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The hazards and risks of hydrogen

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Abstract

An analysis was completed of the hazards and risks of hydrogen, compared to the traditional fuel sources of gasoline and natural gas (methane). The study was based entirely on the physical properties of these fuels, and not on any process used to store and extract the energy. The study was motivated by the increased interest in hydrogen as a fuel source for automobiles.

The results show that, for flammability hazards, hydrogen has an increased flammability range, a lower ignition energy and a higher deflagration index. For both gasoline and natural gas (methane) the heat of combustion is higher (on a mole basis). Thus, hydrogen has a somewhat higher flammability hazard.

The risk is based on probability and consequence. The probability of a fire or explosion is based on the flammability range, the auto-ignition temperature and the minimum ignition energy. In this case, hydrogen has a larger flammability zone and a lower minimum ignition energy—thus the probability of a fire or explosion is higher. The consequence of a fire or explosion is based on the heat of combustion, the maximum pressure during combustion, and the deflagration index. Hydrogen has an increased consequence due to the large value of the deflagration index while gasoline and natural gas (methane) have a higher heat of combustion. Thus, based on physical properties alone, hydrogen poses an increase risk, primarily due to the increased probability of ignition.

This study was unable to assess the effects of the increased buoyancy of hydrogen—which might change the probability depending on the actual physical situation.

A complete hazard and risk analysis must be completed once the actual equipment for hydrogen storage and energy extraction is specified. This paper discusses the required procedure.

Keywords: Hydrogen; Gas explosion; Risk

1. Introduction

Recently, hydrogen has been proposed as a fuel to replace either gasoline and/or natural gas as an energy source. The primary driving force for this is, of course, the fact that hydrogen combustion does not produce carbon dioxide since no carbon is present in the hydrogen molecule. Carbon dioxide has been implicated as a major player in global warming.

Everyone has pictures in their mind of the Hindenburg fire, which occurred on May 6, 1937 and resulted in the deaths of 13 passengers, 22 crew members and one person on the ground. The Hindenburg was the largest zeppelin ever built and was lifted by 200,000 m^3 (7,060,000 ft^3) of hydrogen gas contained in 16 gas bags or cells. The Hindenburg was longer than three Boeing 747 s placed end to end! Speculation continues today as to the cause of the accident. As an interesting historical note, the Hindenburg was originally designed for helium, but the United States military embargo against Germany prevented shipments of helium, resulting in a switch to hydrogen.

The question then arises: is hydrogen safe? Or perhaps, is hydrogen safer than current energy sources, such as gasoline and natural gas? The problem with the word "safe" is that it is difficult to define and various populations perceive safety in different ways. A better approach is to use the concepts of hazard and risk because these words are well-defined and are more suitable for analysis.

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The question then becomes: What are the hazards and risks associated with hydrogen usage and how do these compare to traditional gasoline and natural gas energy sources?

This paper will address the last question. The answers will only be provided in terms of the physical properties of hydrogen, gasoline and natural gas, in this case the flammability and explosion properties. Toxic and environmental hazards are not considered in this evaluation.

A complete risk assessment would require the detailed engineering on the storage and use of hydrogen. Since hydrogen technology related to public transportation is still under development, this information is not currently available and was not completed. However, the information contained within this paper could be used as a starting point for a more detailed and complete risk assessment.

2. Hazard and risk

A number of definitions are required in order to complete a hazard evaluation and risk assessment. Frequently, in the past, this evaluation was not done properly due to an incomplete understanding of these concepts.

Hazard and risk are two words that are commonly used, but frequently not applied correctly. A *hazard* is defined as a ‘‘chemical or physical condition that has the potential for causing damage to people, property, or the environment’’ (AICHE/CCPS, 2000). For fuels, the hazard is due to the physical properties of the fuel—in this case due to the flammable and explosive nature of the fuel.

Risk is ‘‘a measure of human injury, environmental damage or economic loss in terms of both the incident likelihood and the magnitude of the loss or injury’’ (AICHE/CCPS, 2000). In other words, risk is composed of *both* the probability of the accident and the consequences of the accident. If only one of the components is considered, then the risk may be improperly assessed and the means to control the risk may be either inadequate or overdone.

Risk analysis is defined as ‘‘the development of a quantitative estimate of risk based on engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies’’ (AICHE/CCPS, 2000).

Finally, *risk assessment* is ‘‘the process by which the results of a risk analysis are used to make decisions’’ (AICHE/CCPS, 2000).

The hazard identification and risk assessment procedure is shown in Fig. 1. After a complete description of the system is available, the hazards are first identified. The hazards can be due to the physical properties of the materials, operating conditions (temperature and pressure), or procedures used during the operation of the process.

