MEASUREMENT OF HYDROGEN MIXING PROCESS BY HIGH RESPONSE HYDROGEN SENSOR

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ABSTRACT

According to the Global technical regulation on hydrogen and fuel cell vehicles (FCV), fuel cell discharge system at the vehicle exhaust system`s point of discharge, the hydrogen concentration level shall not exceed 4 % average by volume during any moving three-second time interval during normal operation including start-up and shut down [1]. FC stack need to washout by the concentrated hydrogen as the purge gas and how to exhaust gas without exceeding 4 % is the most concerns. Also how to measure hydrogen pulse of millisecond in exhaust is also the rising up issue. In this paper, model of FCV hydrogen discharge system was composed and variety of simple experiments were carried out to control the H_2 concentration and release. In the case which the semiconductor sensor with porous material (average size less than quench distance) were applied to check H_2 concentration, the short pulse of high concentration of H_2 in millisecond was hard to find. In this experiment, the simple exhaust gas model H_2/N_2 flow was used instead of Air/H_2. In the exhaust gas test, experiment was conducted under the atmospheric condition in room temperature with small pressure difference and the fast solenoid valve to create quick hydrogen control. Most of the experiments except the turbulent flow experiments, laminar flow is expected to be dominated when steady state condition is satisfied but the most result discussed here is the measurement of H_2 concentration during the start point at the time of discharge within seconds. The results showed when H_2 was added to N_2 flow, the boundary layer between N_2 and H_2 contained the high concentration of H_2 at the initial wave front and decrease to reach steady state. This H_2 pulse is typical in the FCV exhaust gas and topics of this paper.

1.0 INTRODUCTION

We are on the way of 2020 Tokyo Olympic Games and under the words of clean energy, hydrogen energy applications are prospectively developed: in Fuel Cell vehicle (FCV), cogeneration type of Fuel Cell, combustion of biogas in electric power generation plant etc. But hydrogen is a small molecule with lightweight. This characteristic basic property produces buoyancy, high diffusion constant and high permeability. Leak may occur from hydrogen-based systems through O-ring seals and vent in building or storage facilities containing hydrogen. Leaked hydrogen or unintended concentration of hydrogen as a cloud may escape and lead to an accident, so the leak should be detected as soon as possible for the safety sake [2-3].

Agreement concerning the establishing of global technical regulations for wheeled vehicles, equipment and parts which can be fitted and/or be used on wheeled vehicles is mostly solidified. According to the Global technical regulation on hydrogen and fuel cell vehicles (FCV), fuel cell discharge system at the vehicle exhaust system`s point of discharge, the hydrogen concentration level shall not exceed 4 % average by volume during any moving three-second time interval during normal operation including start-up and shut down. FC stack need to washout by the concentrated hydrogen as the purge gas and how to exhaust gas without exceeding 4 % is the most concerns [7]. Also how to

measure hydrogen pulse of millisecond in exhaust is also the rising up issue. Further more, any single failure downstream of the main H_2 shut off valve shall not result in a H_2 concentration in air of 4 % or more by volume within the passenger compartment. If a single failure down stream of the main hydrogen shut off valve results in a H_2 concentration in air of 4 % by volume within an enclosed or semi enclosed space in vehicle, the main H_2 shutoff valve shall be closed and warning to the driver shall be provided. [8] In this paper, model of FCV hydrogen discharge system was composed of plastic tube with pressure gage, Mass Flow controllers and Solenoid valves. Variety of simple experiments, injection, mixing, change flow rate and change tube inside diameter were carried out to control the H_2 concentration also Nitrogen (N_2) instead of Air. In mixing experiment, H_2 gas was introduced in the N_2 flow to form the various H_2 concentrations. H_2 at the point of discharge was monitored by the real time H_2 monitoring system Sx. The fast solenoid valve was opened within 3 milliseconds to add H_2 gas in N_2 flow, H_2 gas ran through the tube by mixing with N_2, and the wave front at the point of discharge was observed. In the milliseconds following the mixing process the separated phases were shown by the real time H_2 sensor and the wave front concentration of H_2 during stop and release type of motions was topics. In milliseconds diffusion mechanism does not work and Reyleigh-Taylor instability might work [10].

