

Novel Catalytic Processes for Acid Gas Treatment  
in the Natural Gas Industry and Coal-fired Power Plants

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Abstract

LBL developed a catalyst to reduce  $\text{SO}_2$ , using syngas, to sulfur with high efficiency and selectivity while also converting  $\text{NO}_x$  to nitrogen. Several processes using this catalyst are being developed to treat  $\text{H}_2\text{S}$  in natural gas processing plants and  $\text{NO}_x$  and  $\text{SO}_2$  from coal-fired power plants.

Natural gas operations produce large quantities of  $\text{H}_2\text{S}$ , which are currently treated using the Claus process. The Claus process achieves 97% sulfur recovery efficiency by using three catalytic reactors. However, a significant mixture of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  remain in the resultant tail gas. Thus, further treatment is needed in order to comply with stringent environmental standards. Although several tail gas treatment technologies exist, the current methods are very expensive. Consequently a new PROClas process was developed, in conjunction with Parsons Inc., which results in 99.5% sulfur recovery while still using only three reactors.

The versatility of the LBNL catalyst also permits its use in the cleanup of flue gas from coal-fired power plants. The LBNL catalyst is highly effective in recovering sulfur from  $\text{SO}_2$  produced by regenerable  $\text{SO}_2$  processes such as CuO. In addition, development of a process, with a modified catalyst, for the simultaneous reduction of  $\text{SO}_2$  to sulfur and  $\text{NO}_x$  to nitrogen is in progress.

Results to quantify the potential for this type of catalyst in all three applications will be presented.

## 1. Introduction

A suspected source of fine particulate matter ( $PM_{2.5}$ ) in the atmosphere is the secondary aerosol formation from  $SO_2$  and  $NO_x$ . The fine particulate matter has been linked to health and visibility problems.  $SO_2$  and  $NO_x$  are also known to be responsible for the acidification of lakes and streams. In addition,  $NO_x$  is a major contributor to ground level ozone, the primary component of smog. Thus, control of  $SO_2$  and  $NO_x$  emissions from various man-made sources is necessary in order to protect the environment.

Natural gas production operations and oil refineries produce large quantities of  $H_2S$ . Existing  $H_2S$  treatment technology involves the Claus process which can recover about 97% of the sulfur with three catalytic reactors. After the last reactor, a mixture of  $H_2S$  and  $SO_2$  still remain in the tail gas. Before being allowed into the atmosphere the remaining  $H_2S$  in the tail gas must be converted into  $SO_2$ . Since, environmental regulatory agencies continue to promulgate more stringent standards for the emission of  $SO_2$  from oil and gas industries, further treatment of the tail gas from Claus plants is necessary. There are several tail gas treatment technologies currently available but they are very expensive. Using LBNL's  $SO_2$  reduction catalysts, Parsons has advanced an ingenious process, PROClaus, that enables 99.5% overall sulfur recovery while still using only three reactors.

In addition to the pollution problems of natural gas production are coal-fired power plants which emit both  $SO_2$  and  $NO_x$ . Currently, the state-of-the-art method for the control of these two pollutants involves the use of two separated technologies: wet limestone desulfurization systems for  $SO_2$  removal and selective catalytic reduction (SCR) for the removal of  $NO_x$ . In order to reduce the costs associated with the use of two separate systems, extensive research has been performed to develop a technology for simultaneous control of both  $SO_2$  and  $NO_x$ . Over the years, many new processes have been proposed, however most of them have failed to meet expectations. One exception is the CuO process. The CuO process converts  $NO_x$  to  $N_2$ , but produces a high concentration of  $SO_2$  gas. The  $SO_2$  gas is then oxidized to sulfuric acid for conversion to ammonium sulfate fertilizer, which is the route taken by an on-going LEBS (Low Emission Boiler System) project supported by U.S. DOE/FETC. However, elemental sulfur is often preferable to sulfuric acid under many circumstances.

An ideal approach for simultaneous control is the use of a catalyst that enables the simultaneous reduction of  $SO_2$  to elemental sulfur and  $NO_x$  to  $N_2$ . If such a catalyst can be developed, it can use the existing SCR reactor and one can simply replace the SCR catalyst with the new catalyst to achieve the purpose of dual control. The final result is a process that is simpler and much more cost effective.

This paper addresses the role of the LBNL  $SO_2$  reduction catalyst in the aforementioned three processes: PROClaus, CuO, and simultaneous  $SO_2$  and  $NO_x$  catalytic reduction.

## 2. Experimental

### 2.1 Catalyst Preparation

Catalysts composed of a mixture of iron-based metal oxides were supported on  $\gamma$ - $\text{Al}_2\text{O}_3$ . The  $\gamma$ - $\text{Al}_2\text{O}_3$  were granules, 3 mm in diameter by 5 mm in height. Catalysts were prepared by impregnating the carriers with solutions of metal nitrates. Appropriate amounts of metal nitrate solutions were mixed with  $\gamma$ - $\text{Al}_2\text{O}_3$ , and the mixture underwent stepwise heating in an oven up to 600°C for about 0.5 to 20 hrs in order to activate the catalysts. The ratio of the active catalyst to the carrier was about 0.3 by weight.

The prepared catalysts were characterized by a combination of several analytical methods. The surface area was found to be 132 m<sup>2</sup>/g by using a BET surface area analyzer.

### 2.2 Apparatus and Procedure

Experiments were carried out within the range of 200°C and 580°C at 20 degree intervals. The space velocity ranged from 1,000 to 3,000 h<sup>-1</sup>. A gas mixture was prepared that simulates the gas composition of the above mentioned three cases: 1. Claus reactor, 2. CuO process, and 3. Coal-fired power plant.

