H$_2$-F$_2$ Reaction in a Tubular Reactor

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Abstract

Reaction between potentially explosive mixture of H$_2$ and F$_2$ has been studied both experimentally and computationally. It was carried out in a tubular reactor, graduating from one stage to the other, so as to handle the reaction in a safe and sustained manner. The ratio of H$_2$ to F$_2$ flow and the flow rate of nitrogen, affect the reactor temperatures. The experiments have been performed over a wide range of flow ratios to generate reliable data. It was observed that the flame due to reaction between hydrogen and fluorine is formed in front of the fluorine feed nozzle. Numerical simulations have been carried out and temperature profiles predicted by these simulations are compared with experimental ones. Good match is observed between the two. This study will be helpful in designing a large scale H$_2$-F$_2$ flame reactor.
Key words: H$_2$-F$_2$ reaction, turbulent flame, reactor temperature, flame reactor.
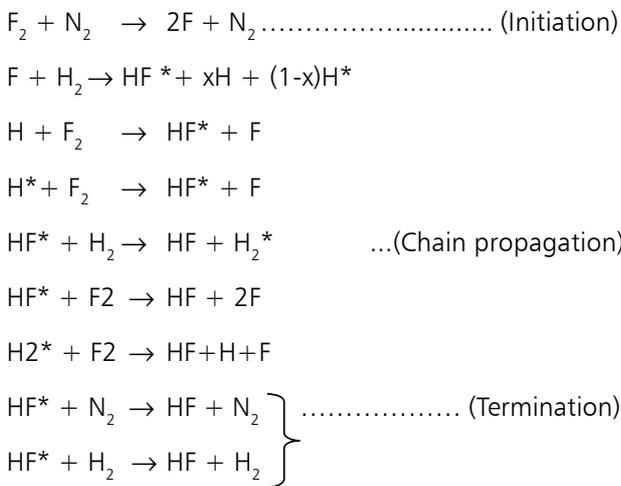
Introduction

The energy needed for many chemical reactions of industrial importance may be provided externally, by heating or internally by carrying out an exothermic chemical reaction in the region of interest. One such example is the reaction between H$_2$ and F$_2$. The reaction between the two produces a high temperature flame. Majority of the published work deals with this reaction in the context of HF lasers [Chen et al. (1975), Kapralova et al. (1976), Kim and Cho (1994)]. Very little work has been reported on its utilization for material processing in chemical and nuclear industries. Scanty information is available for potentially explosive mixtures like H$_2$ and F$_2$.

It was reported by Grosse and Kirshenbaum (1955) that, self ignition takes place whenever fluorine gas issues into hydrogen atmosphere, even at room temperature. Table 1 gives the flame temperature for pure hydrogen-fluorine reaction, mixed in different proportions at atmospheric pressure and room temperature, as reported by Wilson et al. (1951). Basov et al. (1969) consider that the reaction between H$_2$ and F$_2$ involves a branched chain mechanism. According to Sullivan et al. (1975), H$_2$-F$_2$ reaction is of chain type, where free radicals help in the propagation of the reaction steps. In a mixture of F$_2$, H$_2$ and N$_2$, the envisaged reaction steps are as follows:

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Table 1: Theoretical flame temperature by Wilson et al.(1951)

Mole% F_2	Mole% H_2	Theoretical Flame Temperature at 1atm(K)
10	90	1920
33.3	66.7	3550
50	50	4300
66.7	33.3	3800

$F_2 + N_2 \rightarrow 2F + N_2$ ……………............. (Initiation)

$F + H_2 \rightarrow HF * + xH + (1-x)H*$

$H + F_2 \rightarrow HF* + F$

$H* + F_2 \rightarrow HF* + F$

$HF* + H_2 \rightarrow HF + H_2*$ ...(Chain propagation)

$HF* + F2 \rightarrow HF + 2F$

$H2* + F2 \rightarrow HF + H + F$

$HF* + N_2 \rightarrow HF + N_2$ ⎫
……………… (Termination)
$HF* + H_2 \rightarrow HF + H_2$ ⎭