In order to detect low concentration of H_2 in real time at the same time other gases, various kinds of hydrogen detectors existing but each sensor has difficulties to measure 0-100 % concentration of hydrogen. Semiconductor gas sensor, for example, cannot measure 100 % hydrogen. Catalytic gas sensor with filter needs time for hydrogen to penetrate filter. In order to detect hydrogen in real time, mass spectrometer system with differential pumping stage was selected to develop real time monitoring system and applied to H_2/N_2 mixing experiments [5,6]. In hydrogen release experiment on the mountain, high pressure H_2 gas was escaped from the pipe in the air to form the various H_2 concentrations of cloud. H_2 diffusion process was monitored by the real time H_2 monitoring system [5, 7].

2.0 HYDROGEN SENSOR

Photo image of Hydrogen Sensor (Sx) is shown in Fig. 1. Schematic diagram of Sx was shown in Fig. 2. Weight of Sx is 25 kg and portable for the experiment outside mountain [4]. When Sx measure H_2, alarm red light is on. Liquid crystal touch panel is used to control Sx to start by changing valves. Sx has self-calibration system having certain concentration of single to mixed calibration gases. And having these calibration lines for each gas, Sx can monitor and show the concentration of each gas immediately. Real time monitoring is carried out from 2 milliseconds to 12 milliseconds. The real time monitoring system inside volume of Sx is minimized. Sampling inlet of this system is 150-250 μm SUS capillary tube. Gas sample is introduced from capillary through skimmer to ionization chamber. This system having differential pumping system to analyse gas, ionize hydrogen by electron bombardment method (EB). To minimize the humidity influence, Sx having dehumidifier is heated. Mass Spectrometer system works up to m/Z=300 [5, 6]

Figure 1. Sx Hydrogen Sensor.

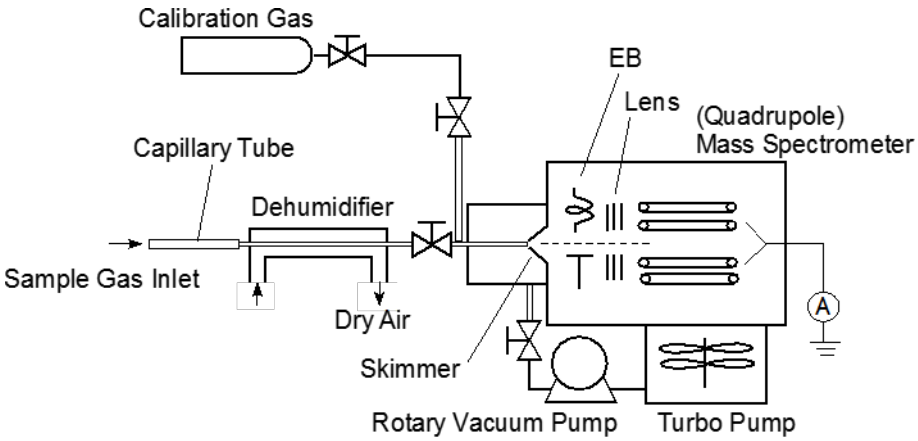

Figure 2. Schematic diagram of Sx system.

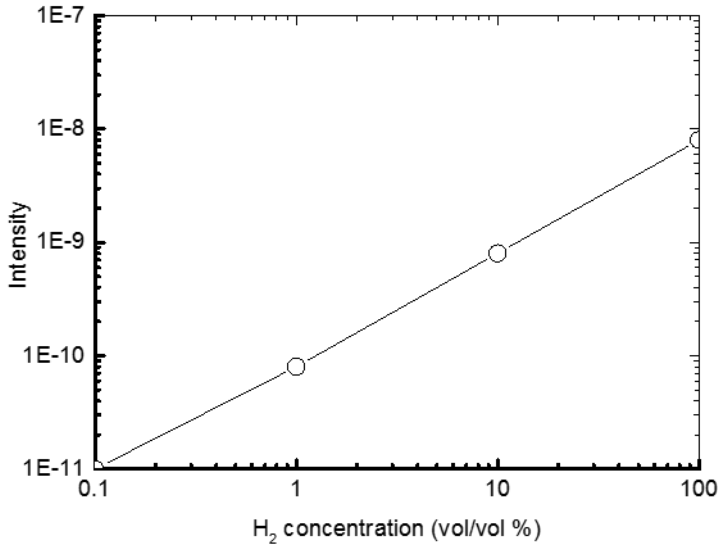

Figure 3. Sx sensor output vs H_2 concentration.

