FIRST JOINT EUROPEAN SUMMER SCHOOL
ON
FUEL CELL AND HYDROGEN TECHNOLOGY

A PRIMER ON HYDROGEN AND FUEL CELL TECHNOLOGY

COURSEWORK ASSIGNMENT

Issue date: 26 August 2011
Submittal date: 15 November 2011

Question 1. Unignited jets and jet fires

by Dr S.L. Brennan

A forklift is used inside an 8 m high warehouse. The forklift is powered by a 45 kW hydrogen fuel cell, and the hydrogen is stored onboard at 350 bar. There is a pressure relief device (PRD) attached to the storage which vents upwards to the surroundings, and there is a lower pressure pipe line feeding hydrogen to the fuel cell. In this question we are interested in unignited and ignited (jet fire) releases from both the PRD and the fuel cell feed line. In all cases we assume the hydrogen leaks at a temperature of 273 K.

In an unignited jet the similarity law (Equation 1) can be used to calculate concentration on the jet axis

.

$$\frac{C_{ax}}{C_N} = 5.4\sqrt{\frac{\rho_N}{\rho_S}}\frac{d_N}{x} \qquad (1)$$

where C_N is the mass fraction of hydrogen at the jet exit (equal to 1 for a 100% hydrogen leak), C_{ax} is the mass fraction of hydrogen at a distance x on the jet axis, d_N is the nozzle diameter, ρ_N,is the density of hydrogen in the nozzle which is dependent on storage pressure and temperature and is equal to 0.0838 kg/m^3 at normal temperature and pressure (NTP) for sub-sonic and expanded sonic jets, ρ_S is the ambient air density which can be taken as 1.205 kg/m^3 (NTP),

Figure 1 below is taken from a presentation at the 11th International Short Course and Advanced Research Workshop entitled “Hydrogen safety: state-of-the-art and recent progress” (full paper by V. Molkov and J-B. Saffers “The Correlation for Non-Premixed Hydrogen Jet Flame Length in Still Air” to be published in the Proceedings of the 10th International Symposium on Fire Safety Science). The graph can be used to estimate the ratio of hydrogen flame length (L_F) to real nozzle diameter (d_N) (y axis) as a function of the dimensionless group that includes the density of hydrogen in the nozzle (ρ_N), which as above, is dependent on storage pressure and temperature (and for sub-sonic and expanded sonic jets is accepted here to be 0.0838 kg/m^3), ambient air density

(ρ_S), which can be taken as 1.205 kg/m^3, velocity of hydrogen at the nozzle (U_N) and the speed of sound in hydrogen at the nozzle (C_N). Please note that the ratio of U_N/C_N (Mach number) is equal to 1 for sonic and super-sonic (under-expanded jets) flows (part of the graph to the right from the dashed line denoted as M=1).

