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# Design and Control of Hot-Gas Desulfurization Systems with High Oxygen Regenerator Feed Gas

**Key Words**: Hot Gas Desulfurization, Design, Control, High Oxygen Regenerator

## 1. Introduction

Hot Gas Desulfurization (HGD) Process consists of two bubbling fluidized-bed reactors (a desulfurizer and a regenerator) operating at high temperatures and high pressure. The removal of $H_2S$ from synthetic gas occurs in the desulfurizer in which the solid MeO is converted to MeS. This reaction has a negligible heat of reaction. The solids are circulated to the regenerator in which the MeS is converted back to MeO by feeding a gas containing oxygen. This reaction is highly exothermic. Therefore, the regenerator feed gas was quite lean in oxygen, the remainder being nitrogen. The large amount of nitrogen serves as an effective heat sink for the exothermic combustion reaction $MeS + 3/2\ O_2 \rightarrow MeO + SO_2$ occurring in the regenerator. However, the compression of this large amount of regenerator feed gas to pressures around 20 atm represents a significant energy and capital cost in the process. If higher $O_2$ concentrations can be used, significant savings in compression capital investment and energy consumption could be achieved. In addition, the smaller gas flowrate yields a smaller diameter regenerator vessel, which also reduces capital investment, and it yields a higher $SO_2$ concentration in the regenerator exit gas, which reduces costs in the sulfur-recovery unit. In steady state design and economic aspect, higher concentration oxygen regenerator case is definitely more favorable. However, we have seen many cases of trade-offs between design and control in many processes. It is important to consider dynamics and control at the early stage of design because of the strong impact of design decisions on the effectiveness of any control system. So, we have studied both design and dynamics at the early stage of design in the hot gas desulfurization system. Based on the study, it is needed to make a reasonable compromise between economics and process controllability.

**2. Objectives**

This paper studies the use of regenerator feeds that have higher oxygen concentrations. Not only steady-state but also dynamic issues are examined. The key issue is identified to be heat-removal limitations which is confirmed by dynamic simulations.

**3. Approach**

Designs for regenerators with feeds having various oxygen concentrations are developed, and a dynamic model of the HGD unit based on Yi and Luyben(1999) is used to converge to the steady-state conditions corresponding to regenerator feed concentrations of 2.5, 5.0, 10 and 21mol% oxygen. The dynamic model is used to compare dynamic aspects of four different oxygen steady-state design cases.

**4. Results and Discussion**

*4-1. Steady-State Designs of Four Different Oxygen Regenerators*

Figure 1 shows the basis case flowsheet with the conditions for the lean regenerator feed gas of 2.5% oxygen concentration. For the pilot-scale unit studied, the flowrate is 10.72kg-mol/hr, and the vessel diameter is 0.23m. This flowrate of feed gas provides enough oxygen to regenerate the solids. The unreacted oxygen in the exit gas is quite small (400ppm). An inlet gas temperature of 549°C permits the regenerator to operate adiabatically since the sensible heat of raising the gas from the cool inlet feed temperature to the high operating temperature of the regenerator removes much of the heat of the exothermic combustion reaction. Some of the heat is also removed by the solids circulation between the cooler desulfurizer (600°C) and the regenerator (750°C).

The physical dimensions used and the calculated steady-state conditions are summarized in Table 1. Designs for regenerators with feeds having various oxygen concentrations are developed, and a dynamic model of the HGD unit is converged to the steady-state conditions corresponding to regenerator feed concentrations of 2.5, 5.0, 10 and 21mol% oxygen.

If the oxygen concentration in the regenerator feed gas is increased to 5mol%, the feed flowrate drops to 5.32kg-mol/hr and the vessel diameter shrinks to 0.16m. This clearly permits a reduction in capital investment (vessel and compressor) and in operating cost (compressor power). The feed temperature required for adiabatic regenerator operation must be decreased from 549°C to 344°C. The impact of these changes on dynamic controllability is the subject of this paper.

