



Programme Area: Carbon Capture and Storage

Project: High Hydrogen

Title: Literature Review of CCGT/CCGE/CHP Systems Operating on High Hydrogen Content Gases

Abstract:

This deliverable is number 1 of 8 in the project and forms the basis of the project direction. It provides information on the current gaps in knowledge of plants operating on High Hydrogen fuels. The report provides an in depth review of the current literature landscape relating to the use of hydrogen rich fuels for both reciprocating engines and gas turbines. All current fuels containing hydrogen are detailed with their other constituent parts. The report identifies the scaling principles to determine how the results from the laboratory can be applied to the plant being constructed for the next phase and real world applications. Appendix A3 Analysis of HSE gas turbine and gas engine incidents database has been removed for confidentiality reasons.

Context:

Hydrogen is likely to be an increasingly important fuel component in the future. This £3.5m project was designed to advance the safe design and operation of gas turbines, reciprocating engines and combined heat and power systems using hydrogen-based fuels. Through new modelling and large-scale experimental work the project sought to identify the bounds of safe design and operation of high efficiency combined cycle gas turbine and combined heat and power systems operating on a range of fuels with high and variable concentrations of hydrogen. The goal of the project was to increase the range of fuels that can be safely used in power and heat generating plant. The project involved the Health and Safety Laboratory, an agency of the Health and Safety Executive, in collaboration with Imperial Consultants, the consulting arm of Imperial College London.

Disclaimer:

The Energy Technologies Institute is making this document available to use under the Energy Technologies Institute Open Licence for Materials. Please refer to the Energy Technologies Institute website for the terms and conditions of this licence. The Information is licensed 'as is' and the Energy Technologies Institute excludes all representations, warranties, obligations and liabilities in relation to the Information to the maximum extent permitted by law. The Energy Technologies Institute is not liable for any errors or omissions in the Information and shall not be liable for any loss, injury or damage of any kind caused by its use. This exclusion of liability includes, but is not limited to, any direct, indirect, special, incidental, consequential, punitive, or exemplary damages in each case such as loss of revenue, data, anticipated profits, and lost business. The Energy Technologies Institute does not guarantee the continued supply of the Information. Notwithstanding any statement to the contrary contained on the face of this document, the Energy Technologies Institute confirms that the authors of the document have consented to its publication by the Energy Technologies Institute.



**Imperial College
London**
Consultants

Harpur Hill
Buxton
Derbyshire SK17 9JN
T: +44 (0)1298 218000
F: +44 (0)1298 218590
W: www.hsl.gov.uk

58 Prince's Gate
Exhibition Road
London SW7 2PG
T: +44 (0)20 7594 6565
F: +44 (0)20 7594 6570
W: www.imperial-consultants.co.uk

**Literature review of CCGT/CCGE/CHP systems
operating on high hydrogen content gases.**

Project no. PE02162

**Updated for general issue 07/09/12
XS/81/12**

Lead Author:
Contributing Authors:

Technical Reviewer:
Editorial Reviewer:
Date Authorised:

**H. Michels (IC)
P. Lindstedt (IC), K. Moodie & R. Santon
(HSL), B.C.R. Ewan (SU).
Dr. S. Hawksworth
Dr. R. Gibson
6th March 2012**

DISTRIBUTION

Paul Winstanley	ETI Project Manager
Matthew Barton	ETI Programme Manager
Karen Russ	HSL Project Director
Hans Michels	Consortium Chief Technologist (Imperial College)
John Gummer	Consortium Project Manager (HSL)
Peter Lindstedt	Imperial College
Keith Moodie	HSL Technical Lead
Roger Santon	HSL Industrial Lead
Stuart Hawksworth	Head of Explosion Safety Unit, HSL
Bruce Ewan	Chementech

PRIVACY MARKING:

Commercial in confidence

Report Authorised for Issue by:	Dr K Russ
Date of issue:	4th March 2012
Project Manager:	Mr. J. Gummer
Technical Reviewer(s):	Dr. S. Hawksworth
Editorial Reviewer:	Dr. R. Gibson
HSL Project Number:	PE02162

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance and advice given by the technical staff from both GE and Jenbacher, for providing an industry perspective with respect to the current operation of gas turbines and gas engines on high hydrogen fuels.

The authors would also like to thank Dr. D. Abbot (EoN) and C. Etheridge (Solar Turbines) for the informative discussions and for their technical inputs.

CONTENTS

1	INTRODUCTION.....	1
1.1	Objectives.....	1
1.2	Scope	1
1.2.1	Range of power plants of interest.....	2
1.3	Search criteria	2
1.4	AbBreviations, Acronyms and Terminology	4
2	TYPES OF POWER PLANT CONSIDERED	5
2.1	Introduction.....	5
2.2	Combined cycle gas turbines.....	5
2.3	Combined cycle gas engines.....	6
2.4	Combined heat and power systems	7
2.5	Heat recovery steam generators	7
2.6	Selective catalytic reduction	8
2.7	Catalytic oxydation.....	9
2.8	Integrated gasification combined cycle	9
2.9	Carbon capture and storage	10
2.10	Emissions using high hydrogen fuels.....	11
3	FUEL TYPES AND SOURCES.....	13
3.1	Introduction.....	13
3.2	Hydrogen	13
3.2.1	Running gas turbines/engines on hydrogen.....	14
3.3	Syngas.....	15
3.3.1	Running gas turbines/engines on syngas	16
3.4	Producer gas	17
3.5	Refinery fuel gas.....	17
3.6	Impurities	17
3.7	Steam	17
3.7.1	Steam injection.....	17
3.7.2	Fire and blast mitigation using water mists	19
3.8	Mixture properties.....	20
3.8.1	Stoichiometry	20
3.8.2	Critical times and distances.....	25
3.8.3	Composition and flammability limits.....	26
3.8.4	Mixing rules	26
3.9	Summary of key findings	26
4	COMBUSTION PROCESSES	28
4.1	Fuel sensitivity and ignition.....	28
4.2	Auto ignition and auto ignition delay times.....	29
4.3	Flame development and flame speed.....	30
4.4	Influence of exhaust gas temperature	30
4.5	Turbulence and flame acceleration.....	31
4.6	Deflagration	32
4.7	Deflagration-to-detonation transition (DDT)	32

4.7.1	Principles of gaseous detonation	32
4.7.2	Self-generated DDT.....	33
4.7.3	Artificially supported DDT	34
4.7.4	Implications for this investigation	34
4.8	Detonation	37
4.9	Combustion enhancement.....	37
4.10	Obstructions and blockage ratio	38
4.11	Wall effects and confinement.....	38
4.12	Potential over-presssures	38
4.12.1	Prediction techniques	38
4.12.2	Experimental measurements	39
4.13	SummarY of key findings.....	39
5	SCALING PRINCIPLES.....	41
5.1	Techniques	41
5.2	Fluid mechanical issues.....	41
5.3	Detonation cell sizes.....	42
5.4	Scaling criteria for WP2/task 3.....	42
5.4.1	Introduction	42
5.4.2	Application to proposed test rig	43
6	CURRENT INDUSTRIAL PRACTICES	44
6.1	Review of existing high hydrogen systems	44
6.2	Combustor developments.....	45
6.3	High H ₂ Hazards associated with current systems	46
6.3.1	Flammable gases in exhaust system.....	46
6.3.2	Analysis and review of actual GT hydrogen concentrations	48
6.4	Fuel used by the ETN (H ₂ -IGCC).....	52
6.5	Typical syngas fuel composition (courtesy of GE)	53
6.6	Strategy for fuel mixture selection to meet industrial interests.....	54
6.7	Calculated exhaust emissions for viper engine.....	56
6.8	Review of HRSG layouts and exhaust systems.....	57
6.8.1	Design rationale.....	58
6.8.2	HRSG layouts.....	58
6.8.3	HRSG equipment.....	61
6.9	Control systems for high hydrogen fuels.....	61
6.9.1	General comments	61
6.9.2	Objectives of control systems.....	62
6.9.3	Protection mechanisms.....	63
6.9.4	Meeting NOx targets	64
6.9.5	Safety aspects during start-up, shutdown and running.....	64
6.9.5.1	Fuel transition	64
6.9.5.2	Over watering on load cut-off.....	65
6.9.5.3	Non-ignition.....	65
6.9.5.4	Fuel heating value changes.....	65
6.9.6	Examples of solution strategies to changes in WI.....	67
6.10	Flame detectors	69
6.11	Summary of key findings	69
7	REGULATORY REGIMES.....	71

7.1	Definitions of standards, regulation and codes of practice.....	71
7.2	Standards re: safety management/control systems for high h ₂ fuels	72
7.3	Standards re: safe handling of high hydrogen fuels.....	74
7.4	Standards re: explosion prevention and protection.....	75
7.5	Standards re: safe design and operation of ccgt/ccge/hrsg systems	78
7.6	Standards re: safe operation of gas turbines	83
7.7	Standards re: safe operation of gas engines	85
8	DISCUSSION.....	89
8.1	Re: fuel types and sources	89
8.2	Re: combustion processes	89
8.3	Re: scaling.....	89
8.4	Current industrial practices	89
8.5	Re: safety and regulatory regimes	90
8.5.1	Safety management systems.....	90
8.5.2	Safe handling of high hydrogen fuels.....	90
8.5.3	Explosion prevention and protection.....	91
8.5.4	Safety design and operation of CCGT/CCGE/HRSG systems.....	92
8.5.5	Safe operation of gas turbines	93
8.5.6	Safe operation of gas engines	95
8.6	Choice of fuel mixtures	96
8.7	Fuels re: gas engines	96
8.8	Implications for Work package two	97
8.8.1	Task one test programme.....	97
8.8.1.1	General implications	97
8.8.1.2	Implications for scale-up	97
8.8.1.3	Implications from use of steam.....	97
8.8.1.4	Implications for detonation cell sizes	98
8.8.1.5	Model systems to be tested.....	98
8.8.2	Consequences for WP2 experimental design	99
9	CONCLUSIONS.....	100
10	RECOMMENDATIONS	102
11	APPENDICES	103
12	BIBLIOGRAPHY	116

EXECUTIVE SUMMARY

This report details an extensive literature review of established facilities, use, operational procedures, hazards and regulatory provisions related to power and heat generation with combined cycle gas turbine and gas engine systems running on high hydrogen fuels or hydrogen only.

It was found that this field of energy generation could be divided in to three sections, according to the use of respectively high, medium and low-grade energy sources. In each of these areas an opportunity exists to increase the efficiency of the generation by hydrogen enrichment. However, the scope for this is limited by associated high temperatures, which may damage the plant and by the explosion and DDT hazards that arise with the reactant hydrogen concentration.

Flame initiation and progression, explosion, detonability, and aspects of associated high overpressures are considered in their scientific and industrial context, including specific aggravating conditions caused by pressure and turbulence; case specific higher risk locations have been identified. Existing control options and scope for development of warning and prevention techniques are reviewed.

Regulatory documentation across the whole field is extensively discussed covering the following aspects: safety management; high hydrogen fuels, explosion prevention and protection; safe operation and design of combined cycle systems; and the safe operation of gas turbines/engines.

Recommendations are made for the amendment and execution of the experimental work of the small scale/laboratory Task 1 of the ETI contract, Work Package 2. Following consultation with and advice from industry, information from international subject groups and opinion expressed by associated experts, it is proposed to investigate three practical multi-component fuel systems plus an additional system using hydrogen, rather than the previously agreed model fuel systems with air.

The report recommends that the scheduling of the hydrogen tests be agreed at the stage gate review. The report also states the changes required to include steam in the experimental programme. These requirements are additional to those for the auto-ignition data.

The Report concludes that the Deliverables detailed in the ETI contract for the literature review, identification of (seven) knowledge gaps, selection of test systems, the review of existing controls and safety provisions and for the scrutiny of Standards or Codes of Practice have all been satisfied and that appropriate recommendations for the work are made.

The review does not make suggestions for Inherent Safety improvements at this stage as this requires a QRA to be undertaken once the characteristics of the selected fuel systems have been quantified.

1 INTRODUCTION

1.1 OBJECTIVES

The objectives of this literature review were:-

- To report from a detailed survey and in house experience on critical properties and operational parameters that may be relevant to the use of gaseous mixtures of high hydrogen content (**high-hydrogen** systems) within CCGT and CCGE power plants;
- To do so with particular focus on the potential of high overpressure generation in the exhausts and heat recovery units (**HRSGs**);
- To identify hazards endemic to, or associated with, such operations and outline appropriate safety provisions and enhancements, including an identification of critical measurement and control techniques and appropriate sensor technology;
- To highlight any areas where current levels of knowledge and expertise are still inadequate to ensure the integrity and safety of combined heat and power (**CHP**) plants running with high-hydrogen fuel systems;
- To select three representative fuel systems including 100% hydrogen, and
- To identify any issues relevant to the conduct of the subsequent work.

1.2 SCOPE

Within its general scope, the review aimed to identify, consider and summarise relevant published work related to operational and safety aspects of CCGT and CCGE systems burning high-hydrogen gas mixtures.

Also within scope were the following specific objectives:-

- Articulating the relationships between mixture composition, pressure, velocity, exhaust gas temperature, ignition, deflagration and deflagration to detonation (DDT) potential.
- Examining data referring to the flammability limits and explosivity of high hydrogen gas mixtures.
- Commenting upon interactions between combustion modes and confinement, such as duct geometry, the influence of obstructions on flame propagation, blockages, catalytic beds and HRSG configurations, with reference to turbulence generation and the resultant flame acceleration.
- Commenting upon scaling criteria applicable to DDTs in exhaust ducts and steam generators.
- Identifying any knowledge gaps key to defining the follow on experimental work programme.

- Reviewing current warning and control technology, together with information relating to rapid composition analysis, flame detection and temperature measuring techniques.
- Reviewing the compositions of the fuel systems of interest as defined in the (RfP., 2010), **and** obtaining fuel composition data from the European Turbine Network (ETN) and the H₂-IGCC European Project.
- Selecting three representative fuel systems including 100% hydrogen.
- Examining safety concerns arising from the presence of high hydrogen fuels in the ductwork of HRSGs as a consequence of operating CCGT/CCGE/CHP direct coupled power generating systems, including those with duct burners, on high hydrogen fuels.
- Reviewing Standards, Codes of Practice and Regulatory Regimes in respect of their applicability to high hydrogen fuelled systems, including assessing current safety systems, and identifying shortfalls and gaps in the current knowledge base.
- Identifying hazards, safety management and safety systems' requirements for high hydrogen content gases in ductwork and HRSGs, including the evaluation of gas turbine and gas engine control systems in so far as they are applicable to high hydrogen fuels.
- Assessing the various exhaust duct configurations currently in use, including their potential impact on the flow and ignition of high hydrogen fuels passing through them.
- Including Information contributed directly by ETI members.

1.2.1 Range of power plants of interest

In respect of this review the gas turbines of interest to the ETI and the project sponsors are those with power outputs ranging from 5 MW up to the largest units of some 250-350 MW. The range of gas engines of interest is from 0.25 MW up to 10 MW.

The basic principles of gas turbines and power generation are given in Appendix A1.

1.3 SEARCH CRITERIA

The search criteria used and the databases examined are listed in this section.

Because of the broad and/or diverse background and interest of the parties involved in the issues, investigation and outcome of the work, some elementary concepts of combustion as well as of common modes of energy and power generation will be summarised and covered as a base-line understanding for this review.

Review of combustion processes within energy and power generating systems and under conditions related to this application was in the first instance based on the reference list provided through the ETI to the consortium, to which were added specific publications and books of perceived interest. A total of 57 references are listed in the bibliography, not all of which are referred to in this review. The main contributing journals were (number of references sourced from each in parentheses):

- Combustion and Flame (6)
- Combustion Science and Technology (4)
- Proceedings of the Combustion Institute (5)
- Journal of Loss Prevention in the Process Industries (4)

- Nuclear Engineering and Design (3)
- International Journal of Hydrogen Energy Engineering (4) and Design

The journal information was extensively abstracted and keyword summaries made.

A separate web search was undertaken focusing on the following search criteria: CHP, CCGT, CCGE, IGCC and HRSG installations combined with standards, high hydrogen and hydrogen fuels, syngas, ducting, gas turbines/engines, safety, ignition, deflagration, DDT and detonation. A search on the suppliers' websites including the engine manufacturers was also made. The relevant articles were either referenced in the main body of the text or added to the list presented in the bibliography attached to this report.

The HSE/HSL Information Centre also carried out a search on our behalf, using the same search criteria given in the previous paragraph, into the design and operation of CCGTs/CCGEs and looking at the key issue of ignition in the ductwork between the turbine and heat exchanger. A total of 110 references were identified as follows:-

- Sixteen references from Healsafe, Mech eng, NTIS and Ei Compendex.
- Sixty-four free format references from NTIS, Chemical Abstracts, Chemical Engineering and Biotechnology Abstracts, Wilson Applied Science and Technology Abstracts and Ei Compendex.
- Twelve references from Oshrom, for HSE's internal reports and references from the Institute of Mechanical Engineers library catalogue.
- Eighteen references from Web of Science.

The CHPA website and the Penwell conference proceedings website were also examined but did not provide anything useful.

The sources of references searched also included the substantial ASME electronic database. A search of the ASME digital library returned a possible 284 hits from the total of 140,623 documents against search terms including gas turbines and hydrogen, and only a further 9 hits against gas engines and hydrogen.

The digital library only contained conference papers from 2002 onwards. The ASME TURBO EXPO series of gas turbine related conferences have run since 1956. The index of papers from 1956 to 2010, and the separate conference list for 2011 include over 18,000 papers. A search of these against similar terms returned a further 94 hits.

The titles and abstracts of these 378 papers showed that they deal almost entirely with engine performance and emission levels. Only two were identified as being of potential relevance to this work.

A list of references was also provided in confidence from Solar (Etheridge, 2011), which have been utilised as part of the review.

A full list of the references found and read is attached in the bibliography section as an Appendix which includes the relevant standards.

1.4 ABBREVIATIONS, ACRONYMS AND TERMINOLOGY

ADT	Auto-ignition Delay Time
API	American Petroleum Institute
ATEX	Atmospheres Explosives
BS	British Standards
CCGE	Combined Cycle Gas Engine
CCGT	Combined Cycle Gas Turbine
CCS	Carbon Capture and Storage
CEN	Comite Europeen de Normalisation
CENELEC	European Committee for Electrotechnical Standardisation
CHP	Combined Heat and Power
COIN	Corporate Operational Information
COS	Carbonyl sulphide
DDT	Deflagration to Detonation Transition
DLE	Dry low emissions
DLN	Dry Low NO _x Combustor
DSEAR	Dangerous Substances and Explosive Atmospheres Regulations
EN	European Standards
ETI	Energy Technology Institute
ETN	European Turbine Network
GE	Gas Engine or General Electric
GT	Gas Turbine
HCV	Higher Calorific Value
HE	High Explosive
HRSG	Heat Recovery Steam Generator
HSE	Health and Safety Executive
HSL	Health and Safety Laboratory
IC	Imperial College
IEC	International Electrotechnical Commission
IFGC	Integrated fuel gas characterisation
IGCC	Integrated Gasification Combined Cycle
ISO	International Organisation for Standards
LCV	Lower Calorific Value
MOU	Memorandum of Understanding
PDTR	Proposed Draft Technical Report
RfP	Request for Proposals
RIDDOR	Reporting of Incidents and Dangerous Occurrences
RP	Recommended Practice
SCR	Selective Catalytic Reduction
SILs	Safety Integrity Levels
STIG	Steam Injection Technology
TIT	Turbine inlet temperature
UHC	Unburnt Hydrocarbons

2 TYPES OF POWER PLANT CONSIDERED

This section provides a brief introductory description of the CCGT/CCGE/CHP/HRSG systems of interest in the context of this review.

2.1 INTRODUCTION

Global energy demand is expected to increase by nearly 35% by 2030, mainly as a result of rapid economic growth and improvements in living standards in developing countries (Bloomberg, 2011). With increasing pressure to curb the phenomenon of global warming and prolong the availability of conventional oil and gas, it is vital to use the remaining sources of fossil fuels more efficiently. Power generation based on gas turbines and gas engines provides a significant portion of global energy demand and as such, it is important to design and operate power plants that do not just provide high efficiency in generating electricity, but also rely increasingly on cleaner gas (such as synthesis gas) and alternative fuels, as opposed to coal.

2.2 COMBINED CYCLE GAS TURBINES

According to Starr (Starr, 2010), the Combined Cycle Gas Turbine (CCGT) is currently one of the most efficient methods for converting the energy in gaseous fuels into electrical energy, achieving efficiencies that have levelled out at just over 60%. The CCGT consists of a gas turbine which produces about two thirds of the power. The waste heat in the exhaust system from the gas turbine is then used to raise steam, which powers a steam turbine producing the remaining third of the power (see also Appendix A1). The steam is raised via a heat recovery steam generator (HRSG), which is situated in the exhaust stream of the primary turbine, and is connected to it by ducting that also serves to expand the flow in order to obtain appropriate velocities for optimum heat transfer. The exhaust gas temperatures are for various thermodynamic reasons relatively low being in the region of 300-600⁰C. This has resulted in large HRSGs often with two or more evaporators operating at different pressures, typically 60-90 bar and 5-10 bar. The larger plants may include up to twelve stages.

The exhaust gas temperature limitations are well recognised. To compensate for this, many industrial scale CCGTs utilise a supplementary duct burner, situated in the gas turbine exhaust. This utilises the residual oxygen in the gas turbine exhaust to raise extra process steam. A fan may be used to supply additional air, which may also enable the burner to be used in the auxiliary mode, whereby it can operate independently to provide heat when the gas turbine is not operating.

Furthermore, because the steam section of the plant provides only about one third of the power, and because the stack losses in CCGTs are high, the amount of useful heat that can be obtained from a CCGT is limited. If the steam turbine units were shut down completely the electrical efficiency would fall to around 37% (Starr, 2010).

Gas turbines intended for CCGT plant usually run at significantly lower pressure ratios than those used in the aerospace sector (Starr, 2003). This has several advantages, which more than compensate for the lower efficiency that results. A lower pressure ratio simplifies the design of the compressor, which is particularly critical since an industrial machine needs to rotate at constant rpm, no matter what the power output.

The specific power from the gas turbine is also higher if the machine is working at optimum efficiency. Pressure ratios are typically in the range of 40:1 to 15:1, based on thermodynamic considerations, as increasing the pressure ratio holds down the turbine outlet temperature with increasing inlet temperature. Thus a low-pressure ratio will result in a relatively higher inlet temperature in to the HRSG to the benefit of the rate of heat transfer (Starr, 2003). HRSG efficiency is also improved by any reductions that can be made in the levels of excess air going into the turbine. These levels are lower than those found in aerospace applications; nevertheless the excess air is typically about three to four times that needed for complete combustion. This mass of excess air, when it leaves the HRSG carries with it a sizeable amount of heat energy, even though typical stack temperatures are of the order of 100-200°C.

Modern gas turbines running on natural gas have turbine inlet temperatures (TIT) of around 1300 °C (with some even above 1400 °C). At the same time, the maximum tolerable metal temperatures of the stator and rotor blades are around 870 °C and 815 °C, respectively (Armstrong, 2004). To avoid the metal temperatures increasing beyond these limits, a combination of air-cooling and blade thermal barriers are used.

The consequential increased mass flow through the turbine also causes enhanced heat transfer. Therefore GE recommends decreasing the turbine inlet temperature by a certain amount if it is desirable to maintain 100 % of the design lifetime (Moliere, 2004). The higher the volume percentage of water vapour, the more the TIT needs to be reduced. Unfortunately, reducing the TIT also has negative impacts on total plant efficiency due to the reduced exhaust gas temperatures. Therefore, economic assessments are needed to draw definitive conclusions.

2.3 COMBINED CYCLE GAS ENGINES

Typical of the gas engines used for Combined Cycle Gas Engine (CCGE) type systems are those of GE Energy (Jenbacher, Waukesha), Caterpillar, Rolls-Royce and others (Jenbacher, 2011). These types of engines are designed from the outset to run on gas (not diesel engine conversions), natural gas, biogas or special gases, and are around 0.25-10 MW in output when used as stationary continuous operation units. Gas engines of this type can be up to 44% efficient, with very low exhaust emissions. They are very durable and highly reliable in all types of applications, particularly when used for CHP applications. They are able to constantly generate the rated output even with variable gas conditions.

Gas engines can usually operate on gases with extremely low calorific value, low methane number and hence a low degree of knock, but also gases with a very high calorific value. Typical gas sources vary from low calorific gas produced in chemical industries, wood gas, pyrolysis gas produced from decomposition of substances by heat (gasification), landfill gas, sewage gas, natural gas, propane and butane which have a very high calorific value. Coke gas is also used as a fuel for gas engines; it is a by-product of coke production from hard coal. Coke gas consists mainly of hydrogen (50 to 60%), methane (15 to 30%) and carbon monoxide, but due to the extremely high hydrogen content of coke gas, specially modified engines are used to generate power from this fuel source. Gas engines are often downrated to utilise higher hydrogen content fuels because of knocking (detonation) in cylinders. The limits on fuel composition are based on autoignition since ignition must occur when sparked and not prior to it. The speed of subsequent flame propagation is also of importance since it determines the rate of heat release following ignition. If this is too high, ignition timing is

compromised, since with increasing flame speed the maximum cylinder pressure is reached sooner. To cope with this the ignition timing would have to be retarded to ensure that the maximum pressure is still achieved at the optimum piston position.

In common with gas turbine plant, although less common, a supplementary duct burner, situated in the gas engine exhaust, may be used to raise extra process steam, utilising the residual oxygen in the engine exhaust as its source of oxygen. A fan may be used to supply additional air, which may enable the burner to be used in the auxiliary mode, whereby it can operate independently to provide heat when the gas engine is not operating.

2.4 COMBINED HEAT AND POWER SYSTEMS

Combined heat and power (CHP), sometimes termed Cogeneration or Total Energy, is the generic term defined as the on-site generation of productive heat and power as a single process. A prime mover, normally a gas turbine or reciprocating gas engine, is coupled to an electricity generator, whilst the heat in the exhaust gas is extracted and used as a heat source. Heat from the reciprocating engine cooling system is also used as a source of low-grade heat, increasing overall thermal efficiency. CHP has been successfully implemented in sectors such as paper manufacture, large hospitals, airports and communal heating, ideally where there is a steady demand for heat and power. The heat may be employed in several ways, including steam or hot water generation using boilers, direct process heating such as drying, or absorption refrigeration. Rankine Cycle systems may be used to extract heat and to drive a turbine and generate more electrical power, increasing overall efficiency.

Shell-type boilers are typically used for low to medium pressure steam, and medium to high temperature hot water and thermal oil. A water-tube boiler is normally used for high-pressure steam, especially if this is superheated to supply a steam turbine in combined cycle configuration. Absorption refrigeration normally uses an arrangement whereby hot water, generated in such boilers, is used as the heat source.

In the context of this investigation, the design of the heat recovery plant of CHP systems may be significant with respect to the potential ignition and subsequent behaviour of high hydrogen fuel/air mixtures in the event of a turbine failure scenario. In water tube boilers, exhaust gases pass over the outside of (normally) finned tubes, while in shell-type boilers these pass through the boiler tubes. The latter presents a completely different configuration with respect to turbulence generation and potential explosion effects. Equally, the direct use of exhaust gases for drying of products that are insensitive to combustion gases, may also present a different situation. These differences will as far as possible be taken into account in the interpretation of the results of the trials to be undertaken in this project.

2.5 HEAT RECOVERY STEAM GENERATORS

According to Starr (Starr, 2003), in Heat Recovery Steam Generators (HRSG), heat exchangers, super heaters and where they are fitted, duct burners are located in large rectangular ducts immediately downstream of the primary power unit exhaust. In order to reduce the velocity of the gas turbine exhaust, the duct opens out in a V-shaped manner, in both the horizontal and vertical directions after the gas turbine; otherwise the pressure drops through the HRSG would be excessive. Swirl vanes are usually

located after the turbine, as the flue gas will otherwise tend to corkscrew up the duct with some force, particularly when the gas turbine is working off design.

The HRSG section of the ductwork, according to (Starr, 2003), is often laid out parallel to the ground, making the HRSG a horizontal type model. This type of duct arrangement leads into a stack, which may be equipped with silencers and selective catalytic reduction systems (SCRs). The alternative vertical layout of HRSGs incorporates the boilers and superheaters within the stack's structure. In a typical horizontal HRSG, the heat transfer tubing is transposed in vertical harp type arrays across the duct. In the vertical form of HRSG the tubing can be in the form of loops, which cross the duct horizontally. Where harps are used these too will cross the duct in a horizontal fashion.

The ducting for HRSGs is extensive due to the huge amounts of air and combustion products going through the gas turbine or gas engine, which can be of the order of 600 kg/s for the largest units. Thermal expansion and the structural integrity of the ductwork are significant design issues because of the sheer size and weight of the units. Ductwork is currently designed to withstand the pressure loads imposed by the gas turbine exhaust stream and the pressure drop through the HRSG and stack. The pressure drop in the HRSG clearly depends upon the velocity and the porosity of the tubing but may typically approach 50-75 mbar, whilst gas turbine exit pressures are typically near atmospheric pressure.

A bypass stack with twin diverter valves may be installed between the engine exhaust outlet and the HRSG in order to firstly, enable the engine to continue to operate and produce electrical power whilst the HRSG is under maintenance or not being used, and secondly, at start-up to enable the engine to be brought up to full speed at the full rate of power increments. In general the HRSG cannot tolerate the same rate of rise of temperature that this implies. A bypass arrangement therefore allows the exhaust flow to be diverted to the HRSG progressively at a low rate thus avoiding extreme thermal shock occurring within the heat exchanger pipe work. Duct velocities and the geometry when a bypass stack is in use may be significantly different to those during normal operation, and consequently great care needs to be taken in our experiments to avoid flammable accumulations and potential incidents. This will be further considered when planning the later parts of our test programme.

2.6 SELECTIVE CATALYTIC REDUCTION

An important issue arising from running CCGT/CCGE systems on high hydrogen fuels is the production of high NO_x emissions. One post-combustion NO_x control method is selective catalytic reduction (SCR). Ammonia is injected into the flue gas and reacts with NO_x in the presence of a catalyst to produce N₂ and H₂O. The SCR system is located in the exhaust path, typically within the HRSG where the temperature of the exhaust gas matches the operating temperature of the catalyst. The operating temperature of conventional SCR systems ranges from 250 to 450°C.

The primary reactions occurring in SCR require oxygen, so that catalyst performance is best at oxygen levels above 2-3%. Several different catalysts are available for use at different exhaust gas temperatures. The longest and most commonly used are base metal catalysts, which typically contain titanium and vanadium oxides, and which may also contain molybdenum, tungsten and other elements. Base metal catalysts are useful between 230°C and 430°C. For high temperature operation (350°C to 650°C),

zeolite catalysts may be used. In clean, low temperature (180-300°C) applications, catalysts containing precious metals such as platinum and palladium are useful. These compositions refer to the catalytically active phase only; additional ingredients may be present to give thermal and structural stability, to increase surface area, or for other purposes.

The mechanical operation of an SCR system consists of a reactor chamber with a catalyst bed, composed of catalyst modules, and an ammonia handling and injection system, with the ammonia injected into the flue gas upstream of the catalyst. In some cases a fluidised bed of proprietary catalyst pellets is used. There are no moving parts, other than spent catalyst, as the SCR process produces no waste products. The catalyst module often consists of a honeycomb or rectangular type structure through which the exhaust gases can pass. The honeycombs may vary in size from 10 mm down to 2 mm depending on the exhaust gas composition. The length of the bed also varies depending on the flow rates and the pressure drop that can be tolerated as the flow passes through the bed. Multiple beds may also be used.

Low temperature SCRs have been developed as they are ideal for retrofit applications where they can be located downstream of the HRSG, thus avoiding the potentially expensive retrofit of the HRSG to locate the catalyst within a hotter zone of the HRSG.

High temperature SCR installations, operating at up to 650°C, have also been developed. The high operating temperature permits the placement of the catalyst directly downstream of the turbine exhaust flange. High temperature SCR is also used on peaking capacity and base-loaded simple-cycle gas turbines where there is no HRSG.

2.7 CATALYTIC OXYDATION

Occasionally, gas engine systems may use an oxidation catalyst to convert CO to CO₂ using the excess oxygen present in the exhaust, thereby releasing heat into the exhaust stream and reducing CO emissions. These systems may operate at up to 800°C (Schneider, 2006). The structure of the system is similar to a crimped ribbon flame arrestor, coated with the catalyst. Although it is not common some gas turbine installations also have oxidation catalysts for CO control during low load operation.

2.8 INTEGRATED GASIFICATION COMBINED CYCLE

Integrated gasification combined cycle (IGCC) power plants (Maurstad, 2005) are believed to be a type of power plant that may be used for electricity generation in the future by replacing the aging coal power plants and increasingly expensive natural gas power plants. The process offers options to eliminate greenhouse gases, to produce hydrogen and/or to produce liquid fuels. The process used by IGCC plants is that of gasifying coal to produce a synthetic gas (syngas). The pollutants are removed from the syngas, and then electricity is generated using a combined cycle gas turbine and an HRSG to create steam, which is used to power a steam turbine-generator.

In the medium and possibly longer-term, gas fuelled CCGT systems are likely to be the major non-renewable power source, with increasing fuel flexibility and (possible) hydrogen addition becoming increasingly likely.

The potential for carbon dioxide sequestration makes IGCC technology even more appealing and environmentally responsible, and if desired, hydrogen can be separated

from the syngas stream. The following as stated by Maurstad (2005), are the main characteristics of an IGCC plant: -

- SO_x , NO_x and particulate emissions are much lower in IGCC plants than from a modern coal plant.
- IGCC plants emit approximately 20% less CO_2 than a modern coal plant.
- IGCC plants use 20-40% less water than a modern coal plant.
- IGCC plants operate at higher efficiencies than conventional coal fired power plants thus requiring less fuel and reducing emissions. Current efficiency is up to 60% when using a high efficiency turbine and other process improvements.
- Costs for electricity, without CO_2 capture, is about 20% higher than in a modern coal plant, but electricity costs are 40% lower than from a natural gas IGCC plant.
- CO_2 can be captured from an IGCC plant much more easily than from a conventional coal plant at an additional cost increase of 25-30% for capture and sequestration, without transportation charges.
- IGCC offers the possibility to capture the hydrogen that is part of the syngas stream in an economic manner.

The syngas combustion process, using low H_2 content and a significant amount of CO , has been known for many years and is used extensively in conventional IGCC applications with E- and F-class turbines.

High H_2 operating experience indicates that in some process gas applications, the concentration of H_2 could be 60%–70% and even reach 90%. For example, Jones (2006) reports that an MS6000B gas turbine is burning refinery gas with a 70% H_2 concentration at the San Roque site in Cadiz, Spain, and that at the Daesan, Korea site, the H_2 percentage can be as high as 95% for this model. The F-class operational experience indicates combustion with lower levels of H_2 concentration, about 44%. These high hydrogen operations are discussed further in Section 6.1.

The H_2 -IGCC project (H2-IGCC, 2011), co-funded by the European Commission's Directorate-General for Energy, has relevance to this review, as its overall objective is to provide and demonstrate technical solutions that will allow the use of state-of-the-art highly efficient, reliable gas turbines (GTs) in the next generation of IGCC plants. The goal is to enable combustion of undiluted hydrogen-rich syngas with low NO_x emissions and also allow high fuel flexibility.

2.9 CARBON CAPTURE AND STORAGE

According to the Dept. of Energy & Climate Change (2011), Carbon Capture and Storage (CCS) technology captures carbon dioxide from fossil fuel power stations. The CO_2 is then transported via pipelines and stored safely, offshore in deep underground structures such as depleted oil and gas reservoirs and deep saline aquifers. Up to 90% of CO_2 from a fossil fuel power station can be captured using CCS technology. CCS can also be transferred and applied to industrial processes to significantly reduce CO_2 emissions.

There are three different capture technologies that can be fitted to fossil fuel power stations: post-combustion, pre-combustion and oxyfuel. Only post-combustion and pre-combustion can be applied to industrial processes.

Post-combustion capture of CO₂ occurs after the burning of fossil fuels. CO₂ is separated from the flue gas (a by-product of burning fossil fuels) through a process called scrubbing. Flue gas is passed through a liquid which causes a chemical reaction and separates the CO₂ ready for transportation and storage. Post-combustion capture technology can be retrofitted to existing fossil fuel power stations.

Pre-combustion capture is where CO₂ is separated or removed prior to the burning of fossil fuels. The pre-combustion technology converts fossil fuels into a gas made up of CO₂ and hydrogen (H₂). These gases are then separated through scrubbing, just like in the post-combustion capture process. H₂ fuels the power plant and the CO₂ is captured, ready for transportation and storage. Only new fossil fuel power plants can be equipped with pre-combustion technology.

Oxyfuel technology burns fossil fuels with nearly pure oxygen. The flue gas produced only contains CO₂ and steam, which are then separated by a cooling process; the water condenses and leaves a flue gas of almost pure CO₂. Oxyfuel technology can be applied safely to new and existing fossil fuel power stations. The technology is still in the development phase and the assignment of appropriate safety provisions will need to be considered for some time yet.

Once pure CO₂ is captured through these technologies, it is compressed into a liquid state (similar density to crude oil) at 70 atmospheres, and is transported via pipeline to offshore storage sites.

A leading process of pre-combustion capture is a system called IGCC (Integrated Gasification Combined Cycle) whereby electricity is generated through gas turbines, as well as steam-powered ones. A benefit of this emerging technology is that less energy is used to remove the CO₂ which improves the power plants' overall efficiency.

According to Zachary (2008), the main impact on IGCC plant with carbon capture and storage (CCS) is the potential for greater use of H₂-rich fuel in the gas turbine. At 90% carbon capture, the expected hydrogen concentrations in the fuel may vary from 30% to 78%. Hydrogen is a fuel with a lower heating value of 120.8 MJ/kg, compared with natural gas, which has a lower heating value of 48.7 MJ/kg. The hydrogen flame temperature is hotter (more NO_x) and flame propagation is faster, thus requiring modified combustor cooling schemes.

