

# CRITERION\* Hydrotreating Catalyst In-Situ Presulphiding Guidelines - Liquid Phase (preferred method) - Gas Phase (alternative method)

## I. Introduction

It has long been recognised that to obtain the maximum activity from Ni/Mo, CoMo, or Ni/W catalyst, they must be presulphided prior to use. Several methods are commonly used to presulphide hydrotreating catalysts. These include in-situ gas phase sulphiding or liquid phase sulphiding - with or without a sulphur spiking agent and ex-situ presulphurised catalyst which can also be activated in a gas or liquid phase. Criterion's preferred in-situ sulphiding method is liquid phase with a sulphur

spiking agent. The preferred method is described in detail below.

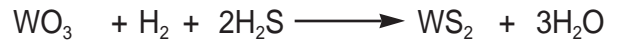
## II. Selection and Calculation of the Quantity of Sulphiding Agent Required for In-Situ Pre-sulphiding

There are several classes/types of sulphur compounds that can be used for sulphiding. These include mercaptans, sulphides, disulphides, polysulphides and sulfoxides. Some of the more frequently used sulphiding agents and their respective physical properties are presented in Table 1.

**Table 1: Physical Properties of Frequently Used Sulphiding Agents**

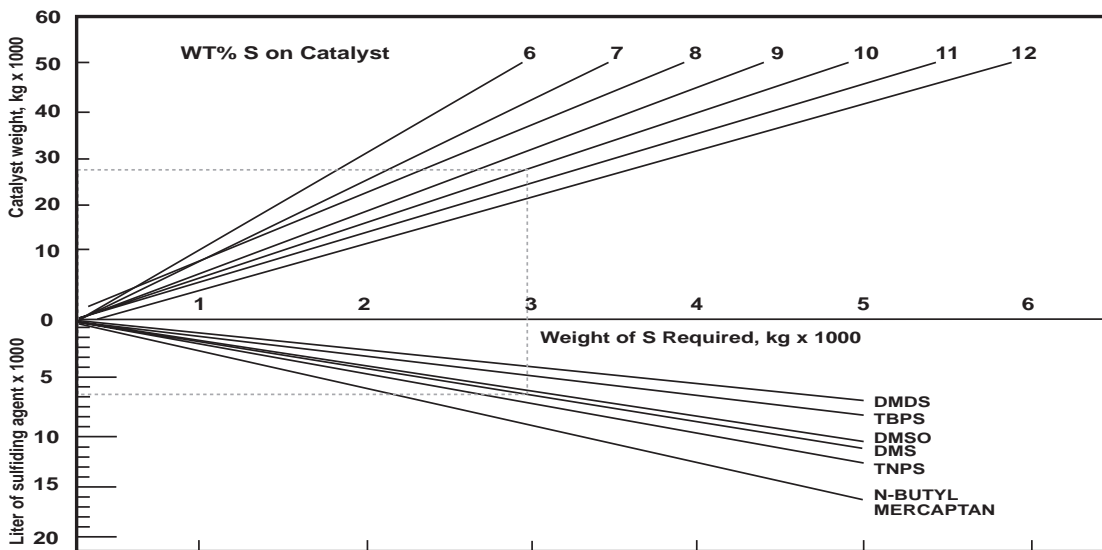
Sulphiding Agent	Wt% Sulphur	Molecular Weight	Specific Gravity @ 20°C (68°F)	Vapor Pressure mm Hg @ 20°C (77°F)	Boiling Point, °C @ 1 atm (°F)	Decomposition Temperatures over HDS catalyst + Hydrogen, °C (°F)	Toxicity, LC <sub>50</sub> Inhalation, ppm	Sulphiding Agent Required	
								Liters per 1000 kg	US Gallons per 1000 lb S
DMDS	68	94	1.06	17	109 (229)	175-205 (350-450)	805	1390	166
DMS	52	62	0.84	398	36 (97)	230-260 (450-500)	40,250	2290	275
DMSO	41	78	1.10	non-volatile	189 (372)	150-175 (300-350)	-	2217	267
N-butyl mercaptan	36	90	0.85	46	96 (205)	150-175 (300-350)	4,020	3270	392
TBPS	54	248	1.10	8 (@38°C)	-	150-200 (300-390)	-	1684	204
TNPS	37	414	1.04	non-volatile	-	150-175 (300-350)	-	2599	313

The total required quantity of sulphur is determined for each catalyst based upon its promoter metals content. The following chemical formulas are used to calculate the stoichiometric amount of sulphur needed for successful presulphiding:

