand correlation for 0.4 and 3.5 seconds compression compared to the adiabatic case, at 500 bar corresponds to 69% of piston travelling. Increasing the total heat transfer coefficient up to 200 times larger than what is estimated requires a considerable increase in the geometry from inside and outside of the compressor which practically is very difficult to reach.

Although increasing the compression time also plays role in decreasing the hydrogen temperature, there is a limitation regarding this parameter. The main reason of that is the considerable reduction of the hydrogen and water speed by increasing the compression time leading to the change of the flow regimes from turbulent to laminar condition. The heat transfer coefficients of the hydrogen and liquid will decrease in the laminar regime, hence decreasing the total heat transfer coefficient.



Figure 2.6 - Studying the role of total heat transfer coefficient at the wall, and compression time on reduction of (a) hydrogen pressure and (b) hydrogen temperature compared to the adiabatic case

2.4 Conclusions

This chapter presents a study on heat transfer analysis of the liquid piston compressor. A model is developed based on the first law of thermodynamics in a reciprocating liquid piston compressor to predict the system temperature and pressure at different time steps. The amount of heat transfer between hydrogen and wall is estimated according to different heat transfer correlations. The results show a small reduction in the hydrogen temperature, between 0.2 and 0.4%, compared to the adiabatic case, due to the large wall resistance and small contact area at the interface of the gas and

liquid. Furthermore, sensitivity analysis of the model shows the key roles of parameters such as: the total heat transfer coefficients at the interface and the wall, and the compression time, in the reduction of hydrogen temperature during the compression procedure. Increasing the total heat transfer coefficient at the interface (10000 times) or at the wall (200 times), leads to 6 % or 20% reduction of the hydrogen temperature, compared to the adiabatic case, at 500 bar, during 0.4 seconds compression, respectively. Increasing the compression time to 3.5 seconds will lead to further reduction of the hydrogen temperature to 22 % or 33 % respectively. Increasing the total heat transfer coefficients requires increasing the total heat transfer area by the same factor. Spraying liquid into the compression chamber can be considered as one of the practical techniques for increasing the total heat transfer area at the interface, and further optimization.
3. Selection of suitable ionic liquid as a replacement for the solid piston

3.1 Introduction

3.1.1 General description of ionic liquids

Ionic liquids are salts that are most commonly defined by the following characteristics [50]. They are entirely composed of ions and consist of organic cations with organic or inorganic anions. Moreover,

- they have melting points below 100 °C, and
- they have very low vapor pressures before starting to thermally decompose.

Ionic liquids are representative of a new class of fascinating liquid materials with a unique set of properties, such as wide electrochemical potential windows, good thermal stabilities, and negligible vapor pressures, which are not achievable with any other class of materials [51,52]. Their definition is different from the classical definition of molten salts [53], for example, sodium chloride (NaCl), which has a melting point of 803 °C [54]. The origin of the melting point reduction is the replacement of the small inorganic cations with bulky asymmetric organic cations [54]. The combination of a larger asymmetric organic cation and smaller inorganic counterparts reduces the lattice energy, consequently decreasing the melting point [55].

The history of ionic liquids began in 1914 when Paul Walden synthesized the first salt, ethylammonium nitrate, with a room temperature melting point [56]. The first patented ionic liquids, alkylpyridinium chloride and dialkyl imidazolium chloride, were used as mixtures with aluminum chloride and were chemically unstable in the presence of water [57]. In 1992, Wilkes and Zaworotko reported the first air and water-stable 1-ethyl-3-methylimidazolium-based ionic liquids $[C_2mim][X]$ (where X = $[CH_3COO]^-$, $[NO_3]^-$, or $[BF_4]^-$). Since that time, hundreds of ionic liquids have been produced [58], studied and used.

The ability to tune the physicochemical properties of ionic liquids by varying the cation-anion combinations [59] has made ionic liquids potential environmentally friendly replacements for volatile organic solvents [60,61], and opened the door to a wide range of industrial applications of ionic liquids [50,55,59,62–65].

3.1.2 Some applications of ionic liquids

The first major industrial application was the BASIL (Biphasic Acid Scavenging Utilizing Ionic Liquids) process, developed by BASF, in which 1-alkylimidazole scavenges the acid from an existing process. This then resulted in the formation of an ionic liquid that could easily be removed from the reaction mixture [64].

Very important developments have been reported in the field of ionic liquids used in gas handling. Ionic liquids have several properties that make them useful in gas storage and handling applications, including low vapor pressures, stability at high temperatures, and solvation for a wide variety of compounds and gases. They also have weakly coordinating anions and cations, which are able to stabilize polar transition states. Many ionic liquids can be reused with minimal loss of activities. Ionic liquids can also be used instead of pressurized cylinders as a transport medium for reactive gases. The gases are dissolved in the liquids at or below atmospheric pressure and are easily withdrawn from the containers by applying a vacuum [66]. The ionic liquid 1-butyl-3-methylimidazolium chloride ([C₄mim][Cl]) has been used for separating hydrogen from ammonia borane in hydrogen storage [67]. In addition, ionic liquids and amines can be used to capture carbon dioxide ((CO_2) and purify natural gases [68–70].

In recent years, the outstanding properties of ionic liquids, such as being liquid at room temperature and having a negligible vapor pressure, good lubrication properties, high-temperature stability, high chemical stability, low compressibility, and low gas solubility make them a suitable option for hydraulic and pneumatic applications [71]. Some examples of ionic liquids in such applications include the replacement of lubrication oil with an ionic liquid in pumps and compressors [71,72], replacement of hydraulic oil with an ionic liquid in diaphragm pumps [73], and replacement of water with an ionic liquid as the lubricant in liquid ring compressors [74] and vacuum pumps [73]. In all these examples, the use of ionic liquids leads to a considerable reduction in the mechanical losses caused by friction and significant improvements in the system efficiency [71,73].

Furthermore, the above-mentioned properties, as well as the ability of safely withstanding the increased temperatures and pressures involved in the compression process, highlight ionic liquids as promising options to replace the solid piston in the conventional reciprocating compressors for compressing hydrogen [28,73]. The use of ionic liquids to replace the solid piston has several advantages compared to the conventional reciprocating compressors in terms of simpler design, the possibility of having a non-cylindrical compression chamber, and the extraction of heat from the operating gas during the compression procedure [75]; consequently, more efficient compressors with longer life spans can be developed [28]. This type of compressor is already used for compressing pure hydrogen in some hydrogen stations [28].

Current patents concerning the application of ionic liquids for compressors are umbrella type, i.e., they cover all possible ionic liquids without specificity [73,74,76]. Sigma-Aldrich, one of the ionic liquid suppliers, reported a theoretically possible number of 10¹⁸ ionic liquids by combining the wide variety of cations and anions. However, a more realistic number might be significantly lower [77]. Because of this large number of combinations and, thus, number of ionic liquids, it is important to systematically investigate their performance for particular applications, so that the number of potential candidates can be reduced. The focus of the following chapter is to find an appropriate ionic liquid as a replacement for the solid piston in the conventional reciprocating compressors for compression of hydrogen. Correspondingly, certain criteria are determined, and a comprehensive review of the relevant properties of ionic liquids has been carried out to find the best candidate that fulfills these criteria. Finally, the best candidate for the replacement of the solid piston is reported.

3.2 Structural features

The structure of ionic liquid and the choice of the cation and anion have a strong impact on the properties, chemistry, and functionality of the ionic liquids. The most commonly used anions and cations are listed in the following sections.

3.2.1 Cation structure

The widely used cations include:

- imidazolium-based ionic liquids,
- pyridinium-based ionic liquids,
- pyrrolidinium-based ionic liquids,
- ammonium-based ionic liquids,
- phosphonium-based ionic liquids.

Figure 3.1 shows the chemical structures of some widely used cations



Figure 3.1- Chemical structure of widely used cations [77]: (*a*) *imidazolium-based,* (*b*) *pyridinium-based,* (*c*) *pyrrolidinium-based,* (*d*) *ammonium-based, and* (*e*) *phosphonium-based*

3.2.2 Anion structure

The commonly used organic and inorganic anions are listed below:

- halide anions (e.g., [Cl]⁻, [Br]⁻, and [I]⁻),
- tetrafluoroborate [BF₄]⁻,
- hexafluorophosphate [PF₆]⁻,
- tris(perfluoroalkyl)trifluorophosphate [FAP]⁻,
- triflate [CF₃SO₃]⁻, which is also known as [OTF]⁻,
- bis(trifluoromethylsulfonyl)imide $[(CF_3SO_2)_2N]^-$, which is also known as $[Tf_2N]^-$,
- thiocyanate [SCN]⁻,

- dicyanamide [N(CN)₂]⁻, which is also known as [C₂N₃]⁻ and [dca]⁻,
- methanesulfonate [CH₃SO₃]⁻,
- alkyl sulfate (e.g., ethylsulfate [EtSO₄]⁻, which is also known as [EtOSO₃]⁻ and methylsulfate [MeOSO₃]⁻), and
- nitrate $[NO_3]^-$.

3.3 Criteria for selecting appropriate ionic liquids for hydrogen compressors

The physical and chemical properties of ionic liquids allow them to meet almost any requirements for use in hydrogen compressors. Among the most important properties of the ionic liquids that can help in the correct choice of replacement for the solid piston in the hydrogen reciprocating compressors are:

- suitable viscosity,
- suitable density,
- negative melting point,
- water immiscibility,
- high corrosion stability,
- low hydrogen solubility,
- low compressibility,
- high chemical stability,
- high thermal stability,
- high heat capacity,
- high thermal conductivity,
- satisfactory tribological behavior.

Many researchers have tried to understand the relationship between the nature and structures of the anion and cation and the physical properties of the ionic liquids. In the following sections, we review the data that have been already presented with respect to the above-mentioned criteria to give insight into which room temperature ionic liquids are suitable replacements for the solid piston in hydrogen compressors.

3.4 Physical and chemical properties

3.4.1 Viscosity

The viscosity is one of the key parameters in the design of any hydraulic system. The viscosity is directly related to issues such as liquid leakage, frictional losses, start-up ease, and the final efficiency of the system. Moreover, the size of the electric motor, pipes, and hoses highly depends on the viscosity of the liquid.

Generally, increasing the viscosity of a liquid increases the volumetric efficiency of the system but, at the same time, decreases the mechanical efficiency of the system [78]. Therefore, appropriate fluids for hydraulic systems are a compromise [78]. Very low viscosity liquids will leak from the

internal seals, causing a loss of volumetric efficiency, whereas very high viscosity liquids make it difficult for the fluid to be pushed through hoses, fittings, and valves, causing a loss of mechanical efficiency [78]. In hydraulic applications, water is considered a thin liquid with low viscosity, whereas honey is considered as an upper-limit example of a thick liquid with high viscosity. In general, over 80% of all consumed hydraulic fluids are divided into three viscosity grades (VG): ISO VG 32, ISO VG 46, and ISO VG 68 [79] Moreover, the National Fluid Power Association recommends a viscosity range of 13–860 mm²/S (cSt) as an acceptable operating viscosity for most pumps and motors [80].

For ionic liquids, a wide range of viscosities has been reported in the literature, with [EMIM]Cl-ALCl₃:1/2 and [bmim][Cl] (supercooled) as lower and upper limit examples, equal to 14 mPa·s (cP) and 40.89 Pa·s, respectively [50]. As a replacement for the solid piston, an ionic liquid with a viscosity in the range of the three viscosity grades for the hydraulic fluid should be selected. However, a viscosity closer to the first viscosity grade, ISO VG32, is desirable because this will reduce the size and losses arising from friction, consequently leading to a more compact and efficient system.

The viscosities of room temperature ionic liquids are affected by the nature of both the cation and the anion. It has been widely reported that increasing the length of alkyl chain on the imidazolium ring will increase the viscosity [81–83]. Such a contribution can be quite significant; for example, Hamill et al. showed that the viscosity of imidazolium-based ionic liquids ([C_n mim][BF4]) could be increased from 66.5 to 314 mPa·s by changing *n* from 2 to 4 and, then, to 6 [84]. At first view, such an observation is quite surprising because many people expected lower viscosities arising from the reduction of the overall contribution of the strong associations (i.e., electrostatic (and hydrogen bond)) to the total interactions [85]. However, in 1996, Bonhote et al. explained this observation as a consequence of the increasing van der Waals forces on increasing the side-chain length [86].

Changing the alkyl chain (from butyl to isobutyl) or fluorination has a similar effect, increasing the viscosity of the ionic liquid [86]. Jacquemin et al. reported the higher viscosity of alkylammoniumbased ionic liquids compared to imidazolium-based ionic liquids with the same anions [85]. Moreover, Bhattacharjee et al. reported that more symmetric cations have a lower viscosity for the same, and sometimes even longer, cation alkyl chain lengths [87].

The nature of the anion, such as anion size, geometry, molar mass, relative basicity, and the ability to participate in hydrogen bonding, can also affect the viscosity of the ionic liquids. Smaller, lighter, and more symmetric anions result in more viscous ionic liquids. It has been shown that the symmetric perfluorinated $[PF_6]^-$ and $[BF_4]^-$ anions, which have stronger H···F interactions, contribute to the formation of ionic liquids with higher viscosities compared to the weakly basic $[Tf_2N]^-$ anion with a negative charge delocalized over the two sulfoxide groups [81,82,88]. In addition, it has been shown that the replacement of three fluorine atoms in the $[PF_6]^-$ anion by pentafluoroethyl groups can reduce the viscosity of the consequent ionic liquids considerably, as can be seen by comparing the viscosities of $[C_4mim][PF_6]$ and $[C_6mim][FAP]$ [89]. In addition, a reduction in the viscosity for imidazolium-based ionic liquids with the 1-ethyl-3-methylimidazolium ([EMIM]⁺) cation and the pyridinium-based ionic liquids with the 1-butyl-3-methylpyridinium

 $([C_4C_1Pyrr]^+)$ cation has been reported in the order of $[CF_3SO_3]^- > [Tf_2N]^-$ and $[FAP]^- > [CF_3SO_3]^- > [Tf_2N]^-$ [90].

In addition, the temperature can affect the viscosity considerably. A considerable reduction in the viscosity with increasing temperature for different ionic liquids has been reported in several studies [85,87,91–93].

The viscosity index (VI) is another important parameter in the selection of hydraulic fluids. It represents the changes in the viscosity with temperature variation. As the VI value increases, the change in the viscosity with the temperature decreases. High VI fluids result in the stable performance of the system within the normal working conditions and lead to good start-up, minimal loss performance at low temperatures, and, also, prevent cavitation issues. However, few studies have investigated this parameter in ionic liquids. Anastas et al. reported the VI value in the range of 125–185 for different imidazolium-based and ammonium-based ionic liquids with the [Tf₂N]⁻ and [BF₄]⁻ anions [94]. Kondo et al. also reported VI values in the range of 122–252 for several imidazolium-based ionic liquids with different anions [95].

Ionic liquids have quite high VI values, even compared to the VI value of the hydraulic fluids (with VI around 90–110) [96]. However, because of the limited number of publications in this area, it is not really possible to find a general order for the ionic liquids cations and anions with respect to the viscosity index.

3.4.2 Density

Knowledge of the ionic liquids density is required for appropriate equipment sizing and the correct selection of the components.

A density range of 1.1–1.6 g/cm³ [60,97], with a lower limit example of [C23guan][Cl] = 0.9 g/cm³ [60] and an upper limit example of [EMIM]Br/AlBr₃ (34-66 mol%) = 2.2 g/cm³ [97], has been reported for the density of the ionic liquids, depending on the type of cation and anion.

With respect to the cation, a reduction in the density with increasing alkyl chain length of the imidazolium cation has been reported in several studies [54,83,85,98–101]. In addition, Tokuda et al. observed the effect of different cations combined with the $[Tf_2N]^-$ anion on the density and found the order 1-butylpyridinium ([bpy]⁺) > 1-butyl-3-methylimidazolium ([bmim]⁺) > N-butyl-N-methylpyrrolidinium ([bmpro])⁺ > N-butyl-N,N,N-trimethylammonium ([$(n-C_4H_9)(CH_3)_3N$]⁺) [100].

The density of the ionic liquids also depends on the molecular weight of the anions; higher densities are expected for higher molecular weight anions [101]. Huddleston et al. reported the increase in the density of ionic liquids with increasing molar mass of the anions in the order $[BF_4]^- < [CF_3SO_3]^- ~ < [PF_6]^- < [Tf_2N]^- [82].$

Temperature also has an approximately linear effect on the density of the ionic liquids. A linear decrease in the density with increasing temperature has been well recorded in several studies [85,98,101,102].

3.4.3 Melting point

Based on the definition, room temperature ionic liquids should have a melting point below 100 °C. A typical melting point range for most ionic liquids is about 0–60 °C [50]; however, negative melting points for ionic liquids are not surprising, and [EMIM]Cl/AlCl₃ = (1:2), which has a melting point of -96 °C (glass transition), has been reported as a lower melting point limit example of ionic liquids [50].

For the operation of ionic liquids in compressors, a melting point of less than 0 $^{\circ}$ C is highly desirable because the compressor should be able to work in countries with cold winter conditions below 0 $^{\circ}$ C.

Generally, it is difficult to find a correlation between the chemical composition of the ionic liquids and their melting point. Katritzky et al. predicted the melting point for 126 structurally diverse pyridinium bromides using a quantitative structure–property relationship and pointed out that the most important factors influencing the melting point of the ionic liquids are the molecular shape and symmetry of the cations, electrostatic intermolecular interactions, and the number of conformational and rotational degrees of freedom in the solid and liquid phases [103]. For a family of quaternary ammonium salts, the melting point only reaches room temperature when the size of the quaternary ammonium cation is large, for example, where the overall number of carbon atoms in the structure is greater than 20 [104].