2.10 EMISSIONS USING HIGH HYDROGEN FUELS

In diffusion combustion systems using hydrogen, nitrogen is added to the hydrogen up stream of the burners to meet the NO_x emission limit (15 ppm). As the firing temperature of a gas turbine operating on hydrogen and nitrogen is lower than that of a turbine operating on conventional IGCC syngas, the additional mass of the inert nitrogen expanding in the turbine section helps compensate for the power loss associated with the lower firing temperature.

Despite the number of dilution additives, namely steam and nitrogen, current high hydrogen fuel technology combustors may still have high levels of NO_x emissions. In diffusion mode, combustion of hydrogen-rich fuel is often therefore limited to 50% hydrogen (Rosenbauer, 2007) to meet emissions targets and control flame stability (See also section 6.2).

In Europe, many initiatives and research activities, such as the Enhanced Capture of CO₂ (ENCAP) program, aim to develop premix burners capable of burning high percentages of hydrogen. The development of the burners is only the first step of the integration process. The impact on the combustion system, either annular or can, must also be evaluated (Zachary, 2008).

Gas engines do not use the addition of nitrogen as a NO_x emission control strategy. They use SCR and /or a lean fuel/air ratio. Schneider (2006) shows the influence of the air/fuel ratio (λ) and the optimum lean burn range for λ of 1.7 to 1.9 for minimum overall emissions.

3 FUEL TYPES AND SOURCES

This section examines the key fuels of interest to this review and their sources.

3.1 INTRODUCTION

The common gas turbines currently in use require clean fuels to avoid corrosion and erosion of critical turbine components and to generate 'clean' exhaust streams. Although there have been efforts to develop gas turbines capable of burning residual oil, higher efficiencies can be achieved by burning clean fuels at higher temperatures. Gas turbine powered CCGTs are currently operated in the main on natural gas, but for economic reasons coupled with the drive for low carbon emissions, alternative fuels are increasingly being considered and used. The fuels of interest in the context of this review are those containing increasingly higher percentages of hydrogen, up to and including 100% hydrogen.

The fuel sources of interest are therefore low carbon fuels such as coal gasification with carbon capture, bio-syngas (thermal gasification of biomass), hydrogen and low cost fuels such as refinery gas, coke oven gas and producer gas. Gas engine special fuels follow along similar lines.

Representative fuel systems are considered, based on future potential fuel sources, which can also be tested generically in the laboratory such that their properties can be readily assessed predominantly in respect of their sub-sonic flame kernel development, DDT potential, and the needs of the project.

3.2 HYDROGEN

At normal atmospheric temperature and pressure, hydrogen is a colourless, odourless, tasteless gas that is only slightly soluble in water; it is the least dense gas known (CUP, 2007). It is the first element in Group 1 of the Periodic Table. Ordinary hydrogen gas is made up of diatomic molecules (H_2) that react/combust with oxygen to form water (H_2O). A jet of hydrogen burns in air with a very hot blue flame. Hydrogen gas must be used with caution because it is highly flammable; it forms easily ignited explosive mixtures with oxygen or air.

Hydrogen has a great affinity for oxygen. With the halogens, it forms hydrogen halides that are strongly acidic in water solution. With sulphur it forms hydrogen sulphide (H_2S), a colourless gas with an odour like rotten eggs; with sulphur and oxygen it forms sulphuric acid. It combines with several metals to form metal hydrides such as calcium hydride. Combined with carbon (and usually other elements) it is a constituent of a great many organic compounds, such as hydrocarbons, carbohydrates, fats, oils, proteins, and organic acids and bases.

Hydrogen possesses high buoyancy and greater diffusivity than other gases. Under ambient conditions, hydrogen has a density of 0.0838 kg/m^3 and a specific gravity of 0.0696 (air = 1). Therefore, hydrogen is approximately 14 times less dense than air, making it the lightest of all gases. The small size of the hydrogen molecule gives it diffusivity greater than that of helium and approximately three times that of nitrogen in air at ambient conditions. Gaseous hydrogen also readily diffuses into solids.

In the case of gaseous hydrogen leaks, its high buoyancy affects gas motion considerably more than its high diffusivity. However, the effects of wind can dominate over diffusion and buoyancy. The buoyancy of hydrogen when it is allowed to rise will create convection currents. As a consequence of these properties, hydrogen gas readily disperses, diffuses and forms ignitable mixtures with air. In an unconfined atmosphere, these mixtures quickly dilute to a level below the lower flammability limit.

The safety relevant parameters of hydrogen are frequently discussed in terms of properties such as flammability limits or ignition energies. Mixtures of hydrogen and air can combust either as a fire, a deflagration or a detonation. Flammability limits, detonability limits, ignition energy and auto-ignition temperature are primary variables used to characterise the circumstances under which combustion may occur. A key to preventing fire, deflagration or detonation is to eliminate ignition sources, as the energy required to ignite a hydrogen/oxidiser mixture is very small. Consequently, many electrical, thermal and mechanical sources of ignition are possible.

The phenomenon of spontaneous ignition of hydrogen during sudden release from a high-pressure system has been postulated because of its negative Joule Thompson co-efficient. However that effect is relatively small and it has been concluded that compression ignition, Joule-Thompson expansion, diffusion ignition and hot surface ignition are unlikely ignition mechanisms for most accidental releases of hydrogen at ambient temperature (Astbury, 2007). Recent work has shown that spontaneous ignition can occur from sudden releases of compressed hydrogen to atmosphere (Astbury, 2007). The work identified certain downstream geometries that have been found to cause spontaneous ignitions.

Some metallic materials used in vessels or other components can undergo a significant loss of their structural strength when exposed to hydrogen. This phenomenon is known as hydrogen embrittlement, and occurs when hydrogen or hydrogen compounds permeate into the lattice structure of the material. At the atomic level, for embrittlement to occur, hydrogen molecules must first dissociate into atoms before they can diffuse into the metallic structure. At temperatures close to ambient, a number of metallic materials are susceptible to hydrogen embrittlement, particularly those with a body-centred cubic crystal lattice structure. This is a particular problem with many ferritic steels if they are subjected to mechanical stresses. The process takes place on freshly generated metallic surfaces that are likely to form on surface defects or other stress concentrations and as a result of stress-induced local plastic deformation processes. Impurities such as hydrogen sulfide dissociate into atomic hydrogen even more easily than molecular hydrogen.

The basic physical and chemical properties of hydrogen are given in Appendix A2 (from NASA-1740, 1997).

3.2.1 Running gas turbines/engines on hydrogen

Currently there is only a limited number of CCGTs running on high hydrogen only fuel and air (Maurstad, 2005). We only came across one verbal reference to turbines having been run on 100% H₂. GE is one of a small number of GT suppliers who offer engines capable of running on fuels with high hydrogen content. Their fuel specifications demand that the maximum hydrogen content is 65%-95% for their E-class GTs, and that the volumetric energy density of the fuel is no less than 7.5 kJ/L. The implication of this is that an amount of CO needs to be left in the fuel, thus limiting the maximum possible degree of CO₂ capture to around 85 % for current designs.

Experiments performed by GE show that NO_x emissions could be kept lower than 10 ppmvd (at 15 % O₂) by diluting hydrogen with nitrogen and steam. A consequence of using a hydrogen rich mixture (hydrogen and nitrogen) as a gas turbine fuel is that the moisture content in the exhaust may be higher. The addition of water/steam for further reductions in NO_x emissions also contributes to higher moisture content. Because of water's physical properties, heat transfer is thereby increased in the turbine both by radiation and convection, which in turn increases the metal temperatures and thus shortens the lifetime of the turbine materials (Maurstad, 2005).

3.3 SYNGAS

Synthesis gas or syngas (NETL, 2010) is a gas mixture comprised of carbon monoxide, carbon dioxide and hydrogen. It is produced by the gasification of a carbon containing fuel to a gaseous product that has some heating value. Some of the examples of syngas sources are: gasification of coal, waste to energy gasification, and steam reforming of natural gas to generate hydrogen. Syngas has up to 50% of the energy density of natural gas.

The production of syngas as a fuel is accomplished by the gasification of coal or municipal waste (Figure 1). Gasification is a clean way to produce electricity, as by first converting the solid feedstock to a gaseous form (syngas), potential pollutants can be captured and reduced to essentially any desired level and then converted to useful by-products or safely disposed of. Gasification is a vital process as it raises the value of low value feedstocks by transforming them to marketable products and fuels. The syngas so produced may contain some trace elements of impurities that need to be removed. They are recovered or redirected to the gasifier; for example, sulphur is recovered in the elemental form or as sulphuric acid and both of these can be marketed.

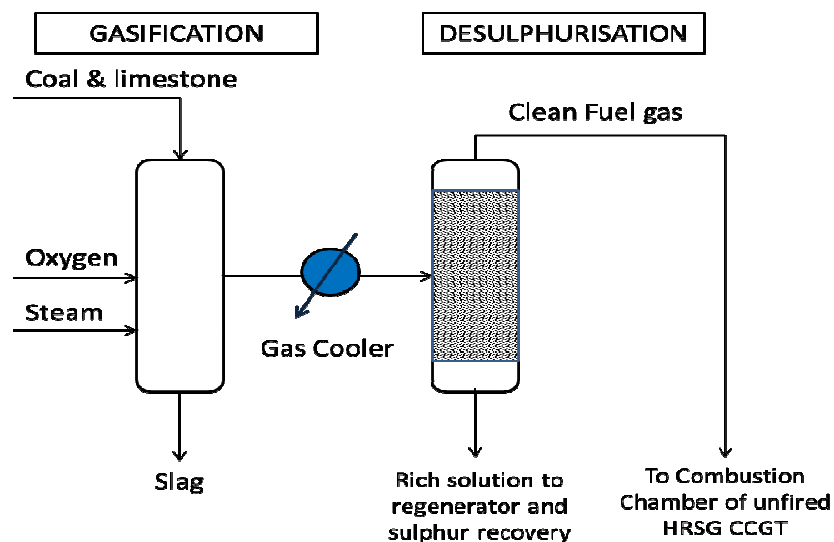


Figure. 1: Production of Synthesis Gas by Coal Gasification

The clean syngas consists mainly of carbon monoxide and hydrogen. Steam is added and the syngas is sent through water-gas shift (WGS) reactors to convert the carbon

monoxide to carbon dioxide and additional hydrogen. After a gas separation process, the hydrogen-rich syngas can be fired in a gas-turbine/steam-turbine generator set to produce electricity. The captured carbon dioxide can be sent for storage or it can be converted to useful products. In addition to efficiently producing electric power, a wide range of highly valued transportation fuels and chemicals can be co-produced from the cleaned syngas, thereby providing the flexibility needed to capitalise on the changing economic market. As a result, gasification provides a flexible technology option for using domestically available resources whilst meeting future environmental emission standards. A further advantage of gasification is that using syngas is potentially more efficient than direct combustion of the original fuel because it can be combusted at higher temperatures or even used in fuel cells.

Syngas is also an intermediate when creating synthetic petroleum for use as a lubricant or fuel, and in the industrial synthesis of hydrogen and ammonia. During the latter process, methane (from natural gas) combines with water to generate carbon monoxide and hydrogen. Another use is as a basic chemical building block for many processes in the petrochemical and refining industries.

Syngas may be burned directly in gas turbines and gas engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic fuel. Gasification can also begin with material such as biodegradable waste which would otherwise have been discarded. In addition, the high-temperature process refines out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels.

3.3.1 Running gas turbines/engines on syngas

Gas turbines need only minor modifications to use syngas as a fuel (Maurstad, 2005), and are available from manufacturers such as GE, Siemens, Rolls-Royce, Alstom and Solar. There are consequences of using syngas as a fuel. It can influence the performance of the gas turbine because of its relatively low heating value; consequently more mass flow of fuel is needed to achieve a certain limiting turbine inlet temperature. In addition nitrogen and syngas saturation contribute to higher mass flow through the turbine and more power output, and when compared with natural gas, there may be a higher fraction of water vapour in the gas turbine exhaust (depending on syngas composition). This again increases the heat transfer and hence puts more strain on materials, and requires a decrease in the turbine inlet temperature to maintain design material life. This reduction means a lower efficiency for the power block (Maurstad, 2005).

Syngas, which typically has only 25 % of the volumetric heating value compared to natural gas, requires roughly a four fold higher flow rate to maintain the same turbine inlet temperature (which is desirable to maintain high efficiency from the power block). Potentially, the increased mass flow of fuel and therefore the higher mass flow rate through the turbine will lead to an increased power output from the turbine. If the fuel is diluted with nitrogen or water for the purpose of NO_x control, the potential for increased gas turbine power output is even higher. However, depending on the gas turbine technology and fuel under consideration, there may be several limitations for the full realisation of this increased power output potential, namely compressor surge, gas turbine torque, turbine inlet temperature and material lifetime (Maurstad, 2005).

3.4 PRODUCER GAS

Another route to the production of fuel gas is by gasification of biomass, which involves the incomplete combustion of biomass. Because of the large variety of sources it is not practical to define a characteristic gas product composition from gasification but the important useful combustible constituents almost invariably including carbon monoxide, hydrogen and traces of methane. The mixture, usually called producer gas, has traditionally been used for running internal combustion engines and also as a substitute for furnace oil in direct heat applications (Rajvanshi, 1986). Because virtually all biomass material can undergo gasification, it is a highly advantageous process to convert wastes such as forestry residues, wood chips, sewage sludge and some plant products to useful energy-rich products, instead of placing them in landfills or discharging to water bodies. This makes the conversion process both an efficient means of producing energy and an environmentally friendly option for the recycling of waste products (US DoE, 2011).

However, gasification of biomass also produces carbon dioxide, water and nitrogen, as well as end-of-process fuel impurities like tar, acids and solid particulates. The former can be carried forward into the gaseous fuel stream to the turbine, but the 'impurities' will generally have to be removed.

Producer gas can be used to power gas turbines, which is especially attractive if the carbon monoxide is further oxidised with steam in the water shift reaction to produce additional hydrogen and carbon dioxide.

3.5 REFINERY FUEL GAS

Waste gases from industrial processes can contain appreciable quantities of hydrogen and thereby offer significant opportunities for CHP generation. For instance, some chemical and refinery waste streams from hydro-cracking processes typically contain 80-95% hydrogen, making them very attractive as a main component in a high-hydrogen fuel. Similarly, hydrogen streams from ammonia manufacture are useful for increasing the hydrogen content of fuel gases used in gas turbines and enhancing electricity generation efficiency, especially in combined cycle power plants.

3.6 IMPURITIES

There are likely to be some impurities in the feedstock for the turbines and gas engines, especially where they have been derived from coal and biomass. However, these will generally have been removed thoroughly to provide a clean fuel gas. They will not affect the combustion process itself and therefore will not feature in our model systems, which will be based on major system components studies only.

However there may still be low-level concentrations of higher hydrocarbons, aromatics and tars in syngas fuels, which may influence the ignition propensity depending on their concentrations. These will also not be considered in the proposed modelling studies.

3.7 STEAM

3.7.1 Steam injection

According to Koivu (2007), utilities worldwide are faced with issues of high energy cost, high capital costs and tightening environmental legislation, and steam injection (STIG)

is a technique which can increase a plant's ability to generate extra power without burning extra fuel and which only requires moderate capital investment. Gas turbines have long been used by utilities for peaking capacity; however, with changes in the power industry, new environmental legislation and increased efficiency, the gas turbine is now being used for base load power generation, as well as to meet peak demand. Much of this growth can be accredited to large (>50 MW) combined cycle plants that exhibit low capital cost and high thermal efficiency. Manufacturers are offering new and larger capacity turbines with more advanced cycles that operate at higher efficiencies. In Europe however, due to increased use of wind power and the need for back up, peaking operations are likely to increase.

As previously explained (e.g. paragraph 2.10) steam injection is also of increasing importance as a means of controlling NO_x emissions from high hydrogen fuels, as means of reducing the combustion temperature of such fuels and of maintaining flame stability.

Steam Injected Gas Turbine (STIG) systems operate as an enhancement to the Brayton cycle. High quality steam is used to increase the power output and improve operating efficiency of the basic Brayton cycle. Steam is typically produced by an auxiliary steam boiler, external steam source or external process source and then injected into the combustion chamber of the gas turbine. The site at which this steam is injected differs according to the design of the particular gas turbine; however, in principle, high-pressure steam is injected into the high-pressure sections of the GT via the combustor fuel nozzles and compressor discharge plenum.

In its most basic form, steam injection works by increasing general mass flow through the GT's power turbine. The increased mass flow generates an increase in the rotational torque and power output. Normally, as mass flow through the power turbine increases so does the mass flow through the compressor stages. While this power increase is beneficial, it is offset by an increase in parasitic load due to the compression of increased air coming into the GT. The beauty of the STIG process lies in its ability to increase the mass flow in the power turbine without increasing the mass flow through the compressor stages. STIG uses high-pressure steam compressed to greater than 35 bar and heated to over 350°C and injects this steam after the compressor. Thus it bypasses the compressor stage, increasing the power generated in the turbine stages without increasing the resulting compression loads.

Steam Injection technology offers a clear improvement over the Brayton cycle whilst providing a fully flexible operating cycle. The amount of steam injected into the combustor can vary between 2% and 10%. The main benefits of STIG are an increase in power output and a decrease in NO_x emissions from the gas turbine particularly when used to control the combustion of high hydrogen fuels. The specific benefits are as follows:-

- 2.5 – 15% reduction in base fuel consumption.
- Reduces NO_x emission.
- Injects maximum steam when electric prices are high.
- Absorbs excess steam when process demand is low
- Flexible process (steam injection 50% - 100% load) output and a decrease in NO_x emissions from the gas turbine.
- 5 to 25 % more power from the base gas turbine.

3.7.2 Fire and blast mitigation using water mists

Although not directly relevant to the selection of the high hydrogen fuels investigated in this review, the use of water mists to mitigate the effects of either a fire or a blast are worthy of inclusion, as they provide a means of suppression that has relevance to the exhaust ducts and HRSGs of CCGT/CCGE systems. Thus in the event of a DDT or detonation occurring in the exhaust system, explosion relief may not prove viable particularly if a detonation occurs, and explosion suppression by water mist may be a viable alternative.

An illustration of the potential for blast suppression is given by Willauer (2009) in which a series of experimental measurements were made using water mists in confined spaces to suppress the blasts resulting from typical military explosives. The effect of water mist on the overpressures produced by the detonation of 22 kg equivalent of high explosives (HE) in a chamber was reported. The overpressures for each charge density were measured with and without mist pre-emptively sprayed into the space. The impulse, initial blast wave, and quasi-static overpressure measured in the blast mitigation experiments were reduced by as much as 40%, 36%, and 35% for 22 kg TNT, when water mist was sprayed 60 seconds prior to detonation at a concentration of 70 g/m³ and droplet Sauter Mean Diameter (SMD) of 54 μm. The results suggest that current water mist technology is a potentially promising concept for the mitigation of overpressure effects produced from the detonation of high explosives.

The mechanism by which mitigation was achieved was dependent on several parameters, including water mist density (the droplet size distribution and its concentration), the geometric complexity of the area being mitigated, and the chemical composition of the explosive.

The results also suggested that the effects are scaleable to larger charges. In addition the mist characterization studies indicated that the mist conditions reached steady state output within seconds of initiating the mist into the chamber. Therefore the pre-emptive application of water mist at concentrations and droplet sizes typically employed for fires' suppression could lead to significant suppression against HE explosives. Finally the results suggest that greater suppression may be achieved with higher mist concentrations in a confined space.

For partially confined explosions, conventional water spray deluge systems have been shown capable of providing beneficial effects against fast deflagrations (Thomas, 2000).

A comprehensive review of fire suppression by water mists is given by Liu & Kim (2000), in which they discuss progress on the research and application of the technology, and conclude that it has been substantial over the last decade (1990's). The paper reviews fundamental studies of water mists, recent water mist applications for the extinguishment of certain types of spray and pool fires in machinery spaces, gas turbine enclosures, combat vehicles, and flammable liquid storage rooms. Up-to-date development of corresponding test and design criteria for the installation of water mist fire protection systems and for the evaluation of the capabilities and limitations of water mist for fire suppression in some application areas, such as machinery spaces, and turbine enclosures, are also discussed.

The use of water mist, or spray, or CO₂, injected into the exhaust duct of a gas turbine or gas engine in the event of an emergency stop, or other scenario that may lead to the introduction of unburnt fuel into the exhaust system, is a potential explosion/detonation mitigation technique, as activation based on systems such as the Kidde-Graviner explosion suppression method may be adaptable for the purpose.

3.8 MIXTURE PROPERTIES

3.8.1 Stoichiometry

A review of the literature indicates that the typical compositions of three generic fuel systems currently used for CCGT/CCGE power generation are as shown in Table 1. Clearly such figures are only an average; the incidental values will depend upon the feedstock, process or gasification technique used. Minor impurities are not considered here. A number of actual syngas and other hydrogen rich fuels are presented and discussed in Sections 6.3 and 6.6. The fuels in Table 1 could form the basis from which a range of other fuels could be generated through the addition of hydrogen.

Table 1: Typical fuel compositions of dry gas (vol. %)

Component	Refinery Fuel Gas (Moliere,2004)	Syngas (Walton, 2007)	Producer Gas from Biomass (Mackalusco,2007)
N ₂	-	1	51
H ₂	20	24	15
CO	-	67	19
CO ₂	-	4	12
CH ₄	50	-	3
C ₂ H ₆	11	-	-
C ₃ H ₈	10	-	-
Others	1 (C ₂ H ₄) 2 (C ₃ H ₆) 3 (C ₄ H ₁₀)	1(H ₂ S) 3 (H ₂ O)	-

These fuel gases can significantly enhance the efficiency of power generation, especially if the hydrogen is also synthesised from renewable energy sources. Additionally, because hydrogen is a light, clean burning fuel (producing water when undergoing combustion), adding hydrogen makes the process more environmentally friendly.

Figure 2 outlines these three generic fuel gas options, alongside three possible hydrogen sources for combustion in the CCGT power generation process.

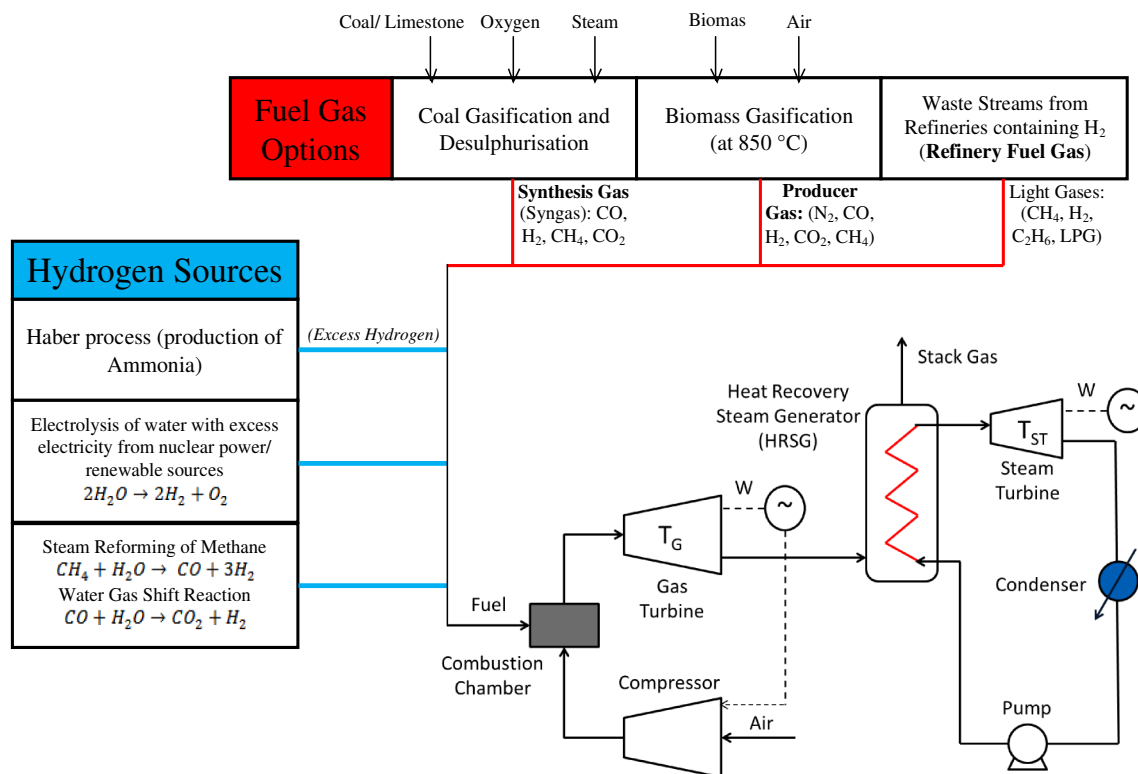


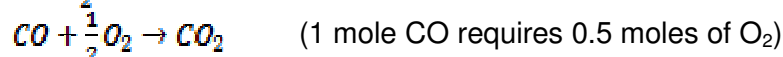
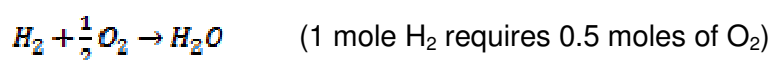
Figure 2: Fuel Gas Options and Hydrogen Sources for CCGT Power Generation

The following sample calculations are carried out using the original compositions of the fuel gases from Table 1, in order to determine the composition of hydrogen gas in the fuel-air mixtures prior to combustion. If, for the sake of argument, it is assumed that the flammability limits for hydrogen in a fuel gas mixture with less reactive constituents to be the same as for pure hydrogen, the results enable an estimate of the amount of pure hydrogen gas that can be mixed with the original fuel gas stream such that the final hydrogen gas on its own in the fuel-air mixture is roughly 4 % by volume (the lower flammability limit (LFL) of hydrogen in air).

- **Synthesis Gas (Syngas from coal gasification)**

Composition: (N₂ - 1%, H₂ - 24%, CO - 67%, CO₂ - 4%, H₂O - 3%, H₂S - 1%)

Combustion Reactions



Taking a basis of 100 moles of synthesis gas, then 24 moles (24%) of H₂ requires 12 moles of O₂ and 67 moles (67%) of CO requires 33.5 moles of O₂. The total amount of oxygen required is 45.5 moles. Assuming air is 21% O₂ and 79% N₂, 216.7 moles of air would be required for stoichiometric combustion of fuel, as shown in Table 2.

Table 2: Fuel-air composition of synthesis gas for combustion under stoichiometric conditions

Component	Amount (moles)	Composition (vol. %)
N ₂	1 + (0.79 x 216.7) = 172.2	54.37
H ₂	24	7.58
CO	67	21.15
CO ₂	4	1.26
H ₂ O	3	0.95
H ₂ S	1	0.32
O ₂	45.5	14.37
Total	316.7	100

For conditions of 300% excess air to reduce peak temperatures in the gas turbine, the amount of air required is 216.7 x 4 = 867 moles. The new fuel-air composition is shown in Table 3.

Table 3: Fuel-air composition of synthesis gas for combustion with 300% excess air

Component	Amount (moles)	Composition (vol. %)
N ₂	1 + (0.79 x 867) = 684.9	70.90
H ₂	24	2.49
CO	67	6.94
CO ₂	4	0.41
H ₂ O	3	0.31
H ₂ S	1	0.10
O ₂	(0.21 x 867) = 182.1	18.85
Total	966.0	100

It is clear from Table 3 that the hydrogen content of the fuel gas stream is below 4% by volume and thus can be increased. The following calculation is carried out to determine the amount of pure hydrogen that can be added to the fuel gas stream, whilst maintaining conditions of 300% excess air after allowing for combustion of the added hydrogen gas.

$$\frac{(24 + x)}{(24 + x) + 76 + (182 + 0.5x) + (683.9 + 2x)} = 0.04$$

$$24 + x = 0.04(3.5x + 965.9)$$

$$24 + x = 0.14x + 38.64$$

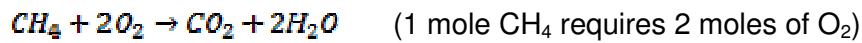
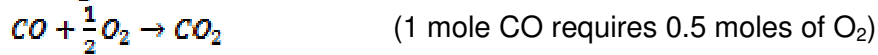
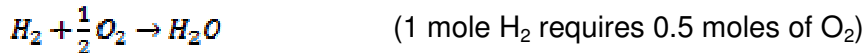
$$x = 17.02 \text{ moles of } H_2$$

Thus, the original synthesis gas stream (100 moles) can be doped with 17.02 moles of pure hydrogen gas such that the hydrogen gas composition in the fuel-air mixture is 4% by volume, under conditions of 300% excess air.

- **Producer Gas (from wood gasification)**

Composition: (N₂ - 51%, H₂ - 15%, CO - 19%, CO₂ - 12%, CH₄ - 3%)

Combustion Reactions



Taking a basis of 100 moles of producer gas, then 15 moles (15%) of H₂ requires 7.5 moles of O₂; 19 moles (19%) of CO requires 9.5 moles of O₂ and 3 moles (3%) of CH₄ requires 6 moles of O₂. The total amount of oxygen required is 23 moles. Assuming air is 21% O₂ and 79% N₂, 109.5 moles of air would be required for combustion of fuel under stoichiometric conditions, as shown in Table 4.

Table 4: Fuel-air composition of producer gas for combustion under stoichiometric conditions

Component	Amount (moles)	Composition (vol. %)
N ₂	51 + (0.79 x 109.5) = 137.5	65.64
H ₂	15	7.16
CO	19	9.06
CO ₂	12	5.73
CH ₄	3	1.43
O ₂	23	10.98
Total	209.5	100

For conditions of 300% excess air to reduce peak temperatures in the gas turbine, the amount of air required is 109.5 x 4 = 438 moles. The new fuel-air composition is shown in Table 5.

Table 5: Fuel-air composition of producer gas for combustion with 300% excess air

Component	Amount (moles)	Composition (vol. %)
N ₂	51 + (0.79 x 438) = 397	73.79
H ₂	15	2.79
CO	19	3.53
CO ₂	12	2.29
CH ₄	3	0.56
O ₂	(0.21 x 438) = 92.0	17.10
Total	538	100

It is clear from Table 5 that the hydrogen content of the fuel gas stream is below 4% by volume and thus can be increased. The following calculation is carried out to determine the amount of pure hydrogen that can be added to the fuel gas stream, whilst maintaining conditions of 300% excess air after allowing for combustion of the added hydrogen gas.

$$\frac{(15 + x)}{(15 + x) + 85 + (37.6 + 0.5x) + 346 + 2x} = 0.04$$

$$15 + x = 0.04 (3.5x + 533.6)$$

$$15 + x = 0.14x + 21.34$$

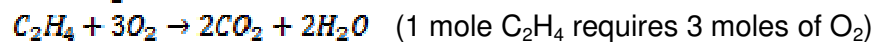
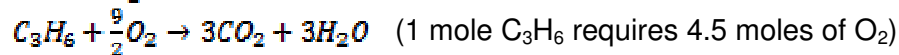
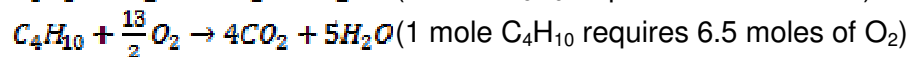
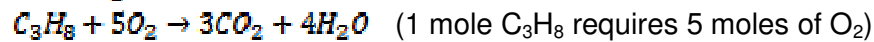
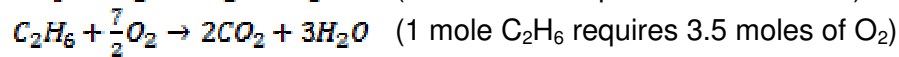
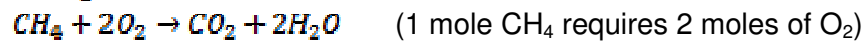
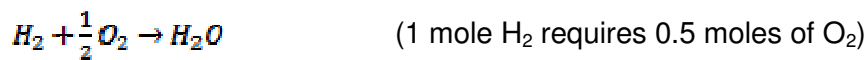
$$x = 7.37 \text{ moles of } H_2$$

Thus, the original producer gas stream (100 moles) can be doped with 7.37 moles of pure hydrogen gas such that the hydrogen gas composition in the fuel-air mixture is 4% by volume, under conditions of 300% excess air.

○ **Refinery Fuel Gas**

Composition: (H_2 - 20%, CH_4 - 50%, C_2H_6 - 11%, C_3H_8 - 10%, C_4H_{10} - 6%, C_3H_6 - 2%, C_2H_4 - 1%)

Combustion Reactions



Taking a basis of 100 moles of producer gas, then 20 moles (20%) of H_2 requires 10 moles of O_2 ; 50 moles (50%) of CH_4 requires 100 moles of O_2 ; 11 moles (11%) of C_2H_6 requires 38.5 moles of O_2 ; 10 moles (10%) of C_3H_8 requires 50 moles of O_2 ; 6 moles (6%) of C_4H_{10} requires 39 moles of O_2 ; 2 moles (2%) of C_3H_6 requires 9 moles of O_2 and 1 mole (1%) of C_2H_4 requires 3 moles of O_2 . The total amount of oxygen required is 249.5 moles of O_2 . Assuming air is 21% O_2 and 79% N_2 , 1188.1 moles of air would be required for combustion of fuel under stoichiometric conditions, as shown in Table 6.

Table 6: Fuel-air composition of refinery fuel gas for combustion under stoichiometric conditions

Component	Amount (moles)	Composition (vol. %)
N_2	$(0.79 \times 1188.1) = 938.5$	72.86
H_2	20	1.56
CH_4	50	3.89
C_2H_6	11	0.82
C_3H_8	10	0.85
C_4H_{10}	6	0.47
C_3H_6	2	0.16
C_2H_4	1	0.08
O_2	249.5	19.37
Total	1288.0	100

For conditions of 300% excess air to reduce peak temperatures in the gas turbine, the amount of air required is $1247.5 \times 4 = 4990$ moles. The new fuel-air composition is shown in Table 7.

Table 7: Fuel-air composition of refinery fuel gas for combustion with 300% excess air

Component	Amount (moles)	Composition (vol. %)
N ₂	$(0.79 \times 4990) = 3992$	78.43
H ₂	20	0.39
CH ₄	50	0.98
C ₂ H ₆	11	0.21
C ₃ H ₈	10	0.20
C ₄ H ₁₀	6	0.12
C ₃ H ₆	2	0.04
C ₂ H ₄	1	0.02
O ₂	$(0.21 \times 4990) = 998$	19.61
Total	5090	100

It is clear from Table 7 that the hydrogen content of the fuel gas stream is below 4% by volume and thus can be increased. The following calculation is carried out to determine the amount of pure hydrogen that can be added to the fuel gas stream, whilst maintaining conditions of 300% excess air after allowing for combustion of the added hydrogen gas.

$$\frac{(20 + x)}{(20 + x) + 80 + (998 + 0.5x) + (3992 + 2x)} = 0.04$$

$$20 + x = 0.04 (3.5x + 5090)$$

$$20 + x = 0.14x + 203.6$$

$$x = \mathbf{213.49 \text{ moles of } H_2}$$

Thus, the original refinery fuel gas stream (100 moles) can be doped with 213.49 moles of pure hydrogen gas such that the hydrogen gas composition in the fuel-air mixture is 4% by volume, under conditions of 300% excess air.

For fuels with a different energy content, these values would of course also be different.

3.8.2 Critical times and distances

Critical times are the primary issue in the context of times and distances. Auto-ignition delay, ignition characteristics, flame development, flame speed and flame acceleration are all time dependent parameters. These tend to reduce with increase in temperature. However, even with time reduction, the distance covered by the process may increase with temperature and the speed of sound (Ciccarelli, 1998). This is therefore an aspect that needs to be investigated for the selected model systems in Task 1 of WP2.

For this project the crucial issue is how long it will take with specific mixture compositions for hazardous conditions to develop and whether these will occur before or after the 'flame' has entered the heat exchanger, where different conditions will apply again.

3.8.3 Composition and flammability limits

If ignition and flame propagation is to be avoided at all cost, then the concentration of the combustible gas in air (or other oxidant) has to be kept below the lower (LFL) or above the upper flammability limit (UFL).

If flame propagation can be tolerated but deflagration to detonation (DDT) is to be avoided at all costs, then the fuel-oxidant system has to be well outside the detonability range as artificial turbulence generation and reflected shock impact can trip the system into a quasi-detonable mode.

For a mixture to be combustible, it obviously has to be within the flammability limits, but approaching the detonable regime requires adequate control, safety and very fast recovery provisions. As already explained in practical situations high air dilutions are frequently used to protect material by lowering the peak temperature in the gas turbine, but equally, mixture enrichment with hydrogen to achieve higher efficiencies are routine practice.

For fuel mixtures with very high hydrogen content in a confined situation, such as the IC test facilities and a turbine duct, limits for the pure material, such as quoted by Nettleton (1987) may be relevant (Table 8). However, for mixtures we have not been able to find any relevant data and, in any event, as the experiments go forward, the composition will continuously change.

Table 8: Flammability/(confined) detonation limits of hydrogen gas (H₂)

	Flammability limits, air (%)		Flammability limits, O ₂ (%)	
	Lower	Upper	Lower	Upper
Hydrogen	4.0/18.3	75.0/58.9	4.0/15.0	95.0/90.0

3.8.4 Mixing rules

Although for practical applications simple mixing calculations, based on Le Chatelier's rule, may be commonly applied, their predictions are profoundly unrealistic for our current interest, because initiation and propagation depend on fundamentally different properties, such as ignition delay times, energy release and external factors. The situation is made more acute by the notable non-linear coupling between parameters such as temperature and ignition delay times.

Without reliable mixing rules, it is virtually impossible to predict the explosivity of fuel mixtures because the ignition delay and rate of reaction can vary significantly even without the current coupling to the flow field. This is a knowledge gap that will not be closed without a specific research programme. Nonetheless, Tables 6-7 show that for refinery fuel the concentration of hydrogen is below its flammability limit, while for synthesis and producer gas it is almost double the LFL.

3.9 SUMMARY OF KEY FINDINGS

1. The properties and concentrations of key fuel components in systems and details of common CCGT processes currently in use have been reviewed.
2. It was found, using simplifying assumptions, that for several of the systems, and with normal air/fuel ratios, the resulting hydrogen content was below the hydrogen LFL and that higher levels of hydrogen should be of greater concern.
3. For the provisionally identified systems, critical times, distances for the development of flame and flame acceleration and to first development of turbulent and kernel combustion as a function of composition and temperature can be determined.
4. Predictive work based on mixing rules for pure component properties are not available or possible; for quality investigation or application experimental work will always be required.

