

Comparison of Sulfuric Acid Plant Catalysts

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Introduction

The contact process for the production of sulfuric acid is based on the oxidation of sulfur dioxide to sulfur trioxide in the presence of a vanadium catalyst. From its beginnings in 1831 when Phillips of Bristol, England patented the oxidation of SO_2 to SO_3 over a platinum catalyst, to the modern plants of today using high activity, low pressure drop, ribbed rings of vanadium catalyst, the contact process and the catalyst it is based on have undergone significant (but subtle) changes, with the vast majority of developments in the last thirty years.

This paper will review the basic principals of the catalytic sulfuric acid process, and using a summary of operating data compare the three catalysts normally used in North America in the areas of conversion efficiency, activity, ignition temperature, loss in activity over time and screening losses. The paper will also review the advantages and problems with extensive plant converter testing using gas chromatography, Reich or other test methods.

Background

Before 1900, essentially all sulfuric acid was produced by the "Chamber" process, where nitrogen oxides were used to catalyze the oxidation of sulfur dioxide to sulfur trioxide. Plant size was small, unusually less than 50 STPD, and product acid strength limited to 65% to 75% sulfuric acid. The development of the chemical (dye) industry and the need for gun powder in the late 1800's necessitated a process to produce high strength sulfuric acid and Oleum. Early work (1870's - 1910) based on platinum as a solid catalyst, usually as platinum impregnated asbestos gauze, was the first technical and economic application of the "Contact" process. The high cost of platinum and its susceptibility to poisoning by many materials (notably arsenic present in the roaster gas streams of the day), led to the development of vanadium pentoxide based catalysts using alkali metal promoters on a porous silica carrier in the early 1900's (BASF patent of 1913). This is essentially the vanadium based catalyst used today. The following table shows the transition from the Chamber to Contact process:

Transition to the Contact Process

	1910	1930	1950	1960	1980
Contact Process %	20	27	75	85	100
Chamber Process %	80	73	25	15	0

Vanadium Catalyst

Vanadium catalyst usually contains 6% - 9% vanadium pentoxide with alkali metal promoters. The promoters are potassium sulfate with an atomic ratio of potassium to vanadium of 2 - 4 and a small amount of sodium sulfate to adjust (lower) the eutectic melt temperature of the mixture. The active components are supported on a highly porous silica base (diatomaceous earth).

In 1948 Topsoe & Nielsen demonstrated catalyst at operating temperatures exists as a melt within the pores of the silica support. The melt consists of vanadium sulfur complexes dissolved in pyrosulfates. In other words, the oxidation of sulfur dioxide to sulfur trioxide is a homogeneous reaction in the liquid film covering the surfaces of the support and not the heterogeneous reaction it would appear to be. The activity of the catalyst is from active species of vanadium pentoxide (V_2O_5), with the mechanism involving changes in the valence of vanadium.

The reaction rate is the result of many factors, including; the solubility of SO_2 , SO_3 and oxygen in the melt, mass transfer limitations, the concentration of the active catalyst components and their solubility's in the melt, the porosity and pore size distribution of the silica support, as well as other less obvious factors (manufacturing process, etc.). The effect and interaction of each variable is not completely defined, so changes leading to improvements are more by trial and error than science. The difference between conversion predicted by rate equations and conversion actually obtained is accounted for by adding a so called "catalyst effectiveness factor" or fudge factor to the rate equation. The reaction rate can be described by the following relationship:

$$r = k [p(SO_2)^l p(O_2)^m p(SO_3)^{-n}] K_{act} K_{eff}$$

- r = reaction rate - g mole SO_2 /g catalyst, sec
- k = rate constant - function on catalyst properties
- $p()^x$ = partial pressure of components
- K_{act} = adjustment factor for catalyst activity
- K_{eff} = adjustment factor for system unknowns

The acknowledgment of the reaction taking place in the liquid melt leads to an understanding of catalyst ignition temperature as the temperature at which the melt first forms. The decrease in activity at low temperature is explained by the precipitation of some of the vanadium

compounds reducing the concentration of the vanadium in the melt. The loss in catalyst activity at high temperature is attributed to the melt exceeding the capacity of the catalyst pores, with the liquid melt forming large inactive globules. The "old wives tale" of catalyst having a memory - once operated at high temperature, it must always be operated at high temperature - is explained by the loss in activity from melt components flowing out of the catalyst.