Bonhote et al. also highlighted the significant role of cation symmetry in achieving high-meltingpoint ionic liquids. However, their studies on series of anions showed a slight influence of Waals interactions on the melting point of the ionic liquids, and the correlation between the hydrogenbonding ability and the melting point was not clear [86]. O'Mahony et al. [105] showed that, although asymmetric cations play a major role in the reduction of the melting point, it is the combination of the cation and anion species that leads to low lattice energies, an important factor in the reduction of the melting point [88].

3.4.4 Water immiscibility

Water is considered to be one of the most significant impurities in ionic liquids. Even hydrophobic ionic liquids can absorb water from the atmosphere [106,107]. The amount of the water absorbed by an ionic liquid can change its physical and chemical properties [85,106,108,109]. A good example of such changes is the reduction of the viscosity with increasing water content, as reported in Refs. [88,109–111]. Water-saturated ionic liquids also have lower densities compared to dry ionic liquids [85].

Moreover, water can also affect the corrosion behavior of the alloys in contact with the ionic liquids and affect the electrochemical reaction and reduce the potential window [88]. Molchan et al. reported that reducing the water content plays an important role in reducing the corrosion rate of alloys in direct contact with imidazolium-based ionic liquids containing the [TCM]⁻ anion [112]. In addition, the thermal stability decreases as the hydrophilicity of the ionic liquids increases. Consequently, the drying of ionic liquids may improve their thermal stability [82,88].

Furthermore, in the presence of water, some ionic liquids may be chemically unstable and decompose, as has been reported for 1-ethyl-3-methylimidazolium ethylsulfate, which decomposes to ethyl-3-methylimidazolium hydrogen sulfate and ethanol under ambient conditions [105].

Water miscibility is an important criterion for selection of the ionic liquid as a replacement for the solid piston in the conventional reciprocating hydrogen compressors. Because the ionic liquid may be in contact with humid air during assembly or maintenance, the drying of the ionic liquid in the vacuum for several days may not be practical.

Apparently, the cation does not play a considerable role in the amount of water uptake from the atmosphere; in contrast, many studies have highlighted the significant role of the anion on determining the hydrophobicity/hydrophilicity of the ionic liquids. Plechkova et al. divided the anions into three groups, categorizing ionic liquids as water immiscible, water miscible, or intermediately miscible. Based on this study the $[PF_6]^-$, $[Tf_2N]^-$, and $[BR_1R_2R_3R_4]^-$ anions form water immiscible ionic liquids, whereas the $[CH_3CO_2]^-$, $[NO_3]^-$, $[BR]^-$, $[Cl]^-$, $[I]^-$, $[Al_2Cl_2]^-$, and $[AlCl_4]^-$ anions form water miscible ionic liquids with moderate water uptake (between the two extremes) [64]. Werner et al. also mentioned the $[Tf_2N]^-$ and $[P(C_2F_5)_3F_3]^-$ anions as lower limit examples and the $[RSO_3]^-$, $[RSO_4]^-$, and $[R_2PO_4]^-$ anions as upper limit examples of water miscibility for ionic liquids [50].

Ionic liquids containing $[FAP]^-$ anions are water immiscible and considered to be hydrophobic ionic liquids with very low residual water contents, e.g., 10–15 ppm or less [113]. A water uptake of much less than the $[Tf_2N]^-$ anion and more than 10 times less than the $[PF6]^-$ anion has been reported for these ionic liquids [113].

3.4.5 Corrosion stability of alloys in contact with ionic liquids

Corrosion is the reaction of a material with its environment because of the thermodynamic instability of these materials in the presence of air, water, or other oxidizing agents. Many general studies have been carried out to achieve an overview of the corrosion of metals and alloys in contact with different types of ionic liquids. It has been shown that, in some cases, severe corrosion problems occur [114–117]. In the case of hydrogen compressors, severe corrosion can lead to hydrogen contamination, costly and time-consuming maintenance, or the leakage of hydrogen, which can result in serious explosions at hydrogen stations. Therefore, special attention is required for selecting the correct choice of cation and anion and the alloy in direct contact with the selected ionic liquid with respect to corrosion issues.

In general, studies have shown that the corrosion stability depends on both the nature of cation and anion and the type of the alloy in contact with the ionic liquids. Uerdingen et al. investigated the corrosion behavior of several metals and alloys in contact with different imidazolium-based and ammonium-based ionic liquids and proved that both the chemical structure of the cation and the type of anion play a significant role on corrosivity of the ionic liquids [118]. A similar trend has been observed by Pisarova et al., who studied the corrosion stability of different alloys in several ammonium-based ionic liquids containing $[Tf_2N]^-$ and $[CH_3SO_3]^-$ anions [119]. However, Wang et al. studied the corrosion behavior of several imidazolium-based and pyrrolidinium-based ionic

liquids with $[dca]^-$ and chloride-chloroaluminate $[AlCl_3]^-$ anions and concluded that the constituent anions played a more significant role than the cations concerning the corrosivity of the ionic liquids in contact with the alloys [120].

Molchan et al. studied the corrosion behavior of alloys in contact with several imidazolium-based ionic liquids with the tricyanomethanide [TCM]⁻ anion and found that, by increasing the alkyl chain length, the corrosion rate could be reduced [112].

With respect to the anion, serious corrosion issues can occur for different metals and alloys when they are in contact with different ionic liquids containing halides, specifically [Cl]⁻. Reddy et al. studied the corrosion behavior of different alloys in four different imidazolium-based ionic liquids for solar collectors and showed an outstanding corrosion resistance in the ionic liquids except for that containing chloride anions [114]. In another study, the high corrosion resistance of titanium in four different types of ionic liquid (including the imidazolium-based and pyrrolidinium-based ionic liquids) was observed, except 1-ethyl-3-methyl-imidazolium chloride aluminum chloride [115]. Similarly, severe corrosion issues have been observed for the alloy 304 SS and copper in aluminum chloride/1-ethyl-3-methylimidazolium chloride ionic liquid [116]. In addition, a study of the corrosion of different ammonium-based ionic liquids with $[Tf_2N]^-$ and $[CH_3SO_3]^-$ showed that, regardless of cation moiety, $[Tf_2N]^-$ showed better performance compared to $[CH_3SO_3]^-$ [119]. In addition, Uerdingen et al. mentioned the possibility of sulfuric acid formation via hydrolysis of ionic liquids containing ethylsulfate and methylsulfate $[EtSO_4]^-$ and $[MeOSO_3]^-$, respectively [118].

Temperature seems to play a fundamental role in increasing the corrosion rate. Perissi et al. studied the corrosion behavior of several metals and alloys in contact with 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide and showed that, at temperatures above 150 °C, serious corrosion occurs [117]. In addition, the viscosity of the ionic liquid is considered an important electrochemical property and plays a role in the corrosion behavior of alloys in contact with the ionic liquids. A highly viscous medium reduces the rate of diffusion-controlled chemical reactions [121]. In contrast, a less viscous medium has faster ion mobilities in the presence of an oxidant, enabling faster electrochemical reactions.

The type of alloy in contact with the ionic liquid is also critical in determining the corrosion rate. Hence, the reported results for each specific ionic liquid can be very different when in contact with different types of alloy.

3.4.6 Hydrogen solubility

Knowledge of the hydrogen solubility in ionic liquids is necessary for the choice of the most efficient and reliable ionic liquid to replace the solid piston for the compression of hydrogen. An ionic liquid with low hydrogen solubility will be a better candidate for use as a replacement for the solid piston.

Although many studies have been carried out to determine the solubility of carbon dioxide in ionic liquids, little information is available on the solubility of hydrogen in ionic liquids. Jacquemin et al. investigated the solubility of carbon dioxide and hydrogen in three different ionic liquids containing the $[Tf_2N]^-$ anion and concluded that hydrogen is two orders of magnitude less soluble than carbon dioxide in these ionic liquids. In addition, a comparison of the solubility of different gases such as

carbon dioxide, ethane, methane, oxygen, nitrogen, argon, and carbon monoxide in different ionic liquids showed that hydrogen has the lowest solubility [122,123].

Imidazolium-based ionic liquids have been reported to have low hydrogen solubilities, for example, 6 mole percent at 450 K and 15 MPa in [EMIM][Tf₂N] [124] and 0.106 mole of hydrogen at 373 K and about 9 MPa in [bmim][PF₆] [125].

Generally, both the cation and anion affect the solubility of hydrogen in ionic liquids.

Cation order with respect to the solubility of hydrogen in different ionic liquids

- Cation order for [X][Tf₂N], obtained by a comparison of Henry's law constants reported by Dyson et al. [126], [bmpy]⁺>[bm₂im]⁺>[bupy]⁺>[bmim]⁺.
- Cation order for [X][Tf₂N], obtained by a comparison of Henry's law constants reported by Finotello et al. [127], [hmim]⁺ > [EMIM]⁺.
- Cation order for [X][BF₄], obtained by a comparison of Henry's law constants reported by Dyson et al. [126], [hmim]⁺ > [bmim]⁺ > [omim]⁺.
- Jacquemin et al. also found the order $[N_{1114}]^+ > [bmim]^+ > [EMIM]^+$ for the $[Tf_2N]^-$ anion [128]
- Raeissi et al., by comparing the hydrogen solubility in different imidazolium-based ionic liquids with the $[Tf_2N]^-$ anion, came to the conclusion that the solubility increases as the alkyl side chain length of the cation increases [124]

Anion order with respect to the solubility of hydrogen in different ionic liquids

- Anion order for [bmim][X], obtained by a comparison of Henry's law constants reported by Dyson et al. [126], $[Tf_2N]^- > [CF_3SO_3]^- > [BF_4]^- > [PF_6]^-$.
- Anion order for [bmim][X], obtained by a comparison of Henry's law constants reported by Jacquemin et al. [122,123,128], [Tf₂N]⁻ > [BF₄]⁻ > [PF₆]⁻.
- Anion order for [EMIM][X], obtained by a comparison of Henry's law constants reported by Finotello et al. [127], [Tf₂N]⁻ > [BF₄]⁻.
- Berger et al. also reported that the hydrogen solubility of $[bmim][PF_6]$ is four times less than that of $[bmim][BF_4]$ [129]

The hydrogen solubility as a function of temperature is not unique, and seems to be different for different ionic liquids. The relevant observations recorded by different studies are listed below:

- Hydrogen solubility in [EMIM][Tf₂N] [124,127], [bmim][PF₆] [122,125,130], [hmim][Tf₂N] [127], and [mmim][MeSO₄][127] increased with increasing temperature.
- Hydrogen solubility in $[N_{1114}]$ [Tf₂N], [bmim][Tf₂N], and [EMIM][Tf₂N] decreased with increasing temperature [128].
- Hydrogen solubility in [EMIM][BF₄] [127], [EMIM][EtSO₄] [131], and [bmim][BF₄] [123] first increased with increasing temperature and then decreased at higher temperatures, having maximum solubilities at about 313.15, 303, and 288.3 K respectively.

3.4.7 Compressibility

Compressibility is an important parameter for selecting a suitable ionic liquid to replace the solid piston in the reciprocating compressors. The problems, which are directly related to the high compressibility of the liquid, are the difficulty in controlling of the compressor if servos fail to maintain the static rigidity, which has an adverse effect on the system amplification, causes a reduction in the volumetric efficiency of the compressor, and finally results in cavitation problems such as metal fracture, corrosive fatigue, and stress corrosion [132]. However, a certain level of compressibility is required to damp the pressure surges caused by switching to achieve the smooth operation of the system [132].

Ionic liquids with low compressibilities are more desirable because they can transmit power more efficiently. However, there have been few investigations into the compressibility of ionic liquids. Nevertheless, generally, ionic liquids have low compressibilities and high potential for hydraulic applications. Regueira et al. studied the compressibility of different ionic liquids compared to conventional hydraulic oils, and concluded that they are more suitable options than the currently employed hydraulic oils [132].

Both the cation and anion affect the compressibility of ionic liquids. Regueira et al. showed that the compressibility of an ionic liquid increases with increasing the alkyl chain length of several different ionic liquids with the $[Tf_2N]^-$ anion [113]. With respect to the anion, similar studies have shown that the compressibility of the imidazolium-based ionic liquids containing the $[EMIM]^+$ cation decreases in the anion order $[Tf_2N]^- > [C_2N_3]^- > [C_nSO_4]^- \sim [PF_6]^- \sim [BF_4]^-$ [113].

In addition, a general trend of decreasing compressibility with increasing pressure [102,132–136], and increasing compressibility with increasing temperature [132,133,135] has been observed for several different ionic liquids.

3.4.8 Chemical stability

The chemical stability is a very important parameter that guarantees that the selected ionic liquid remains stable and is not degraded under real operating conditions. In recent years, many studies have focused on the unique properties of ionic liquids for use in different areas, but very little research has been carried out regarding the stability of ionic liquids in real applications [137,138]. For the application of ionic liquids as a replacement for the solid piston in the reciprocating hydrogen compressors, there are two serious concerns. First, the ionic liquid should remain inert and not react

with the hydrogen at high pressures and temperatures. However, this behavior has not been reported for many types of ionic liquid. Second, the presence of impurities, such as water, which results in hydrolysis and decomposition of the ionic liquids, is a concern. Werner et al. pointed out that heterocyclic cations can be hydrolyzed under extreme conditions [50]. However, the anion seems to play a more significant role in determining the tendency of the ionic liquid toward hydrolysis reactions. Werner et al. mentioned the $[BF_4]^-$ and $[PF_6]^-$ anions as the lower limit examples of hydrolytic stabilities and the $[Tf_2N]^-$, $[CF_3SO_3]^-$, and $[CH_3SO_3]^-$ anions as the upper limit examples of hydrolytic stabilities [50]. The methanesulfate and ethanesulfate anions have been identified as sensitive anions with respect to hydrolysis. However, it has been reported that the sensitivity of alkylsulfates is reduced by increasing the length of the alkyl groups [139].

The $[PF6]^-$ anion has also been reported by Huddleston et al. to be a hydrolytically unstable anion than decomposes and releases HPO₂F₂, H₂PO₃F, H₃PO₄, and highly corrosive HF in the presence of moisture [82]. For similar reasons, Marsh et al. believed that the industrial applications of the $[PF_6]^-$ anion would be very limited [54].

3.4.9 Thermal stability

Knowledge of the thermal stability and decomposition temperature helps us to select an appropriate ionic liquid that fits well to the required operating temperature range of our specific system. In such a specific application as the replacement for the solid piston, the temperature of the ionic liquid can easily increase because of high frequencies, friction, or heat absorption from the hydrogen during the compression procedure [75]. Consequently, ionic liquids with higher thermal stabilities are more desirable.

The decomposition temperature of an ionic liquid depends on the ionic liquid structure. The type of cation and the size of anion seem to play the key roles in this respect. Kroon et al. reported the thermal stabilities of ionic liquids based on the cation and reported the stability in the order phosphonium-based ionic liquids > imidazolium-based ionic liquids > ammonium-based ionic liquids ~ pyrrolidinium-based ionic liquids > pyridinium-based ionic liquids [140]. In addition, it has been reported that the thermal stabilities of imidazolium-based ionic liquids increase with increasing alkyl substitution, as long as linear alkyl groups are used Moreover, based on the work of Awad et al. on a series of the alkyl-imidazolium-based ionic liquids, the thermal stability of ionic liquids increases as the chain length decreased from eicosyl, octadecyl, hexadecyl, decyl, butyl, to propyl [141]. Tokuda et al. observed the effect of different cations combined with the $[Tf_2N]^-$ anion on the thermal decomposition temperature and found the order *N*-butyl-*N*-methylpyrrolidinium ([bmpro]⁺) 1-butyl-3-methylimidazolium $([bmim]^+)$ *N*-butyl-*N*,*N*,*N*-trimethylammonium > > ([(*n*- $C_4H_9(CH_3)_3N^{+} > 1$ -butylpyridinium ([bpy]⁺) [100].

The role of anion size in increasing the thermal stability of ionic liquids has been reported in many studies [82,101,140,142]. The thermal stability increases with increasing the anion size. The relative thermal stability of ionic liquids with various anions combined with the 1-butyl-3-methylimidazolium [bmim]⁺ cation has been recorded in the following orders in several studies:

• $[PF_6]^- > [BF_4]^- \sim [Tf_2N]^- > [CF_3SO_3]^- > [(C_2F_5SO_2)_2N]^- >> [CF_3CO_2]^- ([100])$

- $[Tf_2N]^- > methide > [CF_3SO_3]^- > [BF4]^- > [dca]^- > [Br]^-$ ([101]), and
- $[Tf_2N]^- > [PF_6]^- > [BF_4]^- > [C_2N_3]^- > [Cl]^-([140]).$

MacFarlane et al. reported that the ionic liquids composed of the dicyanamide $[C_2N_3]^-$ anion are not as thermally stable as other ionic liquids consisting of the same cation [143]. This conclusion was obtained by comparing the thermal stability of $[EMIM][C_2N_3]$, which thermally decomposes at 275 °C, with the highest thermal stability for different cation combinations, compared to $[EMIM][Tf_2N]$, which thermally decomposes at 400 °C [86].

For the $[FAP]^-$ anion, depending on the type of cation, thermal stabilities between 220 and 300 °C have been reported. The highest value (300 °C) corresponds to [EMIM][FAP][89].

Furthermore, the halide anions seem to reduce the thermal stability of ionic liquids, which has been well documented in several studies [141,142], and this can also be observed in the anion orders presented by Fredlake et al. [101] and Kroon et al. [140]

A thermal stability range of 230–300 °C, with a lower limit example of [EMIM][OAc] = 200 °C and an upper limit example of $[EMIM][Tf_2N] = 400$ °C, was reported for ionic liquids by Werner et al. [50]. However, the atmospheric conditions may affect the decomposition temperature because there is evidence that, in the presence of oxygen rather than an inert atmosphere, the thermal stability of some imidazolium-based ionic liquids is reduced [141]. In addition, many studies have highlighted the point that the reported decomposition temperatures might be overestimated by the method used for extracting decomposition temperature from thermal gravimetric analysis (TGA) measurements and the fast heating of the samples compared to the conditions of long-term operation [144–147].