The fluorine atoms required to initiate the reaction are formed either by dissociation at higher temperature or by collision of fluorine molecule with another high velocity molecule. Rabideau et al. (1972) found the specific rate constants for $H+F_2$ and $F+H_2$ reactions at 300K to be $2.5\pm0.2 \times 10^{12}$ cm³/mole.sec and $4\pm1 \times 10^{12}$ cm³/mole.sec respectively. The concentration profile presented by Zebib et al. (1975) showed, that H_2 and F_2 never co-existed as the reaction was immediate. In the present work, the reaction between H_2 and F_2 has been carried out in a long tubular reactor, operating at low pressure. Effect of the ratio of F_2 and H_2 flow rates on reactor temperature has also been studied. Nitrogen is always present along with fluorine when it is produced from electrolysis of HF. Therefore, studies on effect of nitrogen flow rates on reactor temperatures were also performed. The experimental data was used to validate a numerical model. The model, thus established, can be used as a tool to simulate cases involving higher reactant flow rates for reactor design and scale up.

Experimental set up

Fig. 1 shows the block diagram for the H_2-F_2 reaction system. The experimental set up consists of a tubular reactor, feeding arrangements and a scrubber. Hydrogen is supplied from a cylinder, while fluorine is generated by electrolysis of hydrogen fluoride in an electrolytic cell using KF.2HF as the electrolyte. The F_2 from the electrolytic cell is premixed with a known quantity of N_2. Flow rates of hydrogen and fluorine mixed with nitrogen are regulated through respective flow control valves. The reactor wall is preheated to 423 K using an on-off temperature controller. Four B-type thermocouples tagged T1 to T4 have been used near the feed nozzles, while five K-type thermocouples are placed away from them. Further details of thermocouple location are given in Table 2. The exit points of fluorine and hydrogen nozzles in (r, è, z) format are at (10,0,140) and (10,180,130) respectively. The reactor wall temperature is controlled by removing the heat of reaction by regulated air/water cooling. One pressure transmitter and two pressure switches are installed in the reactor. Safety interlocks are invoked to guard the reactor from high temperature and pressure surges. HF, F_2 and H_2 sensors are installed appropriately to detect the release of gases and alert for corrective action. As a redundant safety measure, one rupture disc is also attached to the reactor which opens directly to the scrubber. The effluents are routed to scrubber, where HF is neutralized with KOH solution. Excess hydrogen is vented to the atmosphere through a flame arrester and a water seal. The reaction is carried out remotely from control room using PLC and data is recorded through SCADA.

Experimental observations

The cases with varying flow rates of F_2 and H_2 are listed in Table 3. Adiabatic flame temperatures for these cases are also shown in this table, which varies from ~1100 to 3000 K. It was practically impossible to measure this high temperature, that too in a highly corrosive atmosphere. Therefore, the temperature sensors (T1 to T4) were placed in such a way, that they do not lie in the flow path of the fluorine stream. Thermocouple T1 recorded the highest temperature in all the runs. As seen in Figs. 2 and 3,

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Table 2: Location of thermocouples in cylindrical coordinates

Thermocouple	Angle in anticlock wise direction	Radius in mm	Distance in mm from Top of reactor flange
T1	270	4.5	178
T2	90	4	173
T3	197	5.7	161
T4	15	18.5	154
T5	115	26	260
T6	90	25	260
T7	33	20	260
T8	135	16	594
T9	135	16	764

thermocouple T3, which is radially farther from the F_2 nozzle tip as compared to T4, always recorded higher temperature than the latter. It indicates that the flame expands to a radius of ~ 16 mm at a longitudinal distance of 20 mm. Thermocouples T5, T6 and T7 which are relatively closer to the reactor wall, recorded temperatures in the range of 490-570 K, which are much higher than the preset wall temperature. The temperature profile is flattened down the length of the reactor as the difference between T6 and T7 was 60–70 K as compared to 500-700 K, the difference between T1 and T2 placed at the top. During the experiments, no rise in reactor pressure was recorded through the transmitter.