3.0 RESULTS AND DISCUSSION

3.1 Basic Performance and Response of Hydrogen Sensor Sx

Sx can measure hydrogen from 100 ppm to 100% without changing range of concentration up to 2 millisecond intervals by sampling gas from capillary tubing. By sampling high to low concentration of H_2, linear relationship is obtained between the output and the input concentration of hydrogen.

3.2 Experimental set up for Mixing

Nitrogen flow is controlled by Mass flow controller Kofloc (Model 38100SII-V-1, N_2, In 0.15 MPa / Out 0 MPa, 100SLM, 20□, 1 atm) with solenoid valve (CKD AB41-02-7 Minimum Pressure Required (MPR) 0.25 MPa) at the constant flow rate of 5 L/min. Hydrogen is added vertically or coaxially to Nitrogen flow at the constant flow rate and pressure through Mass flow controller Kofloc (Model 3810DS-V, H_2, In 0.20 MPa/Out 0 MPa, 100 SLM, 20□, 1 atm) and solenoid valve

(CKD AB41-02-7 0.25MPa) at the certain flow rates, and start mixing by fast solenoid valve (KOGANEI K2-100SA-09, MPR 0.2-0.5 MPa). The experimental settings for the vertical condition is shown in Fig. 4. In Fig. 4 after mixing H_2 and N_2, mixed flow comes down the stream in plastic pipe of ID/OD=4/6 mm. At the end of tube, discharge point, concentration of H_2 is measured by sampling gas. This tube is open toward atmospheric pressure air. Also schematic diagrams for vertical mixing and coaxial mixing equipment are shown in Fig. 5 and Fig. 6.

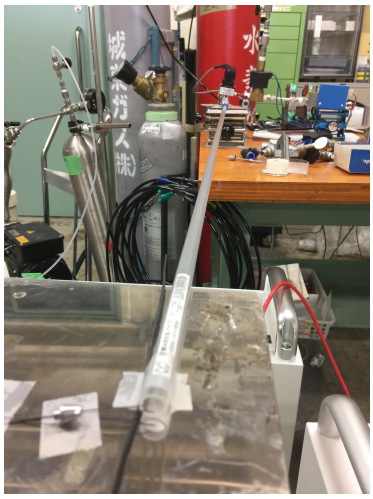

Figure 4. Experimental setup of vertical mixing equipment and sampling gas.

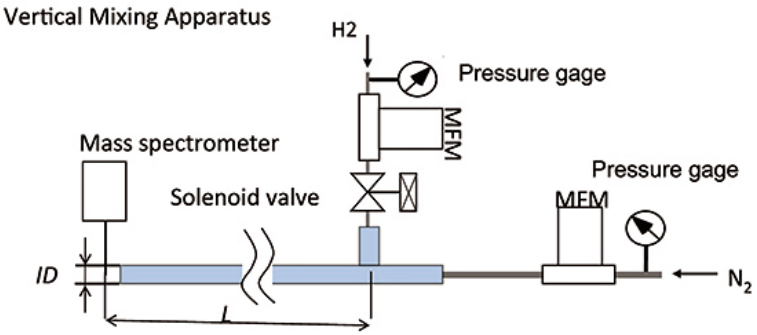

Figure 5. Vertical mixing (right-angle mixing head).

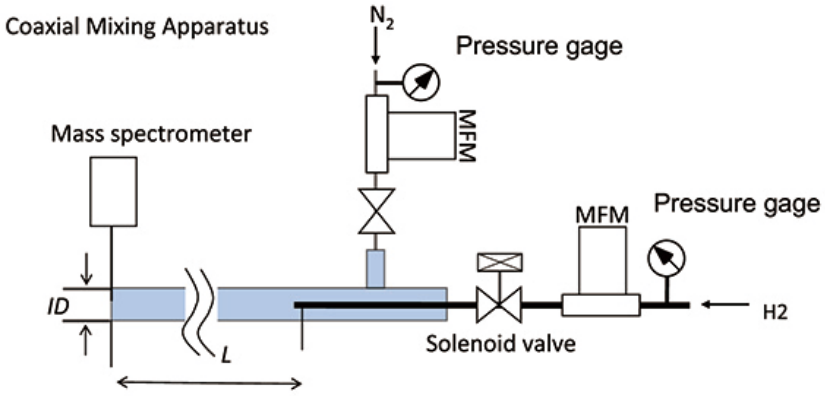

Fig. 6 Coaxial mixing.