The experimental setup was made up of three separate sections: the gas supply section, the main reactor, and the detection and analysis section. Gases were supplied from compressed gas cylinders to flow meters before entering a gas mixer. An appropriate amount of water was continuously injected (using a Cole Parmer Syringe Pump) into the gas mixture at a hot zone before the catalytic reactor. The tubular reactor was fabricated from a 2.8-cm-o.d. and a 1-mm thick quartz tube wall. The entire reactor was mounted inside a tubular furnace. The reactor, which was 9 cm long, included three zones: 1) the inlet or the preheating zone (3 cm long) was packed with 20 mesh quartz chips, 2) the reaction zone (5 cm long) was packed with granules (d-3mm x h-5mm) of activated catalysts on  $\gamma$ -alumina, and 3) the outlet zone (1 cm long) was packed with quartz chips (20 mesh), mainly for the purpose of supporting the catalyst which sat on a perforated quartz plate with seven holes for gas to exit. A thermocouple, reaching the center of the catalytic reactor, provided measurements of the temperature at which the catalytic reactions were taking place. After the last section of the reactor, the gases passed through several treatment steps to collect elemental sulfur and condense water at room temperature. These treatment steps included a trap containing concentrated sulfuric acid solutions, a glass tube filled with silica gel (8 mesh) impregnated with  $\text{P}_2\text{O}_5$  and two sinter glass filters. After removal of sulfur and water, the gases then entered a six-port sampling valve which was used to inject the products

of the catalytic reactions into the gas chromatograph. Finally, the exit gases passed into a scrubber containing concentrated NaOH.

The inlet and exit gases were analyzed by using a gas chromatograph equipped with a column switching valve and a thermal conductivity detector. A 2-meter Porapak QS (polydivinylbenzene, 80-100 mesh) column was employed for the analysis of H<sub>2</sub>S, H<sub>2</sub>O, COS, and SO<sub>2</sub>. Another column with 2-meter 13x molecular sieves (60-80 mesh) was used for analysis of H<sub>2</sub>, O<sub>2</sub>, and CO. The operating conditions were at 60 mA for both columns, and a column temperature of 100°C for the Porapak QS and room temperature for the 13x molecular sieves. The carrier gas was helium.

In the following results and discussion section, the conversion efficiency, selectivity, and yield are represented by C(%), S(%), and Y(%), respectively.

### 3. Results and Discussion

#### 3.1. PROClas Process

A typical gas composition in a Claus plant, including gases into the first stage Claus reactor, tailgas of 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup>-stage of Claus converters is listed in Table 1.

The LBNL catalyst has demonstrated high efficiency and selectivity in converting SO<sub>2</sub>, contained in typical 1<sup>st</sup> Claus catalytic converter as well as 2<sup>nd</sup> Claus catalytic converter tail gas, to elemental sulfur. The LBNL catalyst also converts a substantial fraction of the H<sub>2</sub>S in the tail gas to sulfur.

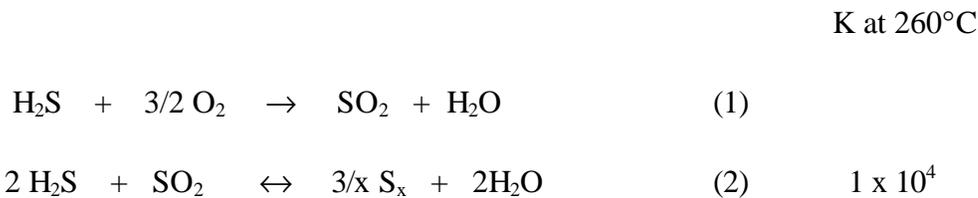
Figure 1 shows the results of the LBNL catalyst in treating a simulated tail gas from a 1<sup>st</sup> stage Claus converter. The experiments were carried out between 200 and 340°C and at a space velocity of 1000 hr<sup>-1</sup>. The conversions of SO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, and CO as a function of temperature are presented in Table 2. From 200 to 320°C, the selectivity of sulfur of the LBNL catalyst is 100%, and all the reacted SO<sub>2</sub> is converted to elemental sulfur. At 340°C, 12.2% of the feed SO<sub>2</sub> was converted to H<sub>2</sub>S. There were no detectable amounts of COS and CS<sub>2</sub>, formed under the experimental conditions employed.

Figure 2 shows the results of the LBNL catalyst in treating a simulated tail gas from a 2<sup>nd</sup> stage Claus converter. The experiments were performed between 200 and 340°C and a space velocity of 1000 hr<sup>-1</sup>. The conversions of SO<sub>2</sub> and H<sub>2</sub>S as a function of temperature are presented in Table 3. From 200 to 300°C, the selectivity of sulfur of the LBNL catalyst is 100%, and all the reacted SO<sub>2</sub> is converted to elemental sulfur. At 320°C and 340°C, 5.9% and 11.0% of the feed SO<sub>2</sub> were converted to H<sub>2</sub>S, respectively. There were no detectable amounts of COS and CS<sub>2</sub> formed under the experimental conditions employed.

Based on the superior performance of LBNL catalyst shown above, Parsons has advanced an ingenious process, i.e. the PROClas (Parsons RedOx Claus) for the treatment of H<sub>2</sub>S gas. The PROClas process combines three catalytic steps into one integrated processing scheme. The three catalytic steps are: Step 1 – A conventional Claus catalytic stage; Step 2. – A Selective Reduction stage that converts SO<sub>2</sub> to elemental sulfur; and Step 3 – A Selective Oxidation stage that converts H<sub>2</sub>S to elemental sulfur. The process chemistry of these three catalytic steps is outlined.

### Claus Reaction

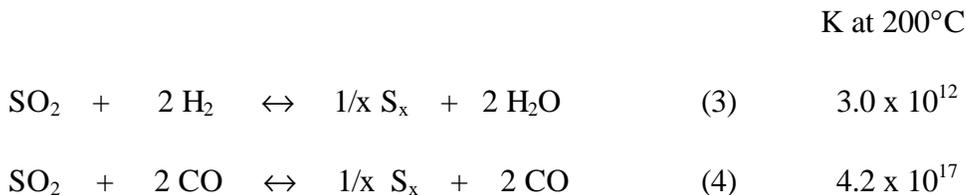
The basic chemical reactions occurring in a Claus process are represented by the following reactions:



In the reaction furnace, one third of the inlet H<sub>2</sub>S is thermally converted to SO<sub>2</sub> in the thermal stage according to reaction (1). The remaining two thirds of the H<sub>2</sub>S is then reacted with the thermally produced SO<sub>2</sub> to form elemental sulfur in the thermal stage and the subsequent catalytic stages according to reaction (2). Claus reaction (2) is thermodynamically limited due to the presence of inerts (such as H<sub>2</sub>O) and a relatively low equilibrium constant (2) over the catalytic operating region.

