HyCoRA – Hydrogen Contaminant Risk Aseessment Grant agreement no: 621223

Deliverable 4.1 Risk assessment: Guidance for the first part of WP1 and WP2 work

Authors: Risto Tuominen, Minna Nissilä, Janne Sarsama, Jari Ihonen

Confidentiality: Public

Report's title Deliverable 4.1 Guidance for the first part of WP1 and WP2 work	
Customer, contact person, address Vasco Ferreira, FCH JU	**Order reference** Grant agreement no: 621223
Project name Hydrogen Contaminant Risk Assessment	**Project number/Short name** HyCoRA
Author(s) Risto Tuominen, risto.tuominen@vtt.fi Minna Nissilä, minna.nissila@vtt.fi Janne Sarsama, janne.sarsama@vtt.fi Jari Ihonen, jari.ihonen@vtt.fi	**Pages** 19/-

Summary

This deliverable describes the progress in HyCoRA WP4 during the first months regarding the specification of a probabilistic risk model for hydrogen fuel quality. The risk model is aimed to capture the knowledge on fuel quality and PEMFCs in automotive applications in the form allowing to assess the risk of fuel quality induced problems in FC powered vehicles and enhance understanding on the right level of fuel quality and required quality assurance (QA) measures.

Considering the most common feedstocks and production technologies, the potential sources of contaminants in the hydrogen fuel chain are described.

The approach taken for modelling the Hydrogen fuel quality risk is explained and the first risk model versions are presented. Centralised production from natural gas (NG) using the SMR-PSA process, and considering carbon monoxide (CO) as single contaminant in the fuel, are used as the starting case for risk modelling.

Finally, the identified challenges in the upcoming risk model development work are summarized together with related recommendations for the work carried out in the other WPs in the first part of the project. In the recommendations, also the feedback from the first OEM workshop has been taken in to consideration.

Confidentiality	Public

Contents

Terms and abbreviations

BN	Bayesian network
FC	Fuel cell
FCEV	Fuel cell electric vehicle
HRS	Hydrogen refuelling station
ID	Influence diagram
IEA	International Energy Agency
ISO	International Organization for Standardization
NG	Natural gas
OEM	Original equipment manufarturer
PEM	Proton exchange membrane
PSA	Pressure swing adsorption
QA	Quality assurance
SMR	Steam methane reforming
WGS	Water-gas shift reactor

A **driving cycle** commonly represents a set of vehicle speed points versus time aimed to mimic real driver behaviour in typical driving conditions; e.g. urban, sub-urban, rural, motorway.. The cycle consists of accelerations and deceleration together with variable speed and idle periods of different durations.

1. Introduction

Fuel cells are known to be prone to certain impurities in the hydrogen fuel affecting adversely in fuel cell performance. Consequently, certain quality of the fuel delivered for use is required. The international standard ISO 14687-2:2012 provides interim quality specifications for hydrogen fuel delievered at refuelling stations and used in proton exchange membrane (PEM) fuel cell applications on road vehicles (ISO, 2012).

The required purity of the fuel obviously affects the production costs and the lucrative selling price of the fuel. Quality requirements being unnecessarily high will hinder the endeavour of rediucing the cost of automotive grade hydrogen to the level required for large scale commercialisation of fuel cell operated vehicles. On the other hand, quality requirements set too low will drastically increase the risk of fuel quality induced problems showing up in the FC vehicle population.

Optimal quality level would be such for which the likelihood of the vehicle owners perceiving problems in vehicle performance is acceptably low, and for which the combined costs of providing the required quality, and the potential costs arising from problems experience in FCEVs' operation, are minimised.

Multitude of variables with uncertainties in knowledge are involved in determining the potential variation in fuel quality and the impact of fuel quality on fuel cell operated vehicles. A risk model considering these variables is thus needed allowing to predict the likelihood of problems appearing in the vehicles, and the associated costs.

1.1 Objectives and scope

In HyCoRA WP4, the objective is to establish a risk model for hydrogen fuel quality risk which provides a systematic framework to:

- quantify the risk of hydrogen fuel quality induced problems and the associated economical impact;
- give information on the right level of fuel quality and required quality assurance (QA) activies;
- explore the influence of different fuel production processes and feedstock on the optimal/required QA;
- explore the influence of uncertanties in current knowledge;
- explore the influence of technology improvements in PEMFCs and FCEVs.

The scope of the work is limited to proton exchange membrane fuel cells (PEMFC) in automotive applications, and automotive grade hydrogen fuel.

1.2 First OEM workshop

The first OEM workshop was arranged on September 30, 2014 in Brussels, with participants representing the automotive industry, hydrogen fuel producers, equipment manufacturers, and research organisations.

The objective of the workshop was to introduce to the participants the risk assment approach adopted in the HyCoRA project to guide the research efforts on the impacts of hydrogen fuel contaminants and the development of quality QA methods and procedures, and to receive OEM's initial feedback on the issues considered most important for modelling the hydrogen fuel quality risk.

The discussions and findings of the OEM workshop have been summarized in a dedicated project deliverable D5.3.

2. Impurity sources in Hydrogen fuel chain

Hydrogen can be produced from a variety of feedstocks, comprising fossil resources, such as natural gas and coal, and renewable resources, such as biomass and water with input from renewable energy sources (IEA, 2006). Also, a variety of process technologies suitable for particular feedstocks, can be used for hydrogen production. Depending on the production technology and the feedstock used, different contaminants are possible in the hydrogen fuel produced. The efficiency of the purification process down-stream the production process finally determines the levels of different contaminants in the hydrogen fuel stream.

In addition to contaminants arising from the fuel production process, specific contaminants may get introduced in the hydrogen fuel in the storage and transportation processes, or as a consequence of maintenance activies performed in the refuelling stations.

In the following sub-chapters, potential sources for different contaminats in the Hydrogen fuel chain are identified, together with brief discussion of their expected significance. The aim here is to cover fuel contaminants, other than particulates, considered relevant for PEM fuel cell applications in automotive (i.e. road vehicle) applications. ISO 14687-2:2012 provides an initial list of contaminants relevant for PEMFCs.

2.1 Production processes (centralised)

The IEA report on 'R&D priorities and gaps in hydrogen production and storage' (IEA, 2006) provides a good overview of both current matured and future potential technologies for hydrogen fuel production. Technologies for both centralised and distributed (i.e. on-site the HRSs) hydrogen production are discussed.