4 COMBUSTION PROCESSES

This section examines the most important parameters that will influence the combustion behaviour of the fuel mixtures proposed for the experimental programme. It also discusses deflagration, DDT and detonation behaviour relevant to the CCGT/CCGE systems that are of interest.

4.1 FUEL SENSITIVITY AND IGNITION

Pure fuels, i.e. CH₄, CO, H₂, etc., exhibit uniquely defined combustion properties which are relatively well known. The characteristics of combustible mixtures containing a single fuel component depend primarily on equivalence ratio, initial and flow conditions. Mixing or diluting fuels introduces new variables as the mixture composition varies. As explained earlier, the composition of process and syngases can fluctuate significantly, which introduces uncertainty to the ignition and combustion process. This uncertainty needs to be evaluated and quantified.

On the other hand, if pure fuels are mixed in a controlled manner, advantageous combustion characteristics of the fuel components can be exploited to enhance combustion efficiency and reduce emissions. A number of authors (Bradley, 2008; Bradley, 2000; Silvestrini, 2008; Chao, 2003; Lee, 1984; Ciccarelli, 2008; Walton, 2007; Cong, 2008; Wu, 2011) have compared combustion phenomena of different undiluted fuels including methane, ethylene, hydrogen, carbon monoxide, propane, iso-octane. The influence of diluents, i.e. H₂O, N₂, Ar, He, or CO₂, on ignition, combustion, and deflagration-to-detonation transition has been studied by several investigators (Veser, 2002; Ciccarelli, 2008; Ciccarelli, 1998; Ciccarelli, 1994; Cong, 2008; Mertens, 2009; Cong, 2008; Williams, 2008; Prathap, 2008). Generally, they reduce the reactivity and sensitivity to explosion and detonation of mixtures by reducing reaction temperature but also affecting the reaction path.

Walton (2007) studied experimentally the ignition behaviour of numerous CO-H₂-O₂-N₂ mixtures using a rapid compression machine. The oxidation of CH₄-CO-H₂ fuel mixtures at different operation pressures, equivalence ratios, mixture compositions, and diluents with respect to burning velocity and ignition delay has been investigated by (Cong, 2008), while Lieuwen et al. (2008) studied the effect of similar mixtures on blowout, flashback, auto ignition and combustion stability. Other studies (Frassoldati, 2007; Cuoci, 2007) have also explored the ignition, combustion and flame structure of CO-H₂ mixtures employing an experimental jet flame and corresponding numerical simulation.

Methane-syngas mixtures over a wide range of equivalence ratios, pressures and initial temperatures have been studied by Cong and Dagaut (2008), who used a jet stirred reactor, while Prathap et al. (2008) studied the effect of different compositions of CO-H₂ fuels on the laminar burning velocity and flame stability for varying equivalence ratios. Sivaramakrishnan et al. (2007) used a shock tube facility to investigate the combustion of CO-H₂ mixtures at pressures up to 500 bar and Williams et al. (2008) explored the effect of syngas composition on emissions and performance utilizing a swirl burner with optical access.

The impact of hydrogen addition to ethane, ethylene, acetylene and carbon monoxide on laminar flame speeds was explored by Wu et al. (2011) using expanding spherical flames, while Bougrine et al. (2011) investigated numerically the effect of hydrogen

addition to methane flames at high pressure and temperature. The blending of hydrogen to pure fuels generally results in a raised reactivity of the mixture, i.e. decreased activation energy and auto ignition delay times, higher flame speed and temperature as well as broader flammability limit. However, the onset of a noticeable effect through hydrogen addition depends strongly on the baseline fuel, i.e. CO, CH₄. While the addition of small amounts of hydrogen has a significant influence on the combustion characteristics of CO, the mole fraction of H₂ is required to exceed about 50% that of CH₄ in order to dominate the reactivity of the mixture (Lieuwen, 2008). A generalized conclusion is however challenging to draw, as ignition, deflagration and onset of detonation are not only highly sensitive to the fuel composition, but its magnitude is also dependent on initial and boundary conditions; hence fuel flexibility analysis appears to require detailed case by case investigations.

Of particular note is the absence of data on the auto-ignition of hydrogen rich mixtures in vitiated environments as may occur in the exhaust duct of gas turbines. This deficiency will have to be addressed as part of WP2 Task 1 of the current programme.

4.2 AUTO IGNITION AND AUTO IGNITION DELAY TIMES

Auto ignition is the initiation of combustion within the reactive mixture with the absence of an externally provided energy source. The phenomenon of auto ignition has received the attention of numerous researchers with different objectives such as investigations of accidents, combustion within diesel engines and flame stability.

Variation of auto ignition behaviour and auto ignition delay time as a function of initial condition, i.e. temperature, pressure, equivalence ratio and type of fuel, has been investigated (Bradley, 2008; Walton, 2007). The influence of diluents such as N₂, Ar, H₂O on the ignition behaviour of syngases has also been analysed through reaction path analysis (Mertens, 2009). The influence of fuel composition on the auto ignition and delay time behaviour has been investigated by Lieuwen et al (2008). The fuel investigated was a CO-CH₄-H₂ mixture where the respective mole fractions as well as the equivalence ratio have been varied. The ignition behaviour of CO-H₂ mixtures has also been analysed (Frassoldati, 2007) by varying the H₂ fraction, equivalence ratio and nitrogen dilution via reaction path and numerical analysis.

The ignition delay and required activation energy depends on fuel, equivalence ratio and initial conditions. Hydrogen mixtures, for example, require low ignition energy while the ignition of CO is more energy intense. Hence, blending CO with H₂ increases the reactivity of the mixture, which is associated with decreasing activation energy and shorter auto ignition delay times.

The general conclusion is that the mixture composition and initial temperature are the most sensitive parameters of auto ignition behaviour.

This is why, as part of the current programme, ignition delay times need to be determined using shock tube measurements for the selected systems. It is hence expected that more reliable data, free from extrapolation/interpolation errors to a greater extent, will thus become available.

4.3 FLAME DEVELOPMENT AND FLAME SPEED

Fuels have characteristic laminar flame speeds which determine the propagation velocity of the flame at laminar flow conditions and certain initial conditions, i.e. temperature, equivalence ratio, etc. However in technical applications, the propagation velocity of the flame front may exceed this laminar flame speed significantly which is attributed to the generation of turbulence intensity in the unburned mixture ahead of the reaction zone. The turbulent flow wrinkles the flame surface, hence increasing the flame surface area, and amplifying the burning rate and burning velocity.

The turbulent flame speed has been investigated numerically (Bradley, 2008; Chan, 1996) for CH₄-air and different H₂-air flames in obstructed ducts, while Silverstrini et al. (2008) have explored the fuel dependency on the flame speed in smooth and obstacle-filled tubes. Experimental studies to investigate turbulent flame speeds of several fuels as a function of equivalence ratio and turbulence intensity have also been carried out (Lee, 1985; Lee, 1984), with other studies (Frassoldati, 2007; Cuoci, 2007) exploring numerically the laminar burning velocity of CO-H₂ mixtures at different pressures.

The influence of equivalence ratio on the flame speed of lean H₂-air mixtures in obstacle-laden tubes was studied by Vesper et al (2002). The impact of hydrogen addition on the laminar flame speed of fuel-air, i.e. ethane, ethylene, acetylene and carbon monoxide, mixtures has also been analysed (Wu, 2011) using expanded spherical flames. Prathap et al. (2008) reported the effects of nitrogen dilution on the laminar burning velocity of spherical syngas flames at atmospheric conditions. Flame propagation of H₂-air mixtures in an open-field experiment has also been studied using image velocimetry (Otsuka, 2007).

The laminar flame speed of a mixture depends primarily on the mixture composition and equivalence ratio, the effect of initial temperature being less pronounced. The turbulent burning velocity, a function of these mixture properties via the laminar burning velocity, is strongly dependent on the flow condition and turbulence generation ahead of the flame front.

The current program has a facility for the determination of the turbulent burning velocity for the selected mixtures. It is hence expected that more reliable data that are free from extrapolation/interpolation errors to a greater extent will become available.

4.4 INFLUENCE OF EXHAUST GAS TEMPERATURE

Auto-ignition in turbulent flow fields is of fundamental importance in the context of risks associated with the propensity of mixtures to form flame kernels that may grow into high-speed deflagrations or detonation. The first step in such an assessment is the procurement of reliable experimental data. The Cabra burner configuration (Cabra 2000; Cabra 2002) has proved particularly useful in this context with experimental data already obtained for the limiting cases of hydrogen and methane fuels. The burner consists of a fuel jet nozzle and a surrounding perforated disk. The fuel nozzle has an inner diameter of 4.57 mm resulting in a high velocity jet and the surrounding disk has a diameter of 210 mm with 2200 holes each with a diameter of 1.58 mm. Each hole stabilizes a premixed flame and thus provides a hot co-flowing low velocity stream. The central fuel jet nozzle extends 70 mm downstream of the plane of the perforated disk to ensure uniform co-flow properties. Gkagkas and Lindstedt (2007; 2009) showed that

calculation methods based on the transported probability density function approach reproduce measured data for both methane and hydrogen fuel mixtures with good to excellent quantitative accuracy. In particular, it has been shown that the geometry permits an assessment of the impact of the fuel reactivity and the temperature of the combustion products on auto-ignition. In the current work, a variant of the Cabra geometry will be used to evaluate the propensity of the selected fuel mixtures to form ignition kernels.

The exhaust temperatures encountered in a practical scenario will be strongly dependent on the design of the gas turbine and the degree of mixing of the unburnt fuel blend with pre-existing combustion products at the exit plane of the combustor. Hence, the problem is not well-defined and it is proposed that the sensitivity to the exhaust temperature is considered as a parameter. The latter should ideally be chosen in a manner that permits a direct comparison of the impact of the fuel mixture reactivity on the propensity to ignition. In past work, temperatures in the range 1045 K to over 1500 K have been used with a particularly pronounced sensitivity observed for hydrogen mixtures. A significant level of dilution is expected in the current application and the focus is likely to be on lower temperatures. A further complication is that the state of the fuel mixture emerging from the gas turbine will be influenced by the overall operating point in terms the resulting premixing taking place prior to the ejection of the fuel blend into the hot combustion products. This effect will be accounted for by varying the stoichiometry of the core fuel jet by dilution and premixing. The focus will be on overall lean fuel mixtures with additional extreme limits also considered.

A range of mixtures for each selected fuel blend will be further assessed in detail in order to provide flow field and scalar statistics by stabilizing turbulent flames against a stream of hot combustion products. The geometry features fractal generated turbulence in order to boost the turbulence Reynolds number (Geipel, 2009; Geipel, 2010; Goh, 2011). The temperature of the hot combustion products, the stoichiometry of the fuel blend and turbulence levels will be varied in order to determine representative burning characteristics.

4.5 TURBULENCE AND FLAME ACCELERATION

The rate of flame acceleration is dependent on the reactivity of the mixture but is primarily governed by the flow condition, i.e. turbulence intensity of the flow. Therefore, flame acceleration phenomena are commonly investigated employing obstacle-laden shock tube facilities (e.g. Johansen, 2009; Silvestrini, 2008; Alekseev, 2001; Beauvais, 1994; Chan, 1996; Lee, 1984; Lee, 1985; Ciccarelli, 2008).

Johansen and Ciccarelli (2009) investigated the initial flame acceleration in a stoichiometric CH₄-air mixture in an obstructed rectangular shock tube using Schlieren photography, while an earlier study (Lee, 1984) determined the flame acceleration of H₂-air mixtures over a wide range of equivalence ratios for different blocking ratios. The impact of different tube diameters and blocking ratios for several fuels over a wide equivalence ratio range has also been studied (Lee, 1985). It was found that increasing the blocking ratio (BR) promotes the initial flame acceleration by elevating turbulence generation, resulting in increased burning rates. The flame acceleration in smooth and obstacle-laden tubes was explored in a number of studies (e.g. Silvestrini, 2008; Ciccarelli, 2008) for different fuels including CH₄ and H₂. Flame acceleration in lean H₂-

air mixtures in integral large-scale experiments has also been investigated (Breitung, 2005).

The effect of venting on the acceleration of a flame front has been studied by Alekseev (2001) for different H₂-air mixtures. Beauvais et al (1994) explored the impact of mixture concentration, initial conditions and geometry of H₂-air mixtures on flame acceleration, while Dorofeev et al (2001) modelled the limits of flame acceleration of hydrogen mixtures by categorizing them as slow flames or choked flames/detonations. The effects of hydrogen concentration and initial temperature have also been studied in obstacle-laden tubes (Cicarelli, 1998). A model for turbulent flame acceleration has been presented (Chan, 1996) and the process of flame acceleration of hydrogen flames via the expansion ratio has also been modelled (Breitung, 2000).

As emphasised above, the acceleration of a flame front is strongly dependent on the flow conditions of the unburned mixture. The mixture composition, i.e. fuel type and equivalence ratio, defines the laminar burning velocity which directly influences the turbulent flame speed and therefore the flame acceleration. Nonetheless, the turbulence generation within the flow field is the most sensitive factor with respect to flame acceleration. An increased initial temperature of the unburned gas mixture results in a damped flame acceleration mechanism as the expansion ratio is decreased.

As part of the current programme, the propensity to DDT will be investigated for the selected systems. Furthermore, for selected cases the flow field will be quantified in order to provide better estimates of the relationship between explosion strength and turbulence levels. The latter also forms an important part of scaling relationships linking laboratory, large scale and practical devices.

4.6 DEFLAGRATION

Flame propagation can be categorised as either a deflagration or a detonation. The former is characterised by subsonic flame propagation, which is sustained by means of heat transfer due to chemical reactions. Deflagration flame propagation is associated with a marginal expansion, an increase of gas velocity and temperature across the flame front. The flame speed in the regime of deflagration, in essence the previously described laminar and turbulent flame propagation speed, is subject to pressure, temperature, equivalence ratio and turbulence intensity.

4.7 DEFLAGRATION-TO-DETONATION TRANSITION (DDT)

4.7.1 Principles of gaseous detonation

As realised long ago, detonation in a gaseous mixture of a fuel and an oxidant is essentially a very simple process. It consists of a shock wave of such intensity that as a result of its pressure rise the temperature of the gas also increases very rapidly. This reduces the auto-ignition delay time of the reactants and increases the rate of ensuing reaction and the expansion of the chemical reaction zone to such levels that the resulting shock wave can sustain the shock front that started the reaction off. This is known as the Positive Feed-back Mechanism. Whether a mixture will in isolation be able to fully sustain a stable detonation is therefore a function of the reactants' composition, energy content, reactivity and Mach number as a function of pressure and temperature, which generally should provide propagation conditions that near stoichiometry are not very different from the independent predictions of traditional C-J-

theory. Ignition delay time is another essential parameter; others, such as detonation velocity and impact loading have to be derived.

Detonation waves are not homogeneous 1-D processes but have a cellular structure. This structure consists of a 3-D process in which the ignition following shock compression occurs at distributed locations behind the shock front. All of these explosion centres send out their individual 3-D shock fronts, which decay, but at their points of interaction once again raise the pressure to such a level that re-ignition takes place. As long as this happens across the area of the explosive front, the detonation will continue to propagate. Enough centres of ignition have to appear, sending out strong enough shock waves, to produce collectively enough new centres of ignition, thus explaining the dependence on fuel mixture reactivity.

There are three groups of main factors that complicate the straightforward application of this simple concept to practical questions about detonability. The first is that even this simple process has to be set in motion from initially non-reactive conditions to a fast deflagration. The second is that the environment in which detonations may occur can influence strongly, positively or negatively, whether a transition to detonation (DDT) can actually take place. The third is whether in a real environment the detonative flame propagation mode of a particular reactant mixture can be stable, needs to be supported or will fail as result of external factors.

Almost everything that determines the first aspect of detonability has been discussed in sections 4.1 – 4.5. These cover what decides whether the nature, condition and environment of a deflagration might be such that a potential transition to a detonation (DDT) can be considered or explained. It is the second and third categories of conditions that are considered in what follows.

4.7.2 Self-generated DDT

If we use the term ‘flame’ as the collective word for any form on non-instantaneous combustion, then, whether any deflagrating flame will be able to enter a deflagration-to-detonation phase depends in essence on whether it has excess reactivity beyond what is required to maintain its present mode of propagation, which should be close to sonic velocity (Rosenbauer, 2007). For a ‘free deflagration’, i.e. one that is not influenced by external factors, this means whether (i) it can of its own accord continue to increase its energy output rate, i.e. as for slower flames (see section 4.4.) and/or (ii) whether under the prevailing conditions, it will increase the size of its flame. The latter is almost entirely dependent on maintaining or increasing the level of flame turbulence and flame kernel development.

This problem has been widely investigated; both theoretical and experimental studies have attempted to define the characteristics of such development. The transfer from fast deflagration to detonation initiation takes place in two phases. In the first, the flame has to accelerate to velocities that are compatible with a gradual strengthening of the wave, leading ultimately to detonation velocities; in the second phase, it has to develop the customary detonation structure. The initial acceleration phase may lead to a quasi-stable strong deflagration phase prior to the transition to detonation velocities (Lindstedt 1989). In cases of weak detonation initiation, e.g. via a spark, the vast majority of time to transition is associated with the transformation of the deflagration to a detonation.

The question whether the flame can then also settle into a detonative mode depends on whether the shock front compression in the transition phase is high enough to produce the temperature that leads to sufficient rapid auto-ignition before the following deflagrating flame catches up with the as-yet unexploded mixture. If it does not, the DDT will fail; if it does, the coalescence of the auto-ignited explosion with the high pressure-high temperature reaction zone sending compression waves forward will cause a momentary explosion peak, which is characteristically twice as high as that of the detonation that is established thereafter (Armstrong, 2004).

4.7.3 Artificially supported DDT

All the artefacts described in 4.4 that can accelerate flame propagation are equally powerful influences in fast deflagrations and can bring these into a DDT regime. In marginal cases this may lead to an enhanced flame propagation condition that the mixture could still have reached and supported of its own characteristic accord but would take a long time or distance to achieve. But more simple, unavoidable conditions also play a role.

The change to the transition mode may never occur, especially where other conditions vary, such as the available distance or time, measure, nature (e.g. surface roughness) or even presence of confinement, the uniformity of mixture composition, temperature and downstream pressure. Yet, it has been shown in laboratories that a genuine state of DDT and possible detonation could be achieved through flame extension by artificially induced turbulence. Shchelkin spirals are examples of aids that allow detonation studies across a composition range in tubes or channels of limited length (Lindstedt, 1988; Lindstedt 1989).

However, when there is not such additional energy availability, artificially induced flame enhancement, as for instance large scale explosions in obstacle filled channels have shown, can still create a 'quasi' DDT and detonation phase that is every bit as hazardous in terms of over-pressure generation and relevance to detonability in a 'non-ideal' environment as a self supporting independent stable detonation. The main artefacts that commonly create such conditions are obstructions, such as surface roughness, pipes and grids, constrictions, step-wise cross channel area variations and non-vented corners. At such points the contact with the obstruction may cause impact pressures, flow acceleration and/or shear, all of which will increase the flame area and hence the energy transfer rate. When such a flame propagation exits the obstructed environment it almost always return to a stable deflagration.

4.7.4 Implications for this investigation

There are numerous records of studies (e.g. Chao, 2003; Teodorczuk, 2008) on aspects of the deflagration-to-detonation transition. These authors comment on details of the mechanism, the conditions in which it may or may not be operative, the circumstances and fuel mixture properties that will promote its engagement and the factors that may accelerate or slow it down. Whether these should be considered in the context of this research will to an extent depend on the outcome of the preceding characterisation of the ignition and flame development of the selected test mixtures. However, some general observations may be made:

- (a) Silvestrini et al (2008) has highlighted how the relative increase in turbulent wall boundary layer thickness in moving to a more narrow confinement can enhance flame velocity and lead to a significant shortening of the run up time and hence

an increased chance of a DDT, while Teodorczuk et al (2008) has demonstrated how moving to a wider confinement will decrease the chance of a DDT. Hence:

The widening of the exhaust duct will delay a potential DDT.

- (b) Chao et al (2003; 2005) have shown that appreciable obstructions/ blockage ratios can significantly shorten the duration of successful DDT for marginally detonable gas mixtures with a 'turbulence scale' (see Section 4.4) of approximately one detonation cell size. In part this is due to the turbulent mixing of the shock condition with the reaction zone that occurs even quicker than the characteristic ignition delay time in the (stable) detonation front. This is similar to what is commonly also observed in sub-sonic flame acceleration (Dorofeev, 1996). Hence:

High-hydrogen mixtures with small cell-sizes, which have not detonated in the exhaust duct, are more likely to DDT within the first banks of a HRSG.

- (c) Additionally, Chan (1996) has described how successive obstacles can lead to step-wise acceleration of the flame; this has particular relevance for the potential of DDT within pipe-arrays, although Dorofeev et al (1996; 2001) have shown that in that instance a minimum distance between obstacle arrays plays a critical role. Hence:

Maximum overpressures associated with fast deflagrations and DDT (or even detonation) may occur in HRSG well beyond the first bank of water tubes, but tight tube arrangements will reduce that hazard.

- (d) A fast deflagration arriving at a significant flow restriction may not only cause a DDT through turbulent mixing within and beyond the open significant channel restrictions, but may also lead to downstream detonations. Where combustion has not taken place, it may also do so by reflecting off the closed parts of the restrictions, causing auto-ignition and localized explosion (Dorofeev, 1996). Similar auto-ignition may take place in corners and other restricted locations where multi-pressure waves are able to congregate. Hence:

The entrance to HRSG arrangements and corners in the duct system are locations where auto-ignition of non-combusted mixtures and acceleration and DDT of existing fast flames are more likely to occur.

- (e) Half-cylindrical obstacles are more suited to flow acceleration than flat surfaces (Kratzel, 1996). Hence:

Piped HRSG fronts favour high flame entrance velocities.

- (f) The width of the characteristic detonation cell size of a mixture is critical for successful DDT through a restriction or blockage. If all other conditions for a satisfactory transition are satisfied, then:

- When the width of the 'orifice' is between 1 and 13 times the width of the detonation cell, the DDT will succeed, although the detonation that results may have a velocity deficit.

- When the width of the 'orifice' is more than 13 times larger than the width of the detonation cell, the ensuing detonation will have the normal CJ-velocity.
- When the width of the orifice is less than the width of the detonation cell, the DDT will fail.

Hence:

Reliable information on detonation cell sizes of the fuel systems investigated in this programme is essential for assessing the DDT risks within the confinements of the test rigs and the scaling to full scale situations. Hence, if detonation characteristics are going to be determined, this will involve cell-size measurements..

- (g) Perhaps most importantly, the research literature puts clear emphasis on understanding how the DDT works and rightly indicates that there are two phases (Starr, 2010). The first is the 'creation of the conditions' for detonation from flame acceleration, turbulence and vortex formation and shock-flame/reactant-product mixing/interaction. The second is the formation of the detonation proper, i.e., the establishment of the cellular structure. Hence:

It is important to remember that the second phase can only be controlled by dimensional constraints or a complete lack of them, and that it is the first phase that needs to be avoided at all costs, by controlling the flame temperature, reactant mixture, vorticity, friction, constriction, blockage ratio, etc.

- (h) Finally, and equally importantly, the earlier comment at the end of section 4.4 about the influence of temperature on the flame acceleration process has to be taken into account. With reference to literature as quoted there (Beauvais, 1994, Dorofeev, 2001, Cicarelli, 1998), flame acceleration was shown to be dependent on confinement, obstruction and blockage ratio, reactant conditions and mixture composition and dilution (Prathap, 2008). However of these, induced and self-generated turbulence and turbulence levels were reported as being the most important. An increase in initial temperature of the unburned mixture was identified as slowing down flame acceleration, whilst other sources highlight that within the combustion zone, temperature rise first has a positive and then at higher levels a negative influence. The crucial question for this investigation is therefore whether from first exposure to high temperature, the combined duration and distance travelled during ADT, ignition, flame development, spontaneous and induced flame acceleration are short enough to lead to any critical detonability condition before the product mixture and any diluents added reach the further turbulence generating but cooling entry into the heat exchanger system. Hence:

It is therefore important to recognise this aspect for its overriding significance. As such factors are rarely reported for real fuel systems (Walton, 2007), or the proposed model mixtures and furthermore as concentration variations play such an important role, the only answers to this problem lie in the successful completion of the WP2 Task 1 experimental programme.

4.8 DETONATION

It follows from Section 4.6 that the only genuine detonation is a stable self-supported process that, driven by the positive feed-back mechanism, will continue to propagate on its own as long as there is no significant change in the basic conditions. Given initial reactant conditions, shock front pressures and temperatures, detonation velocity and impact over-pressures all have characteristic values that can be calculated and measured reasonably well. This also applies in principle to characteristic detonation cell sizes (Ciccarelli, 1998), which are particularly relevant for considering confinement and scaling conditions; for complex systems however, accurate information will have to be determined largely by experiment.

When conditions change, the detonation will adapt: compared with a stoichiometric mixture, generally with air, moving to leaner mixtures will invariably reduce velocity, whilst moving to rich mixtures first tends to increase velocity because of the change in Mach number. Near explosion composition limits, the velocity declines except for fuel-rich soot producing systems. In the present work, this will always be avoided. Because the energy content of the systems reduces away from stoichiometry, the cell size will increase.

The dependence on pressure is not particularly important in this context, but temperature is obviously very important. With its increase, the reaction path extends, but the cell size changes are frequently counter-intuitive. Around stoichiometric mixture make-up there are no great changes, but nearer detonation limits, cell size is reported to decrease with temperature, rather than increase.

Established detonations through constricted/blocked channels

Where quasi DDT has succeeded, mainly through significant confinement or deliberate interference, the following combustion will almost certainly be a 'quasi-detonation'. It will survive as long as a form of artificial flame temperature enhancement, e.g. through shear, continues to supplement the characteristic energy system of the mixture. If this supplement is significantly reduced or ceases, the detonation will generally fail.

This does not mean that a quasi-detonation will be less damaging than a stable detonation which would appear equivalent in velocity, temperature or shock pressure. Indeed, in a semi-obstructed or blocked environment, the very element of artificial support could result in a more powerful impact from perhaps a larger mean molecular fuel and oxidant mass.

With respect to potential issues related to this work, much of the literature related to detonation is written as a follow on from DDT concerns and is far more limited.

4.9 COMBUSTION ENHANCEMENT

Combustion rates can be enhanced by optimising the reactivity of mixtures and by flow conditions, e.g. turbulence intensity. The reactivity of the mixture is dependent on fuel properties, equivalence ratio and initial conditions. Whilst the effects of equivalence ratio and initial conditions have been investigated thoroughly (Beauvais, 1994; Ciccarelli, 1998; Cong, 2008), studies concerning fuel mixtures are of increasing interest, as fuel blending contains a great potential for further enhancement of the combustion process (Cong, 2008; Lieuwen, 2008; Williams, 2008). The addition of H₂ to natural gas, CH₄, or CO gives the advantage of lower activation energy and

increased flame speed. Furthermore, hydrogen blending yields a broader flammability limit, which allows, for example, the combustion of extremely lean mixtures. This affects the combustion beneficially as fuel consumption and emissions may be reduced.

4.10 OBSTRUCTIONS AND BLOCKAGE RATIO

As emphasized earlier, the degree of turbulence intensity plays a prominent role with respect to flame acceleration, flame speed and DDT. The effects of the geometric shape of obstructions and the blockage ratio have been the subject of a number of investigations (Teodorczuk, 2008; Beauvais, 1994; Kratzel, 1996; Lee, 1984). The effect of blockage ratio and obstacle spacing on the flame acceleration has also been reported (Chan, 1996). A sufficiently large blockage ratio (BR), and hence turbulence generation, is necessary to maximise possible flame speeds. Exceeding the optimum BR results in a decreased flame propagation velocity due to flame quenching and momentum loss. As a consequence, a certain mixture is associated with a specific optimum BR as well as obstacle spacing to achieve its maximum flame speed and eventually the transition to detonation (Beauvais, 1994).

4.11 WALL EFFECTS AND CONFINEMENT

The impact of walls has been addressed implicitly in the above discussion. Their effects are two-fold:-

Firstly, even smooth walled tubes provide boundary layer growth behind any compression wave moving ahead of the flame structure and this leads to turbulence generation. The latter is likely to eventually cause transition, provided that there is sufficient confinement length relative to the tube diameter, and that the relevant detonation cell structure of the incipient wave is sufficiently small to fit within the confinement.

Secondly, the presence of walls will reduce the flow divergence and hence any venting of the flow. Many authors have discussed the relative importance of the two effects. For example, Lindstedt and Michels (1988) provided a systematic study of the dependence of the time to transition depending on the mixture reactivity as modulated by the amount of nitrogen dilution in a smooth detonation tube.

It has also been shown in a series of seminal papers by Oppenheim and co-workers e.g. Oppenheim (1966) that transition to detonation may frequently occur via an “explosion in the explosion” taking place in the boundary layer formed along the tube wall. In the current context, it can be expected that such events may be of relevance in the context of combustion wave interactions with obstructions placed in the path of any propagating flame such as in the turbine exhaust ducts.

4.12 POTENTIAL OVER-PRESSURES

4.12.1 Prediction techniques

Prediction techniques for the calculation of over-pressures resulting from explosions have been formulated by a number of commercial vendors. These techniques are typically based on variants on moment closures with a prevalence of eddy-viscosity based methods. A number of these approaches have been reviewed by Arntzen et al (1995) following the completion of major EU projects aimed at gathering reference data

in large-scale explosions. More sophisticated techniques have also been applied and evaluated in the context of explosion initiation in confined flows that are of direct relevance to the current study (Kuan, 2003).

Oran and co-workers have presented extensive studies of flows making more rapid transition to DDT. These studies have traditionally focussed on strong initiation (e.g. via shock wave interactions), but more recently, studies featuring strongly turbulent flows have also been published (Oran, 2007).

The key challenge for all prediction methods is in the interaction of the chemistry of a particular fuel mixture with flow and a sufficiently accurate description of generation of turbulence through interactions with obstructions and boundary layers. The experimental quantification of such effects is also extremely challenging as outlined in Section 4.11.2.

4.12.2 Experimental measurements

Generating accurate data for comparisons with models capable of the *a priori* determination of over-pressures presents a significant challenge. While the accurate measurement of an over-pressure resulting from a particular combination of fuel-mixture reactivity and a particular confinement geometry may appear almost trivial, the reasons for the observed event are typically difficult to describe in detail, depending on a particular combination of mixture reactivity, turbulence generation and confinement geometry. To date, only a very limited number of studies have sought to clarify the underlying mechanisms through the application of time-resolved laser diagnostics for the quantification of flow statistics. The studies by Lindstedt and co-workers (1995; 1998; 2001) are unique in the context of linking turbulence intensities to the strength of an explosion. It must, however, be emphasised that measurements of maximum over-pressures alone are straightforward.

The current programme contains elements aimed at extending such measurements to selected mixtures in the agreed matrix of conditions. Given the complexity of performing the measurements, the most interesting mixtures will be selected for this type of quantification.

4.13 SUMMARY OF KEY FINDINGS

Against the background of a review of the most important phenomenological and scientific aspects of combustion that are relevant to this research programme, the foregoing sections have identified the following salient points.

1. Despite the wealth of theoretical and experimental information available on individual materials and process steps, no integrated models giving a description of compound fuel system behaviour under the conditions of interest to this ETI programme is available.
2. Of particular importance for any system investigated will be the acquisition of accurate and reliable data on auto-ignition/ignition delay times in support of in-house work on turbulent burning velocity, flame acceleration and detonation propensity as a function of initial temperature in clean and obstructed confinement.

3. Associated information on critical times and distances to DDT kernel formation for varying system and confinement conditions will (need to) be collected.
4. Guided by our own knowledge and expertise and reminded or alerted by the wide range of information mentioned in the literature, it will thereby be possible to determine critical parameters for explosivity and detonability system regimes. We will in particular be alert to the implications listed in section 4.7.4 above.
5. The findings will be collected in a suitable form for conditional and scaled application in Tasks 2 and 3 of the programme.

5 SCALING PRINCIPLES

The main scaling principles to be applied to the experimental test rig designs of WP 2 are presented in this section.

5.1 TECHNIQUES

The issue for this project is how the findings from WP 2, Task 1 can be used to predict the combustive flow behaviour and development in the larger scales of WP 2, Tasks 2 and 3. For sub-sonic behaviour the issues are predominantly of a fluid-mechanical nature. For sonic behaviour the detonation cell size plays a dominant role.

5.2 FLUID MECHANICAL ISSUES

Physical modelling of any fire/combustion related problem is based upon matching as many of the most relevant dimensionless parameters as possible. This relies heavily on substantial simplification of any real problem or sound physical insight into the flow under study to assist in the modelling and its interpretation.

The influence of those parameters that are not matched should ideally be negligible. This is rarely the case and assessment of the influence of the neglected parameters is the essence of pragmatic modelling approaches.

In the case of fire modelling, it is recognised that there are some 29 relevant dimensionless groups (Drysdale, 2011), but a practical subset contains the following:

- Geometric similarity
- Froude number (Buoyancy) V^2/gL
- Reynolds number (Turbulence) VL/ν
- Heat release rate (Power output)

In the context of explosions, it can be expected that the Reynolds number will become high as part of the process. The issue of scale separation comes to the fore in the context of assessing the spectrum of scales that a flame will be subjected to during an event. It is probably not unreasonable to assume that Kolmogorov's hypotheses remain valid to a leading order and that flame wrinkling caused by turbulence will occur over a wide spectrum of scales. Hence, it is likely that both the Damköhler (Da) and Karlovitz (Ka) numbers, based on the ratio of a representative chemical (τ_c) and the large integral (τ_l) and fine structure (τ_k) time scales of the turbulence spectrum, will be relevant. The definitions of these scales are available in standard reference texts (e.g. Peters, 2000) and are given below for completeness, where k is the kinetic energy of turbulence, ε its rate of dissipation and ν the kinematic viscosity.

$$Da = \tau_l / \tau_c \quad \text{and} \quad Ka = \tau_c / \tau_k \quad \text{where} \quad \tau_l = k / \varepsilon \quad \text{and} \quad \tau_k = \sqrt{\nu / \varepsilon}$$

The combustion regime present during an explosion will be characterised to a leading order by the above scales. Few attempts have been made to estimate the resulting combustion mode, predominantly due to the absence of relevant velocity statistics. One attempt (Lindstedt, 1998) suggests that even under comparatively benign laboratory conditions, the mode of combustion is located in the distributed reaction zone regime.

5.3 DETONATION CELL SIZES

Scaling for detonating systems can also be done on the basis of detonation cell sizes. Basic characteristics of the detonation cell have been discussed in Sections 4.6 and 4.7. The size of the cell is a measure of the energy content and reactivity of a gaseous system. The higher the reactivity and hence the more explosion centres across the mixture front, the smaller the cell cross-section (width and length) will be. For instance, in a stoichiometric mixture with air, hydrogen, which is very reactive, has a much smaller cell size than methane.

If we dilute detonable stoichiometric gas mixtures, the reactivity will go down. Therefore moving away from stoichiometry into fuel-lean and fuel-rich compositions, the number of ignition sources will decrease and the cell size will increase in proportion to the level of dilution, irrespective of the type of fuel, provided that detonation limits are not reached. As also mentioned elsewhere, temperature increase will also lead to a reduction in detonation cell size (Ciccarelli, 1994).

As the change in cell size thus depends to a large extent on mixture dilution by any non-reactive means (e.g. nitrogen or steam), the rate at which cell sizes change when we move away from stoichiometry is more or less the same for most detonable gas systems. Hence if we know for a specific fuel or fuel mixture the dimensions of the detonation cell at a stoichiometry/equivalence of 1, we can work out what it is away from stoichiometry as long as all components remain detonable. Predictions based on reaction kinetics of complex mixtures is however every challenging.

Alternatively, as the likelihood of a successful DDT depends in part on the ratio of the width of confinement over the detonation cell width, it is possible to obtain an estimate for the feasibility of a DDT in the Task 2 and Task 3 rigs from reliable measurements and/or cell-size calculations of relatively small cell sizes at stoichiometry in Task 1.

The literature reference on this is ambiguous. Dorofeev et al. (2000) carried out experiments on similar rigs at 50 : 1 scale ratio and seem to conclude that the detonation cell size and reaction zone length are more or less proportional to the scaling factor. We can only assume that this means that the ratio of detonation cell size and reaction zone length is more or less fixed.

5.4 SCALING CRITERIA FOR WP2/TASK 3

5.4.1 Introduction

Reduced scale modelling of the geometry and flows from the gas turbine exit through the HRSG and out through the exit stack is complicated because of the differing flow regimes that exist. Immediately downstream of the gas turbine exit the flows are predominately influenced by the high flow velocity and exhaust temperatures, and are therefore governed by the Reynolds Number. Within the HRSG the flow is slowed down due to the rapid expansion in cross sectional area together with a cooling of the flow as heat is lost from the hot gas flow to the steam generating process. Thus the flow on the macro-scale becomes increasingly influenced by buoyancy especially towards the exit stack and is therefore increasingly governed by the Froude Number. However on the micro-scale especially with regards to the flow around the heat exchanger tubes the turbulence will dominate, especially with regard to the vortex

shedding and the turbulent energy dissipation rate and its spectral distribution. Thus the flow particularly if it is combined with the occurrence of an explosion will be expected to be governed by both the Damköhler (Da) and Karlovitz (Ka) numbers, as indicated in Section 5.2.

The issue of arbitrarily choosing the geometric scale can also be overcome by utilising the fact that the buoyancy will increasingly influence the flow through the HRSG and the exit stack. Thus by applying Froude Number modelling as the most appropriate approach globally, the geometric similarity is fixed as a consequence. The heat release rate is scaled with $L^{5/2}$, the velocity with $L^{1/2}$, and the temperatures are the same for the model and full-scale rigs. Matching of Reynolds number is not achieved but this may not be important provided that in both the model and full scale, the flows are fully turbulent and that similar turbulence intensities and spectral distributions are achieved. It is felt that should a flammable mixture exist in the exhaust system then any ignition is most likely to occur within the HRSG, where the velocities are lower and turbulence levels are greatest due to the presence of the heat exchanger tubes.