For the 2.5% and 5.0%$O_2$ cases, the regenerator has enough cool feed gas to permits its adiabatic operation. However, for the 10% and 21% cases, feed gas flowrate is so small that even ambient temperature (25°C) inlet temperature does not provide enough sensible heat removal to permit adiabatic regenerator operation. Some heat must be removed via jacket cooling.

Notice that the jacket heat-transfer area in the regenerator decreases rapidly as the oxygen concentration increases because the flowrate of the gas decreases, which reduces the vessel diameter. At the same time the required jacket heat-removal rate increases because there is less nitrogen in the feed gas to serve as a thermal sink. These two effects result in a rapid decrease in the jacket temperature (Q is increasing and area is decreasing). Heat-transfer coefficients of 150 and 50W/m $^2$-K are used in the bed and free-board portions of the wall, respectively. Table 1 gives the average UA values for each case. Dynamic changes in bed heights are assumed to be negligible.

The presence of large temperature differences between the regenerator (at 750$^o$C) and the jacket indicates that dynamic controllability will be poor because of the limited rangeability of the cooling rate. The temperature differential is already so large that it is difficult to increase it enough to significantly change the heat-transfer rate. This results in poor control of temperature when disturbances occur.

*4-2. Optimum Control Structure for a Hot Gas Desulfurization System*

Figure 2 shows the control scheme used. The scheme is improved from that presented in Yi and Luyben (1999) with one notable addition: the regenerator exit gas oxygen composition is controlled.

The tuning of the regenerator temperature and pressure controllers is different for the different size regenerators and different heat-removal systems because of the different vessel sizes and heat-transfer areas. The relay feedback test is used for each design. The control loops shown in Figure 2 are:

(1) Desulfurizer exit gas $H_2S$ concentration is controlled by changing the setpoint temperature of the desulfurizer temperature controller.

(2) Temperature in the desulfurizer is held by manipulating heat-removal rate. Inlet feed-gas temperature to the regenerator is used to control regenerator temperature when this is possible (the 2.5 and 5mol% cases). Jacket cooling is used in the higher oxygen cases.

(3) Pressures in both vessels are held by manipulating the position of valves in the exit gas streams.

(4) Solids level in the desulfurizer is controlled by manipulating the solid flowrate from the desulfurizer.

(5) Solids flowrate to the desulfurizer is flow controlled.

(6) Regenerator feed gas is ratioed to desulfurizer feed gas through a dynamic lag. This ratio is set by an oxygen composition controller.

(7) Log (ppm $O_2$) Control

In our initial studies(Yi and Luyben, 1999; Luyben and Yi, 2001), the control of the oxygen composition of the regenerator exit gas was found to be quite difficult. This is due to the very small concentration (400ppm) and the resulting large changes in the oxygen composition of the regenerator exit gas. The situation is quite similar to high-purity distillation columns in which composition of impurities in the product streams can *increase* drastically but can *decrease* only slightly. An approach to the high-purity distillation control problem has been successfully used for many years. The idea is transform the variable to be controlled before feeding the signal into the composition controller. The most common transformation is to take the logarithm of the variable. This is what is done in the control scheme shown in Figure 2. The concentration of oxygen in the regenerator exit gas in ``molar ppm'' (mole fraction times $10^6$) is transformed to a new variable ``$\log_{10}$(ppm)'', and this variable is controlled. The log(ppm $O_2$) controller is tuned using a relay feedback test. A 36 second deadtime and two 36 second lags are used in this loop. The ultimate gain is 3.7 and the ultimate period 0.86 hours. The steady-state value of the oxygen is 445ppm, so the log(ppm) variable is 2.648. The span of the log(ppm) oxygen analyzer is set equal to 5.

*4-3. Dynamic Simulation Results of Four Design Cases*

Each case was simulated and tested using two disturbances: a 20% increase in the feed rate $FS_{in}$ to the desulfurizer and an increase in the $H_2S$ concentration of the desulfurizer feed gas from 0.4mol% to 0.5mol%. The latter disturbance is labeled ``+25%$H_2S$'' in the results given in Figures 3 to 6. Both of these disturbance result in higher desulfurizer temperatures in order to keep the product gas at the desired 80ppm$H_2S$ level.