### Selective Reduction of SO<sub>2</sub> to Sulfur

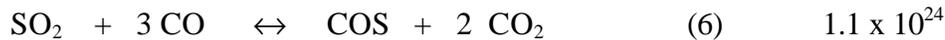
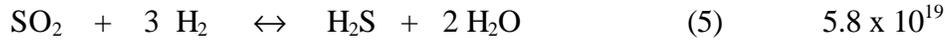
Selective reduction of SO<sub>2</sub> to elemental sulfur by reducing gases (such as H<sub>2</sub> and CO) are represented by the following reactions:



Reactions (3) and (4) are highly favorable thermodynamically and have very large equilibrium constants, as indicated above, over the conventional Claus catalytic operating temperature range.

However, a number of secondary reactions can take place between SO<sub>2</sub> and H<sub>2</sub>/CO producing undesirable by-products such as H<sub>2</sub>S and COS, as represented by the following reactions:

K at 200°C

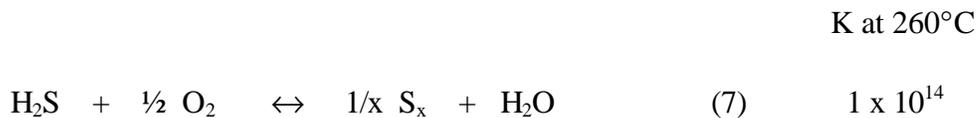


If elemental sulfur production is the process objective, an effective catalyst must not only be able to achieve high conversion of SO<sub>2</sub>, but also achieve high selectivity to elemental sulfur.

Some research has been conducted to develop catalysts for the selective reduction of SO<sub>2</sub> to elemental sulfur by reducing gases such as H<sub>2</sub> and CO. The research efforts focussed on improving the selectivity and conversion efficiency for the production of elemental sulfur at high space velocities and at a temperature range of 400 to 600C, which is much higher than the conventional Claus catalytic operation. In addition, these research efforts focused on flue gas cleanup applications based on more concentrated SO<sub>2</sub> feed streams (3 to 30%) derived from regenerable Flue Gas Desulfurization (FGD) processes or advanced integrated gasification combined cycle (IGCC). However, selective reduction of SO<sub>2</sub> to elemental sulfur under Claus catalytic operating conditions was not explored until LBNL and Parsons started the developmental works a few years ago.

### Selective Oxidation of H<sub>2</sub>S to Sulfur

Selective oxidation of H<sub>2</sub>S to sulfur using H<sub>2</sub>S-shifted operations have been commercialized since the late 1980s (Comprimo's SuperClaus), and combined hydrogenation/selective oxidation operation have been commercialized since the mid-1990s (Parsons BSR/Hi-Activity). Selective oxidation of H<sub>2</sub>S is represented by the following reaction:



Selective catalysts have been developed and commercialized for the reaction between H<sub>2</sub>S and O<sub>2</sub> for the production of elemental sulfur to minimize undesirable by-products such as SO<sub>2</sub> and SO<sub>3</sub>.

The highlights of the PROClas process are:

- Combining three distinct processing steps, two being commercially proven, into one fully integrated process
- Taking advantage of the H<sub>2</sub> and CO produced in the Claus reaction furnace as a reducing gas for processing Step2 – selective reduction of SO<sub>2</sub> to elemental sulfur. No external supply of reducing gas is required.

- Developing a highly selective SO<sub>2</sub> reduction catalyst for Claus type process gas (diluted SO<sub>2</sub> stream and lower operating temperatures as compared to previous research efforts focused on FGD applications).

## Process Description

Figure 3 is a simplified process flow diagram of the 3-stage PROCLaus process.

Acid gas is fed to a Claus thermal stage with a controlled amount of air in which one third of the inlet H<sub>2</sub>S is thermally converted to SO<sub>2</sub> at the burner according to reaction (1). The remaining two thirds of the inlet H<sub>2</sub>S is then reacted with the thermally formed SO<sub>2</sub> to produce elemental sulfur according to reaction (2). Due to the thermodynamic equilibrium of the Claus reaction, only about 60+% of the sulfur is produced in the thermal stage. After waste heat recovery and sulfur condensation, the remaining H<sub>2</sub>S and SO<sub>2</sub> is further reacted in a Claus catalytic converter. The effluent from the 1<sup>st</sup> Claus converter is cooled in a sulfur condenser to recover the produced sulfur. A conventional air demand analyzer is located at the outlet of the sulfur condenser for H<sub>2</sub>S/SO<sub>2</sub> ratio control in the thermal stage and in the Claus converter. The process gas is then reheated prior to entering the second selective reduction converter.

In the 2<sup>nd</sup> converter, more than 90% of the remaining SO<sub>2</sub> is reduced to elemental sulfur, in the presence of a highly selective LBNL SO<sub>2</sub> reduction catalyst, by reducing gases (H<sub>2</sub> and CO) produced in the reaction furnace as well as by H<sub>2</sub>S. The conversion of H<sub>2</sub>S in the selective reduction converter is equivalent to the Claus equilibrium as in a typical 2<sup>nd</sup> stage Claus converter. The effluent from the 2<sup>nd</sup> converter is cooled in a sulfur condenser to recover the produced sulfur and then reheated to the temperature required for the selective oxidation reaction. The reheated process gas is then mixed with process air prior to entering the last converter.

In the 3<sup>rd</sup> converter, more than 90% of the remaining H<sub>2</sub>S is reacted with O<sub>2</sub> to form elemental sulfur in the presence of Parsons Hi-Activity selective oxidation catalyst. The converter effluent is cooled in the last sulfur condenser before the tail gas is routed to a thermal oxidizer. An overall sulfur recovery of up to 99.5% can be achieved with a 3-stage configuration.

## Key Advantages of the PROCLaus Process

The PROCLaus process offers the following distinct advantages over other tail gas clean up processes:

- (1) The performance of the PROCLaus process is not affected by the normal fluctuation of the H<sub>2</sub>S/SO<sub>2</sub> ratio experienced in typical Claus plants. The front-end Claus section of the PROCLaus process operates just like a conventional Claus unit. H<sub>2</sub>S/SO<sub>2</sub> ratio of this section is controlled at 2:1 for optimal sulfur recovery efficiency in accordance with the Claus reaction. Even if the Claus section is operated off-ratio, either lower or higher

than the preferred 2:1 ratio for the Claus section, the incremental amounts of either SO<sub>2</sub> or H<sub>2</sub>S can essentially be converted to elemental sulfur in the subsequent selective reduction stage or the selective oxidation stage. This process feature offers easy and forgiving control as compared to conventional Claus which requires the control of the H<sub>2</sub>S/SO<sub>2</sub> ratio at 2:1; and the SuperClaus which requires the control of the inlet H<sub>2</sub>S concentration to the selective oxidation reactor by operating the Claus section in the shifted-H<sub>2</sub>S mode.