In cases 3 to 11, effect of volumetric excess of hydrogen was studied on reactor temperature profile and the results are shown in Figs. 7a - c. In all the cases, the drop in the value of T1 was in the range of 20-80 K. The net change in T1 decreased at higher fluorine flow rates, suggesting that the effect of excess hydrogen reduces, when higher amount of energy is liberated inside the reactor. At low fluorine flow rate, the heat evolved is comparatively less and the high temperature zone is confined to a small region. As the hydrogen flow increases, more hydrogen molecules reach near the fluorine nozzle where the reaction takes place. Since hydrogen has higher thermal diffusivity, the rate of lateral heat dissipation increases, resulting in increase in temperature being recorded by T4 which is

slightly away from the nozzle radially. As the fluorine flow rate increases, more heat is liberated leading to higher temperatures near the nozzles. The high temperature zone also expands due to local turbulence. Therefore, with higher H_2 to F_2 flow ratio, both T1 and T4 values go down while T7 gains temperature. The gap between the values of T4 and T7 goes on decreasing with increase in hydrogen flow rate. There is almost no variation in the values of T8 as flow of hydrogen increases. This suggests that the effect of excess hydrogen on the reactor temperature is limited to a distance of ~120 mm from the F_2 nozzle tip.

Study on the effect of nitrogen on reactor temperatures was performed through cases 12 to 17. From Figs. 8a - c, drop in temperatures as indicated by T1 and T4 was between 200 and 300 K, when nitrogen flow was increased from ~0.4 slpm to 3.5 slpm. Thermocouples T4 and T7 are located almost at the same radial distance but T7 is ~110mm farther from T4. When the nitrogen flow was varied for 0.2 slpm of fluorine, initially, at lower nitrogen flow rate (0.4 slpm), the value of T4 was more than T7 [Fig. 8(a)]. But, as the nitrogen flow was increased, T7 exceeded T4 by almost 100 K. When the nitrogen flow rate was increased to 3.4 slpm, the drop in T4 was close to 180 K while the rise in T7 was nearly 100 K. The gap between T1 and T7 reduced with increasing nitrogen. The temperatures as indicated by T8 and T9 were almost unaffected. Similar effects of nitrogen flow on reactor temperatures were observed for the other two flow rates of F_2, that is, at 0.3 and 0.4 slpm. Dip in T1 and T4 values and simultaneous rise in the value of T7 imply the expansion of the high temperature jet. More nitrogen adds momentum to the fluorine stream, leading to increase in its velocity. It also results in spreading of species and dissipation of reaction heat to a larger volume. However,

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as observed in the case of excess hydrogen, this effect too appears to be limited to a length of ~120 mm as reactor temperatures below this length did not show any notable change.

Modeling

In order to simulate the reaction under consideration, a 3-D geometry model of reactor was made using GAMBIT 2.2.30. FLUENT version 6.2 was used as a CFD solver and also for post processing. To capture the mixing as well as the reaction phenomena, a fine mesh was adopted near the nozzle exit region. Fluorine and hydrogen issuing into the reactor have lower velocities, and un-mixed flows of these gases are in laminar region. However, when the gases mix and react together, temperature goes up to such an extent, that the flow becomes turbulent. Therefore, a turbulent flow model has been considered here. Species transport model has been used to study the mixture of species in the reactor. As the reaction is instantaneous, the overall rate of reaction is controlled by turbulent mixing. Rate of change due to reaction source has been calculated

by Eddy Dissipation Model (EDM). Mass flow inlet in kg/s is given as the inlet boundary condition for both the nozzles. Thermo-physical properties for all the species namely F_2, H_2, HF and N_2 and their mixture are selected from the Fluent data base. 'Outflow' is given as the outlet boundary condition which assumes zero diffusion $\left(\dfrac{\partial \phi}{\partial x} = 0\right)$ flux at the outflow cells, where ϕ is any flow variable. Inlet gas temperature for both the hydrogen and fluorine gases is given as 423 K. Wall temperature is maintained at 423K. The reactor pressure is given as 1000 mbar (abs).The radiation heat transfer has not been considered in the simulation, due to low emissivity values of flames. Ideal gas law has been used to take care of the density variation due to temperature change. No-slip boundary condition is employed at the walls. Relaxation factors of 0.3, 0.7, 0.8 and 0.8 have been used for pressure, momentum, turbulent kinetic energy and turbulent dissipation respectively. Simulations