4-3-1. 2.5 mol% Oxygen Case

Figure 3 gives the base-case results for the 2.5% oxygen feed. Regenerator inlet temperature is decreased and regenerator feed gas is increased to handle the increases in oxygen supply required by both disturbances. Notice that the peak change in regenerator temperature is about 1.2°C. The changes in regenerator feed temperature are only about 5°C.

4-3-2. 5 mol% Oxygen Case

Figure 4 gives results for the 5% oxygen feed. The regenerator is still adiabatic. Regenerator inlet temperature decreases and regenerator feed gas flowrate increases to handle the increases in load for both disturbances. Now the peak change in regenerator temperature has increased to 4°C, and there is a 10°C decrease in feed temperature.

4-3-3. 10 mol% Oxygen Case

Figure 5 gives results for the 10 % oxygen feed. Regenerator feed gas inlet temperature is held constant at 25$^{o}$C, and heat is transferred through the wall of the regenerator vessel to the jacket. Regenerator feed gas flowrate increases and jacket temperature decreases to handle the increases in load for both disturbances. The changes in jacket temperature are about 10-12$^{o}$C, and regenerator temperature is well controlled (1$^{o}$C excursions).

4-3-4. 21 mol% Oxygen Case

Figure 6 gives results when air is used as the regenerator feed gas (21mol%$O_2$). Regenerator feed gas inlet temperature is held constant at 25$^{o}$C, and heat is transferred through the wall of the regenerator vessel to the jacket. Regenerator feed gas flowrate increases and jacket temperature decreases to handle the increases in load for both disturbances. However, now the peak change in regenerator temperature is 10$^{o}$C. The changes in jacket temperature are quite large: 90-120$^{o}$C.

All of the other runs were made with a 200$^{o}$C temperature transmitter span on jacket temperature, which permits a maximum decrease or increase from steady state of 100$^{o}$C. The thick lines in Figure 6 show that this constrained regenerator jacket temperature results in a loss of control of regenerator temperature after about 1 hour for the $H_2S$ disturbance. Increasing the span permits the system to ride through the disturbance, but the final jacket temperature is about 240$^{o}$C, which represents a drop of 120$^{o}$C from the initial value.

These very large jacket temperature changes indicate the potential for dynamic control problems. If high-oxygen regenerator feed gas is going to be used, particularly in the commercial-scale unit, much more heat-transfer area must be designed into the system if effective regenerator temperature control is to be achieved.

**5. Applications**

This research has studied a pilot-scale unit. Clearly the heat-transfer area problems will be more severe for large commercial-scale HGD units. A simple analysis of this situation is present in this section to get some feel for how bad the problem will be.

We assume a scale-up factor of 1000 and the same gas velocity. Thus for the 21% oxygen case the regenerator feed gas flowrate is 1000 times that of the pilot-scale unit and the cross-sectional area is a factor of 1000 bigger. So the diameter of the commercial unit is 0.08 x $(1000)^{1/2}$=2.53m.  Scaling-up the solids holdup by the same factor of 1000 gives a bed height of only 0.28m, which is unrealistic. So a bed height of 5m and the freeboard height of 15m (total height 20m) is assumed.

The heat-removal rate is 1000 times the pilot-scale value or 44.9x$10^{6}$kJ/hr. Using heat-transfer coefficients of 540 and 180kJ/hr-$m^2$-K for bed and free-board, respectively, gives an impossible temperature difference between the regenerator at 750$^{o}$C and the cooling jacket.

$$\Delta T = \frac{44.9x10^6}{\pi(2.53)[5(540)+15(180)]} = 1070^o C$$

For effective temperature control, a maximum temperature differential of about 300$^o$C seems reasonable. If the height of the regenerator is increased to achieve this $\Delta$T (keeping the same 15/5 freeboard to bed ratio) the total height of the regenerator would have to be about 70m! This looks impractical. Therefore it appears that other methods must be found to increase heat-transfer area in commercial units if high-oxygen feed gas is going to be used.