- (2) No hydrogenation step is required as in the BSR or SCOT type processes since the remaining SO<sub>2</sub> from the last Claus catalytic stage is directly converted to elemental sulfur in the selective reduction stage. Reducing gases are used for direct sulfur production instead of hydrogenation. This process feature offers a major reduction in capital costs as compared to conventional hydrogenation type tail gas treating processes.
- (3) No water removal step is required since both the selective reduction and the selective oxidation catalysts are substantially insensitive to the presence of water vapor in the Claus tail gas. This process feature offers another reduction in capital costs as compared to conventional hydrogenation type tail gas treating processes.
- (4) Within the control fluctuations experienced under actual operating conditions, typical thermal Claus stage produces more than stoichiometric amounts of reducing gases for the subsequent selective reduction reactions which convert SO<sub>2</sub> to elemental sulfur. External reducing gas is normally not required.
- (5) The normal Claus operation and the selective reduction stage reduces the inlet H<sub>2</sub>S concentration to the last selective oxidation stage substantially as compared to the SuperClaus process based on the same number of catalytic reactors adopted. This process feature reduces potential temperature excursion problems across the selective oxidation stage and, subsequently, provides better protection for the direct oxidation catalyst and reduces reactor downtime.
- (6) A 3-stage PROCLaus unit can obtain up to 99.5% overall sulfur recovery, which is substantially higher than other processes, such as the conventional 3-stage Claus and the 3-stage SuperClaus.
- (7) Existing 3-stage Claus plants can be easily modified to 3-stage PROCLaus plants by exchanging the catalysts in the second and the third converters with the selective catalysts, along with minor piping modifications to the last selective oxidation stage. Overall sulfur recovery efficiency can be improved from 95-98% up to 99.5%. Existing 3-stage SuperClaus plants can also be converted easily to PROCLaus by simply exchanging the Claus catalyst in the second converter with the selective reduction catalyst and switching the shifted-H<sub>2</sub>S operation to normal Claus operation. Overall sulfur recovery efficiency can be improved from high-98% up to 99.5%.

- (8) Sub-dewpoint processes require cyclic operation, and routine valve switching and catalytic bed regeneration. Unlike sub-dewpoint operation, the PROClous process is a continuous and steady dry catalytic process without routine sulfur emission spikes.

### Comparison of Tail Gas Clean-up (TGCU) Processes

As discussed in the above section, PROClous process offers a number of advantages over other commercially available tail gas clean-up processes. Table 3 summarizes the comparison results between PROClous and other TGCU processes in (1) number of converters; (2) sulfur recovery; and (3) relative cost (as compared to a 3-stage modified Claus).

As indicated in Table 4, PROClous is the most cost-effective processing scheme that can achieve an overall sulfur recovery of 99.5%.

### 3.2 CuO Process

The CuO process uses copper oxide supported on  $\gamma$ -alumina spheres for simultaneous SO<sub>2</sub> and NO<sub>x</sub> control. The flue gas is contacted with the sorbent/catalyst in an absorber at temperatures near 400°C. SO<sub>2</sub> reacts with copper oxide and oxygen in the flue gas to form copper sulfate. Both copper oxide and copper sulfate act as a catalyst for the selective catalytic reduction of nitrogen oxides by ammonia to nitrogen. The sulfated sorbent is then passed to a regenerator (at 425°C or above) where reducing gases such as syngas are used to reduce the copper sulfate to elemental copper and sulfur dioxide. The regenerated sorbent is returned to the absorber where the elemental copper formed in the regenerator is immediately converted to copper oxide upon contact with oxygen present in the flue gas. The off-gas from the regenerator typically contains the following gas composition:

SO<sub>2</sub>: 25-27%; H<sub>2</sub>O: 25-27%; CO<sub>2</sub>: 12-14%; syngas: 12-14%; N<sub>2</sub>: 18-25%

A simulated off-gas from the copper oxide regenerator, containing 26% SO<sub>2</sub>, 26% H<sub>2</sub>O, and the remaining balance N<sub>2</sub>, was blended with a syngas (with a molar ratio H<sub>2</sub> to CO of 5 in syngas, and syngas to SO<sub>2</sub> of 2.2) to obtain a gas mixture, comprising of 18.7% SO<sub>2</sub>, 18.7% H<sub>2</sub>O, 34% H<sub>2</sub> and 6.86% CO before entering a catalytic reactor. The results (Figure 4) show that the conversion efficiency increases with an increase in temperature. However, selectivity decreases with an increase in temperature due to an increase in H<sub>2</sub>S that accompanies the temperature increase. The sulfur yield is 74% at 360°C and reaches a yield of 90% at 420°C at a space velocity of 1500 h<sup>-1</sup>. Further increases in temperature result in a decrease of sulfur yield: 88%, 83%, and 81.4% at the temperatures 440, 460, and 480°C, respectively.

The above laboratory results suggest that greater than 90% of the SO<sub>2</sub> in the off-gas of CuO process can be directly converted to elemental sulfur with a single stage reactor employing an

LBNL catalyst. Thus, the use of the LBNL catalyst is expected to be cheaper for sulfur recovery, compared with the modified Claus process, where two thirds of the SO<sub>2</sub> is reduced to H<sub>2</sub>S before the mixture enters the conventional multi-stage Claus converters.

### 3.3 Catalytic Reduction of SO<sub>2</sub> and NO<sub>x</sub> (CRSN)

As shown above, the LBNL catalyst is effective for converting SO<sub>2</sub> to elemental sulfur, with an efficiency over 90%, at low SO<sub>2</sub> concentrations (as low as 2900 ppm in tail gas from 2<sup>nd</sup> stage Claus converter) as well as high concentrations (as much as 18.7% in off gas of the CuO process). Also shown above is that the catalyst is capable of reducing SO<sub>2</sub> at a low temperature (between 200°C and 340°C in PROClous process) as well as a high temperature (between 360°C and 540°C in CuO process).

Research is on-going to study the effectiveness of the LBNL catalyst for the reduction of NO<sub>x</sub> to N<sub>2</sub>, in addition to permitting a direct conversion of SO<sub>2</sub> to elemental sulfur. The purpose of this research is to come up with a catalyst that can replace the SCR catalyst such that a simultaneous reduction of NO<sub>x</sub> to N<sub>2</sub> and SO<sub>2</sub> to elemental sulfur can be accomplished in a single step. The conceptual flow diagram of the CRSN process is depicted in Figure 10.