3.4.10 Heat capacity

Heat capacity is defined as the amount of energy per molecule that an ionic liquid can store before its temperature increases. A precise knowledge of the ionic liquid heat capacities is essential for the design, operation, and, finally, optimization of an ionic liquid piston hydrogen compressor. For our specific application, ionic liquids with higher heat capacities are required because this reduces the operating temperature (and temperature restrictions) of the system. In addition, the ionic liquid can be used for long periods inside the compressor before the cooling of the ionic liquid is required.

A range of 300–400 J/mol·K has been reported for the heat capacity of ionic liquids by Werner et al. [50]. Both the cation and anion play a role in determining the heat capacity of ionic liquids. Fredlake et al. reported a general trend of higher heat capacities for molecules of the imidazolium-based ionic liquids containing more atoms [101]. Following this trend, increasing the size of cation and anion increases the heat capacity of the ionic liquids.

Paulechka has shown that the heat capacity in a homologous series of ionic liquids increases as the number of atoms in the alkyl chain of the cation increases [148]. A similar trend can be observed in the results presented by Diedrichs et al. for the $[CF_3SO_3]^-$ anion and Ge et al. for the $[Tf_2N]^-$ anion on increasing the length of alkyl chain of the imidazolium-based ionic liquids [149]. In addition, Ge et al. showed that the heat capacity of the phosphonium-based ionic liquid $[P_{66614}][Tf_2N]^-$ is much higher than those of imidazolium-based ionic liquids with the same anion [150]. However, for the

ammonium-based ionic liquids, the results obtained by Paulechka et al [151] for the molar heat capacity of $[N_{1114}]$ [Tf₂N] show that it is comparable with those of imidazolium ionic liquids obtained by Ge et al. [150].

Similarly, a comparison of the molar heat capacities reported by Fredlake et al. showed that, for the $[bmim]^+$ cation, the molar heat capacity of the ionic liquids combined with different anions decreases in the order of $[Tf_2N]^- > [CF_3SO_3]^- > [PF_6]^- > [BF_4]^- > [CI]^- > [Br]^- [101]$. A similar trend has been observed for the $[bmim]^+$ cation and different anions, i.e., $[CF_3SO_3]^- > [PF_6]^- > [BF_4]^-$ Yu et al. also reported that the molar heat capacity of the ionic liquids decreases in the anion order of $[EtSO_4]^- > [CF_3SO_3]^- > [C_2N_3]^- > [BF_4]^-$ for the $[EMIM]^+$ cation [152]. Furthermore, Feire et al. showed that the molar heat capacity of ionic liquids with the $[EMIM]^+$ cation decrease in the anion order of $[CF_3SO_3]^- > [CH_3CO_3]^- > [C_2N_3]^- > [SCN]^- [153].$

Temperature also plays an important role in the heat capacity of the ionic liquids. The general trend of increasing heat capacity with increasing temperature has been observed in several studies for many kinds of ionic liquids [101,149,152,154–157]. However, the sensitivity of the heat capacity as a function of temperature varies significantly for different ionic liquids depending on the ionic liquid anion and cation.

3.4.11 Thermal conductivity

A knowledge of the thermal conductivity is also required for the design, operation, and, finally, optimization of the ionic liquid hydrogen compressor.

Generally, thermal conductivities ranging from 0.1 to 0.2 W/m·K, similar to those of common organic liquids such as *n*-heptane, toluene, benzene, ethanol, methanol, ethanol, and ethylene glycol at atmospheric pressure [158,159], have been obtained for different types of ionic liquid [145,158–161].

The type of cation and anion plays a role in determining the thermal conductivity of ionic liquids. Froba et al. observed a slight increase in the thermal conductivity with increasing cation chain length (higher molar mass) for imidazolium-based ionic liquids with the $[Tf_2N]^-$ anion [158]. From the results of their work [158], changing the cation of an ionic liquid from an imidazolium-based to an ammonium-based ($[N_{1888}]^+$) cation considerably increases the thermal conductivity. Ge et al. reported that there was no significant effect on the thermal conductivity of imidazolium-based ionic liquids containing the $[Tf_2N]^-$ anion on increasing the alkyl chain length of the cation; however, changing the type of cation from imidazolium-based to phosphonium-based, i.e., $[P_{66614}]^+$, had a strong effect, increasing the thermal conductivity [159]. Chen et al., showed that the type of anion has a significant role in the alkyl chain length effect; as for the pyridinium-based ionic liquids ($[C_npy]^+$) and the imidazolium-based ionic liquids ($[C_nmim]^+$) with the $[BF_4]^-$ anion, the thermal conductivity decreased slightly with increasing alkyl chain length, whereas it had no significant effect on $[C_nmim][PF_6]$ and $[C_nmim][Tf_2N]$ [162].

With respect to the anion, a comparison of the results obtained by Froba et al [158] showed that, for imidazolium-based ionic liquids with the [EMIM]⁺ cation, the thermal conductivity decreases in the anion order of $[C_2N_3]^- > [EtSO_4]^- > [Tf_2N]^-$. In addition, The results obtained by Ge et al. showed

that, for the imidazolium-based ionic liquids containing the $[C_2mim]^+$ and $[C_4mim]^+$ cations, the thermal conductivity decreases in the order $[EtSO_4]^- > [Tf_2N]^-$ and $[CF_3SO_3]^- > [Tf_2N]^-$ [159].

In all the ionic liquid studies, a general trend in the reduction of the thermal conductivity of ionic liquids with increasing temperature has been observed [145,158,159,161,162]. However, Chen et al. emphasized the weak dependence of the thermal conductivity on the temperature [162].

3.4.12 Tribological behavior

The tribological behavior of the ionic liquid is an important factor in selecting a suitable replacement for the solid piston. A suitable choice of ionic liquid can reduce the friction losses and eliminate the oil used as a lubricant in the conventional compressors, consequently reducing the risk of hydrogen contamination and enhancing the overall performance of the compressor.

In general, ionic liquids are promising candidates as replacements for conventional lubricants and natural oils [63,163]. Wang et al. and Liu et al. showed that the imidazolium-based ionic liquids have better tribological performance in terms of friction-reducing ability and load-carrying capacity compared to conventional lubricants such as liquid paraffin [164], phosphazene, and perfluoropolyether (used as lubricants for gas tribune engines and space applications) [165]. Reeves et al. investigated the tribological performance of several phosphonium-based ionic liquids and concluded that they have better tribological behavior compared to petroleum-based lubricants and natural oils [166]. In addition, Qu et al. came to the conclusion that the ammonium-based ionic liquids compared to hydrocarbon oils showed 30% less friction and better tribological behavior in steel ball bearings on aluminum alloy [167]. An important point that should be taken into consideration regarding the tribological performance of ionic liquids is tribocorrosion, which must be avoided by careful choice of the ionic liquid and the alloys with which they are in contact.

Because they consist of large, asymmetrical ions, ionic liquids can be absorbed onto surfaces and produce a thin protective film that keeps the moving parts separated. Under extreme pressure conditions, ionic liquids can react to form a protective tribofilm [163]. Studies have shown that the overall structure of the ionic liquid, both the cation and anion structure and the type of alloy in contact with the ionic liquid, can affect the tribological behavior.

On increasing the alkyl chain length of the imidazolium cation, the wear is reduced, and better tribological performance has been observed [164,168,169]. A similar trend has been observed for large changes in the alkyl chain length of phosphonium-based ionic liquids [170], but does not necessarily apply to smaller changes in the alkyl chain length [171].

In addition, it has been shown that for the $[Tf_2N]^-$ anion, the phosphonium-based [170] and ammonium-based [167,172] ionic liquids showed better tribological performance compared to the imidazolium ones. Furthermore, Somers et al. showed that the $[FAP]^-$ and $[Tf_2N]^-$ phosphonium-based ionic liquids show better tribological behavior than the imidazolium-based ionic liquids with the $[FAP]^-$ anion and the two pyrrolidinium-based ionic liquids with the $[Tf_2N]^-$ anion because the first anion–cation combinations can avoid the tribocorrosion issues that are probably caused by the reaction of fluorine with the aluminum substrate in the latest alloy combinations [173].

With respect to the anion, generally, $[CF_3SO_3]^-$, $[Tf_2N]^-$, and $[FAP]^-$ anions exhibit better tribological behavior than the $[PF_6]^-$ and $[BF_4]^-$ anions. A tribochemical reaction has been observed for the $[PF_6]^-$ anion combined with the alkyl-imidazolium cation while investigating its application as lubricants for steel/steel contact [164].

Jimenez et al. also showed that, although $[PF_6]^-$ and $[BF_4]^-$ combined with the alkyl-imidazolium cations work well as additive oils, some tribocorrosion process has been observed when they are used as neat lubricants. However, the tribological behavior improved and no tribocorrosion process occurred when the $[CF_3SO_3]^-$ anion was substituted with the $[PF_6]^-$ and $[BF_4]^-$ anions [168]. The $[Tf_2N]^-$ anion has also been shown to have better tribological behavior compared to the $[BF_4]^-$ anion in alkyl-imidazolium-based ionic liquids when used as a lubricant for steel–steel contact [174]. In addition, the $[FAP]^-$ anion showed even lower friction and better tribological behavior compared to the the tribulation of the tribological behavior compared to the the tribological behavior compared

3.5 Anions and cations suitable for ionic liquids hydrogen compressors

Based on the above review, our cation and anion choices have been narrowed, allowing us to find the best ionic liquid to replace the solid piston for the compression of hydrogen.

3.5.1 **Potential anion choices**

Of the most commonly used anions presented in section 3.2.2, two anions, $[Tf_2N]^-$ and $[CF_3SO_3]^-$, were selected as the best candidates. The other anions presented in section 3.2.2 were eliminated in this step as they could not satisfy some of the important criteria defined in section 3. The main reasons for eliminating these anions are presented in table 3.1.

Anion	Eliminating reasons
Halides (e.g., [Cl] ⁻ , [Br] ⁻ , [l] ⁻)	Corrosion issues
Tetrafluoroborate [BF ₄]	High viscosity, low chemical stability, tribocorrosion issues
Hexafluorophosphate [PF ₆] [–]	High viscosity, chemically unstable, tribocorrosion issues
Tris(perfluoroalkyl)trifluorophosphate [FAP] ⁻	More viscous than $[Tf_2N]^-$
Thiocyanate [SCN]	Lower heat capacity compared to $[Tf_2N]^-$ and $[CF_3SO_3]^-$
Dicyanamide [N(CN) ₂] [–] , also known as [C ₂ N ₃] [–] and [dca] [–]	Very low viscosity, lower thermal stability than $[Tf_2N]^-$
Methanesulfonate [CH ₃ SO ₃] ⁻	Lower heat capacity compared to $\left[Tf_2 N \right]^-$ and $\left[CF_3 SO_3 \right]^-$

Table 3.1 -Main reasons for eliminating some of the most commonly used anions

Alkysulfate (e.g.,	ethylsulfate [E	tSO₄] [−] , also known
as [EtOSO ₃] [−] and	methylsulfate	[MeOSO₃] [−])

Decomposes in the presence of water and, consequently, serious corrosion issues

Nitrate [NO₃]⁻

Water miscible

3.5.2 Potential cation choices

Taking into account the parameters such as lower viscosity, lower hydrogen solubility, and higher thermal stability, between the cation choices of the imidazolium-based, pyridinium-based, and pyrrolidinium-based ionic liquids presented in section 3.2.1, the imidazolium-based ionic liquids are the best candidates. However, with respect to the alkyl chain length for the imidazolium-based ionic liquids, taking into account parameters such as lower viscosity, lower melting point, and lower hydrogen solubility, our cation choice is 1-ethyl-3-methylimidazolium ([EMIM]⁺).

For the ammonium-based and phosphonium-based ionic liquids, because of the considerable advantages such as higher heat capacity (only the phosphonium-based ionic liquids), good tribological behavior, higher thermal stability, and higher thermal conductivity compared to the imidazolium-based ionic liquids, several ammonium-based and phosphonium-based ionic liquids are also selected for further investigation. Therefore, our cation selections are narrowed to:

- 1. 1-ethyl-3-methylimidazolium ([EMIM]⁺),
- 2. trihexyltetradecylphosphonium $([P_{66614}]^+)$,
- 3. butyltrimethylammonium $([N_{1114}]^+)$, and
- 4. methyltrioctylammonium $([N_{1888}]^+)$.

3.5.3 Final candidate

Between all the possible cation and anion combinations our choices are narrowed to the five following candidates:

- 1. 1-ethyl-3-methylimidazolium triflate ([EMIM][CF₃SO₃]),
- 2. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]),
- 3. trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($[P_{66614}]$ [Tf₂N]),
- 4. butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($[N_{1114}]$ [Tf₂N]), and
- 5. methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($[N_{1888}]$ [Tf₂N]).

Figure 3.2 presents chemical structure of the selected ionic liquids



Figure 3.2- Chemical structure of the selected ionic liquids: (a) $[EMIM][CF_3SO_3]$; (b) $[EMIM][Tf_2N]$; (C) $[P_{66614}][Tf_2N]$; (d) $[N_{1114}][Tf_2N]$; (e) $[N_{1888}][Tf_2N]$

As mentioned in Section 4.5, further investigation is required with respect to corrosion to guarantee the safe performance of ionic liquids in direct contact with construction materials for hydrogen compressors. Correspondingly, we have investigated the corrosion behavior of the five selected ionic liquids with stainless steels and nickel-based alloys as construction material for ionic liquid hydrogen compressors at 23 °C [176] and 80 °C, and found that all the selected ionic liquids have high corrosion stability in contact with the mentioned alloys and can be safely used for our application. The detail of the corrosion study is explained in chapter 4.

Table 3.2 presents the viscosities of the five selected candidates.

Ionic liquids	Dynamic viscosity (mPa·s)	Kinematic viscosity (mm ² /s)
[EMIM][CF ₃ SO ₃]	40	28.99
[EMIM][Tf ₂ N]	32	21.05
[P ₆₆₆₁₄][Tf ₂ N]	304	286.79
[N ₁₁₁₄][Tf ₂ N]	99	71.22
[N ₁₈₈₈][Tf ₂ N]	530	460.87

Table 3.2 - Dynamic and kinematic viscosities of the five selected ionic liquids at 25 °C and atmospheric pressure (provided by the manufacturer [177])

Considering that lower viscosities are more suitable for the required viscosity range and our specific application, among the five choices, $[EMIM][CF_3SO_3]$, $[EMIM][Tf_2N]$, and $[N_{1114}][Tf_2N]$, which

have lower viscosities, are the best candidates. In contrast, the two other ionic liquids $[P_{66614}][Tf_2N]$ and $[N_{1888}][Tf_2N]$ with relatively higher viscosities are more suitable for use as lubricants instead of hydraulic oils in any type of compressor for the compression of hydrogen. However, further investigation is required with regard to lubricating applications because the type of the material or alloys in direct contact with the ionic liquid is also critical with respect to the tribocorrosion issues.

Between the three final choices, $[EMIM][Tf_2N]$ and $[EMIM][CF_3SO_3]$ have viscosities in our desired range. The two final choices are both reliable options; however, taking into account the parameters such as better water immiscibility, higher thermal stability, lower melting point, and higher heat capacity, the ionic liquid $[EMIM][Tf_2N]$ is recommended as the best candidate for the replacement of the solid piston in the conventional reciprocating hydrogen compressors. Table 3.3 summarizes the thermophysical properties of our final candidate, $[EMIM][Tf_2N]$.

 Table 3.3 - Thermophysical properties of [EMIM][Tf₂N], the best candidate for replacement of the solid piston in the conventional reciprocating hydrogen compressors

Thermophysical properties of	Thermophysical properties of the ionic liquid [EMIM][Tf ₂ N]								
Dynamic viscosity at 25 °C	40 (mPa·s) [177] *								
Kinematic viscosity at 25 °C	28.99 (mm²/s) [177]*								
Viscosity index	185 [94]								
Density at 25 °C	1.52 (g/mL) [177] *								
Melting point	-17±2 °C [101]								
Henry's law constant	2600 ± 12 (atm) [127]								
Isothermal compressibility	5 × 10 ⁴ (1/MPa) [113]								
Decomposition temperature	400 °C [86]								
Heat capacity at 25 °C and 101.325 kPa	509.2 ± 7.9 (J/ mol·K) [178]								
Thermal conductivity at 25 °C and 101.325 kPa	0.1209 ± 0.0041 (W/ m·K) [158]								

*Data provided by the supplier [177]

3.6 Conclusions

The unique properties of ionic liquids highlight them as a promising option to replace the solid piston in conventional reciprocating hydrogen compressors. Hence, this chapter aims to summarize and discus the literature concerning ionic liquids and the effect of the ionic liquid structure, as well as the temperature, on their properties to find the best ionic liquid candidate for the replacement of the solid piston.

For application to the compressor, an ionic liquid with suitable viscosity, suitable density, negative melting point, water immiscibility, high corrosion stability, low hydrogen solubility, low compressibility, high chemical stability, high thermal stability, high heat capacity, high thermal conductivity, and good tribological behavior is required. Correspondingly, the roles of the cation,

anion, and temperature have been extensively reviewed to find ionic liquids that fulfill our requirements. Finally, the choices are narrowed down to five ionic liquid candidates:

- 1. 1-ethyl-3-methylimidazolium triflate ([EMIM][CF₃SO₃]),
- 2. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N])
- 3. trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($[P_{66614}]$ [Tf₂N]),
- 4. butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($[N_{1114}][Tf_2N]$), and
- 5. methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($[N_{1888}]$ [Tf₂N]).