## 6. Conculsions

It has explored the steady-state and dynamic implications of using regenerator feed gases with higher oxygen concentrations in a hot gas desulfurization system. Steady-state economics favor higher oxygen because the vessel is smaller, less feed gas is needed and the concentration of $SO_2$ in the gas fed to the sulfur-removal plant is higher. However, dynamic control deteriorates. Jacket heat-transfer area decreases and the required heat-transfer rates increase. Both act to increase the required differential temperature driving force. This means very low jacket temperatures and this results in poor regenerator temperature control.

Large-scale systems will have even less heat-transfer area per vessel volume than the pilot-scale unit studied in this study, so control problems will be even more severe in commercial-scale units unless additional heat-transfer area beyond that provided by jacket cooling can be designed into the system.

## References

Yi, C.K., and Luyben W.L., **1999**. Dynamic Model and Control Structures for a Hot-Gas Desulfurization Fluidized Process. Ind. Eng. Chem. Res. 38(11): 4290-4298.

Luyben W.L., and Yi, C.K. **2001**. Dynamic Modeling and Control of a Hot-Gas Desulfurization Process with a Transport Desulfurizer. Ind. Eng. Chem. Res. 40(4): 1157-1167.

Table 1. Steady state designs of four different oxygen regenerators

| Oxygen conc. in reg. feed gas | mol% $O_2$ | 2.5 | 5 | 10 | 21 |
|---|---|---|---|---|---|
| Inside diameter of regenerator | m | 0.23 | 0.16 | 0.12 | 0.08 |
| Height of regenerator | m | 2 | 2 | 2 | 2 |
| Bed height | m | 0.287 | 0.287 | 0.287 | 0.287 |
| Volume of regenerator | $m^3$ | 0.083 | 0.040 | 0.023 | 0.010 |
| Heat transfer area of bed | $m^2$ | 0.207 | 0.144 | 0.108 | 0.072 |
| Heat transfer area of freeboard | $m^2$ | 1.24 | 0.861 | 0.646 | 0.431 |
| MeS fraction in desufurizer | wt% | 20.27 | 21.50 | 22.62 | 23.02 |
| MeS fraction in regenerator | wt% | 6.86 | 8.11 | 9.25 | 9.63 |
| Solid holdup | kg | 14.3 | 7.16 | 3.58 | 1.71 |
| Gas feed rate to regenerator | kg-mol/h | 10.72 | 5.32 | 2.65 | 1.10 |
| Reg. feed gas temperature | °C | 549 | 344 | 25 | 25 |
| Jacket temperature | °C | Not needed | Not needed | 670 | 364 |
| Desulfurizer temperature | °C | 602 | 605 | 608 | 609 |
| Required heat transfer | M kJ/h | 0 | 0 | 8.65 | 44.9 |
| Average UA | kJ/h/K | - | - | 355 | 116 |

