# Hydrogen from Exhaust Gas Fuel Reforming:

# Greener, Leaner and Smoother Engines

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**The University of Birmingham**

# Hydrogen as a Fuel

| Property | | Gasoline | Methanol | Methane (Nat.gas) | Hydrogen |
|---|---|---|---|---|---|
| Formula | | C7.1H12.56 | CH3OH | CH4 | H2 |
| Boiling Point | deg C | 30 - 190 | 65 | -161 | -253 |
| Flammability limits | % vol. | 1.0 - 7.6 | 6.7 - 36 | 5.3 - 15 | 4 - 75 |
| Max burning velocity in air | m/s | 0.5 | 0.48 | 0.4 | 2.9-3.5 |
| Net ignition energy in air | mJ | 0.24 | 0.215 | 0.29 | 0.02 |
| Quenching distance | mm | 2.84 | 1.8 | 1.9 | 0.6 |
| Heat of evaporation | MJ/kg | 0.4 | 1.25 | gas | gas |
| Lower Calorific Value | MJ/kg | 40-45 | 20 | 50.01 | 120.5 |
| Energy density (15C/100kPa) | MJ/m3 | 33750 | 15840 | 33.4 | 10.3 |
| Mixture Calorific Value (20C) | MJ/m3 | 4.44 | 3.24 | 3.13 | 2.95 |

# Use of Hydrogen in IC Engines

- **As a pure fuel**
  - **Long term strategy**
- **As an additive to fossil fuels**
  - **Lean/Diluted Burn**
  - **Exhaust Gas Recirculation**
- **Problems:**
  - **Production Thermoeconomics**
  - **Storage on board**
- **Solution: Production on-board**

# Off-board produced hydrogen

- **Remote energy & $CO_2$ cost**
- **Lack of distribution infrastructure**
- **Storage problems for use on board**
  - **hydrides:**

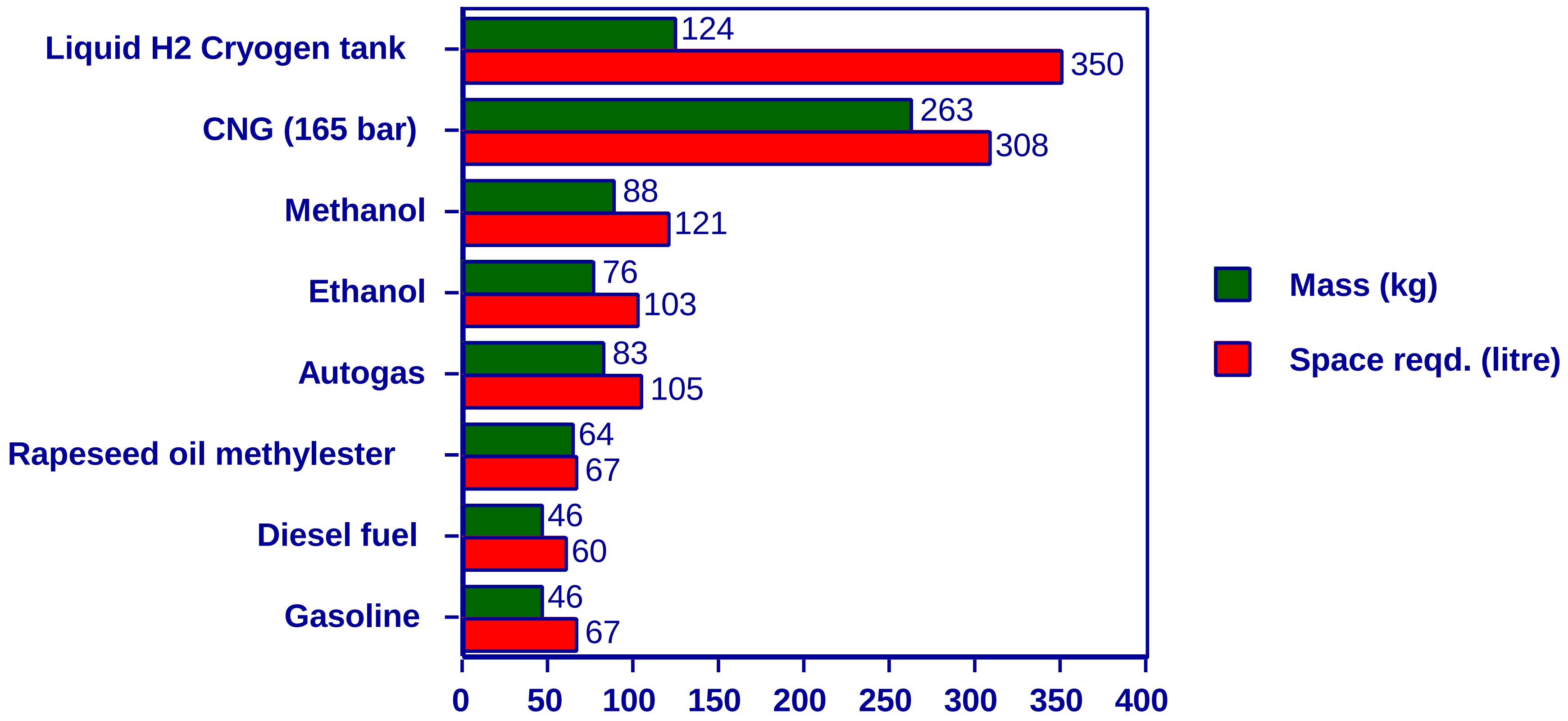
    **weight & range penalty**
  - **compressed $H_2$:**

    **bulk**
  - **liquid $H_2$ - best,**

    **high energy cost for liquefaction**

# Fuel storage requirements

## Storage requirements for fuels equivalent to 55 litres gasoline




*Source: Volkswagen Documentation "Alternative Fuels"*

# On-board Production of Hydrogen: Fuel Reforming

- **Production of hydrogen on-board from hydrocarbons or alcohol**
- **Three main reaction paths**
  - **steam reforming** e.g. $CH_4 + H_2O = CO + 3H_2$
  - **direct partial oxidation** $2CH_4 + O_2 = 2CO + 2H_2$
  - **thermal decomposition** $CH_3OH = CO + 2H_2$
- **Exhaust gas reforming**
  - **direct contact between exhaust gases and HC fuel over catalyst**
  - **combination of all three fundamental processes, e.g.**

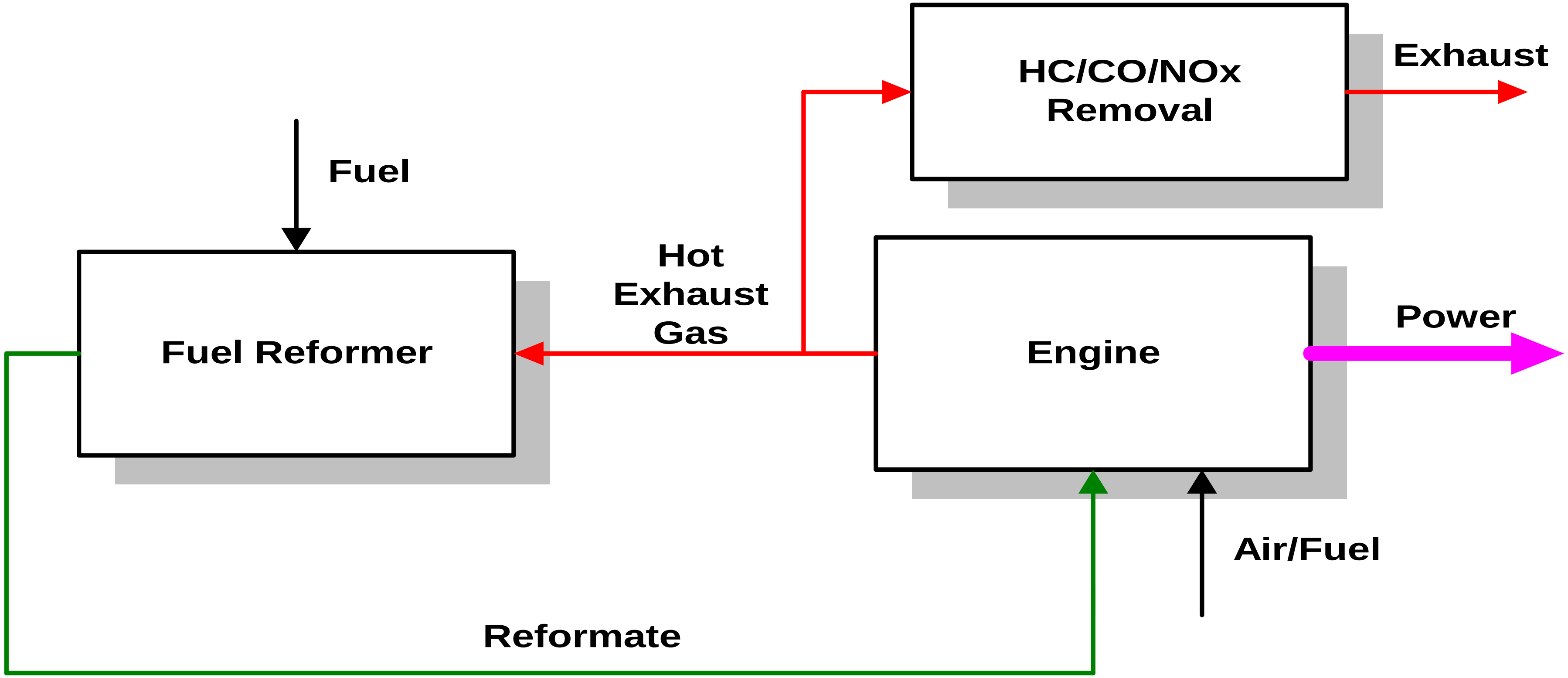
$$CH_4 + 0.33(CO_2 + 2H_2O + 7.52N_2) = 1.33(CO + 2H_2 + 1.88N_2)$$

$$D_RH = 220 \text{ kJ/kmol} \quad \text{(endothermic)}$$

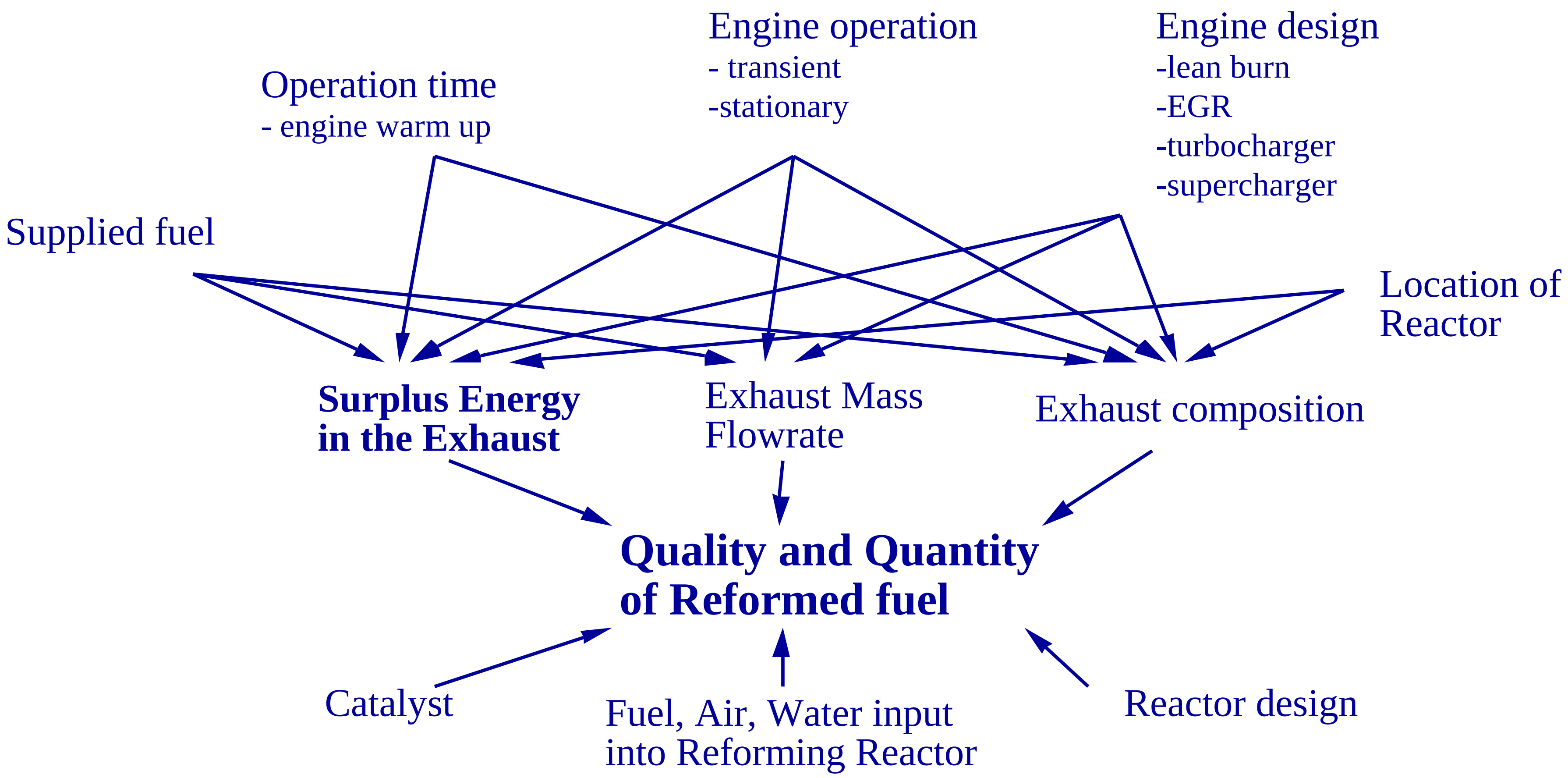
**combustion of reformed fuel:**

$$(CO + 2H_2 + 1.88N_2) + 1.5(O_2 + 3.76N_2) = CO_2 + 2H_2O + 7.52N_2$$

# Engine-Reformer System



# Parameters affecting the Quality and Quantity of Reformed Fuel



# Main modes of fuel reforming with exhaust gas

- **High exhaust temperature (>800-900 degC)**
  - **High hydrogen yield (over 30% in reformed gas)**
  - **Energy recovery from exhaust gas to increase CV of fuel**
  - **All or most fuel could be reformed**
  - **Possible at high engine load**
- **Lower temperature (500-700 degC)**
  - **Up to 20% hydrogen obtainable**
  - **Temperature may be boosted by partial oxidation**
  - **Mainly for hydrogen enrichment of EGR to improve combustion**
  - **Possible at part load, maybe at idle**