According to (Corbo et al , 2011), currently almost half of the hydrogen used worldwide comes from steam methane reforming (SMR) of natural gas (48%). Other major technologies used in hydrogen production are based mainly on partial oxidation of refinery oil (about 30% of production) and coal gasification (18% of production). Only 4% of the produced hydrogen derives from water electrolysis.

In current and near term, *steam methane reforming from natural gas* can be considered to remain the dominant method for large-scale production of hydrogen fuel. In medium and long term, large centralised production plants based on biomass or fossil fuels with CO_2 capture and storage, as well electrolysis using renevables and nuclear energy, are envisioned to gain weight (IEA, 2006). To be successful, centralised hydrogen production obviously requires large market demand, as well as an efficient hydrogen transmission and distribution infrastructure.

2.1.1 Steam methane reforming (SMR) of hydrocarbon feedstock

Steam rmethane reforming (SMR) involves the endothermic conversion of methane and water vapour into hydrogen and carbon monoxide, as shown in Figure 2.1. The heat for this process is often supplied from combustion of some of the methane feedgas and the tail-gas from the PSA process containing the unrecovered H_2 and the non-H_2 species in the reformate gas. The SMR process typically occurs at temperatures of 700 to 850 °C and pressures of 3 to 25 bar. (IEA, 2006; Papadias et al., 2009)

The produced syngas coming out from the steam reformer contains approximately 12 % CO, which can be further converted to CO_2 and H_2 in the water-gas shift (WGS) reactor.The reformate gas exiting the WGS reactor at around 170 °C is cooled down to separate out the bulk of water in the gas flow before directing it to purification. (Papadias et al., 2009)

In addition, ta desulphurizer unit may be placed in the feedgas flow before the steam reformer to remove sulphur compounds in the feedgas to ppb levels (ISO 14687-2:2012).

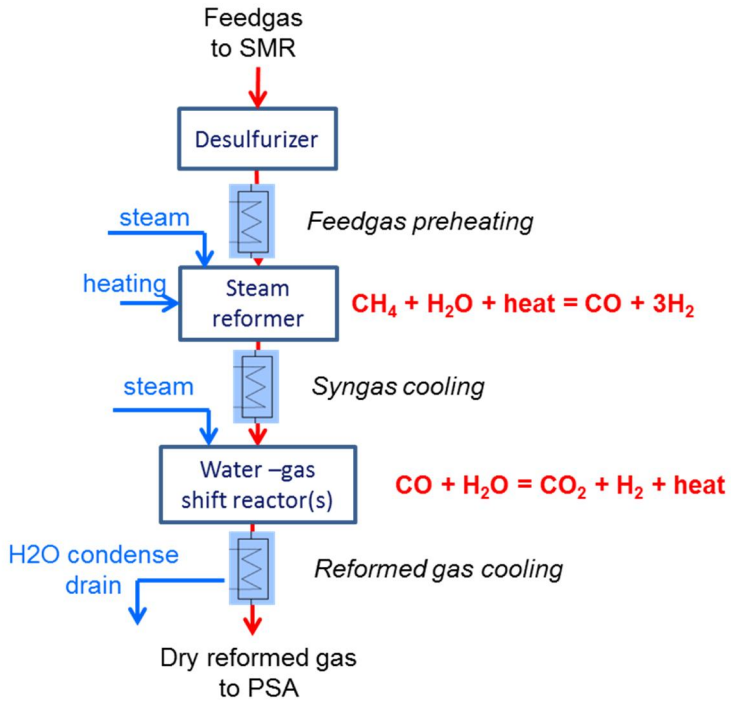

Figure 2.1 Steam methane reforming (SMR) process

Impurities:
Along the enriched concentration of hydrogen, the reformed gas flow will contain notable concentrations of CH_4, CO_2, CO and N_2. Examples of the effect of main process parameters on these concentrations can be found in Papadias et al., 2009.

The ISO 14687-2:2012 standard Annex C summarizes the expected presence of impurities in the reformed gas as:

- no presence of oxygen and hydrocarbons other than methane CH_4;
- no presence of sulphur (due to desulphuriser in the process and the capture by catalysts in the steam reformer and water-gas shift reactor);
- formaldehyde (HCHO) and formic acid (HCOOH) may be present at concentration levels of 10 to 100 ppb;
- depending on nitrogen content in the feedstock, ammonia (NH_4) may be present at levels of 100 to 1000 ppm, but it is dissolved and mainly removed in the drain water.

2.1.2 Industry by-product production

Many industrial processes produce hydrogen as a by-product. Surplus hydrogen from these industrial processes could be used to fuel both transport and stationary applications during the transition phase towards a hydrogen economy. (Roads2Hy, 2007)

Industrial surplus hydrogen comprises production margin available from users like refineries or ammonia industries, waste by-product hydrogen from chemical industries (e.g. chlorine production), or valorised by-product hydrogen from chemical industries. (Roads2Hy, 2007)

Impurities:
Potential impurities in the hydrogen product would depend on the industrial process from which hydrogen comes out as by-product, and the purification methods applied.

2.1.3 Other production technologies

Not within the scope of the current report. Potential future technologies for hydrogen fuel production are outlined e.g. in the IEA report (IEA, 2006)

2.2 Purification processes

Because of other constituents than hydrogen typically present in the hydrogen fuel mixture produced using the different methods and feedstock, the fuel needs to be purified before its delivery for use. The purification needs to be done according to the quality specifications (i.e. grade), if any, issued for the intented use domain.

Currently, the ISO 14687-2:2012 standard provides the quality specifications for hydrogen fuel for automotive grade hydrogen fuel product.

Hydrogen fuel can be purified using Pressure Swing Adsorption (PSA) or gas purifiers. Gas purifiers are based on the use of selected adsorbent materials or membrane technology.

Pressure Swing Adsorption (PSA) is a dominant purification technology used in hydrogen production. Over 85% of current global hydrogen production units use PSA technology for hydrogen purification (Ref.?).

2.2.1 Pressure Swing Adsorption (PSA)

The PSA technology is based on physical binding of gas molecules to an adsorbent material. The binding force acting between the gas molecules and the adsorbent material depends on the gas component, type of adsorbent material, partial pressure of the gas component and operating temperature. Highly volatile gas components with low polarity, such as hydrogen, are practically non-adsorbable as opposed to molecules like N_2, CO, CO_2, hydrocarbons and water vapour. (Linde AG, 2013)

A qualitative ranking of adsorption forces of different gas components is shown in Figure 2.2.

