Claus catalyst pore structure optimization

Detailed calculation procedure gives guidelines for the most efficient catalyst properties

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The modified Claus process is used to recover elementary sulfur from hydrogen sulfide present in gases from refineries, natural gas, etc. A wide range of catalysts dedicated to sulfur recovery and based on the Claus process are available. The selection procedure is not a trivial task; different aspects need to be considered and many experimental tests must be done. A procedure has been developed that attains the catalysts’ physical parameters, which provides relevant information about catalyst performance in the Claus reaction.

The Claus reaction consists of hydrogen sulfide (H₂S) and sulfur dioxide (SO₂) reacting in the vapor phase to produce sulfur and water. In the first stage, one-third of the H₂S is oxidized, producing H₂S and SO₂ in a 2:1 ratio. Due to thermodynamics, conversion is about 70% at this stage and three to four catalytic stages are needed to obtain 95% to 98% conversion. The reactions are:

\[ 3 \text{H}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{SO}_2 + \text{H}_2\text{S} \]

\[ 2 \text{H}_2\text{S} + \text{SO}_2 \rightleftharpoons 3/n \text{S}_2 + 2 \text{H}_2\text{O} \]

The most widely used Claus catalyst in sulfur recovery units is non-promoted spherical activated alumina. Properties associated with optimum non-promoted Claus catalyst include high surface area, appropriate pore size distribution and enhanced physical properties. These catalysts provide the necessary sites to catalyze the conversion of H₂S and SO₂ to elemental sulfur. In addition, they are capable of efficiently converting the more stable COS and CS₂, present in low concentrations. The reactions are:

\[ \text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2 \]

\[ \text{CS}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{S} + \text{CO}_2 \]

Usually, the hydrolysis reactions are verified at the first reactor—a 360°C outlet temperature ensures its completion.

**Claus reaction effectiveness factor.** Catalysts are highly porous materials, and typically show some aspects of pore diffusion control. The effectiveness factor, \( \eta \), for a catalyst is defined as the ratio of the average reaction rate, \( r' \), divided by the rate at catalyst’s surface, \( r \). When the reaction rate presents constraints due to the porous structure of the catalyst pellet, the true reaction rate is given by:

\[ r' = \eta r \text{ and } \eta = f(\phi) \]

where \( \phi \), the Thiele modulus, is the ratio of the reaction rate to the diffusion rate and is given by:

\[ \phi = R/3 ( r p / D, C_2)^{1/3} \]

The effectiveness factor includes various potential rate-controlling factors such as the intrinsic catalytic reaction rate, both inter- and intra-particle mass and heat transfer rates, and the catalyst particle physical properties.

Effectiveness factor calculations for Claus reactions involve considerable complexity due to the presence...
Table 1. Intrinsic rate expressions for Claus reaction

<table>
<thead>
<tr>
<th>Author</th>
<th>Catalyst</th>
<th>E, J/mol</th>
<th>b</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>McGregor (1972)</td>
<td>CoMo</td>
<td>1.24 E-3</td>
<td>53.5</td>
<td>1</td>
</tr>
<tr>
<td>Dalla Lana (1976)</td>
<td>CoMo</td>
<td>0.24 E-3</td>
<td>27.7</td>
<td>1</td>
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<tr>
<td>George (1974)</td>
<td>CoMo</td>
<td>1.24 E-3</td>
<td>16.5</td>
<td>1</td>
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<tr>
<td>Quatt (1980)</td>
<td>CoMo</td>
<td>1.24 E-3</td>
<td>27.7</td>
<td>1</td>
</tr>
<tr>
<td>El Masry (1985)</td>
<td>CoMo</td>
<td>1.24 E-3</td>
<td>27.7</td>
<td>1</td>
</tr>
</tbody>
</table>

*Equation for optimization procedure calculation
**Low activation energy due to diffusional limitations

Table 2. Catalytic converters effectiveness factor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reactor 1</th>
<th>Reactor 2</th>
<th>Reactor 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>320</td>
<td>275</td>
<td>220</td>
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<tr>
<td>Vol% H2S</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>GHSV, h⁻¹</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Φ</td>
<td>6.58</td>
<td>8.1</td>
<td>2.8</td>
</tr>
<tr>
<td>η</td>
<td>0.14</td>
<td>0.12</td>
<td>0.31</td>
</tr>
</tbody>
</table>