Sulfur dioxide to sulfur trioxide equilibrium is determined by the following equation:

$$K_p = \frac{p(\text{SO}_3)}{p(\text{SO}_2) p(\text{O}_2)^{1.5}}$$

A typical equilibrium curve showing operating lines for a four bed single or double absorption system is shown in Figure 1. The figure shows the change in the equilibrium curve resulting from the removal of SO₃ in the interstage absorber (upper equilibrium line), and the reason the double absorption process increases conversion of SO₂ to SO₃ from 98.5% to 99.7%.

A review of the equilibrium equation indicates increasing pressure will increase equilibrium conversion. Figure 2 shows the effect of increasing pressure. In the example shown, increasing pressure from 1.3 bar (3.8 psi) to 10 bar (127 psi) will increase equilibrium conversion in a first catalyst stage from 63% to 75%. In the late 1960's, I did extensive work developing and evaluating a pressure process for sulfuric acid production - looking at single absorption at pressure versus double absorption. The conclusion of that work indicated double absorption could not be avoided at reasonable pressures to meet 99.7% conversion, eliminating the pressure process from economic consideration. In the mid 1970's, Krebs built a plant at PCUK in France based on the pressure process. The plant was a double absorption unit operating at 70 psi. Analysis indicated capital cost savings compared to the conventional double absorption route to be small (< 10%), with the plant experiencing extremely high corrosion and low energy efficiency.

Another route to increased conversion is to increase the oxygen concentration in the converter gas by using enriched air or pure oxygen. Analysis indicates improved conversion efficiency, but not enough to eliminate double absorption. A process using pure oxygen was evaluated in the late 1960's as an alternate to double absorption. The system was not economically sound due to the continuing cost of oxygen. No plants based on pure oxygen have been built. A number of spent acid regeneration plants use enriched air to overcome capacity limitations in the gas cleaning sections of the plant, and oxygen use to enrich the gas in the contact section is being used in a few places. The cost is a balance of the need for additional capacity versus the continuing cost of oxygen.

Catalyst Shape and Composition

In the 1960's and early 1970's catalyst was in the form of pellets, usually 1/4" and 5/32" diameter by 0.3" to 0.6" long (6 mm & 4 mm diameter by 8 mm - 15 mm long). The catalyst normally contained 6% to 8% V₂O₅, and was sold in North America by many vendors:

Stauffer
Cyanamid
BASF
Catalyst & Chemicals

Allied
Monsanto
Topsoe
Imperial Smelting

In the mid to late 1970's lower pressure drop through the catalyst bed was achieved by the use of a larger diameter pellet, 8 mm in diameter or 5/16" rather than 6 mm diameter. This size pellet was heavily promoted by Monsanto as 516 catalyst. At about the same time Topsoe introduced the ring shape catalyst to the North American market. Topsoe claimed significantly lower pressure drop and greater dust holding capacity. Initial installations used ring catalyst to top off the pellets in the first catalyst bed. Data showed lower initial pressure drop, and lower rate of pressure drop build-up (greater dust holding capacity). Complete first beds of ring catalyst showed acceptable activity and conversion while maintaining the low pressure drop and pressure drop build-up. Ring catalyst allowed an increase in operating time between turnarounds from 12 months to 18 - 24 months. It took a number of years for ring catalyst to be accepted and used in the entire converter. Now the three principal catalyst suppliers to North America (Topsoe, BASF, Monsanto) all offer ring shaped catalyst - with pellet and 516 catalyst essentially obsolete. The most recent change in catalyst shape has been the ribbed ring, offered by Topsoe as "Daisy" and BASF as "Star" rings, providing about 20% lower pressure drop than the normal 10 mm rings.

In addition to catalyst shape changes, in the last twenty years catalyst composition changes have provided improved performance permitting 99.7% conversion in a double absorption plant with increasing SO₂ gas strengths (9.5% - 10% in the 1970's to 11.5% - 11.75% today). A catalyst with 6% - 8% V₂O₅ is used in the first and second beds of the converter to attain resistance to activity loss at high temperature and maintain high temperature strength (reduced screening loss). The lower vanadium content - lower activity is offset by the higher average operating temperature of the upper beds, resulting in a high reaction rate and acceptable catalyst loading and approach to equilibrium. A catalyst with 7% to 9% V₂O₅ is used in the third and fourth catalyst beds to provide higher activity, lower ignition temperature and high reaction rate at the lower average operating temperature. The higher vanadium, lower bed catalyst has 10% to 20% greater activity than the 6% - 8% V₂O₅ upper bed catalyst.