Figure 2.2. Qualitative ranking of adsorption forces of gas components (Linde AG, 2013)

In the PSA process, the hydrogen-rich reformate gas mixture is fed through a pressurised adsorber vessel (typically a set of 3 to 6 vessels) containing suitable adsorbent materials (zeolites, activated carbons, silica and alumina gels) selected to capture the contaminants in the gas flow. The process works at constant temperature and uses the effect of alternating pressure and partial pressure to perform adsorption and desorption of the feed gas impurities

in the adsorbent material. Adsorbtion is carried out high pressure (typically 10 to 40 bar) while desorption is done at slightly above atmospheric pressure (Linde AG, 2013).

The PSA process comprises four basic process phases: (i) adsorption, (ii) de-pressurisation, (iii) regeneration, and (iv) re-pressurisation (Linde AG, 2013). The adsorber vessels work in parallel in different phases in order to provide continuous hydrogen product flow. Minimum of four vessels is needed to provide continuous supply of purified hydrogen (Linde AG, 2013).

In the adsorption phase, the feed gas flows through an adsorber vessel at the pressure of the feed gas. Impurities in the feed gas get selectively adsorbed on the surface of the adsorbent materials and the purified hydrogen exits from the top of the vessel. After a defined time, the adsorption phase of the vessel is stopped and the feed gas flow is switched to another (regerated and re-pressurised) adsorber vessel to take over.

The saturated adsorbent in the first vessel is regenerated by desorption of the impurities from the adsorber materials when vessel pressure is reduced. Regeneration is completed by purging the desorbed impurities into the PSA tail-gas system with purified hydrogen obtained from another vessel being in the de-pressurization phase. Before a new adsorption phase is started, the regenerated vessel is re-pressurised using hydrogen from a vessel under de-pressurisation. (Linde AG, 2013)

The maksimum amount of a particular impurity removed from the feed gas stream within one cycle corresponds to the difference of adsorption loading to desorption loading in the corresponding pressures (Linde AG, 2013).

In the PSA process a portion of the hydrogen is required in use for the regeneration process. This limits the maximum possible hydrogen recovery rate to less than 90%.

Impurities:
Failures in controlling the PSA process variables (e.g. T, p), or responding to variation in quality (i.e. impurity levels) of the feed gas entering the PSA process, can lead to break out of impurities from the PSA process. This break-out is selective regarding the different contaminats in the feed gas.

The risk of halogenates from the SMR process passing through the PSA purification process should be very small.

2.2.2 Gas purifiers

2.2.2.1 Adsorption purifiers

Adsorption purifiers are based on electrochemical adsorption of impurities in the inlet gas on the adsorbent materials. The adsorbent materials are selected based on the impurities present in the inlet gas and required to be removed. The purifiers are operated at constant temperature and pressure.

The purifier units need to be replaced before getting saturated, the expected saturation determining the expected purifier unit lifetime. The replaced units are typically not regenerable. However, some purifiers can be regenerated off-line by the manufacture.

Typically fairly high purity inlet gas is required for reasonable purifier service life. Since no hydrogen is lossed for regeneration of the adsorbents, hydrogen recovery rate for adsorption purifiers is 100%.

Impurities:
Saturation of the purifier unit would lead to unpurified output gas. Exposure to unexpected impurities in the inlet gas, or unexpectedly high levels on the known impurities, could shorten the time to saturation

2.2.2.2 Membrane purifires

Membrane purifiers use a specifically designed membrane to trap the impurities in the inlet gas flow and let only the pure gas to permeate through the membrane to the outlet. Membrane purifiers do not require regeneration or replacement as the impurities trapped on the inlet side can be continuously vented. In principle, membrane purifires have unlimited lifetime. Pembrane purifiers produce a high pressure drop in the gas flow, are sized according to the required flow rate.

Palladium membrane purifiers use palladium alloy which is selectively permeable only to hydrogen rejecting permeation of any other substance. Even high-ppm or percentage level impurities in the inlet hydrogen flow can be removed to parts-per-billion levels in the output using palladium membrane purifiers (http://www.saespuregas.com/Products/GasPurifier/Hydrogen/Palladium-Membrane/Home.html).

Similar to adsorption purifiers, 100% hydrogen recovery rate is provided.

Impurities:
Micro leaks across the membrane can degrade output gas purity.

Membrane purifier is non-selective regarding the different contaminants in the hydrogen product that get leaked across a defective membrane. This could simplify the monitoring of product gas purity as monitoring only a single (easy to measure) component (e.g. CH_4) could be sufficient.

Since micro leaks are non-selective for the contaminants, the ratio of contaminants should be the same in the purified hydrogen and the tail gas. This opens the possibility to follow only a single contaminant in the purified hydrogen, if the concentrations of all contaminants are measured in the tail gas.

2.3 Storage and transport processes (centralised production)

In principle, hydrogen can be stored in gaseous or liquid form, or chemi- or physisorbed in particular solid materials (IEA, 2006). Storage in gaseous form in pressurized tanks or in liquid form at cryogenic temperature (about -253 °C) in isolated tanks are the two most common storage methods currently in use.

Suppliers currently transport hydrogen to HRSs by dedicated pipelines or over roads using tube trailers and cryogenic liquid hydrogen tankers. Gaseous hydrogen is also being transported to HRSs in high-pressure bottles or bottle racks.

Impurities:
Impurities may become introduced in the transported hydrogen fuel from from compression of the gas for transportation, from the connectors used for loading and unloading the transport units (i.e. cleaning agents etc. used), or from the transport units when they are returned to use after maintenance.

2.4 Refuelling Stations (HRS)

A refuelling station may be supplied by a hydrogen production unit located on-site, or by hydrogen delivered to the site from centralised production units. In the latter case, the refuelling station only comprises a hydrogen storage of sufficient volume and the arrangement needed for hydrogen dispensing to FCEVs.

2.4.1 On-site production and purification

Distributed on-site production at refuelling stations can be based on steam reforming of hydrocarbons, especially natural gas, or water electrolysis (IEA, 2006). Hydrogen production

from natural gas by the SMR-PSA process is seen as the most likely near-term pathways in on-site production (Papadias, et al., 2007; ISO 14687-2:2012).

Distributed production would utilise the existing natural gas or water and electric power infrastructures and reduce the need for hydrogen fuel transportation. Higher production costs and lower production efficiency would be expected for the smaller-capacity facilities compared to centralised plants.The competitiveness of distributed hydrogen production would thus depend on the transportation distance. (IEA, 2006)

2.4.1.1 SMR-PSA process using hydrocarbon feedstock

In principle the same technology as in centralised hydrogen production, but in smaller scale can be used for distributed on-site production. Natural gas (NG) is expected to be the most typical feedstock used.