# Hydrogen enrichment

- **Increases flame speed**

| | Gasoline | Methane | Hydrogen |
|---|---|---|---|
| burning velocity in air (m/s) | 0.5 | 0.4 | 2.9-3.5 |

- **Reduces emissions of hydrocarbons**

| | | | |
|---|---|---|---|
| Quenching distance (mm) | 2.84 | 1.9 | 0.6 |

- **Allows higher levels of EGR (thus reduced NOx) with good combustion stability**

# Exhaust Reforming of Liquid Fuels (n-Heptane and Gasoline)

**University of Birmingham:**

- **ML Wyszynski, MR Jones, H West, R Chen, Y Jamal, T Wagner (Mechanical Engineering)**
- **RS Lehrle, J Riches, D Sarson (School of Chemistry)**

**D Bradley, CGW Sheppard (University of Leeds)**

**B Parsons, D Szczupak, R Lee (Jaguar Cars)**

**S Wallace, D Richardson, S Shillington, M Davies (Rover Group)**

**Drs P Hawker & RJ Brisley, Dr J Frost (Johnson Matthey)**

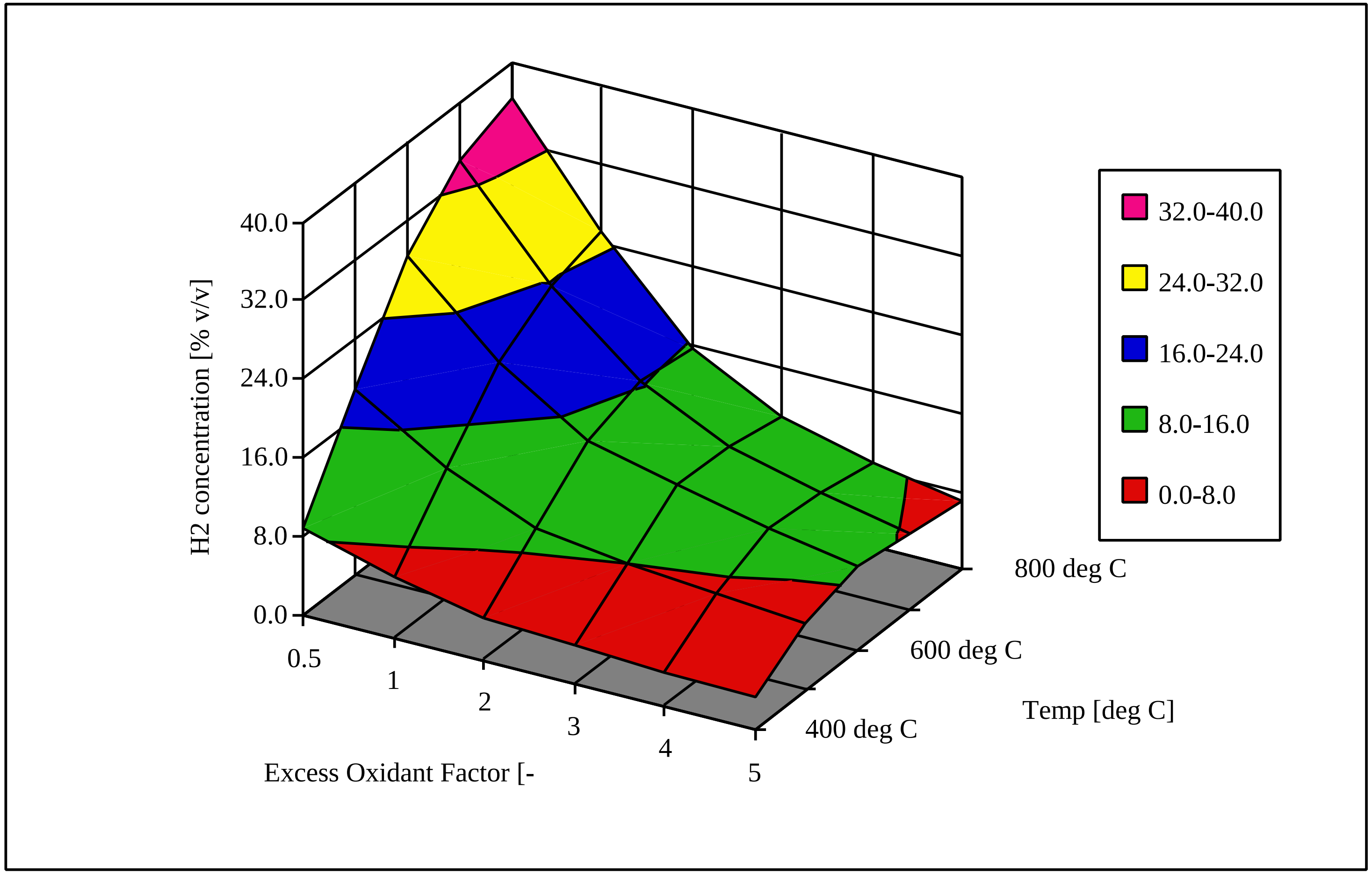
**M Shaw (Inco Alloys International)**

**Dr R Mortier, Mr S Orszulik (Castrol Ltd)**

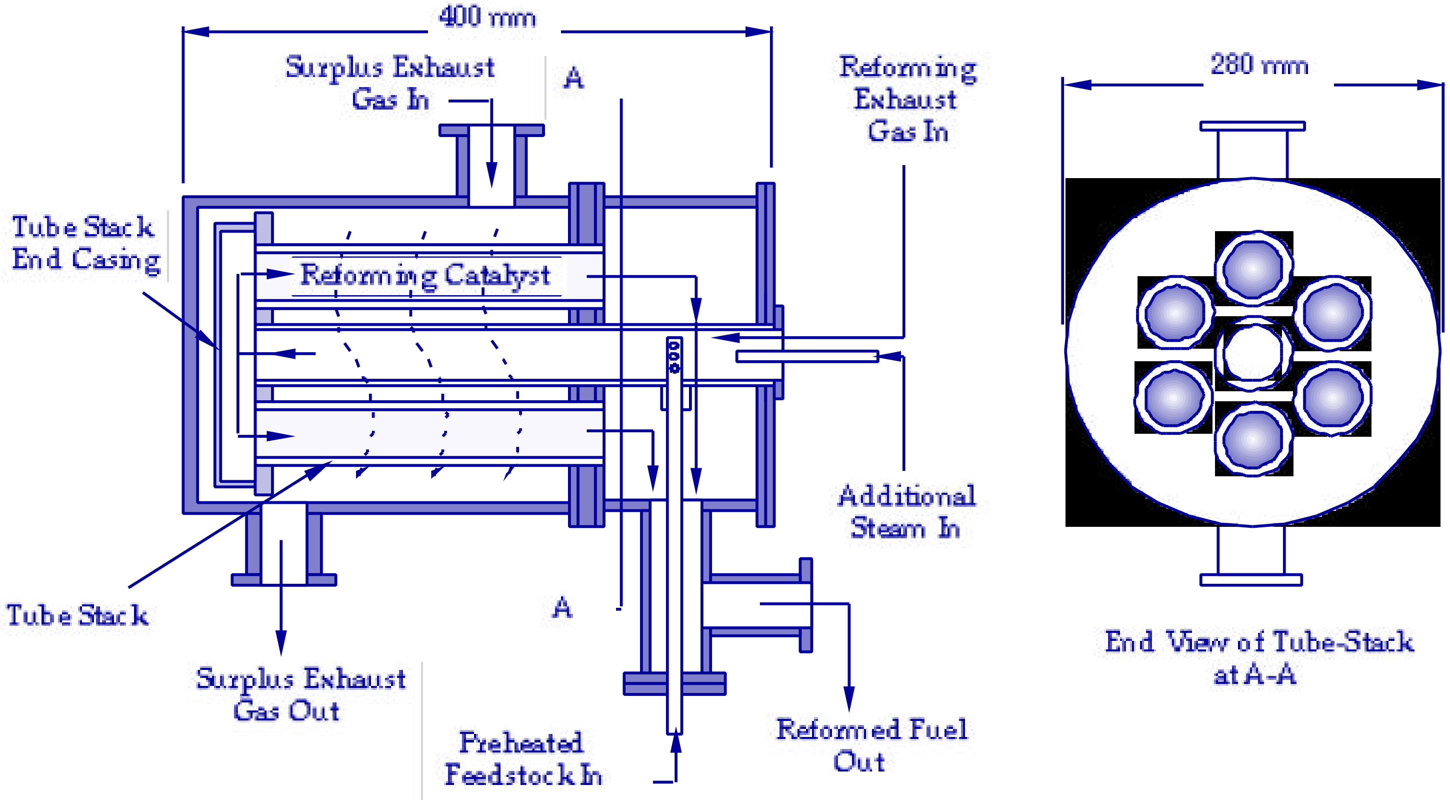
**SERC - MPVI, British Gas**

# Exhaust Gas Reforming of Gasoline

## Calculated Hydrogen Concentration vs. Excess Oxidant Factor and Temperature, p=1.013 bar, Equivalence ratio 1.0



# First reforming reactor



# High temperature reforming results

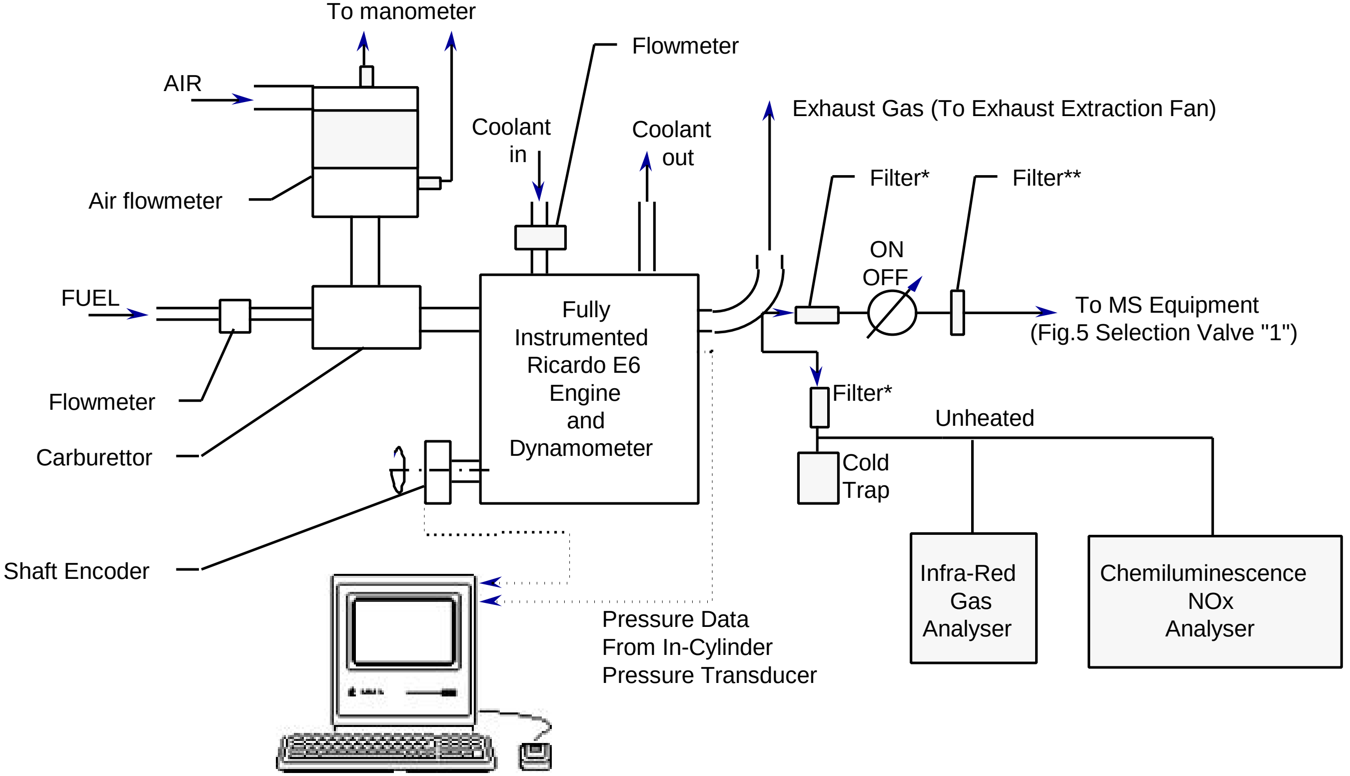
- **n-Heptane:**
  - Peak Proportion of Hydrogen = 32.2%
  - Peak Proportion of CO = 20.9%
  - Highest Reactor Thermal Efficiency = 128%

- **Unleaded Gasoline**
  - Peak Proportion of Hydrogen = 19.8%
  - Peak Proportion of CO = 12.0%
  - Highest Reactor Thermal Efficiency = 97.2%

# High/Low temperature reforming results

| Component (vol %) | HTRF-4 (n-heptane, 950 degC) | RF-3 (vol %) (ULG, 650 degC) |
|---|---|---|
| Hydrogen | 23.00 | 4.81 |
| Carbon monoxide | 11.00 | 1.68 |
| Carbon dioxide | 8.40 | 14.52 |
| Nitrogen | 45.90 | 78.81 |
| Methane | 3.70 | 0.14 |
| Ethane | 1.20 | 0.01 |
| Ethene | 5.50 | 0.05 |
| Propene | 1.30 | 0.08 |