(Both H_2 and N_2 introduced coaxially straight direction)

3.3 Diameter of tube

Three types of transparent plastic tube (Inside/Outside diameter; 4 mm/6 mm, 6 mm/8 mm, 10mm/13mm) at the length of 1000mm is used. Plastic tube is connected to vertical mixer and the concentration of H_2 is monitored by H_2 sensor Sx by time at the end of tube by sampling. The experiment is started by open up H_2 solenoid valve to introduce 100% H_2 at thee flow rate of about 2l/min at the pressure of 0.2 MPa. At the beginning of experiment there are some H_2 leak from solenoid valve and observed gradual increase of H_2 concentration, but the effect is negligible. H_2 flow mixed with N_2 flow and should reach about 40 % of hydrogen content in steady state flow. The result shown in Fig. 7 and the concentration of H_2 has peak top about 60 %. Also the width of peak top becomes wider when the diameter of pipe becomes bigger. These peak top might changes peak height and peak width. In this paper we call this as H_2 spike.

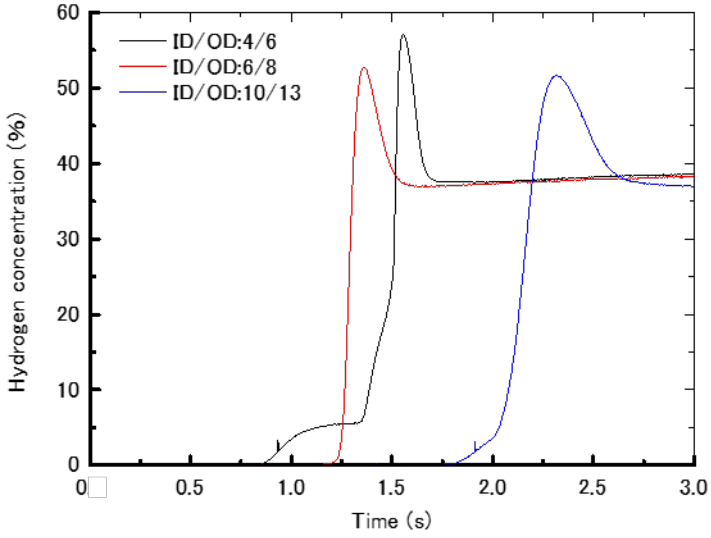

Figure 7. H_2 spike head vs tube inside diameter.

(ID: Inside diameter of tube, OD: Outside diameter of tube

3.4 H_2 Pressure Effect

Using the vertical mixer of 4 mm inside diameter at the length of 12400 mm, hydrogen pressure is changed from 0.1 to 0.5 MPa to add on the N_2 flow. When the experiment starts, the solenoid valve of H_2 is opened. After opening of the solenoid valve, hydrogen start flow and mixed with N_2 flow and discharged at the end of tube where Sx sampling is taking place. The result showed the concentration change by time. At the front boundary of mixed gas, H_2 concentration is high and gradual decrease of H_2 concentration to reach steady state, theoretical concentration of H_2. The maximum concentration of H_2 and steady state concentration are analyzed. By monitoring the concentration change from the start of this experiment to reach equilibrium concentration, the top, the maxim concentration of H_2 to steady state showed peak called spike. The spike observed in experiments by changing experimental condition was compared and analyzed. The spike appeared within a second. Hydrogen pressure effect toward the spike head is analyzed in Fig. 8. By changing the introduced hydrogen pressure from 0.1 to 0.5 MPa using Vertical Mixer, the hydrogen concentrations at the top of the spike are measured. In normal experiment of hydrogen mixing with nitrogen, the mixing process takes place within seconds and reaches the desired hydrogen concentration by changing flow rate of both gases. In this spike head analysis, the concentration of hydrogen is monitored in millisecond. Some kinds of over expecting hydrogen concentration is analyzed by the following process. The observed hydrogen concentration is subtracting from the expected value (the equilibrium concentration of hydrogen) as the over expecting concentration. The over expecting concentration is integrated by time to create the spike area. The increase of hydrogen pressure increases the area of spike head in Fig. 8. So we can say that the spike head concentration of hydrogen decreases with the increase of the inside diameter of tube. The width of spike head increases with the increase of the inside tube diameter.