Impurities:
Impurities characteristic to steam reforming of natural gas are possible (cf. Ch. 2.1.1). The levels of impurities in the hydrogen product are determined by the effectiveness and control of the PSA process.

2.4.1.2 Water electrolysis

In water electrolysis process, water is split into hydrogen and oxygen through the application of electrical energy:

$$H_2O + \text{electricity} \rightarrow H_2 + ½\ O_2$$

Along the basic process for splitting hydrogen from water, additional processes have been developed, comprising (IEA, 2006):

- Alkaline electrolysis
- PEM electrolysis
- High-temperature electrolysis

Of these, the alkaline electrolysis (Figure 2.3) represents a mature technology, with a significant operating record in industrial applications (IEA, 2006).

Alkaline electrolysers use an aqueous KOH solution (Potassium hydroxide) as an electrolyte that usually circulates through the electrolytic cells. Commercial electrolysers usually comprise a number of electrolytic cells arranged in a stack. Alkaline electrolysers are suited for stationary applications and are available at operating pressures up to 25 bar.(IEA, 2006)

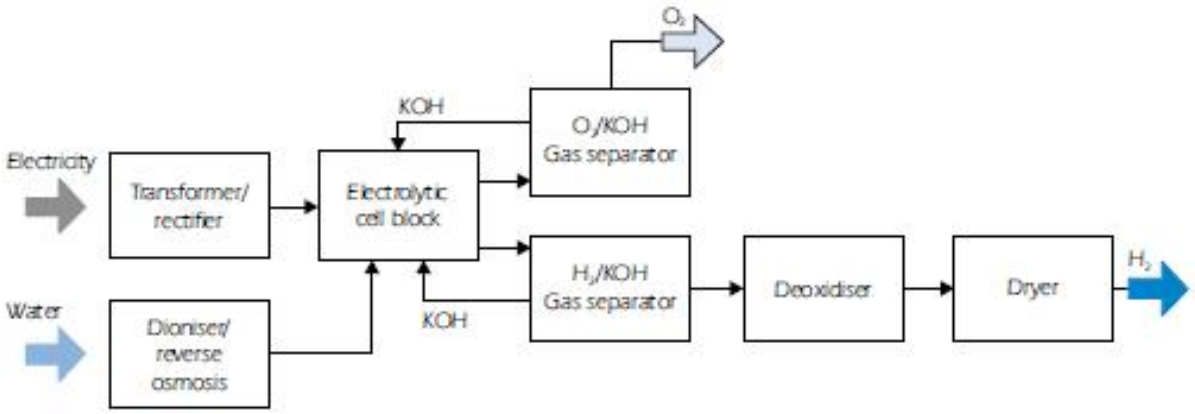

Figure 2.3. Alkaline electrolysis process (IEA, 2006)

Impurities:
Impurities coming from the feed water, and passing the process, are also possible.

The risk of halogenates from the production process should be very small.

2.4.2 On-site storage and dispensing

Refuelling stations would typically comprise a storage tank (pressurized gas 200 – 300 bar), a compressing unit, a high-pressure tank (850 – 1000 bar) and the dispenser arrangement. Gaseous hydrogen may also be delivered and stored at stations compressed in bottles. Cryogenic liquid storages are also used.

Impurities: .
Potential sources for introducing impurities in the closed system are station maintenance actions. Traces of impurities in the hydrogen fuel may come from materials used for cleaning or lubrication of parts. Remains of nitrogen or helium may also be entered from inert gas purge used in preparing station systems for safe maintenance.

3. Quality assurance in Hydrogen fuel chain

3.1 Specifications of hydrogen fuel for PEM fuel cells in road vehicles

ISO 14687-2:2012 standard specifies the hydrogen fuel quality requirements by providing the maximum concentrations for selected individual contaminants at the dispenser nozzle.

The stated requirements apply to hydrogen fuel for PEM fuel cells in road vehicles, and they are not production process or feed stock specific.

3.2 Quality assurance approaches for on-site fuel supply

ISO 14687-2:2012 Annex C describes, as an example case, a common QA practice for on-site hydrogen fuel production from natural gas (NG) using the SMR-PSA process.

The recommended approach outlined briefly in the standard Annex C comprises:

- in-line monitoring of CO;
  CO is used as canary species for the presence of other contaminants in the fuel. Confirmation that CO content is less than the specified limit indicates that other impurities, except water and inert gases, are present at less than their specified limits.
- in-line monitoring of water content;
- estimation of the max content of inert gases in the product hydrogen based on maximum content of inert gases in the feed stock and certain SMR-PSA process parameters;
- for back-up of the in-line monitoring of CO content, batch sampling at dispenser nozzle and laboratory analysis of all impurities using standar analytical methods;
  The frequency of sampling and analysis is to be determined by the hydrogen supplier.

Regarding other technologies or processes used for on-site fuel production and purification, the current ISO standard directs the users of those to specify similarly QA requirements for the production.

3.3 Quality assurance approaches for off-site fuel supplies

According to ISO 14687-2:2012, ‘the off-site supplier (primary distributor) should specify the analytical requirements for qualification tests and lot acceptance requirements’. No further guidelines are provided for this.

4. Modelling of the Hydrogen fuel quality risk

The hydrogen fuel quality risk comprises of:

- the risk of fuel cell operated vehicles (FCEVs) experiencing (severe) adverse effects due to quality of the hydrogen fuel used, and
- the likelihood of hydrogen refuelling stations (HRSs) delivering hydrogen fuel of such malign quality.

Fuel quality refers here to small concentrations of contaminants (i.e. impurities) in the hydrogen fuel that, if present, affect adversely on PEM fuel cell performance.

Figure 4.1 shows the top view of the HyCoRA risk model for considering the hydrogen fuel quality risk.