The most recent catalyst development (re-invention of a 1948 discovery) is the so called "Cesium Catalyst". Cesium catalyst is really a 6% - 8% V₂O₅ catalyst with the formulation adjusted by substituting cesium for a portion of the potassium promoter. The use of cesium doubles the activity of the catalyst in the low temperature region, permitting continuous operation at bed inlet temperatures in the 720 F - 730 F region. The high cost of cesium promoted catalyst (about 2.5 times standard catalyst) limits its use to special applications.

The various catalyst shapes are shown in Figures 3 and 4. The following tables compare catalyst size and composition.

Shape

		Pellet	Pellet	Ring	Ribbed Ring
Diameter	mm	6	8	10	12
Length	mm	8	12 - 15	9 - 14	10
Pressure Drop	"H ₂ O	1.0	0.9 - 0.95	0.5	0.4

Composition

	V ₂ O ₅ Content	Comments
Upper Bed Catalyst	6% to 8%	High Temperature Operation Hardness & Temperature Resistance
Lower Bed Catalyst	7% to 9%	Low Temperature Operation High Activity - Softer Catalyst
Cesium Catalyst	6% to 8%	High Activity at Low Temperature (720 F) Can be Sticky at High Temperature

Catalyst Operation Analysis

Over the last ten years Acid Engineering & Consulting, Inc. has been involved with the operation of over one-hundred sulfuric acid plants around the world. In many cases data collected included information on various catalysts, including conversion efficiency, ignition temperature, loss in activity, screening loss, pressure drop and pressure drop build-up. A statistical analysis was performed on the data and the resulting observations are presented below. The analysis was made for the three main North America catalyst suppliers, Topsoe, BASF, and Monsanto, identified and supplier "A", "B", and "C". Note: If the analysis is on target, acid plant operators should be able to connect the supplier with their performance data.

Conversion Efficiency - The data suggests little significant difference in overall conversion efficiency between the three suppliers. Conversion efficiency analysis was complicated by many operating plants with more than one manufacturers catalyst in the converter, and many with two or three suppliers catalyst in a particular bed. Although there was some statistical difference, one could not use the conversion efficiency difference to tell which catalyst was in a particular converter.

Loss in Activity - The reduction in activity of a particular catalyst over time was determined by a review of catalyst suppliers activity test results and operating data showing changes in bed inlet and exit temperatures and conversions over time. The results were based on plants operating with high converter inlet SO₂ concentrations resulting in bed 1 exit temperatures of 1140 F to 1160 F. The table below summarizes the activity loss over an 18 month to 24 month period for ring catalyst.

Loss in Activity (18 - 24 Months)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	20% - 35%	9% - 12%	9% - 13%
Bed 2	8% - 12%	5% - 8%	5% - 8%
Bed 3	< 5%	< 5%	< 5%
Bed 4	< 5%	< 5%	< 5%

The data indicates supplier "A" upper bed catalyst loses activity at a significantly higher rate than the others, about 2 to 3 times the activity loss between turnarounds. This would suggest a formulation problem resulting in the melt solution leaving the pores of the catalyst when operating at high temperature. The data is consistent over many years, eliminating the possibility of a bad batch or run of catalyst causing the results. In fact, for many years this supplier recommended limiting first bed exit temperature to less than 1125 F.

Screening Loss - Data for screening loss was based on ring catalyst, vacuum screened per suppliers instructions, usually by the same two commercial catalyst screening companies. The wide variation in the data for a particular supplier is attributed to operating time at high temperature, screening rate and the amount of broken pieces returned to the converter.

Screening Loss (% of Bed)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	25% - 40%	10% - 15%	11% - 16%
Bed 2	20% - 30%	9% - 15%	10% - 15%
Bed 3	15% - 20%	8% - 14%	8% - 14%
Bed 4	12% - 17%	8% - 12%	8% - 12%

The data is consistent, indicating a problem with supplier "A" catalyst, especially in the high temperature area, suggesting a formulation problem (high screening loss and loss in activity). The data is from many plants over a number of years with more data points for beds 1 and 2, and limited data for beds 3 and 4.

Pressure Drop Build-up - Data for sulfur burning plants was analyzed to determine differences in the rate of pressure drop build-up over an 18 month operating period between turnarounds. The analysis was complicated by unknown variations in the ash content of the sulfur and the amount of broken pieces returned to the converter after screening. After some

adjustment for bed area, gas velocity, etc., the data indicated no significant difference in the rate of pressure drop build-up between the three catalysts.