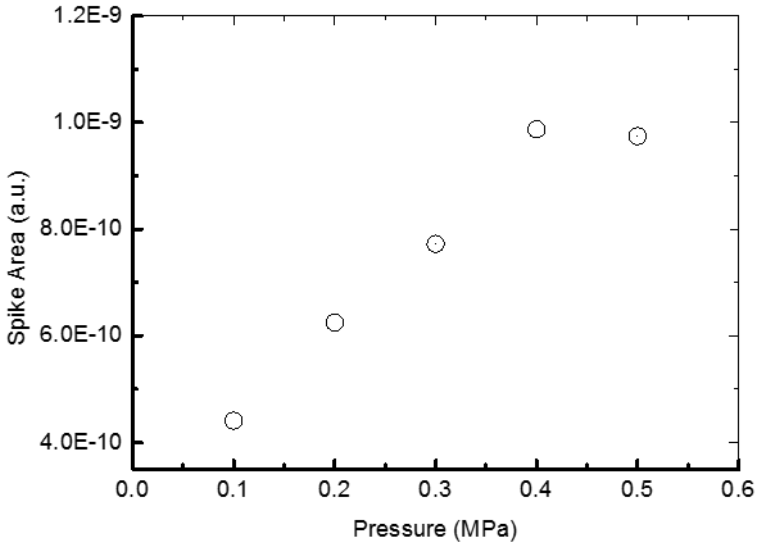

Fig. 8 H_2 spike head vs. pressure. (a.u; arbitrary unit)

3.5 Reynolds Number

The vertical mixer attached with plastic tube of ID/OD 4 mm/6 mm, length of 12400 mm is used to check Reynolds Number effect. Sampling point is the end of tube. In this experiment the ball valve (Swagelok 1/4 inch ball valve) is used instead of solenoid valve attached after Mass Flow Meter

(MFM). The condition for experiments varies by Reynolds Number, 200-13000 at the H_2 pressure of 0.2 MPa, Reynolds Number 1500-20000 at the H_2 pressure of 0.5 MPa. The increase of Reynolds Number decreases the area of spike head. This means that in turbulent flow the spike head made of the high concentration H_2 decrease but still survived in the long tube.

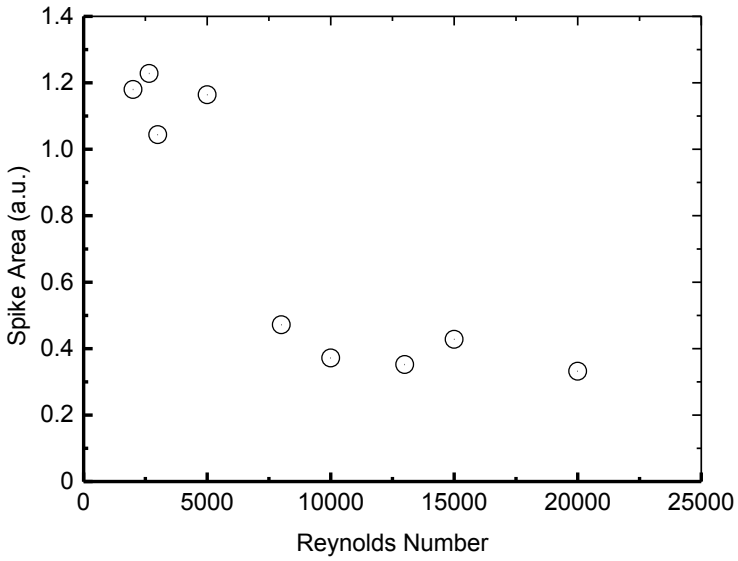

Figure 9. H_2 Spike head vs Reynolds Number.

3.6 Length of tube H_2

Similar experiments are conducted by changing the length of pass from 10 to 12400 mm. The concentration measurement is conducted at the end of each tube respectively. The result is shown in Fig.10. The spike head remains at the length of up to 12400 mm. The high concentration of H_2 penetrates 12400 mm length tube without diffusion.