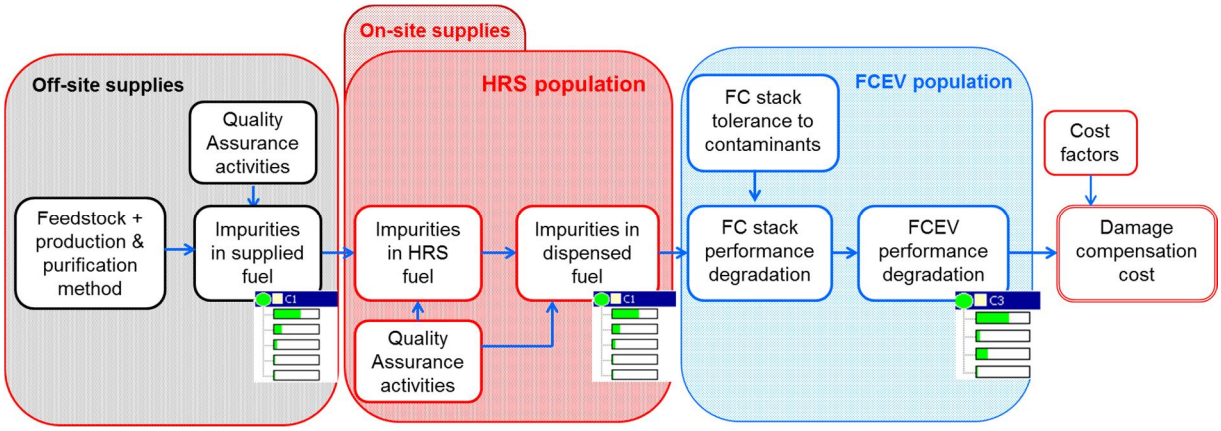

Figure 4.1 HyCoRA risk model – top view

Population of FCEVs uses hydrogen fuel from a population of HRSs. The HRSs are supplied either by on-site production (dedicated to a single HRS) or by a population of off-site production facilities supplying multiple HRSs.within economically feasible distance around the facility.

In the risk model, the potential variation in fuel quality in hydrogen fuel production is transferred to potential variation in quality of the hydrogen fuel dispensed at the HRSs.

In this context we can consider that every FCEV refuelling (i.e. a random FCEV visiting a random HRS) poses a risk situation that can turn up as no or different levels of degradation in FC stack and vehicle performance experienced by the vehicle user within the operating period before next refuelling.

If we can relate a compensation cost factor (i.e. utility) to the different levels of vehicle performance degradation or damage, the model would allow to calculate *the expected damage compensation cost per FCEV refuelling* arising from fuel quality.This 'risk cost' could be taken into account e.g. in fuel or vehicle pricing depending on the accountable stakeholder.

As shown in Figure 4.2, the risk model could be extended to cover also the expected damage of malign fuel quality on customer (and the public in general) perception of the technology and its reputation as a credible choice for automotive power. This damage to technology reputation could arise from the problems experienced in the FCEVs, as well as from unavailability of HRS stations for refuelling because of their shutdowns for decontamination.

HRS unavailability for refuelling however affects mainly the reputation of the hydrogen fuel distribution technology as being reliable. The coverage of the HRS network obviously

impacts the importance that is given for an individual refuelling station being available and the grade of impact on technology reputation.

Negative impacts on public perception of the hydrogen technology can be seen to have high significance for the automotive industry as the market roll-out of hydrogen powered vehicles is to start just now. At least in principle, the damage compensation costs and the impacts of fouled technology reputation could be combined into a single risk measure called 'overall economic risk'. Defining a credible value function for technology reputation is however considered to be difficult.

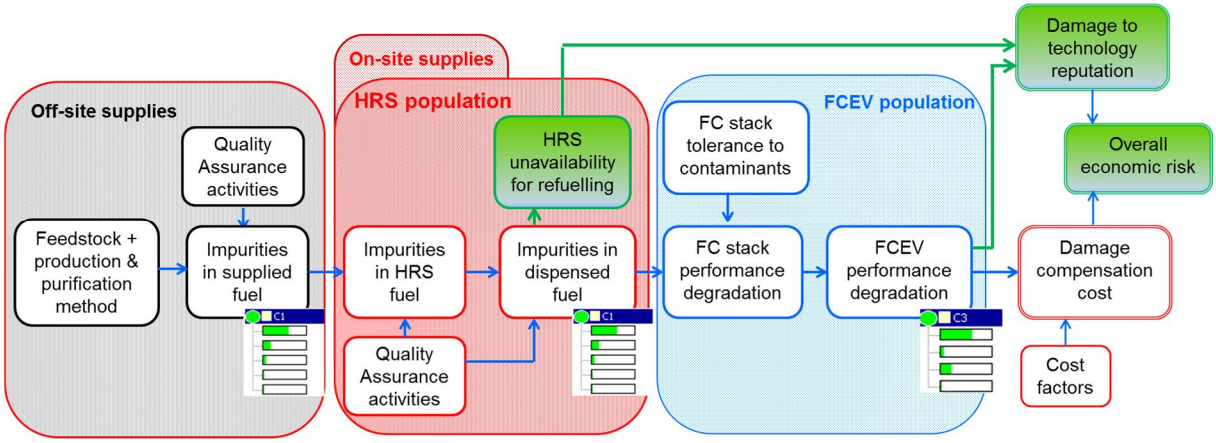

Figure 4.2 HyCoRA risk model with technology reputation effects

4.1 Modelling approach

In order to clarify the risk modelling process and keep it better manageable, a step-wise process for building the risk model gradually has been selected. This implies developing the first risk model versions aroud a relevant example case with limited scope. Once found feasible, the model scope can be expanded from there to include the most likely hydrogen fuel production methods and feedstocks, and all important contaminants.

Hydrogen produced centrally from natural gas (NG) by steam methane reforming (SMR) and purified by pressure swing adsorption (PSA) was selected as the starting case for establishing the model for Hydrogen fuel quality risk. Furthermore, carbon monoxide (CO) was selected as the single fuel contaminant of high relevance to start with.

The FCEV population considered is limited to PEMFC operated passenger cars in private use, thus excluding taxes, buses, lorries, etc. Also, modelling the economic impact from malign fuel quality is limited to consider damage compensation costs only.

Once become convinced of the feasibility of the limited risk model, it can be expanded to comprise also other hydrogen production methods and other significant fuel contaminants. The most relevant other production methods to be modelled comprise distributed, on-site production by water electrolysis and by SMR-PSA process from natural gas, and by-product production from industrial processes, e.g. the chlorine – alkaline process.Other significant fuel contaminants would comprise sulphur, halogenates and ammonia.

Bayesian networks (BN) will be used as the first choice to model the fuel quality risk in quantitative terms. Fuel quality risk is measured as the likelihood of experiencing fuel impurities induced adverse effects in the FCEV population and associated damage compensation costs.

Bayesian network (BN) model is a directed acyclic graph model comprised of nodes and directed arcs. Acyclic implies that loops leading back to a node are not allowed. In the model,

nodes represent random variables with an associated probability distribution for their possible values/states (continuous or discrete). Directed arcs indicate the conditional probabilistic dependence between the connected variables. Direction of the arc indicates the direction of the dependence. A conditional probability table is defined for each node to specify the probability of the variable being in a particular state considering each combination of the states of the parent node variables.