Experiments were performed using syngas as the reducing gas and a stoichiometric ratio of syngas to SO<sub>2</sub> and NO<sub>x</sub>, i.e.  $(\text{CO} + \text{H}_2)/(\text{SO}_2 + \text{NO}) = 1.91$ . The flue gas composition was assumed to be 3000 ppm SO<sub>2</sub>, 300 ppm NO, and 6% H<sub>2</sub>O. The conversion efficiency and selectivity of both SO<sub>2</sub> and NO were determined between 320 and 460°C, varying the composition of syngas (H<sub>2</sub>/CO = 0.4, 0.75, 1.0, 3.0, and 5.0) and at a space velocity of 1000 ml/g.h. The results are shown in Figure 5-9. The removal efficiency of NO increases as temperature increases. The efficiency reaches 90% at 340°C, and increases to 100% at 420°C. The removal efficiency of SO<sub>2</sub> also increases with an increase in temperature. The SO<sub>2</sub> removal efficiency is greater than 80%, 90%, and 95% at temperatures greater than 320°C, 380°C, and 400°C, respectively. However, the production of H<sub>2</sub>S increases with the increase in temperature. The production of H<sub>2</sub>S also increases with an increase in the ratio of H<sub>2</sub> to CO in syngas. The environmental regulation is such that the release of H<sub>2</sub>S is absolutely forbidden. In order to circumvent this problem, an H<sub>2</sub>S oxidation step such as the last stage in the Parsons' PROClous process, i.e. the Hi-activity converter, may be employed following the LBNL catalytic converter for the oxidation of H<sub>2</sub>S to SO<sub>2</sub> before the gas is vented to the air.

## CONCLUSIONS

The PROClous process combines the conventional Claus processing step with two selective reaction steps in a 3-stage configuration which enhances the overall sulfur recovery up to 99.5%. The PROClous process utilizes two highly selective catalysts for direct reduction of SO<sub>2</sub> and direct oxidation of H<sub>2</sub>S to elemental sulfur. This innovative processing scheme

overcomes the sulfur yields limitation dictated by the Claus equilibrium. In addition, it eliminates the requirements of:

- Operating the Claus stages off-ratio as in the SuperClaus process, which reduces the recovery efficiency of the Claus stages as well as increasing the inlet H<sub>2</sub>S concentration to the last direct oxidation stage.
- Having a hydrogenation step since SO<sub>2</sub> is converted directly to elemental sulfur in the presence of the highly efficient LBNL catalyst.

Parsons is currently in discussion with several natural gas producers and oil refineries in converting their existing 3-stage Claus plants to PROClous. Preliminary design, revamping requirements, and estimated costs have been identified. PROClous process's technological, operational and economic edges over other commercial TGPU processes will certainly revolutionize how an efficient and cost-effective SRU/TGPU should be designed.

In summary, the status of the LBNL catalyst for commission in conjunction with the aforementioned three applications is at different developmental stages. The PROClous is at the commercial stage. The CuO tail gas with a syngas composition (H<sub>2</sub>/CO=5, and syngas/SO<sub>2</sub>=2.2) has been successfully demonstrated in the laboratory (Table & Figure 4). Tests with other syngas compositions are in progress. Indications are such that the conversion efficiency of more than 90% with a single reactor is achievable and that it is ready for the next step: a pilot plant demonstration. The catalytic process for simultaneous reduction of SO<sub>2</sub> to sulfur and NO<sub>x</sub> to N<sub>2</sub> is still in the R&D stage. Parametric study on the use of a reducing gas, such as syngas (H<sub>2</sub> & CO), NH<sub>3</sub>, and H<sub>2</sub>S, or the combination of these reducing gases are necessary to determine a practical and optimal condition.

**Table 1. Typical Claus Tailgas Compositions**

Sources	H <sub>2</sub> S(%)	SO <sub>2</sub> (%)	H <sub>2</sub> (%)	CO(%)	H <sub>2</sub> O(%)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	COS(%)
Claus Inlet	6.74	3.37	1.59	0.23	27.22	2.29	58.54	0.48
After 1 <sup>st</sup> stage	1.85	0.92	1.63	0.24	32.97	2.34	60.02	0.48
After 2 <sup>nd</sup> stage	0.58	0.29	1.64	0.24	34.46	2.36	60.40	0.48
After 3 <sup>rd</sup> stage	0.29	0.15	1.64	0.24	34.80	2.36	60.49	0.48

**Table 2 – LBNL Catalyst Test Results for First Stage Claus Tail Gas**

Temp., °C	C (SO <sub>2</sub> %)	C (H <sub>2</sub> S%)	C (H <sub>2</sub> %)	C (CO%)
200	95.9	74.3	13.5	8.6
220	93.3	71.1	15.9	9.8
240	92.4	61.6	19.2	23.3
260	91.8	52.7	24.1	36.9
280	89.5	42.6	45.9	41.9
300	93.4	26.8	51.6	74.9
320	95.6	9.8	57.7	88.1
340	97.2	-12.2	59.1	100.0

**Table 3 – LBNL Catalyst Test Results for Second Stage Claus Tail Gas**

Temp., °C	C (SO <sub>2</sub> %)	C (H <sub>2</sub> S%)
200	86.2	56.2
220	88.7	47.5
240	88.8	32.8
260	91.5	24.6
280	94.3	19.5
300	96.3	15.7
320	96.8	-5.9
340	96.0	-11.0

**Table 4 – Comparison of TGCU Processes**

<b>Process</b>	<b>No. of Converters</b>	<b>Sulfur Recovery,%</b>	<b>Relative Cost</b>
Modified Claus	3	97.0	1.00
<b>PROClaus</b>	<b>3</b>	<b>99.5</b>	<b>1.15</b>
Sub-Dewpoint	3	99.0	1.20
Sub-Dewpoint	4	99.5	1.40
SuperClaus	3	99.0	1.15
SuperClaus	4	99.3	1.30
BSR/Hi-Activity	4	99.5	1.35
BSR/Amine or SCOT	3 + amine	99.9	1.70