Of the five choices, [EMIM] $[CF_3SO_3]$, $[EMIM][Tf_2N]$, and $[N_{1114}][Tf_2N]$ have relatively low viscosities and are, thus, the best candidates for the replacement of the solid piston, whereas the two other choices are more appropriate for use as lubricants in any type of compressor for the compression of hydrogen. Finally, $[EMIM][Tf_2N]$ is recommended as the best candidate to replace the solid piston in the conventional reciprocating hydrogen compressors.

4. Corrosion study of stainless steels and nickel-based alloys in contact with the selected ionic liquids

4.1 Introduction

Corrosion is an important factor for selecting an appropriate combination of ionic liquids and construction materials in all the applications of ionic liquids for pneumatic and hydraulic systems. Corrosion of components which are in direct contact with the ionic liquid is of course highly undesirable since it can cause serious problems such as reduced efficiency, leakage of explosive gases, reduced strength, contamination by the corrosion products, and costly maintenance including shut down of the entire production line. Therefore, it is essential to evaluate the corrosivity of the materials in contact with the ionic liquids under relevant conditions.

The corrosion behavior of seven metals and alloys including nickel, titanium, aluminum, copper, manganese, 304 SS and carbon steel was evaluated in several imidazolium- and pyrrolidinium-based ionic liquids with different anions at 25 °C based on the potentiodynamic polarization. The results indicated that nickel had the highest corrosion resistance in the studied ionic liquids, while copper, aluminum and carbon steel showed serious corrosion problems. Moreover, it has been proved in this study that the constituent anions play more significant role, compared to the cations, in corrosivity of the ionic liquids towards materials [120]. Another study has reported a very low corrosion rate of carbon steel alloy (1018) in several imidazolium-based ionic liquids at 25 °C based on the potentiodynamic polarization for solar plant applications [179]. Also, very low corrosion current densities have been reported in a room temperature corrosion study of alloys (copper, nickel, AISI 1018 steel, brass, Inconel 600) in 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide based on the potentiodynamic polarization for vessels and pipes that are applicable in solar power plants [117]. In another study, the corrosion behaviors of stainless steel 316 and carbon steel 1018 were investigated in four different imidazolium-based ionic liquids for solar collectors based on the potentiodynamic polarization at ambient temperature. The results showed active/passive behavior and outstanding corrosion resistance in ionic liquids, except in those that contained a chloride anion [114]. In addition, the corrosivity of pure titanium was evaluated in four different types of ionic liquids mainly at 30 °C based on the potentiodynamic polarization, and electrochemical impedance spectroscopy in a glove box. The results showed high corrosion resistance of titanium in all the ionic liquids expect 1-ethyl-3-methyl-imidazolium chloride aluminum chloride, due to the formation of passive layer [115]. Furthermore, corrosion resistance of nickel has been evaluated in 1-butyl-1methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide based on the situ electrochemical polarization. The pitting corrosion was observed above 500 mV [180]. Another study using the potentiodynamic polarization and electrochemical impedance spectroscopy at ambient temperature, showed a very high corrosion resistance of nickel in aluminum chloride/1-ethyl-3methylimidazolium chloride ionic liquid, while pitting corrosion occurred for AISI 316 before formation of passivation layer at higher potentials and copper corroded severely [116]. A similar study showed an outstanding corrosion resistance of 304 SS and severe corrosion behavior of titanium in this ionic liquid [181]. Moreover, the corrosion behavior of copper, nickel and titanium has been studied in both Lewis acid and basic 1-butyl-3-methyl-imidazolium chloride based on the potentiodynamic polarization and electrochemical impedance spectroscopy at 30 °C. It was observed that nickel showed the highest corrosion resistance while titanium and copper severely corroded however the corrosion mechanism was not the same in acidic and basic ionic liquids. The study also emphasized on the more important role of anion on corrosion rate than the cation [182].

In addition, high temperature corrosion was also to a large extent concerned in the last decades, as it has its basis in many problems of materials degradation at high temperatures. In hydraulic and pneumatic industries, an increase in the operating fluid temperature due to several reasons, such as high frequencies, friction and heat absorption from other media in the system, may happen. Consequently, additional attention must be paid to the corrosion behavior of engineering alloys in the ionic liquids at elevated temperatures.

The corrosion behavior of copper, nickel, AISI 1018 steel, brass, Inconel 600 in 1-butyl-3methylimidazolium bis(trifluoromethanesulfonyl)imide at elevated temperatures based on the potentiodynamic polarizations for vessels and pipes that are applicable in solar power plants showed the fundamental role that temperature plays in the corrosion rate. It has been observed that above 150 °C, copper heavily corroded while at 275 °C, localized corrosion phenomena observed in inconel, carbon steel and nickel, and at 325 °C the pitting corrosion was observed in brass [117]. In another study, the corrosion resistance of austenitic stainless steel, carbon steel, nickel-based alloy C22, brass, copper and aluminum alloy (AlMg₃) was investigated using the rotating cage method in seven different imidazolium- and ammonium-based ionic liquids up to 90 °C [118]. It has been proved in this study that both the chemical structure of the cation and type of anion play a significant role on the ionic liquids corrosivity. Stainless steel 304 showed the highest corrosion resistance in water-free and water-diluted ionic liquids at ambient and elevated temperatures, whereas brass and copper faced severe corrosion problems in the studied ionic liquids [118]. In addition, the corrosion behavior of mild steel was evaluated as a function of the alkyl chain length in the cation of 1-alkyl-3methylimidazolium tricyanomethanide ($[C_n mim]$ TCM, n=2, 4, 6) ionic liquids for CO₂ capture applications. The immersion test was used at 70 °C and 80 °C, and the results showed that the rate of corrosion decreased with an increase in the cation alkyl chain length. It also proved that the reduction of water content and removal of oxygen from the ionic liquid are the two significant factors in decreasing the corrosion rate [112]. Furthermore, the surface corrosion of different metal and alloys (Inconel, bronze, and carbon steel) was studied in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, after a 20-day immersion test at 225 °C. The result showed the formation of corrosion layers was due primarily to the decomposition product of ionic liquids. However, absorption of decomposed products on the surface of alloys restrained the surface corrosion [183].

The application of ionic liquids in the pneumatic and hydraulic technologies is quite new, and to the authors' knowledge, so far only one study has been conducted in this field which investigates the corrosion resistance of several ionic liquids as a lubricant oil in an oxygen screw compressor, using the rotating cage at 120 °C [72]. However, no information was given on the type of ionic liquids and it was only mentioned that stainless steel was very stable. The aim of this chapter is to investigate the corrosion behavior of different stainless steels and nickel-based alloys as construction materials for ionic liquid hydrogen compressor in contact with the five ionic liquids selected in chapter 3, at 23 °C and 80 °C, under atmospheric pressure.

4.2 Experimental part

4.2.1 Materials

Five ionic liquids are selected in chapter 3 and provided by Iolitec [177] are tested. These five ionic liquids are:

1-ethyl-3-methylimidazolium triflate ([EMIM][CF₃SO₃]) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P₆₆₆₁₄][Tf₂N]) butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([N₁₁₁₄][Tf₂N]) methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ([N₁₈₈₈][Tf₂N])

The information regarding the chemical formulae and the purities of the selected ionic liquids are summarized in table 4.1.

Table 4.1- Chemical formulae and purities of ionic liquids provided by the manufacturer [177]

lonic liquids	Chemical formulae	Purity	Anion purity	Cation purity	Halides
[EMIM][CF3SO3]	$C_7H_{11}F_3N_2O_3S$	>99%	99.6%	99.1%	<100 ppm
[EMIM][Tf2N]	$C_8H_{11}F_6N_3O_4S_2$	>99%	99.9%	99.9%	<100 ppm
[P66614][Tf2N]	$C_{34}H_{68}F_6NO_4PS_2$	>98%	>98%	>98%	
[N1114][Tf2N]	$C_9H_{18}F_6N_2O_4S_2$	>99%	99.9%	99.8%	<100 ppm
[N1888][Tf2N]	$C_{27}H_{54}F_6N_2O_4S_2$	>99%	>99 %	>99 %	<100 ppm

The density, dynamic and kinematic viscosity of the selected ionic liquids, provided by the manufacturer [177] at 25 °C, and at atmospheric pressure, are given in table 4.2.

Table 4.2 - Density, dynamic and kinematic viscosity of the selected ionic liquids at 25 °C and
atmospheric pressure (provided by the manufacturer [177])

Ionic liquids	Density(g/mL)	Dynamic viscosity (mPa∙s)	Kinematic viscosity (mm ² /s)
$[EMIM][CF_3SO_3]$	1.38	40	28.99
[EMIM][Tf ₂ N]	1.52	32	21.05
[P ₆₆₆₁₄][Tf ₂ N]	1.06	304	286.79
[N ₁₁₁₄][Tf ₂ N]	1.39	99	71.22
[N ₁₈₈₈][Tf ₂ N]	1.15	530	460.87

In addition, in order to see the effect of temperature on the viscosity, the dynamic viscosities of the selected ionic liquids at 80 °C, and at atmospheric pressure are presented in table 4.3.

Ionic liquids	Dynamic viscosity				
	(mPa∙s)				
[EMIM][CF ₃ SO ₃]	9.84±0.11 [153]				
[EMIM][Tf ₂ N]	7.83±0.2 [184]				
[P ₆₆₆₁₄][Tf ₂ N]	14.1 [97]				
[N ₁₁₁₄][Tf ₂ N]	14.7±0.2 [87]				
[N ₁₈₈₈][Tf ₂ N]	30.8* [185]				

Table 4.3 - Dynamic viscosity of the selected ionic liquids at 80 °C, and atmospheric pressure

* predicted viscosity based on third-degree polynomial curve fitting of dynamic viscosity data for the temperature range of between 20-60 °C presented in [185]

All of the austenitic stainless steels alloys: AISI 316L, AISI 321, AISI 347 and the nickel-based alloys: Inconel[®] 625 and Hastelloy[®] C-276, were provided as wires by Sigma Aerospace Metals LLC [186]. Table 4.4 presents the typical chemical composition of stainless steels and nickel-based alloys, which were investigated in this study.

Table 4.4 - Chemical composition of the alloys

Elements, weight %													
Alloy type	Ni	Со	Cr	Мо	W	Fe	Si	Mn	С	AI	Ti	Other	Nb+Ta
AISI 316L	10-13	-	16.5-18.5	2-2.5	-	Bal.	1.0	2.0	0.03	-	-	N Less 0.11	-
AISI 321	9-12	-	17-19	-	-	Bal.	1.0	2.0	0.08	-	0.4-0.7	-	-
AISI 347	9-13	-	17-19	-	-	Bal.	1.0	2.0	0.08	-	-	-	0.8
Inconel [®] 625	62	1.0	21.5	9.0	-	5.0	0.5	0.5	0.1	0.4	0.4	-	3.5
Hastelloy [®] C-276	57	2.5	15.5	16	3.75	5.5	0.08	1.0	0.02	-	-	V 0.35	-

For the reference electrode compartment, silver sulfate (Ag_2SO_4) with purity of 99.9% (provided by Heraeus [187]) was used.

4.2.2 Electrode preparation

The working electrodes are sealed to determine the surface area of the electrodes. Alumina tubes with inner and outer diameters of 2 and 4 mm respectively, are used for preparation of the alloys working electrodes. A coating paste, CC180W, which was provided by CeProTec [188], is used to seal the electrodes inside the tubes, and fixing the area, exposed to the electrolyte. The diameter of the wires varied between 0.8 to 1 mm and the geometrical working electrode area of all of the tested alloys, is in the range of 8 to 20 mm² (see figure A1 in the appendix A which illustrates one of the working electrodes tested in this study).

A platinum wire of 0.4 mm in diameter, provided by Dansk Aedelmetal A/S [189], serves as a counter electrode. A silver wire of 0.5 mm in diameter, also provided by Dansk Aedelmetal A/S

[189], located in the reference compartment of the Pyrex cell serves as a reference electrode. The ionic liquid $[N_{1114}][Tf_2N]$ saturated with silver sulfate (Ag_2SO_4) is used as an electrolyte for the reference electrode compartment in all of the corrosion experiments. The reliability of this reference electrode has been previously reported elsewhere [190,191]. At room temperature, the potential of the Ag/Ag_2SO_4 electrode is approximately 0.7 V more positive than of the standard hydrogen electrode [192].

4.2.3 Gravimetric method and scanning electron microscopy

Five samples of each alloy are prepared as thin cylindrical discs that were cut from the tested alloy wires, and their faces are grinded with a P1200 grit silicon carbide paper (provided by Struers [193]) to achieve a reproducible surface finish. Then, the samples are washed with acetone to remove any polishing residue, dried in the oven, and weighed using an analytical balance with an accuracy of 0.01 mg. The weighted samples are placed in small Pyrex vessels filled with the ionic liquids and placed in the furnace at 80 °C. After 120 hours of immersion, the samples are rinsed with acetone, dried in a furnace, and finally weighed again at room temperature.

To obtain more information about the corrosion behavior of the tested alloys, cross-sections of the samples after the immersion test are studied using scanning electron microscopy (SEM). All the samples are mounted in PolyFast phenolic hot mounting resin with a carbon filler, provided by Struers [193]. SEM measurements are made using a Zeiss EVO MA10 scanning electron microscope.

4.2.4 Electrochemical corrosion cell

The corrosion test is performed in an electrochemical cell with a special design that was built in our laboratory. The cell (shown in Figure 4.1) is open to the atmosphere and represents a typical three-electrode configuration that consists of the working, counter and reference electrodes. The two working and reference compartments are separated with a porous frit, which is shown as position 7, figure 4.1. The counter electrode (position 4 in figure 4.1) is placed in the same compartment where the working electrode is located. The spiral form of the counter and reference electrodes (platinum and silver wires) ensures a high surface area.

For the measurements at 80 °C, the cell is immersed in the temperature-controlled water bath. A Chromel-Alumel PFA coated thermocouple, which was provided by Omega [194], is used to measure the temperature inside the electrochemical cell. The thermocouple is located in the same compartment with the working electrode. A temperature tolerance of ± 3 °C is allowed during the experiment.

A potentiostat model VersaSTAT 3 with the VersaStudio software by Princeton Applied research [195] is used for the electrochemical measurements. Once the open-circuit potential is established, then the steady-state cyclic voltammetry technique with a scan rate of 5 mV/s is performed at 80 °C under atmospheric pressure. The potential window is 2 V, starting at -1 V, then going to 1 V and ending at -1 V, all against the reference electrode potential.



Figure 4.1 - Electrochemical cell: (1) Working electrode; (2) Reference electrode (Ag wire); (3) Thermocouple; (4) Counter electrode (Pt wire); (5) Hot water bath; (6) Porous frit; (7) Saturated Ag₂SO₄; (8) Electrolyte (ionic liquids)

4.3 Results and discussion at 23 °C

Figures 4.2-4.6 present Tafel plots for stainless steels and nickel-based alloys in [EMIM][CF₃SO₃], [EMIM][Tf₂N], [P₆₆₆₁₄][Tf₂N], [N₁₁₁₄][Tf₂N], and [N₁₈₈₈][Tf₂N] at 23 °C. The cyclic Tafel voltammograms provide valuable information regarding the possible corrosion mechanisms [196]. Figures 4.2-4.6 indicate that for all the alloys tested a passivation layer is formed quite easily. By changing the direction of the polarization from anodic to cathodic, the voltametric curves, in high anodic region close to 1 V vs. the reference electrode, show a decrease of the current value at the reversed scan. This fact can be explained by passivation of the electrode with the metal oxide layer [189].



Figure 4.2 - Tafel plot for the alloys tested in [EMIM][CF₃SO₃] at 23 °C



Figure 4.3- Tafel plot for the alloys tested in [*EMIM*][*Tf*₂*N*] *at* 23 °*C*



Figure 4.4- Tafel plot for the alloys tested in $[P_{66614}][Tf_2N]$ at 23 °C



Figure 4.5 - Tafel plot for the alloys tested in $[N_{1114}][Tf_2N]$ *at 23 °C*



Figure 4.6 - Tafel plot for the alloys tested in $[N_{1888}][Tf_2N]$ at 23 °C

Furthermore, valuable data such as corrosion current density (i_{corr}), corrosion potential of the electrode (E_{corr}), and electrochemical stability window (potential window), can be obtained from the Tafel plots. Figure 4.7 shows the schematic view of Tafel plot and the estimated corrosion current density, corrosion potential and potential window for the stainless steel alloy AISI 316L in [EMIM][Tf₂N]. As shown in figure 4.7 for the stainless steel alloy, the corrosion current density can be estimated from the intersection point of the vertical line through E_{corr} , and the extrapolated linear portions of the anodic and cathodic polarizations [196,197]. Table 4.5 shows the estimated corrosion current densities in the five mentioned electrolytes, which are obtained from figures 4.2-4.6.



Figure 4.7 - Schematic view of the Tafel plot and the estimated corrosion current density, corrosion potential and potential window for the stainless steel alloy AISI 316L in [EMIM][Tf₂N] at 23 °C

i _{corr} (10 ⁻⁵ mA/cm ²)								
	[EMIM][CF ₃ SO ₃]	[EMIM][Tf ₂ N]	[P ₆₆₆₁₄][Tf ₂ N]	[N ₁₁₁₄][Tf ₂ N]	[N ₁₈₈₈][Tf ₂ N]			
AISI 316L	0.8	1.6	0.8	4	1.8			
AISI 321	0.8	1.1	0.8	3.2	0.8			
AISI 347	2.5	1.3	1.3	8	2.5			
Inconel [®] 625	5	4	3.2	16	5			
Hastelloy [®] C-276	1.8	2	1	10	2			

Table 4.5 - Corrosion current densities for the stainless steels and nickel-based alloys in the ionicliquids tested at 23 °C

It can be seen from table 4.5 that the corrosion rate of the materials studied here in the mentioned ionic liquids is very small even in the worst case (Inconel® 625 in $[N_{1114}][Tf_2N]$ with $i_{corr} = 16 \times 10^{-5}$ mA/cm²). Therefore, all of the alloys can be safely used as construction materials for all of the components in direct contact with the ionic liquids tested. Since the estimated corrosion current densities for all of the alloys tested in each electrolyte are comparable, parameters such as corrosion potential and electrochemical stability window can be utilized for a detailed comparison of the corrosion resistance.