Table 3: Gaseous flow rates and adiabatic flame temperature

Case no.	Flow Rate, F_2 (slpm)	Flow Rate, H_2 (slpm)	Flow Rate, N_2 (slpm)	Adiabatic flame temp in K
1	0.44	2	0.52	2488
2	0.5	2	0.5	2691
3	0.2	0.63	0.4	2682
4	0.2	0.85	0.4	2367
5	0.2	1.27	0.4	1954
6	0.3	0.95	0.45	2830
7	0.3	1.27	0.45	2487
8	0.3	1.91	0.45	2025
9	0.4	1.27	0.5	2911
10	0.4	1.7	0.5	2545
11	0.4	2.54	0.5	2067
12	0.2	0.85	0.9	1933
13	0.2	0.85	3.4	1090
14	0.3	1.27	1.9	1715
15	0.3	1.27	3.4	1333
16	0.4	1.7	1.5	2043
17	0.4	1.7	3.5	1500

have been carried out with flow rates of hydrogen, fluorine and nitrogen as given in Table 3. The steady state condition is assumed and the solution was iterated until the stipulated convergence criterion of residue $< 10^{-4}$ was achieved for each run.

Modeling results and comparison with experimental observations

Initially, simulation was carried out using 0.75 and 1mm grids, in order to verify the grid independency. The difference in temperatures at various locations for both the grid sizes as shown in Fig. 2 is not significant. However, there is a large difference between the computational time requirements for the two grid sizes. Therefore, further simulations were carried out with 1 mm grid size. In order to check the effect of turbulence model, simulations were carried out for 'case 2' using both standard k- ù and standard k- å models. The temperature values of T1 through T9 are compared with the experimental data in Fig. 3. It is seen that the predictions with k-å model are closer to the experimental data. Therefore, k-å model for turbulence was chosen for simulations. The temperature contours are presented in Fig. 4 for cases 1 and 2. It can be seen that, reaction flame does not touch the reactor wall, and its length is around 120 mm in both the cases. Experimentally also, high temperatures are observed at locations of T5, T6 and T7 at ~120 mm from the nozzle, which further confirms the hypothesis. Fig. 5 shows the Y velocity contours for the two cases. From this figure, it is seen that velocity in the downward direction is predominant near the fluorine nozzle. A part of the hydrogen flow has upward motion suggesting some recirculation in the region near the hydrogen feed nozzle. The nozzles were inspected after the reaction had been carried out. Both the nozzles were found to be intact and clean, as if they have been passivated with diluted fluorides. One of the reasons attributed to the occurrence of this phenomenon, could be some length taken for hydrogen molecules to diffuse, mix with fluorine molecules and react. This observation is further confirmed by the simulation results shown in Fig. 6 where, hydrogen streamlines are seen bending towards the fluorine streamlines and intersecting them slightly away from the nozzle tip. Since the velocity of hydrogen stream is lower, it is dragged by the relatively high velocity fluorine and nitrogen stream. The validated model used for cases 1 and 2 was deployed in simulating another 15 cases as mentioned in Table 3. Fig. 9 shows the comparison of simulated and experimental reactor temperature readings for few selected cases. There is a good match between the two. The computed data follows the experimental trend of increase and decrease in temperatures when a particular parameter is changed.

Conclusion

The reaction between hydrogen and fluorine has been carried out in a tubular reactor for different flow rates of reactant gases and also has been computationally simulated. The assumption made during the simulation that the reaction between hydrogen and fluorine is instantaneous and the flow field is turbulent has produced results, which match well with experimental observations. The reaction between hydrogen and fluorine takes place along the axis of fluorine flow jet. The flame does not form right at the nozzle tip because of insufficient fuel present locally. The flame temperature is affected by parameters such as excess of hydrogen and fraction of nitrogen present in the fluorine. With increasing flow of hydrogen, the temperature near the nozzle drops while the reactor temperature away from them increases. The drop in temperatures near the nozzle area is substantial with increasing nitrogen flow rate. The computational results also show similar behaviour. The good match between the experimental results and the numerical predictions validate the computational model. This tool can now be used to assist in the design of a scaled up H_2-F_2-flame reactor.

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