Next, the scenarios are identified. The scenarios are ‘‘a description of the events that result in an accident’’ (Crowl & Louvar, 2002). The accident begins with an incident. An *incident* is defined as the loss of containment or control of material or energy. The incidents should be identified without regard to importance or initiating event, otherwise some critical incidents might be overlooked. Most incidents are followed by a series of events that propagate the accident. This could include fires, explosions and toxic releases. Finally, the *incident outcome* is ‘‘the physical manifestation of an incident’’ (AICHE/CCPS, 2000). The incident outcome includes human injury, environmental damage and loss of production and equipment. A particular piece of equipment might have dozens of scenarios. Each of these would need to be identified.

Next, both the probability and consequence of the scenario are estimated for all of the scenarios identified. The probability can be estimated using actual equipment reliability data, published data, or estimated based on generic data or mathematical models. The consequence can be estimated using traditional consequence estimation methods (AICHE/CCPS, 1999).

The probability and consequence estimates are then combined to determine the risk.

Finally, a risk acceptance procedure is applied. This can be done using a fixed risk acceptance criteria, or a number of other approaches (AICHE/CCPS, 2000).

There are two important observations from Fig. 1 that are important to this work. First, both the probability and consequence must be determined in order to complete a risk assessment. Second, once the scenarios are identified, the scenario must be applied in exactly the same way to each of the candidate fuels. If the scenarios are applied inconsistently for each fuel, then the results cannot be compared.

This has been the problem with some past efforts to study the risks associated with hydrogen. A well-known video on the internet, prepared by Professor Michael Swain of the University of Miami, shows two vehicle fires. In the first vehicle, a liquid leak of gasoline is ignited beneath the vehicle. The resulting fire destroys the entire vehicle. For the second vehicle, the hydrogen relief valve located on the top of the vehicle trunk is activated and the hydrogen plume is ignited. Little damage results to this vehicle. The video and paper (Swain, 2005) imply that hydrogen is ‘‘safer’’ than gasoline.

The study by Swain (2005) has three problems. First, probability is not considered in the study, only the consequence. Second, the scenarios for the two fuels are not identical—for the hydrogen the release occurs on top of the trunk while for the gasoline the leak occurs beneath the vehicle. The proper risk assessment procedure requires that the scenarios be applied to both fuels in the identical fashion. Third, only one scenario is considered—a proper risk assessment requires a study of all identifiable scenarios. If the hydrogen plume were ignited beneath the vehicle, we believe the damage from the hydrogen flame would be equivalent to the gasoline damage.