Comparison Summary

Overall the catalyst comparison indicates supplier "A" has a problem with its upper bed ring catalyst when operated at high gas strength - high temperature (exit temperatures above 1130 F), resulting in excessive loss of activity over time and screening losses two to three times the others. In fact, the high screening loss and subsequent make-up with fresh catalyst obscures the activity loss problem, so overall plant conversion efficiency is maintained. Based on the analysis, supplier "B" and "C" catalyst are close in all aspects studied, with supplier "A" upper bed catalyst of lower overall performance.

Cesium Promoted Catalyst

Cesium promoted catalyst is offered by the three North American suppliers. The high cost, about 2.5 - 3 times conventional catalyst, has limited use to special situations. Cesium catalyst is rarely used in sulfur burning plants, but has found some advantages in spent acid regeneration and metallurgical plants. The catalyst has been used as a top layer of the first catalyst bed to provide operation at 720 F - 730 F, reducing gas heat exchanger requirements, while allowing restart of the plant when the catalyst bed is at 600 F.

Early installations of cesium promoted catalyst experienced severe pressure drop build-up. Pressure drop in some plants increased 30" to 60" H₂O in a few months. Investigation indicated the plants experiencing the problem were operating at first bed inlet temperature of 780 F to 820 F, while plants without problems operated at 720 F to 740 F. The operating data indicates the cesium catalyst becomes very sticky at elevated temperatures. Recently, Topsoe has reformulated their cesium catalyst so it can be operated at low or high temperature without the pressure drop build-up problem. The other suppliers are expected to produce an adjusted formulation in the near future.

Converter Testing

Traditionally catalyst performance evaluations are made by reviewing bed inlet temperatures and temperature rise, inlet SO₂ gas strength and overall conversion efficiency. Changes in these operating variables, although small from day to day, are good indicators of catalyst bed performance over time. Recently, one catalyst supplier has offered portable gas chromatograph testing of converter systems. The tests provide the composition of gas into and out of each catalyst bed. Comparing actual bed conversion with calculated conversion and equilibrium would be a superior way of determining catalyst activity - performance.

Acid Engineering & Consulting, Inc. has reviewed the results of a number of gas chromatograph tests of converter systems. In most cases, the test data was consistent with evaluations based on traditional methods, and was a useful tool in determining catalyst activity - replacement requirements for an upcoming turnaround. In a number of cases, the test results were obviously incorrect and the interpretation of the results flawed and self-serving. Objectivity comes into question when the one doing the testing is selling catalyst or testing his own catalyst to show how good it is, or how bad a competitors is. In one case, the test data indicated 7% to 8% conversion of SO₂ to SO₃ in the sulfur furnace - well above equilibrium. This was coupled with extremely low conversion in the first catalyst bed, indicating low catalyst activity and the need for additional replacement catalyst. In another case, a spent acid regeneration plant was experiencing conversion efficiency problems (very low first bed temperature rise) after a major plant modification. The catalyst in the first bed was changed, but the same problem persisted. Gas chromatograph tests (purchased with the replacement bed of catalyst) were run at various O₂/SO₂ ratios (0.72 to 0.92) and SO₂ gas strengths (9.4% - 10.7%). Note: Most sulfur burning plants operate at O₂/SO₂ ratios of 0.75 to 0.77 and SO₂ gas strengths of 11.5% - 11.75%. The test results are summarized below:

Plant Test Data

	Run 1	Run 2	Run 3
O ₂ /SO ₂ Ratio	0.72	0.86	0.92
Overall Conversion	90.8%	94.2%	95.4%
Bed 1 Catalyst Activity	104%	83%	82%

Note: Catalyst activity dropped 22% between test runs 1 and 3. This was reported as "catalyst activities are in the normal range".

The conclusion presented by the testing company - catalyst supplier was the plant design at 0.75 O₂/SO₂ ratio and 97% conversion in a single absorption plant was not possible with the catalyst type, volume and O₂/SO₂ ratio. However, the catalyst supplier - testing company would be happy to study ways to achieve plant conversion and capacity, although they stated "there are no clear cut, low cost ways to do this". Note: Acid Engineering & Consulting, Inc. adjusted plant operating conditions and in four hours the plant was able to meet design capacity at an O₂/SO₂ ratio of 0.75 with conversion exceeding 98%. In this case, knowledge and experience was able to do what blind or self-serving testing could not do - get the plant operating at or above design without additional catalyst or costly modifications.