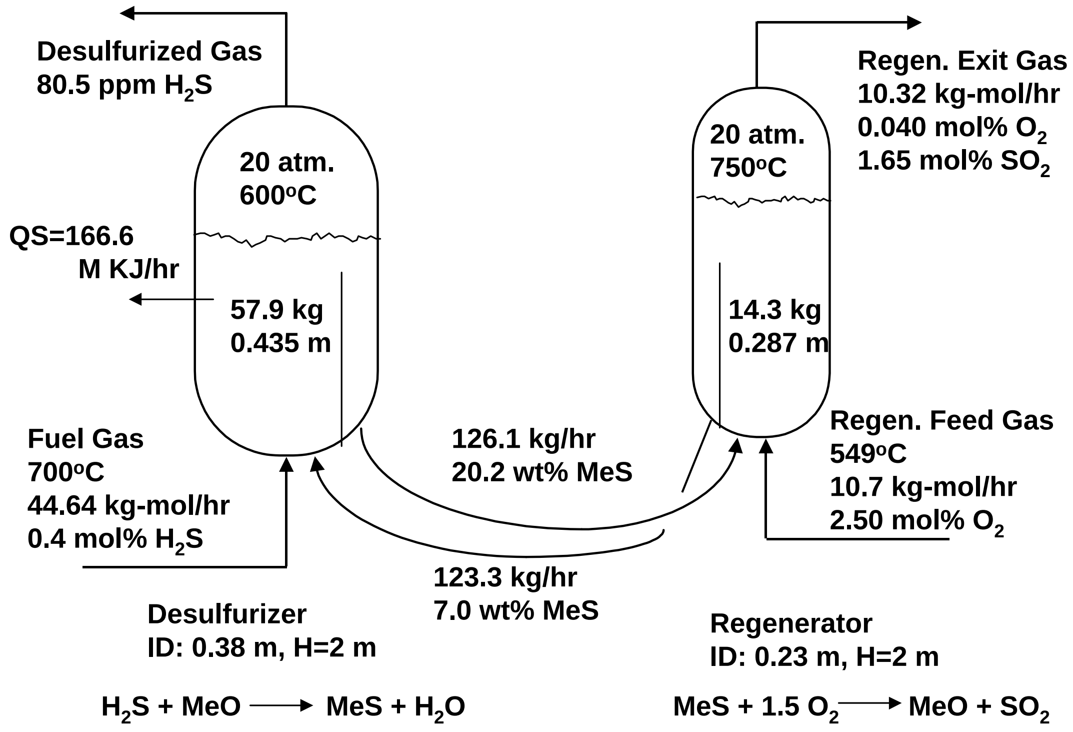


**Figure 1. Steady-state design of 2.5% oxygen case.**

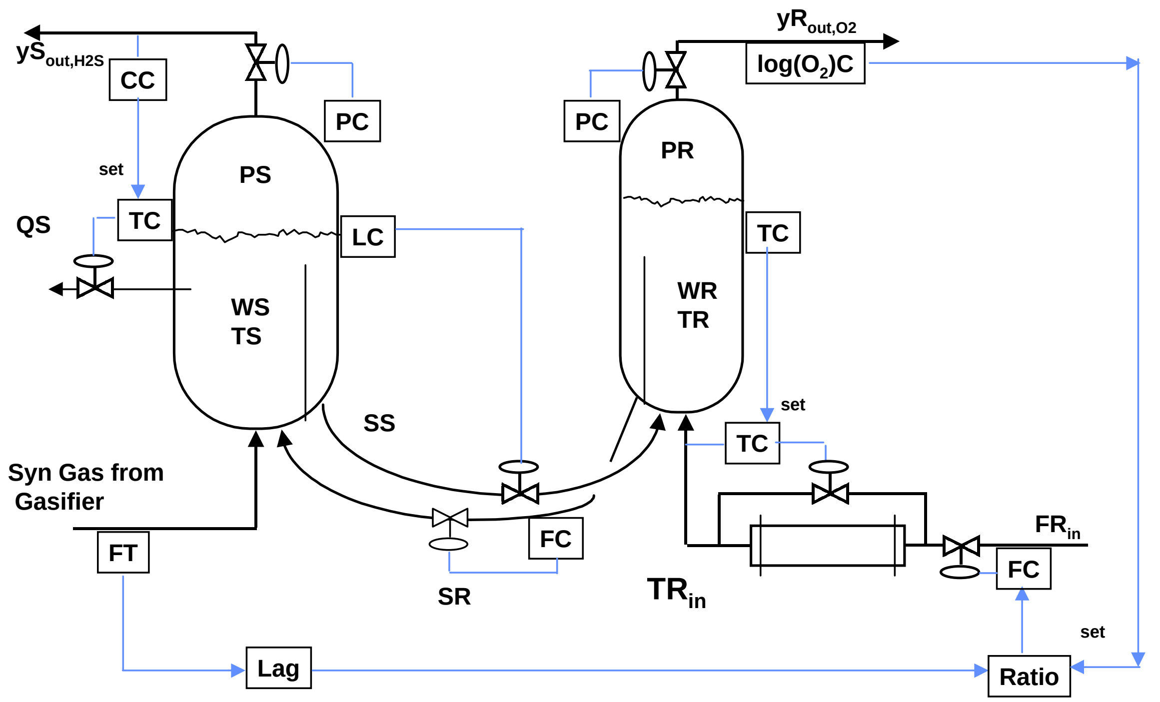