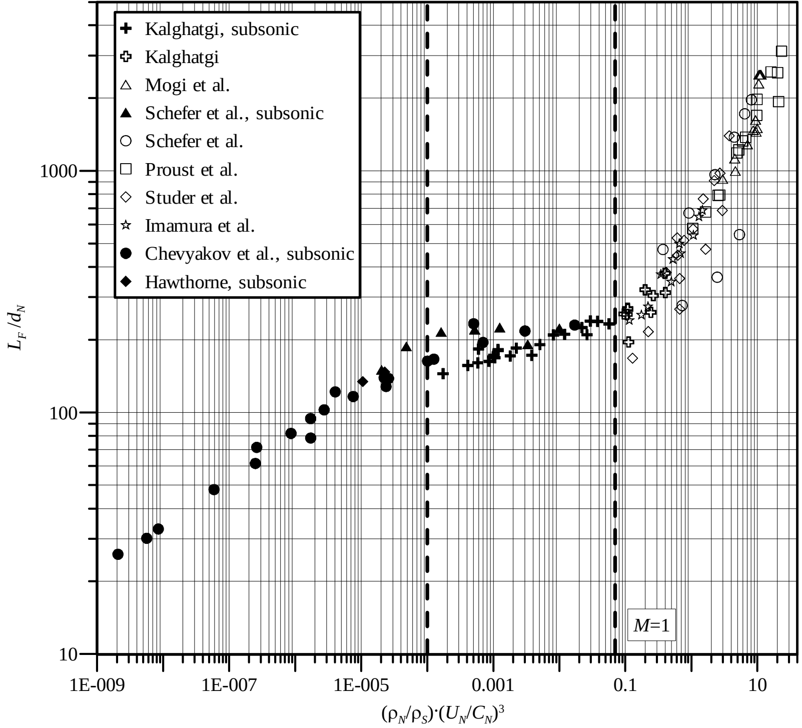

Figure 1. Jet flame length correlation.

a. Calculate the diameter of the PRD for the forklift onboard storage which obeys the following safety strategy: in the case of upward release from the onboard storage we would like to exclude formation of a flammable layer under the ceiling. To realize this strategy the concentration on the jet axis at the ceiling should be less or equal to 4% by volume (corresponding to 4% by volume the mass fraction of hydrogen is C_{ax}=0.00288). The density of hydrogen in the nozzle exit, calculated by the under-expanded jet theory for a storage pressure of 350 bar, and a temperature of 273 K at the leak exit is 14.6 kg/m^3.

(15 Marks)

b. What would be the flame length for the PRD diameter calculated in (a) if the release is ignited?

(15 Marks)

c. Admit that a pipe is placed after the PRD orifice (calculated in part a). Consider such a pipe with a diameter of 6 mm. Assume that the mass flow rate (density*velocity*area) is conserved between the PRD exit and exit from the pipe of 6 mm diameter, and that temperature is the same in both locations (i.e. neglect cooling due to expansion and heating due to heat transfer from the pipe to the flow).

i. Please demonstrate that the flow from 6 mm pipe exit is still choked flow. Hint: hydrogen is choked when the pressure ratio across the orifice is greater than or equal to 1.9 (in this case the density of hydrogen at the nozzle exit at NTP will be greater than 0.0838 kg/m^3); assume the speed of sound in hydrogen at 273 K equal to 1255 m/s.

(15 Marks)

ii. Will the flame length from 6 mm pipe change compared to the case of a release directly from the PRD orifice to the atmosphere? If “no”, please explain. If ”yes”, please calculate a new value.

(15 Marks)

d. The fuel cell powering the forklift has an electrical efficiency of 45%. If the heat of reaction (combustion) of hydrogen is accepted as 152.34 kJ/g then determine the flow rate (in g/s) needed to feed the fuel cell.

(15 Marks)

e. Hydrogen is fed to the fuel cell at the rate calculated in part (d) at a pressure of 1.5 bar (abs.). The pipe is ruptured. Please use equation $\sqrt{2\Delta P/\rho}$ to estimate the velocity of hydrogen. The speed of sound in the hydrogen is 1255 m/s. What is the minimum pipe diameter sufficient to feed this fuel cell and what would be the flame length from this pipe?

(15 Marks)

f. The diameter of the pipe used to feed the fuel cell is expanded to 5 mm, the mass flow rate remains the same and the speed of sound in hydrogen is 1255 m/s, calculate the new L_F/d_N and flame length.

(15 Marks)

g. The jets in parts (b) and (c) were under-expanded, and in (e) and (f) were “traditional” momentum-controlled jets. Describe how an increase in the diameter for the same mass flow rate had a different effect on flame length in each case.

(10 Marks)

Question 2. Polymer Electrolyte Membrane (PEM) fuel cells

by Dr B.G. Pollet

a. What are the main differences between a Fuel Cell and an Electrolyser?

(20 Marks)

b. Briefly describe the main requirements for a flow field plate (also called a Bipolar Plate) to be used in a PEM fuel cell.