The major difficulty of Froude number scaling, namely maintaining a constant heat release rate (power output), is overcome in this the experimental phase of the project as the power outputs of the system are known and constant. Radiation is not scaled, but again this is not considered important in the area of the application under consideration, namely downstream of the gas turbine/gas engine exhaust outlet.

5.4.2 Application to proposed test rig

By way of an example, the experimental rig proposed for this ETI sponsored programme is based upon the use of a R-R Viper gas turbine as the replicate power source, which has a rated output of 3.6 MW. Taking a horizontal HRSG design supplied by GE as the typical layout of a CCGT/HRSG unit, and based upon a 380 MW total output from the gas turbine (Frame 9FA), then from the equivalence of power output, the equivalent model scale is: -

$$380/3.6 = L_{fs}^{2.5} / L_m^{2.5}.$$

Thus the geometric scale in this case would be 1:6.4, and the size of the model HRSG would be 0.156 per unit length. A complication when comparing power outputs is recognising that in an actual power generation system the turbine is connected to a power generator, which is not the case with the R-R viper engine whose total output is directed towards creating thrust. Therefore, it is suggested that another way of comparing the two is to use the ratio of their respective fuel consumptions when running on similar fuels. This results in an "output" ratio of: - 14.3/0.233 and a geometric scale of 1:5.2. This and the previous value give a representative range for the length scale to be used.

In addition the flow velocities on the model should be of the order of $1/6.4^{1/2} = (0.4U_{fs})$ of those in the full size CCGT, whilst the temperatures should be similar. This scaling approach has been applied to smaller units with similar results, thus establishing its validity, although noting that the geometric scaling ratio is specific to each individual design considered.

6 CURRENT INDUSTRIAL PRACTICES

This section discusses existing high hydrogen power plants, and provides a brief discussion of combustor developments in so much as they impact the use of high hydrogen fuels, the hazards associated with using high hydrogen fuels, and issues arising from the layouts used for HRSGs.

The issue of the selection process is also reviewed in the light of real gas turbine systems and representative fuel systems suggested for the follow-on experimental laboratory test programme, based on the information in this Chapter and that in Chapter 3.

Information relating to control systems for high hydrogen fuelled gas turbines is also included.

6.1 REVIEW OF EXISTING HIGH HYDROGEN SYSTEMS

Walton et al (2007) point out that the successful operation of gas turbines using syngas (including hydrogen fuel concentrations >90%) has been demonstrated at numerous facilities in the United States and abroad over the past few years, although there have been difficulties. The syngas mixtures can vary widely in the relative hydrogen and carbon monoxide concentrations, complicating turbine operation and design. The high-temperatures associated with the hydrogen combustion can lead to high nitrogen oxide emissions, and existing dry low-NO_x gas-turbine technologies are not amenable to the high mass flow rates and fuel concentrations (from 15% to 40%) required for syngas mixtures. As a result, the current approach is to fire syngas with high levels of dilution (typically using nitrogen or steam).

Todd and Battista (2000) state that significant progress has been made in the development of market applications for hydrogen fuel use in gas turbines. These applications include integrated gasification combined cycle (IGCC) and other types of process/power plants. Development of a new application using gas turbines for significant reduction of power plant CO₂ emissions has initiated extensive efforts to expand the range of hydrogen combustion capabilities. Testing program results also show the feasibility of hydrogen use for 20-90% CO₂ emission reduction with control of NO_x emissions to below 10 ppmvd at 15% oxygen.

Jones (2006) points out that GE gas turbine product experience with H₂ content fuel gas is extensive including E-class and advanced F-class units. Feasibility of high H₂ fuel combustion with low emissions has been demonstrated at F-class conditions using the proven syngas MNQC combustor. He also states that there are over 20 sites operating GE gas turbine power plants using high hydrogen fuels with the Daesan installation operating at up to 95% hydrogen, and most of the others operating in the 60-80% regime.

Chun et al (2001) describe the petrochemical plant at DAESAN, owned and operated by SAMSUNG General Chemicals which has two co-generation units driven by a Frame 5P commissioned in 1988 and a Frame 6B commissioned in 1997. GE Energy Products-Europe (GEEPE) supplied these gas turbines. They have proven to be efficient, reliable and adaptable to changing fuels. Indeed, the Frame 6B (a 40 MW machine) routinely accommodates a wide range of petrochemical by-product gases with over 95% hydrogen in the main fuel.

Wolf et al (1992) discuss the safety aspects and environmental considerations of operating a 10 MW cogeneration gas turbine burning coke oven gas with 60% hydrogen content. The power plant was a dual fuel arrangement using light distillate oil as the secondary fuel. An inert nitrogen buffer was considered necessary for safety reasons when switching between fuels, in order to prevent oxy-hydrogen formation at the transition point. Sophisticated control and regulation systems, details of which are not given in the paper, were developed and because of the increased hazards, explosion proofing was also provided. Controlling the NO_x emissions was a major problem.

The GE experience of running gas turbines on high hydrogen fuels in respect to a CO₂ constrained environment is also summarised by Shilling and Jones (2003). They point out that hydrogen/N₂ is an acceptable fuel for gas turbines using IGCC combustors.

Schneider (2006) describes the successful operation of gas engines running on various hydrogen containing fuels including coke gas (55 to 70 % H₂), pyrolysis gas from domestic waste gasification (35% H₂) and wood gas (15-40% H₂).

6.2 COMBUSTOR DEVELOPMENTS

According to GE, over the past 20 years, manufacturers of gas turbine combustors have been striving to keep pace with a changing regulatory landscape. Originally burners were developed for burning natural gas and have since been modified to cope with alternative fuels.

One of the prominent pollutants that needed to be dealt with was NO_x. Early gas turbine combustors employed a diffusion flame that inherently had good stability but poor emission characteristics. When emissions needed to be controlled, water or steam was used as a diluent and NO_x was brought down to less than 50 ppm at the expense of reliability and performance.

In order to meet more stringent emissions requirements, Dry Low NO_x (DLN) combustors have been developed by most of the major gas turbine manufacturers. DLN combustors employ lean, premixed combustion for achieving low NO_x and CO emissions. The cooler flame temperatures of the lean premixed flames are the primary mechanism for producing lower NO_x levels. In order to achieve both acceptable CO and NO_x emissions, a very narrow range of fuel/air ratios must be maintained. It should also be noted that combustion systems with different NO_x and CO limits would have wider or narrower ranges of fuel/air ratio in which they can operate, although when the fuel/air ratio drops below the target operating range, CO emissions will increase sharply because the lean blowout limit is being approached.

Such premixed designs include features such as multiple and independently supplied fuel nozzles and staged combustion, and rely on careful design and operation in order to maintain flame holding aerodynamically. This has implications for the monitoring and control system, which needs to have greater sensitivity to factors such as fuel calorific value, density and flame instability. The combination of design and control enable the real time distribution of fuel within each individual combustor to optimise temperature distributions both for stability and emissions.

DLN combustion technology can offer extended combustion intervals, which may lead to reduced maintenance costs, as utilising a dry system eliminates water usage and associated costs.

Although to date running diffusion flame type burners on hydrogen has been explored extensively and fully characterised by GE (Danner, Private communication), premixed burners running on hydrogen only are not commercially available at present. A major problem with a hydrogen only fuel is that NO_x production can be up to 400 ppm, if not controlled.

6.3 HIGH H₂ HAZARDS ASSOCIATED WITH CURRENT SYSTEMS

6.3.1 Flammable gases in exhaust system

One of the main driving issues is that the use of high hydrogen fuels introduces the possibility that flammable mixtures may enter into the exhaust system and into the HRSG in the event of a gas turbine flameout or gas engine failure, as can be deduced from, in the case of a hydrogen only fuel, the information given in Table 9 (Abbott, 2011).

Table 9: GT performance data for a range of fuels.

	Gas turbine performance data				NG Base case	Equivalent Fuel Flow*			
	ISO base rating (MW)	Efficiency (%)	Exhaust Flow (kg/s)	Exhaust Temp. (°C)		NG (kg/s)	H ₂ (kg/s)	COG (kg/s)	Syn-Gas (kg/s)
Siemens SGT-200	6.75	31.5	29.5	466.1	0.45	0.18	0.56	1.88	4.82
GE Frame 6B	43	33.1	145.1	542.2	2.71	1.08	3.42	11.42	29.23
R-R RB211 GT62	29.87	37.6	95.9	497.2	1.66	0.66	2.09	6.98	17.87
GE Frame 9FA	254.1	37	642.9	598.9	14.31	5.72	18.08	60.37	154.54
Siemens SGT5-4000F	292	39.8	692.2	577.2	15.28	6.11	19.32	64.49	165.06

*Fuel flow to achieve same overall power output with the same efficiency and airflow as natural gas base case.

The above values are based on the assumed calorific values (CVs) (MJ/kg) shown in Table 10 (Abbott, 2011).

Table 10: Assumed calorific values (MJ/kg) for several fuels.

Natural Gas	Hydrogen	Coke Gas	Oven	Syngas	Bio-syngas
48	120	37.98		11.38	4.44

It is apparent that for the range of power plants considered, hydrogen/air mixtures of between 8-12% hydrogen by volume may enter the exhaust stream in the event of a flameout and a delay in closing the main fuel supply valve. These values are for running at full power under steady conditions; failure during acceleration to reach full power may increase the fuel quantity by up to 20% (Abbott, Personal Communication). These concentrations are above the LFL for hydrogen and may well approach the concentrations associated with the DDT regime especially at elevated temperatures.

In the case of a CCGT system, GE (Danner, Personal Communication) has analysed the quantity of fuel that might be expelled through the exhaust if the machine flames out and the gas valve closes instantly. The fuel quantity is the residual fuel in the piping at pressure and at the instant of valve closing. The complete analysis of the fuel quantity purged during the trip of a 7FB IGCC gas turbine running syngas is provided in Table 11.

Table 11: Exhaust and fuel flows for a range of GE gas turbines running on syngas.

Frame Size	Nominal rating (MW)	Nominal Air Flow (kg/s)	Air through Machine purge (kg)	through during Total Flow Shutoff (kg)	Gas to Average estimated gas flow rate (kg/s)
9FB	284	656.5	4330	40.45	5.78
9E	127.6	419.1	2765	25.9	3.7
7FB IGCC	232	533.6	3520	32.72	4.67
7EA	83.5	300	1979	18.18	2.6
6FA	77.1	212.3	1400	13.18	1.88
LMS 100PA	103.2	219.5	1010	9.55	1.36
LM 6000PC	43.3	128.7	644	5.91	0.84
LM 2500PE	23.1	71.5	472	4.55	0.65

The above data are based upon the following assumptions:-

- The unit is operating at full load speed.

- For multi-mode fuel systems, the mode with the largest volume between the shut-off valve and nozzles is operating.
- There is total loss of flame for some reason, e.g. due to forced fuel supply valve closure on removal of electrical output or partial flameout producing asymmetry in outlet temperature profile.
- All nominal rating values are based on natural gas operation with the exception of the 7FB IGCC machine, which is based on the syngas IGCC rating.
- All values are based on a detailed simulation of a 7FB IGCC machine trip and assume immediate flame out following fuel valve closure.
- Total gas flow is considered a worst case for each machine.
- The expected LFL for IGCC syngas (approx. 35% H₂) is 7.9% by volume with a molecular weight of 19.8.
- The gas flow rate is the average over the purge time of 7 seconds.

Essentially, the simulation captures what is required to purge one volume of syngas from the fuel line in a plug flow fashion following a simulated closure of the Speed Ratio Valve and opening all of the purge nitrogen valves connected to the fuel line. The simulation shows that the entire volume of syngas is purged within about 7 seconds of the valve tripping on a 7FB IGCC machine. The total amount of fuel purged is approximately 0.9% by weight of the total air that passes through the gas turbine during that purge period.

The analysis is also based on the simulation of the 7FB IGCC machine, which operates at a 17:1 pressure ratio. All of the other machines run similar pressure ratios with the exception of two of the aero-derivative machines. It is assumed that an equivalent ratio of fuel to air is expelled into the other machines following a valve trip since most of the flow comprising the one volume turnover is a result of the pressure in the fuel line. In the case of the LM6000PC, the fuel to air ratio was adjusted upward by the square root of the pressure ratio relative to the 7FB = $\sqrt{(30/17)} = 1.3$ times 7FB fuel to air ratio (1.2% fuel/air). For the LMS100PA, the flow was adjusted upward by a similar ratio = $\sqrt{(40/17)} = 1.5$ (1.35% fuel/air). Since the target is for a one-volume turnover of the fuel, this would mean that the relative amount of air that goes through the machine would be decreased to hold the required ratio of fuel to air.

This analysis is somewhat artificial as it assumes that a flameout occurs immediately following closure of the fuel valve. This is a very optimistic assumption, as in practice the flameout must first of all be detected, the fuel shut off valve closed and the fuel trapped in the line allowed to decay through the exhaust system. This process may take several seconds in total to complete, thus there is a period when unburnt fuel and air are able to flow under pressure through the hot turbine and into the exhaust system.

6.3.2 Analysis and review of actual GT hydrogen concentrations

The range of different hydrogen sources results in a wide range of concentrations in the primary fuel and a corresponding range in calorific values. The material limitations required for turbine entry temperatures will require appropriate levels of dilution prior to turbine entry and therefore the downstream hydrogen concentrations which can arise during a flameout condition will be limited by the dilution levels typically required to maintain material stability.

Table 12 below summarises information provided by GE (Danner, Private Communication) and Abbott (Abbott, 2011) regarding a range of GT systems, and

provides basic information on the exhaust flow rates, input chemical energy rates and output powers.

Table 12: Gas turbine flow rates and input powers.

	Output Power (MW)	Input chemical energy flow rate for NG (MW)	Exhaust flow rate (kg/s)	Exhaust flow rate per input MW of chemical energy (kg/s/MW)
Siemens SGT-200	6.75	21.2	29.5	1.4
GE Frame 6B	43.0	127.4	145.1	1.1
R-R RB211 GT62	29.9	78.0	95.9	1.2
GE Frame 9FA	254.1	672.6	642.9	1.0
Siemens SGT5-4000F	292	718.2	692.2	1.0
		Input chemical energy based on 37% efficiency		
GE 9FB	284.0	767.6	656.5	0.9
GE 9E	127.6	344.9	419.1	1.2
GE 7FB IGCC	232.0	627.0	533.6	0.9
GE 7EA	83.5	225.7	300.0	1.3
GE 6FA	77.1	208.4	212.3	1.0
LMS 100PA	103.2	278.9	219.5	0.8
LM 6000PC	43.3	117.0	128.7	1.1
LM 2500PE	23.1	62.4	71.5	1.1

The last column in this table indicates the ratio of exhaust gas flow rate per unit of input chemical power and therefore provides a relation between the fuel flow rate and the total gas flow rate appearing in the exhaust. When the calorific value and composition of the primary fuel are known, the final column in the table allows an estimation of the molar flow rate of fuel versus the molar flow rate of exhaust, which in turn enables an estimate of the mole fraction of hydrogen in the exhaust when flameout occurs.

It can be seen that the ratio lies in the range 0.8 - 1.4, and choosing a value at the lower end of this range provides a conservative basis for the calculation of the hydrogen mole fraction in the exhaust on flameout. This calculation requires a discussion on fuel gas compositions for the various types.

Some information has already been provided in the report in this area and some real representative examples are collected in Table 13. These are considered to represent the likely sources of fuels incorporating hydrogen, and the following summary briefly describes the basis for their choice. Within this table, the number of kg/s of fuel gas is calculated per MW of chemical power supplied (1/CV).

As has been explained in the Introduction and is also highlighted in the Appendix, hydrogen is the main fuel of interest and its use in pure form must be considered. There are several postulated sources of such hydrogen streams, e.g. as an energy storage 'vector' arising from renewable sources such as wind and wave. A more likely source is from gasification processes, which are 'oxygen blown', and which incorporate carbon capture, but other sources include specific refinery processes producing concentrated streams of hydrogen, which are likely to be used for power and steam generation on-site.

There are a number of gasification processes using fossil fuel as the input fuel, which give rise to different output gas mixes and these are sufficiently different to justify individual consideration. The main technologies available are described as Sasol-Lurgi, GE (Texaco), Shell and ConocoPhillips. The output compositions from these processes will depend on the manner of the gasification and subsequent gas processing. For 'air-blown' gasifiers, the output fuel stream will have a significant nitrogen component, while for 'oxygen-blown' gasifiers, which require an air separation unit (often drawing from the gas turbine), the fuel stream is almost nitrogen free. In addition, 'shifting' the carbon monoxide from the gasification will increase the hydrogen content and introduce additional carbon dioxide. The various operation options will result in hydrogen/carbon monoxide molar ratios that can range from 0.5:1 up to 2:1 with varying degrees of nitrogen and carbon dioxide. Several composition cases are cited by Todd and Battista (2000) and three of these have been chosen to represent typical hydrogen contents. In addition to these, there is the possibility of carbon capture following carbon monoxide shifting.

In the case of oxygen-blown gasifiers, this will result in mainly hydrogen streams and is represented by the pure hydrogen case above. Therefore a further case has been included, which represents an air-blown gasifier with carbon capture, and which contains some nitrogen in the fuel stream.

Coke oven gas has a high level of hydrogen but is normally low in inert gases and carbon monoxide. The 20 - 30 mol% levels of hydrocarbon contribute significantly to the calorific value and as with refinery gas, result in a lower molar flow rate of fuel per MW of chemical power input.

Refinery gas can take a wide range of compositions. Typically these will have both hydrogen and hydrocarbon content. For those mixtures with very high hydrogen mole fractions, the analysis of exhaust hydrogen is similar to that of the pure hydrogen case and the mixture taken for Table 1 is considered a representative one.

Biofuel provides the raw material for bio-syngas production and being already partially oxidised will be expected to have a lower final calorific value. Partial oxidation of the biofuel provides the energy for the gasification process and the final gas stream will therefore contain a nitrogen component unless upstream air separation is used, resulting in this being the fuel with the lowest CV value of the group.

A number of syngas mixtures and other reported hydrogen rich fuels, which have been used in actual gas turbine installations, are presented in Table 13. These can be compared with those in Table 1 and reflect the variability which different classes of high hydrogen fuels may have depending on their specific source.

With the information in Tables 12 and 13 and their reported operating conditions, it is now possible to make an estimate of the possible range of mole fractions of hydrogen

in the exhaust following a flameout event. This assumes that the non-fuel gas in the exhaust is excess air. Since the molecular masses of both the fuel stream and this excess air are known, and since the flow rates of both streams have been related to a common input chemical power (1 MW), then the fuel mole fraction in the exhaust can be calculated. Each fuel stream has different fractions of hydrogen and the hydrogen mole fraction can then be estimated by applying this value to the fuel mole fraction in the exhaust. Table 14 collects these values together and the final result is given in the last column. It can thus be seen that four of these fuel compositions could in the event of a flameout result in hydrogen concentrations being above the LFL for at least the time that it takes the detection system to react and close off the fuel supply.

Table 13: Representative fuel gas sources incorporating hydrogen.

Fuel stream	Fuel composition (mol%)							CV (MJ/kg)	Avg Mol Wt	Fuel kg/s/MW
	H ₂	CO	CH ₄	H/C	N ₂	CO ₂	H ₂ O			
Hydrogen	100							120.00	2.00	0.0083
Syngas 1	14.5	23.6	1.6		49	5.6	5.7	9.47	24.40	0.106
Syngas 2	34.4	35.1	0.3	0	0	30.2		8.21	23.85	0.122
Syngas 3	61.9	26.2	6.9	0	2.2	2.8		25.65	11.53	0.039
Syngas +CCS	47	1	1		41		10	8.85	14.66	0.113
COG	61.6	6	23	2.2	5.4	1.2		42.42	9.60	0.024
Refinery Gas	28		28	34	3.5	6.5		41.00	23.8	0.024
Bio Syngas	18	20	7	2	30	23		6.50	26.5	0.154

NB: Syngases 1 - 3 and Syngas + CCS are taken from Todd & Battista (2000). COG is taken from Wolf & Perkovec (1992). Refinery Gas is taken from Dragomir et al (2010). Bio-Syngas is taken from Demirbas (2008).

Table 14: Estimation of hydrogen mole fraction in exhaust on flameout.

Fuel stream	Fuel kg/s/MW	Fuel kmol/s/MW	Exhaust kg/s/MW	Excess air kg/s/MW	Excess air kmol/s/MW	Fuel/Exhaust mol fraction	H ₂ mol fraction in exhaust
Hydrogen	0.0083	0.0042	0.9	0.8917	0.0314	0.117	0.117
Syngas 1	0.106	0.0043	0.9	0.7944	0.0280	0.134	0.019
Syngas 2	0.122	0.0051	0.9	0.7782	0.0274	0.157	0.054
Syngas 3	0.039	0.0034	0.9	0.8610	0.0303	0.100	0.062
Syngas +CCS	0.113	0.0078	0.9	0.7870	0.0277	0.218	0.102
COG	0.024	0.0025	0.9	0.8764	0.0309	0.074	0.045
Refinery Gas	0.024	0.0010	0.9	0.8756	0.0308	0.0321	0.0090
Bio Syngas	0.222	0.0058	0.9	0.6778	0.0239	0.181	0.033

6.4 FUEL USED BY THE ETN (H₂-IGCC)

A memorandum of understanding has been agreed between the Health and Safety Laboratory (HSL) and the European Turbine Network (ETN) to exchange specific information relating to the high hydrogen fuels to be utilised by both organisations in the course of their investigations.

Thus according to Geris (Private communication, MOU, 2011), the overall objective of the H₂-IGCC project is to provide and demonstrate technical solutions, which will allow the use of state-of-the-art, highly efficient, reliable gas turbines in the next generation of Integrated Gasification Combined Cycle (IGCC) power plants. Such gas turbines are to be suitable for combusting undiluted hydrogen-rich syngas derived from a pre-combustion CO₂ capture process, with high fuel flexibility.

The recognised challenge is to operate a stable and controllable gas turbine on hydrogen-rich syngas with emissions and process parameters similar to current state-of-the-art natural gas turbine engines. This objective will have significant implications for the combustion technology, hot gas path materials, the aerodynamic performance of turbomachinery components, and the system as a whole.

The project addresses these issues in four sub-projects, which cover the areas of combustion (SP1), materials (SP2), turbomachinery (SP3) and overall systems analysis (SP4).

SP4, which is also analysing the gasification process, provides the fuel composition for the other subprojects besides several other items of information. The fuel composition, shown in Table 15, is used as a reference throughout all sub-projects, and reflects the current status of the project. It is defined at the interface of the fuel injector to the gas turbine combustor, at a temperature of 30⁰C and a pressure of 38.7 bar(a).

Table 15: H₂ rich syngas at combustor fuel nozzle.

Fuel Component	Unit Mol %	Unit Wt %
H ₂	85.82	27.28
CO	1.17	5.18
H ₂ O	0.04	0.11
CO ₂	4.03	27.97
H ₂ S	TRACE	TRACE
COS	TRACE	TRACE
NH ₃	TRACE	TRACE
N ₂	8.93	39.46
SELEXOL	TRACE	TRACE

The lower heating value (LHV) for the fuel is 33248.47 kJ/kg, and the higher heating value (HHV) is 39202.73 kJ/kg. The combustion chamber fuel flow rate is 3.675 kmol/s or 23.308 kg/s.

The composition represents the reference fuel for the H₂-IGCC project and does not cover any deviation from this composition which might be due to shut down of the CO₂ capture unit etc. The fuel composition reflects a pre-combustion carbon capture efficiency of 90%. The fuel mass flow corresponds to an air mass flow of about 683 kg/sec in a 100% load case (775 MWth).

For some of the (experimental) activities in SP1 (combustion) and SP2 (materials), simplified 2-/3-/4-component mixtures have been defined and will be used for reasons of practicality.

6.5 TYPICAL SYNGAS FUEL COMPOSITION (COURTESY OF GE)

Table 16 gives the typical fuel composition for a moisturised syngas fuel, with nitrogen dilution for NO_x control (with a nitrogen to fuel ratio of approximately 1.1), as defined by GE.

Table 16: Moisturised syngas fuel composition.

Fuel Component	Volume fraction
CO	0.5818
CO ₂	0.0069
H ₂	0.2360
H ₂ O	0.0802
N ₂	0.0868
CH ₄	0.0002
Ar	0.0081
H ₂ S	0.000018
COS	0.000009

A GE gas turbine type 7FB in an IGCC plant when running on the above fuel produces the exhaust composition shown in Table 17, which has a molecular weight of 29.217.

Table 17: Exhaust composition for 7FB gas turbine.

Exhaust Component	Volume fraction
N ₂	0.7334
O ₂	0.1126
CO ₂	0.0803
H ₂ O	0.0642
Ar	0.0095

The CO emissions are 5.92 ppm and the NO_x emissions are 25 ppm at 15% O₂. The unburnt hydrocarbons (UHC) are zero.

6.6 STRATEGY FOR FUEL MIXTURE SELECTION TO MEET INDUSTRIAL INTERESTS

Table 1 in Section 3 has identified three generic fuel mixtures and Table 13 has shown actual reported hydrogen rich mixtures derived by various routes. It is noted that the gas mixtures in Table 1 can be used as a basis for approximating most of the gas mixtures in Table 13 by the addition of hydrogen.

For example, the refinery gas mixture of Table 1 becomes close to that of coke oven gas by addition of hydrogen to the 58% level and adding hydrogen to the basic syngas mixture of Table 1 can reproduce each of the three syngas mixtures with different H₂/CO ratios.

The options for deriving these gas mixtures from the generic set in Table 1 are shown in Table 18. It is noted that pure hydrogen is also one of the choices, which represents some of the special cases identified above, e.g. oxygen blown gasification with carbon capture.

Table 18: Fuel options based on the generic hydrogen mixtures of Table 1.

Component	Pure H ₂	Refinery Fuel Gas	COG	Syngas 1	Syngas 2	Syngas 3	Producer Gas from Biomass	Syngas + CCS
N ₂		-	-	1	1	1	51	27
H ₂	100	20 + H ₂ →	58	24 + H ₂ →	48	60	15 + H ₂ →	55
CO				67	46	35	19	10
CO ₂				4	3	2	12	6
CH ₄		50	26				3	2
C ₂ H ₆		11	6					
C ₃ H ₈		10	5					
Others		1 (C ₂ H ₄) 2 (C ₃ H ₆) 3 (C ₄ H ₁₀)	5	1 (H ₂ S) 3 (H ₂ O)	3	2		

The various fuel mixtures discussed in the previous sections are collected together in Table 19 below for comparison.

Table 19: Summary of high hydrogen fuel mixtures.

Fuel stream	Fuel reference No.	Fuel composition (mol%)						
		H ₂	CO	CH ₄	H/C	N ₂	CO ₂	H ₂ O
Hydrogen	1	100						
Refinery gas (Moliere)	2	20		50	27			
Syngas(Walton)	3	24	67			1	4	3
Producer gas (biomass)	4	15	19	3		51	12	
ETN reference fuel	5	85.8	1.2			8.9	4	0.04
GE syngas Fuel	6	23.8	58	0.02		8.7	0.6	8
Syngas 1	7	14.5	23.6	1.6		49	5.6	5.7
Syngas 2	8	34.4	35.1	0.3			30.2	
Syngas 3	9	61.9	26.2	6.9		2.2	2.8	
Syngas+CCS	10	47	1	1		41		10
COG	11	61.6	6	23	2.2	5.4	1.2	
Refinery Gas	12	28		28	34	3.5	6.5	
Bio Syngas	13	18	20	7	2	30	23	

The basis for selection of a representative group of 3 fuels (plus hydrogen) for future experimental investigations is influenced by a number of factors. A major source of high hydrogen gaseous fuel is likely to originate from the gasification of solid fuels, which can thereby take advantage of the significant efficiency gains associated with combined cycles for electricity generation. It is therefore necessary to include a syngas source. It is also likely that a significant proportion of syngas will be derived by means of air blown gasifiers without carbon capture, and Syngas 1 (Fuel 7, Table 19) is representative of such a low calorific value fuel.

It is also recognised that the need for CO₂ removal will continue to exert pressure on gasification systems operators to capture the CO₂, and therefore a second choice would include an air blown syngas produced by a CCS process and characterised by the Syngas +CCS (Fuel 10) in Table 19. It is noted that oxygen blown syngases with CO₂ capture are effectively hydrogen streams and are already represented by the pure hydrogen choice.

A further likely gaseous fuel stream will be associated with refinery or coke production processes and is likely to have a significant hydrocarbon content. Given the very large material flows associated with industries such as steel making, it is considered that coke oven gas is likely to be the more prevalent fuel stream and therefore the third choice would be COG (Fuel 11).

In summary therefore, the proposed fuel choices for the experimental study are shown in Table 20.

Table 20: Proposed high hydrogen fuel mixtures to be used in the experimental programme.

Fuel stream	Fuel reference No.	Fuel composition (mol%)						
		H ₂	CO	CH ₄	H/C	N ₂	CO ₂	H ₂ O
Hydrogen	1	100						
Syngas 1	7	14.5	23.6	1.6		49	5.6	5.7
Syngas+CCS	10	47	1	1		41		10
COG	11	61.6	6	23	2.2	5.4	1.2	

6.7 CALCULATED EXHAUST EMISSIONS FOR VIPER ENGINE

The calculated exhaust emissions for the R-R Viper gas turbine being used for the larger scale experimental work of Work Package 2; Tasks 1 & 2 are shown here for comparative purposes.

Reaction Engines (Bond, 2011) have experience of running a Viper engine on butane fuel and have previously studied the exhaust products as part of that activity. The Viper Mk522 Jet Engine has been found to operate satisfactorily on butane fuel as an alternative to kerosene, for which it was designed. Calculations have been made using

the Gordon and McBride chemical equilibrium code to assess the composition of the engine exhaust when operating on butane.

The mixture ratio in the primary zone is within the combustion limits for air/butane and probably close to stoichiometric. The excess air is used to cool the combustion chamber and then dilute the combustion products to give the desired overall turbine entry temperature with cool regions close to the wall at turbine entry.

Calculations were performed at combustion chamber primary zone conditions and at propelling nozzle entry conditions to determine the best estimate of the exhaust composition. The Viper 522 normally operates at a mass mixture ratio (air/fuel) between 60 (100% design speed) and 90 (85% design speed). The ignition mixture ratio limits at 1 atm are between 5.4 and 27.2 and the stoichiometric mixture ratio is 15.463. The molecular weight of the air was assumed to be 28.966.

The combustion calculations were performed for iso-butane, C₄H₁₀ as being representative of commercial butane with a heat of formation taken as -31452 cal/mole. The air entering the combustion chamber has increased enthalpy due to being compressed by the compressor. The work to supply this enthalpy increase is extracted by the turbine from the flow. Thus for the primary combustion zone calculation, the air enthalpy was taken as 1492 cal/mole but for the nozzle entry calculation the enthalpy was taken to be -10 cal/mole. The mixture ratio in the primary zone was taken to be 15 at an absolute pressure of 5.6 bar, and in the nozzle entry to be 66 at an absolute pressure of 1.7 bar. The calculated exhaust composition was as shown in Table 21, with a molecular weight of 28.8480. The fuel consumption on butane is approximately 9% less than when running on kerosene.

Table 21: Calculated exhaust composition for Viper 522 gas turbine.

Components	Mol fraction	Mass fraction
Ar	0.00913	0.0126
CO ₂	0.02994	0.0457
H ₂ O	0.03705	0.0231
NO	0.00053	0.0005
N ₂	0.76617	0.7446
O ₂	0.15718	0.1743
H ₂ O (s)	0.00000	0.0000

The fuel consumption figures for the Viper 522 engine when running on butane are:-

- 100% design speed 0.400 kg/sec (max 5 minutes)
- 98.5% design speed 0.393 kg/sec (Maximum continuous run speed).
- 85 % design speed 0.233 kg/sec (Maximum cruise speed, MK 202).
- 92% design speed 0.284 kg/sec.

6.8 REVIEW OF HRSG LAYOUTS AND EXHAUST SYSTEMS

This section examines the available information concerning the various exhaust configurations that are used on CCGT/CCGE/HRSG systems.

6.8.1 Design rationale

In respect of designing HRSGs as part of a combined cycle unit, the performance of the turbine or gas engine, followed by the HRSG, has the most important impact on the unit's efficiency. The key HRSG parameters that need to be optimised include steam pressures, temperatures, flows, pinch points, approach temperatures and HRSG exit gas temperatures. Thus the flue gas from the turbine/engine enters the HRSG and is reduced in temperature by the superheater, reheater, drum evaporative surfaces and economiser before it enters the stack. Condensate from the combined cycle condenser enters the de-aerator and flows through the economiser, steam from which flows to the superheater and then to the high-pressure turbine. Steam from the high-pressure steam turbine flows through the reheater and then to the intermediate pressure turbine.

Most HRSG designs are of the multiple pressure type with duct firing and other capabilities that can make the design complicated; optimisation often depends on the use of suitable software design tools or parametric approaches, such as described by Zhao et al (2003). In such systems the objective is to demonstrate the impact on the cost of electricity of the various design parameters, such as the exhaust gas pressure drop. Pinch points and approach temperatures are also important HRSG design parameters as reducing them increases cycle efficiency. However, optimisation involves fairly complicated heat transfer calculations and steam cycle heat balances to avoid operational problems.

HRSG exhaust stacks often include SCRs as well as a range of rectangular heat exchanger units, together with a separate exhaust gas bypass stack or an integrated bypass and heat exchanger unit. In addition there are circular designs where the silencer, bypass and heat exchanger are combined in a compact package providing the lowest weight, plot space and life cycle costs. The latter are available for up to 50 MW engines.

A bypass stack with twin diverter valves may be installed between the engine exhaust outlet and the HRSG for two reasons. Firstly it enables the engine to continue to operate and produce electrical power whilst the HRSG is under maintenance. Secondly at start-up, it enables the engine to be brought up to full speed at the full rate of power increments. In general the HRSG cannot tolerate the same rate of rise of temperature that this would imply. A bypass arrangement allows the exhaust flow to be diverted to the HRSG progressively at a low rate avoiding extreme thermal shock. Gas engine systems normally use a bypass around the HRSG or heat exchanger rather than a bypass stack.

Since there is evidence that a significant proportion of exhaust explosion (and other) incidents occur at start-up, the conditions at start-up may be particularly relevant to this work. The effects of duct velocity and geometry associated with a bypass stack may be significant and it may be possible to derive relevant related risk reduction recommendations. However it needs to be borne in mind that back up fuels, which are not of high hydrogen content, are often used during start-up.

6.8.2 HRSG layouts

The paper by Nessler et al (2001) states that to mate efficiently the Rankine steam cycle with high-temperature gas turbines, new HRSGs were needed that could operate at substantially higher flue-gas temperatures. New HRSG designs were also required to match each incremental jump in gas-turbine size, as combined cycle units grew

larger and larger. Perhaps the most important development in HRSG design has been the move from single to dual-pressure steam production. This change, which enabled lower stack temperatures and thus greater recovery of thermal energy from the gas turbine exhaust, has increased thermal efficiency of a combined-cycle plant by nearly 4%. Later designs have gone one-step further, from dual to triple-pressure steam.

HRSG manufacturers also offer a choice between horizontal or vertical flue-gas paths. Vertical designs, which were originally developed in Europe where the major suppliers of this kind are still located, offer a smaller footprint and are less vulnerable to thermal cycling problems than the horizontal designs commonly applied in North America.

Since vertical HRSGs no longer require forced-circulation pumps, not even for start up, due to design improvements of the evaporator systems, both HRSG types offer the same overall efficiency, although the choice of type of HRSG may be made for other reasons. Vertical type installations are more popular for lower power output installations, presumably because of size constraints. The various advantages and disadvantages of the two designs are summarised in Table 22, which is reproduced from Nessler et al (2001).

Table 22: Horizontal vs. Vertical Type HRSG from Nessler et al (2001).

Horizontal HRSG	Vertical HRSG	
	Horizontal HRSG	Vertical HRSG
Output and Efficiency	Equal	Equal
Surface Area for equal Output	Similar, except the reheater and super heater section might require slightly more heating of the surface area mainly due to less advantageous flue gas flow distribution with regard to temperatures and mass flow	Base

Table 22 (cont.) : Horizontal vs. Vertical Type HRSG from Nessler et al (2001) continued.

Plot Plan Area for equal Output	Up to 30% more, mainly due to the opening angle of the inlet duct and the stack, and if supplementary firing systems, SCRs, CO Catalysts, etc. are required	Base
Emission control	Requires more HRSG length	Requires more HRSG height; cleaning of downstream fouled surfaces has to be carried out carefully, not to poison the catalyst.
Supplementary Firing	Readily installed in the HRSG inlet duct or within the boiler surface area	Readily installed in the HRSG inlet duct; difficult to install within the boiler surface area
HRSG enclosure/Boiler house	Free standing, self supporting enclosure	Attached to and supported by the HRSG structure, light enclosure
Natural Circulation	State of the art	Special design considerations, though state of the art
Modularized/Standard concepts	Typical	Typical
Erection Area, prefabrication on site	Equal, though more crane area is required for pressure part (harps) mounting which typically lasts 5 weeks for large GT CCPP	Equal, though heavy transportation (120 ton) may be required on site, typical time needed for boiler surface mounting: 3 weeks for large GT CCPP.
Cycling	State of the art design experiences severe cycling problems at super heater and reheater stages; design considerations cost effective	Less vulnerable if properly designed
HRSG Cost (ready to run)	Equal	Equal
O&M Cost	Higher number of and larger textile expansion joints, boiler surface replacements not possible, repair by blocking of tubes, cost effective	Replacement and blocking of tubes possible
Regular Inspections	Headers and surfaces not easy to access	Header and surface inspection carried out, accessing through manholes without requirement for additional auxiliaries

GE (Danner, personal communication) has provided the following information about the flows and temperatures through a typical (GE-designed) HRSG as exemplified for a 9FB powered IGCC unit. However, the overall values should be relatively constant across a range of turbines with the volume being primarily related to the flow rate of the driving machine (the HRSG for a Frame 6 being proportionately smaller).