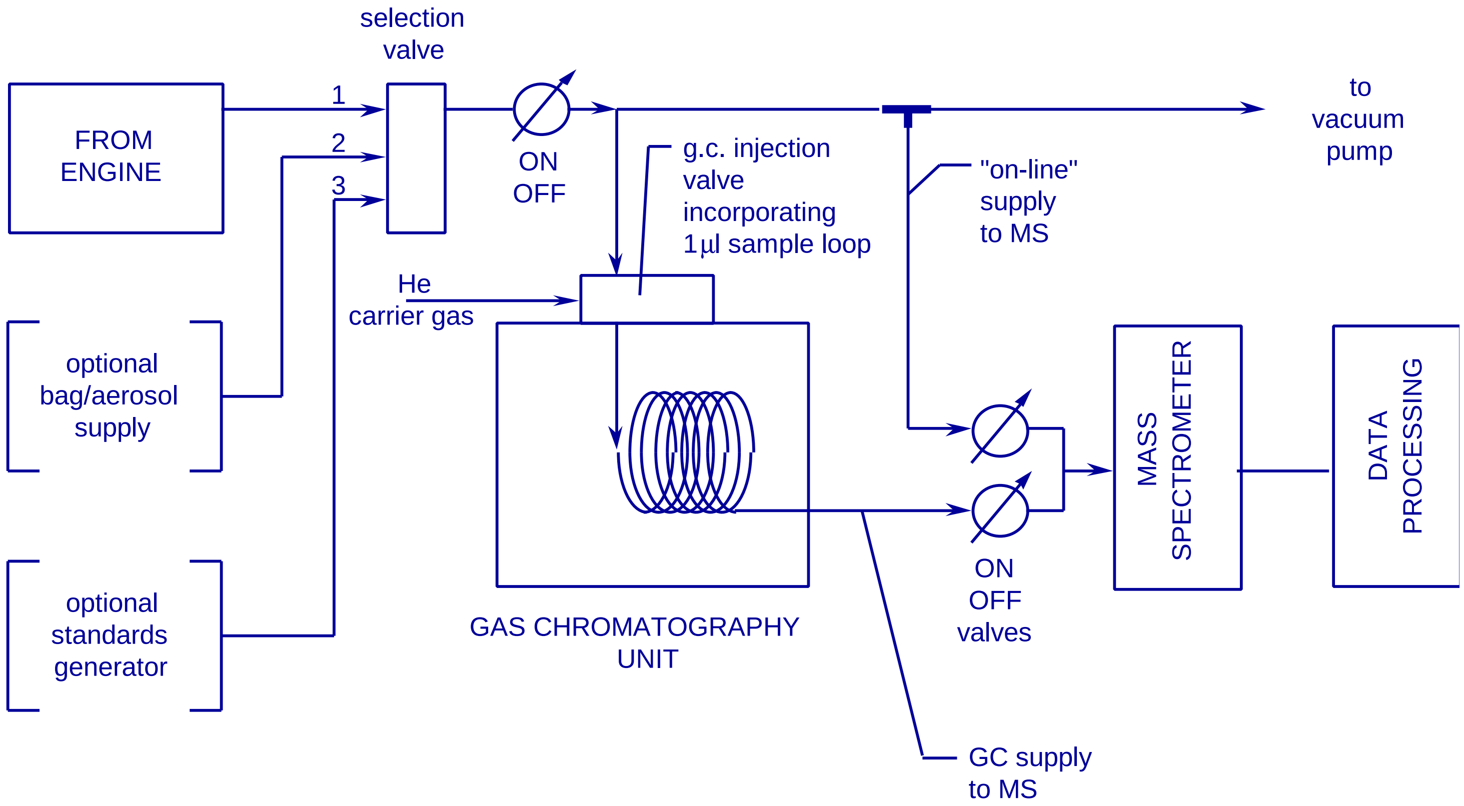
# Initial test rig




Filter* refers to cylindrical glass fibre - packed filters
Filter** refers to glass fibre paper filters
All transfer lines are Heated to in excess of 150 degC unless specified otherwise

**Engine-based Experimental Equipment**

# Emission equipment for HC speciation




**Arrangements for sample transmission (all gas lines at>150oC, unless indicated otherwise)**

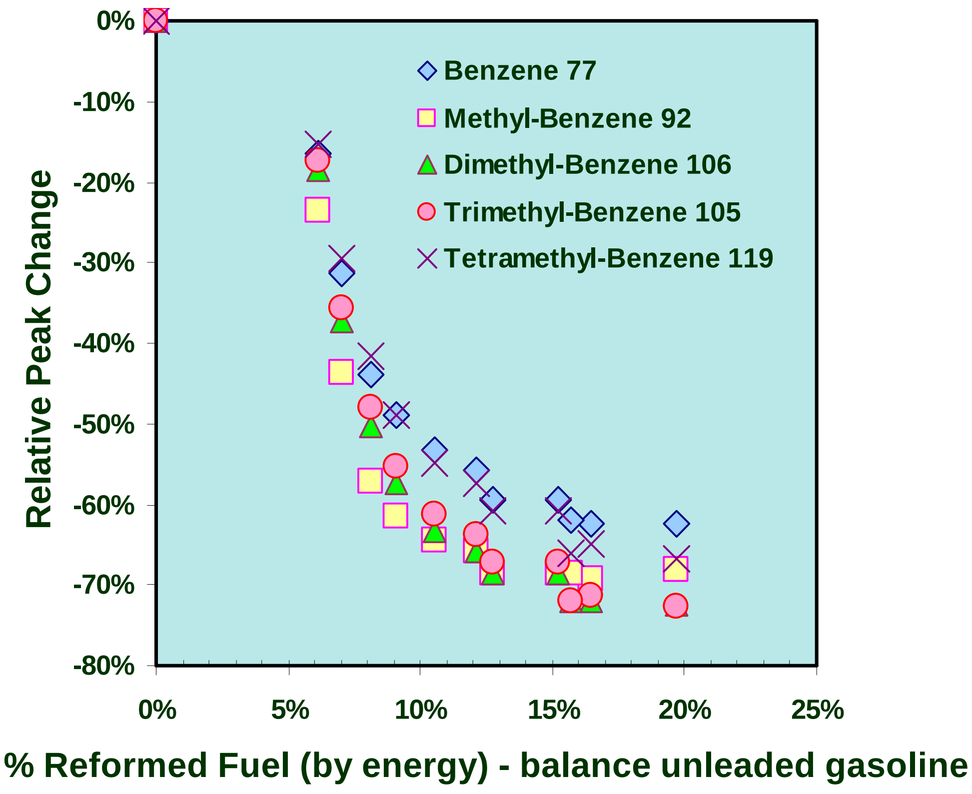
# Results of E6 Engine Tests with Reformed Fuel Added to Gasoline

- 5 to 20% of Energy Input from Reformed Fuel, balance Gasoline
- Constant Compression Ratio, Ignition Timing, Load, Speed and Throttle Setting (4/10 or 10/10)
- With the Increase of Reformed Fuel Input:
  - Decrease in Equivalence Ratio, NO and HC
  - Large Reduction (up to 70%) in Emissions of Aromatic Hydrocarbons
  - Increase in Overall Fuel Conversion Efficiency

# Gasoline:
# Reduction of Aromatics Emissions
### by the addition of reformed fuel

- gasoline operation, Ricardo E6 engine
- reformed fuel: 23% $H_2$, 11% CO, 8.4 % $CO_2$, 11 % $C_1$-$C_3$ HC, balance $N_2$
- individual HCs measured on-line using Mass Spectrometry

Changes in Species Content (relative to Argon Content)
Ricardo E6, CR 8, 2400 rpm, 2.6 bar imep, throttle 4/10, ign. 25 deg BTDC



# Reforming of Natural Gas to Improve Combustion in High EGR Dilution CNG Engines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  - The University of Birmingham
- **S. Clarke, M.J. Davies, D. Richardson, S.A.C. Shillington, S. Wallace**
  - Rover Group Ltd
- **A.K. Bhattacharya, P. Hayden, J.S. Sarginson**
  - University of Warwick
- **J.C. Frost, S.E. Golunski**
  - Johnson Matthey plc

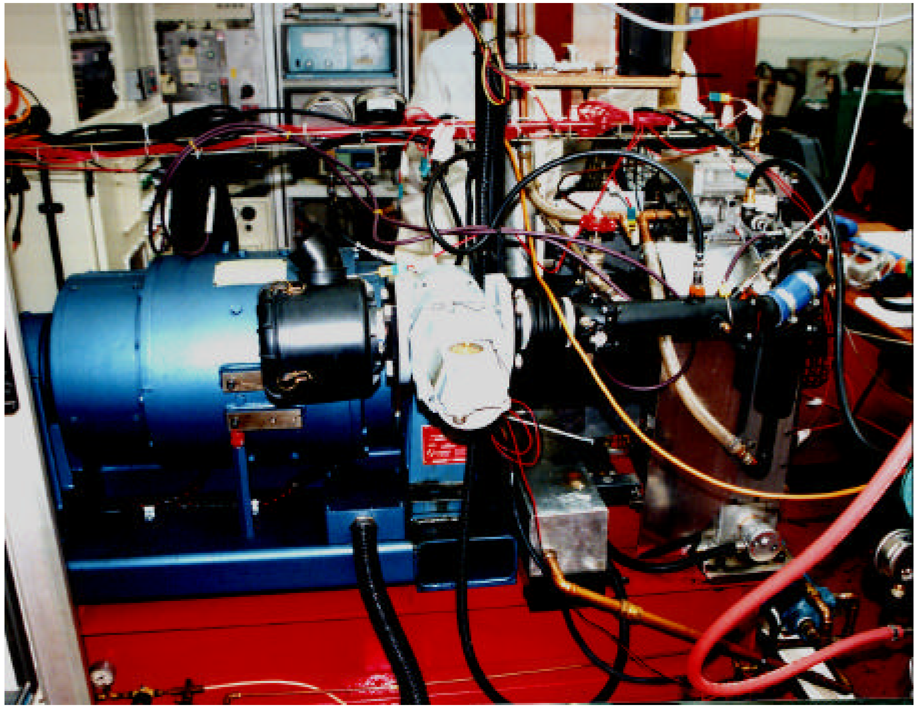
# Natural Gas as a vehicle fuel

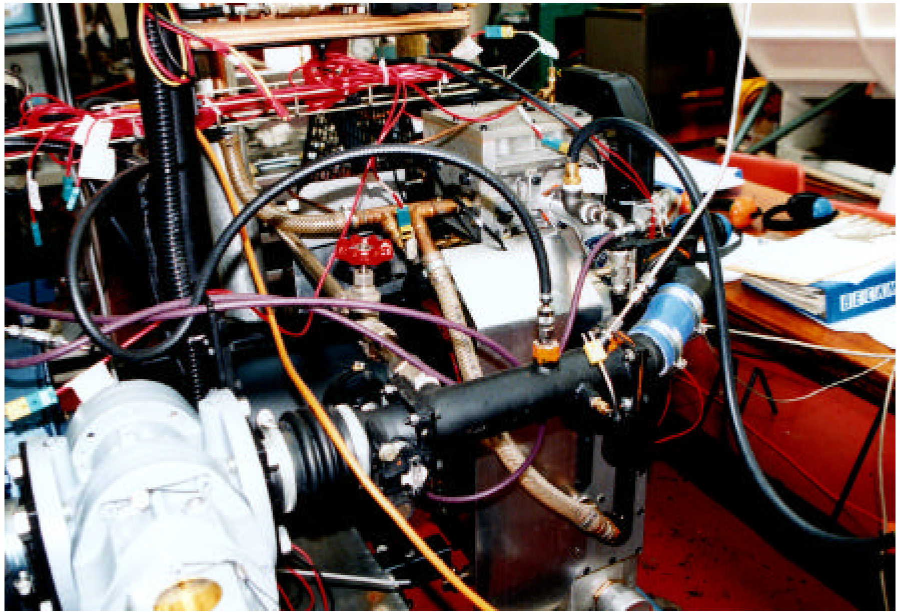
- **Benefits**
  - – ‘Clean burning’
  - – Low CO, HC and particulate emissions
  - – Gaseous under normal conditions
  - – Excellent antiknock properties (equivalent RON 130)

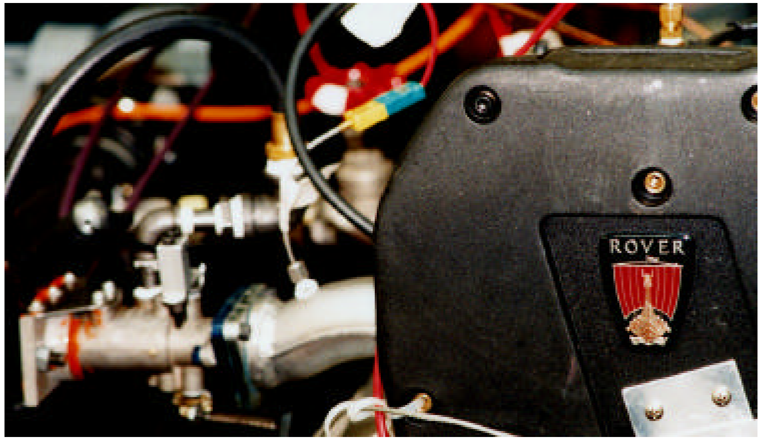
- **Disadvantages**
  - – High $NO_x$ emissions
  - – Low flame speed
  - – Difficult to burn at high dilution
  - – Difficult to burn with high EGR fraction

# The Test Engine

- Purpose built ‘Medusa’ (R. Stone) single cylinder engine
- One quarter of Rover K16 (1800/4) cylinder head
- Instrumentation
  - Pressure transducer mounted in cylinder
  - Digital shaft encoder for crank angle
  - Thermocouples and pressure gauges
- Analysis
  - In-house LabVIEW based software performs data acquisition, analysis and statistics
  - Output includes peak and average pressures, average and percentage COV of IMEP