Table 4.6 presents the corrosion potentials of the stainless steels and nickel-based alloys in the tested ionic liquids, which are obtained from figures 4.2-4.6. It can be assumed that the corrosion

potentials, in the Tafel voltammograms on figures 4.2-4.6, correspond to the potentials at which we have started the electrochemical oxidation of the alloys during the anodic polarization (the corrosion potential of the stainless steel alloy AISI 316L in [EMIM][Tf₂N] is shown in figure 4.7). The cathodic processes could be the reduction of oxygen or electrolytes. However further studies of the chemistry and electrochemistry of the tested ionic liquids are required to obtain a detailed understanding of these processes. Lower corrosion rates is expected for the more positive values of the corrosion potentials, as reported previously [198].

E _{corr} , mV (vs. Ag/Ag ₂ So ₄)								
[EMIM][CF ₃ SO ₃] [EMIM][Tf ₂ N] [P ₆₆₆₁₄][Tf ₂ N] [N ₁₁₁₄][Tf ₂ N] [N ₁₈₈₈][Tf ₂								
AISI 316L	671	629	731	404	752			
AISI 321	551	454	669	356	689			
AISI 347	533	570	733	406	708			
Inconel [®] 625	504	619	696	418	697			
Hastelloy [®] C-276	451	361	561	345	566			

Table 4.6 - Corrosion potentials of the stainless steels and nickel-based alloys in the ionic liquids tested

Table 4.7 presents the electrochemical stability windows (potential windows) obtained on the stainless steels and nickel-based electrodes in the tested ionic liquid electrolytes, derived from figures 4.2-4.6. The electrochemical stability window is the potential range at which there is not any faradaic activity in the electrochemical system. The potential window obtained on the stainless steel alloy AISI 316L in [EMIM][Tf₂N] is shown is figure 4.7.

Table 4.7 – Electrochemical stability windows obtained on the stainless steels and nickel-based alloys in the ionic liquids tested

Potential window, mV								
[EMIM][CF ₃ SO ₃] [EMIM][Tf ₂ N] [P ₆₆₆₁₄][Tf ₂ N] [N ₁₁₁₄][Tf ₂ N] [N ₁₈₈₈][Tf								
AISI 316L	1201	1321	1582	1104	1137			
AISI 321	1103	988	1440	1103	1162			
AISI 347	1208	1269	1482	1117	1154			
Inconel [®] 625	1101	1263	1206	1125	1275			
Hastelloy [®] C-276	1094	709	1172	1104	1142			

As it can be seen from tables 4.6 and 4.7, and corresponding figures 4.2-4.6, among the three stainless steel alloys tested, AISI 316L and AISI 347, show higher corrosion resistance than AISI 321 in all of the ionic liquids tested.

The high corrosion resistance of AISI 316L can be explained by 2-2.5 wt. % of molybdenum in the structure of AISI 316L. However, the highest contents of molybdenum are only possible in the high nickel alloys, adding a small amount of molybdenum, even one or two percent, to stainless steels can considerably increase the corrosion resistance of these alloys [199,200]. Molybdenum decreases the

corrosion rate by stabilizing the previously formed passive films [201]. In addition, 0.8 wt. % of niobium and tantalum in the structure of AISI 347, and its role in the formation of an oxide layer can explain the high corrosion resistance of AISI 347 [202]. The lowest corrosion resistance of AISI 321 indicates that molybdenum, tantalum, and niobium play more important roles in increasing the corrosion resistance of the alloys than titanium.

Comparing the corrosion resistance of the nickel-based alloys (with a nickel content above 55 wt. %) with stainless steel alloys (with a nickel content 9-13 wt. %) in all of the ionic liquids tested (figures 4.2-4.6, and tables 4.6 and 4.7) shows that high nickel concentration does not have a considerable effect on the corrosion rate.

Hastelloy[®] C-276 shows the poorest corrosion resistance in [EMIM][CF₃SO₃], [EMIM][Tf₂N], $[P_{66614}]$ [Tf₂N], $[N_{1114}]$ [Tf₂N], and $[N_{1888}]$ [Tf₂N]. Thus Hastelloy[®] C-276 has the highest corrosion rate of all the alloys in all the electrolytes tested. This could be due to the lack of niobium and tantalum in the structure of Hastelloy[®] C-276 (compared to Inconel[®] 625), since small amounts of niobium and tantalum could increase the stability of the passivation layer [202,203].

4.4 Results and discussion at 80 °C

4.4.1 Immersion test

After 5 days of immersion, neither serious damage on the surface of the alloy samples nor any considerable changes in the color of ionic liquids are observed. Table 4.8 shows the amount of changes in the weight of alloy samples after 120 hours of immersion in the tested ionic liquids at 80 °C. Other than a slight increase in weight, no significant changes were detected using an analytical balance. The formation of an oxide layer around the samples, as a known factor reported in many corrosion studies [204,205], explains the slight increase in the samples weight. Figure 4.8 shows SEM images of the stainless steel alloy AISI 347 after 120 hours of immersion in [EMIM][CF₃SO₃] at 80 °C, with the highest weight gain percentage. The formation of thin oxide layer on the sample surface can be observed in figure 4.8.

gain weight, 10 ⁻⁵ g (weight gain percentage *)									
	[EMIM][CF ₃ SO ₃] [EMIM][Tf ₂ N] [P ₆₆₆₁₄][Tf ₂ N] [N ₁₁₁₄][Tf ₂ N] [N ₁₈₈₈][Tf ₂ N]								
AISI 316L	34 (0.77%)	4 (0.1%)	7 (0.24%)	6 (0.24%)	6 (0.2%)				
AISI 321	8 (0.19%)	2 (0.04%)	23 (0.55%)	5 (0.15%)	1 (0.02%)				
AISI 347	27 (0.78%)	9 (0.34%)	9 (0.37%)	3 (0.13%)	4 (0.17%)				
Inconel [®] 625	14 (0.33%)	12 (0.27%)	21 (0.64%)	16 (0.54%)	4 (0.13%)				
Hastelloy [®] C- 276	10 (0.34%)	4 (0.14%)	8 (0.29%)	1 (0.05%)	10 (0.46%)				

Table 4.8 – Amount of weight gain and weight gain percentage of the stainless steels and nickelbased alloy samples, after 120 hours of immersion in the tested ionic liquids at 80 °C

*Weight gain percentage is calculated based on ((weight after immersion – weight before immersion)/weight before immersion)×100



Figure 4.8 – SEM of the cross-section of the AISI 347 sample after 120 hours of immersion in [EMIM][CF₃SO₃]

4.4.2 Electrochemical measurements

Figures 4.9-4.13 show Tafel plots of austenitic stainless steels and nickel-based alloys measured in $[EMIM][CF_3SO_3]$, $[EMIM][Tf_2N]$, $[P_{66614}][Tf_2N]$, $[N_{1114}][Tf_2N]$, and $[N_{1888}][Tf_2N]$, at 80 °C.



Figure 4.9 - Tafel plot for the tested alloys in [EMIM][CF₃SO₃] at 80 °C



Figure 4.10 - Tafel plot for the tested alloys in [EMIM][Tf₂N] at 80 °C



Figure 4.11 - Tafel plot for the tested alloys in $[P_{66614}][Tf_2N]$ at 80 °C



Figure 4.12 - Tafel plot for the tested alloys in $[N_{1114}]$ [Tf₂N] at 80 °C



Figure 4.13 - Tafel plot for the tested alloys in $[N_{1888}]$ *[Tf₂N] at 80 °C*

Figures 4.9-4.13 show that similar to 23 °C by changing the direction of polarization from anodic to cathodic, the current values of the reverse voltametric curves are reduced in high anodic region close

to 1 V vs. the reference electrode. This fact indicates the passivation of almost all of the electrodes in this region with the metal oxide layer at 80 °C. However, further investigation is required to better understand of the nature of the passive layer.

Table 4.9 presents the estimated corrosion current densities of all tested alloys in the five studied electrolytes at 80 °C.

i _{corr} (10 ⁻⁵ mA/cm ²)								
	[EMIM][CF ₃ SO ₃]	[EMIM][Tf ₂ N]	[P ₆₆₆₁₄][Tf ₂ N]	[N ₁₁₁₄][Tf ₂ N]	[N ₁₈₈₈][Tf ₂ N]			
AISI 316L	4	5	2	6.3	3.2			
AISI 321	5	3.5	2	5.6	5			
AISI 347	5	4	3.2	10	6			
Inconel [®] 625	20	8	8	25	8			
Hastelloy [®] C- 276	10	6.3	1.3	31.6	4			

Table 4.9 - Corrosion current densities for the stainless steels and nickel-based alloys in the testedionic liquids at 80 °C

Although a considerable increase in the corrosion rate can be expected at elevated temperatures, the corrosion current density values, as estimated from the Tafel plots (shown in table 4.9), are very low, which indicates a small corrosion rate for all of the alloys in any of the five tested ionic liquids at 80 °C. It can be seen from table 4.9 that even in the worst case (Hastelloy® C-276 in [N₁₁₁₄][Tf₂N] with $i_{corr} = 31.6 \times 10^{-5}$ mA/cm²), the corrosion current density value is very low and is comparable to the corrosion current density and corrosion rate values for one of the most corrosion-stable metals in an aggressive solution of hot phosphoric acid (tantalum $i_{corr} = 31.5 \times 10^{-5}$ mA/cm² equal to corrosion rate $< 1 \mu$ m/year) [198]. In general, materials can be considered outstanding corrosion-resistant materials when the corrosion rate is less than 20 µm/year [206]. Consequently, a primary evaluation of the results shows that all of the alloys tested in this study can be safely used as construction materials for all of the components in direct contact with the five ionic liquids tested at elevated temperatures and up to 80 °C. Table 4.10 shows the ratio of corrosion current densities of the stainless steels and nickel-based alloys in the tested ionic liquids at 80 °C compared to 23 °C.

i _{corr _80 °C} / i _{corr _23 °C}								
	[EMIM][CF ₃ SO ₃]	[EMIM][Tf ₂ N]	[P ₆₆₆₁₄][Tf ₂ N]	[N ₁₁₁₄][Tf ₂ N]	[N ₁₈₈₈][Tf ₂ N]			
AISI 316L	5	3.1	2.5	1.6	1.8			
AISI 321	6.2	3.2	2.5	1.8	6.2			
AISI 347	2	3.1	2.5	1.2	2.4			
Inconel [®] 625	4	2	2.5	1.6	1.6			
Hastelloy [®] C- 276	5.6	3.1	1.3	3.2	2			

 Table 4.10 – Ratio of the corrosion current densities at 80 °C to corrosion current densities at 23 °C

 for the stainless steels and nickel-based alloys in the ionic liquids tested
table 4.10 shows that the rate of corrosion current densities increases at 80 °C compared to that at 23 °C. Depletion of the protective layer and a reduction of viscosity at higher temperatures can play a role in the corrosion current density rate increase. The viscosity will significantly decrease with an increase in temperature based on the Arrhenius equation [91]. A dramatic reduction in viscosity at 80 °C compared to that at 25 °C can be seen from table 4.2 and 4.3. Generally, the viscosity of an ionic liquid is an important electrochemical property, and a highly viscous medium decreases the rate of diffusion-controlled chemical reaction [121].In contrast, a less viscous medium has faster ion mobilities in the presence of oxidant, which facilitates faster electrochemical reactions.

Table 4.11 presents the corrosion potentials of the stainless steels and nickel-based alloys in the tested ionic liquids at 80 °C, which are obtained from the Tafel plots (figures 4.9-4.13).

E _{corr} , mV (vs Ag/Ag ₂ So ₄)					
	[EMIM][CF ₃ SO ₃]	[EMIM][Tf ₂ N]	[P ₆₆₆₁₄][Tf ₂ N]	[N ₁₁₁₄][Tf ₂ N]	[N ₁₈₈₈][Tf ₂ N]
AISI 316L	503	374	620	252	417
AISI 321	428	461	536	83	309
AISI 347	522	508	629	242	479
Inconel [®] 625	321	502	569	272	407
Hastelloy [®] C-276	265	324	394	45	245

Table 4.11 - Corrosion potentials of the stainless steels and nickel-based alloys in the tested ionicliquids at 80 °C

A comparison of the results obtained in table 4.11 at 80 °C, with those reported in table 4.6 for 23 °C shows the reduction of corrosion potentials at higher temperatures. This is consistent with an increase in corrosion current densities at 80 °C, as shown in table 4.10.

It can be seen from table 4.11 that among all of the tested alloys, AISI 347 is remarkable at 80 $^{\circ}$ C because it has high corrosion potentials in all of the ionic liquids tested. As explained before, the high corrosion resistance of AISI 347 at 80 $^{\circ}$ C can be attributed to the presence of approximately 0.8% niobium and tantalum in the structure of this alloy.

Figure 4.14 shows the Tafel plot for the stainless steel alloy AISI 347 in all five ionic liquids tested.



Figure 4.14 – Tafel plot for AISI 347 in [EMIM][CF_3SO_3], [EMIM][Tf_2N], [P_{66614}][Tf_2N], [N_{1114}][Tf_2N], and [N_{1888}][Tf_2N] at 80 °C.

It can be seen from figure 4.14 and tables 4.9 and 4.11 that the stainless steel alloy AISI 347 shows the highest corrosion resistance in $[P_{66614}][Tf_2N]$, $[EMIM][Tf_2N]$ and $[EMIM][CF_3SO_3]$ ionic liquids.

In general, similar to 23 °C, a comparison of the corrosion potentials of the two nickel-based alloys (Inconel® 625 and Hastelloy® C-276) with the stainless steel alloys at 80 °C shows that there is no noteworthy improvement in the corrosion rate of high nickel concentration alloys in the tested electrolytes. Table 4.11 shows that Hastelloy® C-276, with the nickel content above 55 wt. %, is the least corrosion-resistant alloy at 80 °C.

4.4.3 Role of ionic liquid cation and anion

Although AISI 347 and Hastelloy[®] C-276 shows a similar corrosion behavior in all of the ionic liquids tested, different corrosion behaviors are observed for AISI 316L and Inconel[®] 625 in different electrolytes. As can be seen in figure 4.10 and table 4.11, AISI 316L shows a relatively poor corrosion resistance in [EMIM][Tf₂N] compared to the stainless steel alloys AISI 347 and AISI 321 and the nickel-based alloy Inconel[®] 625. In contrast, stainless steel AISI 316L is one of the most stable alloys in other electrolytes, with a relatively high corrosion resistance close to that of AISI 347. In contrast, as seen from figure 4.9 and table 4.11, Inconel[®] 625, with a relatively high corrosion resistance (comparable with AISI 347) in [EMIM][Tf₂N], [P₆₆₆₁₄][Tf₂N], [N₁₁₁₄][Tf₂N], and [N₁₈₈₈][Tf₂N], shows a relatively poor corrosion resistance compared to the other alloys in [EMIM][CF₃SO₃]. Such differences show the role of both cation and anion of ionic liquids in the corrosion behavior of the tested alloys in different ionic liquid-based electrolytes. Such dependencies have also been reported previously [118].

4.4.4 Role of ionic liquid water absorption

In addition to viscosity and the nature of the cations and anions of ionic liquids, water miscibility is an important parameter in ionic liquids that can affect the corrosion behavior of alloys. Water is reported to be one of the most significant impurities in the ionic liquids that can change the physical and chemical properties of the ionic liquids [106,108,109] because even hydrophobic ionic liquids can absorb some amount of water from the atmosphere [106,107].Water can affect the electrochemical reaction and reduce the potential window [88]. In addition, an increase in the water content in an ionic liquid has been shown to decrease viscosity [88,109–111]. Enhancing the cations and anions mobility and increasing the transport of molecular species in ionic liquids are consequences of a reduction in ionic liquid viscosity [207]. The significant role of reducing the water content in decreasing the corrosion rate has been reported in [112]. To investigate the role of water content in the corrosion rate of the tested alloys, the water content of five tested ionic liquids is measured at 25 °C under atmospheric conditions using Karl Fischer Titration. The samples are used directly from the bench without any attempt for drying or purification and the results are shown in table 4.12.

Ionic Liquids	Water content (ppm)
[EMIM][CF ₃ SO ₃]	1683
[EMIM][Tf ₂ N]	792
[P ₆₆₆₁₄][Tf ₂ N]	442
[N ₁₁₁₄][Tf ₂ N]	1007
[N ₁₈₈₈][Tf ₂ N]	1046

Table 4.12 - Water content of the five tested ionic liquids at 25 °C under atmospheric conditions

It can be seen from tables 4.9, 4.11, and 4.12 that all of the stainless steels and nickel-based alloys show the best corrosion resistance behavior (the lowest corrosion current densities and the highest corrosion potentials) in $[P_{66614}][Tf_2N]$, with a relatively high viscosity and the lowest water content compared to the other ionic liquids in this study.

Generally, as discussed above, the low corrosion current densities at 23 and 80 °C prove the possibility of selecting all of the alloys tested as construction materials for components that are in direct contact with the five ionic liquids. However, the final choice may depend on several parameters, such as the operating temperature and pressure of the system, limitations in selecting a material for a specific application, ease of fabrication, mechanical properties, hydrogen embrittlement, and price. Among all the alloys tested, AISI 316L is the cheapest with high corrosion resistance in all the ionic liquids studied here, and very high resistance to hydrogen embrittlement [208–210]. Therefore, it is recommended as one of the promising candidates for construction materials of the components in direct contact with the tested ionic liquids.

