



Programme Area: Carbon Capture and Storage

Project: High Hydrogen

Title: Proposed Representative Fuel Systems

Abstract:

A brief summary report of only six pages supporting Stage Gate 1 for discussions to identify the fuel mixtures we should utilize in the test program

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.

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Proposed Representative Fuel Systems: Summary.

It was agreed with ETI that the proposed choice of the three representative fuel systems would be reviewed and agreed prior to the submission of the literature review. The following therefore summarises the selection process.

Three representative fuel systems are suggested, based on future potential fuel sources, which can also be tested generically in the laboratory such that their properties can be readily assessed in respect of their DDT potential, and the needs of the project. The issue of the selection process is also reviewed in the light of real gas turbine systems. This provides additional information, which shows that certain high hydrogen fuels could potentially result in fuel mixtures exceeding the LFL in the exhaust stream following a flameout.

A review of the literature shows that the typical composition of the three most generic fuel systems currently used for CCGT power generation may be represented 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.

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

| 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.

Since hydrogen is the main area of interest its use as a fuel in pure form must also 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. A number of composition cases are cited by Todd and Battista (D.M. Todd, R.A. 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, results 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 having the lowest CV value of the group.

A number of syngas 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.

Based on the fuels of Table 13 and their reported GT operating conditions, it is 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 can be 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/M W |
|-------------------------|-------------------------|------|-----------------|---------|----------------|-----------------|------------------|---------------|------------------|---------------------|
| | H ₂ | CO | CH ₄ | H/ C | N ₂ | CO ₂ | H ₂ O | | | |
| Hydrogen | 100 | | | | | | | 120.0 | 2.0 | 0.0083 |
| Syngas 1 | 14.5 | 23.6 | 1.6 | | 49.0 | 5.6 | 5.7 | 9.5 | 24.4 | 0.106 |
| Syngas 2 | 34.4 | 35.1 | 0.3 | 0 | 0 | 30.2 | | 8.2 | 23.9 | 0.122 |
| Syngas 3 | 61.9 | 26.2 | 6.9 | 0 | 2.2 | 2.8 | | 25.7 | 11.5 | 0.039 |
| Syngas +CCS | 47 | 1 | 1 | | 41 | | 10 | 8.9 | 14.7 | 0.113 |
| COG | 61.6 | 6 | 23 | 2.2 | 5.4 | 1.2 | | 42.4 | 9.6 | 0.024 |
| Refinery Gas | 28 | | 28 | 34 | 3.5 | 6.5 | | 41.0 | 23.8 | 0.024 |
| Bio Syngas | 18 | 20 | 7 | 2 | 30 | 23 | | 6.5 | 26.5 | 0.154 |

NB: Syngases 1 - 3 and Syngas + CCS are taken from (D.M. Todd, R.A. Battista, 2000). COG is taken from (J. Wolf, & M. Perkovec., 1992). Refinery Gas is taken from (R. Dragomir et Al, 2010). Bio-Syngas is taken from (A. 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 | 0.89 | 0.0314 | 0.117 | 0.117 |
| Syngas 1 | 0.106 | 0.0043 | 0.9 | 0.79 | 0.0280 | 0.134 | 0.019 |
| Syngas 2 | 0.122 | 0.0051 | 0.9 | 0.78 | 0.0274 | 0.157 | 0.054 |
| Syngas 3 | 0.039 | 0.0034 | 0.9 | 0.86 | 0.0303 | 0.100 | 0.062 |
| Syngas +CCS | 0.113 | 0.0078 | 0.9 | 0.79 | 0.0277 | 0.218 | 0.102 |
| COG | 0.024 | 0.0025 | 0.9 | 0.88 | 0.0309 | 0.074 | 0.045 |
| Refinery Gas | 0.024 | 0.0010 | 0.9 | 0.88 | 0.0308 | 0.0321 | 0.0090 |
| Bio Syngas | 0.222 | 0.0058 | 0.9 | 0.68 | 0.0239 | 0.181 | 0.033 |

Two further sources of high hydrogen fuel gas composition are detailed below (Tables 15, 16) and originate from the high hydrogen fuel to be used by the ETN consortium together with a representative high hydrogen fuel as recognised by GE.

The ETN is also analysing the gasification process, and provides, besides several other items of information, the fuel composition for the other sub-projects. The following 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).

Table 16 below 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 | Mol % |
|-----------------------|--------------|
| CO | 58.1 |
| CO ₂ | 0.69 |
| H ₂ | 23.6 |
| H ₂ O | 8.0 |
| N ₂ | 8.7 |
| CH ₄ | 0.02 |
| Ar | 0.8 |
| H ₂ S | 0.0018 |
| COS | 0.0009 |

The various fuel mixtures discussed above have been collected together in Table 17 for comparison.

Table 17: Collected 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 the future experimental investigations is influenced by a number of factors as discussed in the following.

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 likely that a significant proportion of syngas will be derived by means of air blown gasifiers without carbon capture, and Syngas 1 (Fuel 7) is representative of such a group of low calorific value fuels.

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) entry in Table 17. It is noted that oxygen blown syngases with CO₂ capture are effectively hydrogen streams and already represented by the pure hydrogen choice.

A further likely gaseous fuel stream will be those associated with refinery or coke production processes and which are likely to have 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 18.

Table 18: 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 | |