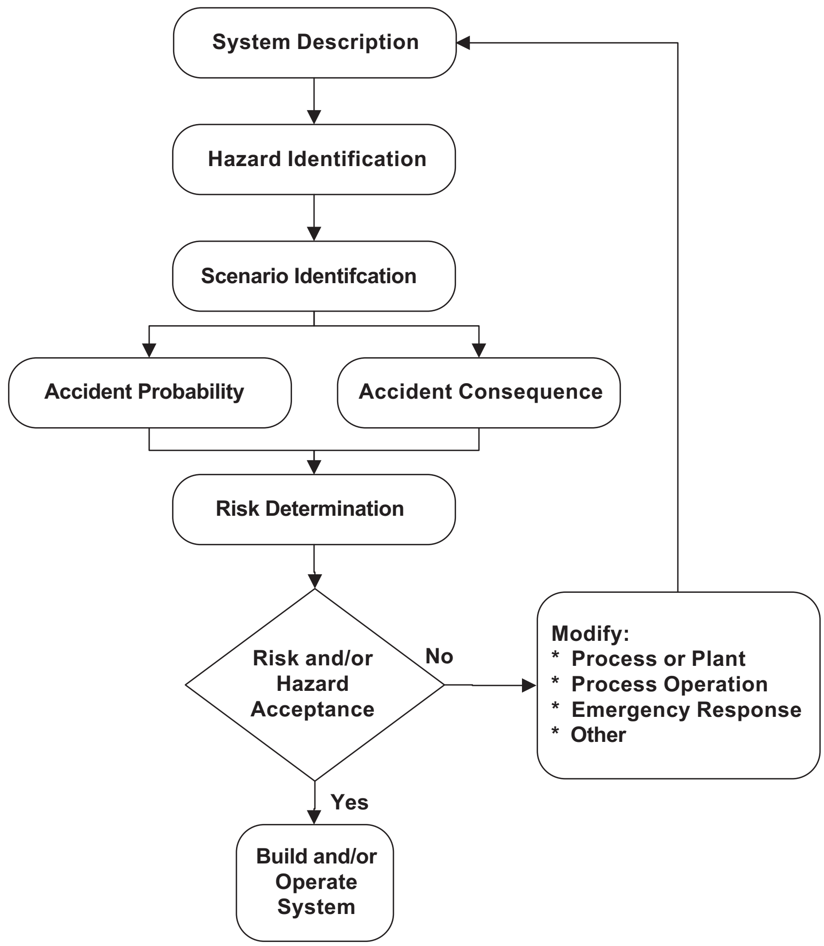

Fig. 1. The hazard identification and risk assessment procedure (Crowl & Louvar, 2002).

3. Physical properties of fuels related to risk

Since fuels have flammable and explosive hazards, this paper will focus on properties related to these hazards. Toxic or environmental hazards are not considered.

Table 1 is a list of the parameters used to characterize flammable and explosive materials. Also provided is an indication of the direction the property must go to increase the hazard, whether the property is related to the probability or consequence, and also some supplemental comments on the property.

The hazards of the fuel are related to all of the physical properties, i.e. any one of the properties might cause a source for hazard. However, only some of the properties are related to probability and some are related to consequence. For instance, the flammability range is related to the probability since the wider the range the greater the probability that the fuel will ignite. Likewise, the heat of combustion is related to the consequence since the heat release causes the damage.

Hydrogen and methane are both gases and are easy to compare while gasoline is a liquid and somewhat difficult

Table 1
Physical properties related to the probability and consequence of a fuel fire and/or explosion

Property	Direction of increased hazard	Probability and/or consequence?	Comments
Physical state (solid, liquid, gas)	Solid→ liquid→gas	Probability	Difficult to assess.
Vapor pressure (liquids only)	Higher	Probability	
Flammability limits (vapor only)	Lower LFL or wider range	Probability	
Flash point temperature (liquids only)	Lower	Probability	Not unique—related to flammability limits
Auto-ignition temperature	Lower	Probability	
Ignition energy (vapor only)	Lower	Probability	
Heat of combustion	Higher	Consequence	
Max. pressure during combustion	Higher	Consequence	
Deflagration index	Higher	Consequence	

to compare. Some of the properties in Table 1 only apply to liquids (vapor pressure and flash point) while some properties (flammability limits, ignition energy, maximum pressure during combustion and deflagration index) apply only to gases or the vapor above a liquid. The procedure defined for determining the auto-ignition temperature applies only to liquids, but the liquid vaporizes in the apparatus prior to ignition.

The flammability limits for gases and the flash point temperature for liquids are related. That is, the theory is that the flash point temperature occurs when the vapor concentration above the liquid is at the flammability limit. Since these two properties are related, this paper will only use the flammability limits for the subsequent analysis.

There are additional properties used to characterize the flammable and explosive hazards of materials beyond those shown in Table 1. This includes the flammability zone, the limiting oxygen concentration, and the flammable limits in pure oxygen. However, any release of these fuels in practical application would most likely be into an air atmosphere, not one enriched with oxygen. Thus, these properties were not included in the table.

The vapor pressure of a liquid is related to the flammability limits. However, this was included in the list of properties in order to assist in the comparison between the liquid and gaseous fuels.

The deflagration index is determined using pressure—time data from combustion in a closed vessel. The index is determined from the maximum slope of the pressure–time data during the combustion. Once the maximum slope is known, the index is computed from (Crowl & Louvar, 2002):

$$K_G = \left(\frac{dP}{dt}\right)_{max} V^{1/3}. \tag{1}$$

The deflagration index is an indication of the "robustness" of the explosion. The higher the deflagration index the more robust the explosion and the greater the consequences of the explosion.

The maximum pressure during the combustion is also determined from pressure–time data from combustion in a closed vessel. The higher the maximum pressure the greater the consequences of the explosion.

Tables 2–4 list the physical properties for the three fuels. Gasoline is a blend of materials with no fixed composition. For gasoline, no directly measured values are available in the open literature for the maximum pressure and deflagration index. The estimated maximum pressure of 8 bar for gasoline is most likely near the correct value since this is a typical pressure increase for most hydrocarbons. The value for the deflagration index for gasoline is estimated using octane and propane. A range of 100–150 bar m/s is shown since this is a common range for these flammable materials. The conclusions drawn in this paper are not dependent on a specific value of the deflagration index and are valid over the range shown.