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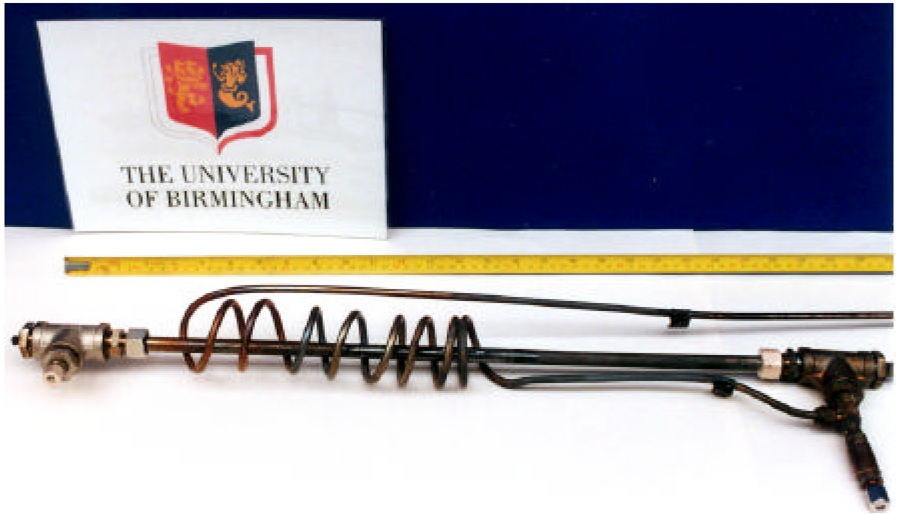
THE UNIVERSITY
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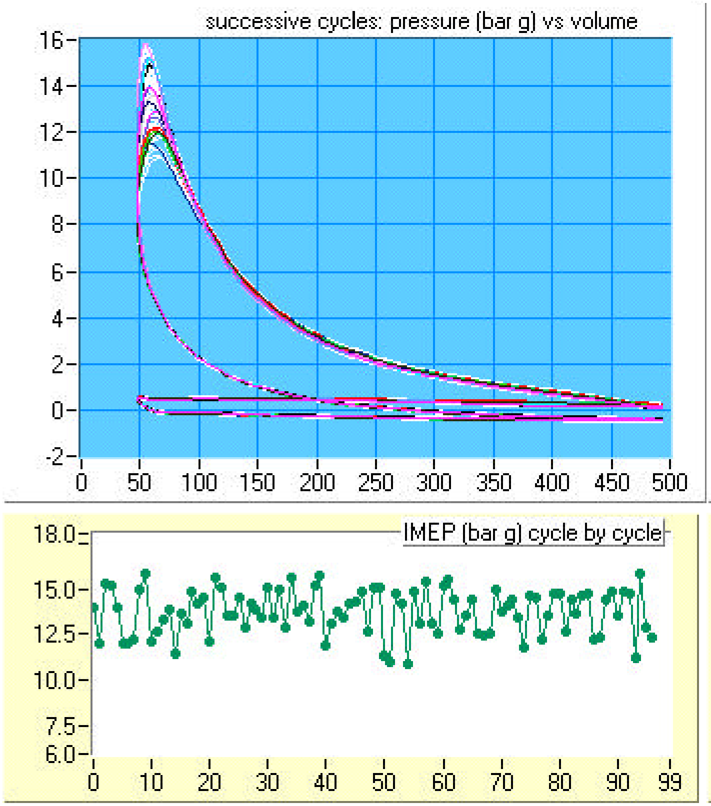
# Exhaust Gas Recirculation

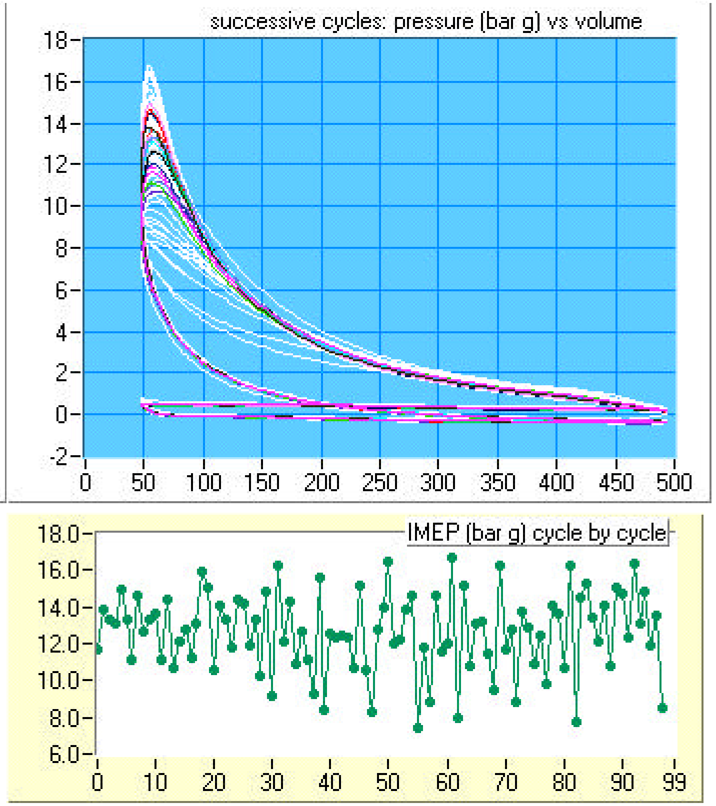
- Addition of exhaust gases to inlet charge
  - dilution reduces flame temperature and speed
  - similar effect to ‘lean burn’
  - reduces $NO_x$ more effectively than same volume excess air
  - allows engine to run stoichiometric with respect to oxygen
  - three way catalytic converter can be used
  - less throttling: reduced pumping losses
- Limit to amount of EGR tolerated
  - high levels lead to unacceptable combustion variability

# Typical pressure data for low / high COV of IMEP




**1.44 % COV of IMEP**

**NG, baseline (no EGR)**, 2000 rpm, 2.04 bar IMEP, 97 cons. cycles, inlet manif. press. -0.06/-0.36 bar, ign -37 deg (BTDC), ave. delay 29 deg, 50% burn +9.4 deg, total duration 67 deg, COV peak pressure 8.87%, (990513/d3a)




**16.79 % COV of IMEP**

**NG, approx 12% EGR**, 2000 rpm, 1.99 bar IMEP, 99 cons. cycles, inlet manif. press. -0.06/-0.31 bar, ign -56 deg (BTDC), ave. delay 46 deg, 50% burn + 11 deg, total duration 91 deg, COV peak pressure 17.09 % (990513/d25a)

**Both sets: noise elimination using 3pt smoothing with 1% trigger, 5 passes**

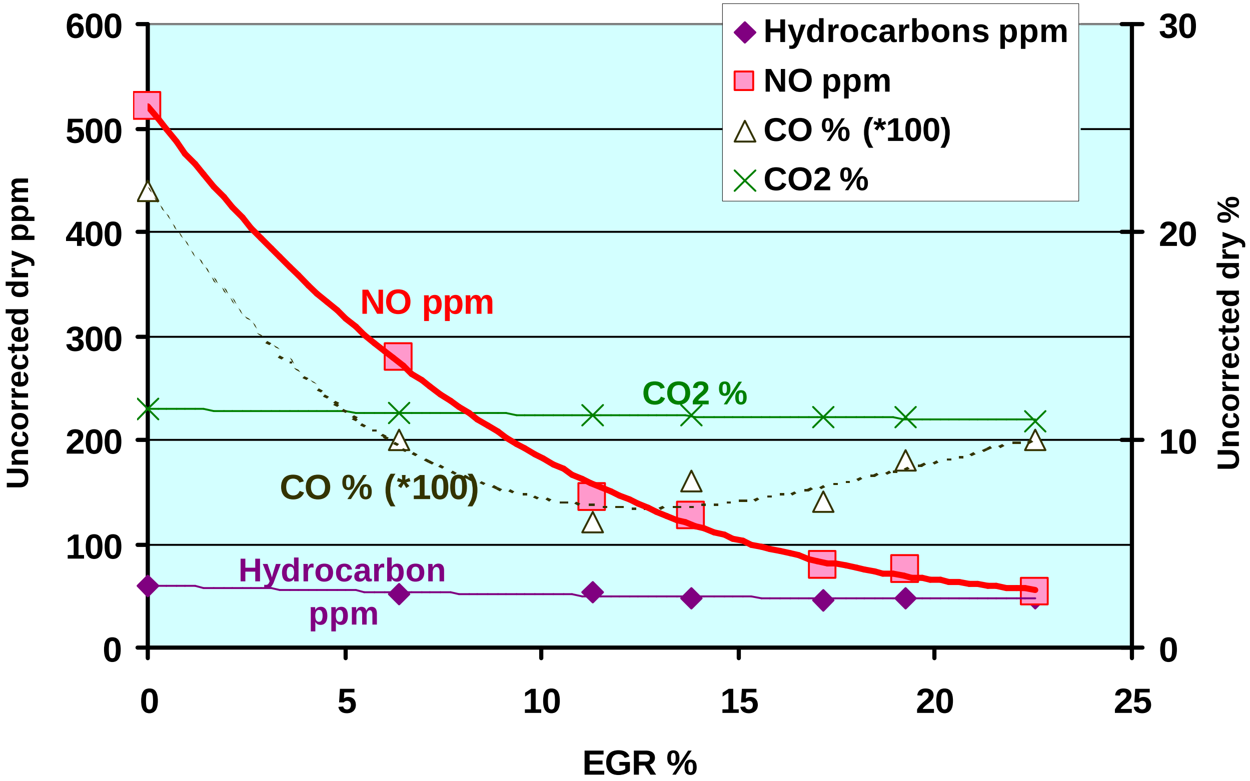
**IMEP: indicated mean effective pressure (equivalent of indicated power)**

**COV: coefficient of variation**

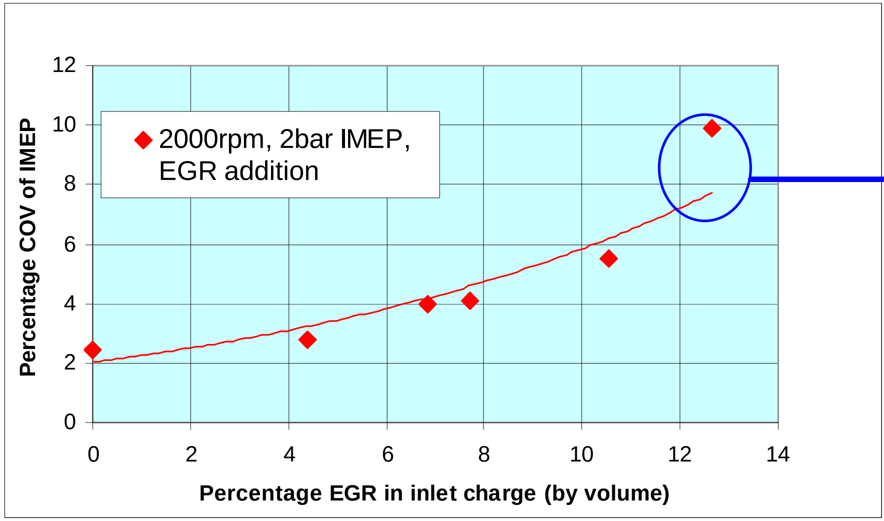
**5% COV of IMEP is normally acceptable**

# Variation of Emissions Levels with EGR Proportion

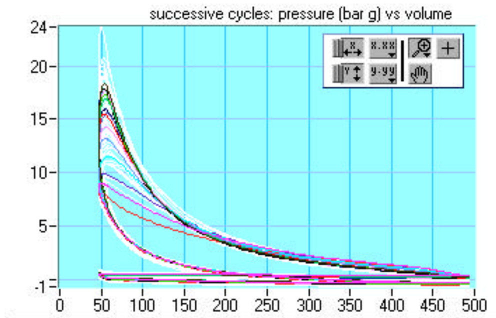
**Exhaust emissions with varying EGR proportion at 2000rpm, 2bar IMEP, fixed ignition timing strategy**

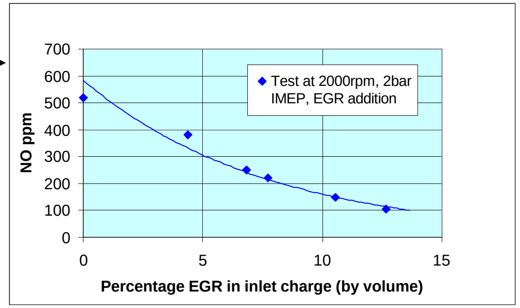


# Effect of EGR and hydrogen on stability

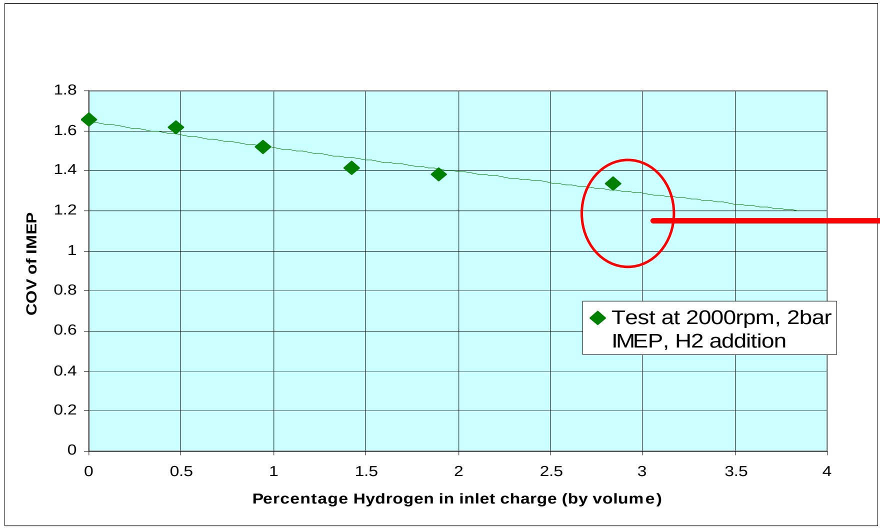



Increase in COV of IMEP with increased levels of EGR: p-V diagram for consecutive cycles shows high variability

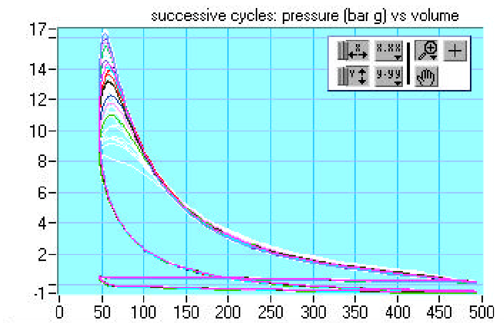



Reduction in NO emission corresponding to a given volumetric percentage of EGR. Reduction of the order of 80% but stability not maintained.




The effect of hydrogen addition on COV of IMEP. p-V diagram shows little variability.