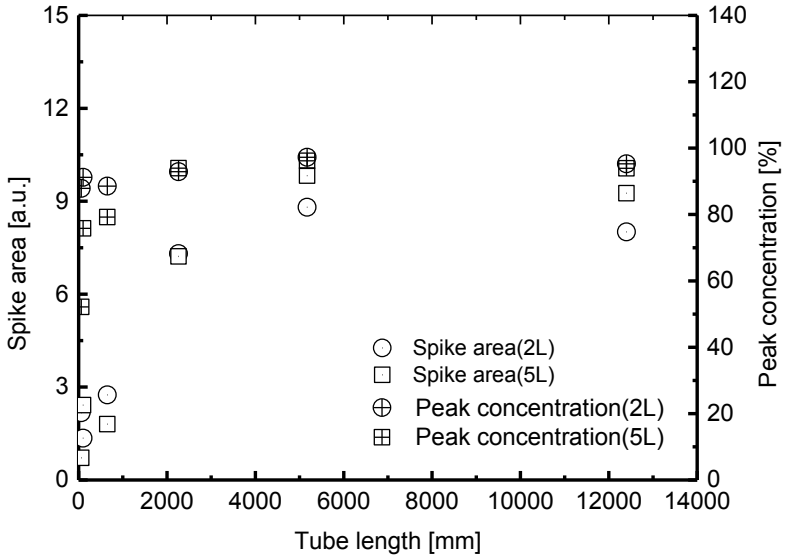

Figure 10. H2 spike head vs tube length.

3.7 Length of tube He

In Fig.11, Spike Head analysis is taken place by changing gas to Helium. In He case, the spike area is low but the similar phenomena are observed in the experiment.

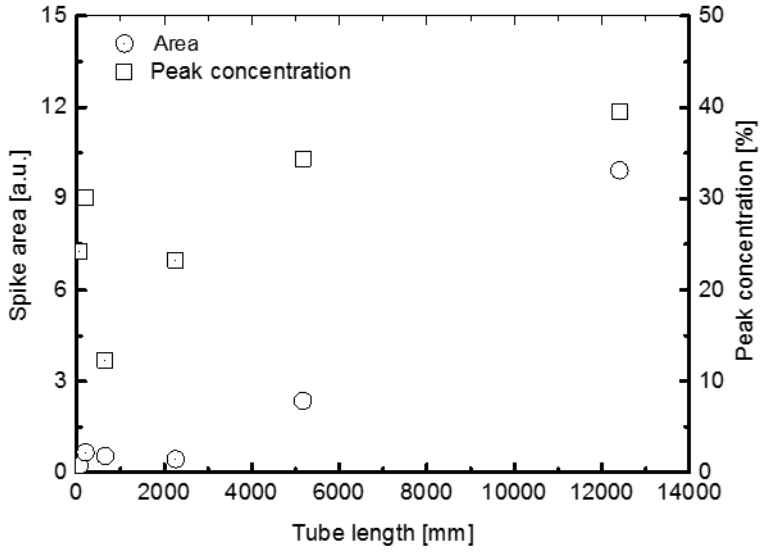

Figure 11. He spike head vs. tube length.

3.8 Types of valves

In Fig.12, the Spike heads are observed by changing the type of valves. The result shows that the spike heads are observed in all experiment and valves with narrow controller like needle type enhance the spike height and area.

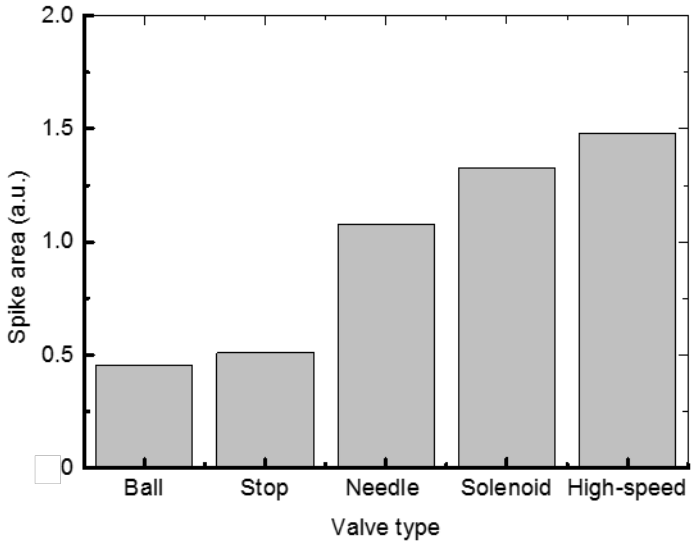

Figure 12. H_2 spike head vs valve type.

3.9 Various Gases H_2, He and O_2 and coaxial mixer

The results show that the spike heads are observed in all gas experiments and the lighter molecular weight enhances the spike height and area. The experiment using coaxial mixing equipment with plastic tube at the length of 12400 mm carried out and same spike is observed

Table 1. Spike area of gases.