Table 2
Physical properties for hydrogen at 1 atm, 298 K

Property	Value	Units	Reference
Physical state (solid, liquid, gas)	Gas		
Vapor pressure (liquids only)	Gas		
Flammability limits (vapor only)	4.0–75%	Volume % fuel in air	Kuchta (1985)
Flash point temperature (liquids only)	Gas		
Auto-ignition temperature	572	°C	Glassman (1996)
Ignition energy (vapor only)	0.018	mJ	Glassman (1996)
Heat of combustion	285.8	kJ/mol	Suzuki (1994)
Max. pressure during combustion	6.8	Bar gauge	Bartknecht (1993)
Deflagration index	550	Bar m/s	Bartknecht (1993)

Table 3
Physical properties for methane at 1 atm, 298 K

Property	Value	Units	Reference
Physical state (solid, liquid, gas)	Gas		
Vapor pressure (liquids only)	Gas		
Flammability limits (vapor only)	5.3–15%	Volume % fuel in air	Lewis and Von Elbe (1987)
Flash point temperature (liquids only)	Gas		
Auto-ignition temperature	632	°C	Glassman (1996)
Ignition energy (vapor only)	0.280	mJ	Glassman (1996)
Heat of combustion	890.3	kJ/mol	Suzuki (1994)
Max. pressure during combustion	7.1	Bar gauge	NFPA 68 (2002)
Deflagration index	55	Bar m/s	NFPA 68 (2002)

4. Results

Table 5 compares the hazards between hydrogen and methane while Table 6 compares hydrogen with gasoline. The comparison was done by comparing hydrogen individually with each of the fuels. For each physical property a qualitative decision was made with respect to which chemical represented the greatest hazard. The chemical with the highest hazard was given a value of "1". This was done for all of the properties, and the totals added at the bottom of the table. The hazards were all considered of equal value—no attempt was made to apply weighting factors.

Comparing hydrogen with methane (Table 5) shows that hydrogen represents a greater hazard with respect to the flammability range, the very low ignition energy, and the deflagration index. Methane has a higher heat of combus-

Table 4
Physical properties for gasoline at 1 atm, 298 K

Property	Value	Units	Reference
Physical state (solid, liquid, gas)	Liquid		
Vapor pressure (liquids only)	0.34	Bar	Rose and Cooper (1977)
Flammability limits (vapor only)	1.3–7.1%	Volume % fuel in air	Kuchta (1985)
Flash point temperature (liquids only)	−43	°C	Sax (1984)
Auto-ignition temperature	440	°C	Kuchta (1985)
Ignition energy (vapor only)	0.25	mJ	Estimated
Heat of combustion	5512	kJ/mol	Suzuki (1994)
Max. pressure during combustion	8	Bar gauge	Estimated—see discussion in paper.
Deflagration index	100–150	Bar m/s	Estimated—see discussion in paper.

Table 5
Comparison of hydrogen and methane hazards at 1 atm, 298 K

Property	Hydrogen	Methane	Comment
Physical state (solid, liquid, gas)	?	?	Both are gases, but hydrogen is more buoyant, which may reduce hazard in open space
Flammability limits (vapor only)	1	0	Much wider for hydrogen
Auto-ignition temperature	—	—	About the same
Ignition energy (vapor only)	1	0	Ignition energies may be comparable near the flammable limits—more study required
Heat of combustion	0	1	
Max. pressure during combustion	—	—	They are about the same
Deflagration index	1	0	Much higher for hydrogen
Totals	3	1	

tion. Thus, by this analysis, hydrogen represents greater hazard. Both hydrogen and methane are gases, but hydrogen is more buoyant and may disperse more quickly in an open space. In a confined space, such as a garage, it is expected that the buoyancy of the hydrogen will have less of an effect on the dispersion. A more detailed study on this issue is required and the physical state issue is left with a question mark in Table 5.

Table 6 compares hydrogen with gasoline. In this case hydrogen is a gas while gasoline is a liquid. Clearly, it is more difficult to contain high pressure hydrogen gas compared to liquid gasoline. However, hydrogen gas is buoyant and is believed to disperse quickly. Gasoline liquid is easier to contain, but contains a higher energy content. Thus, the hazard identification is incomplete and the physical state issue is left with a question mark in Table 6.