4.5 Conclusions

The compatibility of various austenitic stainless steels and nickel-based alloys as construction materials, in contact with the five different ionic liquids, selected in chapter 3 is investigated with respect to corrosion at 23 and 80 °C and atmospheric air. At 80 °C, the role of parameters, such as

temperature, viscosity, ionic liquid cation and anion, and ionic liquid water absorption on the corrosion behavior of alloys are investigated using gravimetric test, cyclic polarization and Tafel plots. Under the tested conditions, the following findings were presented:

- The corrosion rate increases with increasing temperature. However, very low corrosion rates of the tested alloys in the studied ionic liquids are observed. Consequently, all of the alloys are safe to use as construction materials for the ionic liquid hydrogen compressors and/or other hydraulic and pneumatic components that are in direct contact with the studied ionic liquids at elevated temperatures up to 80 °C.
- The reduction of current on the reverse voltametric curves compared to the current of forward ones, in high anodic region close to 1 V vs. the reference electrode shows the formation of a passivation layer on almost all of the alloys.
- Nickel-based alloy, Hastelloy[®] C-276 shows the poorest resistance to corrosion in all the tested ionic liquids. A comparison of the corrosion resistance of the nickel-based alloys with stainless steel alloys in all of the tested ionic liquids shows that high nickel concentration does not play a significant role on corrosion rate of the tested alloys in the selected ionic liquid-based electrolytes.
- Considering the observed corrosion rates, prices, and resistance to hydrogen embrittlement, for all of the tested stainless steels and nickel-based alloys, stainless steel AISI 316L is recommended as the construction material for all of the components which are in direct contact with the studied ionic liquids in an ionic liquid hydrogen compressor.

<u>At 23 °C:</u>

• AISI 316L and AISI 347 show a higher corrosion resistance than AISI 321, in all the tested ionic liquids. A small addition of molybdenum, tantalum, and niobium in the structure of the alloys can increase the corrosion stability of the alloys in selected ionic liquids.

<u>At 80 °C:</u>

- Small weight gain of the tested alloys and SEM analysis confirms the formation of an oxide layer after the exposure of the alloys to the selected ionic liquids.
- A small addition of tantalum and niobium in the alloys structure can enhance the corrosion stability of alloys that were tested in the studied ionic liquid-based electrolytes at 80 °C.
- The stainless steel alloy, AISI 347, shows outstanding corrosion stability in all five tested ionic liquids.
- The preliminary investigation of the tested alloy behavior in the studied ionic liquid-based electrolytes proves the importance of both the cation and the anion roles of the ionic liquids in determining the corrosion resistance of the tested alloys.

• Reducing the viscosity and enhancing the water content of an ionic liquid can play a key role in increasing the corrosion rate. All of the tested alloys have the highest corrosion resistance in the $[P_{66614}][Tf_2N]$ ionic liquid, with a relatively high viscosity and the lowest water content.

5. Design and fabrication of the prototype

5.1 Introduction

The liquid piston compressor appears to be a promising option to address the many problems in conventional compressors. The history of the liquid piston dates back to 1909, when the first internal combustion liquid piston pump known as the Humphrey pump was introduced. The Humphrey pump used a column of liquid with a combustion chamber at one end to pump the liquid without applying any type of solid piston. A historical review of this technology showed that the pump has a superior thermodynamic cycle and higher efficiency compared to conventional alternatives [211].

Such concept has been used in piston engine compressors to utilize the combustion of hydrocarbon fuels for compressing air into high-pressure supply tanks by a slug of water, which leads to functionality and performance improvement [212,213].

The engineering team of the U.S. DOE hydrogen program has developed a liquid piston compressor for compression of hydrogen using hydraulic oils [29] by spraying hydraulic oil into the head of the compression chamber. For a single prototype unit, they showed that a significant improvement in efficiency and 50% reduction in cost, compared to conventional hydrogen compressors with the same flow rate and compression ratio, can be obtained [29].

As it is mentioned in the previous chapters, recently, a company called "Linde" developed a new type of compressor for the compression of hydrogen in hydrogen refueling stations using ionic liquids. In the designed compressor, the ionic liquid is directly pumped into the compression chamber/chambers to compress the hydrogen and it is sent back to the hydraulic system [214]. It has been proved that substituting hydraulic oil with an appropriate ionic liquid in a diaphragm pump leads to a remarkable improvement of approximately 10 to 30% in volumetric efficiency [73].

In the present work, we have used the advantages of both the liquid piston concept and ionic liquid as a replacement for the solid piston, while introducing a custom-designed hydraulic to pneumatic transformer to integrate our designed pneumatic and hydraulic systems. As will be discussed later in the present study, directly using an ionic liquid in our system may require either a complicated and custom-designed hydraulic system or a task-specific ionic liquid (specifically designed for our case), which in both cases, will result in a considerable increase in the final production cost of the compressor, and hence, is not desirable. The proposed system can avoid direct contact of the ionic liquid with the hydraulic system. The designed compressor can be used for compression of hydrogen to the required pressure of up to above 700 bar [215] in hydrogen refueling stations and reduce the total hydrogen costs.

The following sections briefly described the design procedure for the three main parts of the compressor, namely the pneumatic system, hydraulic to pneumatic transformer, and hydraulic system, as well as the selection of components for the prototype unit.

5.2 Advantages of the selected ionic liquid compared to water and hydraulic oils

Substituting the solid piston of the conventional reciprocating compressor with an ionic liquid is clearly the first step; however, the type of ionic liquid that behaves as close as possible to the solid piston was crucial to guarantee a reliable performance and long lifetime of the system. As explained in chapter 3 the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) is selected as the best candidate to be used as replacement for the solid piston.

In general, the following advantages can be obtained by using the ionic liquid as replacement for the solid piston compared to water and hydraulic oils:

A. Advantages of the selected ionic liquid compared to both water and hydraulic oils

- Negligible vapor pressure [50], resulting in a higher volumetric efficiency and pure hydrogen as final product (no contamination of hydrogen with water and hydraulic oil)
- Satisfactory tribological behavior [63,163], which eliminates the application of oil as lubricant in our system; therefore, no contamination of hydrogen with hydraulic oil

B. Specific advantages of the selected ionic liquid compared to water

- Much higher viscosity than water [97], which can prevent leaks in seals, and hence, improvement in volumetric efficiency and avoiding the risk of cavitation due to negative pressures
- High corrosion stability [176], which avoids corrosion problems that can occur due to the presence of water in the system
- Much higher molar heat capacity [157], which reduces both the operating temperature of the system and cooling requirements
- Prevents the growth of bacteria and algae, which can occur due to the presence of water in the system [78].

C. Specific advantaged of the selected ionic liquid compared to hydraulic oils

- Higher viscosity index value, which leads to a reliable system operation within the normal working condition, easy start up, considerable reduction of losses at low temperatures, and avoid cavitation problems such as metal fracture, fatigue corrosion, and stress corrosion
- Higher thermal stability [163], which avoids decomposition of the liquid during the operation and provides a safe and reliable performance
- Possibility of having lower compressibility [132], which leads to improvement in volumetric efficiency, better control of the system, and avoid cavitation problems

5.3 Design of a prototype

The basic concept of the liquid piston compressor technology is to directly compress the hydrogen in the compression chamber by a column of liquid driven as a part of the hydraulic system. Our studies

regarding ionic liquid behavior and pneumatic and hydraulic systems showed that directly using ionic liquids in hydraulic systems may cause the following problems:

- Risk of corrosion in hydraulic components, as an incorrect selection of the ionic liquid and component material in contact with the ionic liquid can cause serious corrosion issues. In order to avoid such issues, a comprehensive corrosion study of different ionic liquids in contact with all the hydraulic components is required. This will be time consuming, and may lead to a requirement for costly task-specific ionic liquids or a custom-designed hydraulic system made of expensive materials.
- Risk of hydrogen penetration in the hydraulic system in case of any failure in the hydraulic components or control procedure. In order to ensure a safe performance of the hydraulic system in such cases, ATEX-certified hydraulic components, which can significantly increase the cost, are required.
- Requirement for a strictly airtight hydraulic system, which can be extremely costly. Even hydrophobic ionic liquids can absorb some amount of humidity in the atmosphere. This can affect their properties and intensify the corrosion issues [106–109]. Therefore, it is highly desirable to have an airtight hydraulic system and avoid direct contact of the ionic liquid with the atmosphere in long-term applications.
- No possibility of minimizing the amount of ionic liquids in the system. As ionic liquids are expensive, it is highly desirable to minimize their amount. However, fulfilling such condition in the hydraulic system may not be very easy as the reservoir should be filled with more hydraulic oil than what is really required to ensure a satisfactory performance of the pump.

To solve the above problems, we proposed a hydraulic to pneumatic transformer for integrating our designed pneumatic and hydraulic systems. Two candidate solutions are proposed and evaluated; then, the best option is chosen for the fabrication stage.

5.3.1 Design specification

Thoroughly defining the main design parameters is fundamental for the proper arrangement of the system elements and correct selection of components. Our main design parameters are as follows:

Maximum Operating pressure: The maximum operating pressure of the system is required for the proper arrangement and selection of the pneumatic and hydraulic components. We have designed our hydraulic and pneumatic system in such a way that the system can easily build up a high pressure above 700 bar; however, in the selection of components, we have limited our operating pressure to 300 bar with a pressure ratio of 3, due to the safety regulations and restrictions of the university.

<u>Maximum Operating temperature</u>: The maximum operating temperature of hydrogen is required for the correct selection of components. The hydrogen maximum operating temperature of approximately 140 °C is estimated based on the thermodynamic model, assuming a compression of hydrogen from 100 bar to 300 bar and an inlet hydrogen temperature of approximately 29 °C.

Maximum volume flow rate and operating frequency:

The maximum volume flow rate of hydraulic oil and operational frequency of the system play a key role in determining the correct selection of the pump and the electric motor for the hydraulic system. The maximum volume flow rate is selected based on the expected Reynolds-number of the hydrogen flow inside the compression chamber. We are targeting a Reynolds-number above 2300 in order to have the possibility of investigating a turbulent behavior of flow inside the compression chamber.

The Reynolds-number for hydrogen flow is calculated by the thermodynamic model using equation 5.1, and assuming the same speed of the hydrogen and ionic liquid inside the compression chamber.

$$Re = \frac{\rho_{liq\backslash gas} VID_{comp-ch}}{\mu_{liq\backslash gas}} \quad \text{where} \quad VI = \frac{\dot{v}_{IL}}{A_{comp_ch}}$$
(5.1)

Where $\rho_{liq\backslash gas}$, $\mu_{liq\backslash gas}$, $A_{comp-ch}$, $D_{comp-ch}$, and \dot{v}_{IL} are the density and viscosity of the liquid or hydrogen, cross-sectional area of the compression chamber, diameter of the compression chamber, and ionic liquid volume flow rate respectively.

5.3.2 Design of pneumatic system

In the pneumatic system, the hydrogen enters the compression chamber from the inlet line. During the compression stroke, the energy of the hydraulic system will be transferred to the pneumatic system by the column of ionic liquid, which compresses the hydrogen. Finally, the compressed hydrogen will be released from the outlet line after it reaches the required pressure. Figure 5.1 shows the piping and instrumentation (PI) diagram of the designed pneumatic system.



Figure 5.1 - PI diagram of the designed pneumatic system

The inlet and outlet lines consist of the following:

Three solenoid valves (position 1, 5, and 9): The first solenoid on/off valve (pos. 1) is located at the beginning of the inlet line. It is normally open and will be automatically closed in an emergency case (leakage and high concentration of hydrogen in the environment), disconnecting the hydrogen source from the rest of the components. The second and third solenoid valves at the inlet (pos. 5) and outlet (pos. 9) lines will be opened and closed automatically allowing the hydrogen to enter and be released from the compression chamber.

Filter (position 2): A filter (pos. 2) is provided to avoid the presence of any type of particle in the system.

Check valves (position 3, 12): Two check valves are installed at the inlet (pos. 3) and outlet (pos. 12) lines to allow the hydrogen to flow in the required direction.

Pressure relief valves (position 4, 10): Two pressure relief valves are installed at the inlet (pos. 4) and outlet (pos. 10) lines to avoid undesirable overpressures and protect the system components.

Manual on/off valves (position 6, 8): Two manual on/off valves at the inlet (pos. 6) and outlet (pos. 8) lines are normally open during operation, while providing the possibility of disconnecting the chamber from the inlet and outlet lines for easier maintenance.

Metering valve (position 11): A properly adjusted metering valve (pos. 11) is installed at the outlet line to control the hydrogen volume flow rate, and avoid hydrogen auto-ignition due to rapid release of hydrogen.

Compression chamber (position 7): The compression chamber (pos. 7) is a high-pressure vessel for compressing the hydrogen; it has to be equipped with a safety rupture disc to avoid explosion in case of overpressurization. In addition, a thermocouple (pos. 7-a) and a pressure transducer (pos. 7-b) are tightly installed on the head of the compression chamber in direct contact with hydrogen to monitor the hydrogen pressure and temperature during the compression process, evaluate the compressor performance, and control the system. Monitoring of the surface temperature of the chamber is performed for verification of the theoretical model and further optimization of the process.

Scenarios related to failure of any component or overpressure are considered in the valve arrangement and location of pressure relief valves to minimize the risks and component damages in case of any accidents.

5.3.3 Design of hydraulic to pneumatic transformer

The following two solutions are suggested to transfer the hydraulic power to the pneumatic system (hydrogen) while separating the ionic liquid from the hydraulic system

<u>A commercially available accumulator</u>: The accumulator (shown in figure 5.2-a) consists of a cylinder with a floating piston, which separates the ionic liquid from the hydraulic oil. The hydraulic oil will be pumped into the accumulator through a hydraulic circuit to move the sliding piston, which

consequently transfers the same amount of force to the ionic liquid side for pressurizing the hydrogen inside the compression chamber.

<u>A custom-designed dual cylinder</u>: The dual cylinder (shown in figure 5.2-b) consists of a back-toback cylinder unit including a piston rod between the two cylinders for transferring the hydraulic power from the hydraulic side to the ionic liquid side. This option will provide the possibility of taking advantage of different surface areas of the cylinders (larger cylinder diameter in the hydraulic oil side and smaller cylinder diameter in the ionic liquid side) in order to reach the required pressure in the pneumatic side while providing a lower pressure in the hydraulic side.



Figure 5.2 - schematic of (a) accumulator and (b) dual cylinder

5.3.3.1 Evaluation of different concepts

A comparison of the two solutions shows that the custom-designed dual cylinder will provide more benefits.

First, it will slightly reduce the hydraulic power consumption and save more energy. The reason for the power reduction can be explained by equation 5.2 [216]:

$$W_{pump} = \frac{\dot{v}_{oil}\Delta p}{\eta_{pump}\eta_{el}}$$
(5.2)

where W_{pump} , \dot{v}_{oil} , Δp , η_{pump} , and η_{el} are the required power for pumping, volume flow rate of hydraulic oil, pressure drop across the pump, pump efficiency, and electric motor efficiency

respectively. By comparing the accumulator concept with the dual cylinder concept, the result of ($\dot{v}_{oil}\Delta p$) would be approximately the same for both. As it can be observed in equations 5.3 and 5.4, the two parameters of volume flow rate (\dot{v}_{oil}) and pressure drop (Δp) increase and decrease with the factors of $(D_{oil}/D_{IL})^2$ and $(D_{IL}/D_{oil})^2$ respectively for the dual cylinder (D_{oil} is the diameter of cylinder containing hydraulic oil and D_{IL} is the diameter of cylinder containing ionic liquid, shown in figure 5.2-b. On the other hand, η_{pump} is a function of the volume flow rate (\dot{v}_{oil}) [216] and increases with increasing \dot{v}_{oil} . Consequently, a lower power consumption will be expected for the dual cylinder with a higher volume flow rate correspondingly a higher (η_{pump}).

Second, it will be a safer design as the ionic liquid will be completely separated from the hydraulic oil and there will be no risk of hydrogen penetration into the hydraulic system in case of any failure.

Therefore, the concept of a custom-designed dual cylinder is selected for integrating into the designed pneumatic and hydraulic system.

The diameters of the cylinders should be determined as follows to achieve the required pressure in the compression chamber, assuming the same force in the hydraulic and ionic liquid side:

$$F_{oil} = F_{IL} \to P_{oil} A_{oil} = P_{IL} A_{IL}$$
(5.3)

where *F* and *P* are respectively the force and pressure of the hydraulic oil inside the hydraulic oil cylinder (oil) and the ionic liquid inside the ionic liquid cylinder (IL), and A_{oil} and A_{IL} are respectively the cross-sectional areas of the cylinders containing hydraulic oil (oil) and ionic liquid (IL) in the hydraulic to pneumatic transformer.

Figures 5.3 and 5.4 show the drawing of the designed hydraulic to pneumatic transformer, and figure 5.5 shows the 3D configuration of the cylinders containing (a) the hydraulic oil, and (b) ionic liquid.



Figure 5.3 - Drawing of the custom-designed dual cylinder hydraulic to pneumatic transformer: the part shown in red color is the holder, the left side shows the cylinder containing hydraulic oil, and the right side shows the cylinder containing the ionic liquid in the hydraulic to pneumatic



Figure 5.4 - Detailed drawing of the cylinder containing ionic liquid as part of the hydraulic to pneumatic transformer



Figure 5.5 - The 3D configuration of cylinders containing (a) hydraulic oil and (b) ionic liquid as parts of the hydraulic to pneumatic transformer

Assuming the same speed of piston rod between the hydraulic oil and ionic liquid cylinder will provide the same speed of the ionic liquid inside the ionic liquid cylinder VI_{IL} and hydraulic oil inside the hydraulic oil cylinder VI_{oil} ; therefore, the volume flow rate of the ionic liquid \dot{v}_{IL} can be estimated as follows:

$$\mathcal{V}_{IL} = \mathcal{V}_{oil} = \frac{\dot{v}_{oil}}{A_{oil}} \Longrightarrow \dot{v}_{IL} = \dot{v}_{oil} \frac{A_{IL}}{A_{oil}}$$
(5.4)

5.3.4 Design of hydraulic system

The hydraulic system is mainly responsible for providing the required pressure and volume flow rate (correspondingly, the speed of the cylinder movement) in the pneumatic part. The gas will be compressed in a cycle inside the compression chamber following the four steps below:

- 1. Filling the compression chamber with hydrogen
- 2. Pressurizing the system to the required pressure by pumping hydraulic oil toward the pneumatic side
- 3. Releasing the hydrogen
- 4. Depressurizing the system by sending back the liquid to the hydraulic oil reservoir

Figure 5.6 shows the PI diagram of the designed hydraulic system and the hydraulic to pneumatic transformer.