**Figure 2. Optimum control scheme of a hot gas desulfurization system.**

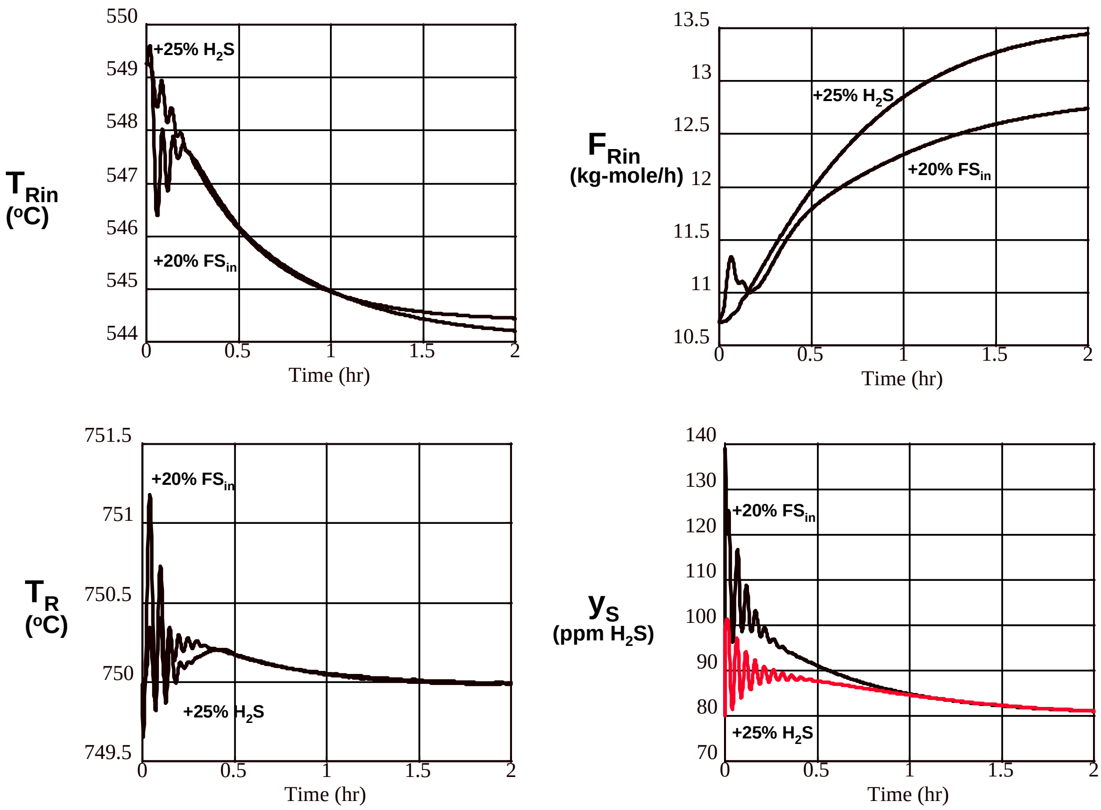


**Figure 3. Dynamic simulation results of 2.5% oxygen case.