Table 6
Comparison of hydrogen and gasoline hazards at 1 atm, 298 K

Property	Hydrogen	Gasoline	Comment
Physical state (solid, liquid, gas)	?	?	Difficult to determine
Flammability limits (vapor only)	1	0	Wider for hydrogen, but gasoline LFL is lower.
Auto-ignition temperature	—	—	About the same
Ignition energy (vapor only)	1	0	Ignition energies may be comparable near the flammable limits—more study required
Heat of combustion	0	1	A lot higher for gasoline
Max. pressure during combustion	—	—	About the same
Deflagration index	1	0	Much higher for hydrogen
Totals	3	1	

Table 7
Comparison of hydrogen and methane fire/explosion probability at 1 atm, 298 K

Property	Hydrogen	Methane	Comment
Physical state (solid, liquid, gas)	?	?	Both are gases, but hydrogen is more buoyant.
Flammability limits (vapor only)	1	0	Much wider for hydrogen
Auto-ignition temperature	—	—	About the same
Ignition energy (vapor only)	1	0	Ignition energies may be comparable near the flammable limits—more study required
Totals	2	0	

With respect to the other properties in Table 6, hydrogen has a wider flammability limit, but gasoline has a lower LFL—in this case the wider flammability range was assigned the greater hazard. Hydrogen also has a lower ignition energy and a higher deflagration index over gasoline. Thus, this analysis shows that hydrogen represents the greater hazard.

Tables 7 and 8 compare hydrogen to methane and gasoline based on the physical properties related to fire and/or explosion probability. In both cases hydrogen represents a greater fire and/or explosion probability due to the wider flammability range and the low ignition energy.

Tables 9 and 10 compare hydrogen to methane and gasoline based on the physical properties related to fire

Table 8
Comparison of hydrogen and gasoline fire/explosion probability at 1 atm, 298 K

Property	Hydrogen	Gasoline	Comment
Physical state (solid, liquid, gas)	?	?	Difficult to compare since hydrogen is a gas and gasoline is a liquid. Hydrogen gas escapes easily, but gasoline has higher energy content.
Flammability limits (vapor only)	1	0	Wider for hydrogen, but gasoline LFL is lower.
Auto-ignition temperature	—	—	About the same
Ignition energy (vapor only)	1	0	Ignition energies may be comparable near the flammable limits—more study required.
Totals	2	0	

Table 9
Comparison of hydrogen and methane explosion consequence at 1 atm, 298 K

Property	Hydrogen	Methane	Comment
Heat of combustion	0	1	Higher for methane
Max. pressure during combustion	—	—	About the same
Deflagration index	1	0	Much higher for hydrogen
Totals	1	1	

Table 10
Comparison of hydrogen and gasoline explosion consequence at 1 atm, 298 K

Property	Hydrogen	Gasoline	Comment
Heat of combustion	0	1	Much higher for gasoline
Max. pressure during combustion	—	—	About the same
Deflagration index	1	0	Much higher for hydrogen
Totals	1	1	

and/or explosion consequence. In this comparison the fuels came out about equal. Methane and gasoline have a higher heat of combustion (per mole) and hydrogen has a much higher deflagration index.

5. Conclusions and recommendations

Table 11 summarizes the results of this study. It is important to recall that this study is only a preliminary assessment of the hazards and risk of hydrogen compared to traditional fuels based only on physical properties—a more detailed and complete risk assessment procedure is required once the specific designs for storage and use of hydrogen are detailed.

Table 11
Summary of results

	Hydrogen	Methane	Gasoline
Hazards	3	1	1
Probability	2	0	0
Consequence	1	1	1

The results show that hydrogen represents a greater hazard over methane and gasoline due to the wider flammability limits, lower ignition energy and higher deflagration index.

Hydrogen also represents a greater risk, primarily due to the increased probability of a fire and/or explosion. This is due to the wider flammability limits and the lower ignition energies. The consequences of a fire and/or explosion of these fuels appear to be about equal, but the very high deflagration index for hydrogen probably warrants further study.

The buoyancy of hydrogen must also be considered in future hazard and risk studies. Anecdotal studies have been completed (Swain, 2005) indicating that hydrogen disperses so quickly that it is unlikely to create a flammable mixture of any large volume. A rigorous study of this phenomenon must be completed. This study must include mathematical modeling followed by extensive experimental studies. These studies can then be used to identify the situations where dispersion may not be significant and larger volumes of flammable gas may accumulate.

Hydrogen also has two additional hazards not studied in this work. First, hydrogen burns with a colorless flame, so it is difficult to detect. Second, unlike most common gases, hydrogen self-heats when it leaks from a high-pressure source. The impacts of these two phenomena must be considered in future hazard and risk assessment studies.

It is recommended that a full risk assessment be completed for these fuels once the actual hardware designs for storage and use are in the preliminary stages. This risk assessment must include (1) identification of all of the scenarios that can lead to an accident, (2) evaluation of all of the scenarios using experimental data coupled with mathematical modeling, and (3) determination of the risk based on both probability and consequence.

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