Figure 5.6 - PI diagram of the designed hydraulic system and hydraulic to pneumatic transformer

The main components of the hydraulic system are as follows:

Pump and electric motor (position 15 and 16): a variable displacement pump (pos. 15) powered by an electric motor (pos. 16) will provide the required pressure in the pneumatic part.

Proportional flow-regulating valve (position 19): an electrical proportional flow-regulating valve (pos. 19) will regulate the actual hydraulic oil volume flow rate by changing the size of the opening.

By using the so-called "load-sensing system," the pump will maintain a constant pressure drop across the flow-regulating valve (pos. 19). If the opening of the flow-regulating valve (pos. 19) is small (4 mA) the pump reduces the volume flow rate in order to maintain the pressure drop, while still running with the same speed. If the flow-regulating valve (pos. 19) is fully opened (20 mA), the pump will angle the swashplate to obtain the same pressure drop through the flow-regulating valve (pos. 19). Correspondingly, the volume flow rate and the speed of cylinder movement will be regulated.

Proportional pressure-regulating valve (position 20): an electrical proportional pressureregulating valve (pos. 20) is mounted in the load-sensing line in order to control the maximum operating pressure. This pressure valve should be manually adjusted to the maximum operating pressure (corresponds to 20 mA). Therefore, the valve will never allow the pressure to be higher than the maximum system pressure (if the receiving signal is \geq 20 mA).

When the proportional flow-regulating valve (pos. 19) and the proportional pressure-regulating valve (pos. 20) are adjusted to the required movement speed and pressure, the system is ready to run in cycles.

Safety relief valve (position 22): an extra safety relief valve (pos. 22) is added to the system. This is usually adjusted 20 bars higher than the maximum normal operating pressure to avoid undesirable overpressure and protect the components if the proportional pressure-regulating valve (pos. 20) fails.

2-/3-way valve (position 24): a 2-/3-way valve will direct the hydraulic oil from the inlet line toward the hydraulic oil cylinder during pressurization and from the hydraulic oil cylinder toward the oil tank during depressurization. During the depressurization, the hydrogen pressure will force the ionic liquid and hydraulic oil to return to the ionic liquid cylinder and oil tank respectively.

Operating ON/OFF valve (position 21): an operating ON/OFF valve (pos. 21) will start/stop the cylinder movement. The operating ON/OFF valve is a normally open valve to start up the system relief, as there is no pressure requirement during the return cycle. Therefore, the pressurization process is started by closing the ON/OFF valve (pos. 21), and when the cylinder of the compression chamber is moved to the total adjusted stroke (compressed the hydrogen to the required pressure), the 2-/3-way valve (pos. 24) will be deactivated, and the ON/OFF valve will be relieved to stop the pump force by closing the load-sensing line to the oil tank. Then the system is ready to move the cylinder backward again.

Check valve (position 23): a check valve (pos. 23) is installed between the proportional flow-regulating valve (pos. 19) and 2-/3-way valve (pos. 24) to move forward the hydraulic oil in the desired direction toward the hydraulic oil cylinder.

Filters (position 18 and 31): a hydraulic filter is installed in both the inlet (pos. 18) and outlet (pos. 31) of the hydraulic line to protect the hydraulic components from damage due to contamination of hydraulic oils. A bypass valve parallel to the filter is installed at the lines in the case of filter clogs; however, the filter must be replaced before the pressure drop reaches the bypass valve set value.

Generally, hydraulic oils can pick up contaminating particles (rust from metal and polymer particles from seal), which can clog the tiny clearances in precision valves and cylinders, and also cause corrosion [78]; therefore, having a filter at both the inlet and outlet lines is important. In addition, a clogging indicator on the filter is a good option to provide a visual or electrical indication; it must have a set value lower than the bypass valve value.

Oil tank (position 13): the oil tank (pos. 13) will provide a source of room temperature hydraulic oil at atmospheric pressure. The oil tank is basically an oil storage tank including an oil sight glass (pos. 13-a) and a sensor (pos. 14) for sensing the liquid level inside the tank. It is connected to the atmosphere through an oil breather (pos. 13-b); it has a pump (pos. 15) and return line to deliver and accept the hydraulic oil.

Sensors (position 17, 26, 28, 29, and 30): a pressure transmitter (pos. 17) is installed at the inlet of the hydraulic line to measure the hydraulic oil pressure. In addition, a pressure sensor (pos. 28), a piston position sensor (transducer with floating magnet) (pos. 26), a temperature transmitter (pos. 29), and flow meters (pos. 30) are installed between the compression chamber and ionic liquid cylinder to monitor the ionic liquid temperature, pressure, and speed and appropriately control the system.

Oil cooler (position 32): an oil cooler unit can be added to the system if there is a requirement for cooling the hydraulic oil due to significant increase in the operating temperatures of the hydraulic oil.

5.4 Fabrication of a porotype

A prototype of the ionic liquid piston compressor is built as proof of concept. Commercially available components are selected for the hydraulic and pneumatic systems to provide a realistic picture of an industrial system, with all the data on pressure drops, flows, and dynamic behavior being taken from catalogues and technical manuals.

The list of key components together with corresponding pictures and the challenging issues for the component selection are briefly presented in the following sections.

5.4.1 Components selection

As mentioned above, several corrosion tests were performed to examine the compatibility of commercial stainless steel and nickel-based alloys in contact with the selected ionic liquid [176,217], Finally, stainless steel alloy AISI 316 with high corrosion resistance and relatively cheaper production cost is selected as the material for all components in direct contact with the ionic liquid.

5.4.2 Pneumatic components

Figure 5.7 shows a prototype of the designed pneumatic system corresponding to the PI diagram illustrated in figure 5.1, which consists of 12 main parts. Figure 5.7-a shows the components of the inlet line shown in figure 5.1; the two black components are the two solenoid valves, pos. 1 and 5. Figure 5.7-b demonstrates the components of the outlet line shown in figure 5.1; the black component is the solenoid valve pos. 9. In both figure 5.7-a and 5.7-b the silver component standing on the middle of the holder is the compression chamber (pos.7)



Figure 5.7 - the prototype of the designed pneumatic system, (a) inlet line, (b) outlet line

To reduce any risk of explosion, a small compression chamber with 1 L size is selected. The list of pneumatic components used for building the prototype is presented in table 5.1 along with the maximum operating temperatures and pressures, and the suppliers.

Table 5.1- Li	ist of pneumatic	components	used for	building	the prototype
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Component	Туре	Supplier
Solenoid valves (pos. 1, 5, 9)	Valve (SS-AFSS6) and Actuator (VRX25DIS2C)	Swagelok A/S [218] and Valpes A/S [219]
Filter (pos. 2)	SS-4TF-2 (204 °C maximum temperature)	Swagelok A/S [218]
Check valves (pos. 3, 12)	SS-CHS4-10 (204 °C maximum temperature)	Swagelok A/S [218]
Pressure relief valves(pos. 4, 10)	SS-4R3A1	Swagelok A/S [218]
Metering Valve (pos. 11)	SS-31RS4 (93 °C maximum temperature)	Swagelok A/S [218]
Manual on/off valves (pos. 6, 8)	A455VB2	Swagelok A/S [218]
Compression chamber (pos. 7)	Parr pressure vessel instrument 4653, fixed- head mounting with stand (w/o heater) (size:1 L/ diameter = 63.5 mm, length = 33.3 mm) (414 bar maximum pressure, 350 °C maximum temperature)	Parr Instrument Company [220]
Thermocouple (pos. 7-a)	Туре Ј	Parr Instrument Company [220]
Pressure transducer (pos. 7-b)	PARA1905E7 (517 bar maximum pressure, 125 °C maximum temperature)	Ashcroft A/S [221]

Monitoring of the operating temperature of hydrogen during the compression process is required, as there are some limitations for some of the components with respect to the maximum operating temperature.

5.4.3 Hydraulic to pneumatic transformer

Figure 5.8 shows the prototype of the custom-designed hydraulic to pneumatic transformer corresponding to figure 5.3.



Figure 5.8 - Prototype of the hydraulic to pneumatic transformer; the red dotted arrows show the direction in which the ionic liquid will be pumped into the compression chamber, and the blue arrows show the direction in which the ionic liquid will return to the ionic liquid cylinder

The cylinder connected to the hydraulic circuit is a slave cylinder of the cylinder containing the ionic liquid. As shown in figure 5.8, the ionic liquid will be pumped into the compression chamber when the slave cylinder moves forward (shown with arrow direction in red color), and the ionic liquid will return to the ionic liquid cylinder when the slave cylinder moves backward (shown with arrow direction in blue color).

The cylinder containing the hydraulic oil is a commercially available high-pressure hydraulic cylinder (diameter = 140 mm, mass = 49.6 kg, working pressure = 250 bar, test pressure = 375 bar) provided by Fjero A/S [222], while the cylinder containing the ionic liquid is a custom-built cylinder made of stainless steel AISI 316 (diameter = 100 mm, mass = 42.1 kg, test pressure = 300 bar provided by Fjero A/S [222] to fulfill our design requirements. Operating the dual cylinder at a pressure close to the test pressure caused a minor deflection of the cylinder construction; therefore, two extra upper stringers have been added to the original design to avoid flexing problems.

Based on equation 5.3 and the diameter of the cylinders and compression chamber, a minimum pressure of 153 bar (as friction losses and pressure drops are neglected in equation 5.3) should be provided by the pump to reach the required maximum operating pressure of 300 bar in the ionic liquid side and the compression chamber. An ATEX-certified ultrasonic device is installed in the cylinder containing the ionic liquid to track the liquid level and measure the speed inside the compression chamber.

5.4.3.1 O-ring Selection

The next challenge for a satisfactory performance of the transformer is the correct selection of seal ring for the custom-built cylinder in order to avoid any reaction between the O-ring and ionic liquid and any leakage in the system. A differential thermal analysis (DTA) is performed for four different O-ring types (Viton, PTFE, EPDM, and NBR90) in contact with the selected ionic liquid. Figure 5.9 shows the corresponding results between 50 to 225 °C. In addition, for better understanding of the ionic liquid behavior in long-term contact with the O-rings, different O-ring types are kept inside the

selected ionic liquid in an oven at 160 °C for 19 h as shown in figure 5.10-a, and for 2 weeks as shown in figure 5.10-b.



Figure 5.9 - DTA analysis of different O-ring types with the selected ionic liquid ([EMIM][Tf₂N])



Figure 5.10- Ionic liquid with different O-ring types kept in an oven at 160 $^{\circ}C(a)$ for 19 h and (b) for 2 weeks

Figure 5.9 shows the result of DTA versus temperature for the ionic liquid itself and five different Orings in contact with the ionic liquid. The presence of peaks in the DTA versus temperature curve represents the reactions between the O-ring and ionic liquid that can occur at certain temperatures. As there is no peak observed in figure 5.9, the presence of the ionic liquid ([EMIM][Tf₂N]) in contact with any of the O-ring types does not seem to be a problem. However, figures 5.10-a and 5.10-b show that the color of the ionic liquid in contact with EPDM and NBR90 has slightly and significantly changed after 19 h and 2 weeks respectively. Therefore, the two O-ring types of Viton and PTFE are more reliable candidates. Viton is selected as our final choice for the ionic liquid cylinder.

5.4.4 Hydraulic components

A range of 0 to 28 L/min is determined for the hydraulic flow rate corresponding to the maximum ionic liquid flow rate of 14.28 L/min inside the compression chamber. Assuming that hydrogen will move with the same speed as the ionic liquid inside the compression chamber, our thermodynamic model shows that the ionic liquid maximum volume flow rate of 14.28 L/min inside the compression chamber can compress the hydrogen in approximately 2 s from 100 to 300 bar corresponding to a Reynolds-number of 3882 to 6260. Consequently, the appropriate electric motor and pump are selected to provide the maximum volume flow rate of 28 L/min in the hydraulic system.

Figure 5.11 shows the prototype of the designed hydraulic system corresponding to the PI diagram shown in figure 5.6.



Figure 5.11- Prototype of the designed hydraulic system; some of the visible components are marked in the figure including (16) electric motor, (19) flow-regulating valve, (20) pressure-regulating valve, (21) operating ON/OFF valve, and (23) check valve The list of the main hydraulic components used for building the prototype and their suppliers is presented in table 5.2 .

Component	Туре	Supplier
Pump (pos. 15)	REXROTH, A10VSO NG 28 BR 31 PA (passfeder)	Genuine Metaris A/S [223]
Electric motor (pos. 16)	IEC-50Hz-1500 rpm-15kW-Bg.160L-IM B5/V1	Hoyer A/S [224]
Flow-regulating valve (pos. 19)	SE 2-3/36-G24 (0-36 L/min flow rate)	HAWE A/S [225]
Pressure-regulating valve (pos. 20)	PMVS41-44/G (5-330 bar pressure range)	HAWE A/S [225]
Safety relief valve (pos. 22)	MV64 BR (275 bar pressure)	HAWE A/S [225]
Operating ON/OFF valve (pos. 21)	GS2-1-N24 (24 V DC)	HAWE A/S [225]
Check valve (pos. 23)	B 2-3 check valve ½"	HAWE A/S [225]
Oil sensor (pos. 13-b)	HMFB-VT	HEMOMATIK A/S
Pressure transmitter (pos. 17)	MBS 3050-3611-1GB04 (060G3583)	Danfoss A/S [226]
Piston position sensor (pos. 26)	Micropulse transducer BTL5-E10	Balluf A/S [227]
Pressure sensor (pos. 28)	Pressure range (0-400 bar), ATEX 3x03-1503.37	UK Flowtechnik A/S [228]
Temperature transmitter (pos. 29)	Pt100, 3 wire, ATEX PPL8-P-A-3-S-A-20-A30-A-2-017	UK Flowtechnik A/S [228]
Flow meters (pos. 30)	High-pressure axial turbine flow meter (345 bar maximum pressure, ATEX) RN3/15/1/HP/EX (1.2-10 L/min) RN3/15/2/HP/EX (2-20 L/min)	UK Flowtechnik A/S [228]

Table 5.2- List of hydraulic components used for building the prototype

All sensors between the ionic liquid cylinder (pos. 27) and compression chamber (pos. 7) are ATEX-certified, as there might be a risk of hydrogen penetration in these components.

In addition, a terminal box consisting of the following parts is provided by Fritz Schur Teknik A/S [229] for the hydraulic unit:

- Soft starter for 15 kW electric motor

- 24 V DC power converter
- DIN rail and 2 pieces amplifier card EV1G1-24V (amplifier for proportional pressure and flow valves)
- 24 V DC supply for pressure transmitter
- 24 V DC supply for ON/OFF valve (pos. 21) relay-controlled
- 24 V DC supply for 2-/3-way valve (pos. 24) relay-controlled
- Emergency stop on the terminal box
- Pressure filter gauge 24 V DC (indication lamp on the front cover of the terminal box)
- Return filter gauge 24 V DC (indication lamp on the front cover of the terminal box)
- Oil level gauge 24 V DC (indication lamp on the front cover and electric motor stop)

5.5 Control procedure

The control procedure is the final but a key step in system functionality. The designed compressor should be controlled through the following procedure:

Step 1 (setting the values):

- Set the speed based on the required operating flow rate for the proportional flow-regulating valve (pos. 19) using the amplifier card EV1G1-24V
- Set the pressure based on the maximum operating pressure for the proportional pressureregulating valve (pos. 20) using the amplifier card EV1G1-24V
- Set the minimum liquid level inside the ionic liquid cylinder
- Set the required inlet pressure of the hydrogen inside the compression chamber
- Set the required maximum operating pressure of the hydrogen inside the compression chamber
- Set the maximum operating temperature of the hydrogen inside the compression chamber
- Set the time between the end of pressurization and releasing of hydrogen

The set values must be constant until a new value is added.

Step 2 (cycle begins: hydrogen enters the chamber):

- Open the solenoid valve (pos. 5) for hydrogen to enter the compression chamber
- Close the solenoid valve (pos. 5) when the pressure measured by the pressure transducer (pos. 7-b) reaches the required inlet pressure of the hydrogen inside the compression chamber set in step 1

Step 3 (start of pressurization process):

- Set the voltage to operate the ON/OFF and 2-/3-way valves (pos. 21 and 24)
- Correspondingly, start filling the cylinder containing hydraulic oil (pos. 25) at the speed set for the proportional flow-regulating valve (pos. 19) in step 1

The ON/OFF valve and 2-/3-way valve (pos. 21 and 24) are simple changeover valves (24 V DC, approximately 30 W).

The ON/OFF valve and 2-/3-way valve (pos. 21 and 24) will run in a cycle signal based on the pressure signal from the pressure transducer (pos. 7-b) as explained in the next steps.

WARNINGS:

The compression procedure must stop if any of the following cases occurs:

- If the pressure measured by the pressure sensor (pos. 28) is more than the pressure measured by the pressure transducer (pos. 7-b). The same value is expected, unless there is an error somewhere in the system.
- If the hydrogen detector in the room is activated, which means that there is hydrogen leakage (simultaneously, the solenoid valve (pos. 1) should be closed immediately).
- If the temperature measured by the thermocouple (pos. 7-a) is higher than the maximum operating temperature inside the compression chamber set in step 1.
- If the liquid level measured by the piston position sensor (pos. 26) is less than the minimum liquid level inside the ionic liquid cylinder set in step 1.