**

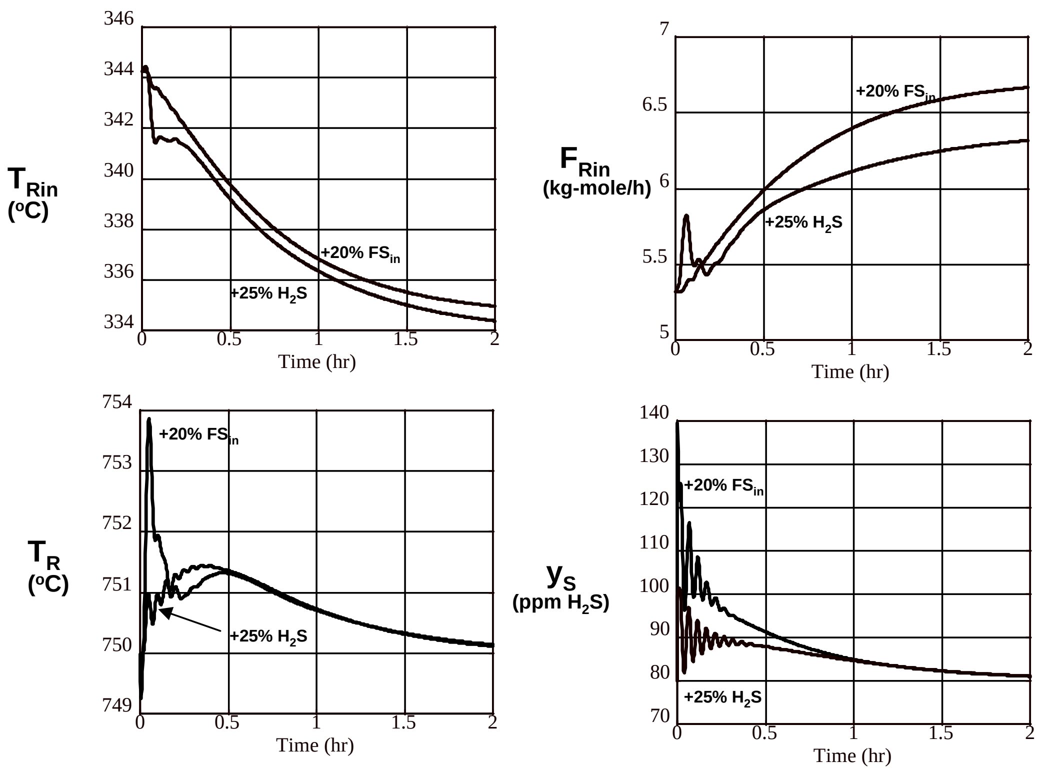


**Figure 4. Dynamic simulation results of 5% oxygen case.**

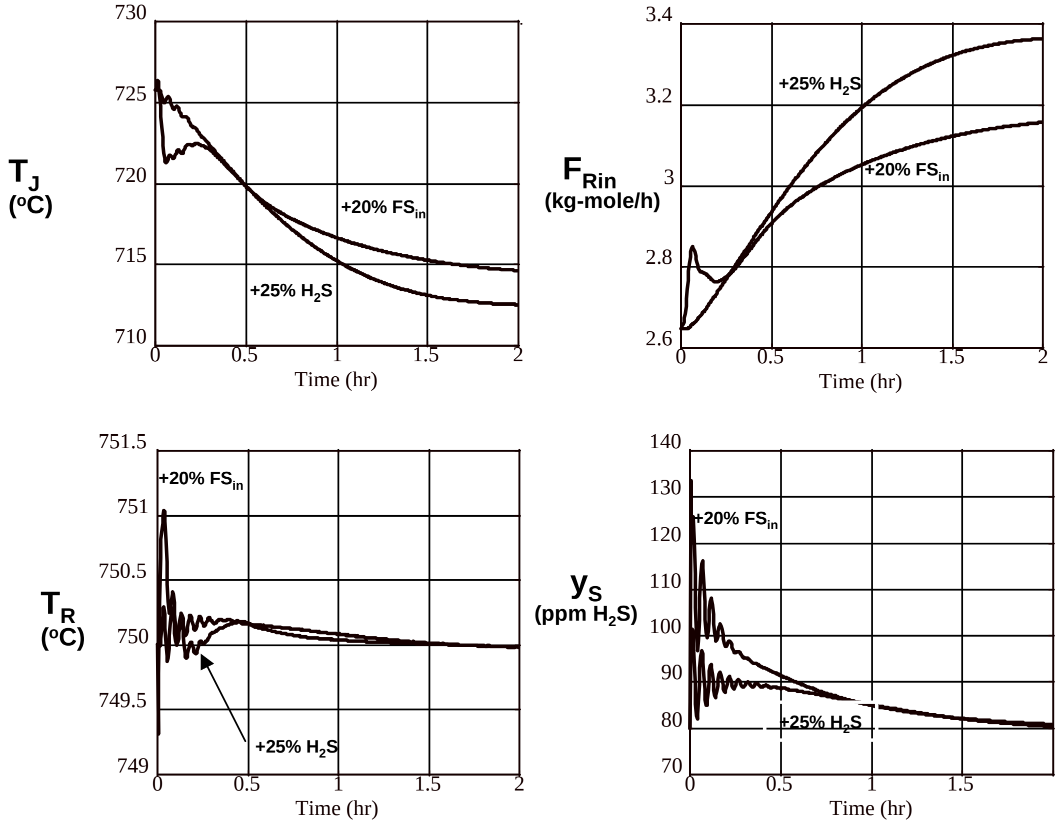