*Atmospheric operating pressure

Table 3. Alumina physical properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρs, g/cm³</td>
<td>3.16</td>
</tr>
<tr>
<td>ρw, g/cm³</td>
<td>1.24</td>
</tr>
<tr>
<td>Vmacro, cm³/g</td>
<td>0.085</td>
</tr>
<tr>
<td>Vmicro, cm³/g</td>
<td>0.404</td>
</tr>
<tr>
<td>εmacro</td>
<td>5.26</td>
</tr>
<tr>
<td>εmicro</td>
<td>25</td>
</tr>
<tr>
<td>ρs</td>
<td>0.14</td>
</tr>
<tr>
<td>ρw</td>
<td>0.56</td>
</tr>
<tr>
<td>S, m²/g</td>
<td>325</td>
</tr>
<tr>
<td>d, cm</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Random pore model. A catalyst pellet’s pore structure can be conveniently characterized by its pore size distribution determined by porosimetry. For bimodal pore structures, the relevant quantities are:

- \( V_{macro} \) is the macropore volume
- \( V_{micro} \) is the micropore volume
- \( r_{macro} = 1/V_{macro} \) is the macropore average radius
- \( r_{micro} = 1/V_{micro} \) is the micropore average radius
- \( \rho_s \) is the solid density

According to a typical alumina bimodal pore distribution, the limit between micropore and macropore is set around 100 Å. Because pores smaller than 15 Å have no Claus catalytic activity, Hg porosimetry is suitable for catalyst characterization. Micropore and macropore average radius and volume are obtained this way. The following properties can be derived from:

\[
p_0 = 1 / \left( \frac{\rho_s}{V_{macro}} + \frac{\rho_w}{V_{micro}} \right)
\]

\[
ε_{macro} = \frac{V_{macro}}{P_t} \rho_p
\]

\[
ε_{micro} = \frac{V_{micro}}{P_t} \rho_p
\]

The surface area of the catalyst is directly related to its pore structure. For bimodal pore structures, such as alumina, integral properties allow a reasonably good correlation:

\[
S = 2 V_{macro} / r_{macro} + 2 V_{micro} / r_{micro}
\]

Besides surface area, pore structure also determines the diffusive characteristics of the support. The random pore model of Wakao and Smith is used in these calculations, since it matches with alumina diffusivity measurements. The random pore model considers both Knudsen diffusion (small pores) and bulk diffusion (large pores) and accounts for the transition region.

These equations are needed for the random pore model:

\[
D_3 = 0.001853 T^{0.6} (1/M_A + 1/M_B)^{0.4} / P_t \sigma_{AB} \Omega_{AB}
\]

\[
D_{klmacro} = 9.7 \times 10^3 r_{macro} (T/M_A)^{0.4}
\]
Fig. 4. Effectiveness factor vs. particle size.

\[ D_{kmicro} = 9.7 \times 10^3 r_{micro} (T / M_A)^{1/2} \]

\[ 1/D = (1/D_A + 1/D_k) \]

With all these equations, the effective diffusivities are computed from:

\[ D_{eff} = D_{macro} \epsilon_{macro}^2 \]

\[ + \epsilon_{micro}^2 (1 + 3\epsilon_{macro}) D_{micro} / (1 - \epsilon_{macro}) \]

Catalyst optimization procedure. The optimization procedure calculates effectiveness factors for the Claus reaction over alumina catalyst as a function of alumina pore structure parameters. The calculation assumes that \( V_{macro}, V_{micro}, r_{macro}, \) and \( r_{micro} \) are the independent variables, their values to be optimized so that the effectiveness factor is maximized. The calculation sequence is presented in Fig. 3.

Besides the explicit constraint on the independent variables, two implicit constraints were used. One was the pellet density—experience indicates that excessively low pellet densities may result in physical erosion and mechanical crushing. The other was surface area—fresh catalyst surface area ranges in excess of 330 m\(^2\)/g, but the surface area decline for alumina-based Claus catalysts is quite rapid. All the catalysts lost substantial surface area in the first few days of operation, after which the surface area loss begins to level out; realistic surface areas are about 250 m\(^2\)/g and deactivated aluminas have surface areas around 120 m\(^2\)/g.

The optimization technique was an adaptive random search (ARS) algorithm.\(^7\) The method is a sequential search technique that effectively finds global optima for problems involving nonlinear objective functions subject to explicit and implicit nonlinear inequality constraints. The ARS optimization randomly generates a point close to the actual values of the independent variables; an objective function then accepts or rejects the new points and restricts the search space until an optima is found. Although the method presents some inefficiency and is slower than formal ones, the increasing power of personal computers allows their use for larger-scale tasks.

Optimization results. Effectiveness factors were obtained for average operating conditions in modified Claus unit catalytic converters, as stated in Table 2.

The second converter has the most unfavorable results and was used as the base case. Commercial catalyst physical parameters are presented in Table 3.

Reactor pressure drop restricts catalyst size, and small sizes diminish the diffusion constraints. A 0.6-cm diameter was used here. The selection was made according to the effectiveness factor sensitivity to the pellet size as shown in Fig. 4.