- The gas path volume is 5548 m³, with a tube volume of 432 m³ for the total HRSG.
- The percentage of the cross section that the tubes comprise (which will also vary through the HRSG due to fin density) is 66%.

- The “solidity” varies slightly through the HRSG due to varying fin density.
- The inlet temperatures at the entrance to the HRSG are 708⁰C.
- The temperatures after each of the four heat exchangers are respectively: 354⁰C, 346⁰C, 245⁰C, and 175⁰C, whilst the outlet to stack temperature is 166⁰C.
- The pressure drop across the HRSG inlet to outlet is 383 mm water gauge.
- The velocities through the HRSG are an inlet velocity of 23 m/s and a stack exit velocity of 6 m/s.
- Where a SCR assembly is fitted, the inlet temperature is 354⁰C with a gas side pressure drop of 50 mm water gauge.

The heat exchangers can be considered as evenly divided sections through the HRSG. Clearly, the velocities are a function of the pressure / temperature driven local density, with pressure being a minor term in the equation.

6.8.3 HRSG equipment

The following equipment may be found in the CCGT/CCGE/HRSG exhaust system and should be considered for its potential to generate turbulence or quenching in the context of DDT in the event of ignition. In the case of any unburnt buoyant gases entering the exhaust system, consideration must also be given to ensuring that they cannot accumulate in “dead” spaces.

- Swirl vanes – used for gas turbines to reduce corkscrewing of gases in the exhaust duct.
- Turbocharger – used by gas engines to pressurise combustion air supply taking energy from exhaust.
- Oxidation catalytic bed for (gas engine) CO emission reduction.
- High and low temperature SRC catalytic treatment plant.
- High angle transition ducts, with bends - gas turbine.
- Pipework with bends - gas engine.
- Diverter valve to bypass stack.
- Silencer to reduce pressure fluctuations that may lead to in-duct burner instability.
- Supplementary and/or auxiliary burners.
- Explosion relief panels or (gas engine) relief panels.
- HRSG – Vertical and horizontal types.
- Gas engine – Shell/tube heat exchanger with exhaust gases in tubes.
- CHP hot water generator of the fire tube type and CHP plant generally.

6.9 CONTROL SYSTEMS FOR HIGH HYDROGEN FUELS

6.9.1 General comments

According to Wilbraham (Private communication, 2011), the control issues associated with high hydrogen fuels including syngas, is really a result of the chemical kinetics of the fuels. Syngases also contain high levels of CO. Not only is CO toxic, which requires gas sniffers in the GT enclosure and on all fuel lines/manifolds, but also CO is an extremely energetic reactant at pressure. In many cases CO is much more important than H₂ when above about 5 bar pressure. This is apparent from chemical kinetic

simulations to determine flame strain rates. These increase dramatically as the CO content is increased.

Thus the reason why H₂ and CO are a problem is really down to flame stability. As stated above, high flame strain resistance means that the reacting flame front is more difficult to contain in an aerodynamically stabilized burner. Hydrogen has a high flame strain resistance, but this is a result of the high flame speed. The engineering problem is to hold the flame. Most premixed burners cannot be used for LCV fuels for this reason as it becomes increasingly difficult to hold the flame as the H₂ and CO content increases. Most gas turbine suppliers will not offer a dry low emissions (DLE) solution for anything in the LCV range. This is because the associated high-pressure loss to hold such a flame aerodynamically would be a serious hit on GT efficiency.

The result is therefore more to do with (1) knowing when the combustor flame is burning through the flametube, (2) knowing when a flameout has happened, and (3) controlling the fuel flows during GT load change, either island mode or load shed.

Most GTs operating with LCV fuels will start on a premium fuel and switch over to the LCV fuel. This then requires control of the fuel metering and knowing if the flame has moved. It is possible that the efficiency of combustion could be reduced during a fuel switchover, which would be a problem for any HRSG (boiler) used in conjunction with the GT. As is the case with premium fuels, all power plant operators are most concerned about unburnt fuel entering downstream plant equipment; so fast response flame detectors (to see flame-outs in the combustors) are frequently requested.

6.9.2 Objectives of control systems

The primary objectives of gas turbine control, when used for electricity generation, are to maintain rotation speed and phase matching with the grid supply and to achieve the target power demand.

Some of the operational processes involved in achieving these objectives can have a potential impact on exhaust gas compositions, and the following is a brief summary of the main operating stages that are designed to avoid unsafe conditions both downstream and within the gas turbine itself. These stages apply in general to gas turbine systems but relate specifically to GE control systems as given in Johnson et al (1996) and Barker et al (2000).

Start-up stages:-

1. Initial cranking of the turbine by means of Diesel engine or electric motor.
2. Unfired cranking up to 25 - 30% of full speed, which also allows gas path purging.
3. At ignition speed, igniters are turned on, followed by the firing fuel flow.
4. Monitoring of flame detection following ignition and cross firing within a specified period, typically 60 seconds.
5. In the event of non-ignition or incomplete cross-firing (detected by asymmetry in the turbine exhaust temperature profile) fuel is cut off and a purge sequence is followed;
 - purge will allow up to five volume changes in gas path.
 - a restart sequence will then automatically follow.

6. On ignition, fuel flow is reduced to a warm-up value for a specified period.
7. Following warm-up, fuel flow is increased and at a turbine speed of around 50% of maximum, an acceleration sequence is then initiated automatically to minimise thermal fatigue during start-up.
8. External cranking power is discontinued at around 50% power.
9. On turbine approach to running speed, phase synchronising with the grid is implemented followed by connection of the breaker.
10. Increase of the generator load to target value.

Shutdown stages:-

12. Initiated by operator or as an automatic response in event of contact breaker opening;
 - remains reversible while turbine speed is above 95%.
13. Automatic unloading of unit.
14. Breaker opens when reverse power is detected at 5% level.
15. Gas turbine fuel flow driven to minimum value to maintain flame.
16. Deceleration of turbine to ~ 30% speed when fuel is cut off;
 - fired shutdown reduces thermal fatigue on hot parts.
17. Gradual slowdown and cool down - may take several hours.

The operator sets the running conditions for the turbine, by specifying an output load for electricity generation. This will involve an increase in fuel supply rate followed by feedback control on the fuel supply valve to maintain turbine speed as the load on the generator reaches target. Automatic fine-tuning of the fuel control valve is then aimed at maintaining this speed and hence the supply frequency by minimising the error between grid and turbine frequency.

Part load running conditions are achieved at intermediate fuel supply rates and adjustment of the compressor inlet guide vanes.

6.9.3 Protection mechanisms

Key safety requirements for normal start-up and running include stable flame throughout the combustors, maintaining turbine inlet temperature within an upper limit, maintaining turbine speed within an upper limit and mechanical integrity of system.

Many GT systems are equipped with UV flame detection sensors located within several of the combustors to establish that flame exists within the system. Others will use the temperature distribution in the exhaust stream as a flameout indicator. The absence of flame within one or more combustors manifests itself as a non-uniform circumferential distribution of temperature in the exhaust stream. This temperature distribution is monitored and in the event of a partial flame-out, the shutdown system would be initiated.

Turbine inlet gas temperatures are monitored and used to set an upper limit on fuel supply rate and hence power output. Temperatures up to 1600°C are now accessible (MHI, 2011). A number of condition monitoring systems are also now available for GT systems (Hewitt et al, 2004). These include turbine blade temperatures using pyrometric methods, which can provide real time information on the effectiveness of blade cooling. Pressures and temperatures are monitored routinely at several points in

the compressor and turbine pathway and in the exhaust system, and dynamic pressure monitoring can now also provide information about the onset of flameout and the excitation of severe acoustic modes. Vibration monitoring allows continual assessment of mechanical integrity by signalling changes in the frequency composition of the system.

Removal of electrical load, for example by the opening of the electrical contact breakers, would result in turbine overspeed and this would automatically force a reduction of fuel supply to a minimum level to maintain combustion (Johnson et al, 1996).

6.9.4 Meeting NO_x targets

NO_x levels are strongly influenced by the maximum temperatures within the combustor. The wider the distribution of these around the chosen mean values, the greater will be the NO_x levels. Combustor design choice is influenced by the choice of fuel to be used. For natural gas fuelled combustors, the reduction of peak combustion temperatures is best achieved by using premixed fuel/air mixtures, enabling NO_x levels down to 25 ppm. Such combustors belong to a class of dry low NO_x designs (DLN) and premixing requires careful design and operation of the flow system to avoid flame blow-off at high flow-rates and flashback into the mixing zone at low flow-rate levels.

For premixed fuel/air mixtures that contain hydrogen, the limiting H₂ fuel concentration is 10% by volume in order to avoid flashback problems. As a consequence of this, existing high hydrogen fuels, which typically contain more than 25% hydrogen, are unable to use this combustor choice and will rely on more conventional diffusion based combustor designs (Moliere, 2000). Such designs are much more robust with respect to flame blowout but can suffer from greater NO_x levels. The reduction of flame temperatures in diffusion designs is normally achieved by additional dilution using inerts such as nitrogen, steam (wet control) or carbon dioxide. Such dilution is most effective when injected directly into the flame zone.

For nitrogen addition, this is normally achieved using nitrogen from an air separation unit, which may be part of an oxygen blown gasification system within an overall CCGT plant.

The NO_x level can be monitored by continuous exhaust gas sampling and whilst it is not a critical operating parameter, the measurement allows adjustment of diluent flow to minimise the NO_x emission. Published data on the effectiveness of diluent addition indicates that steam/fuel flow rates can be up to 2 kg/s with steam (as given by Todd, and Battista, 2000) and that emission levels can be reduced to around 25 ppm.

6.9.5 Safety aspects during start-up, shutdown and running

6.9.5.1 Fuel transition

Many gas turbine systems will operate satisfactorily with both liquid and gaseous fuels, as well as mixtures, by using suitably designed dual fuel supply nozzles. A common operational sequence for these is the change over from one fuel to the other, known as fuel transition, involving a switch over during a period of around 30 seconds.

Since there are risks with this procedure associated with flameout, the control hardware and algorithms in place to affect the change need to be robust. This is now a well-developed procedure for GT systems and the same methods are used for transition involving hydrogen rich systems.

For hydrogen rich fuels, the turbine is always started using an alternative fuel, e.g. natural gas or propane. An example of the protections used for transition to syngas operation are given by GE Energy (2010) and involve a rigorous inerting protocol with nitrogen and compressor air to ensure that the supply lines for the inactive fuel are continuously purged when not in use.

6.9.5.2 Over watering on load cut-off

The use of inert, e.g. steam, to mitigate NO_x formation requires careful control under abnormal running conditions. An example would be the opening of the electrical breakers and removal of turbine load. The rapid fuel reduction to avoid overspeed will in these cases be accompanied by a rapid shut-off of the inert to avoid a flame blowout due to 'over-watering'.

6.9.5.3 Non-ignition

Non-ignition during start-up has been referred to above and has the potential to transfer unburnt fuel into the downstream ducts. Two important mitigating factors around this scenario involve: (1) the fact that start-up fuels never use a high hydrogen mixture but rather a start-up fuel, e.g. natural gas, meaning that only deflagration events are feasible in the downstream ducting, and (2) that the non-ignition purge sequence is automatically built into the start-up procedure.

6.9.5.4 Fuel heating value changes

There has been considerable discussion within the GT community about the increase in variability of gaseous fuel characteristics. For natural gas, this may arise due to the use of different sources, whilst for hydrogen rich gas, this may arise for a number of reasons associated with the gasification or other processes involved.

The main characteristics of interest are the fuel calorific value and the density. The starting point for discussion would assume that the gas turbine fuel nozzle design and compressor stages are arranged based on pre-chosen fuel properties. In particular, the fuel density and calorific value will determine the limiting rate of heating via combustion for a particular nozzle choice and differential pressure.

In simple terms, the mass flow rate (W) of gaseous fuel discharged through the nozzle is given by:-

$$W = C_D A \sqrt{2\rho\Delta p} \quad (\text{kg/s})$$

where C_D = Fuel nozzle discharge coefficient.

A = The nozzle area. (m²)

ρ = Fuel gas density. (kg/m³)

Δp = Differential pressure across the fuel nozzle. (N/m²)

In volumetric terms, the flow rate (G , m³/s) becomes:-

$$G = \frac{W}{\rho} = \frac{C_D A}{\sqrt{\rho}} \sqrt{2\Delta p}$$

when the volumetric higher heating value of the fuel is HHV (MJ/m³), and the heat supply rate (Q, MJ/s) is given by G x HHV, thus when the nozzle parameters remain constant, this is:-

$$Q = \frac{K_{fuel}}{\sqrt{\rho}} HHV \quad (\text{MJ/s})$$

For convenience, this flow-rate parameter is referenced with respect to air flowing through the same nozzle under the same conditions at 15°C and 1 atm pressure.

This new parameter, the Wobbe Index (WI, MJ/m³), then provides the basis for comparison of the heat supply rates for different fuels under the same nozzle operating conditions, i.e.

$$WI = \frac{HHV}{\sqrt{\rho_{fuel}/\rho_{air}}} = \frac{HHV}{\sqrt{SG_{fuel}}}$$

where SG_{fuel} is the specific gravity of the fuel with respect to air at the reference condition.

There is a direct operational implication resulting from a change in HHV of the gaseous fuel and this is linked directly to power generation, where any algorithm relating fuel rate to power will be upset by a change in the Wobbe index value.

The safety implications of a change in HHV are associated particularly with the flame stability margins available to those operating with premixed fuel/air systems. The need to maintain power at a prescribed level combined with the sensitivity of flame fronts to the WI value has resulted in solutions directed mainly at natural gas fuel burning systems. Some of these solutions may also be applicable to high hydrogen containing mixtures.

The WI value of natural gas can vary for a number of reasons. The main changes are linked to composition, which may include small amounts of higher hydrocarbons, and changes in ambient conditions. Considering that ambient temperatures may vary from -20 to +40°C, this implies a density change of around $\pm 10\%$. In addition to this absolute change, there are the issues of the rate of change of fuel properties and the extent to which control hardware can match these time scales. This is particularly relevant when close to a flame blowout limit. In the event that the control system, which would act to restore heat input rate via a feedback action on the fuel valve, is slower than this rate of change of fuel properties, one of the mechanisms to reduce this rate of change is to buffer the fuel supply via an appropriately sized mixing vessel.

Based on the simple behaviour of a well mixed system, with a fixed volume V (m³) and volumetric flow rate G (m³/s), the step response of the system is given by :

$$C = C_2 - (C_2 - C_1) \exp\left(-\frac{Gt}{V}\right)$$

where C is the instantaneous concentration following a change in input concentration from C_1 to C_2 .

For a 250 MW turbine operating at 37% efficiency, the fuel flowrate for methane would be 13.5 kg/s. For a combustor operating at 20 bar and fuel at 25 bar supply pressure, the fuel density at ambient temperature is around 16.0 kg/m³ and the volumetric flowrate is then 0.84 m³/s. Allowing for the outlet concentration to rise to 95% of its changed value implies $G t / V = 3$ and, if a timescale for valve response t is set at 3 seconds, then a buffer vessel volume of 0.84 m³ is required. This is a modest volume at the normal operating pressures and provides a simple method to accommodate response time limitations of monitoring and control systems.

6.9.6 Examples of solution strategies to changes in WI

1. GE has implemented a solution for both composition variation of natural gas and vaporised LNG fuels as well as ambient condition variation. This solution, referred to as the OpFlex Wide Wobbe control system (Healey & Frederick, 2007), is based around a computer-based algorithm, which interprets the data provided by pressure, temperature and fuel flow rate, through a comprehensive understanding of the aero-thermal behaviour of the GT system. This understanding provides the necessary basis for adjusting the fuel flow rate and air/fuel ratio via other control elements such as IGVs and, since this response is algorithm based, it enables very short response times for control commands (e.g. 50 msec). The result is a wide tolerance to WI changes (20% quoted) and the ability to respond to WI rates of change of 18%/min.
2. Mitsubishi has developed an Advanced Combustor Pressure Fluctuation Monitor (A-CPFM), which detects flame instabilities arising from fuel heating value changes when operating under lean conditions (Koenke et al, 2006). This self-tuning system automatically adjusts the air bypass valve and fuel flows to maintain appropriate fuel/air ratios and has been demonstrated with 3 - 4% changes in fuel LHV.
3. Siemens has pursued a different approach by making a direct measurement of the Wobbe index using a fast response Wobbe index meter upstream of the combustion system (Nag et al, 2007). This is referred to as the Integrated Fuel gas Characterisation (IFGC) system. This measurement provides a feed-forward signal to the engine control systems to adjust fuel rates and air/fuel ratios in anticipation of the any change to the incoming fuel. The finite time required for the control hardware to respond is allowed for by the inclusion of a buffer tank between the meter and the combustor (as shown in Figure 3).

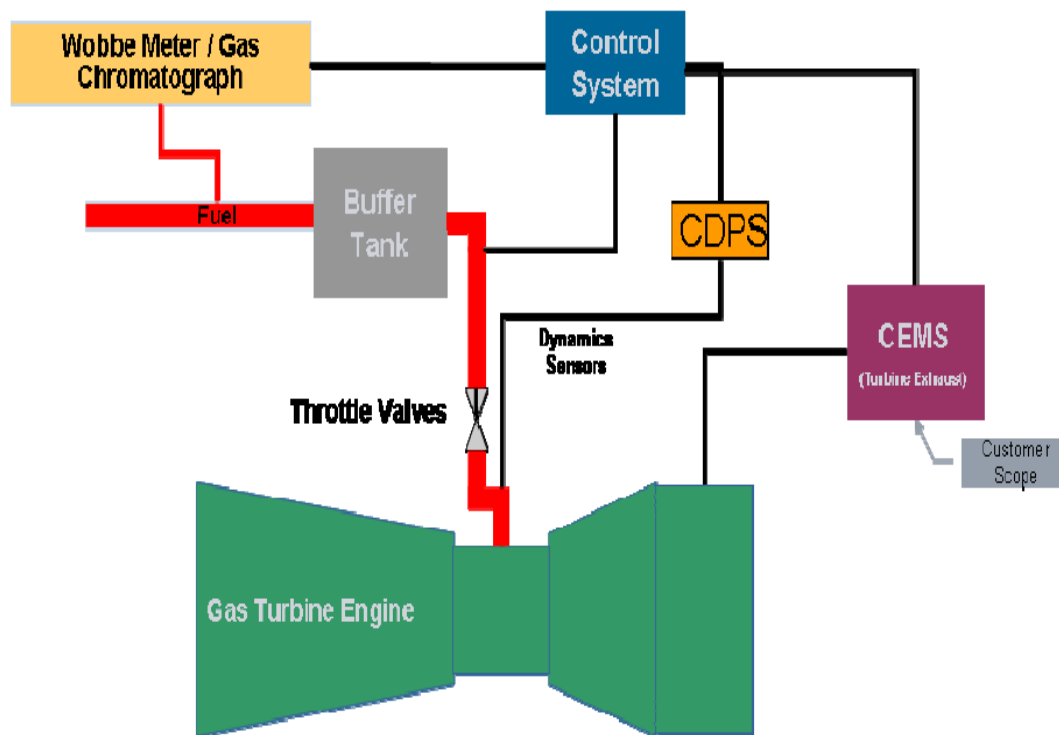


Figure 3: Schematic showing placement of buffer tank.

As shown in Figure 3, a gas chromatograph is also included alongside the Wobbe meter. In this case, the GC provides gas composition data in parallel but is not used for control purposes. In general, GC instruments can be used to calculate the Wobbe index but their response times are too slow to provide active control.

4. Given the slow response times of GC instruments, Alstom has pursued a different strategy by measuring the gas composition optically (Hansen, 2008). For a given fuel type such as LNG, where the possible components are well defined, i.e. C_1 , C_2 and C_3 , the fast response of an infrared (IR)-based measurement is well suited to engine control. Fortunately these hydrocarbons are IR active and have good component signatures enabling measurements on a millisecond timescale. For Alstom GT systems, the combustion system is particularly sensitive to C_2 and C_3 and the measurement of these provides the basis for direct intervention in the fuel control via active fuel staging between multiple fuel inlets to maintain flame stability and emissions control.

These strategies to deal with WI changes have been directed at LNG fuelled systems, since the pre-mixed nature of these requires greater attention to combustion stability. However, where similar concerns are to be avoided with hydrogen rich diffusion based combustion systems, a number of the above strategies are also valid. These include particularly fuel buffering, fast WI measurement, and real-time optical measurements for some of the fuel components (unfortunately IR measurement is not an option for hydrogen).

It is noted that existing practice with diffusion type combustion systems using high hydrogen mixtures indicates less concern with Wobbe index measurement due to the good stability of the flames within these combustors (Danner, GE, Private communication, 2012). Whilst WI may also vary for these fuels, providing that the variation is within the limits of operation of the fuel supply nozzles and controller, the existing feedback systems, which maintain turbine speed, are considered sufficient to cope with these.

6.10 FLAME DETECTORS

Flame detectors (optical) are frequently used for gas turbines, but they are prone to contamination and giving false readings. Thermocouples are often used, in the combustor burner and the GT interduct. A combination of crosschecking these thermocouples can diagnose flameout very quickly, and this has been successfully used in small GTs for about 20 years. Other systems include detection based on engine characteristics such as compressor pressure and power algorithms.

Recent improvements in flame detection, using a new range of SiC detectors, as opposed to the previous Geiger-Muller tube based designs, has resulted in a better matching of detector sensitivity range (peak at 275 nm) to flame radiation peak emission (310 nm) and better overall flame sensitivity. Quoted response times of 25 msec are much faster than any of the mechanical components of the control system that would respond to a flameout condition.

6.11 SUMMARY OF KEY FINDINGS

The main findings of this section may be summarised as follows:-

1. There is a wide range of hydrogen content in high hydrogen fuels depending on source and processing background and this presents a challenge in selecting a small number to represent possible deflagration scenarios.
2. It is recommended that for further study we increase the number of representative fuel systems from three to four, this will include three multi-component fuel systems plus an additional one of hydrogen and these reflect the range of hydrogen levels in common use. This choice is influenced by the likely dominance of these sources. Note that the current contract covers only three systems.
3. There is a significant body of experience by several GT manufacturers in operating high hydrogen and combined cycle systems.
4. Procedures for start-up and shutdown of GT systems are well established for natural gas systems.
5. The monitoring and protection arrangements for GT systems are well established for natural gas fired GT plant and most of these are transferable to H₂ rich systems.

6. Dual fuel systems are also well established and fuel transition procedures are robust.
7. High hydrogen fuels start up on natural gas (or propane) and use the same fuel transition principles.
8. Several options exist for monitoring variability in fuel properties and providing active control of the combustion system in response.
9. DLN combustor designs are used for premixed natural gas fuels. Diffusion flame combustors are currently used for H₂ levels above ~ 10%. Future systems may include undiluted non-diffusion concepts. The flame stability is much greater for these. However, it is noted that research programs continue to investigate possibilities for premixed combustion with higher hydrogen fuels with the aim of lower average temperatures and NO_x levels.
10. For some high hydrogen fuels, with normal air/fuel ratios, the exhaust can have H₂ levels above 5% in the event of a flameout.

7 REGULATORY REGIMES

In this section the various standards that have potential relevance to the safe operation of CCGT/CCGE/HRSG systems on high hydrogen fuels are identified and their key sections identified and discussed.

7.1 DEFINITIONS OF STANDARDS, REGULATION AND CODES OF PRACTICE

The purpose of regulations, standards and codes of practice is to ensure safe and reliable design and operation of a product or facility. The development of appropriate codes, standards and regulations will be essential when hydrogen becomes a significant energy carrier because they are required to establish a market receptive environment for commercialising hydrogen based products and systems.

Regulations give general legal requirements to ensure that the construction and use of a particular application is carried out safely. However, regulations do not say how this should be achieved in practice.

In the EU and UK, codes of practice and standards serve as guidelines and are developed typically by companies and associations to provide practical guidance. They support the free exchange of goods and services, and promote safety and common understanding. While standards are developed by standardisation organisations through a development process involving workgroups consisting of a wide range of interested parties, codes of practice may be developed by a few or only a single company or association. Because of the more rigorous development process, standards generally have a wider acceptance than codes of practice.

The notion of “Code” is used differently in the USA, where it refers to a standard or collection of rules made binding by a local or national government.

Unlike regulations, standards and codes are not legal documents; however standards may be included or referred to in regulations and through the regulation may be made legally binding. In some cases, standards are drafted to provide a means of compliance with regulations made to implement European Directives, in which case the standard is said to be harmonised with the regulation and becomes a harmonised standard. Compliance with a harmonised standard is one way to ensure compliance with the relevant regulations. In some cases, CEN and CENELEC, the European counterparts to the international standardisation organisations ISO and IEC, have adopted international standards and harmonised these with European Directives. The reason for the parallel structure is that the European standards can have a legal force in Europe as opposed to the international standards.

In addition to the European and international standardisation bodies, there are national bodies such as the US National Fire Protection Association (NFPA), the American Petroleum Institute (API) and the British Standards Institute (BSI), which are relevant for the construction and operation of hydrogen installations. Some national bodies have adopted standards from other national or international bodies; thus a standard may have different ID numbers or codes in different countries.

7.2 STANDARDS RE: SAFETY MANAGEMENT/CONTROL SYSTEMS FOR HIGH H₂ FUELS

This section examines those standards relating to risk and safety management issues arising from the use of high hydrogen fuels. It also examines the control of hazards and risk mitigation. Standards relating to those control systems that are applicable to fuels and high hydrogen fuels are also included in this section.

The standard ISO-PDTR-15916 (2010) entitled “Basic considerations for the safety of hydrogen systems” states that as hydrogen has inherent hazards, a hydrogen system or facility should have inherent safety features. Although not specifically referring to CCGT/CCGE systems, it is reasonable to interpret the standard as being applicable to these systems. The standard goes on to state that typical inherent safety features include fail-safe design, automatic and passive safety operation, caution devices and warning devices.

A fail-safe design involves measures such as redundant safety features (example.g. pressure-relief devices), back-up critical components and systems, fail-safe positions for valves and similar components (e.g. valves should automatically go to the safe position in the event of a power failure), and single-fault or dual-fault tolerance as needed, depending on the consequence of the hazard.

Automatic safety design includes features such as remote monitoring of critical information, remote operation and automatic limiting of operating conditions (e.g. pressure or flow rate) or automatic operation of appropriate equipment if hydrogen is detected. This would include operations such as: closing shutoff valves, turning ventilation on or off as appropriate and initiating appropriate shutdown operations.

A hydrogen system should include caution and warning devices as necessary to alert personnel in the event of any abnormal condition, malfunction or failure. Such devices should provide the personnel with adequate time to respond to the event.

In respect of the risks and safety management issues arising from explosive atmospheres generally, several standards have been developed for explosion prevention and protection. Part 1 of the relevant standard (BS-EN-1127, 2011) covers the basic concepts and methodology, including risk assessment and risk reduction methods. This standard is covered in more detail in section 8.3: Explosion prevention and protection.

The international standard (IEC-61508, 2010) entitled "Functional Safety of Electrical/Electronic/Programmable Electronic Safety-related Systems" is intended to be a basic functional safety standard applicable to all kinds of industry. It defines functional safety as: “part of the overall safety relating to the EUC (Equipment Under Control) and the EUC control system which depends on the correct functioning of the E/E/PE safety-related systems, other technology safety-related systems and external risk reduction facilities.” The standard covers the complete safety life cycle and needs interpretation to develop sector specific standards. It has its origins in the process control industry sector.

The technical standard (IEC-61511, 2003) and associated standards sets out practices in the engineering of systems that ensure the safety of an industrial process through the use of instrumentation. Such systems are referred to as *Safety Instrumented Systems*. The title of the standard is "*Functional safety - Safety instrumented systems*

for the process industry sector". The standard defines the functional safety requirements established by IEC-61508 (2010) in process industry sector terminology, while other standards (e.g. IEC-61511, 2003) focus attention on one type of instrumented safety system used within the process sector. The scope of IEC-61508 (2010) includes: initial concept, design, implementation, operation and maintenance through to decommissioning. It starts in the earliest phase of a project and continues through start-up. It contains sections that cover subsequent modifications, along with maintenance activities and the eventual decommissioning activities.

Integral to the above standards (IEC-61508, 2010; IEC-61511, 2003) is the concept of **Safety Integrity Levels** (SILs), which are defined as a relative or target level of risk-reduction provided by a safety function. In simple terms, SILs are a measure of the performance required for a Safety Instrumented Function (SIF). The requirements for a given SIL are not consistent among all of the functional safety standards. In the European Functional Safety standards based on the IEC-61508 (2010) standard, four SILs are defined, with SIL 4 being the most dependable and SIL 1 being the least. A SIL is determined by risk assessment based on a number of quantitative factors in combination with qualitative factors such as development process and safety life cycle management.

Two further related relevant standards that are harmonised to the machinery Directive are EN ISO 13849-1: 2008 "Safety of machinery. Safety-related parts of control systems. General principles for design" and EN 62061: 2005 "Safety of machinery. Functional safety of safety-related electrical, electronic and programmable electronic control systems". EN 62061 is based on the principles of IEC 61508 and uses the same terminology, but is restricted to electrical, electronic and programmable systems, whereas EN ISO 13849-1 is also applicable to pneumatic, hydraulic and mechanical safety systems. However it uses different terminology, with Performance Level instead of Safety Integrity Level.

A recommended practice (RP) publication (API-556, 2011), concerning the instrumentation and control systems for fired heaters and steam generators, is also available. It provides guidelines that specifically apply to instrument, control and protective system installations for gas fired heaters in petroleum production, refineries, petrochemical and chemical plants. It specifically excludes fired steam generators used to recover heat from combustion turbines. Nevertheless it does include some useful information concerning primary measuring and actuating instruments, controls, alarms and protective systems as they apply to fired heaters.

Guidelines for the selection or evaluation of heat recovery steam generator (HRSG) systems have also been provided (API-534, 2007). Details of related equipment designs are considered only where they interact with the HRSG system design. This publication does not provide rules for design, but indicates areas that need attention and offers information and description of HRSG types available to the designer or user to aid in the selection of an appropriate system. The HRSG systems discussed are those currently used in industry. Many of the individual features described in these guidelines are applicable to any type of HRSG system.

7.3 STANDARDS RE: SAFE HANDLING OF HIGH HYDROGEN FUELS

This section reviews the current standards information regarding the safe handling and storage of hydrogen and high hydrogen gas mixtures. It also reviews the potential explosive atmospheres and the potential consequences that can result .

The ISO technical report (ISO-PDTR-15916, 2010) referred to in Section 8.2 in respect of the inherent safety aspects covered, is primarily a guideline for the use of hydrogen in its gaseous and liquid forms as well as its storage in either of these or other forms (hydrides).

The report identifies the basic safety concerns and risks, as well as describing the properties of hydrogen that are relevant to safety. Detailed safety requirements associated with specific hydrogen applications are considered in separate International Standards. In respect of its applicability for the design and operation of CCGT/CCGE/HRSG systems, it provides basic information regarding the properties of hydrogen, identifying the associated hazards, particularly its deflagration/DDT characteristics, its flammability limits and its ease of ignition. All of these need consideration with regard to the use of hydrogen and high hydrogen fuels, especially in off design situations where the risk of flammable gases entering the exhaust streams is real and needs to be quantified.

A section in the standard refers to the use of hydrogen for power generation and highlights the importance of certain auxiliary components that provide essential support for primary functions such as:

- Hydrogen storage or a source of hydrogen.
- Fluid delivery lines to connect hydrogen to the reaction system.
- Flow controls.
- Pressure-relief systems that are incorporated into the design of the above mentioned components.
- Detection components.

The standard also points out that fixed-hydrogen systems must be located and served according to specific requirements found in locally relevant safety standards. These standards identify specific construction and materials requirements, as well as location for storage structures, based on the quantity of hydrogen, whether it is gaseous or liquid. Hydrogen designs should account for all possible circumstances anticipated during the life of the system's operation, and the designs should place the system in a safe state for all reasonable failure modes.

The standard states that the environmental effects arising from the use of hydrogen systems are anticipated to be benign. With very few exceptions, pure water is the only reaction product. The exception is air-breathing systems that combust hydrogen at high temperatures, such as gas turbines and gas engines, as they will produce unacceptable quantities of nitrogen oxides (NO_x) if steps are not taken to control them. The effects of hydrogen gas escaping into the atmosphere (e.g. boil-off gas from liquid storage) are negligible since the hydrogen will soon react with something else. Hydrogen is also very buoyant so that releases into the open atmosphere will rapidly disperse.

ISO-PDTR-15916 (2010) also emphasises the need to use only those materials that are suitable for hydrogen service and the conditions to which they will be exposed. Materials that are in contact with other materials should be both compatible with each other, and with hydrogen and the use conditions.

Material considerations for a hydrogen system involve both metals and non-metals (such as polymers and composites). Some of the considerations that are involved in selecting a material include: temperature effects, hydrogen embrittlement effects, permeability and porosity, and compatibility of dissimilar metals if used together.

A US standard referring to the properties, use, handling and storage of hydrogen is available (NASA-NSS-1740.16, 1997). Although cancelled in 2005, much of the basic information remains relevant and is either used or referenced in the ISO Standard (ISO-PDTR-15916, 2010).

7.4 STANDARDS RE: EXPLOSION PREVENTION AND PROTECTION

This section considers those standards that are applicable to the prevention and protection from explosions resulting from the presence of flammable atmospheres in enclosed spaces.

Several standards have been developed for explosion prevention and protection. Part 1 of the British standard (BS-EN-1127, 2011) covers basic concepts and methodology, including risk assessment methods and risk reduction techniques. It is applicable to any equipment, protective systems and components intended for use in potentially explosive atmospheres, under atmospheric conditions, and applies at all stages of their use. These atmospheres can arise from flammable materials being processed, used or released by the equipment, protective systems and components or from materials in the vicinity of the equipment, and/or from the materials of construction of the equipment.

The preventive and protective measures described in the standard will not provide the required level of safety unless the equipment, protective systems and components are operated according to their intended use and are installed and maintained according to the relevant codes of practice or requirements. The standard does specify general design and construction methods to help designers and manufacturers in achieving explosion safety in the design of equipment, protective systems and components. It does not apply, however, to the design and construction of systems containing controlled combustion processes, unless they can act as ignition sources in potentially explosive atmospheres.

The standard specifies methods for the identification and assessment of hazardous situations, through hazard identification, risk assessment and risk reduction, using the principles given by the relevant standard (ISO-12100, 2010): “Safety of machinery - Risk assessment and risk reduction.”

According to the standard, the safety of equipment, protective systems and components can be achieved by eliminating hazards and/or limiting the risk by using: (a) appropriate design (without safeguarding), (b) safeguarding, (c) information for use as supplied by the manufacturer, and (d) any other preventive measures. Measures in accordance with (a) prevention and (b) protection against explosions are dealt with in

Clause 6 of the standard, whilst measures according to (c) are dealt with in Clause 7 of the standard.

Another important standard (BS-PD-CEN-TR-15281, 2006) gives guidance on inerting for the prevention of explosions. It primarily covers the addition of inert gases to a flammable gas stream in order to render it safe. As such, it is of doubtful utility for the CCGT/HRSG or CCGE/HRSG systems of interest here due to the enormous quantities of inerting gas that would be required, together with the timescales involved. As noted in section 3.7.2 however, inert gas or water mist suppression in the exhaust system following an emergency stop or similar scenario may provide mitigation against explosion risks.

The standard NFPA-68 (2008) provides guidance for the design, location, installation, maintenance and use of devices and systems that vent the combustion gases and pressures resulting from a deflagration (as a result of ignition of a flammable gas) within an enclosure so that structural and mechanical damage is minimized. It should be used as a companion to NFPA-69 (2008).

The standard NFPA-69 (2008) on explosion prevention systems describes the minimum requirements for installing systems for the prevention of explosions in enclosures that contain flammable concentrations of flammable gases, vapours, mists, dusts or hybrid mixtures. This standard provides basic information for design engineers, operating personnel and authorities having appropriate jurisdiction and has several relevant sections about minimizing the risk and potential outcomes from deflagrations. Deflagration prevention and control for unoccupied enclosures seeks to prevent the rupture of the enclosure. Gas turbine acoustic enclosures are generally protected when necessary against explosions by ventilation systems designed and validated in accordance with ISO 21789 to ensure that the consequences of the ignition of any foreseeable accumulation of a dangerous fuel gas cloud are reduced to a safe level. Design criteria are given by Ivings et al (2004).

The determination of explosion limits and auto ignition temperatures of gases and vapours are covered by other relevant standards (BS-EN-1839, 2003; BS-EN-14522, 2005). The determination of explosion pressure and the rate of explosion pressure rise are covered by an additional document (BS-EN-13673, 2003).

The general principles for leak detection systems are also covered by BS-EN-13160 (2003). Performance requirements and test methods of stationary hydrogen detection apparatus designed to measure and monitor hydrogen concentrations are covered by an ISO standard (ISO-26142, 2010).

Equipment for use in potentially explosive atmospheres is covered by both the European and the international standardisation organisations. CEN covers the non-electrical equipment with part 1 of the relevant standard (BS-EN-13463, 2009), and has developed terms and definitions for equipment and protective systems intended for use in explosive atmospheres (BS-EN-13237, 2003).

Electrical apparatus to be placed in an explosive atmosphere is considered by the international standard series, IEC 60079 (2007) and the equivalent CENELEC standard series (BS-EN-60079, 2007). The relevant standards (BS-EN-60079, 2007) are divided into several parts, where the most relevant sections cover general requirements (part 0); classification of hazardous areas (parts 10-1); electrical installations in hazardous

areas (other than mines) (part 14); inspection and maintenance of electrical installations in hazardous areas (other than mines) (part 17); and repair and overhaul for apparatus used in potentially explosive atmospheres (other than mines or explosives)(part 19).

The CEN standard (BS-EN-ISO-4126, 2004) is harmonised with the Pressure Equipment Directive (PED) (ED-97-9-EC, 1999), and covers a variety of safety devices for protection against excessive pressure. When dealing with gaseous or liquefied hydrogen under pressure, the PED is applicable, but in addition, the ATEX directives are also applicable due to the potentially explosive atmospheres that may exist.