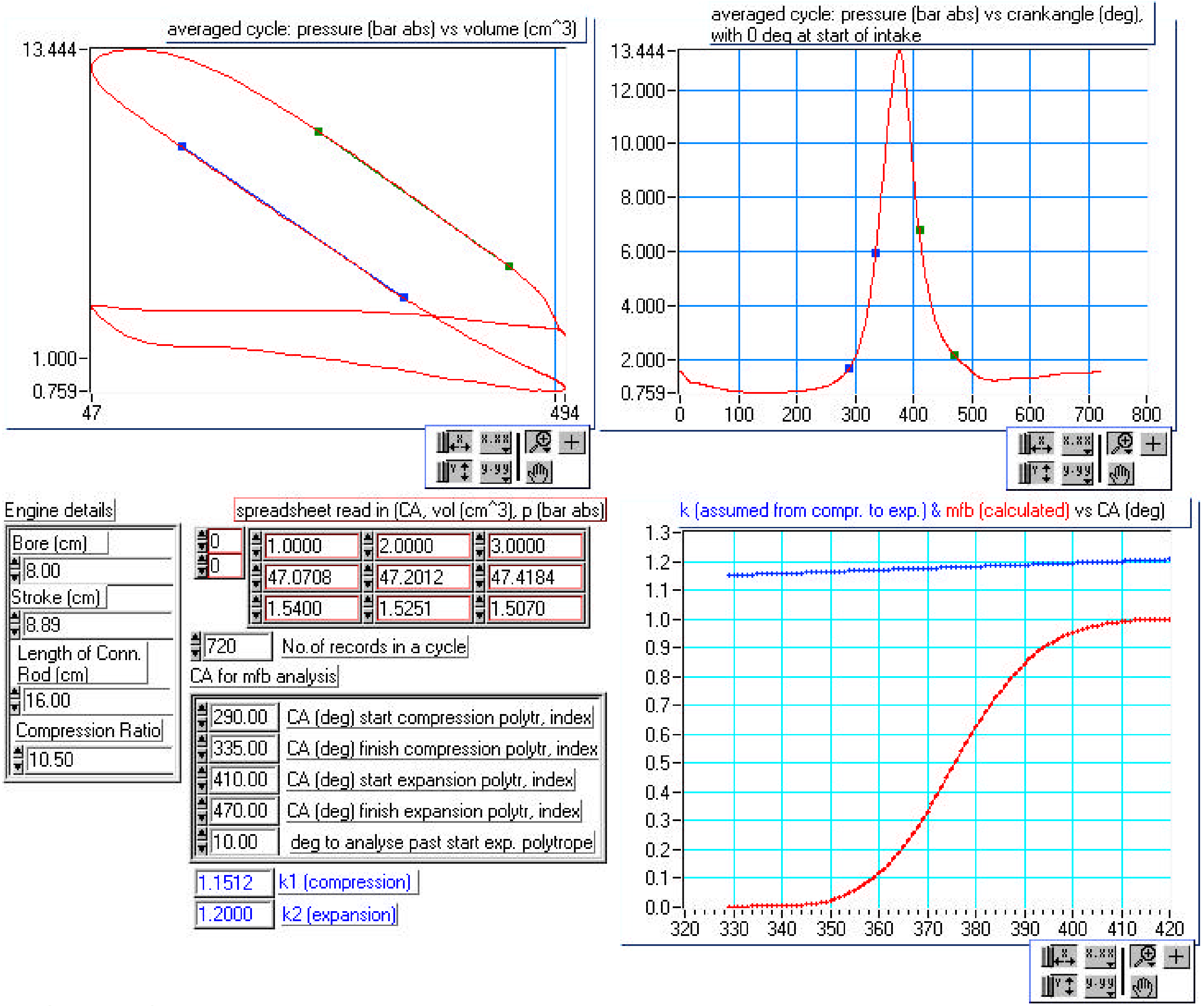


# Analysis of Pressure Data for Burn Duration

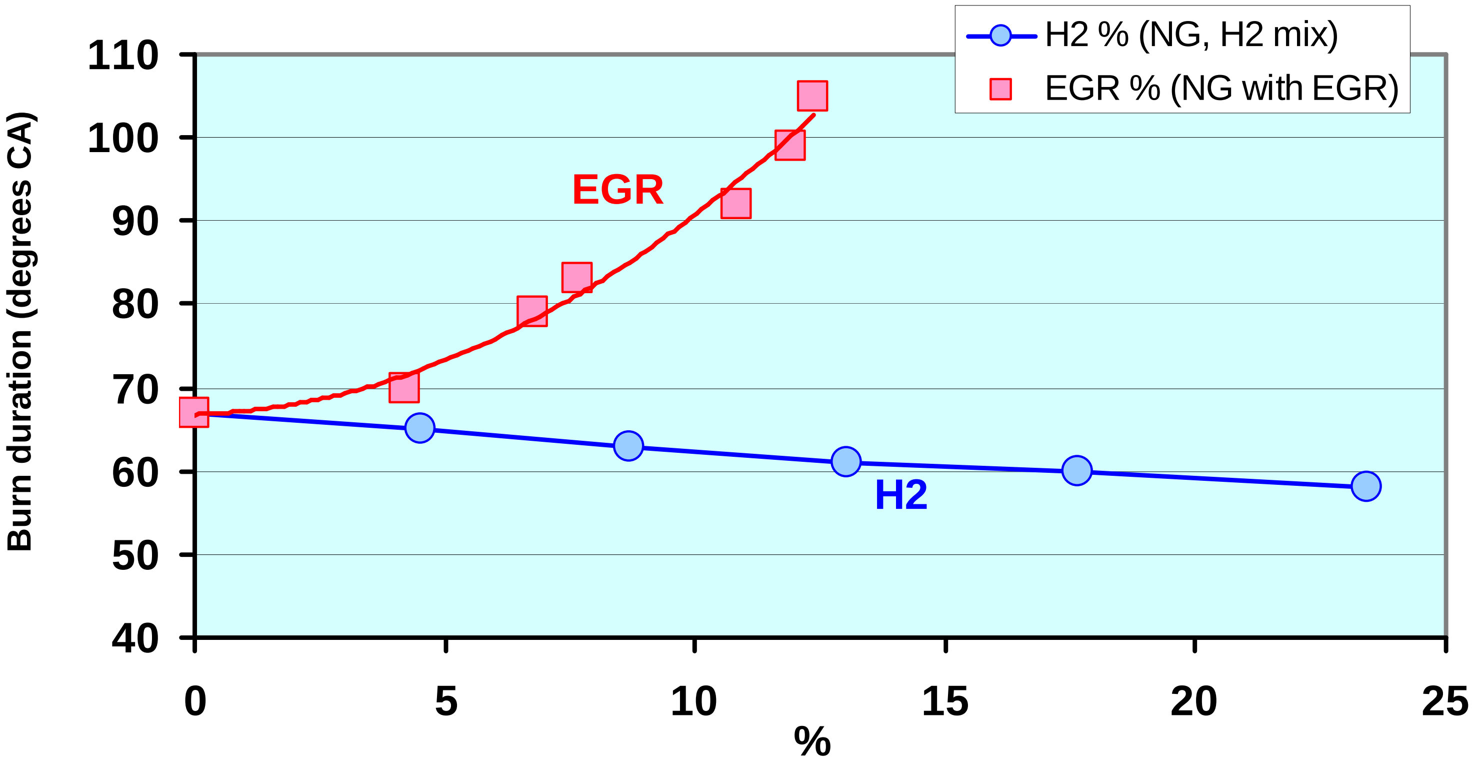
**Ignition at 329 deg CA**

**(31deg BTDC)**

**Combustion delay of 25 deg CA before first 5% of fuel is burned**



# Effects of Hydrogen and EGR on Burn Duration

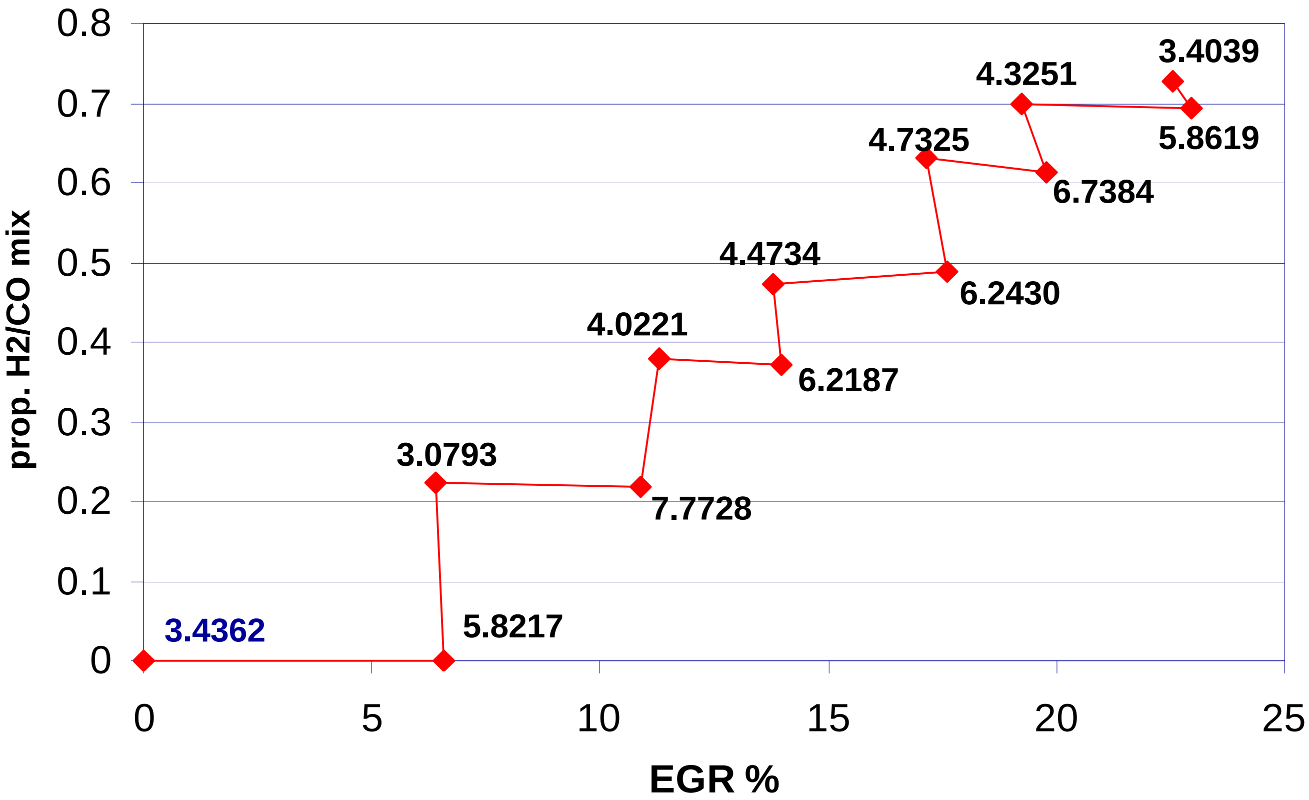


# Envelope of Benefits Testing

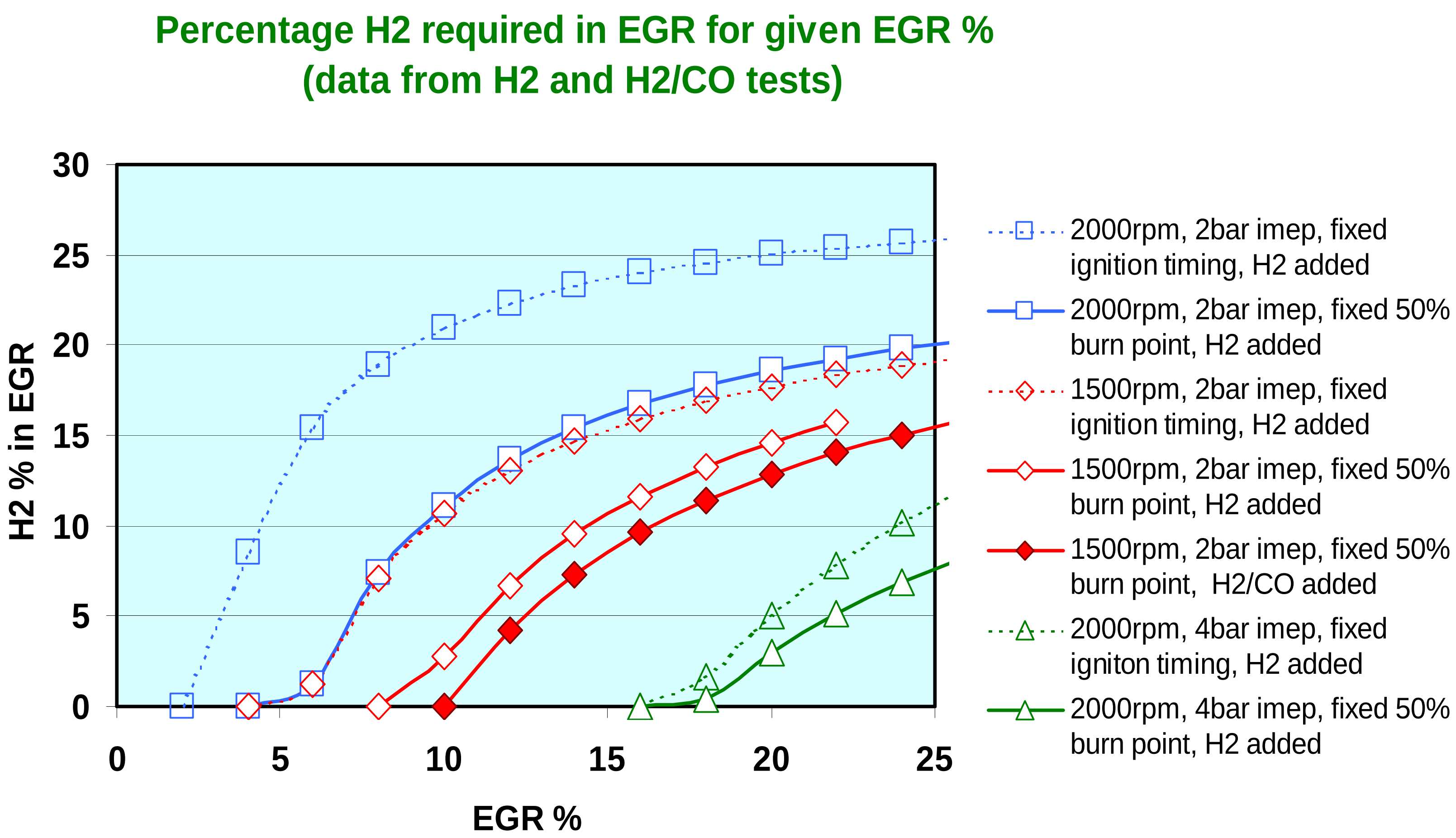
- **Aim**
  - envelope of benefits for addition of hydrogen and synthetic reformate at high levels of EGR
- **Procedure**
  - Increase proportion of EGR until combustion unacceptably variable
    - » signified by COV of IMEP greater than 5%
  - Record full data set
  - Increase proportion of hydrogen or synthetic reformate until COV within set limit
  - Record full data set
- **Data obtained tracks line of 5% COV of IMEP in steps**