(20 Marks)

c. What would you need to build a PEM fuel cell stack – please draw a diagram and write the electrochemical reactions in your answer?

(20 Marks)

d. Why do conventional PEM fuel cells have operating temperature limits?

(20 Marks)

e. Why is there great interest in developing PEM fuel cells that can operate at higher temperatures, for hydrogen fuel cell cars?

(20 Marks)

Question 3. Deflagrations and detonations

by Dr A.E. Dahoe

In the questions that follow you shall be studying the following papers:

[1] Tang M.J. and Baker Q.A. A new set of blast curves from vapor cloud explosion. Process Safety Progress, 18:235-240, 1999.
[2] Tang M.J. and Baker Q.A. Comparison of blast curves from vapor cloud explosions. Journal of Loss Prevention in the Processes Industries, 13:433-438, 2000.
[3] Molkov V., Makarov D., and Schneider H. LES modelling of an unconfined largescale hydrogen-air deagration. Journal of Physics D: Applied Physics, 39:4366-4376, 2006.
[4] Dorofeev S.B. A flame speed correlation for unconfined gaseous explosions. Process Safety Progress, 26(2):140-149, 2007.
[5] Dorofeev S.B. Evaluation of safety distances related to unconfined hydrogen explosions. International Journal of Hydrogen Energy, 32:2118-2124, 2007.
[6] Ciccarelli G. Critical tube measurements at elevated initial mixture temperatures. *Combustion Science and Technology*, 174:173-183, 2002.
[7] Stamps D.W., Slezak S.E., and Tiezen S.R. Observations of the cellular structure of fuel-air detonations. Combustion and Flame, 144:289-298, 2006.
[8] Ngo T., Mendis P., Gupta A., and Ramsay J. Blast loading and blast effects on structures - An overview. *Electronic Journal of Structural Engineering*, 7:76-91, 2007. Special Issue: Loading on Structures.

You are expected to apply the material described in these papers to answer the questions further on.

Figure 1 shows a picture of an enclosure containing a fuel-cell stack. The stack is operated by continuous stream of hydrogen and air. There is a concern that the continuous hydrogen stream may leak into the enclosure to form a combustible mixture. The dimensions of the enclosure are 0.7m by 0.8m by 1m. And the concern is that 5 to 15 grams of hydrogen might mix with the air contained by the enclosure.

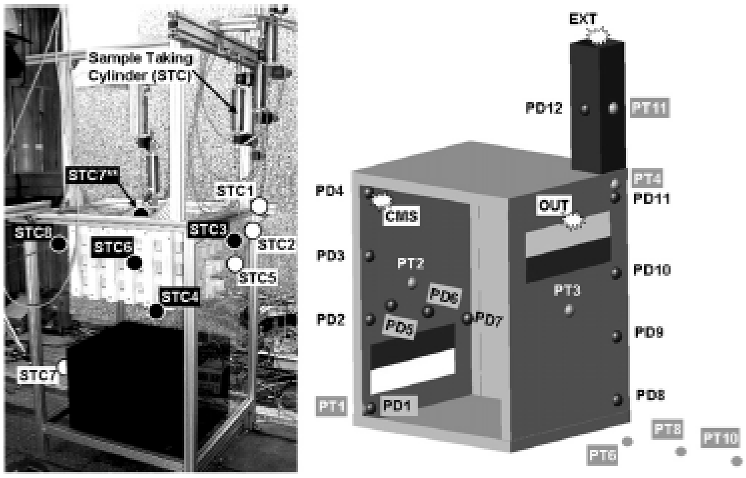

Figure 1. Enclosure containing a fuel-cell stack. From: Ref. [10].Friedrich A., Veser A., Stern G., and Kotchourko N. Hyper experiments on catastrophic hydrogen releases inside a fuel cell enclosure. International Journal of Hydrogen Energy, 36:2678-2687, 2011.

a. When 5 to 15 grams of hydrogen would mix with the air in the enclosure would like to know which amounts would cause the combustion to remain in the deflagration or pose a detonation risk. Apply your knowledge of flammability and detonation limits to calculate the amount of hydrogen below which combustion can only occur in the deflagration mode, and, beyond which detonation may occur.