Since HRSG manufacturers are operating on the international market, different codes and legislative rules have to be considered. For HRSGs to be installed in EU countries, application of the PED has been obligatory since May 2002. As part of this approach the PED contains Essential Safety Requirements, which are defined in terms of general safety objectives. Although the European Committee for Standardisation CEN has the mandate to develop “harmonised standards”, which, when followed, will give a presumption of conformity with the directive, the HRSG manufacturer is under no compulsion to use them, since no design code specific to HRSGs exists.

The two European Directives for controlling explosive atmospheres (ATEX, 2006) describe the equipment and work activities that are allowed in an environment with an explosive atmosphere.

- Directive **99/92/EC** (also known as 'ATEX 137' or the 'ATEX Workplace Directive') gives the minimum requirements for maintaining better health and safety protection of workers potentially at risk from explosive atmospheres. The text of the Directive and the supporting EU guidelines are available on the EU website.
- Directive **94/9/EC** (ATEX, 2006) (also known as 'ATEX 95' or 'the ATEX Equipment Directive') on the approximation of the laws of Members States concerning equipment and protective systems intended for use in potentially explosive atmospheres. The text of the Directive and EU produced supporting guidelines are available on the EU website.

In the UK, Directive 99/92/EC is implemented by the **Dangerous Substances and Explosive Atmospheres Regulations 2002** (DSEAR, 2002). Similar legislation applies in each EU member state. The requirements of DSEAR apply to most workplaces where a potentially explosive atmosphere may occur. Some industry sectors and work activities are exempted because there is other legislation that fulfils its requirements. These exemptions are listed in regulation 3 of DSEAR.

DSEAR requires employers to eliminate or control the risks from dangerous substances. The main duties under DSEAR may be summarised as follows:

- To carry out a risk assessment.
- To eliminate or reduce risks from dangerous substances.
- To identify and classify places where explosive atmospheres may occur.
- To select appropriate equipment for use in hazardous areas.

Other duties include the verification of safe design, arrangements for dealing with accidents, incidents and emergencies, information, instruction and training, and the marking of hazardous areas, pipework and vessels.

Under DSEAR, employers must classify areas where hazardous explosive atmospheres may occur into zones. The classification given to a particular zone, its size and location, depends on the likelihood of an explosive atmosphere occurring and its persistence if it does. Schedule 2 of DSEAR contains descriptions of the various classifications of zones for gases, vapours and dusts.

The relevant standard (BS-EN-60079-10-1, 2007) provides guidance for assessing the extent and type of zone, and can be used as a guide to complying with the requirements of DSEAR. However, it cannot give the extent and type of zone in any particular case, as site-specific factors need to be taken into account. Furthermore, the standard is currently under revision and contains some significantly misleading guidance. In particular the methodology for the estimation of the effectiveness of ventilation by estimating the parameter V_z for excluding the need for classification is invalid. An alternative methodology has been published (Webber et al, 2011). This is of particular relevance to lower pressure applications (less than 20 barg gas) and therefore to gas engine installations.

7.5 STANDARDS RE: SAFE DESIGN AND OPERATION OF CCGT/CCGE/HRSG SYSTEMS

This section reviews the various standards and codes of practice that have some relevance to the safe design and operation of CCGT/CCGE/HRSG systems. The review considers mainly European and North American standards. It also includes those standards dealing with external enclosures housing the gas turbine or gas engine, which may, if not adequately ventilated, be at risk of unconfined/confined gas explosions.

Where there is the risk of a flammable atmosphere developing in an enclosed space, the usual practice is to seek to ensure that the general body is maintained below the LFL for the gas mixture in question. In the case of hydrogen or high-hydrogen fuels, which may for whatever reason enter the exhaust stream without combusting (i.e. an engine flameout), then the hydrogen gas concentration should not be allowed to exceed a fraction of the LFL, typically 25%, although occasionally an excursion does occur. Some means of mitigation may therefore be required, as clearly such a limitation as this cannot be met in practice following a flameout.

A code that provides for the safe design and operation of these systems is provided via the Boiler and Combustion Systems Hazards Code (NFPA-85, 2011). The code is intended for natural gas or similar fuels. Although it does not specifically state that it applies to high hydrogen fuels, it contains useful and relevant guidance taking the characteristics of the fuel into account.

The section dealing with installing and commissioning specifically states that the boiler, HRSG, engine exhaust system, or pulverized fuel system shall not be released for operation before the installation and checkout of the required safeguards and instrumentation system have been successfully completed.

It also requires that the party responsible for the erection and installation of the equipment ensures that all pertinent apparatus is installed and connected in accordance with the system design, and that the owner or owner's representative, the engineering consultant, the equipment manufacturer and the operating company prohibit operation until the safeguards have been tested for correct operation as a system. After installation but before initial operation, coordinated tests of all systems are to be undertaken, and documentation of the plant equipment, the system and maintenance activities updated to reflect changes in the status of equipment and operating procedures.

The standard NFPA-85 (2011) also states that the fuel-burning system shall function to convert continuously any ignitable input into unreactive products of combustion at the same rate that the fuel(s) and air reactants enter the combustion chamber. The fuel-burning system shall also be sized to meet the operating requirements of the unit and be compatible with other component systems.

It also requires the flue gas ducts, fans and stack are sized and arranged to remove the products of combustion at the same rate at which they are generated by the fuel-burning process during operation of the unit.

Section 8 of the standard NFPA-85 (2011) "Heat Recovery Steam Generators and other Combustion Turbine Exhaust Systems" applies to all fired and unfired HRSG systems or other combustion turbine exhaust systems and their associated combustion turbines, but does not dictate the methods or details of the combustion turbine manufacturer's product or control system. It identifies specific functional considerations for proper interfacing related to the safety aspects of the combined combustion turbine and the HRSG or other combustion turbine exhaust systems, with the express purpose of:

- Contributing to operational safety.
- Preventing explosions, implosions and uncontrolled fires in HRSG sections and other exhaust system ductwork.
- Establishing minimum requirements for the design, installation, operation and maintenance of heat recovery steam generators and their fuel burning, air supply and combustion products' removal systems.
- Coordinating operating procedures and components, control systems, interlocks and structural design.
- Establishing training programs in equipment operation and maintenance, for both new and existing personnel, to ensure that minimum standards for operation and maintenance are understood and followed.

Sub-section 8.5.1 of the standard requires the HRSG or other combustion turbine exhaust systems to be sized and arranged to maintain combustion turbine exhaust gas backpressure within design limits and to remove the products of combustion at the same rate that they are generated by the fuel-burning process during operation of the unit. The HRSG enclosure or other combustion turbine exhaust systems is to be capable of withstanding the design pressure without permanent deformation due to yield or buckling.

This sub-section also requires that there is expansion provision for the movement of the combustion turbine exhaust duct, the HRSG enclosure and other combustion turbine exhaust systems. These expansion joints shall withstand at least the highest design pressure for which they are designed.

The Appendices to this standard (NFPA-85, 2011) recognise and comment on the complexity of CCGT/HRSG systems and the limitations of the code. The simplest combined cycle plant automatically has certain hazards that are common to all designs. Coupling various designs of heat recovery units with combustion turbines of varying characteristics in different configurations (such as varying damper arrangements) can produce unique hazards. The code recognises both the potential ineffective use of the combustion turbine as the source of the purge and potential sources of substantial fuel entering the HRSG from normal and false starts, stating that these are major considerations that need to be addressed.

The standard lists numerous conditions that can arise from operation of a system that produces explosive conditions. The most common of these, which are also taken into account in Section 11.4.1, are as follows:

- Interruption of the fuel or air supply or ignition energy sufficient to result in momentary loss of flames followed by restoration and delayed re-ignition of an accumulation.
- Fuel leakage into an idle combustion chamber and the ignition of the accumulation by a spark or other source of ignition.
- Repeated unsuccessful attempts to light off without appropriate purging, resulting in the accumulation of an explosive mixture.
- Accumulation of an explosive mixture of fuel and air as a result of loss of flame or incomplete combustion and the ignition of the accumulation by a spark or other ignition source, such as could occur when an attempt is made to relight a burner(s).
- Purging with an airflow that is too high and stirs up smoldering combustible materials.

The code suggests that improved instrumentation, safety interlocks and protective devices, proper operating sequences, and a clear understanding of the problems by both designers and operators can greatly reduce the risks and actual incidence of explosions.

In the final Appendix to this standard (NFPA-85, 2011), differences in the operation of the HRSG combustion turbine system compared with a conventional multiple burner boiler are discussed. Some of these are as follows:

- The combustion turbine is an internal combustion engine. The engine burns a lean mixture of fuel with compressed air. The hot, pressurised combustion gases expand from the combustor through a series of rotating turbine wheel and blade assemblies, resulting in shaft power output and hot turbine exhaust gas discharge to the HRSG. Turbine exhaust gas is hot and has reduced oxygen content relative to air.

- The design of the HRSG differs from that of a regular steam generator in that, in most cases, the HRSG is designed to utilise the residual heat from the combustion turbine exhaust gas, with some supplementary firing by the duct burner, if necessary.
- Because the combustion turbine is a volumetric machine, combustion turbine exhaust gas is discharged within closely prescribed limits, with the oxygen content varying as a function of load.
- Separate purge requirements exist prior to combustion turbine light-off and prior to duct burner light-off.
- Air-fuel ratios controlled by duct burners are not recommended. As vast quantities of turbine exhaust gases far in excess of the theoretical air requirements of the fuel are utilised, fuel-rich conditions cannot inherently occur under normal controlled operating conditions.
- Many types of burners are available for HRSG systems. The burner can consist of a number of parallel tubes or runners placed in the duct to provide the required heat release. This is commonly used for gaseous fuels and is referred to as a grid burner. Alternatively, wall-mounted burner systems with parallel flame holders in the duct can be used for liquid fuels.

A similar code to NFPA-85 (2011) can be found in the Australian Standard for Industrial and Commercial Gas-fired Appliances (AS-3814, 2009). This standard seeks to provide minimum requirements for the safe operation of gas-fired industrial appliances and other large appliances for commercial applications, which are not covered by other standards. It should not be regarded as a design specification or as an instruction manual in the UK as it has been based on the gas rules and regulations currently in force in Australia. It can be taken as applying to gas turbines in as much as it defines a forced draught burner as one where the combustion air/oxygen are provided under pressure, and similarly for a gas engine where suction by mechanical means is provided. The bulk of the standard does not apply to CCGT/CCGE systems where the exhaust gases are used for steam generation in a HRSG, as it assumes that the exhaust gases are vented directly in accordance with the Australian standard for flues.

The standard suggests that explosions are the main hazard on the firing side of the equipment, the basic cause being ignition of a combustible mixture in the combustion chamber or associated ductwork. The magnitude and intensity of the explosion depends on both the quantity of combustibles present and the proportion of air with which they are mixed. The standard states that explosions may be the result of one or more of the following:

- Improper design of equipment or control systems.
- Equipment or control system malfunction, including valve leakage.
- Interruption and restoration of gas or air supply causing loss of flame followed by delayed ignition of the resultant accumulation of a combustible mixture.
- Flame failure on a burner and subsequent ignition of the resultant accumulation of a combustible mixture.

In the current edition of the standard, several sections have been expanded to cater for changing technology; e.g. the use of LEL monitoring or the inclusion of systems that are commonly found on gas-fired turbines that were not previously covered adequately. The appendices have also been expanded to cover information on maintenance of appliances, the configuration of gas/air ratio control systems as well as valve train requirements for gas-fired turbines.

The current version also has a section (3) dealing with engine start-ups including the ignition procedures/sequences to be followed. It is not clear whether this section is intended to apply to the CCGT/CCGE systems of interest for this review, but a section dealing specifically with the start-up gas rate does impose some restrictions on the gas concentrations at start-up. For instance, during start-up the percentage of gas in the exhaust mixture must not exceed a specified percentage of the LEL of the gas in question. For propane, 25% of LEL is specified at 13% stoichiometric. This may have unintended consequences for running gas turbines and gas engines on hydrogen or high hydrogen fuels.

The current version also has a section (5.8) that applies specifically to gas engines and gas turbines, where the latter comply with the relevant British Standard (BS-ISO-21789, 2009).

Section 5.8.3 mentions HRSGs under turbine purging. Thus where a heat recovery system is installed and there is supplementary firing fitted, it is acceptable to purge with turbine exhaust gases provided that under all load conditions, the temperature of the purge gases does not exceed 450 °C for natural gas or 80% of AIT for other fuels, and the temperature is interlocked. Where the heat recovery system is initially purged prior to a turbine start up, provided that a leakage detection system is fitted to the supplementary firing burners, then re-purging is not required. The integrity of the safety shut off valves must be checked prior to a start up of the supplementary burners.

Section 5.8.11 (Extinction Safety Time) does have interesting criteria for shut down times. Thus on loss of flame, the flame detection and gaseous fuel shutdown system shall have a combined maximum response time (extinction time) of no more than 3 seconds or shall limit the release of unburned gaseous fuel to an amount that prevents damage to the plant or injury to personnel. Where the shutdown time exceeds 3 seconds, calculations shall be provided to ensure compliance with the intent of this clause.

An ASME code (ASMEPTC4.4, 2009) is applicable to gas turbine steam generators. The code establishes procedures for conducting performance tests on heat recovery steam generators used to recover gas turbine exhaust energy. The HRSG may include supplementary burners. The code is intended for determining the performance of HRSGs using what are currently considered good engineering practices. Sections 5-3 and 5-4 are useful in the context of this review as they give the gas flow equations for obtaining the HRSG and gas turbine energy balances respectively.

Another similar ASME code is applicable to IGCC power plants (ASMEPTC47, 2007). As with ASMEPTC4.4 (2009), this code provides procedures for performance testing of integrated gasification combined cycle power plants to determine fuel gas flow and quality, thermal efficiency (heat rate) and power output at specified operating conditions. The code also covers a defined range of primary fuel characteristics but is limited to those IGCC systems using gas and steam turbines.

In the UK, the HSE publishes various Codes of Practice (COPs) and guidance notes relating generally to safety in the process industries. One such document relevant to this review is HSE guidance note HSEPM84 (2003), which deals with the control of safety risks at gas turbines used for power generation. Santon (1998) provides some further information about explosion hazards.

The guidance is aimed at manufacturers, suppliers and operators of gas turbines (GTs) used for electrical power generation. The guidance draws attention to the associated hazards and describes ways in which the risks can be eliminated or reduced to an acceptable level. It also recognises that hydrogen and biogas derivatives (including waste streams produced on site) are increasingly being used. The choice of fuel is considered to depend on commercial and environmental considerations. The guidance note recognises that each type of fuel has its own particular hazards arising from its physical and chemical properties.

The guidance is primarily aimed at the hazards arising from the high-pressure fuel supply to the gas turbine as well as from the enclosures in which the gas turbine may be housed. It does not specifically cover any hazards arising from the presence of flammable mixtures in ductwork downstream of the turbine exhaust and connecting it to an HRSG. It does, however, recognise the explosion hazards that may arise in enclosures, suggesting means of mitigation based on limiting the size of the detectable flammable gas cloud.

The guidance states that explosions occurring within fired plant at start-up, due to the ignition of accumulated fuel, are a well-recognized hazard and measures should be adopted to control this hazard. Such measures should include adequate gas path purging (at least three volume changes) before start-up, a high standard of isolation to prevent leakage during shutdown and a controlled duration for attempted ignition based on flame or combustion detection. These precautions are normally inherent within the GT control package provided by the manufacturer.

The guidance also states that for those hazards identified by a risk assessment and which are addressed by precautions inherent within the GT control package, safety-related systems should be identified, specified, implemented, tested and maintained in accordance with the principles of relevant standards (IEC61508, 2010; IEC61511, 2003) as appropriate.

7.6 STANDARDS RE: SAFE OPERATION OF GAS TURBINES

This section examines those standards dealing with the safe operation of gas turbines in CCGT/CHP systems.

The current international standard for non-motive gas turbine safety (BSISO 21789, 2009) contains a set of recommendations for the safe design of gas turbines. It covers the safety requirements for gas turbine applications using liquid or gaseous fuels and the safety related control and detection systems and essential auxiliaries for all types of open cycles (simple, combined, regenerative, reheat, etc.) used in onshore and offshore applications, including floating production platforms. It details the anticipated significant hazards associated with gas turbines (based on the requirements of the Machinery Directive in anticipation of harmonisation, which is currently in progress) and

specifies the appropriate preventative measures and processes for reduction or elimination of these hazards. It addresses the risks of injury or death to humans and risks to the environment.

Gas turbine packages are generally specified using international and national standards. Safety is promoted using additional safety codes and standards, which are relevant for gas turbines and other technologies. The standard approaches gas turbine safety from an international perspective based on the content of existing recognised ISO and IEC standards to the greatest extent possible. Where no ISO or IEC standard exists, other codes or standards (such as EN, NFPA, etc.) are included.

Section 4 of this standard lists the significant hazards associated with gas turbines and indicates the corresponding preventative measures that should be used to reduce or eliminate the risks. Fire and explosions are key hazards that are listed, and in respect of this review links to Section 5.11.3, extinction safety time. This states that on the loss of flame, the flame detection and fuel shutdown systems shall have a combined maximum response time that limits the release of unburned fuel to an amount that prevents dangerous consequences.

Section 5.9.7 of the standard deals with the hazards of recirculation and specifically with the avoidance of flameout.

In respect of explosion protection, Section 5.12.4 states that: “where the potential exists for the exhaust system to contain an explosive atmosphere, or gases or vapours that can create an explosive atmosphere, the exhaust system shall be purged before gas turbine start-up. The purge flow rate should be sufficient to minimise un-purged voids. At least three complete volume changes of the gas turbine and downstream exhaust system equipment shall be undertaken. The volume is measured up to the base of any main chimney or to that point where, under all load conditions, the exhaust gas temperature of any flammable gases or vapours that can be present is below 80 % of the AIT, measured in degrees Celsius.”

The standard also discusses explosion controls, referring to preventing an explosion from attaining its maximum explosion pressure through either injecting extinguishing agents (BS EN 1127, 2011) or using explosion relief panels sized in accordance with the relevant standard (NFPA68, 2008).

The standard also refers to the application of SILs to protection systems, although it is less onerous in this context than alternatives (e.g. HSE PM 84, 2003); it states that “where this International Standard states that the risk of a potential hazard shall be reduced to a tolerable level, and that hazard is associated with a safety related control function in conjunction with the associated system components, a qualitative or quantitative risk assessment method shall be applied for the events to define the corresponding safety requirements and/or safety integrity level (SIL) of the protection system.”

The international standard (BS ISO 3977, 2004) is related to the design and procurement of gas turbine system applications and is based primarily on the ASME 133 series on gas turbines, as well as related standards (API 616, 2011; API 11PGT, 1992). The standard environmental design point of any gas turbine system is 15°C, 60% relative humidity and sea level elevation. The standard is divided into nine sub-

sections and covers procurement, design requirements, installation and reliability. It contains relatively little safety related information.

An American Petroleum Institute standard (API 616, 2011) gives the minimum requirements for open, simple and regenerative-cycle combustion gas turbine units for mechanical drive, generator drive or process gas generation. All auxiliary equipment required for operating, starting and controlling gas turbine units and for turbine protection is either discussed directly in the standard or referred to in other publications. Specifically, gas turbine units that are capable of continuous service firing gas or liquid fuel or both are covered by the standard. It also applies to both industrial and aero-derivative gas turbines.

As is the case with most API publications, the standard is published as an aid to the procurement of standardised equipment and materials. Consequently it concentrates upon the design and performance requirements of gas turbines. It has little to say about the main subject matter of this review except under Section 5.8: Fuel System, where it refers to the fuel flow control valve being designed and positioned to control the fuel flow to the gas turbine under all reasonably foreseeable operating conditions. It requires a second device to ensure tolerable fuel flow should failure of the primary valve lead to a dangerous situation. It also refers to the need for two shut-off valves positioned to cut off the fuel in the event of a dangerous situation arising that could result in a dangerous failure of the gas turbine. Dangerous is not however defined in this context.

The standard IGEM/UP/9. Edition 2 (2010) is published by the Institution of Gas Engineers and Managers (IGEM). It covers the application of natural gas and fuel oil systems for firing gas turbines and their interactions with gas and oil firing for supplementary and auxiliary fired burners. Whilst it therefore primarily deals with natural gas and oil fuels, it considers gas safety issues in more detail than other standards and many of its recommendations (such as those dealing with isolation and purging) are relevant to all gaseous fuels. The risk of an exhaust system explosion is noted and pre-purge is given as the preventative measure. A substantial section of the standard describes this process and the associated limitations. The requirements are similar to and build on those of ISO 21789. Specifically IGEM/UP/9 requires a purge prior to every ignition attempt, whilst ISO 21789 permits this to be omitted subject to risk assessment. In addition, IGEM/UP/9 requires that where a plant by-pass is fitted, the sequential operation of dampers shall be proved to ensure that the purge has been performed correctly. (Note that damper linkage failure was the cause of an exhaust over-pressurisation incident.)

7.7 STANDARDS RE: SAFE OPERATION OF GAS ENGINES

This section examines those standards dealing with the safe operation of gas engines in CCGE systems.

There are at least three relevant general standards and several related marine based standards.

EN 12601, "Reciprocating internal combustion engine driven generating sets. Safety" is a wide ranging standard harmonised to the Machinery Directive. It deals superficially with all the hazards associated with this type of machinery, in many cases by reference

to other standards. Fire hazards are limited to liquid fuel hazards, and explosion risks are not mentioned.

The scope of IGEM/UP/3, "Gas fuelled spark ignition and dual fuel engines", published by IGEM, is restricted to 1st family (Town Gas), 2nd family (Natural Gas) or 3rd family (LPG) gases as fuel, although it may be appropriate for other gases taking their characteristics into account. It is therefore appropriate to consider it as a minimum standard for application to high hydrogen fuels taking the relevant fuel properties such as density, flame speed and energy content that may affect safety into account. It contains the following sections:

- Engine installation;
- Gas supply pressures and pipework;
- Facilities for testing and purging during commissioning;
- Venting;
- Area classification (by reference to other publications);
- Air supplies for cooling combustion and ventilation;
- Exhaust system requirements;
- Essential (safety) system requirements;
- Engine design and operation;
- Ancillary equipment.

The following measures stated in the standard are all relevant for high hydrogen fuel applications.

The standard requires a pre-start exhaust system 3 volume purge, and in common with other gas utilisation equipment, isolation by means of two safety shut-off valves, with valve proving at every shut-down and/or start-up for systems of over 1.2 MW throughput. (This is not optional as it is in the relevant standard BS ISO 21789 (2009) in relation to GTs.) Shut-off pressures and valve closure times are specified. (A maximum of one second is specified for valves up to 100 mm nominal bore, and a maximum of up to three seconds for larger valves.)

IGEM/UP/3 requires spark ignition circuits to remain in operation on shutdown to clear gas/air mixtures from the engine and exhaust, and start-up to be delayed until hot surfaces have cooled following a shut-down.

In addition, IGEM/UP/3 recommends that "consideration shall be given to the application of temperature monitoring of cylinder exhausts, of detonation-sensitive monitoring systems, etc. that are able to detect any failure of gas inlet valves, exhaust valves or fuel injectors that might lead to an explosion or fire in the exhaust system."

IGEM/UP/3 requires that "to prevent unburnt gas from entering the exhaust system, the air/fuel ratio control system shall maintain the ratio to within the flammability limits for the particular fuel being used during steady start-up, operation and during speed or load transients."

Other recommendations include overall safety measures regarding control and operation.

The DNV STANDARD 2.11 (Det Norske Veritas, 1999) is a short standard designed primarily for marine applications, but is not specifically restricted to them or to any specific gas. It is relevant to land installations. It deals with dual fuel engines whereby

pilot oil is injected into gas used in compression ignition engines, as well as gas-only spark ignition engines. In the latter case, it specifies the following precautions designed to mitigate the risk of an explosion in the exhaust.

The starting sequence must be such that fuel gas is not admitted to the cylinders until ignition is activated and the engine has reached a minimum rotational speed. If the engine monitoring system has not detected ignition within ten seconds of opening of the gas injection valve, the gas supply is to be shut off automatically and the starting sequence terminated.

When restarting after a failed start attempt, admission of fuel gas to the cylinders is not to be possible before the exhaust gas system has been purged with a volume of air at least equal to 3 times the volume of the exhaust gas system before the turbocharger(s). Purging may be carried out through e.g. running the engine on starting air for a predetermined number of revolutions.

The exhaust receiver is to be equipped with an explosion relief vent of sufficient dimensions to prevent excessive explosion pressure in the event of ignition failure of one cylinder followed by ignition of the unburned gas in the receiver. The explosion venting is to be led outside the machinery space.

As an alternative to explosion venting, documentation may be accepted showing that the exhaust system has sufficient strength to contain the worst-case explosion without damage. Compliance with these requirements would be difficult, if not impossible, for machines operating on hydrogen based fuels with detonation potential.

The DNV standard is particularly onerous with respect to (in effect) area classification and the requirements for protected electrical equipment and double walled fuel pipework. These requirements are not normally met.

Germanischer Lloyd (GL) (2011) classification rules, chapter 6, section 16, "Use of Cargo as Fuel" contains relevant requirements similar to the DNV code. Fuel is required to be in double walled pipework or a ventilated duct. Fuel isolation by double block and bleed is specified, but the higher standard of valve proving is not required. Explosion relief for both inlet and exhaust systems is required.

The maritime IGC-Code (2010) prescribes the design and constructional standards of bulk LNG carrying ships and the equipment they should carry. Chapter 16 contains provisions for using boil-off gas from LNG cargoes as fuel for boilers, gas turbines and internal combustion. For the use of methane boil-off gas from LNG cargoes as an engine fuel, dual fuel engines are mandatory.

The code gives several precautions that are designed to mitigate the risk of an explosion in the exhaust. Gas nozzles should be fitted in such a way that the flame of the oil fuel burner ignites the gas fuel. A flame scanner should be installed and arranged to ensure that gas flow to the burner is cut off unless satisfactory ignition has been established and maintained. An installation should be provided for purging the gas supply piping to the burners by means of inert gas or steam, after these burners have been extinguished. Arrangements should be made that, in case of flame failure of all operating burners for gas or oil or for a combination thereof, the combustion chambers of the boilers are automatically purged before relighting. Arrangements should also be made to enable the boilers to be manually purged.

Interestingly, the Chinese Classification Society version of the document “Rules for Construction and Equipment of Ships Carrying Liquefied Gases in Bulk”, includes an additional requirement, namely that the exhaust gas, scavenging and air inlet manifold are to be protected against explosion in the event of failure of timing mechanism or extinguishing of the cylinder. The relief valves against explosion, if fitted, are to be so arranged as to discharge to atmosphere in a safe location.

Other marine classification societies also publish relevant rules for gas-fired engines for marine use. It is understood that the requirements are all generally based on the IGC code, with some individual variations.

In addition to the above, VISA is an institution that makes guidelines and safety requirements for natural gas-fired applications in The Netherlands. Parts C-1 / C-7 "Richtlijnen voor het gebruik van aardgas in gasmotoren" (Guidelines for the use of natural gas in gas engines) and Parts C-8 / C-14 "Veiligheidsvoorschriften voor aardgasmotoren" (safety requirements for gas engines) are relevant and are used by the gas engine industry.

8 DISCUSSION

This section discusses and appraises the various documents reviewed in the previous sections. The key findings with their implications for the project are discussed. Significant conclusions can only be arrived at after the results of WP2, Task 1 are available.

8.1 RE: FUEL TYPES AND SOURCES

The fuel systems proposed are simplified generic models of three common categories of fuel types currently in use that cover the range of source energy contents. The options of variable fuel oxidant ratios and dilution with air or nitrogen extend the range of practical fuel mixes.

8.2 RE: COMBUSTION PROCESSES

Consequences of known and recorded general and specific aspects of combustion of these fuel systems have been reviewed. The relevant characteristics and hazards of their use, particularly in the areas of deflagration and DDT, for CCGT and CCGH energy production and therefore for the model situations of WP2, Task 2 and 3 have been highlighted in this review.

8.3 RE: SCALING

The techniques for scaling and their application have been considered in Sections 4 and 5. However the issue of overpressures can only be discussed once the critical mixture make-ups, the temperature conditions, the nature of the combustive or explosive character and the most hazardous locations in (model) duct configurations have been better identified by the findings of WP2, Task 1.

The results from Task 1 (and possibly some of task 2), may also influence the structural strength requirements of the Task 3 test rig, should the results suggest that there is a possibility of exceeding the current maximum design pressure of the Task 3 test rig. A recently agreed contract variation will enable more accurate predictions to be made of the maximum design pressure of this rig with a view to producing the most economical design.

8.4 CURRENT INDUSTRIAL PRACTICES

A large body of literature has been reviewed, and the main conclusions regarding current industrial GT practice have been indicated.

The well-established practices developed for natural gas burning have been applied where possible to high hydrogen systems. Good practices, such as system purging, N₂ blocking of inactive lines are well established and the manufacturers are confident about the robustness of the procedures. Whilst human error remains a possible cause for hazardous incidents, the main risk scenarios associated with start-up and shutdown are automated. The likelihood of possible ingress of any hydrogen rich fuel into exhaust ducts is thereby minimised by the use of such features as alternative start-up fuels, fired shutdowns etc.

8.5 RE: SAFETY AND REGULATORY REGIMES

This section discusses the many issues arising from the foregoing examination of the standards discussed in Section 9. In particular it discusses their relevance and shortcomings with respect to the future safe use of high hydrogen fuels in CCGT/CCGE/HRSG power plants.

8.5.1 Safety management systems

Safety management systems described in the literature, standards or legislative texts are mostly generic in nature. They may apply to suppliers and/or users of equipment. For example, ISO-9001 (2008) provides a certified basis for quality which is increasingly regarded by many customers as a pre-requisite qualification for their suppliers and which would have general implications for gas turbine and gas engine suppliers, including suppliers for high hydrogen applications. The novelty and perceived enhanced hazards of such applications may encourage use of this standard as a criterion for suppliers. There are however no directly relevant industry-specific derivatives of the standard relating to gas turbines or gas engines.

Risk assessment is frequently recommended by safety related standards and required by legislation. In the UK, regulations such as the Management of Safety Regulations and DSEAR require risk assessments to be carried out by users in general terms or specifically in relation to explosion hazards respectively. Standards such as ISO-14121-1, 2007, EN 1127-1, 2001, DSEAR, 2002 and the HSE publication (HS(L)21, 2009) provide relevant guidance.

The HSE guidance (HSE PM 84, 2003) on the “Control of safety risks at gas turbines used for power generation” recommends that both suppliers and users should apply risk assessment methods. It includes statements, which are equally relevant to the use of high hydrogen fuels in gas engines.

In the evaluation of new and less well-defined hazards, risk assessments are both more difficult but more necessary. The gas turbine applications safety standard (ISO-21789, 2009) applies to the suppliers of equipment and discusses risk assessment at clause 5.2 in terms that are equally relevant to gas engines.

Thus in summary, the use of Safety Management Systems is a legal requirement that applies to power generation activities irrespective of the fuel used. Undertaking appropriate risk assessments is key to the safe operation of such activities and to ensuring compliance.

8.5.2 Safe handling of high hydrogen fuels

As discussed in Section 8, ISO has issued a technical report (ISO/PDRT-15916, 2010) that deals with the issues relating to the safe use and handling of hydrogen, which can also be applied to high hydrogen fuels. It provides a comprehensive listing of the properties of hydrogen emphasising its very low ignition energy, its relatively low AIT, wide flammability limits, high flame speed and incompatibility with certain materials. All of these properties are important in appreciating the potential hazards if flammable high hydrogen mixtures are allowed to enter the confined volume of the exhaust stream and the HRSG. Clause 7.7 contains a concise and valuable summary of good practice in “Recommended practices for organisations”. It deals with areas including

organisational policies and procedures, hazard assessment, design, safety and operational reviews, maintenance and quality control programmes, and training.

The report recognises the numerous potential applications for hydrogen referring specifically to fuel cells, *internal combustion engines, gas turbines, and all applications that use these components*. It also recognises the applicability to CHP units to produce electricity (and heat) on demand and notes that such systems may be further integrated and used to stabilise power grids and to capture waste heat for heating or industrial processes.

The report also emphasises the need for an inherent safety approach to the design of systems, and by way of an example, places a requirement on the supplier to provide protection against over-pressurisation within the system. It states that vessels and piping that confine or potentially confine hydrogen should be protected with a pressure-relief system.

The report considers excessive pressures arising from explosions and the need for explosion relief, as the deflagration/detonation potential is recognised and discussed. However, if the potential for deflagration and detonation cannot be eliminated, then hydrogen system design and operations should take into account the possibility of their occurrence. This includes designs with sufficient strength to withstand the high pressures or remote operation in order to protect facilities and personnel. There is an understanding that explosion relief may not be feasible in some circumstances because of the very high flame speeds involved.

The information contained in this technical report is broad, general and attempts to cover all aspects of hydrogen safety. The degree to which the guidelines are applied will vary according to the specifics of the application (such as the conditions and quantity of hydrogen involved, and the way in which the hydrogen is used). Industrial users should find that large portions of the guidelines are applicable to their particular operations, i.e. gas turbine manufacturers. The report provides sufficient information for equipment manufacturers to achieve the appropriate levels of safety through design, coupled with appropriate care in installation. The manufacturers should also use the guidelines to ensure that they provide sufficient specific information for the users to operate them, in the environment for which they are intended.

It is also worth pointing out that hydrogen has been used safely by industry for many decades in many different applications, particularly in aerospace applications as, NASA-NSS-1740.16, 1997 refers. Its use should not present any insurmountable problems, despite the potentially large quantities hydrogen involved.

8.5.3 Explosion prevention and protection

This review of legislation and standards with specific reference to the potential for an explosion in the downstream plant when operating on high hydrogen fuels indicates that the ATEX workplace directive is the major piece of legislation relevant to CCGT and CCGE applications. It was implemented in the UK by the DSEAR Regulations and by similar regulations in other EU Member States.

Assuming that a reasonably practicable regime can be provided to protect against injury with respect to the regulations and the general requirements of the Health and Safety at Work etc Act (1974) (HSWA), there remains a risk of equipment damage as a result of an explosion in the downstream plant.

The standard NFPA 68 (2008) is often used as an authoritative basis for explosion relief design. It was first published in 1945 and has been revised frequently as the technology of explosion relief sizing and design has advanced. It has been approved as an American National Standard. An alternative harmonised European standard for gas explosion venting is BS-EN 14994 (2007), compliance with which ensures compliance with DSEAR. A harmonised standard, which specifies requirements for explosion-pressure-resistant and explosion pressure shock-resistant equipment, is BS-EN 14460 (2006).

The Machinery Directive, implemented in the UK by The Supply of Machinery (Safety) Regulations and by similar regulations in other EU Member States, contains general requirements relating to fire and explosion risks. Depending upon the extent of supply and the extent to which the assembly of equipment has therefore been CE marked as compliant with the Directive, these requirements may apply to the hazard of an explosion in the exhaust systems of CCGT and CCGE applications and therefore may have an overall legal certification relevance to the mitigation of such risks.

The only viable protection for most of the plant and systems downstream from a gas turbine or gas engine is explosion relief, although this is probably impractical with the very large HRSG designs currently in use and unlikely to be effective against a detonation. However, explosion-pressure-resistant design may be suitable for smaller gas engine exhaust pipes. It is often used for gas engines, in particular for marine applications as required by classification society rules and, in other cases, as a result of the risk assessment depending upon the fuel and/or location of the plant.

8.5.4 Safety design and operation of CCGT/CCGE/HRSG systems

Six codes were identified and reviewed as having relevance to this review. None of the codes state that they apply to high hydrogen or all hydrogen fuels, nor do they specifically exclude them.

The NFPA 85 (2011) standard was considered to be one of the most relevant and although it is called a boiler and combustion code, it has several relevant passages and sections that apply to gas turbines and gas engines in the context of combined cycle systems. It states in its scope that it applies to: "Fired or unfired steam generators used to recover heat from combustion turbines [HRSGs] and other combustion turbine exhaust systems at any heat input rate."

This code clearly puts the onus on both the manufacturer and operator to ensure that the system is fit for purpose by making sure the design meets the standards specified in the code, and that it is installed and commissioned to an acceptable level with the operators having appropriate training in the safe use of the system.

The code makes it clear that in combined cycle systems, the gas turbine or gas engine is designed and constructed to prevent the formation of hazardous concentrations of combustible gases existing under normal and off-design operating conditions. This has implications for the response of the engine control systems especially if the fuel is virtually all hydrogen.

As a means of mitigating the consequences of an explosion, this code suggests that improved instrumentation, safety interlocks and protective devices, proper operating sequences and a clear understanding of the problems by both designers and operators can greatly reduce the risks and actual incidence of explosions. This should however

be read in the context of the ATEX Directive and DSEAR, which give a clear set of requirements for controlling explosion hazards.

The Australian code (AS 3814, 2009) is similar to NFPA 85, although of more limited application to the systems of interest in this review. It does apply to gas turbines but with open flue designs. The current version, however, deals with engine start-ups including the ignition procedures/sequences to be followed. It is not entirely clear whether this applies when a HRSG is fitted. If it does, then this may have unintended consequences for running gas turbines and gas engines on hydrogen or high hydrogen fuels since meeting the start-up conditions may be virtually impossible.

The current version of the code AS 3814 mentions HRSGs with supplementary firing fitted, where it is acceptable to purge with turbine exhaust gases provided that under all load conditions, the temperature of the purge gases does not exceed 80% of AIT for the fuel. The other relevant codes do not appear to impose such a condition, which in the case of hydrogen would be very difficult to meet as most gas turbine exhaust temperatures are above the AIT of hydrogen.

This code also imposes a maximum response time of three seconds in the event of a flameout, or a limit to the release of unburned gaseous fuel to an amount that prevents damage to the plant or injury to personnel. Where the shutdown time exceeds 3 seconds, calculations shall be provided to ensure that the intent of this clause is met.

There are two codes ASME PTC 4.4 (2009) and ASME PTC 47 (2007) which establish: procedures for conducting performance tests on heat recovery steam generators used to recover gas turbine exhaust energy, and procedures for performance testing of integrated gasification combined cycle power plants respectively. These codes are more applicable to test engineers when checking the performance of installed plant than defining appropriate safety criteria for the safe use of hydrogen and high hydrogen fuels.