The analysis of effectiveness factor sensitivity to model parameters is shown in Figs. 5 to 8. The model parameters \( V_{macro} \) (Fig. 5), \( V_{micro} \) (Fig. 6), \( r_{macro} \) (Fig. 7) and \( r_{micro} \) (Fig. 8) were varied independently, keeping the others constant.

Macropore volume improves the effectiveness factor, although pellet density decreases as macropore volume grows. At 0.5 ml/g, pellet density reaches 0.81 g/ml—a somewhat low value that affects catalyst crushing strength and attrition properties. Macropore volume controls alumina surface area, as has been stated. The Claus catalyst needs more than a 250-m\(^2\)/g surface area to obtain equilibrium conversions. Micropore volumes lower than 0.3 ml/g will threaten this objective. Increasing macropore radius has a moderate effect on effectiveness, reaching a 0.23 value for 50,000-Å pores. Micropore radius has a low effect on the effectiveness factor.

A preliminary optimization was made with liberal constraints. The pore structure tends to converge toward low pellet densities and low surface area. Results are shown in Table 4 (Case 1). The optimized catalyst performance is not affected by pore diffusion.
Table 4. Optimization results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base case</th>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{ex}}$, g/cm$^3$</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>$\rho_p$, g/cm$^3$</td>
<td>1.24</td>
<td>1.61</td>
<td>1.61</td>
</tr>
<tr>
<td>$V_{\text{macro}}$, cm$^3$/g</td>
<td>0.085</td>
<td>1.00</td>
<td>0.300</td>
</tr>
<tr>
<td>$V_{\text{micro}}$, cm$^3$/g</td>
<td>0.404</td>
<td>0.31</td>
<td>0.379</td>
</tr>
<tr>
<td>$r_{\text{macro}}$, Å</td>
<td>5,226</td>
<td>100,000</td>
<td>30,000</td>
</tr>
<tr>
<td>$r_{\text{micro}}$, Å</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>$S$, m$^2$/g</td>
<td>325</td>
<td>248</td>
<td>300</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.12</td>
<td>0.97</td>
<td>0.50</td>
</tr>
<tr>
<td>$d$</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Since effectiveness is close to 1. Unfortunately, the low pellet density (0.61 g/ml) and low surface area make its industrial use unfeasible.

Regarding the preceding analysis, the optimization constraints were changed to a surface area greater than 300 m$^2$/g to obtain Claus equilibrium conversions. The minimum allowed pellet density is 0.9 g/ml. Macropore volume and radius are limited to 0.3 ml/g and 30,000 Å, respectively. Table 4 (Case 2) presents the optimization results.

Catalysts with areas over 300 m$^2$/g, macroporosities over 0.15 ml/g and macropore radii as high as allowed by pellet density should have good performance. To avoid small pores collapsing due to thermal and hydrothermal aging in the reactor, microporosity volume should be increased and the pore radius set around 25 Å.

Macroporosity has a paramount role in catalyst performance. Effectiveness increases are around 40%, providing faster diffusion, ingress and egress of the reactants and reaction products. This fact allows higher flowrates and equivalent conversions at higher space velocities. A higher pore radius allows closer operations to the dew point and liquid sulfur is more easily desorbed during shutdown or sub-dew-point operation.

\[ C_e \] reactant concentration (units as a function of rate equation)
\[ d \] catalyst diameter, cm
\[ D_A \] bulk diffusivity, cm$^2$/s
\[ D_{\text{eff}} \] effective diffusivity, cm$^2$/s
\[ D_k \] Knudsen diffusivity, cm$^2$/s
\[ D \] combined diffusivity, cm$^2$/s
\[ M_A \] molecular weight
\[ D_v \] pore volume differential
\[ p_{\text{H2S}} \] H$_2$S partial pressure, atm
\[ p_{\text{H2S, eq}} \] H$_2$S equilibrium partial pressure, atm
\[ p \] total pressure, atm
\[ R \] catalyst radius, cm
\[ r_{\text{macro}} \] macropore radius, Å
\[ r_{\text{micro}} \] micropore radius, Å
\[ r \] catalyst surface reaction rate
\[ r \] average reaction rate
\[ S \] surface area, m$^2$/g
\[ T \] temperature, K or °C
\[ V_{\text{macro}} \] macropore volume, cm$^3$/g
\[ V_{\text{micro}} \] micropore volume, cm$^3$/g

Greek symbols:
\[ \epsilon \] porosity
\[ \eta \] effectiveness factor
\[ \Phi \] Thiele modulus
\[ \Phi \] modified Thiele modulus
\[ \Psi \] factor as defined in Eq. 7
\[ \rho_s \] solid density
\[ \rho_p \] pellet density
\[ \Omega \] Lennard-Jones constants

NOMENCLATURE

**LITERATURE CITED**


**BIBLIOGRAPHY**