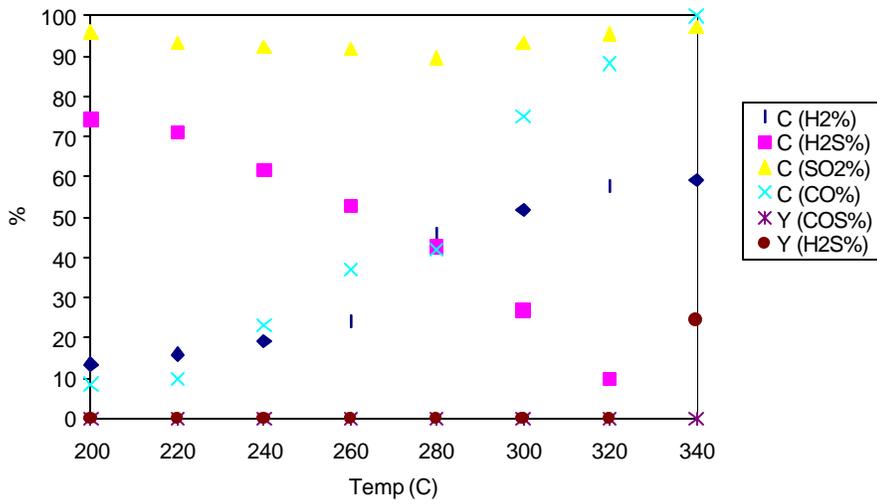


Figure 1. The reduction of SO<sub>2</sub> in tailgas from the 1<sup>st</sup> stage Claus converter at a space velocity of 1000 ml/g.h.

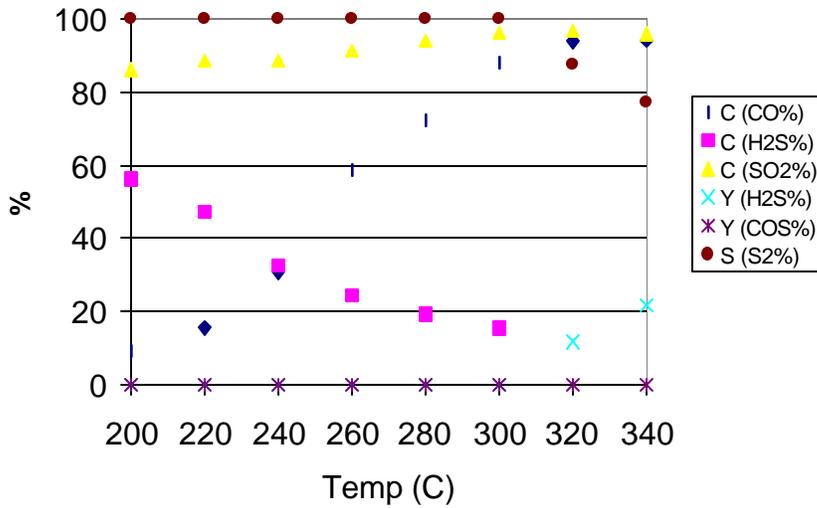
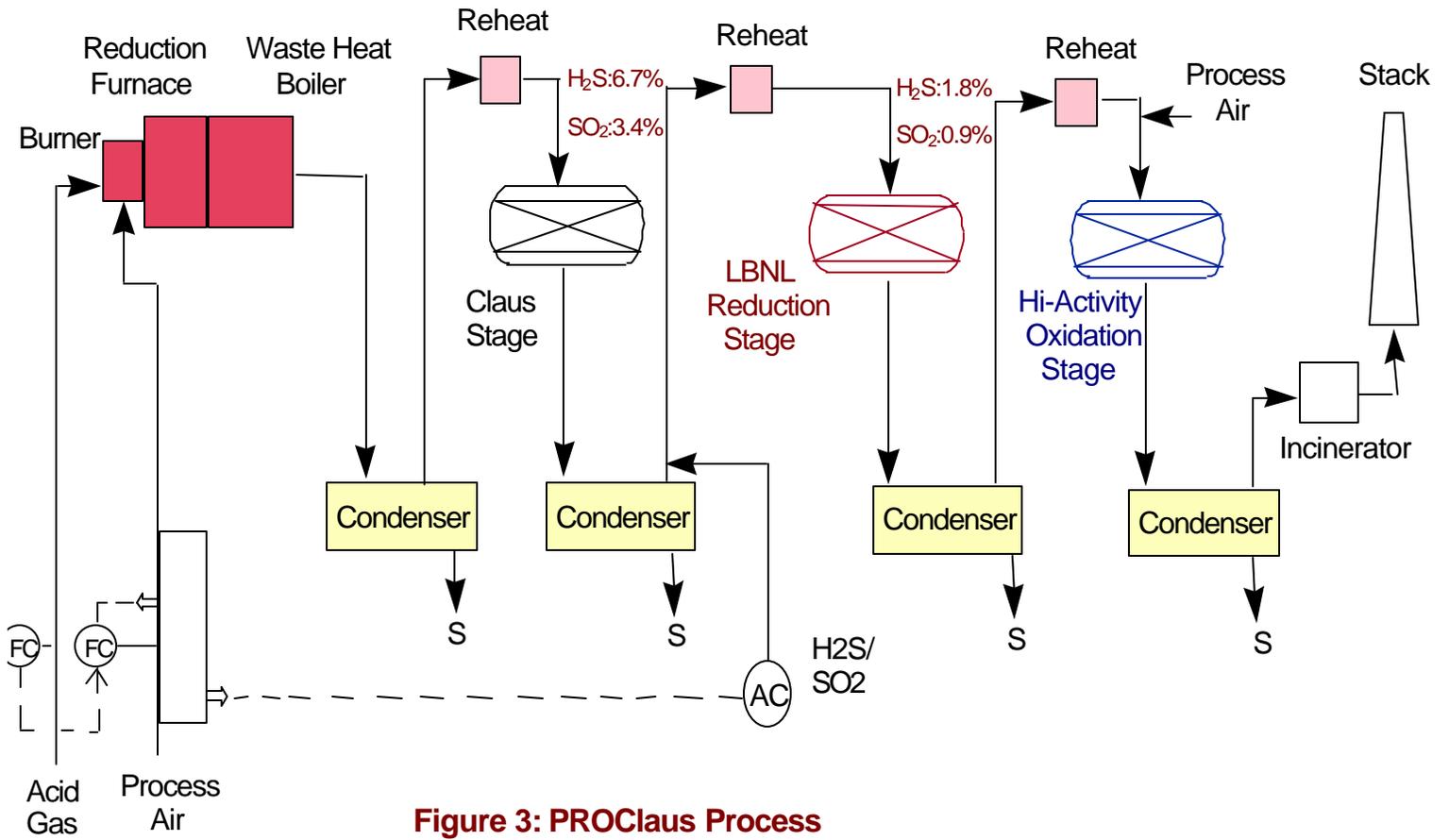


Figure 2. The reduction of SO<sub>2</sub> in tailgas from the 2<sup>nd</sup> stage

Claus converter at a space velocity of 1000 ml/g.h.