BN model allows to capture complete set of scenarios regarding some variable of interest, and the dependencies between those scenarios. With the BN model, the joint marginal distributions regarding the model variables can be calculated.

BN model also allows probabilistic backward inference given the information (i.e. evidence) on some of the model variables. As a simple example (cf. Figure 4.4) , knowing the impurity concentration in vehicle fuel tank and the fuel level at the previous refuelling on a vehicle experiencing problems in operation, would allow to make inference on the likelihood of the fuel that was dispensed in the previous refuelling being contaminated.

4.2 Qualitative risk models

4.2.1 ID model for CO contamination in HRS dispensed fuel

Figure 4.3 shows the tentative Influence Diagram (ID) model for considering the risk of CO contamination in HRS dispensed fuel. This tentative risk model, considering hydrogen supply by centralised production from natural gas (NG) using the SMR-PSA process, was represented and discussed in the first OEM workshop in the HyCoRA project.

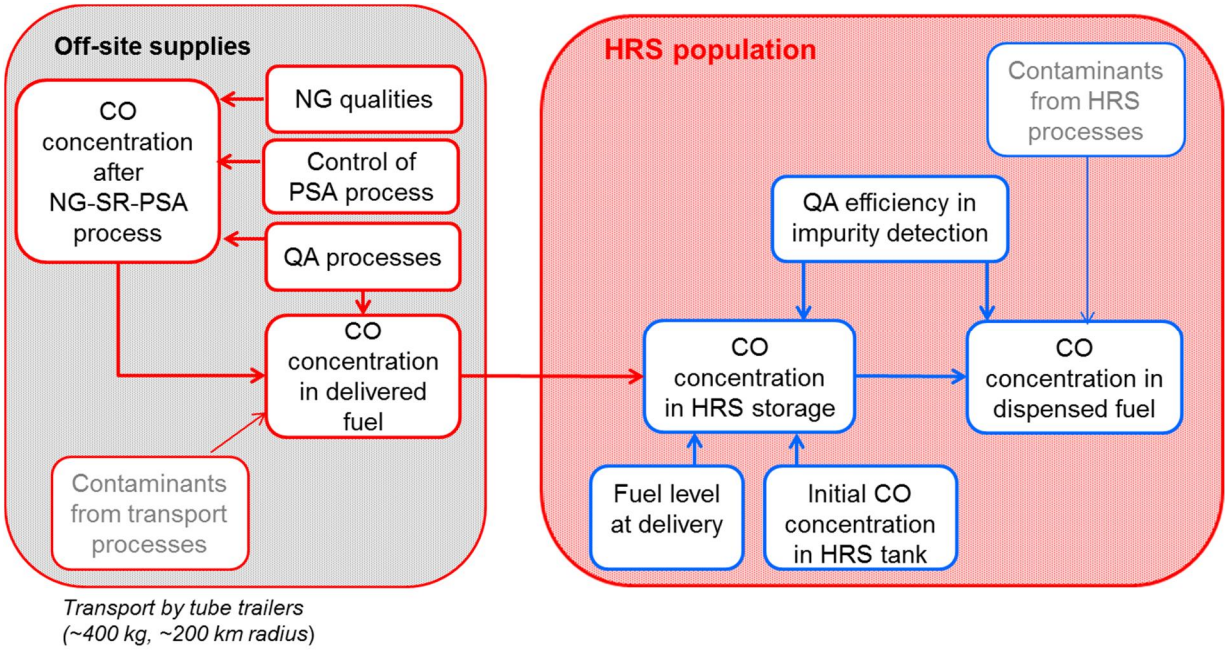

Figure 4.3 Tentative ID model for CO contamination in HRS dispensed fuel

The hydrogen-rich gas reformate produced from natural gas by steam reforming (SR) and subsequent water-gas shift reaction (WGS) contains naturally notable quantity of CO as imupurity and requires purification before it can be used as fuel. In large scale production, the purification is typically done using the PSA process.

CO concentration in the hydrogen fuel delivered from cetntralised production plants to refuelling stations (HRSs) is determined by the efficiency and reliability of the PSA process in removing CO from the hydrogen product. Purity of the produced hydrogen can be ensured by

thoroughly controlling the PSA process parameters and/or by monitoring the CO concentration in the produced fuel or in the deliveries to HRSs.

The storage and transport processes of hydrogen fuel are not conceivable sources for additional CO contamination.

The CO concentration in a particular delivery from a production plant is spreaded to the set of HRSs supplied by that delivery. Resulting CO concentration at each HRS may however be different depending on variation between the stations in initial CO concentration in HRS stoarage tank and fuel storage level at the time of delivery.

The CO concentration in the fuel dispensed to FCEVs from HRSs depends on efficiency of the QA processes employed in HRSs in detecting substandard fuel quality and preventing dispensing of the contaminated fuel. QA efficiency is determined by the delay in and reliability of the detection. QA efficiency is likely to be different for different contaminants and impurity levels.

In case of no QA, or totally inefficient QA process, the CO concentration in the dispensed fuel follows directly the CO concentration in the HRS storage tank. Efficient QA, on the other hand, will stop delivery of the contaminated fuel once detected, and thus reduce the possibility of FCEVs to refuel contaminated fuel. The probability of unacceptable CO concentrations in the dispensed fuel will then get lowered compared to CO concentrations in the fuel in the HRS storage tank.

The storage and dispenser processes at HRSs are not conceivable sources for additional CO contamination.

4.2.2 ID model for FCEV performance degradation due to CO contamination in fuel

Figure 4.4 shows the tentative Influence Diagram (ID) model for considering the risk of FCEV performance degradation in case of CO contamination in the fuel used. This tentative risk model was represented and discussed in the first OEM workshop.