# Combustion Stability

**The proportion of synthetic reformate (75% H2 / 25% CO) added to the mains NG fuel vs. % EGR. 2000rpm, 2bar IMEP, fixed ignition timing. %COV shown for each data point.**



# Hydrogen in EGR needed for 5% COV of IMEP

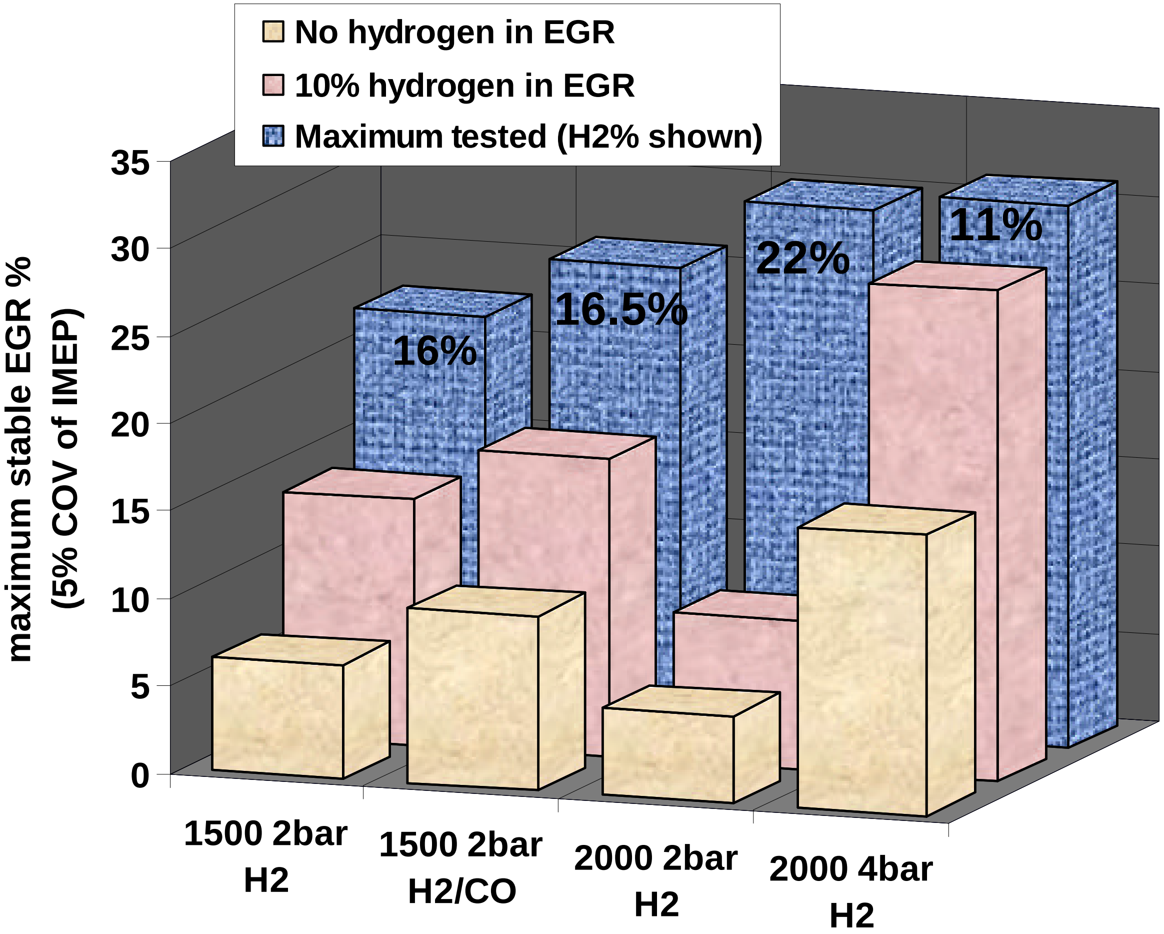


# Extension of EGR tolerance

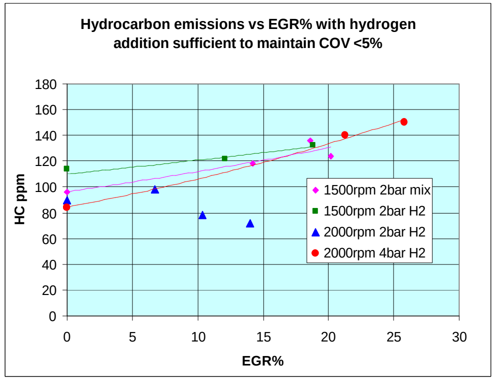
**The extension to EGR tolerance available through the use of reformed EGR.**

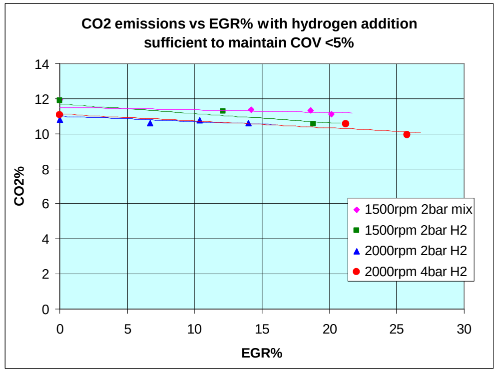
**Bars show maximum volumetric EGR percentage available with a COV of IMEP no greater than 5%.**

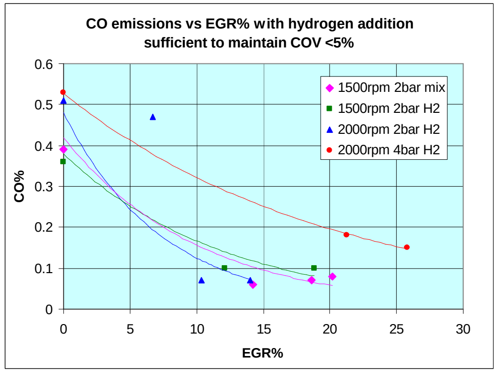
**Series are for EGR with no hydrogen content, 10% hydrogen, and the maximum hydrogen percentage tested for each operating condition.**

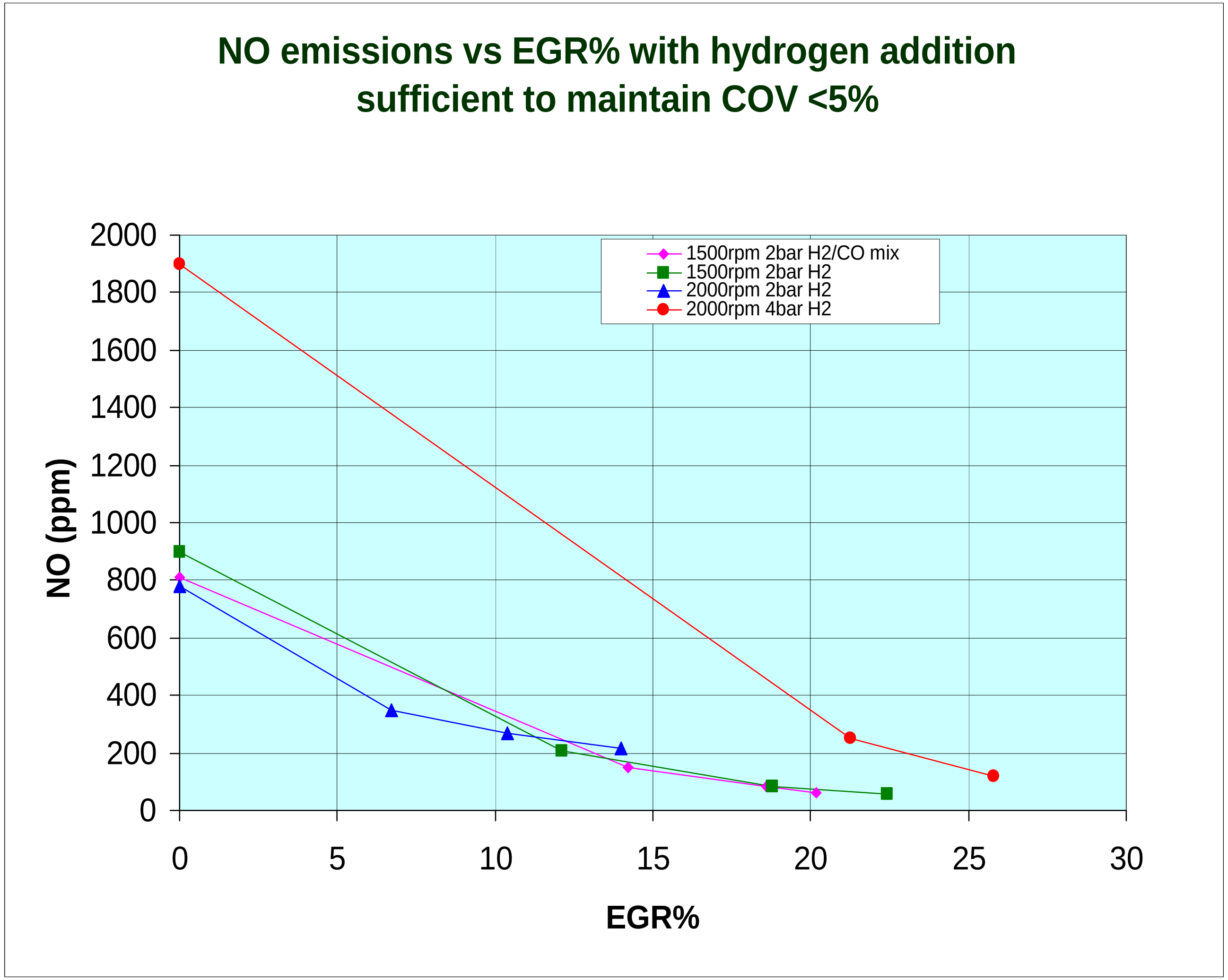


# Emissions Results



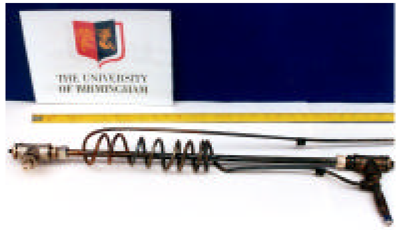



# Reforming Catalyst: Test Rig

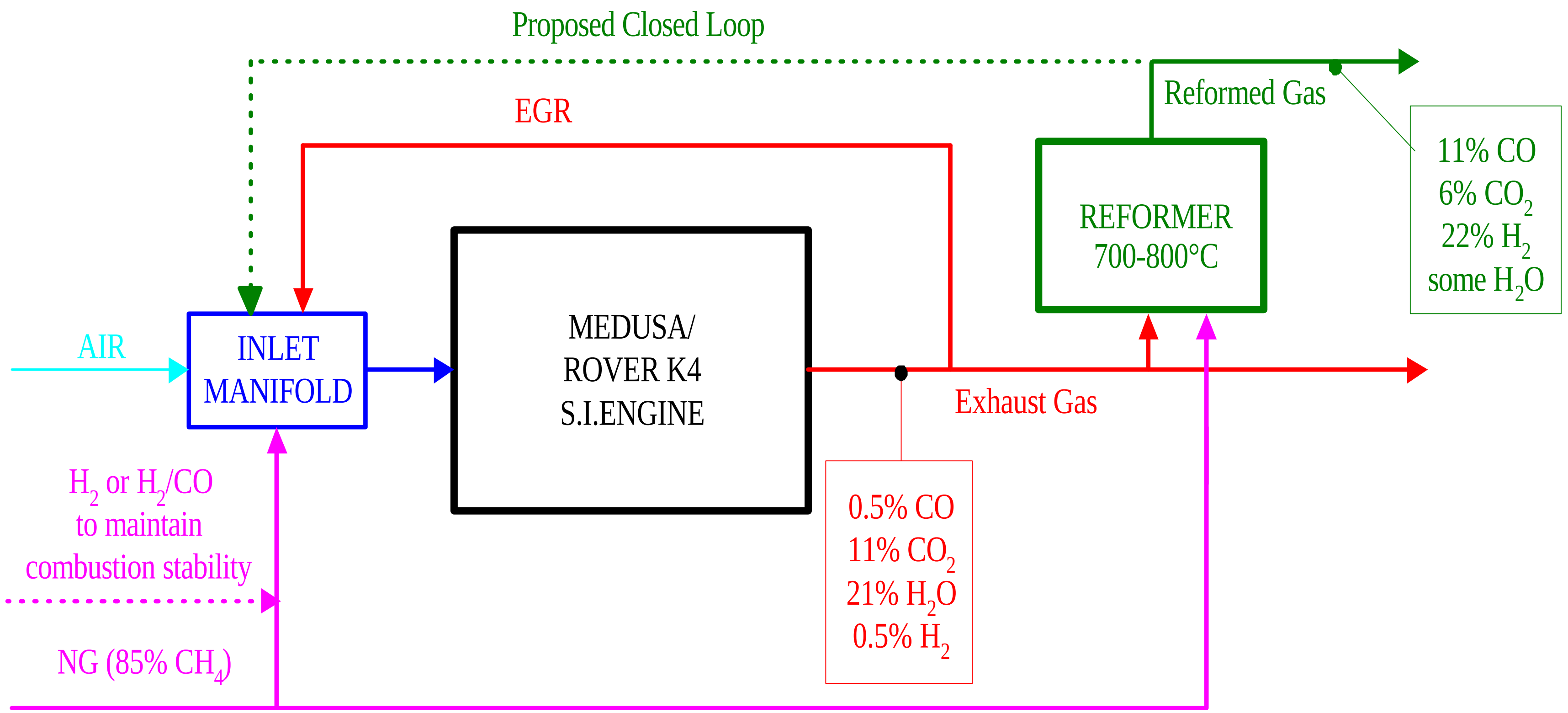
## Designed & constructed to test performance of catalysts