(10 Marks)

b. What is the Rankine-Hugoniot diagram? Describe the features of this diagram i.e. derive expressions for Hugoniot curve, the Rayleigh lines, the detonation and deflagration branches and the Chapman-Jouget points. Using the Rankine-Hugoniot diagram point out the differences between deflagrations and detonations, and, explain why detonations are more dangerous than deflagrations.

(10 Marks)

In the questions that follow you shall be applying the program GASEQ, made available from: www.gaseq.co.uk/ and http://193.61.145.225/MScHSE/Software/.

Consider the chemical reactions:

$$v'_{H_2} H_2 + v'_{O_2} O_2 + v'_{N_2} N_2 \leftrightarrow v''_{H_2} H_2 + v''_{O_2} O_2 + v''_{N_2} N_2 + v''_{H_2O} H_2O \tag{1}$$

and

$$v'_{H_2} H_2 + v'_{O_2} O_2 + v'_{N_2} N_2 \leftrightarrow v''_{H_2} H_2 + v''_{O_2} O_2 + v''_{N_2} N_2 + v''_{H_2O} H_2O + v''_{OH} OH + v''_{H} H + v''_{O} O + v''_{HO_2} HO_2 + v''_{H_2O_2} H_2O_2 \tag{2}$$

c. Calculate (using GASEQ) the constant volume adiabatic flame temperature and final pressure of the mixtures formed after releases of 5.0g, 5.5g, 6.0g, 6.5g, 7.0g, 7.5g, 8.0g, 8.5g, 9.0g, 9.5g, 10.0g, 10.5g, 11.0g, 11.5g, 12.0g, 12.5g, 13.0g, 13.5g, 14.0g, 14.5g, and, 15.0g, while assuming the reaction products on the right hand side of equation (1). Assume initial conditions of 298.15K and 1 bar. Make a graph of the adiabatic flame temperature versus the hydrogen concentration (in vol%). Repeat this calculation while assuming the reaction products on the right hand side of equation (2) and add these results to the graph. Why is there a difference between the results obtained using the product species in equations (1) and (2)?

(10 Marks)

d. Apply GASEQ (Problem type CJ Detonation) to compute the Chapman-Jouget conditions of the hydrogen-air reaction at initial conditions of 298.15K and 1 bar. Perform these calculations for mixtures formed after releases of 5.0g, 5.5g, 6.0g, 6.5g, 7.0g, 7.5g, 8.0g, 8.5g, 9.0g, 9.5g, 10.0g, 10.5g, 11.0g, 11.5g, 12.0g, 12.5g, 13.0g, 13.5g, 14.0g, 14.5g, and, 15.0g, while assuming the reaction products on the right hand side of equation (1). Make a graph of the shock velocity, the velocity of the product mixture, the pressure and the temperature. Are you able to explain the difference between the pressures obtained for the deflagrations under c) and detonations on the basis of these graphs?

(10 Marks)

e. Apply GASEQ (Problem type CJ Detonation) to compute the Chapman-Jouget conditions of the hydrogen-air reaction at initial conditions of 298.15K and 1 bar. Perform these calculations for mixtures formed after releases of 5.0g, 5.5g, 6.0g, 6.5g, 7.0g, 7.5g, 8.0g, 8.5g, 9.0g, 9.5g, 10.0g, 10.5g, 11.0g, 11.5g, 12.0g, 12.5g, 13.0g, 13.5g, 14.0g, 14.5g, and, 15.0g, while assuming the reaction products on the right hand side of equation (1). Make a graph of the shock velocity, the velocity of the product mixture, the pressure and the temperature. Are you able to explain the difference between the pressures obtained for the deflagrations under c) and detonations on the basis of these graphs?