Step 4 (hydrogen release):

- Open the solenoid valve (pos. 9) when the pressure measured by the pressure transducer (pos. 7-b) reaches the required maximum operating pressure of the hydrogen inside the compression chamber set in step 1
- To postpone the hydrogen release based on the time set in step 1 (only for the first tests), deactivate the 2-/3-way valve (pos. 24) and open the ON/OFF valve (pos. 21) to start the system relief

Step 5 (start of depressurization: cycle ends):

- Close the solenoid valve (pos. 9) when the liquid level measured by the piston position sensor (pos. 26) reaches the minimum liquid level inside the ionic liquid cylinder set in step 1
- At the same time, deactivate the 2-/3-way valve (pos. 24) and open the ON/OFF valve (pos. 21) to start the system relief
- Correspondingly, the hydraulic oil in the cylinder is driven back to the oil tank (pos. 13); the cycle is back to the start position and can start again

Steps 1 to 5 can be run under "one cycle" (only one cycle until the system is started manually again) or "repeated cycle" (a new cycle will start again until the system will be stopped manually again).

6. Conclusion

6.1 Concluding remarks

This PhD thesis presents the design, modeling, and fabrication of a new compressor consisting of pneumatic, hydraulic, and hydraulic to pneumatic transformer for compression of hydrogen in hydrogen refueling stations. The proposed compressor addresses the limitations of the current technology and the previously designed compressors using the liquid piston concept and ionic liquid, by introducing a custom-designed hydraulic to pneumatic transformer and benefitting from the advantages of the hydraulic systems.

The presented thermodynamic model investigating the heat transfer phenomena inside the compression chamber indicates the possibility of cooling gas during the compression by further optimization of the key parameters such as the total heat transfer coefficient at the interface, total heat transfer coefficient at the wall, and compression time.

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[EMIM][Tf_2N]$) fulfilled our criteria for suitable viscosity, suitable density, negative melting point, water immiscibility, high corrosion stability, low hydrogen solubility, low compressibility, high chemical and thermal stability, high heat capacity, high thermal conductivity and satisfactory tribological behavior. Therefore this ionic liquid is recommended as a reliable replacement for the solid piston in the conventional reciprocating hydrogen compressors.

In addition, corrosion behavior of the selected ionic liquid in contact with several commercially available stainless steels and nickel-based alloys proves the high corrosion stability of the selected ionic liquid in the tested alloys. Considering parameters such as high corrosion stability, price and resistance to hydrogen embrittlement, the stainless steel alloy AISI 316 is selected as the construction material for the compressor components which are in direct contact with the selected ionic liquid.

The designed compressor can provide the required pressure for hydrogen stations while offering the following advantages compared to conventional compressors:

- Simpler design
- Higher efficiency
- Less noise due to the elimination of the solid piston
- Fewer moving parts
- Longer life span and less maintenance
- Simpler sealing system
- Flexible frequency and possibility of controlling of the liquid piston velocity, and pressure ratio, by a pump
- Flexible geometry and possibility of internal cooling during compression
- Considerable energy saving due to the significant reduction of sliding friction

The new design has high potential to be used as an alternative to the conventional reciprocating compressors in hydrogen refueling stations to reduce the hydrogen costs and timelines for penetration of the hydrogen fuel cell vehicles into the market.

6.2 **Recommendation for future work**

Testing the performance of the fabricated prototype would provide valuable information about the functionality of the employed models, design process, as well as the selected components and material. Future efforts should also be directed towards optimization of the heat transfer inside the compression chamber, consequently maximizing the amount of heat that can be extracted from the gas during the compression process. In this regard, appropriate technologies should be identified to increase the total heat transfer coefficient at the interface between hydrogen and ionic liquid and the total heat transfer coefficient at the wall, which are pointed out in this research as critical parameters in reduction of the hydrogen temperature.

In the recent years, novel approaches have been proposed to improve the functionality of compressors. Examples of these approaches include insertion of bores inside the compression chamber [31], spraying liquid into the chamber [29], or changing the liquid piston velocity during the compression process (optimal trajectory) [230]. Comprehensive analysis of the advantages and disadvantages of each of the above-mentioned techniques is required.

Furthermore, due to the novelty of applying ionic liquids in compression technology, there is no available library on thermophysical properties of the suitable ionic liquids which can be used in different software like EES or Matlab for making thermodynamic and heat transfer models. Development of such libraries, specifically for the five ionic liquids with triflate and bis(trifluoromethylsulfonyl)imide as anion choices and three different cation types of imidazolium-, phosphonium-, and ammonium-based as cation choices which are narrowed down in this work will be a great help on improvement of such models and employing these ionic liquids in similar engineering applications.

In addition, improvement of the proposed control procedure based on the requirements of the leading compressor manufacturers is required for better performance of the compressors and mass production of this technology.

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A Further information on the corrosion study



Figure A1- Picture of the working electrode (1) The fixed area of the electrode exposed to the electrolyte; (2) Coating paste (CC180W); (3) Alumina Tube

B Thermodynamic model (One of the EES codes)

PROCEDURE IFPROP(dis_liq;num;T_gas;T_liq;h_flam_gas;h_flam_liq:T_ref;h_flam)

IF num<=dis_liq THEN

T_ref=T_liq h_flam=h_flam_liq

ELSE

T_ref=T_gas h_flam=h_flam_gas

ENDIF end

PROCEDURE Tstot (dis;dis_liq;dis_gas;T_s2_n[1..dis]: T_s2_n_liq;T_s2_n_gas)

 $\label{eq:t_s2_n_liq} T_s2_n_liq=(sum(T_s2_n[1..dis_liq]))/dis_liq\\ lim_liq=dis_liq+1\\ T_s2_n_gas=(sum(T_s2_n[lim_liq..dis]))/(dis-dis_liq)$

end

PROCEDURE QDEF (dis;dis_liq;dis_gas;Q_dot_losw_n[1..dis]: Q_dot_gas_tot;Q_dot_liq_tot) Q_dot_liq_tot=sum(Q_dot_losw_n[1..dis_liq]) lim_liq=dis_liq+1 Q_dot_gas_tot=sum(Q_dot_losw_n[lim_liq..dis]) end

PROCEDURE NUCAL(Re_num_liq_D;;Re_num_gas_D;Re_num_gas_D_swr;pr_liq_eq;pr_gas_eq;mu_gas_0;mu_gas_eq:N us_gas;Nus_liq)

"for the laminar flow"

a_lam_liq=0,664 m_lam_liq=1/2 n_lam_liq=(1/3)

a_lam_gas=0,664 m_lam_gas=1/2 n_lam_gas=(1/3)

"for the turbulent flow"

a_turb_liq=0,026 m_turb_liq=0,8 n_turb_liq=0,3

a_turb_gas=0,75

m turb gas=0,8 n turb gas=0,6 if Re num lig D <=2300 then "critical Re 2300 based on incropera" Nus_liq=a_lam_liq*(Re_num_liq_D^m_lam_liq)*(pr_liq_eq^n_lam_liq) else Nus lig=a turb lig*(Re num lig D^m turb lig)*(pr lig eg^n turb lig) endif if Re num gas D swr <=2300 then Nus_gas=a_lam_gas*(Re_num_gas_D_swr^m_lam_gas)*(pr_gas_eq^n_lam_gas) else Nus_gas=a_turb_gas*(Re_num_gas_D_swr^m_turb_gas)*(pr_gas_eq^n_turb_gas) endif end "compression cycle, system 1" \$integraltable time;p; T gas;T liq; H;dis_liq;dis_gas;H_liq;H_gas;UA_liq_gas;Q_dot_link;Q_dot_liq_tot;Q_dot_gas_tot;Q_dot_losw_n[1..10];Q_d ot_axial_n[1..9];Q_dot_los_out[1..10];num[1..10];T_s2_n[1..10];R_convairw[1..10];Nus_gas;Nus_liq;h_flam_g as;h_flam_liq;Re_num_liq_D;Re_num_gas_D;Re_num_gas_D_swr "time domain for the integral table" tau=0,44 [s] tau_0=0 [s] TT=time "-----pump conditions------pump conditions------Q pump=0,0014 [m3/s] "flow rate of liquid" m_dot=Q_pump*rho_liq_0 "mass flow rate of the liquid goes into chamber" "determining the type of liquid and gas" Gas\$='Hydrogen' Lig\$='Water' "fixed parameters used in the model" a=9,81 [m/s2] T am=298,15 [K] "ambient temperature, assuming 25 degree" "ambient pressure" p_atm=101325 [Pa] T max=1000[K] "initial conditions for high pressure hydrogen vessel" p_hy_vessl=20000000 [Pa] "the hydrogen pressure coming out of the vessel" T_hy_vessl=298,15 [K] h hy vessel =enthalpy(Gas\$; T=T hy vessl;p=p hy vessl) "initial conditions of liquid and gas in compression chamber" p 0= 10000000 [Pa] "the inlet gas pressure in compressor chamber, after pressure valve" "assuming constant enthalpy around the pressure valve" T_0=temperature(Gas\$;p=P_0; h=h_hy_vessel) "start temperature of liquid and gas" rho_liq_0=Density(Liq\$;T=T_0;P=p_0) "density of liquid; assume constant value, assuming incompressible liquid; assume T liq 0=T gas 0 and T pmp out will be mixed with this " rho gas 0=Density(Gas\$;T=T 0;P=P 0) "the initial density of hydrogen" mu_gas_0=Viscosity(Gas\$;T=T_0;P=P_0)

"vessel dimension-	["]
D=0,08 [m]	"Vessel diameter"
H=0,2 [m]	"Vessel hieght"
t_vessel=0,022 [m]	"vessel thickness"
A=(pi*D^2)/4	"cross sectional area of vessel"
v total=A*H	"vessel size (m^3=1 lit) this the volume of Lig+gas"
v lig $0=0.1$ *v total	"initial volume of liquid"
v_gas_0=v_total-v_liq_0	"initial volume of gas"
"Initial mass ostimation	
M das - rbo das 0^{*} das 0	"it will be constant during the compression procedure"
M lig 0-rbo lig 0*V lig 0	"initial mass value of lig"
M = 0 - M = 0	"initial total mass of liquid and gas"
IM_t_0=IM_gas+IM_IIq_0	initial total mass of liquid and gas
" Mass ba M t-M t 0=integral(m dot:time:tau	alance inside the compression chamber " 0:tau)
$M_{II}q=M_{t}-M_{t}0$	"mass of water added to control volume"
v_liq=M_liq/rho_liq_0	" amount of liquid volume added to the chambr;V_liq=dv_liq"
v_gas=v_gas_0-v_liq	"gas volume changing by time; v_gas"
v_dot_liq=m_dot/rho_liq_0	"volume flow rate of the liquid"
v_dot_gas=v_dot_liq	"volume flow rate of the gas"
" estimatio	on of T_gas and P by time"
"first law	of thermodynamic for the system (gas)"
M_gas*(u_gas-u_gas_0)=integral(Q	_dot_link+Q_dot_gas_tot+p [*] v_dot_gas;time;tau_0;tau)
u_gas_0=IntEnergy(Gas\$;T=T_0;P=	:P_0)
u_gas=IntEnergy(Gas\$;T=T_gas;P=	P)
rho_gas=M_gas/v_gas	
p=pressure(Gas\$;T=T_gas;v=1/rho_	_gas)
" estimation of	Q dot losw (gas heat transfer through the walls)"
"estimation of inside and outside cyli	nder walls area and gas height"
H gas= $(4^*v gas)/(pi^*D^2)$	
H lig=H-H gas	
$D2 \text{ metal}=((D+2^{*}t \text{ vessel})^{2})-D^{2}$	
$A_metal=(pi^*(D2_metal))/4$	
"determining unknown gas, liquid, ar	nd metal characteristic for the following relationship"
T film=(T gas+T am+T lig)/3	
k stainless=k ('Stainless AISI316':	T=T film)
K gas=Conductivity(Gas\$:T=T gas:	P=p)
K_liq=Conductivity(Liq\$;T=T_liq;P=p)
Call	
	e DiRe num das Diswrint lig egint das egimu das Oimu das egil
us_gas;Nus_liq)	5_D,1\e_110111_9a5_D_5w1,p1_114_e4,p1_9a5_e4,1110_9a5_0,1110_9a5_e4.14
h flam gas=(Nus gas*K gas)/D ef	f gas
h_flam_liq=(Nus_liq*K_liq)/D	
dis=10	"

dis_liq=round((H_liq/H)*dis) dis_gas=dis-dis_liq L dis=H/dis

Duplicate i=1;dis num[i]=i

CALL IFPROP(dis_liq;num[i];T_gas;T_liq;h_flam_gas;h_flam_liq:T_ref[i];h_flam[i])

A_inside_wall_n[i]=pi*D*L_dis A_outside_wall_n[i]=pi*(D+2*t_vessel)*L_dis

 $\label{eq:ual_losw_n[i]=1/(R_convw_n[i]+R_condvessw_n[i]) \\ R_convw_n[i]=1/(h_flam[i]^*A_inside_wall_n[i]) \\ R_condvessw_n[i]=ln(((1/2)^*D+(t_vessel/2))/((1/2)^*D))/(\ 2^*pi^*L_dis^*k_stainless) \\ Q_dot_losw_n[i]=UA_losw_n[i]^*(T_s2_n[i]-T_ref[i]) \\ \end{array}$

end

"------ determining heat transfer coefficients ------" Duplicate i=1;dis Q_dot_los_out[i]=UA_air[i]*(T_am-T_s2_n[i]) UA_air[i]=1/(R_convairw[i]+R_condvessw_air_n[i]) R_convairw[i]=1/(h_nat_air_ck[i]*A_outside_wall_n[i]) h_nat_air_ck[i]=100 R_condvessw_air_n[i]=ln(((1/2)*D+(t_vessel))/((1/2)*D+(t_vessel/2)))/(2*pi*L_dis*k_stainless) end

"------ solving wall equation based on finite difference -------

duplicatej= 1;dis-1 Q_dot_axial_n[j]= (k_stainless*A_metal*(T_s2_n[j+1]-T_s2_n[j]))/L_dis end

"energy balance at the wall for gas side and liquid side"

duplicatej= 1;dis-2 -Q_dot_losw_n[j+1]+Q_dot_axial_n[j+1]-Q_dot_axial_n[j]+Q_dot_los_out[j+1]=0 end

-Q_dot_losw_n[1]+Q_dot_axial_n[1]+Q_dot_los_out[1]=0 -Q_dot_losw_n[dis]-Q_dot_axial_n[dis-1]+Q_dot_los_out[dis]=0

CALL QDEF (dis;dis_liq;dis_gas;Q_dot_losw_n[1..dis]: Q_dot_gas_tot;Q_dot_liq_tot)

"----- estimation of T_W by time; also pressure is connected (connecting pump and water side to gas side)---------"

"------ calculating the inlet enthalpy flow of water base on isentropic efficiency of pump------" eta_is_pump=0,7 "isentropic efficiency of the pump, assumed" eta_is_pump=(h_sliq+h_liq_0)/(h_liq_out-h_liq_0) h_liq_0=Enthalpy(Liq\$;T=T_0;p=p_atm) s_liq_0=Entropy(Liq\$;T=T_0;p=p_atm) h_sliq=Enthalpy(Liq\$;s=s_liq_0;P=P) T_pump_out=Temperature(Liq\$;h=h_liq_out;P=p)

(M_liq+M_liq_0)*u_liq-M_liq_0*u_liq_0=integral(-Q_dot_link+Q_dot_liq_tot+m_dot*h_liq_outp*v_dot_gas;time;tau_0;tau)

u_liq_0=IntEnergy(Liq\$;T=T_0;P=P_0) T_liq=temperature(Liq\$;u=u_liq;P=p) "----- estimation of heat transfer between liquid and gas only by conduction------" Q_dot_link=UA_liq_gas*(T_liq-T_gas)

Q_link=integral(Q_dot_link;time;tau_0;tau) UA_liq_gas=1/(R_cond_liq+R_cond_gas)

R_cond_liq=H_liq/(K_liq*A) R_cond_gas=H_gas/(K_gas*A)

"-----estimation of Re number of liquid side and gas side------"

Re_num_liq_D_ch=(4*m_dot*rho_liq_eq)/(pi*D*mu_liq_eq*rho_liq_0) "if we define it as: Re_num_liq_D=(rho_liq_eq*vel_gas*D)/(mu_liq_eq) Re_num_liq_L=(4*m_dot*H_liq)/(pi*(D^2)*mu_liq_eq) mu_liq_eq=Viscosity(Liq\$;T=T_liq;P=p) rho_liq_eq=density(liq\$;T=T_liq;P=p) pr_liq_eq=Prandtl(Liq\$;T=T_liq;P=p)

Re_num_gas_D=(rho_gas_eq*vel_gas*D)/(mu_gas_eq) Re_num_gas_L=(rho_gas_eq*vel_gas*H_gas)/(mu_gas_eq) vel_gas=v_dot_gas/A mu_gas_eq=Viscosity(Gas\$;T=T_gas;P=p) rho_gas_eq=density(Gas\$;T=T_gas;P=p) pr_gas_eq=Prandtl(Gas\$;T=T_gas;P=p)

"------calculation RE based on Swirl------calculation RE based on Swirl-------

"see Adiral 1972"

Re_num_gas_D_swr=(rho_gas_eq*vel_gas_swr*D_eff_gas)/(mu_gas_eq)

omega=(1/0,42)	"compression frequency, for reaching the pressure ratio of 500
Vel_gas_swr=2*omega*(D_eff_gas/2)	" swirl velocity is calculated based on two times of compression
	"Note: since you times omega by D_eff gas/ 2, you will get eq.
16 Adiral, not times it again in Re eq"	

D_eff_gas=vol_gas/Area_gas vol_gas=6*v_gas Area_gas=(pi*D*H_gas)+(2*pi*(D/2)^2)

" it is equal to vol_gas = 6*(pi*(D^2)/4)*H_gas "

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