- Catalyst loaded into mini-reactor
- Mounted inside temperature-controlled tube furnace at 700ºC
- Controlled flow of exhaust gas and 10% by volume natural gas
- Gas Hourly Space Velocity = 10^5 (similar to TWC)
- Lines heated to prevent condensation of water
- Samples of reactor product taken at regular intervals

# Schematic and Typical Results

**Reforming reactor is fed exhaust gas and natural gas (ratio 10:1) producing hydrogen rich reformed EGR stream.**



# Catalyst Testing: Results

Catalyst test results using an engine-linked micro reactor system. Progressive improvement in performance can be seen, with iteration 3 capable of producing an EGR stream containing more than 20% $H_2$.

| Analyte | Reactor Inlet (typical) | Reactor product (%) @700 degC, 6hrs, PGM Cat. Iteration 1 | Reactor product (%) @724 degC, 2¼hrs, PGM Cat. Iteration 2 | Reactor product (%) @690 degC, 2¼hrs, PGM Cat. Iteration 3 |
|---|---|---|---|---|
| $H_2$ | 0.6 | 5.8 | 18.4 | 21.9 |
| $O_2$ | 0.7 | 0.2 | 0.1 | <0.1 |
| $N_2$ | 77.1 | 72.7 | 63.2 | 60.6 |
| CO | 0.4 | 2.2 | 8.1 | 11.4 |
| $CO_2$ | 11.7 | 11.3 | 8.1 | 5.9 |
| $CH_4$ | 9.2 | 8.6 | 3.1 | 1.3 |
| $C_2H_6$ | 0.61 | 0.34 | 28 vpm | 247 vpm |

# Conclusions - reforming of Natural Gas:

- **Use of EGR with addition of reformed fuel offers significant emissions improvements**

- **Tolerance of NG engine to EGR (as measured by combustion stability) can be greatly extended by addition of reformed fuel**

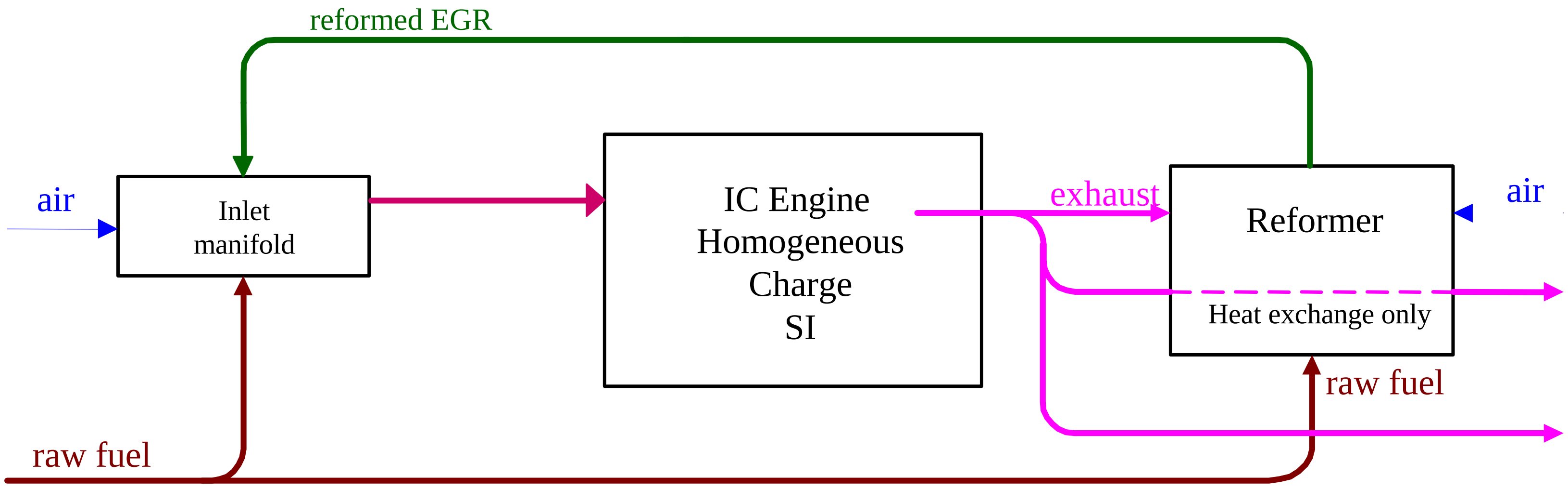
- **Currently available prototype catalysts can be used to produce a reformed fuel of the required composition (over 20% hydrogen) from exhaust gases with natural gas added**

# Proposed Applications of Fuel Reforming

**To extend utilisation of fuels, reduce emissions, improve efficiency:**

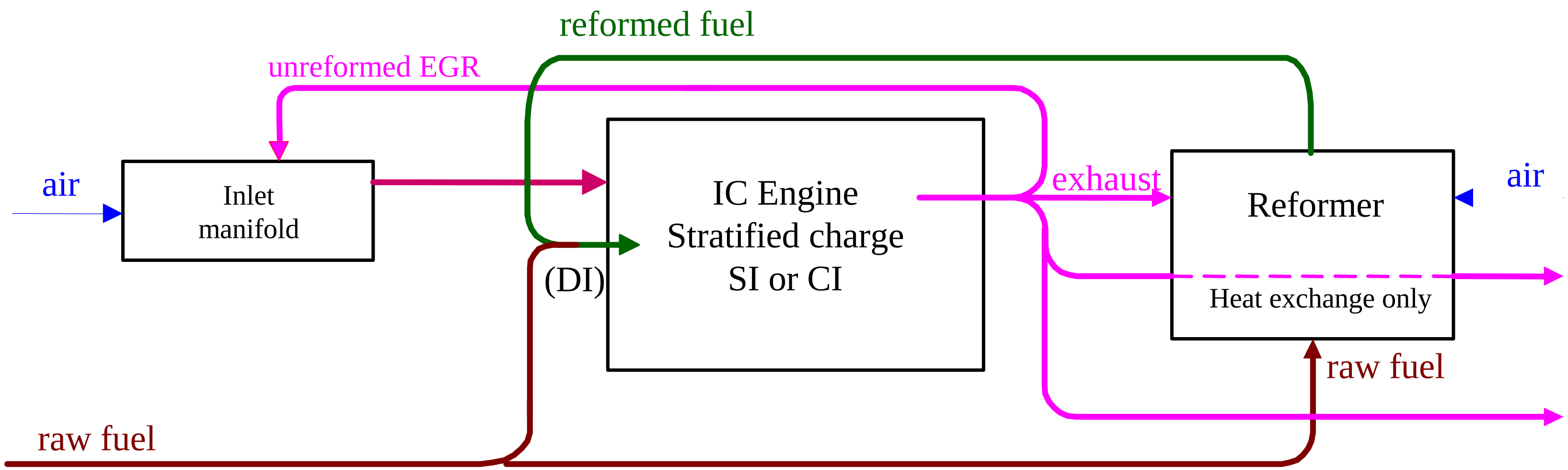
- **fuel reforming for efficiency improvements and reduction of emissions in homogeneous stoichiometric modes of operation of liquid and gas fuelled engines with EGR,**
- **HCCI (Homogeneous Charge Compression Ignition) mode with fuel reforming to deliver controlled proportions of hydrogen and active radicals**
- **hybrid ICE / electrical vehicle propulsion, where IC engine and fuel reforming system can be optimised for one or two regimes**
- **reforming hydrogen-containing fuels so that different fuels can all be used in a specified IC engine type,**
- **selective use of reforming to convert a single strategic fuel to become usable in any IC engine,**
- **the use of reforming to enhance low quality diesel fuels and bio-diesel mixtures,**

# Possible Modes of Operation of an Engine / Reformer System - 1



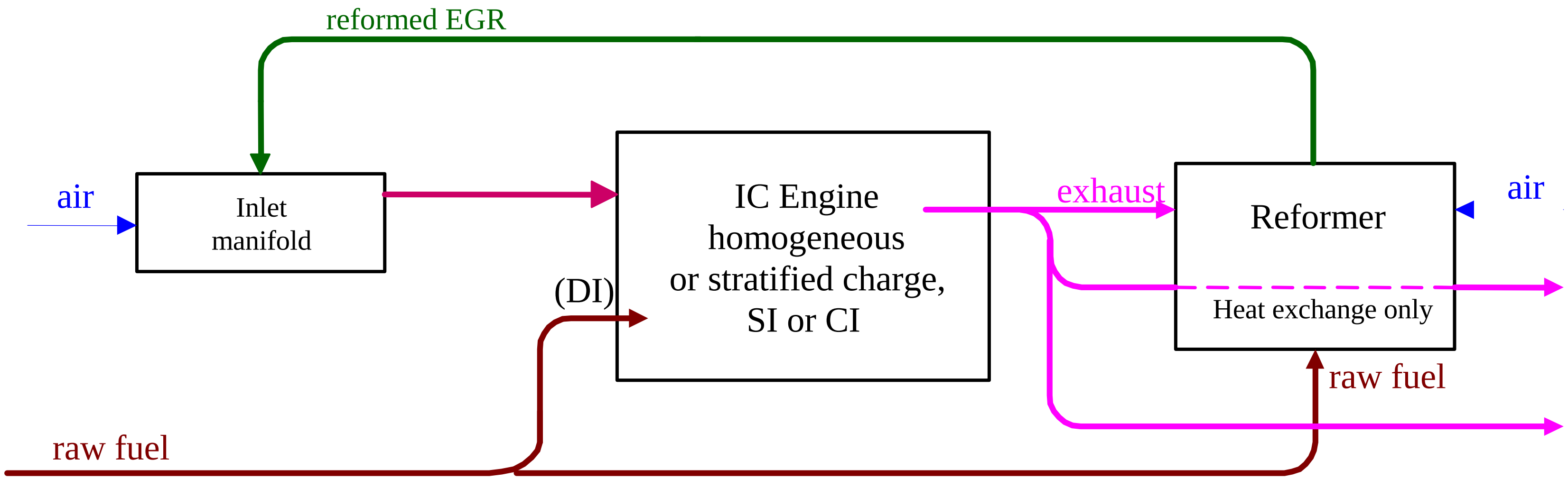

1: Some fuel reformed and returned as reformed EGR to improve combustion and reduce emissions at high dilution.

# Possible Modes of Operation of an Engine / Reformer System - 2




2: Some fuel reformed and mixed with raw fuel for direct injection to chamber. Unreformed EGR can be used, reformed fuel used to improve combustion of difficult sprays.

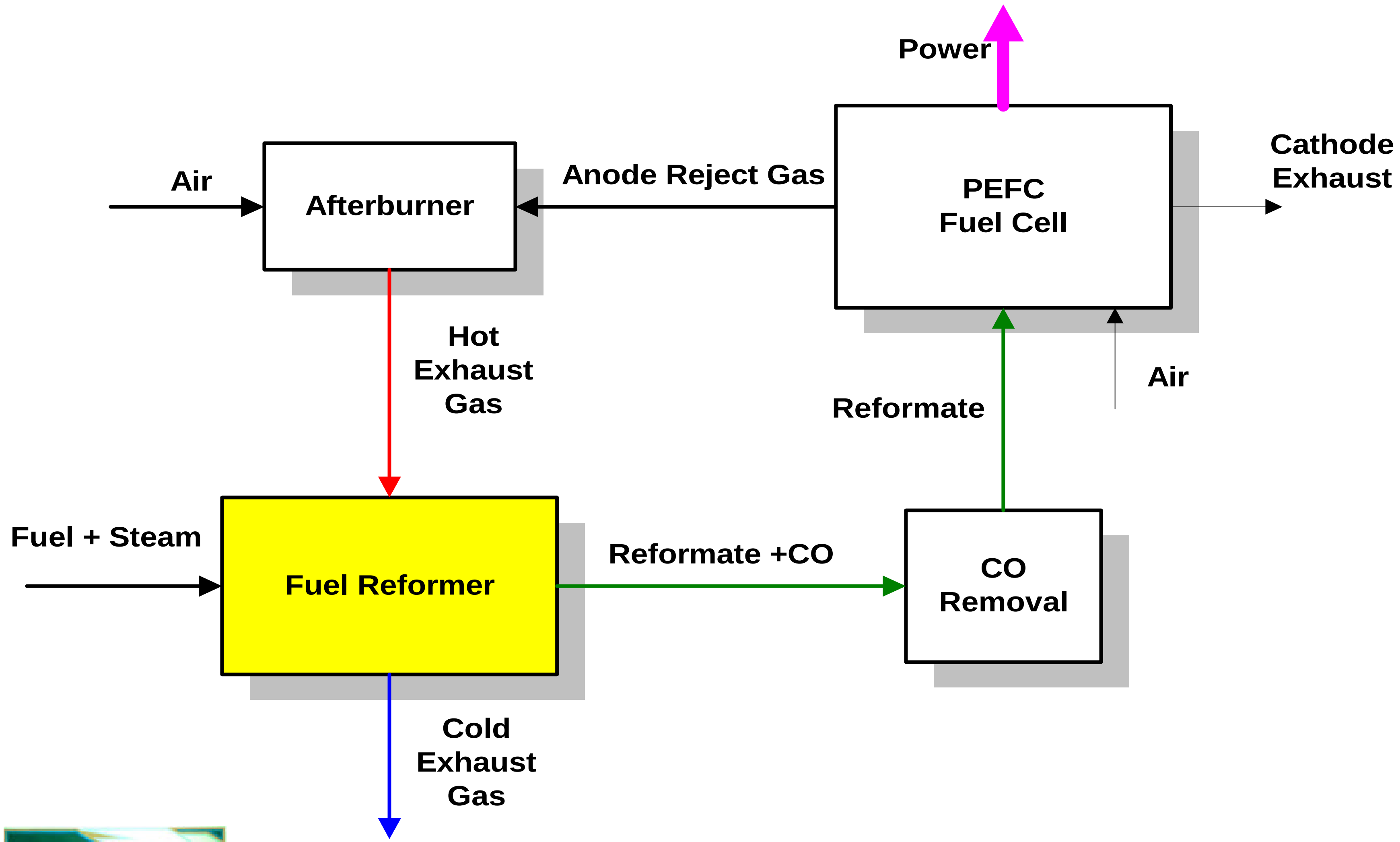
# Possible Modes of Operation of an Engine / Reformer System - 3