**Figure 3: PROClas Process**

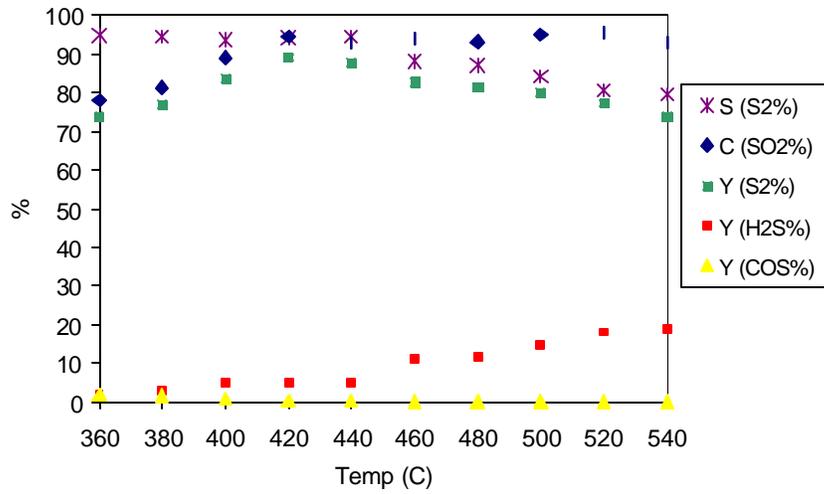


Figure 4. The reduction of SO<sub>2</sub> in the off-gas produced by a CuO regenerator

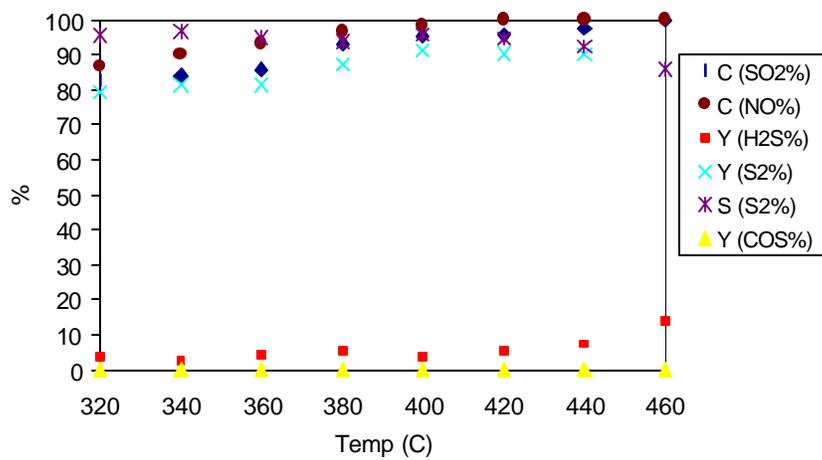


Figure 5. Simultaneous catalytic reduction of SO<sub>2</sub> and NO<sub>x</sub> by syngas with H<sub>2</sub>/CO=0.4 at a space velocity of 1000mL/gh

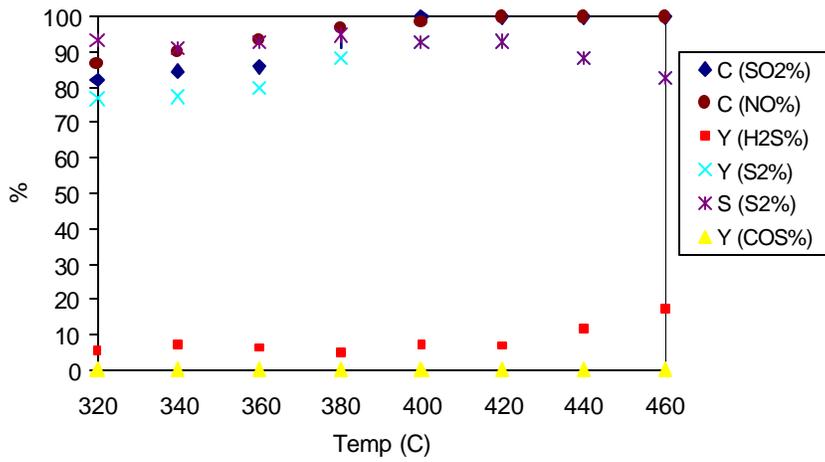
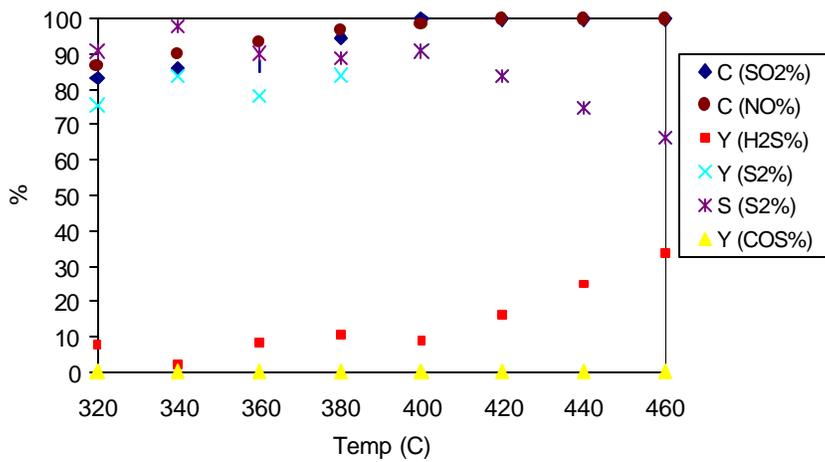


Figure 6. Simultaneous catalytic reduction of SO<sub>2</sub> and NO<sub>x</sub> by syngas with H<sub>2</sub>/CO=0.75 at a space velocity of 1000mL/gh