(10 Marks)

Figure 2 shows a house on top of a garage that will be used to park hydrogen fuelled cars. The dimensions of the garage are: length = 25 m, width = 20 m, height = 5 m. The cars are equipped with an on-board storage tank designed to contain compressed hydrogen gas. The on-board fuelling system is protected by a pressure relief device that will discharge the content of the high pressure storage tank in a controlled manner when actuated. To cope with unexpected hydrogen releases in the garage a ventilation system consisting of tubes fitted with ventilators have been installed as shown in Figure 1. Air enters the garage continuously in the centre at roof level and leaves the garage through a tube system as shown in Figure 1. The conditions in the garage are 1 bar and 300 K. The cars are parked near the ventilation tubes (see Figure 2) to prevent hydrogen released accidentally from dispersing into the entire space. Released hydrogen is entrained into the ventilation tubes and purged into the atmosphere outside the garage. The diameter of the ventilation tubes is 30 cm.

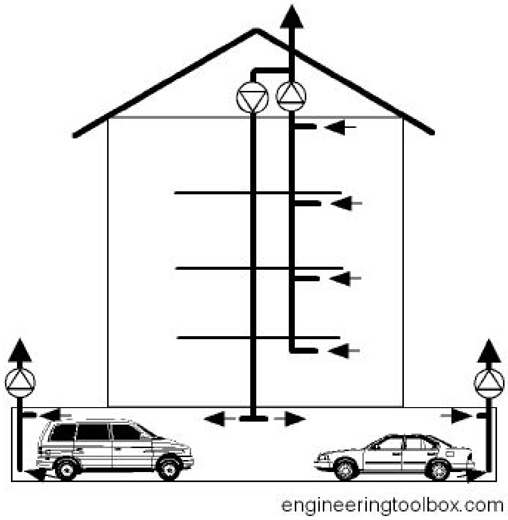

Figure 1. Garage beneath a house.

f. (i) Comment on whether or not a stoichiometric hydrogen-air mixture would detonate if it entered the ventilation tubes and ignited. Make use of the papers in Refs. [6] and [7] to motivate your answer.
(ii) It has been suggested to prevent detonation in the ventilation tubes by diluting hydrogen-air mixtures using steam. Steam generators capable of delivering steam at conditions of 1 bar and 420 K are available for this purpose. These will be installed near the inlets of the ventilation tubes, such that they are activated upon detection of hydrogen. Suppose now that a stoichiometric hydrogen-air mixture would be entrained into the ventilation tubes at a rate of 10 litre per second. Estimate the minimum steam generation capacity (in litres per second) to dilute the hydrogen-air mixture so that it will not detonate within the ventilation tubes upon ignition? Consult the papers in Refs. [6] and [7]. Make assumptions concerning the concentration and temperature of the hydrogen-air-steam mixture using these papers.

(10 Marks)

Figure 3 shows a mock-up of a 10m - radius hemispherical shell, filled with a 29.7 vol% hydrogen-air mixture. At time t = 0 (ms) the mixture is ignited to deflagration at the centre of the hemispherical cloud upon which a hemispherical flame begins to develop (see Figure 4). The flame propagates in the radial direction, away from the ignition point, and continues to grow until the combustible vapor cloud is consumed. The behaviour of the flame radius as a function of time, covering a radial trajectory of up to 20m is shown in the upper left part of Figure 5. The behaviour of the overpressure generated by the vapour cloud explosion at distances of 5m, 35m and 80m is shown in the other three sub-figures of Figure 5.