Conclusion

This work was intended to provide an understanding of sulfuric acid plant catalysts and to present a comparison of the three catalysts used in North America. Data from many plants over a number of years was reviewed, adjusted and evaluated to obtain comparative catalyst performance. The data indicated suppliers "B" and "C" catalyst to be about equal in each of the areas examined, with supplier "A" catalyst of lower performance (activity loss over time and high screening loss).

If some have a better understanding of sulfuric acid plant converter operation and catalysts, and supplier "A" is encouraged to improve their catalyst, the time and effort spent on this work will have been justified.

Figure 1

Converter Equilibrium

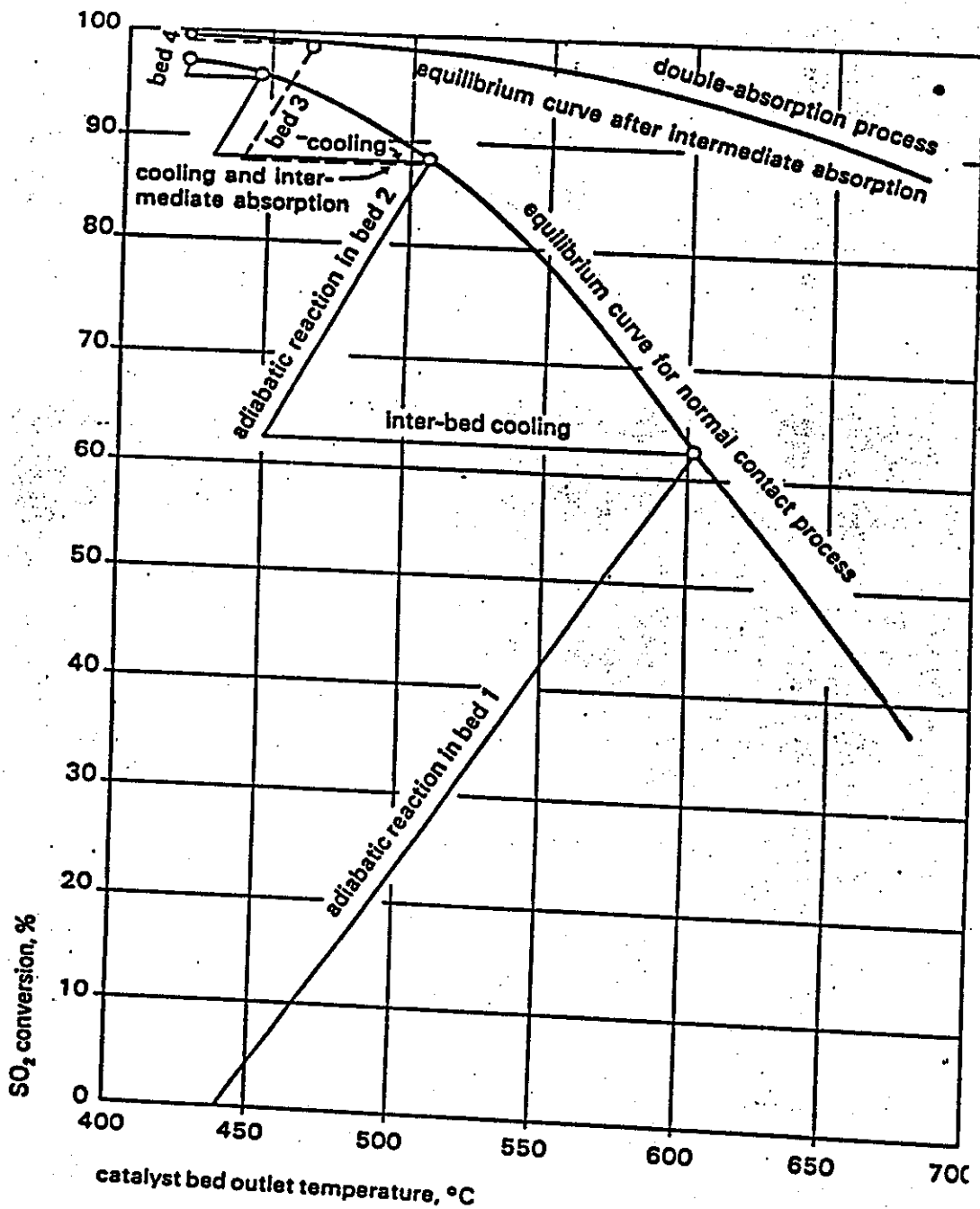


Figure 2

Pressure Effect on Equilibrium

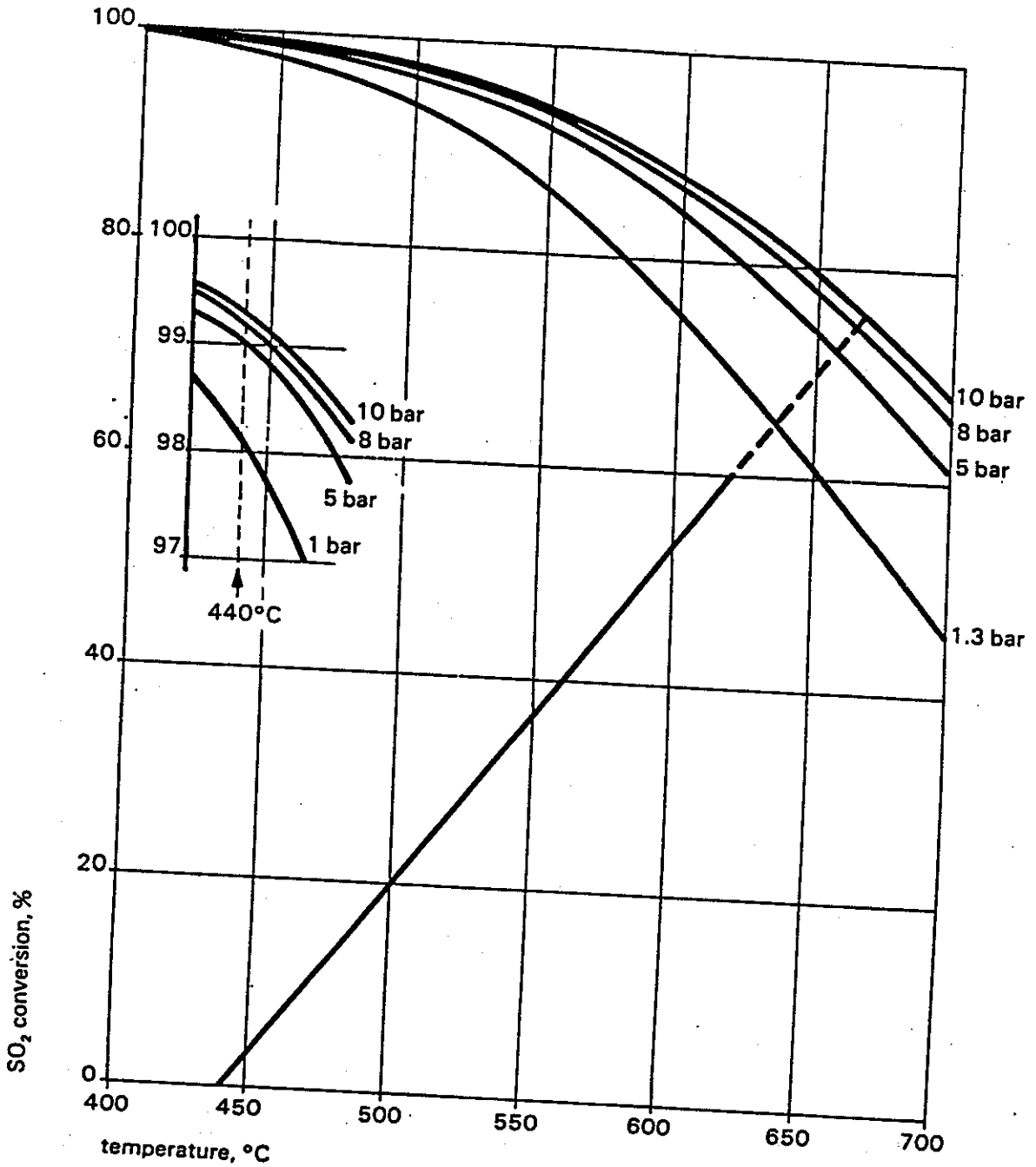


Figure 3
Catalyst Shapes & Sizes

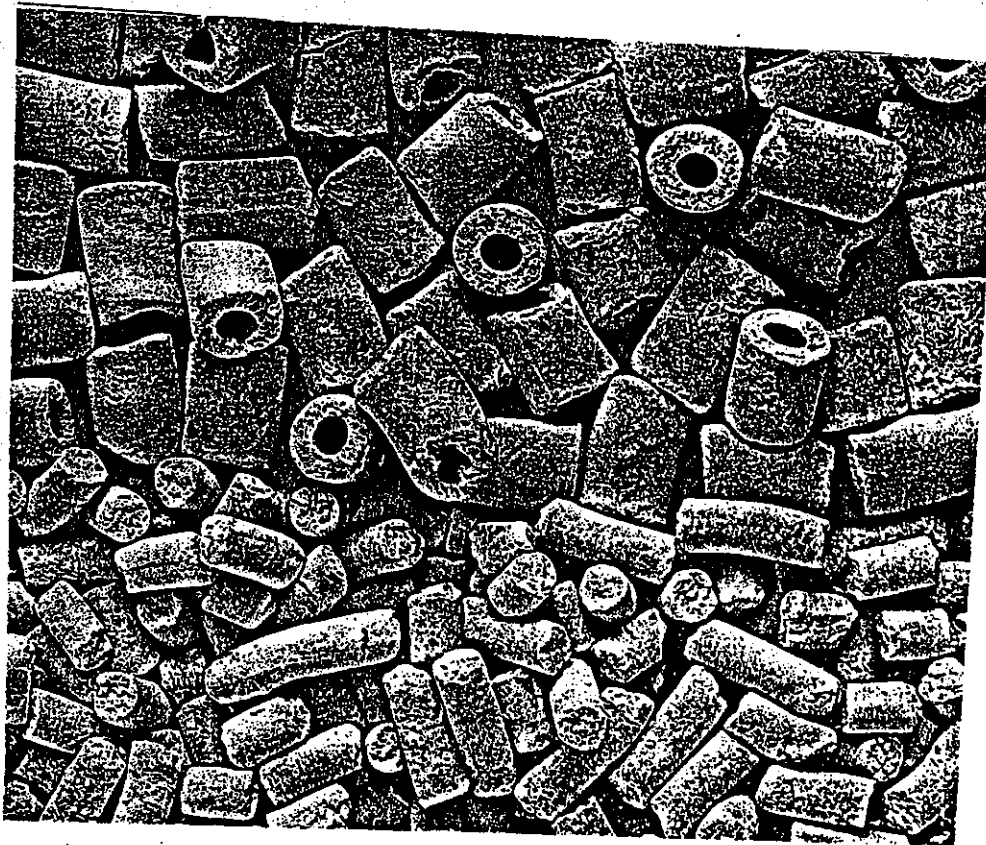
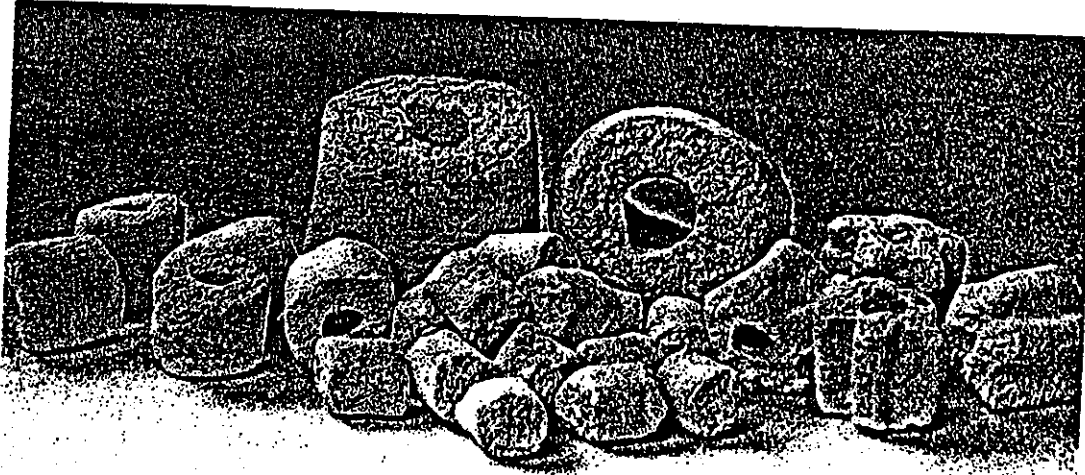


Figure 4

Catalyst Shapes & Sizes