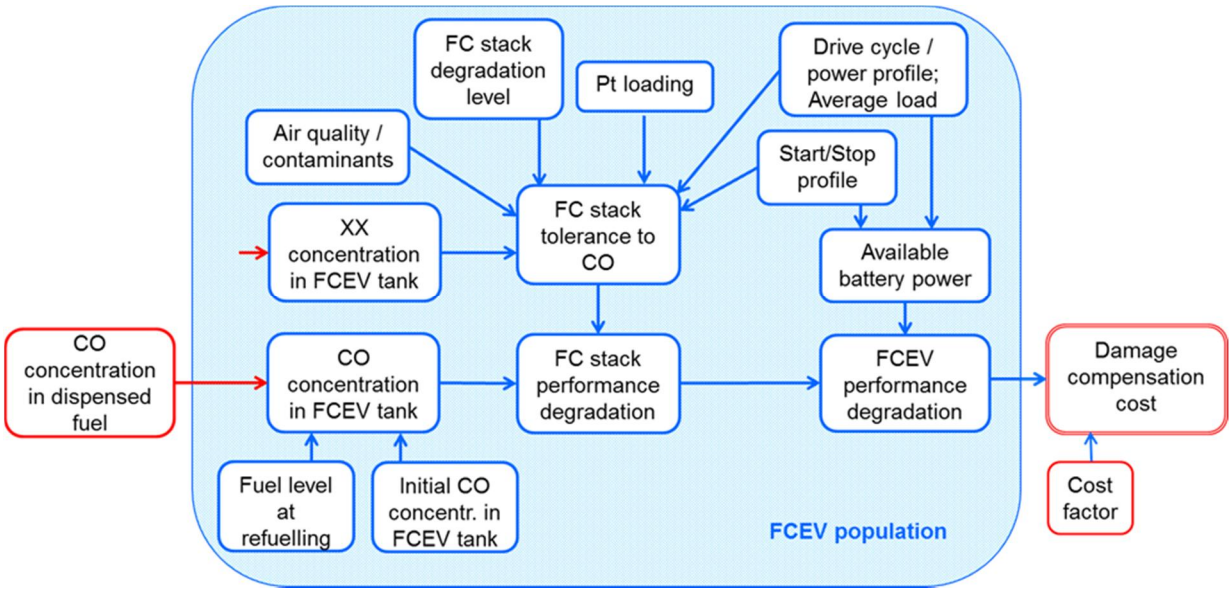

Figure 4.4 Tentative ID model for FCEV performance degradation due to CO contamination in fuel

PEM fuel cells are (selectively) sensitive to contaminants in the hydrogen fuel used. This is shown as degradation of the FC stack output as the stack cells get exposed to contaminated fuel. The severity of performance degradation depends on the contaminant(s), concentration of the contaminant(s) in the vessel fuel tank, and FC stack tolerance to the contaminant(s), as indicated in Figure 4.4

CO concentration in the fuel tank of an FCEV after a refuelling at a HRS is determined by the CO concentration in the fuel at the dispenser of the visited refuelling station, the initial CO concentration in vessel's fuel tank, and the the tank fuel level at the time of refuelling.

FC stack tolerance to CO exposure depends mainly on FC stack condition, the presence of (particular) other contaminants in the fuel or the air of the driving environment, and how the vessel is operated before the next refuelling. FC stack condition takes into account the intial stack dimensioning and the degradation expected in the cells over time. The degradation is affected by vessel age and operating history. The drive profice specifying at what power levels, and for how long, the FC stack is required to operate, as well as the frequency and duration of stop periods, also determine FC stack tolerance to CO exposure.

FCEVs are typically hybrid vehicles equipped with an energy compensation device such as battery or super-capacitor designed to fill-in gaps between the vehicle operation required energy output and the energy supply available from the FC stack, e.g. in quick accelerations of vehicle speed. This design feature may allow to drive the FCEV with reduced FC power so that the FC stack performance degradation is reduced while the user will perceive no or only minor adverse effect in FCEV operation. This further complicates the assessment of the risk of user perceived FCEV performance degradation. The availability of sufficient 'battery power' is affected by the battery capacity and the drive power profile, and the battery recharging possibility during vehicle stop periods as indicated in Figure 4.4.

Taking into account the fact that CO is a reversible contaminant, a more detailed tentative model is outlined in Figure 4.5 for considering FC stack performance degradation risk in case of fuel CO contamination. In the model, the anode catalyst CO poisoning and recovery are adressed as separate processes affecting fuel cells performance.

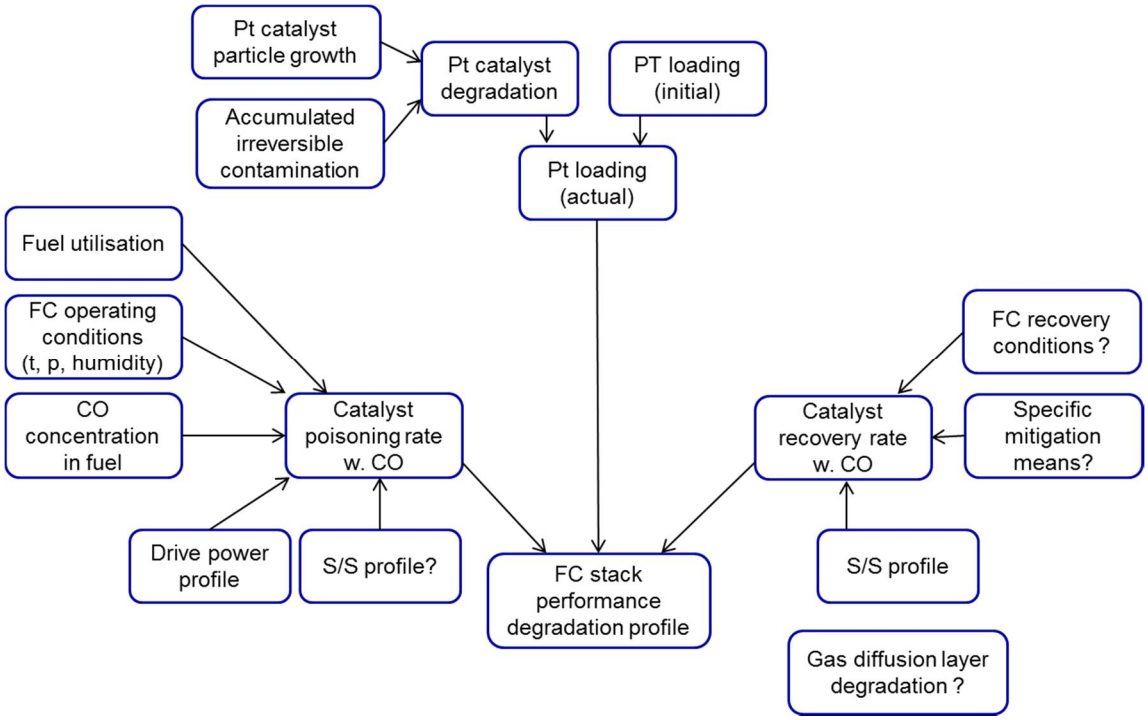

Figure 4.5 ID model for PEMFC stack performance degradation by CO

In the model, FC stack voltage output is assumed to be determined by the active anode Pt catalyst surface area available at the point of refuelling for hydrogen to react. This is affected by the initial amount of platinum catalyst (i.e. initial Pt loading: mg/cm^2 or m^2/cm^2) and the Pt catalyst degradation taking place over time and reducing the active catalyst surface area. CO in the hydrogen fuel adsorbs on the catalyst surface and further reduces the active catalyst surface area available for power production. On the other hand, oxidation of CO on the catalyst surface to CO_2 is started as soon the CO level in the fuel cells is reduced or the stack operation is stopped, allowing rapid recovery of the active catalyst surface area.