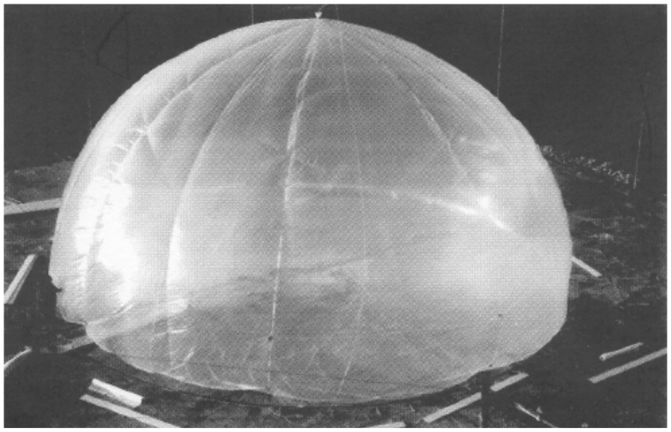

Figure 3: Hemispherical balloon mock-up containing a 29.7 vol% hydrogen-air mixture. From: Pfortner H. and Schneider H. Ballonversuche zur Untersuchung der Deflagration von Wasserstoff Luft Gemischen (Abschlussbericht). PNP Sicherheitssofortprogramm: Prozessgasfreisetzung - Explosion in der Gasfabrik und Auswirkungen von Druckwellen auf das Containment. ICT Internal Report, Fraunhofer Institut für Chemische Technologie, Pfinztal, Germany, 1983.

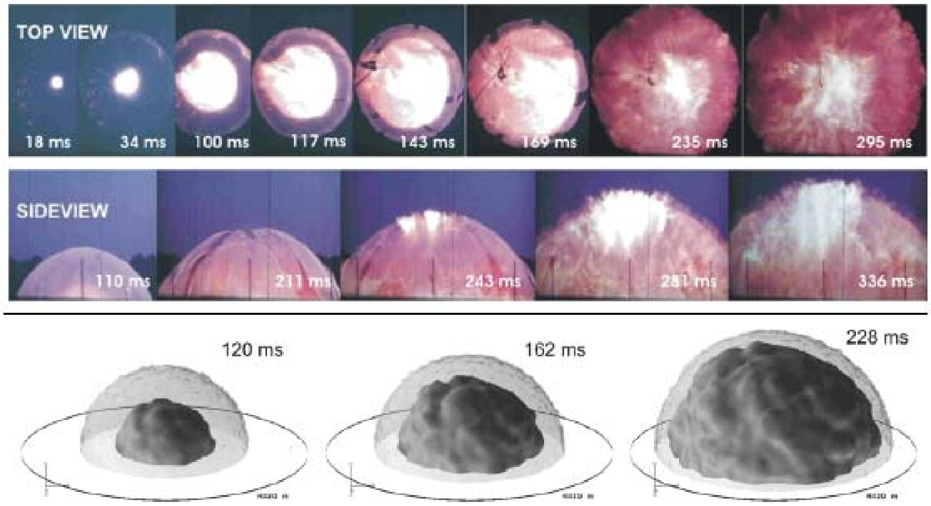

Figure 4: Snapshots of the propagating flame during an explosion of the 10m radius hemisphere filled with a 29.7 vol% hydrogen-air mixture. From: Molkov V., Makarov D., and Schneider H. LES modelling of an unconfined largescale hydrogen-air deflagration. Journal of Physics D: Applied Physics, 39:4366-4376, 2006.