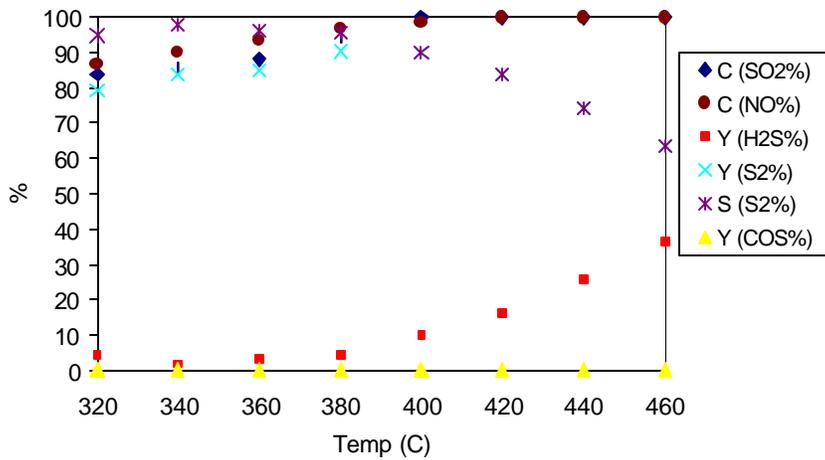


Figure 7. Simultaneous catalytic reduction of SO<sub>2</sub> and NO<sub>x</sub> by syngas with H<sub>2</sub>/CO=1.0 at a space velocity of 1000mL/gh

Figure 8. Simultaneous catalytic reduction of SO<sub>2</sub> and NO<sub>x</sub> by syngas with H<sub>2</sub>/CO=3.0 at a space velocity of 1000mL/gh

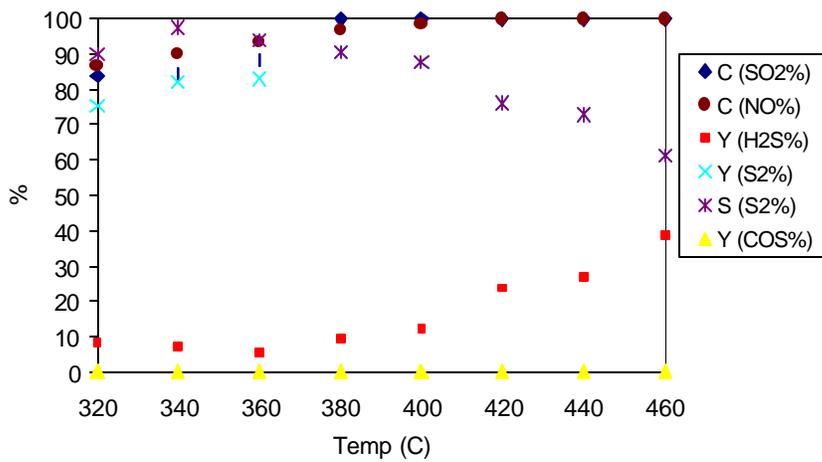
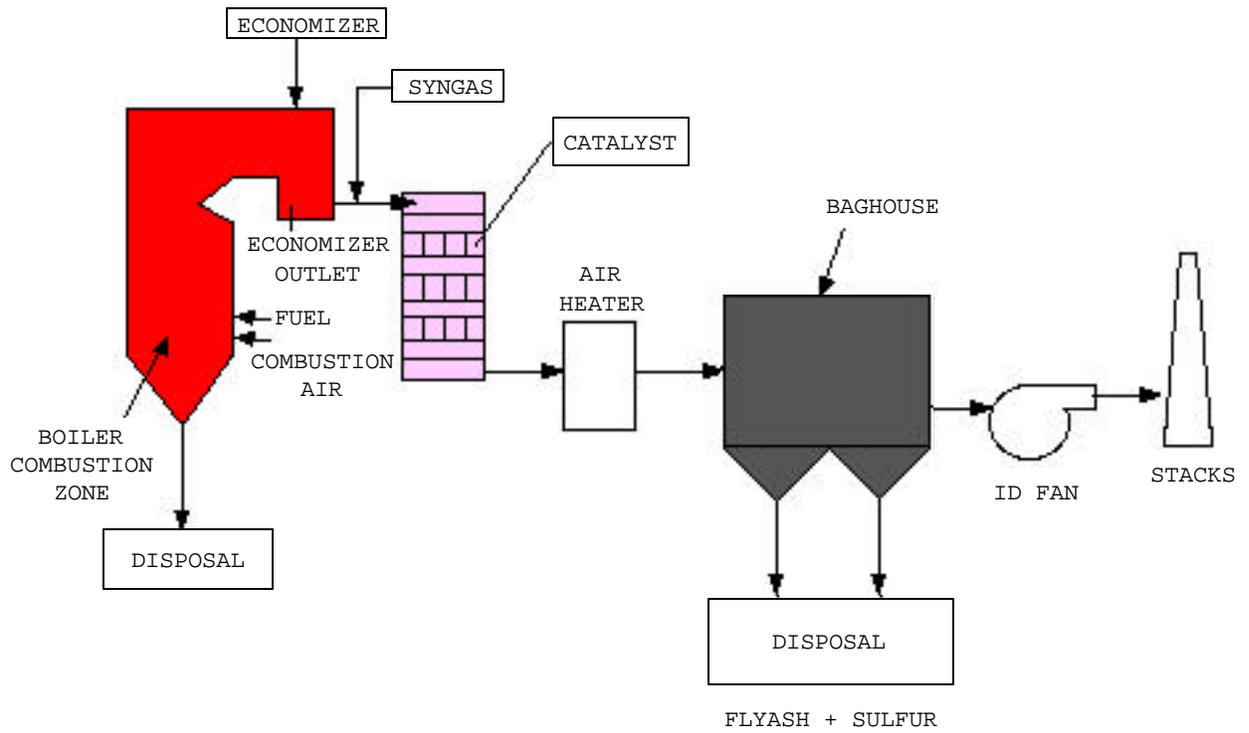


Figure 9. Simultaneous catalytic reduction of SO<sub>2</sub> and NO<sub>x</sub> by syngas with H<sub>2</sub>/CO=3.0 at a space velocity of 1000mL/gh

syngas with  $H_2/CO=5.0$  at a space velocity of 1000mL/gh



**Figure 10: A Conceptual flow diagram of a catalytic process for Simultaneous Reduction of  $\text{NO}_x$  and  $\text{SO}_2$**