Pt catalyst degradation can be defined as the proportion of the initial active anode Pt catalyst surface area lost over fuel cell life. This degradation is due to FC 'aging effects', more specifically, particle growth taking place in the Pt catalyst over (calendar) time and the surface poisoning by irrereversible contaminats accumulated on Pt catalyst surface over previous operation history. Both of these are are affected by the age distribution of the FC stacks and FCEVs.

Catalyst poisoning rate by CO exposure is affected by FC operating conditions, and especially CO concentration in the fuel and the drive profile specifying at what power levels, and for how long, the FC stack is required to operate. The power level defines the hydrogen fuel supply, and together with the fuel CO concentration and duration on that power level, the total amount of CO introduced to poison the catalyst surface.

Catalyst recovery rate from CO poisoning is determined by the oxidation rate of CO. CO oxidation is provided mainly by oxygen passing through the membrane from the cathode. The recovery rate depends on the conditions and the FC system design providing specific means for mitigation. The start and stop profile determines the frequency and the time durations available for catalyst recovery processes.

The aim in automotive applications is to reduce the initial Pt catalyst loading from the currently high levels at both the anode and cathode. Obviously, the lower the initial Pt loading is, the more susceptible the FC systems become to age-related effects and for catalyst poisoning contaminants, like CO. In current FC stack designs, typically having about 10% of the intial active catalyst surface area still available at the anode is enough to ensure reasonable power output.

4.3 Quantitative risk models

Since the qualitative risk models specified in Influence Diagram (ID) format are directly usable for Bayesian Network (BN) models, the main activities in specifiying the quantitative risk models relate to (i) simplifying the models where necessary or useful to facilitate the quantification, (ii) specifying the range of variation and the relevant states/levels for each variable in the BN model, and (iii) defining and filling in the conditional probabilities regarding the BN model variables.

4.3.1 BN model for CO contamination risk in HRS dispensed fuel

No BN model is produced yet.

4.3.2 BN model for CO contamination induced FC stack performance degradation risk

No BN model is produced yet. The BN model will be based on the ID model shown in Figure 4.5.

The National Renewable Energy Laboratory (NREL) has collected and published data on operating of the FCEVs in the U:S, covering the time period 2005 – 2009 (NREL, 2012). This data can be used as initial estimates regarding variation in the FCEV operation related risk model variables.

5. Conclusions and recommendations

5.1 WP progress and identified challenges

Development of the hydrogen fuel quality risk model has been started using carbon monoxide (CO) as an example case of potential fuel contaminants.

Based on the work done thisfar in developing the risk models and the feedback received in the first OEM workshop, following challenges for the risk modelling have been identified:

- There may be no or very limited quantitative data available from hydrogen producers on variation in the quality of the produced and delivered hydrogen fuel. Hydrogen quality is currently controlled by monitoring the SMR and PSA process parameters or by pass / fail criteria (with respect to the fuel specification of ISO 14687-2:2012).

- Data regarding the PSA process may be difficult to obtain. ANL may be able to provide the PSA model for the project use for simulations. However, data exists only for limited number of contaminants for PSA modelling.

- The cost factors regarding degraded FCEV performance, and especially the monetary value of the damage incurred to technology reputation, can be difficult to estimate.

- Considering the user perceived vehicle performance degradation taking into account the energy compensation devices in hybrid vessels can be rather complicated due to differences in dimensioning of such devices and the utilisation of self-diagnostic features between car models and makes. It may then be necessary to limit the scope of the risk model only on impacts of FC stack performance.

- Validation of the risk model that will be produced in the project against real world data would be difficult. In short term, only semi-validation by a thorough peer review may be possible..

5.2 Recommendations for first part of WP1 and WP2 work

The effects of the gas diffusion layer degradation and water management on the catalyst CO poisoning and recovery processes could be further clarified in WP1.

The effects of CO_2 on FC performance in combination with CO are not known well. Maybe this could be clarified experimentally in WP1.

The OEM workshop adviced to include formic acid and formaldehyde on the list of contaminants that are further studied in WP1. Both species are problematic to measure with the levels specified in the current standard (ISO 14687:2-2012), while the specified levels are suspected to be unnecessarily low. The experimental effort for providing data for the possible revision of the limits would be reasonable.

Furthermore, haloganates were considered difficult to measure. In order to support possible revision of the requirements in the current standard (ISO 14687:2-2012), the risk of

halogenate contamination in the fuel should be quantified regarding the different production methods and supply chain operations.

In the measurement campaign of dispensed hydrogen fuel quality performed in WP3, also the background information regarding the HRSs should be collected. This would comprise data on fuel supplies to the station, maintenance and decontamination activities carried out in the station, and QA measures in use, Such data would be needed in order to draw conclusions regarding the effects of these issues on the quality variations measured in the dispensed fuel.

6. References

IEA, 2006. Hydrogen production and stotrage; R & D Priorities and Gaps. IEA – Hydrogen Co-ordination Group. International Energy Agency, 2006. 33 p. http://www.iea.org/publications/freepublications/publication/hydrogen.pdf

ISO 14687-2:2012. Hydrogen fuel – Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles. ISO 2012. 17 p.

Linde AG Engineering, Hydrogen recovery by Pressure Swing Adsorption. 5 p. http://www.linde-engineering.com/internet.global.lindeengineering.global/en/images/HA_H_1_1_e_12_150dpi19_6130.pdf

NREL, 2012: National Fuel Cell Electric Vehicle leraning Demonstration Final Report. K. Wipke, et al.Technical report NREL/TP-5600-54860, July 2012. 102 p.

P. Corbo et al., Hydrogen Fuel Cells for Road Vehicles, Green Energy and Technology, DOI: 10.1007/978-0-85729-136-3_2, Springer-Verlag London Limited 2011.

Papadias et al., 2009. Hydrogen quality for fuel cell vehicles – A modelling study of the sensitivity of impurity content in hydrogen to the process variables in the SMR-PSA pathway. International Journal of hydrogen Energy 34 (2009) 6021 - 6035.

SAES Pure Gas. Micro-channel Palladium Hydrogen Purifiers. Product sheet. http://www.saespuregas.com/cm/Products/Gas-Purifier/Hydrogen/Palladium-Membrane/Home.html