No	Gas	Cmax(%)	Ceq(%)	Time(s)	Area(a.u)	Cmax/Ceq
1	H_2	76.9	14	0.47	0.18	5.5
2	He	39	7.5	0.83	0.17	5.2
3	O_2	65.3	43.8	0.21	0.07	1.5
4	CO_2	45.5	26.5	0.21	0.05	1.7
5	CH_4	41	27.2	0.15	0.03	1.5
6	Ar	49.7	19	0.32	0.08	2.6

Cmax: Spike top concentration of gas

Ceq: concentration of gas after stabilization of flow

3.10 H2 Spike Model

In Fig. 13, our millisecond H_2 monitoring shows the over expecting concentration of hydrogen phase, the spike. And this over expecting hydrogen concentrations is analysed by changing experimental conditions. These data shows in every case, the spike head is appeared and demonstrated that the high concentration phase start to run as front flow in tube. By mixing of H_2 with N_2 in steady state regime, laminar flow with diffusion mechanism by concentration gradient might work to reach equilibrium concentration. But the establishment of steady state flow and the concentration gradient by Fick`s law do not work within second considering diffusion constant of H_2. This mixing mechanism is almost like injection of H_2 into N_2. Reyleigh-Taylor instability might be comprehensive to understand the H_2 spike [10]. Even considering the complex system of FC stack in FCV with bent and narrow path for H_2, acceleration and deceleration path of H_2, the exhaust gas from FCV is simple pulse and width of less than second.

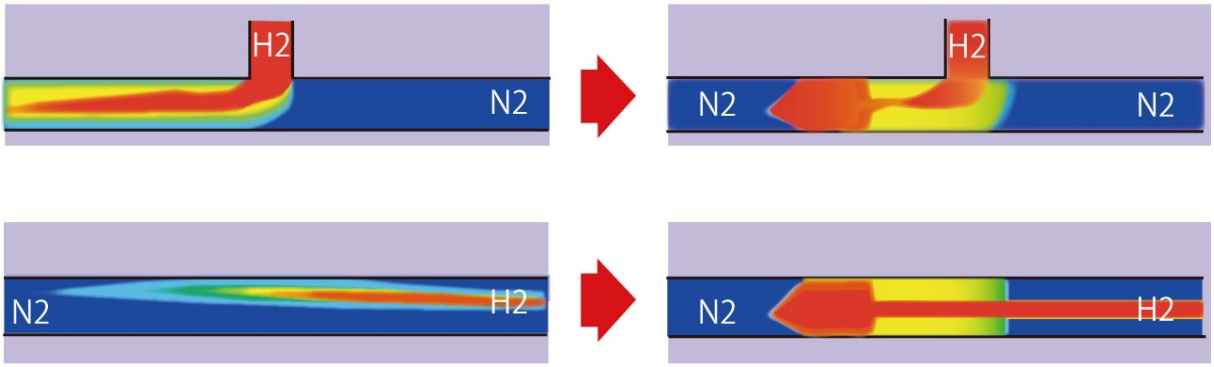

Fig. 13 H2 Mixing Model.

(Before and after experiments)

4.0 CONCLUSION

Simple H_2 purge model experiment to demonstrate the existence of cloud in exhaust gas from FC stack was conducted and at the point of discharge the real time H_2 monitoring was took place. Instead of H_2 and N_2 gases mixing process thought to be smooth diffusion process and end with the final intended concentration. Our experimental result shows hydrogen injection within milliseconds demonstrated the existence of hydrogen cloud, the spike. This spike head always appeared, when the pressure H_2 on front of the solenoid valve is changed. Changing the kinds of valves, the diameter of tube, the length of the tube, and even the Reynolds number up to 20000, this spike head flow with high hydrogen concentration always appeared. Even other gas showed the similar spike head with high concentration. These 2 milliseconds interval measurements are carried out by using the real time monitoring system Sx. The mass cloud of hydrogen move separately from N_2 and heterogeneously rather than diffusing homogeneously. Also head of spike is observed in millisecond monitoring by Sx. Our actual data showed difference from the perception before conducting experiment and simulation. The high concentration phase of hydrogen clouds survives and moves upward by buoyancy or flow forming spike head rather than homogeneously diffusing.

ACKNOWLEGMENT

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