3: Fuel directly injected to chamber, some fed into reformer to produce reformed EGR

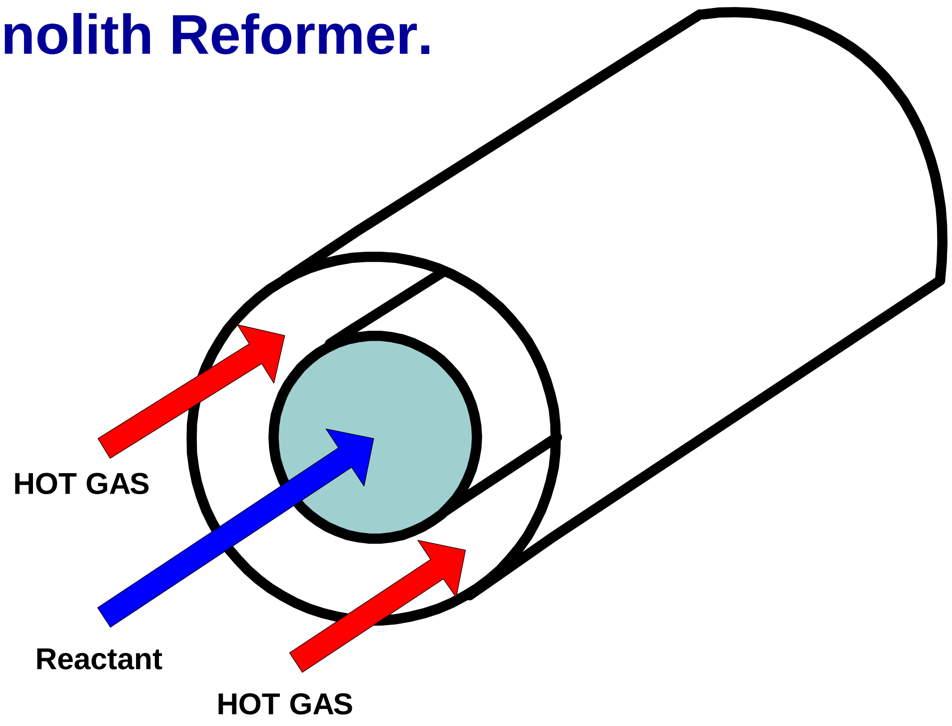
- 3a. For stoichiometric range of GDI operation: energy recovery from exhaust
- 3b. For CI engines: reduction of smoke by very lean but combustible 'end gas' containing reformed EGR
- 3c. For HCCI: with very early direct injection of fuel and reactivity of charge controllable by reformed EGR

# Methanol Reformer in a PEFC Propulsion System



# Dynamic Response of a Methanol Steam Reformer

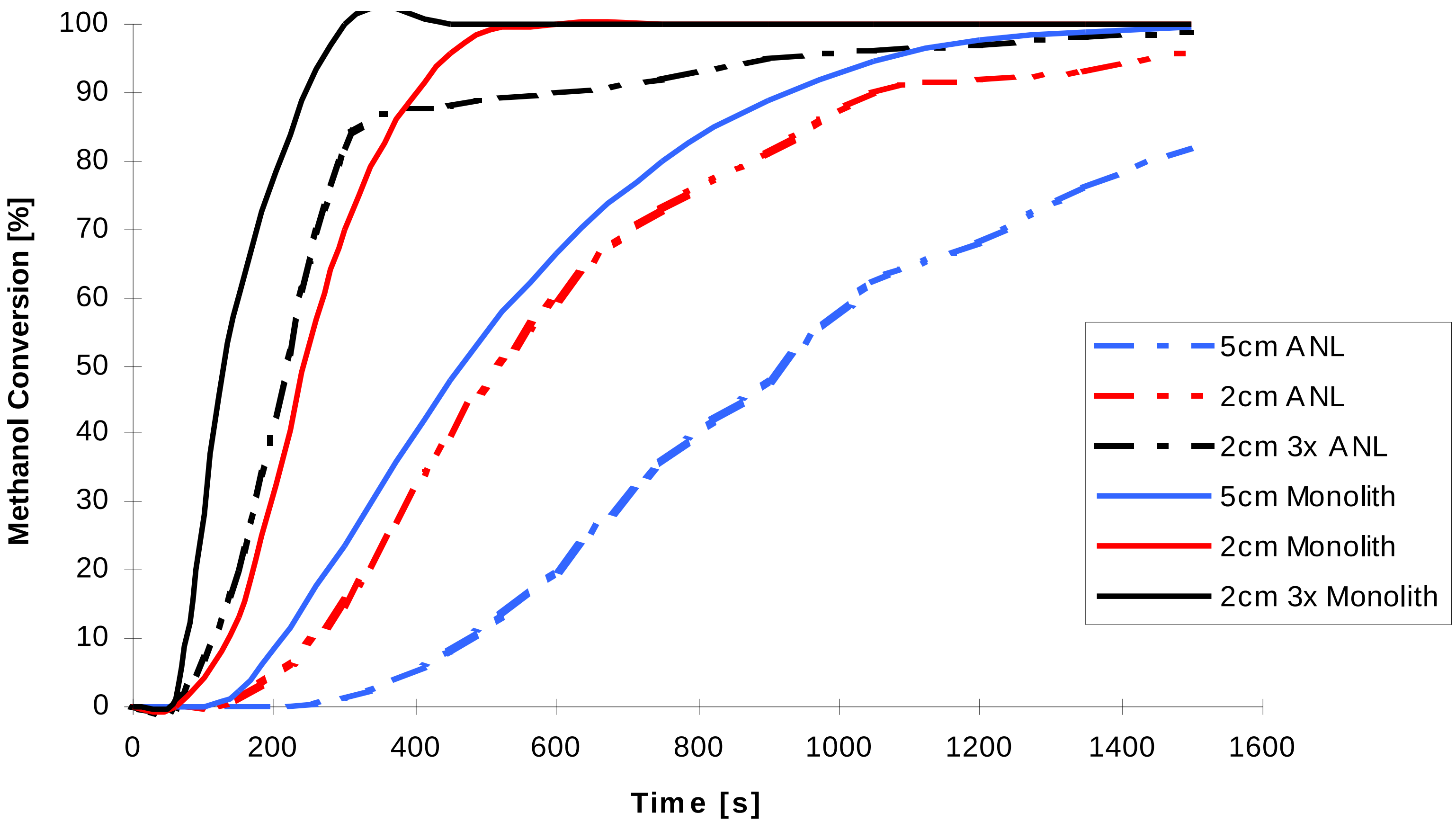
- Simulations carried out by ANL to optimise the warm-up performance of their methanol reformer (packed bed).
- Simulate performance of a Monolith Reformer.




**Reactant : $CH_3OH$, $H_20$**

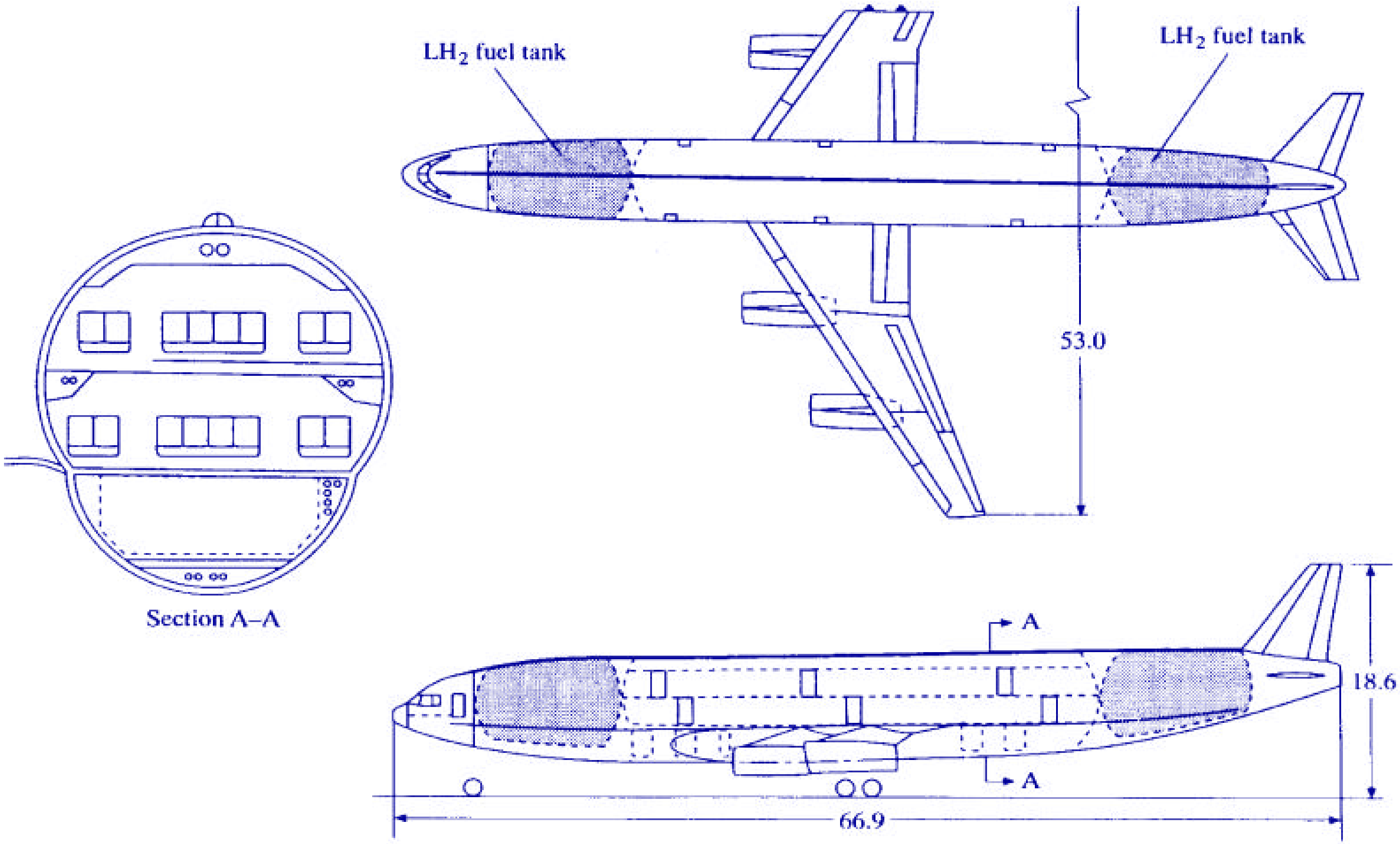
**Reformate : $H_2$, $CO_2$, CO**

# Methanol Conversion Predictions



# Hydrogen for aviation - 1

## Design studies of liquid H2 and kerosene fuelled airliners




source: ProcInstMechEng Vol211 (1997) PtG, p.6

# Hydrogen for aviation - 2

# Hydrogen for aviation - 3

## Comparison: Kerosene vs. Liquid H2 fuelled long-range passenger aircraft, designed for 400 passengers, 10200 km (5500 nm), Mach 0.85 cruise

| | Kerosene | Liquid H2 |
|---|---|---|
| Take-off gross weight (kg) | 237280 | 177640 |
| Total fuel weight (kg) | 86530 | 27940 |
| Wing area (m2) | 389.0 | 312.5 |
| Wing loading, take-off (Pa) | 5983 | 5575 |
| Weight fractions (percentage) | | |
| Fuel | 36.5 | 15.7 |
| Payload | 16.8 | 22.5 |
| Structure | 26.0 | 30.7 |
| Propulsion | 6.4 | 12.3 |
| Equipment, etc. | 14.3 | 18.8 |
| Energy used (kJ / seat km) | 778.1 | 705.5 |

*source: ProcInstMechEng Vol211 (1997) PtG, p.6*

# Hydrogen as a Fuel

| Property | Unit | Gasoline | Methanol | Methane (Nat.gas) | Hydrogen |
|---|---|---|---|---|---|
| Formula | | C7.1H12.56 | CH3OH | CH4 | H2 |
| Molar mass | kg/kmol | 98 | 32 | 16 | 2 |
| Boiling Point | deg C | 30 - 190 | 65 | -161 | -253 |
| Density liquid | kg/m3 | 730 - 780 | 792 | 424 | 71 |
| gas (STP) | | | | 0.72 | 0.09 |
| Vapour pressure | bar | 0.45 - 0.9 | 0.317 | gas | gas |
| Ignition Temp. in Air | deg C | 371 | 470 | 632 | 572 |
| flammability limits | % vol. | 1.0 - 7.6 | 6.7 - 36 | 5.3 - 15 | 4 - 75 |
| flammability limits | equiv. ratio | 0.71 - 2.5 | 0.54-2.93 | 0.47 - 1.43 | 0.1 - 2.0 |
| max Burning velocity in air | m/s | 0.5 | 0.48 | 0.4 | 2.9-3.5 |
| Flame Temperature in air | K | 2470 ?<br>2394 (liq.C8H18) | 2230 | 2326 | 2524 |
| Net ignition energy in air | mJ | 0.24 | 0.215 | 0.29 | 0.02 |
| Quenching distance | mm | 2.84 | 1.8 | 1.9 | 0.6 |
| stoichi. A/F ratio (mass) | - | 14.7 | 6.44 | 17.2 | 34.2 |
| stoichi. A/F ratio (volume) | - | 6.85 | 7.14 | 9.52 | 2.38 |
| Heat of evaporation | MJ/kg | 0.4 | 1.25 | gas | gas |
| Lower Calorific Value | MJ/kg | 40-45 | 20 | 50.01 | 120.5 |
| Energy density (15C/100 kPa) | MJ(LCV)/m3 | 33750 | 15840 | 33.4 | 10.3 |
| Mixture density (20C/100 kPa) | kg/m3 | 1.551 | 1.206 | 1.139 | 0.862 |
| Mixture Calorific Value (20C) | MJ(LCV)/m3 | 4.44 | 3.24 | 3.13 | 2.95 |
| CO2 prod. on-board/ energy | g/MJ (LCV)<br>(liq C8H18) | 69.4<br>(liquid) | 68.9 | 54.8 | 0 |