In the UK, the HSE's COP (PM-84, 2003) deals with the control of safety risks at gas turbines used for power generation. This guidance is aimed at manufacturers, suppliers and operators of gas turbines and draws attention to the associated hazards in particular with turbine enclosures and as such it is not directly relevant to the exhaust/HRSG systems of immediate interest. Nevertheless it does contain useful information on explosion hazards arising external to the combined cycle unit but within the turbine hall.

Thus in summary there are no Codes of Practice or Standards that apply specifically to CCGT/CCGE/CHP systems intended to run on hydrogen or high hydrogen fuels. However several existing codes, because of their catch-all approaches, are relevant to their design and use with such fuels.

8.5.5 Safe operation of gas turbines

The following are considered to be the foreseeable failure scenarios that could lead to the presence of flammable gas/air mixtures and a subsequent explosion in gas turbine exhaust systems and downstream equipment, taking into account the scenarios listed by standards, such as NFPA 85 (2011) and AS 3814 (2009):-

- Inadequate isolation during shutdown so that gas accumulates in the exhaust, is not effectively purged before start up and is ignited by the exhaust at start up.

- Insufficient purging after a failed or repeated start-up.
- Incomplete purging due to HRSG configuration.
- Temporary ignition spark (or pilot flame) failure at start up.
- Control system failure, such as un-covenanted fuel stoppage and immediate restart causing flame failure or loss of power.
- Flame failure at fuel changeover.
- Flame failure due to a transient fuel composition change.
- Flame failure due to transient phase change, i.e. slug of liquid in gas, or vice-versa.
- Flame failure due to a transient fuel pressure change.
- Flame failure due to a transient combustion air supply failure.
- Undetected flame failure.

GE (Danner, Private communication) are of the opinion that most of the above are very unlikely, with a lean mixture blow out or a complete loss of electrical power being the most likely cause of flameout. Mitigation against many of these failure scenarios is already included in the relevant standards such as IGEM/UP/9 and ISO 21789.

Gas turbines would not be expected to start up on high hydrogen fuels, but on natural gas or another conventional fuel, until stable operation has been achieved. This would avoid the risk of high hydrogen mixtures in the exhaust system arising from spark failure, over fuelling or other start up hazards. Redundant systems of flame detection and ignition spark plugs have been recommended (Wolf, 1992). Nitrogen buffering and compressor discharge air purge are used to reduce the risks of flammable mixtures, fuel stream mixtures, and backflow arising within the fuel delivery systems. Modern engine control systems with high reliability should also mitigate the risks from fuel changeover, speed management and fuel pressure control.

It should be noted that in the event of a flame failure, subsequent fuel shut off and engine shutdown, there are a number of delays that will arise to allow fuel time to pass into the downstream sections. There will be delays associated with the detection of flame failure, with the control system decision to shut down, and with the closure of the isolation valve, as well as with the depressurisation of the fuel delivery pipework between the valve and the combustion cans. Each of these individual delays may be very small, but the total delay need only be a few seconds to result in a significant amount of fuel being lost into the duct and downstream equipment.

It has been suggested that following a flame failure when the engine is already hot, any unburnt fuel passing into the turbine section of the engine would be immediately ignited by the hot blades and/or engine walls and be burnt before passing into the downstream duct. There is no evidence in the literature that supports this proposal or suggests that it has been directly tested. Indeed the historical occurrence of explosions in the exhaust system following a fuel changeover tends to contradict the idea, and it is possible that turbulence and the absence of an effective ignition delay would suppress ignition. However high hydrogen and low AIT fuels may behave differently.

It does therefore appear that there is a risk of a flammable atmosphere and a possible ignition occurring in the exhaust transition duct leading from the gas turbine or in the exhaust pipes from a gas engine. The likelihood of this may increase with the use of high hydrogen fuels, although establishing whether this is in fact the case is the purpose of the project. This risk should, therefore, be included in a DSEAR risk

assessment, which needs to show that there is minimal risk of injury, or that the risk can be controlled in another way, such as by providing explosion protection. The regulations require the avoidance of sources of ignition. Auxiliary or supplementary burners would represent sources of ignition, but even in their absence, hot surfaces may also represent sources of ignition.

Clearly there is a recognised need to mitigate any risks arising in exhaust ducts as a consequence of using high hydrogen fuels. The hazard, however, cannot be adequately quantified until the experimental programme has been completed and the results assessed. At this stage it is sufficient to recognise the existence of a potential problem and the need to deal with it in due course through discussion with the relevant authorities.

Explosion protection is defined as including explosion relief venting, explosion suppression, pressure shock resistant plant, and pressure resistant plant. It appears that GT exhaust systems are subject to this requirement unless it has been eliminated by the risk assessment. HSE have been consulted on this matter and the preliminary view is that the interpretation above is correct.

8.5.6 Safe operation of gas engines

The following are considered to be foreseeable failure scenarios that could lead to the presence of flammable gas/air mixtures and a subsequent explosion in gas engine exhaust systems and downstream equipment, taking into account the scenarios listed by standards such as NFPA 85 and AS 3814:-

- Inadequate isolation during shutdown, or after multiple start-up attempts, so that unburnt mixture has accumulated in the exhaust, and has not been effectively purged before a successful start-up.
- Total external power failure followed by a black restart without an adequate purge.
- Engine control system failure.
- Ignition failure in one or more cylinders of spark ignition engines leading to the passage of unburnt mixture into the exhaust.
- Engine inlet valve failure, such as valve stuck open, so that unburnt mixture passes through the cylinder when the exhaust valve opens.
- Engine exhaust valve failure so that unburnt mixture passes through the cylinder when the inlet valve opens.
- Ignition failure due to a transient fuel composition change.
- Automatic air/fuel ratio control failure.
- Over fuelling due to a transient fuel composition change.
- Over fuelling due to a transient fuel pressure change.

Mitigation against many of these risks is already included in the relevant standards such as IGEM/UP/3, DNV standard 2.11, and the IGC Code, and is discussed in Section 8.7 of this review. In many cases, modern engine control systems would detect a fault and take remedial action immediately.

The explosion of excess fuel in the exhaust system of a reciprocating engine is not unusual. This suggests that a flammable mixture released into the exhaust system of a

gas engine may subsequently ignite from the hot surfaces in the system and it does not always ignite immediately at the exit from the cylinder.

It has been concluded following discussions with Jenbacher that the most likely failure scenarios for gas engine exhaust explosions are the first three of the above list.

Original equipment manufacturers (OEMs) of gas engines sometimes install explosion relief on the exhaust system. At least one company supplies relief valves specifically for this application. IGEM/UP/3 states "Consideration shall be given to the need for exhaust system explosion relief panels to protect persons nearby from injury in the event of failure of any part of the system including expansion bellows." An appendix to IGEM/UP/3 provides design guidance. DNV 2.11 requires explosion relief or for the exhaust system to be explosion pressure resistant without damage. The IGC Code, the principal maritime code, makes no reference to this requirement, although at least one national version of it does.

It appears that explosion relief is more commonly used in association with gas engines than with gas turbines. Thus in common with GTs, it appears that gas engine exhaust systems are subject to this requirement if it is not shown to have been eliminated by a risk assessment. HSE have been consulted on this matter and the preliminary view is that the interpretation above is correct.

8.6 CHOICE OF FUEL MIXTURES

The selection of fuel systems to be tested has been based on the review of Chapters 3 and 6 and make-up details were given in Section 9.1. It is possible that as result of the work of Task 1 and of post-contract comments from ETI sponsors, some changes may still have to be made, either because of external comments or problems in accommodating all of the mixture components. At this stage, the consortium does not envisage this, as long as the total number of components does not exceed 5 and steam addition can in practice be realised.

Should such changes have to be made, then further consideration will be given to incorporating them into the experimental programme forming Tasks 2 and 3 of WP2.

8.7 FUELS RE: GAS ENGINES

The gas engine industry has experience of using high hydrogen fuels with hydrogen levels up to 70%. Typical fuel gases are from the steel industry, bio-gas, syngas, pyrolysis gas, coke gas and wood gas (Schneider, 2006). Engines can operate on low CV gases (3% H₂, 20% CO, with CO₂ and N₂) and whilst 100 % H₂ has been tested satisfactorily, engines have to be de-rated because of knocking (detonation) in the cylinders. There are no specific limiting factors for hydrogen. The limits on fuel composition are the risk of auto-ignition, since ignition must occur when sparked and not before, and also if the flame speed is too high then the ignition timing is further compromised. Knocking can also occur following spark ignition if the end gas auto-ignites before the flame arrives, this is normally an issue with low burning velocity mixtures. The three selected fuel gases, plus 100% hydrogen, are equally appropriate as model gases for the gas engine investigations. taking start-up and lean burn considerations into account as necessary.

8.8 IMPLICATIONS FOR WORK PACKAGE TWO

In this section the implications of the findings from the review are considered with respect to their possible impact on the follow on experimental test programme.

8.8.1 Task one test programme

8.8.1.1 General implications

Based on the undertakings of the Contract agreed for this Programme with ETI, the Consortium Documents and the details of the Review of WP1 discussed in the preceding Sections 2 – 8, we reviewed the envisaged undertakings of the Programme for WP2, Task 1, both in terms of the systems to be investigated and the nature of the investigations.

In Section 6 we compared the initially proposed three model fuel systems, based on the RfP information, with current practices and specifically declared focus and interest from industry. On the strength of this review, we concluded in Section 6.6 that three multi-component fuel systems and 100% hydrogen would most closely satisfy current industrial demand. This has three important consequences for programme WP2 as follows.

8.8.1.2 Implications for scale-up

The most important is the switch from the relatively simple model systems with no more than two common fuel components to the very practical industrial multi-component fuel systems, which are of more limited scope but more direct interest to industry. This creates challenges for applying science-based analysis but also opportunities for comparing existing analytical methods with the results from the more complex fuel mixtures. It is intended that this new knowledge be applied in scale-up predictions required for WP2.

This was of greatest importance for the 100% hydrogen system. Although itself of course a one component system of one of the most investigated fuels, its behaviour in the large scale tests of Tasks 2 and 3 and the complex environment of the latter is likely to be among the most hazardous of the entire programme. However much will be learned from the preceding tests with the other proposed fuel mixtures and the pure hydrogen work would be scheduled accordingly.

Given that the design of systems utilising hydrogen continue to evolve, and that operation with pure hydrogen is still the subject of ongoing research, we would intend to complete the work on the three fuel mixtures for WP2 Tasks 1 & 2 in order that the experience gained can then be applied to the pure hydrogen fuel.

An added advantage would be that, within current contract provisions, this strategy would maximise the use of approved resources on the investigation of the three systems proposed.

8.8.1.3 Implications from use of steam

The recommendation on fuel choice indicates that some of the systems will contain some water vapour. This was anticipated in the project specification and will be

accommodated by the inclusion of a precision steam generator, which will match the accuracy of the existing fuel mixing system.

8.8.1.4 Implications for detonation cell sizes

A third consequence is related to the more complex mixtures as well as to the introduction of steam and specifically relates to our proposed detonation work. For simple systems, our 50 mm diameter detonation tube would be able to cope with near stoichiometric mixtures including hydrogen. Calculated cell sizes would be marginally possible for validation; the change of cell sizes with composition changes are known and raising the temperature would shrink the cell-sizes. This confirms the suitability of our existing equipment.

The extension of predictive capability for more complex fuel mixtures is more challenging and judgements will need to be made regarding the suitability of existing tube diameters. For example, adding steam is a means of slowing down reactivity and hence increasing cell sizes (Ciccarelli et al, 1994).

We are confident that, with modifications, we will be able to deal with this too, but it makes the preparation for and the execution of the detonation work more complex. We will in due course report on how this will be addressed.

8.8.1.5 Model systems to be tested

Based on these findings, considerations and solutions, we proposed to investigate as follows: (but see also now Appendix 3).

1. Three model systems, based on the main components of more complicated real systems:

Model A: A low energy model, simulating synthesis gas from coal gasification processes without carbon capture and containing 10 – 20% hydrogen. Model *fuel* constituents: 14.5% H₂, 23.6% CO, 1.6% CH₄; diluents: 49% N₂, 5.6% CO₂, 5.7% H₂O.

Model B: A low energy model, simulating synthesis gas from coal gasification processes, which include carbon capture and containing 40 - 50% hydrogen. Model *fuel* constituents: 47% H₂, 1% CO, 1% CH₄; diluents: 41% N₂, 10% H₂O.

Model C: A medium energy model, simulating gas originating from coking or refinery processes which includes over 50% hydrogen and other significant hydrocarbon components. Model *fuel* constituents: 61.6% H₂, 6% CO, 23% CH₄, 2.2% other H/C(C₂, C₃); diluents: 5.4% N₂, 1.2% CO₂.

Subject to satisfactory progress and findings as detailed in Section 6.1.2, we will also investigate:-

Model D: A high-energy model, representing a limiting condition where hydrogen is available from a pure source, e.g. refinery processes, electrolysis, and containing 100% H₂.

2. We would test these systems for their auto ignition delay, ignition characteristics, flame development and flame acceleration, ability for and susceptibility to turbulence and propensity for flame kernel development and DDT potential.
3. We would carry out the tests for (worst case) equivalence ratios of “1” with air and varying reactant temperatures. The nitrogen normally found in the real systems will be treated as part of the air make-up.
4. We would also carry out these tests with equivalence ratios of “0.5” with (excess) air and with additional nitrogen as used in CCGTs for NO_x reduction purposes.

In due course:

5. We will investigate the changes of characteristic properties for enrichment with hydrogen; for Model D up to 100% by progressively reducing the 2:1 contribution of methane and ethane. For model A, we will also investigate the effect of propane, as a highly reactive additive.

Note however, that these model mixtures would not satisfy the needs of the ETI sponsors and that alternative choices and an associate test matrix have been listed in Appendix 4.

8.8.2 Consequences for WP2 experimental design

Some results of the explosion phenomena investigated as part of WP2, Task 1 may necessitate a review of the provisional designs for WP2, Tasks 2 and 3. Although a full range of consequences cannot be identified without progress with, if not completion of, Task 1, some of these can be anticipated at this point.

- To match the quality of results from WP2, Task 1, the inclusion of steam at an adequate rate will almost certainly require some equipment adaptation.
- It is not expected that the information from Dorofeev (2000) will affect the scale up estimation, but it will be positively considered, tested and judged and if unexpectedly proven, may require some redesign.
- The findings on detonation cell sizes may influence our appreciation of the process development in the Task 2 facility and hence of its design requirements and instrumentation, although that is unlikely at this stage.
- The results from modelling, approved as a predictive input on hazardous zones in subsequent tasks, can only partly be tested on Task 2; depending on the findings, they may influence preparations for Task 3 and any subsequent work on hydrogen in all three Tasks of WP2.

9 CONCLUSIONS

1. The hazard regimes for operating CCGT and CCGE power generation systems with enhanced or high hydrogen fuels have been identified. Assuming equivalent reactant/air ratios near “1”:
 - a. If at the temperature regimes of interest the system can be kept or brought outside the flammability regime, e.g. by supplementary air through by-pass or directly in to the exhaust duct, then there are no hazards for ignition of non-combusted fuel. Favourable conditions for this can be created by adequate mixture dilution, although this is only true for some failure scenarios.
 - b. If in thorough testing under the above conditions of mixtures within the fuel flammability regime, no spontaneous or artificial turbulence/kernel formation can be detected, then the system will be safe, as long as over-pressures from deflagrations can be safely contained. Favourable conditions for this can be created by mixture dilution, duct design and rapid remedial action.
 - c. If turbulence or flame kernel generation can be detected then the potential for artificial or spontaneous DDT is present along with the generation of very high over-pressures from stable or quasi detonations. In that case even a perfectly designed exhaust system provides no adequate protection as DDT may be generated within the entry zone of the HRGS. Favourable conditions can only be created by rapid remedial action.

As for the Deliverables required in the project (Schedule 5):

- A detailed report of our review is hereby presented.
- We have assessed the level of current knowledge, which covers a wide range of characteristic behaviours and explosion hazards of gas mixtures used for CHP generation. However, the currently available literature gives no specific quantitative information. This is a **gap**.
- We have repeatedly and extensively referred to references on the likely behaviour of gaseous systems in exhaust ducts and HRSG systems of power plants, and highlighted the likely areas for specific hazards such as turbine exhausts, duct corners and HRSG entrance, including and specifically within the heat exchangers.
- On the basis of the three most prominent types of fuel systems used, we have selected three fuel systems that in a simplified composition could represent the main character, hydrogen enrichment potentials and nature of the explosive hazards in exploitation for CHP generation. We wish to defer the investigation of hydrogen until information on three industrially used systems at least has been obtained from Task 2. This will allow a test programme with progressively stronger mixtures to establish were the high and over-pressures in the turbine and exhausts systems are likely to occur.

- The particular areas where knowledge is insufficient or non-existent or impossible to realise (further **gaps**) in the context of the current hydrogen rich fuel streams are:
 - Qualitative information relating to possible outcomes following ignition.
 - Quantitative information relating to the understanding of actual outcomes following ignition.
 - Mixing rules for extrapolation and/or interpolation of results.
 - Probability of ignition related to mixture strength in a turbulent flow field.
 - Probability of DDT related to mixture strength following ignition.
 - Scaling behaviour suitable for estimation of extrapolation and/or interpolation of results.
- Current CCGT systems when operating on high hydrogen fuels may, following a flameout, result in hydrogen concentrations exceeding the LFL entering the exhaust system.
- No Standards or Codes of Practice were found that apply specifically to CCGT/CCGE/CHP systems operating on high hydrogen fuels.
- Several existing Standards and Codes of Practice have relevant sections that should be applied when considering high hydrogen fuels.
- Where there is a foreseeable risk of a flammable mixture entering the exhaust system and the HRSG, then the ATEX regulations (EU only) should be complied with in order to mitigate the risk of an explosion.

10 RECOMMENDATIONS

It is recommended that:

- This report is assessed, discussed and approved by ETI.
- In particular, the proposed fuel systems are considered and alternatives debated if required. Specifically the restriction to five fuel system components, the introduction of steam and the deferment of hydrogen all need to be discussed.
- The separately reviewed and submitted test matrix for WP2, Task 1 is discussed and approved.
- Additional funding for equipment to extend the work to the use of steam is considered and approved.
- The revised situation regarding the detonation work is discussed and resolved.
- The result of the review of the use of the BAE software is reported.
- The option for external purchase for ADT data is discussed and a decision made on whether to proceed with purchasing it from a Chinese or UK source.
- The possibility, following a flameout, that any unburnt fuel may burn off as it goes through the hot turbine is investigated, particularly for the high hydrogen fuels of interest.
- The potential application of the ATEX directive to CCGT/CCGE systems is discussed further with the UK regulator.

11 APPENDICES

Appendix A1: Basic gas turbine principles.

The power plants of interest to this investigation are all more efficient developments from the simple open circuit gas combustion systems in which a gas turbine or gas engine drives an electricity generator and the exhaust gases go to waste, as shown in Figure A1.

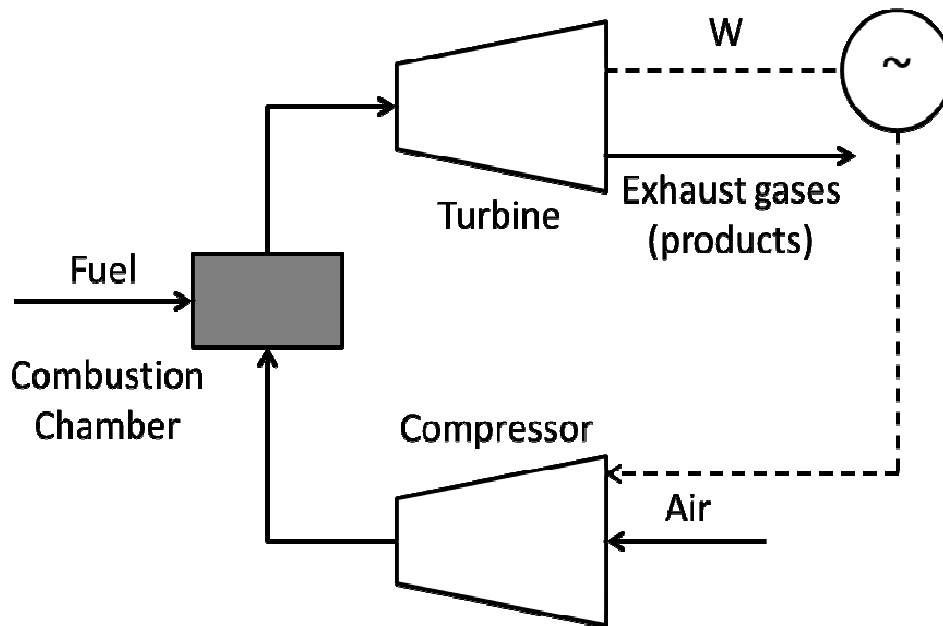


Figure A1: *Open Circuit Gas Turbine Power Plant*

Increased sophistication is achieved in Combined Heat and Power Systems (**CHP**), which can be 'Open' or 'Closed' Cycle. The most common combined plant consists of an open circuit gas turbine and a closed cycle steam plant.

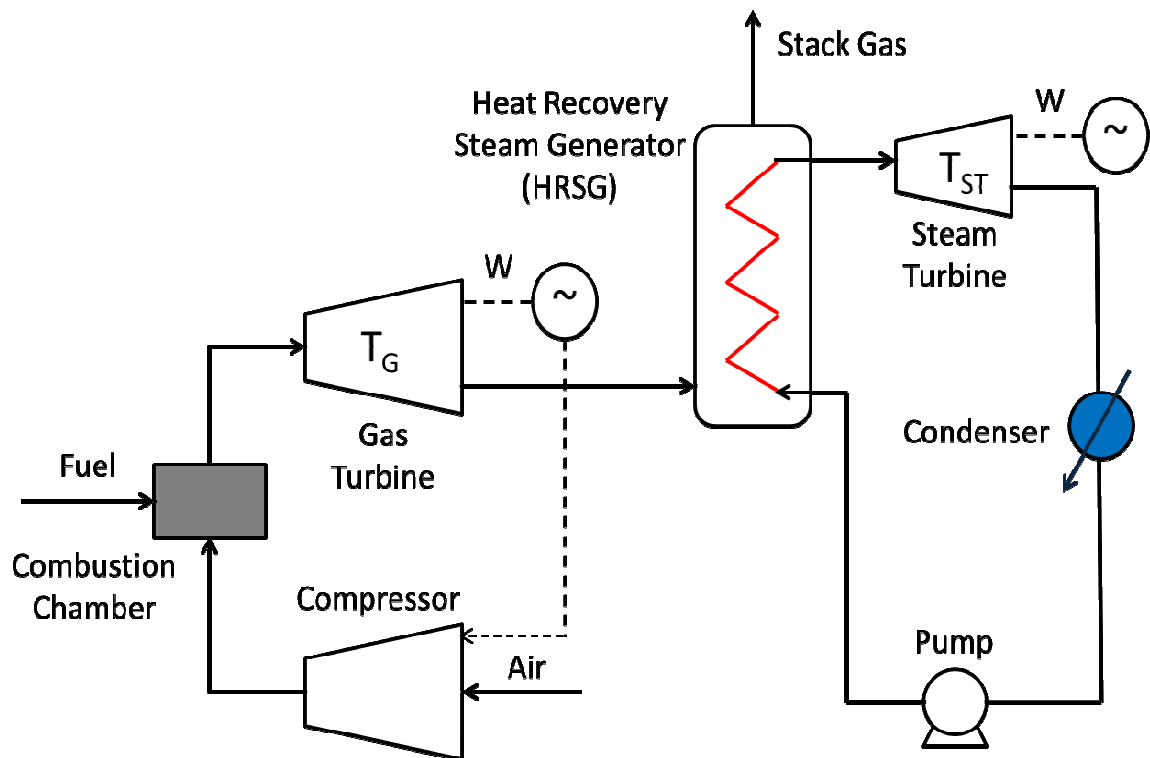


Figure A2: Unfired HRSG Combined Cycle Gas Turbine (CCGT) Power Plant.

Of the configurations in existence, the most widely used CHP plants are of the heated exhaust system type, in which the gas turbine exhaust heats a steam turbine cycle, as shown Figure A2. Supplementary heating of the gas turbine exhaust stream and a higher temperature intake into the heat recovery steam generator (**HRSG**) may be used, depending on the presence or supply of air, which will allow a better and more efficient distribution of energy generation over the two cycles.

In conventional thermal power plants, represented as a block diagram in Figure A3, fuel energy (F) is used to produce useful work (W) and the residual heat (Q) is rejected to a low temperature heat sink. In order to maximise the economic benefit of operating the plant, it is important to maximise the efficiency of power generation by obtaining greater useful work (W) out and reducing residual heat rejected (Q) for a given fuel energy input (F).

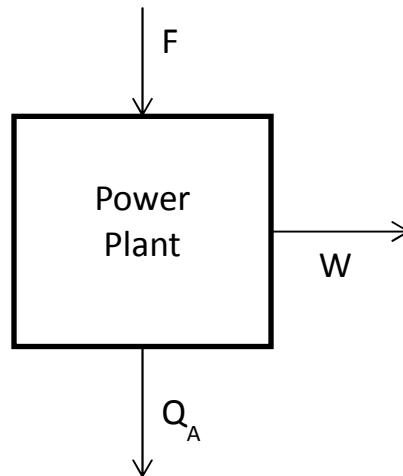


Figure A3: *Basic Power Plant*

It is important to distinguish between a closed circuit power plant (or heat engine) and an open circuit power plant. Traditional power plants are cyclic, involving a fluid passing around a closed circuit, through a thermodynamic cycle, in which heat (Q_B) received from a high temperature source is used to produce work output (W) to drive an electric generator, while the residual heat (Q_A) is rejected to a sink at a lower temperature.

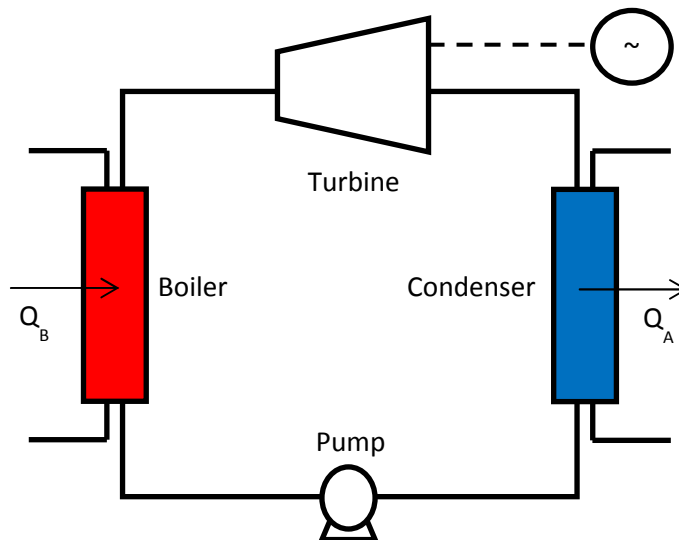


Figure A4: *Steam Turbine Power Plant*

The most common type of cyclic power plant is the steam turbine power plant, shown in Figure A4, following the Rankine cycle. With water as the working medium, this arrangement generally requires strong, bulky, expensive alloys, rather than relatively inexpensive steel, to withstand high pressure and avoid corrosion. These alloys limit

the maximum steam temperature in the cycle, while the lower temperature is fixed by the boiling point of water. Conventional steam turbine power plants have an efficiency of around 35-40%.

A gas turbine power plant operates similarly on a closed circuit, following the Joule-Brayton cycle, with a compressor used to pressurise the working fluid instead of a pump (Horlock, 2002). However, it is more likely for a gas turbine plant to operate on an open circuit, with internal combustion, as was shown in Figure 1. Fuel is fed to the combustion chamber and burned in the presence of pressurised air from the compressor. The combustion products are expanded through a turbine (connected to an electric generator) and exit the plant as exhaust gases. Thus, there is no 'circulating' fluid in this arrangement and the open circuit plant cannot be said to operate on any particular thermodynamic cycle with more or less similar efficiency as the steam turbine.

The above system is very basic and traditional, and several modifications to these single cycles have been proposed in the past to increase overall efficiency. However these changes were not able to achieve a high enough overall efficiency, or would have involved excessive capital expenditure in order to do so. As a result, in more recent times, the most important developments from the conventional power plant have been the Combined Cycle Power Plant. Its fundamental principle is the operation of two thermodynamic cycles, such that the 'higher' (upper or topping) cycle produces power, and is able to transfer part or all of its rejected heat to a 'lower' (bottoming) cycle, which in turn also generates power. This arrangement enables a greater work output for a given initial fuel energy supply. Thus, a higher overall plant efficiency can be attained, but this system requires a higher mean temperature of heat supply and/or a lower temperature of heat rejection.

**Appendix A2: Selected Thermophysical, Chemical, and Combustion Properties
of Gaseous Hydrogen (NASA-NSS-1740.16, 1997).**

Hydrogen:

Molecular Weight 2.01594

NORMAL TEMPERATURE AND PRESSURE (NTP)

Density of GH₂ 0.083764 kg/m³
 Density of air (for comparison) 1.198 kg/m³
 Specific heat at constant pressure Cp 14.89 kJ/kg·K
 Specific heat ratio $\gamma = C_p/C_v$ 1.383
 Enthalpy 4097.7 kJ/kg
 Internal Energy 2888.0 kJ/kg
 Entropy 64.44 kJ/kg·K
 Velocity of sound (adiabatic) 1294 m/s
 Viscosity 8.81 $\mu\text{Pa}\cdot\text{s}$
 Thermal conductivity 19.14 mW/m
 Dielectric constant 1.00026
 Compressibility factor 1.0006
 Index of refraction 1.00012

CRITICAL POINT

Temperature 32.976 K
 Pressure 1,292.8 kPa abs
 Density 31.43 kg/m³
 Specific heat at saturation Cs (very large)
 Specific heat at constant pressure Cp (very large)
 Specific heat ratio $\gamma = C_p/C_v$ (large)
 Enthalpy 38.49 kJ/kg
 Internal Energy 2.83 kJ/kg
 Entropy 17.6 kJ/kg·K
 Velocity of sound 350 m/s
 Viscosity 3.5 $\mu\text{Pa}\cdot\text{s}$
 Thermal conductivity (Anomalously large)
 Dielectric constant 1.098
 Compressibility factor 0.3025

NORMAL BOILING POINT (NBP)

Normal Boiling Temperature (NBT) 20.268 K
 Pressure 101.3 kPa
 Density of vapor 1.338 kg/m³
 Density of liquid 70.78 kg/m³
 Heat of vaporization 445.6 kJ/kg
 Specific heat at saturation of vapour -16.51 kJ/kg·K
 Specific heat at saturation of liquid 9.38 kJ/kg·K

COMBUSTION PROPERTIES

Equivalent vol gas @ NTP/vol liquid @ NBT 845.1
 Pressure required to maintain NBP liquid density
 in NTP GH₂ (fixed volume, no venting) 172 MPa
 Joule-Thomson inversion temperature 193 K
 Heat of combustion (low) 119.93 kJ/g

Heat of combustion (high)	141.86 kJ/g
Limits of flammability in NTP air	4.0 to 75.0 vol %
Limits of flammability in NTP oxygen	4.1 to 94.0 vol %
Limits of detonability in NTP air	18.3 to 59.0 vol %
Limits of detonability in NTP oxygen	15 to 90 vol %
Stoichiometric composition in air	29.53 vol %
Minimum energy for ignition in air	0.017 mJ
Autoignition temperature	858 K
Hot air-jet ignition temperature	943 K
Flame temperature in air	2318 K
Thermal energy radiated from flame to surroundings	17 to 25%
Burning velocity in NTP air	2.65 to 3.25 m/s
Detonation velocity in NTP air	1.48 to 2.15 km/s
Diffusion coefficient in NTP air	0.61 cm ² /s
Diffusion velocity in NTP air	<2.0 cm/s
Buoyant velocity in NTP air	1.2 to 9 m/s
Maximum experimental safe gap in NTP air	0.008 cm
Quenching gap in NTP air	0.064 cm
Detonation induction distance in NTP air	L/D ≈100
Limiting oxygen index	5.0 vol %

Vaporization rates (steady state) of liquid pools without burning	2.5 to 5.0 cm/s
Burning rates of spilled liquid pools	0.5 to 1.1 mm/s
Energy of explosion (Theoretical explosive yield)	≈24 (g TNT)/(g H ₂) 0.17 (g TNT)/(kJ H ₂) 2.02 (kg TNT)/m ³ NTP GH ₂) 1.71 (g TNT)/(cm ³ NBP LH ₂)

Appendix A3: Mixture Properties and Test Strategy.

Following discussions at the WP1 Stage Gate review meeting it is apparent that a systematic study of the impact of gradually increasing the reactivity of fuel blends, by hydrogen addition on the strength of deflagrations and potential deflagration to detonation transitions is essential. Such a study contrasts with the testing of specific mixtures that would provide valuable information for the blends considered, but preclude more general conclusions. The exchange of information at the meeting was particularly welcome because of the opportunity to clarify the expectations of the sponsors and the current brief note aims to build on the Stage Gate review by proposing a fuel blend and test strategy as outlined below. A brief background to the laboratory scale equipment is also provided.

A3.1. Fuel Blends.

Mixture compositions obtained from a comparatively wide range of sources were reported in WP1 and strongly suggest that the principal fuel components of interest represent three classes of reactivity through H_2 , CO and CH_4 . It can also be noted that more reactive hydrocarbons may be present in some mixtures. The latter applies particularly to refinery gas, where the content may exceed 25%, but also to coal oven gas and bio-derived syngas where the amount is reduced by an order of magnitude to around 2%. The three named components will therefore represent the core of the WP2 Task 1 programme.

The fuel mixtures will also include different single additional diluents including nitrogen and carbon dioxide. In some cases, water (steam) may also be present. The principal effect of the diluents is to act as such. Comparatively modest differences in fuel blend behaviour can be caused by the influence of diluents due to molecular transport properties and in the context of third-body efficiencies for chain terminating reactions. However, such effects are expected to be at least tertiary compared to the importance of (i) binary and (ii) ternary blending of the principal fuel components and (iii) the impact of more reactive hydrocarbons in selected cases. Hence, for the purposes of the current phase of the investigation, the principal diluent is proposed to be nitrogen with some consideration also given to carbon dioxide.

In practical use all fuel blends will be significantly diluted, either as part of the application dependent preparation of the combustible mixture and/or as a consequence of the mode of operation of the practical device. In particular, it should be noted that conditions relevant to gas turbine combustors can be expected to lead to a significant dilution of the fuel stream. Such effects will be taken into account in the experimental study.

A3.2. Test Strategy.

The proposed strategy (for the lab based testing) will initially feature binary fuel blends of H_2/CH_4 and H_2/CO starting from the case of 100% H_2 and with the gradual addition of the second component. For screening purposes the mixtures will focus on the more reactive end of the spectrum with mixtures ratios of hydrogen to carbon monoxide of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60 and 30/70 prior to dilution. The proposed range covers the majority of H_2/CO ratios identified as detailed in Section 6.6. A narrower range of mixtures is proposed for the H_2/CH_4 blends encompassing 100/0,

90/10, 80/20, 70/30, 60/40 and 50/50 in line with the obtained mixture information. Hence, we prefer to use 13 binary fuel combinations prior to assessing the influence of any more reactive hydrocarbons and the use of ternary mixtures of H₂/CH₄/CO. The implications in terms of overall workload of using a large number of mixtures can be mitigated by moderate changes in the overall work programme, notably by emphasising the importance of detonability rather than detonation behaviour of mixtures.

The majority of ternary mixtures detailed in Section 6.6 are low on the CH₄ component and hence it can be expected that the overall reactivity will be dominated by H₂ and CO. A potential exception is coal oven gas where a high level of H₂ and a modest amount of CO is combined with a comparatively large amount of CH₄. However, the corresponding H₂/CH₄ ratio is covered by the proposed binary mixtures and a comprehensive investigation of synergetic effects for ternary mixtures will require a large additional test matrix. It is hence proposed that such an investigation awaits the outcome of the results obtained for the binary mixtures before the need for such work is assessed.

The addition of more reactive hydrocarbons for refinery gas, coal oven gas and bio-derived syngas presents a further challenge that would require a systematic study that includes the selection of a representative hydrocarbon or a range thereof. Again, it is proposed that such an investigation awaits the outcome of the results obtained for binary mixtures. Nevertheless, it is recognised that such hydrocarbons may substantially alter the ignition behaviour and that it is likely that a further investigation would be desirable.

The dilution factor depends upon the actual combustion device. In general, it will be assumed that overall lean premixed combustion will be used and/or that significant dilution of the fuel stream will take place prior to conditions of relevance to the current investigation. Hence, it is likely that the overall hydrogen concentration in the mixture prior to combustion will not exceed 25% by volume in a fully premixed mode and, perhaps, less than half of that in the context of a gas turbine combustor. With the further dilution expected in a gas turbine engine, the proposed test matrix will therefore move the hydrogen content towards the lower flammability limit.

A3.3. Test Matrix.

The final test matrix features a large number of fuel blends resulting from the instigation of a systematic study. As outlined above, we are fully supportive of this strategy and in order to reduce the number of experiments, parameters of tertiary impact (e.g. the nature of the diluent) will be assessed computationally through the determination of ignition delay times.

In order to reduce the overall size of the overall test matrix, we will at this stage use only one (fuel lean) stoichiometry and two dilution levels corresponding to gas engines and gas turbines and one diluent. We also aim to use only one temperature for the combustion products, as low as practically possible, for the Cabra and opposed jet burner experiments. The current stretching of the envelope will require more initial experimentation in order to determine optimal conditions for a consistent comparison basis.

The detonability tests will be performed using a fuel reactivity assessment in terms of (i) the propensity to auto-ignition in turbulent flow fields (Cabra burner), (ii) the strength of the deflagration phase as characterised by the turbulent burning velocity and (iii) the strength of explosion kernels (e.g. DDT propensity) as obtained in an obstructed detonation tube with optical access. The order of the experiments follows the above list and is aimed at clarifying the potential risk of DDT in the laboratory experiments and to provide an assessment of potential precautions in terms of remote operation of the shock tube facility. The experiments will be performed by starting with the least reactive mixture along each leg of the ternary diagram and then move up the diagram by progressively adding hydrogen to the system.