**Figure 5. Dynamic simulation results of 10% oxygen case.**

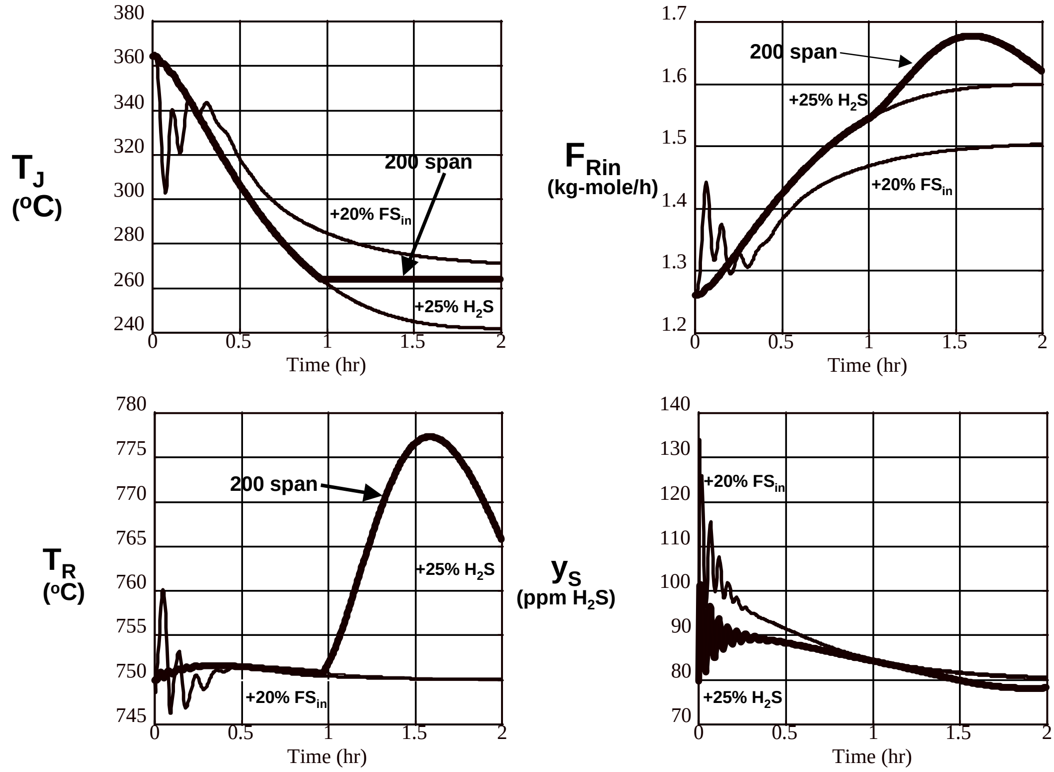


**Figure 6. Dynamic simulation results of 21% oxygen case.**