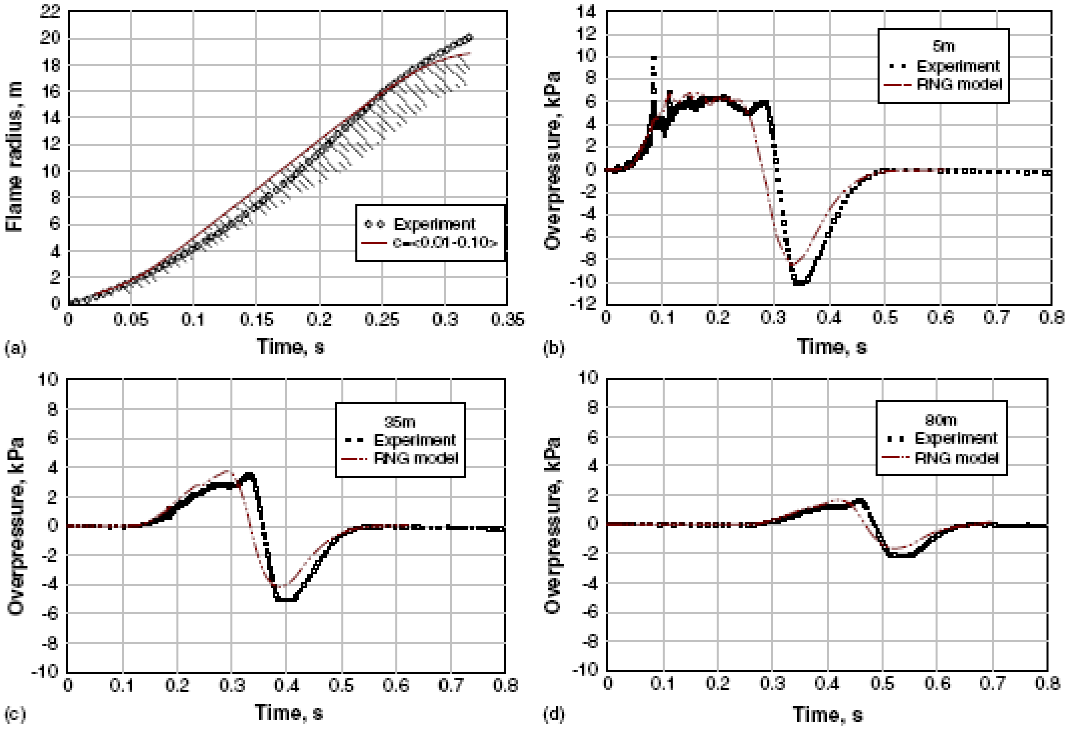

Figure 5: (a) Flame radius. (b) Over-pressure at 5m from centre of explosion. (c) Over-pressure at 35m from centre of explosion. (d) Over-pressure at 80m from centre of explosion. From: From: Molkov V., Makarov D., and Schneider H. LES modelling of an unconfined largescale hydrogen-air deagration. Journal of Physics D: Applied Physics, 39:4366-4376, 2006.

g. For unconfined spherical deflgrations, Ref. [5] provides a correlation of the form

$$S_f = C S_L^{4/3} \chi^{-1/3} R_f^{1/3} \qquad (3)$$

for the flame speed. Refer to Ref. [5] for the meaning of the symbols in this expression. Use the data in Figure 5.a to determine the value of C and χ in equation (3).

(10 Marks)

h. Compute the overpressure of the vapour cloud explosion of the hemispherical hydrogen-air cloud in Figure 3 at stand-off distances of 35m and 80m. Use equation (3) with the values for C and χ obtained under g) for the flame speed. Apply the methodology given by Ref. [1] to calculate the overpressure at stand-off distances of 35m and 80m. Compare your flame trajectory and overpressure with the data given in Figure 5.

(10 Marks)

i. Explain how the pressure profiles in Figure 5 can be used to assess the potential of an explosion to cause mechanical damage.

(10 Marks)

j. Refer to Ref. [8], Ngo T., Mendis P., Gupta A., and Ramsay J. Blast loading and blast effects on structures - An overview. *Electronic Journal of Structural Engineering*, 7:76-91, 2007. Special Issue: Loading on Structures. Explain the Single Degree of Freedom (SDOF) model and describe how it is applied to assess the response of a structure to a blast load. In your answer, address the idealisation of the waveform, the equation of motion for the SDOF, the inclusion of the structural mass and resistance in the equation of motion, and how the solution of this equation of motion can be used to assess structural response to blast waves.

(10 Marks)