The matrix of conditions identified on the basis of mixtures given in this appendix, features, in addition to the pure hydrogen case, seven H₂/CO blends and five H₂/CH₄ blends. Each experiment needs to be repeated three times in order to assess reproducibility. Accordingly, the number of tests to be performed for the CO blends will amount to 7 mixtures x 3 repetitions x 3 configurations x 2 dilution levels = 126 experiments. The corresponding figure for the CH₄ blends is 90 experiments. The total projected effort is accordingly 234 following the addition of the pure hydrogen case.

The resulting test matrix is substantially larger than the 124 tests originally envisaged. Some economies may be made for the opposed jet configuration, where it is expected that less repetitions will be required. However, this saving is likely to be offset by the need to establish the minimum practical operating temperature in the Cabra burner configuration. The number of test points (mixtures) can naturally be reduced, though in our view that would be detrimental to the programme as we are expecting a non-linear behaviour of the fuel reactivity as the hydrogen content is increased.

A3.4. Possible Additional Tests.

The above formulation of the test programme suggests the possible formulation of two additional Work Packages addressing ternary mixtures, including the impact of more reactive hydrocarbons.

A3.3.1. Ternary Mixtures of H₂:CO:CH₄

A number of practical systems are likely to be well characterised by the binary mixtures discussed above. There are, however, systems where synergistic effects between fuel components may come to the fore. Examples include certain types of syngas, coal oven gas, refinery gas and bio-derived syngas. In order to explore such effects it is suggested that H₂:CO ratios are varied as 2:1, 1:1 and 0.5:1 with, in each case, the CH₄ content varied as 0.1, 0.25 and 0.50. The resulting test matrix would be sufficient to identify synergistic effects. The man-month effort is aimed to be around 65% of the binary fuel blend test programme with no additional investment in equipment necessary.

A3.3.2. Ternary Mixtures of H₂:CO and more Reactive Hydrocarbons (HCs)

There are three systems where the impact of more reactive hydrocarbons may play a significant role. These are refinery gas, bio-derived syngas and, possibly, coal oven gas. The variation in hydrocarbon content is large and spans from a few percent in coal oven gas and bio-derived syngas to being the dominant component in some types of refinery gas. In the former cases, the more reactive hydrocarbon may act as an

initiator, while in the latter case a major contribution to the overall heat release can be expected.

The following test matrix is proposed starting from a basis of H₂:CO ratios varied from 2:1, 1:1 and 0.5:1. For each case, the content of the reactive hydrocarbon would be varied as 1, 0.5 and 0.1 relative to the amount of hydrogen. The test matrix is comparatively large as, ideally, at least two hydrocarbons of different reactivities should be considered. Typical choices would be propane and ethylene. However, the low temperature chemistry of longer alkanes suggest that consideration should be given to a fuel component such as n-heptane due to the possibility of triggering ignition at lower temperatures (< 1000 K). The man-month effort estimated is around 65% for each selected hydrocarbon component with no additional investment in equipment necessary.

A3.5. Laboratory Scale Testing.

There are significant uncertainties regarding the actual temperature and flow conditions experienced during an ignition event in the practical devices under consideration. However, it can be expected that ignition will occur in a mixture of a combustion products and fresh reactants and that both stratification and turbulence will be present at the point of ignition. It is further expected that ignition will occur at comparatively low temperatures. The challenge of deriving information regarding the relative propensity to cause violent deflagrations and/or deflagration to detonation transition (DDT) under such conditions is significant. Hence, a novel combination of a wide range of methods will be applied with results critically appraised in order to provide recommendations for the subsequent larger scale experimental testing.

A3.5.1. Fuel Reactivity Assessment via Ignition Delay Times (IDT)

The conventional way of determining fuel reactivity rests upon the use of ignition delay times obtained from shock tube experiments in a laminar flow environment. The method provides data related to the underlying chemistry and can be expected to provide valuable information regarding the reactivity of the selected fuel blends. The resulting data can also be used to validate chemical reaction mechanisms and is of direct relevance to shock initiated DDT. However, the application of the technique at lower temperatures (e.g. < 1000 K) presents device dependent challenges due to non-ideal behaviour and the need to consider longer measurement times. Hence, information in the current work will be obtained at a higher temperature, around 1450 K, in order to determine the relative reactivity of the mixtures considered. Preliminary work at Xi'an Jiaotong University has shown that the ignition delay time is reduced by around 2/3 for fuel rich methane mixtures when 20% of hydrogen is added with the overall stoichiometry kept constant. The approach does not account for the influence of turbulence and/or the strength of the deflagration phase. Accordingly, the data is valuable, but not sufficient, and must be augmented as outlined below.

A3.5.2. Fuel Reactivity Assessment via Auto-ignition in Turbulent Flow Fields

The actual conditions experienced in a practical device present significant challenges in terms of deriving even a relative assessment of the reactivity of different fuel blends. The Cabra burner geometry has been successfully used to study the auto-ignition of high velocity nitrogen diluted hydrogen streams (25/75 H₂/N₂) injected at ambient temperatures in a co-flowing stream of dilute combustion products at temperatures

down to 1045 K. Due to the nature of the shear layer driven mixing, the temperature at the point of ignition will be lower. In the current work, the geometry will be used at as low a temperature as can be achieved while still covering the fuel reactivity range of interest. The work will directly determine the impact of fuel reactivity on auto-ignition when fuel blends are injected into combustion products in a turbulent flow field. The geometry arguably presents conditions that are as close to the practical environment as can reasonably be achieved in a small-scale laboratory context. As part of the experiment, the flame lift-off height and temperatures will be monitored.

A3.5.3. Fuel Reactivity Assessment via Turbulent Burning Velocities

The propagation speed of the developing turbulent flame resulting from an ignition event, be it forced or through auto-ignition, will have a direct impact on the strength of the subsequent deflagration. Hence, the outcome is of direct relevance to the assessment of the impact of fuel reactivity on the deflagration phase and also provides an indication of the DDT propensity. It is important to note that the impact of the higher diffusivity of hydrogen is taken into account. In the current work, an opposed jet geometry, featuring fractal-generated turbulence will be used with flames stabilised against a stream of hot combustion products. The selected turbulent Reynolds number and other conditions will be chosen to provide as consistent a comparison basis as the range mixture reactivity permits. The turbulent burning velocity and velocity statistics will be determined using Particle Image Velocimetry (PIV). It may be noted that Fairweather et al. (Fairweather, 2009) have shown experimentally that the turbulent burning velocity for a H₂/CH₄ mixture at the proposed lower reactivity end of the current range (50/50) increases by around a factor of 2 as compared to the pure methane case. A reduced propensity to extinction was also observed.

A3.5.4. Determination of the DDT Potential in Obstructed Shock Tubes

The initial stages of DDT will be studied using a rectangular (72 x 34 mm) shock tube with optical access and with inserted obstacles generating Reynolds numbers around 120,000 and correspondingly high turbulence levels. The configuration has been shown to be able to generate explosion over-pressures in excess of 1 bar for stoichiometric methane-air mixtures. It is expected that substantially higher over-pressures will be generated for the current hydrogen enriched mixtures. The experiments will accordingly provide a significant link between the alternative methods used for the assessment of the impact of fuel reactivity on DDT potential and the larger scale experiments planned at HSL. Flow field statistics will be determined using high speed PIV for selected cases of particular interest.

A3.5.5. Determination of DDT in Small Scale Laboratory Experiments

The final configuration to be used features a conventional round shock tube with an internal diameter of 50 mm. The tube will be used to study flame acceleration and DDT in a conventional environment. The tube diameter is expected to be impose restrictions on the ability to study DDT for the less reactive mixtures. However, the configuration will provide a link to the corresponding larger scale experiments to be performed at the HSL. This particular work items is to be reviewed due to a greater emphasis on detonability and the deflagration phase.

A3.5.6. Summary of priorities for WP2, Task 1

The decisions given above can be summarised as follows:

1. The general objective is to obtain adequate information on the behaviour and hazard implication of the ternary fuel matrix of H₂:CO:CH₄.
2. Most important is the binary system H₂:CO, which for this reason is our first priority.
3. Of almost the same importance is the binary system H₂:CH₄, which is therefore our second priority.
4. Most ternary systems have little CH₄, thus are close to (2) above; a fuller study will be deferred as a first future option.
5. In terms of energetic behaviour our next concern would be the above systems with the addition of reactive hydrocarbons. Incorporating this in the present work would complicate matters and is therefore deferred as a second future option.
6. In practical situations the above fuel systems are diluted, we will therefore investigate (1) and (2) as lean fuel mixtures.

A3.6. In-budget programme for WP2, Task 1.

The full programme needed will exceed the limits set by the contract (see A4.3). To facilitate an immediate start of WP2, Task 1 within budget, we will in first instance investigate a more coarse test matrix by skipping alternative H₂ dilutions from A4.5 (1) and (2) and investigate pure H₂ and mixtures with 20, 40 and 60% CO and mixtures with 20, 40 and 50% CH₄. With 3 repetitions and 2 dilution levels in the 3 test configurations of A4.5.2, A4.5.3 and A4.5.4 the matrix will result in $7 \times 3 \times 2 \times 3 = 126$ test configurations. This slightly exceeds the number quoted and approved in the budget, but we will accommodate this.

The consequences are:

1. We will apply for additional funding to supplement the work to the full number of 234 required tests (see A4.3 above).
2. We will reconsider the need for detonation work as part of WP2, Task 1 and report at our earliest opportunity.
3. We will offer optional work on;
4. H₂:CO:CH₄ systems (see A4.5.4)
5. Hydrocarbon enriched systems (see A4.5.5)

A3.7. Relevance of WP2, Task 1 results for WP2, Task 2.

Given the first large scale model configurations of the 9 m long circular duct of 600 -700 mm diameter, with the VIPER turbine at one end and an initially open other end and subject to the application of scaling methods, the results of WP2, Task 1 will inform as follows:

1. The ignition delay time (IDT) data for non-turbulent flow generated in A4.5.1 will provide information on the time and distance to ignition from the turbine end.
2. The Cabra burner data generated in A4.5.2 will inform on (i) the impact of turbulence on the ignition delay times, (ii) the impact of mixing of the fuel stream with combustion products and (iii) provide an assessment of the impact of hydrogen enrichment relative to mixtures considered "safe" to use.
3. The data from A4.5.3 will indicate the reactivity of the combustion initiated turbulent flow, following (i) or (ii), and the strength of the subsequent deflagration phase.
4. The data from the rectangular shock tube in A4.5.4 will add to the information from either (i) or (ii) and (iii) to indicate for the mixtures investigated any risk of incipient DDT along the length of the test facility.

-

12 BIBLIOGRAPHY

- Abbott, D. (2011) *Private Communication*, E.ON Energy Ltd.
- Alekseev, V., Kuznetsov, M., Yankin, Y., & Dorofeev, S. (2001). Experimental study of flame acceleration and the deflagration-to-detonation transition under conditions of transverse venting. *Journal of Loss Prevention in the Process Industries*, 14 (6), 591-596.
- API-534. (2007). *Heat recovery steam generators*.
- API-556. (2011). *Instrumentation, control, and protective systems for fired heaters*.
- API-618. (2011). Gas turbines for the petroleum, chemical and gas industry services. *American Petroleum Institute*, 5.
- API-RP-11PGT. (1992). *Recommended practice for packaged combustion gas turbines. 1st Edition*.
- Armstrong, P. (2004). ITM Oxygen for Gasification. *Gasification Technology Conference*. Washington DC.
- Arntzen, B.J., Hjertager, B., Lindstedt, R.P., Mercx, W.P.M. and Popat, N., (1995) Investigations to Improve and Assess the Accuracy of Computational Fluid Dynamic Based Explosion Models, *Journal of Hazardous Materials*, 45:1-25.
- AS-3814. (2009). *Industrial and commercial gas fired appliances*. Australian Standard.
- ASME-PTC-4.4. (2009). *Gas turbine heat recovery steam generators*.
- ASME-PTC-47. (2007). *Integrated gasification combined cycle power generation plants*.
- Astbury, G., & Hawksworth, S. (2007). Spontaneous ignition of hydrogen leaks: A review of postulated mechanisms. *International Journal of Hydrogen Energy*, 2178-2185.
- ATEX. (2006). *94/9/EC Equipment Directive and 99/92/EC Workplace Directive*.
- ATEX. (1999). *99/92/EC Minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres*.
- Barker, W., Cronin, M., 'Speedtronic Mark VI Gas turbine Control system', GE Document GER-4193A. 2000.
- Beauvais, R., Mayinger, F., & Strube, G. (1994). Turbulent flame acceleration-mechanisms and significance for safety considerations. *International Journal of Hydrogen Energy*, 19 (8), 701-708.
- Bloomberg. (2011). *Exxon Mobil Forecasts 35% Global Energy Demand Growth by 2030*. Retrieved July 11, 2011 from <http://www.bloomberg.com/news/2011-01-27/exxon-mobil-forecasts-35-global-energy-demand-growth-by-2030.html>
- Bond, A., (2012). *An assessment of the exhaust composition of the Viper jet engine using Butane fuel*. Reaction Engines. VCC-REL-RP-0001.
- Bougrine, S., Richard, S., Nicolle, A., & Veynante, D. (2011). Numerical study of laminar flame properties of diluted methane-hydrogen-air flames at high pressure and temperature using detailed chemistry. *International Journal of Hydrogen Energy*, 36, 12035-12047.
- Bradley, D., Lawes, M., & Liu, K. (2008). Turbulent flame speeds in ducts and the deflagration/detonation transition. *Combustion and Flame*, 154 (1-2), 96-108.
- Bradley, D., Sheppard, C., Woolley, R., Greenhalgh, D., & Lockett, R. (2000). The development and structure of flame instabilities and cellularity at low Markstein numbers in explosions. *Combustion and Flame*, 122 (1-2), 195-209.
- Bray, K. (1980). Turbulent flows with premixed reactants. In P. a. Libby (Ed.), *Turbulent Reacting Flows* (Vol. 44, pp. 115-183). Heidelberg: Springer Berlin.
- Breitung, W., & Royl, P. (2000). Procedure and tools for deterministic analysis and control of hydrogen behavior in severe accidents. *Nuclear Engineering and Design*, 202 (2-3), 249-268.
- Breitung, W., Dorofeev, S., Kotchourko, A., Redlinger, R., Scholtyssek, W., Bentaib, A., et al. (2005). Integral large scale experiments on hydrogen combustion for severe accident code validation-HYCOM. *Nuclear Engineering and Design*, 235 (2-4), 253-270.

- BS-EN-1127. (2011). *Explosive atmospheres - Explosion prevention and protection - Part 1: Basic concepts and methodology*.
- BS-EN-13160. (2003). *Leak detection systems: general principles*.
- BS-EN-13237. (2003). *Potentially explosive atmospheres: terms and definitions for equipment and protective systems intended for use in potentially explosive atmospheres*.
- BS-EN-13463. (2009). *Non-electrical equipment for potentially explosive atmospheres: basic methods and requirements*.
- BS-EN-13673. (2003). *Determination of the maximum explosion pressure, and the maximum rate of explosion pressure rise of gases and vapours*.
- BS EN ISO 14121-1:2007 *Safety of machinery. Risk assessment. Principles*
- BS-EN-14522. (2005). *Determination of the auto ignition temperatures for gases and vapours*.
- BS-EN-14460. (2006). *Explosion resistant equipment*.
- BS-EN-14994. (2007). *Gas explosion venting systems*.
- BS-EN-1839. (2003). *Determination of the explosion limits for gases and vapours*.
- BS-EN-60079. (2007). *Explosive atmospheres*.
- BS-EN-ISO-4126. (2004). *Safety devices for protection against excessive pressure*.
- BS-ISO-21789. (2009). *Gas turbine applications - Safety*.
- BS-ISO-3977. (2004). *Gas turbines - Procurement: Part3 - design*.
- BS-PD-CEN-TR-15281. (2006). *Inerting for the prevention of explosions*.
- Cabra,R.,Turbulent jet flames in a vitiated coflow, *Tech. Rep. CR-2004-212887*, NASA, 2000.
- Cabra,R., Myhrvold,T., Chen, J.Y., Dibble, R.W., Karpets,A.N., and Barlow,R.S., Simultaneous laser Raman–Rayleigh–LIF measurements and numerical modeling results of a lifted turbulent H₂/N₂ jet flame in a vitiated coflow, *Proc. Combust. Inst.* 29 (2002), pp. 1881-1888.
- Chan, C., Sitar, J., Beauvais, R., & Mayinger, F. (1996). Modeling maximum flame speeds. *Nuclear Engineering and Design*, 166 (3), 463-469.
- Chao, J., & Lee, J. (2003). The propagation mechanism of high speed turbulent deflagrations. *Shock Waves*, 12 (4), 277-289.
- Chao, J., Otsuka, T., & Lee, J. (2005). An experimental investigation of the onset of detonation. *Proceedings of the Combustion Institute*, 30 (2), 1889-1897.
- Chun, M.K., Song, H.K., Moliere, M. Kandel, E., & Lallemand, R., *Daesan Unit Burns 95 per cent Hydrogen Fuel*, Modern Power Systems, 19 (12), 27, (December 1999)
- Ciccarelli, G., & Dorofeev, S. (2008). Flame acceleration and transition to detonation in ducts. *Progress in Energy and Combustion Science*, 34 (4), 499-550.
- Ciccarelli, G., Boccio, J., Ginsberg, T., Finrock, C., Gerlach, L., Tagawa, H., et al. (1998). *The effect of initial temperature on flame acceleration and deflagration-to-detonation transition phenomenon*. U.S. Nuclear Regulatory Commission, Office of Nuclear Regulatory Reserach, Washington DC.
- Ciccarelli, G., Ginsburg, T., Boccio, J., Economos, C., Finrock, C., Gerlach, L., et al. (1994). *High-Temperature Hydrogen-Air Steam Detonation Experiments in the BNL Small-Scale Development Apparatus*. U.S. Nuclear Regulatory Commission, Office of Nuclear Regulatory Research, Washington DC.
- Ciccarelli, G., Ginsburg, T., Boccio, J., Economos, C., Sato, K., Kinoshita, M., (1994). *Detonation cell size measurements and prediction in hydrogen-air-steam mixtures at elevated temperatures*. Combustion and Flame 99:212-220. (1994).
- Ciferno,J.P., Marano J.J. (2002) Benchmarking Biomas Gasification Technologies for Fuels, Chemicals and Hydrogen Production [Online] 19-20 Available from: <http://www.acribd.com/doc/52659768/26/Syngas-Composition>.

- Cong, T., & Dagaut, P. (2008). Experimental and detailed kinetic modeling of oxidation of methane and methane/syngas mixtures and effect of carbon dioxide addition. *Combustion Science and Technology*, 180, 2046-2091.
- Cong, T., Dagaut, P., & Dayma, G. (2008). Oxidation of Natural Gas, Natural Gas/Syngas Mixtures, and Effect of Burnt Gas Recirculation: Experimental and Detailed Kinetic Modeling. *Journal of Engineering for Gas Turbines and Power*, 130 (041502).
- Cuoci, A., Frassoldati, A., Ferraris, G., Faravelli, T., & Ranzi, E. (2007). The ignition, combustion and flame structure of carbon monoxide/hydrogen mixtures. Note 2: Fluid dynamics and kinetic aspects of syngas combustion. *International Journal of Hydrogen Energy*, 32, 3486-3500.
- CUP. (2007). *Hydrogen properties, Columbia Electronic Encyclopedia, 6th edition*. Columbia University Press.
- Demirbas A. Hydrogen Production from Carbonaceous Solid Wastes by Steam Reforming, *Energy Sources, Part A*, 30:924–931, 2008.
- Dept. of Energy and Climate Change. UK. www.decc.gov.uk. Carbon Capture and Storage. 2011.
- Det Norske Veritas (DNV) (1999). *Gas Burning Internal Combustion Engine Installations*. Standard for Certification No. 2.11.
- Directive 1999/92/EC. *ATEX workplace Directive*. 1992.
- Dorofeev, S., Kuznetsov, M., Alekseev, V., Efimenko, A., & Breitung, W. (2001). Evaluation of limits for effective flame acceleration in hydrogen mixtures. *Journal of Loss Prevention in the Process Industries*, 14 (6), 583-589.
- Dorofeev, S., Sidorov, V., Dvoinishnikov, A., & Breitung, W. (1996). Deflagration to Detonation Transition in Large Confined Volume of Lean Hydrogen-Air Mixtures. *Combustion and Flame*, 104, 95-110.
- Dorofeev, S., Sidorov, V., Kuznetsov, M., Matsukov, I. D., Alekseev, V. I., *Effect of scale on the onset of detonations*. *Shock Waves* (2000) 10: 137-149.
- Dragomir R., Drnevich R. F., Morrow J., Papavassiliou V., Panuccio G., Watwe R., Technologies for improved refinery gas utilization, NPRA 2010 Meeting Phoenix AZ .
- Drysdale, D. (2011). *An Introduction to Fire Dynamics, 3rd Edition*. John Wiley & Sons, Ltd.
- DSEAR. (2002). *Dangerous Substances and Explosive Atmospheres Regulations*.
- ED-97-9-EC. (1999). *Pressure Equipment Directive*.
- EN 12601:2010, Reciprocating internal combustion engine driven generating sets. Safety
- EN 62061: 2005, Safety of machinery. Functional safety of safety-related electrical, electronic and programmable electronic control systems.
- EN ISO 13849-1: 2008, Safety of machinery. Safety-related parts of control systems. General principles for design
- Etheridge, C. *Private Communication* Solar Inc.
- Fairweather, M, Ormsby, M.P., Sheppard, C.G.W. and Woolley, R. (2009) Turbulent burning rates of methane and methane-hydrogen mixtures, *Combustion and Flame*.156:780-790.
- Frassoldati, A., Faravelli, T., & Ranzi, E. (2007). The ignition, combustion and flame structure of carbon monoxide/hydrogen mixtures. Note 1: Detailed kinetic modeling of syngas combustion also in presence of nitrogen compounds. *International Journal of Hydrogen Energy*, 32, 3471-3485.
- Freedman, S.I. (2007) Chapter 9. Gast Turbines. *Energy Conversion*. [Online] 9-9 –9-10. Available from: <http://www.crcnetbase.com/doi/abs/10.1201/9781420044324.ch9>
- GE Energy, '*Compressor Discharge Air (CPD) and Inert Purge System*. (7FB IGCC Turbine), GEK 116632a, April 2010.
- Geipel, P., Experimental Research on Turbulent Reacting Flows using Gaseous and Liquid Fuels, *PhD Thesis, Imperial College, 2009*.

- Geipel, P., Goh, K.H.H., and Lindstedt, R.P., Fractal-Generated Turbulence in Opposed Jet Flows, *Flow Turbulence Combust* 85:397-419 (2010).
- Gkagkas K., and Lindstedt, R.P., Transported PDF modelling with detailed chemistry of pre- and auto-ignition in CH₄/air mixtures, *Proc. Combust. Inst.* 31 (2007), pp. 1559-1566.
- Gkagkas, K. and Lindstedt, R.P., The impact of reduced chemistry on auto-ignition of H₂ in turbulent flows, *Combust. Theory. Model.* 13:607-643 (2009)
- Goh, K.H.H., Geipel, P. and Lindstedt, R.P., The stability of flames burning against hot exhaust products in fractal generated turbulence, *5th European Combustion Meeting, Cardiff, June 28 – July 1, 2011.*
- Gamezo, V.N., Ogawa, T. & Oran, E.S. (2007) Numerical simulations of flame propagation and DDT in obstructed channels filled with hydrogen–air mixture, *Proceedings of the Combustion Institute* 31: 2463-2471.
- Germanischer Lloyd Rules and Programs 13.0 (2011)
- H₂-IGCC. (2011). *H2 IGCC Energy without CO2 - European Project.* (E. T. (ETN), Producer) From <http://www.h2-igcc.eu/default.aspx>
- Hansen, T., 'Meeting Gas Quality Challenges', *Power Engineering*, May 2008.
- Healy, T., Frederick, G., 'Tuning for LNG on the fly', *Turbomachinery International*, 48(5), 24 - 26, 2007.
- Hewitt, G., Futter, D., Roby, D., Rea, S., Goy, C., 'Combustion Dynamics and Exhaust Gas Monitoring for CCGT Plant', Powergen Europe Conference, Barcelona, May, 2004.
- Horlock, J. (2002). *Elementary Thermodynamics of Power Plants.* Combined Power Plants, 2.
- HSE Books HS(L)21. (2009). *A guide to health and safety regulation in Great Britain.*
- HSE Publications. L134 (2003). *Design of plant, equipment and workplaces.*
- HSE-GD-PM-84. (2003). *Control of safety risks at gas turbines used for power generation.* HSE Guidance Note PM84. HSE Books.
- HSE. *The Supply of Machinery (Safety) Regulations.* 1992.
- IEC-61508. (2010). *Functional Safety of Electrical/Electronic/Programmable Electronic Safety-related Systems.*
- IEC-61511. (2003). *Functional Safety - Safety instrumented systems for the process industry sector.*
- IGC. (2010). *The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk.* IGC-Code.
- IGEM-UP-3. (2006). *Gas fuelled spark ignition and dual fuel engines.* The Institute of Gas Engineers and Managers, UK.
- IGEM-UP-9. (2010). *Application of Natural Gas and fuel oil systems to gas turbines and supplementary and auxiliary fired burners.* The Institute of Gas Engineers and Managers, UK. IGEM.
- ISO-12100. (2010). *Safety of machinery - Risk assessment and risk reduction.*
- ISO-26142. (2010). *Hydrogen detection apparatus: stationary applications.*
- ISO- 9001. (2008) *Quality management systems — Requirements.*
- ISO-PDTR-15916. (2010). *Basic considerations for the safety of hydrogen systems.*
- Ivings, M.J., Lea, C.J., Ledin, H.S., Pritchard, D.K., Santon, R.C. and Saunders, C.J., (2004). *Outstanding safety questions concerning the use of gas turbines for power generation – Summary report,* HSL report CM/04/02, Health and Safety Laboratory, Buxton, UK.
- Jenbacher (2011). *Private Communication.*

- Johansen, C., & Ciccarelli, G. (2009). Visualization of the unburned gas flow field ahead of an accelerating flame in an obstructed square channel. *Combustion and Flame*, 156 (2), 405-416.
- Johnson, D., Miller, R. W., Ashley, T., 'Speedtronic Mark V Gas turbine Control system', GE Document GER-3658D. 1996
- Jones, R.M., (2006). *Gas turbine fuel flexibility for a carbon constrained world*. Workshop gasification technologies, Bismark, ND.
- Koeneke, C., Haruta, H., Kawakami, T., 'Update on MHI Self-Tuning Combustion Dynamics System ACPFM', *Power-Gen International Conference*, Orlando, November 2006.
- Koivu, T.G., (2007) New technologies for steam injection (STIG) etc. 17th Symposium Industrial application of Gas Turbines(IAGT) Canada. October 2007.
- Kratzel, T., Burkhardt, A., Eichert, H., & Fischer, M. (1996). Instationary highly turbulent hydrogen tube combustion processes in obstacle areas. *International Journal of Hydrogen Energy*, 21 (1), 45-52.
- Kuan T.S., Lindstedt, R.P. and Vaos, E.M., (2003) Higher Moment Based Modeling of Turbulence Enhanced Explosion Kernels in Confined Fuel-Air Mixtures, *Advances in Confined Detonations and Pulse Detonation Engines*, ISBN 5-94588-012-4, Torus Press, pp. 17-40.
- Lee, J., Knystautas, R., & Chan, C. (1985). Turbulent flame propagation in obstacle-filled tubes. *Symposium (International) on Combustion*, 20 (1), 1663-1672.
- Lee, J., Knystautas, R., & Freiman, A. (1984). High speed turbulent deflagrations and transition to detonation in H₂-air mixtures. *Combustion and Flame*, 56 (2), 227-239.
- Lieuwen, T., McDonell, V., Petersen, E., & Santavicca, D. (2008). Fuel Flexibility Influences on Premixed Combustor Blowout, Flashback, Autoignition, and Stability. *Journal of Engineering for Gas Turbines and Power*, 130 (011506).
- Lindstedt, R.P. & Michels, H.J. (1988). Deflagration to Detonation transition in mixtures of alkane LNG LPG constituents with O₂/N₂. *Combustion and Flame*, 72, 63-2.
- Lindstedt, R.P. and Michels, H.J., Deflagration to Detonation Transitions and Strong Deflagrations in Alkane and Alkene Air Mixtures, *Combustion and Flame*, 76:169-181 (1989).
- Lindstedt, R.P. and Sakthitharan, V., (1995) Transient Flame Growth in a Developing Shear Layer, *in Turbulent Shear Flows 9*, Eds. J.H. Whitelaw, F.W. Schmidt, F. Durst and K. Suzuki, (Springer-Verlag, Berlin), pp. 389-409.
- Lindstedt, R.P. and Sakthitharan, V., (1998) Time Resolved Velocity and Turbulence Measurements in Turbulent Gaseous Explosions, *Combustion and Flame*, 114:469-483.
- Lindstedt, R.P. and McCann, H.A. (2001) Time Resolved Flow Characteristics of Confined Turbulent Gaseous Explosions. Presented at 18th ICDERS, Seattle.
- Liu, Z. & Kim, A.K. *A review of water mist fire suppression systems: fundamental studies*. National Research Council, Canada. NRCC-41910. 2000.
MHI Press release, May 2011, <http://www.greencarcongress.com/2011/05/mhij-20110527.html>, accessed 21/1/12.
- Mackaluso, J. (2007). *The use of syngas derived from biomass and waste products to produce ethanol and hydrogen*. Retrieved July 28, 2011 from <http://ejournal.vudat.msu.edu/index.php/mmg445/article/viewFile/236/292>
- Maurstad, O. (2005). An Overview of Coal based Integrated Gasification Combined Cycle (IGCC) Technology. *MIT LFEE 2005-002 WP*.
- Mertens, J., Kalitan, D., Barrett, A., & Petersen, E. (2009). Determination of the rate of H+O₂+M -> HO₂+M (M=N₂, Ar, H₂O) from ignition of syngas at practical conditions. *Proceedings of the Combustion Institute*, 32, 295-303.
- Moliere, M. (2004). *Hydrogen-fuelled gas turbines: status and prospects*. 2nd CAME-GT Conference. Bled, Slovenia.

- Molière, M., 'Stationary gas turbines and primary energies : A review of fuel influence on energy and combustion performance', *Int. J Therm. Sci.* 39, 141-172 (2000)
- Mori, H., Uematsu, K., & Aoki, S. (1998). A Study of Hydrogen Combustion Turbines. *ASME Turbo Expo 98-GT-394*.
- Nag, P., Lagrow, M., Wu, J., Abou-Jaoude, K., Engel, J., 'LNG Fuel Flexibility in Siemens' Land- Based Gas Turbine Operations', Electric Power Conference, Chicago, may, 2007.
- NASA-NSS-1740.16. (1997). *Safety standards for hydrogen systems: Guidelines for Hydrogen System Design, Materials Selections, Operations, Storage, and Transportation*. National Aeronautics and Space Administration. Washington DC: Office of Safety and Mission Assurance.
- NCEAC. (2011). *Northwest Clean Energy Application Center*. (U.S. Department of Energy) Retrieved August 21, 2011 from Promoting CHP, District Energy, and Waste Heat Recovery: <http://www.chpcenternw.org/AboutCleanEnergy/CombinedHeatandPowerCHP/CHPEmissions.aspx>
- NETL. (2010). *The National Energy Technology Laboratory*. Retrieved 2010 from Coal and Power Systems: <http://www.netl.doe.gov/technologies/coalpower/gasification/>
- Nettleton, M. (1987). Gaseous detonations - their nature, effects and control. *Environmental Progress*, 6 (3), A7.
- Nessler, H. Eisenkolb, P. (2001). *Developments in HRSG technology*. 7th Industrial & Power Gas Turbine O&M Conference. 2001.
- NFPA-68. (2008). *Standard on explosion prevention systems*.
- NFPA-69. (2008). *Standard on explosion prevention systems*.
- NFPA-85. (2011). *Boiler and combustion systems hazards code*.
- Oppenheim, A.K. & Urtiew, P.A. (1966) Experimental observations of the transition to detonation in an explosive gas, *Proceedings of the Royal Society A*, 295.
- Otsuka, T., Saitoh, H., Mizutani, T., Morimoto, K., & Yoshikawa, N. (2007). Hazard evaluation of hydrogen-air deflagration with flame propagation velocity measurement by image velocimetry using brightness subtraction. *Journal of Loss Prevention in the Process Industries*, 20 (4-6), 427-432.
- Prathap, C., Ray, A., & Ravi, M. (2008). Investigation of nitrogen dilution effects on the laminar burning velocity and flame stability of syngas fuel at atmospheric condition. *Combustion and Flame*, 155, 145-160.
- Rajvanshi, A. (1986). Chapter 4: Biomass Gasification. In D. Y. Goswami, *Alternative Energy in Agriculture* (Vol. 2, pp. 83-102). CRC Press.
- RfP (2010). Request for proposal issued by ETI, July 2010.
- Rules for Construction and Equipment of Ships Carrying Liquefied Gases in Bulk, China Classification Society
- Rosenbauer, G. (2007). Siemens power generation approach to carbon capture and storage. *Power-Generation Europe*. Madrid.
- Santon, R. (2005). A Review of UK Onshore and Offshore Installations. *Institution of Diesel and Gas Turbine Engineers*.
- Santon, R. (1998). Explosion hazards at gas turbine driven power plants. *ASME*.
- Santon, R.C., Kidger, J.W. and Lea, C.J.,(2002) Safety Developments in Gas Turbine Power Applications. ASME GT-2002-30469.
- Santon, R.C., Ivings, M.J. and Pritchard, D.K., (2005) A New Gas Turbine Enclosure Ventilation Design Criterion. ASME GT-2005-68725.
- Schneider, M., (2006) Utilisation of Low BTU Gases in Spark Ignition Reciprocating Engines,2006) *Institution of Diesel and Gas Turbine Engineers*.
- Shilling, N., Jones, R. M., The response of a gas turbine to a CO₂ restrained economy. Gasification Technology Conference. Oct. 2003.

- Silvestrini, M., Genova, B., Parisi, G., & Trujillo, F. (2008). Flame acceleration and DDT run-up distance for smooth and obstacles filled tubes. *Journal of Loss Prevention in the Process Industries*, 21 (5), 555-562.
- Sivaramakrishnan, R., Comandini, A., Tranter, R., Brezinsky, K., Davis, S., & Wang, H. (2007). Combustion of CO/H₂ mixtures at elevated pressures. *Proceedings of the Combustion Institute*, 31, 429-437.
- Starr, F. (2003). Background to the design of HRSG systems and implications for CCGT plant cycling. *OMMI*, 2 (1).
- Starr, F. (2010). *Future Challenges for CHP in the UK and Continental Europe*. Claverton Energy Research Group.
- Tang, C., Huang, Z., Chun, J. J., Wang, J., et Al. *Explosion characteristics of hydrogen-nitrogen-air mixtures at elevated pressure and temperatures*. *Int. Journal of hydrogen energy* 34 (2009) 554-561.
- TC197HydTec. (2010). *Basic considerations for the safety of hydrogen systems*. TC 197 Hydrogen technologies. International Organization for Standardization.
- Teodorczuk, A. (2008). Scale effects on hydrogen-air fast deflagrations and detonations in small obstructed channels. *Journal of Loss Prevention in the Process Industries*, 21 (2), 147-153.
- Thomas, G. O., The controlling mechanisms during explosion mitigation by water sprays. *Process Safety and environmental Protection.. Vol 78. pp339-354*. 2000.
- Todd, D. M., Battista, R. A., 'Demonstrated Applicability of Hydrogen Fuel for Gas Turbines', Proceedings of Gasification 4 the Future, Noordwijk, Netherlands, April 2000.
- Veser, A., Breitung, W., & Dorofeev, S. (2002). Run-up distances to supersonic flames in obstacle-laden tubes. *J. Phys. IV France*, 12 (7), 333-340.
- VISA (Netherlands) Parts C-1 / C-7 "Richtlijnen voor het gebruik van aardgas in gasmotoren" (Guidelines for the use of natural gas in gas engines) and Parts C-8 / C-14 "Veiligheidsvoorschriften voor aardgasmotoren" (safety requirements for gas engines)
- Walton, S., He, X., Zigler, B., & Wooldridge, M. (2007). An experimental investigation of the ignition properties of hydrogen and carbon monoxide mixtures for syngas turbine applications. *Proceedings of the Combustion Institute*, 31, 3147-3154.
- Webber, D., Ivings, M., & Santon, R. (2011). Ventilation theory and dispersion modelling applied to hazardous area classification. *Journal of Loss Prevention in the Process Industries*, 24 (5), 612-621.
- Willauer, H.D., Ananth, R., Farley, J.P., Willaims, F. W., *Blast mitigation using water mist: test series II*. Naval Research Laboratory. Washington DC. NRL/MR/6180-09-9182. 2009.
- Williams, F. (1976). Qualitative Theory of Nonideal Explosions. *Combustion Science and Technology*, 12 (4-6), 199-206.
- Williams, T., Shaddix, C., & Schefer, R. (2008). Effect of Syngas Composition and CO₂-diluted Oxygen on Performance of a Premixed Swirl-Stabilized Combustor. *Combustion Science and Technology*, 180, 64-88.
- Wolf, J., & Perkovec, M. (1992). Safety Aspects and Environmental Considerations for a 10MW Cogeneration Heavy Duty Gas Turbine Burning Coke Oven Gas with 60% Hydrogen Content. *ASME Turbo Expo 92-GT-042*.
- Wu, F., Kelley, A., Zhu, D., & Law, C. (2011). Further study on effects of hydrogen addition on laminar flame speeds of fuel air mixture. *7th US National Combustion Meeting*, 7 (LE10).
- Zachary, J. (2008). CO₂ capture and sequestration options-Impact on tubomachinery design. *ASME Turbo Expo*. Berlin.
- Zhao, Y., et Al. (2003). Modelling and cost optimisation of combined cycle heat recovery generator systems. *ASME Turbo Expo*. Atlanta USA.