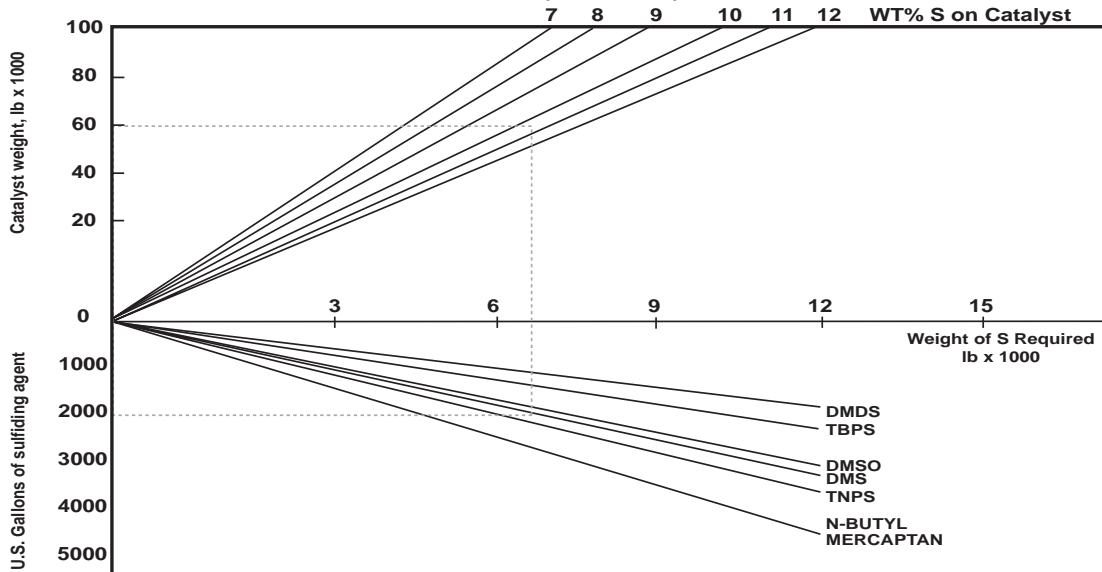


For convenience, Figures 1 and 2 indicate the volume of sulphiding agent required for a given catalyst weight and recommended sulphur addition in metric and U.S. units. Table 2 is a tabular form of the calculations presented in these two figures.

**Figure 1**  
**VOLUME OF SULPHIDING AGENT REQUIRED**  
(Metric Units)



**Figure 2**  
**VOLUME OF SULPHIDING AGENT REQUIRED**  
(U.S. Units)



**Table 2: Calculation of Quantity of Sulphiding Agent Required**

Example: Calculate quantity of DMDS required to sulphide 25,000 kg (60,000 lb) of CRITERION 424 hydrotreating catalyst.

	Metric Units	US Units
1. Determine the weight of catalyst to be sulphided in the 1000's of kg or 1000's of lb.	25	60
2. Determine the stoichiometric amount of sulphur addition in wt % required for the particular catalyst.	10.8	10.8
3. Calculate the 1000's of kg or 1000's of lb of S required by multiplying the results of Step 1 times the results of Step 2 divided by 100.	2.70	6.48
4. Determine the liters of sulphiding agent per 1000 kg S or the U.S. gallons of sulphiding agent per 1000 lb S for the selected sulphiding agent from Table I.	1390	166
5. Calculate the volume of sulphiding agent required (liters or U.S. gallons) by multiplying the results of Step 3 times results of Step 4.	3751	1075

It is the intent of the presulphiding procedure to add the stoichiometric amount of sulphur to the catalyst. It is common to use an excess amount of sulphur compound to ensure that the catalyst is fully sulphided. Prior to concluding the presulphiding procedure, a sulphur balance should be conducted to confirm that the desired amount of sulphur has been taken up by the catalyst.

### III. Preferred Commercial Presulphiding Procedure (Liquid Feed)

#### Dry Out

Catalysts are normally shipped/supplied dry, but due to their high surface area can readily adsorb moisture when exposed to the atmosphere (or other potential high moisture conditions). Our R&D has shown that  $\approx 1$  wt %  $H_2O$  on the catalyst can interfere with presulphiding. Consequently,

a dry out step is recommended after the catalyst is loaded. Gas phase dry out is more common, but liquid phase dry out with a virgin feed stock is also practiced. The gas phase dry out is described below.

After the catalyst is loaded, purge the system thoroughly with inert gas after pressure testing. Adjust the reactor pressure to 15-35 barg (200-500 psig) with hydrogen. Establish maximum hydrogen gas rate, once-through or recycle, and heat to 150°C (300°F) at 30°C/hr (50°F/hr). Once-through, dry hydrogen gas provides the best drying. Use of a gas stream that is wet or contains condensed hydrocarbons could exhibit an exotherm due to the heat of absorption. Maintain maximum cooling on condensers to remove as much water as possible in the separator. Drain water from the separator as needed.

Maintain hydrogen circulation at 177°C (350°F) for at least 1 hour and until no more than 4 liters/hr (1 gallon/hr) of free water is taken out of the separator.

#### **Initial feed in with sulphiding agent**

Reduce hydrogen gas rate to minimum recycle or once-through rate (Be aware of compressor surge limitations). Reduce reactor temperature to 120°C (250°F) in order to control the potential exotherm from the heat of absorption. Introduce virgin feed stock (such as naphtha, kerosene, or distillate) at maximum possible feed rate to ensure complete catalyst wetting. Continue for four hours. After completing catalyst wetting, increase hydrogen gas rate back to normal.

Discount the sulphur content of the feed stock and add sufficient sulphiding agent to the feed stock in order to provide 1-2 wt% sulphur, based on density of the feed. Feedstocks containing unsaturated compounds should not be used for presulphiding. It is best if the final boiling point is 340°C (640°F) or less.

Initial sulphiding of the catalyst should normally be done at 205-230°C (400-450°F) by adjusting the reactor inlet temperature. Some sulphiding compounds, e.g. dimethyl sulphide, may require reactor temperatures in excess of 230°C (450°F) to initiate sulphiding. The sulphiding agent may accumulate on the catalyst if a large amount of the sulphiding agent is injected prior to the catalyst beds reaching the sulphiding agent's decomposition temperature. This could cause a high exotherm when the sulphiding agent's decomposition temperature is reached. In order to minimise this potential exotherm, the temperature of the catalyst beds should be increased so that the introduction of sulphiding agent onto the catalyst coincides with the catalyst beds reaching the sulphiding agent's decomposition temperature.

Care should be taken not to exceed 245°C (475°F) anywhere in the catalyst bed during initial sulphiding before H<sub>2</sub>S breakthrough. Depending upon feed sulphur concentration and the resultant exotherm, reactor temperatures could reach into an undesirable 315-375°C (600-700°F) range. Above 245°C (475°F), coking and/or promoter metal oxide reduction will occur before sulphiding is complete.

Sulphur concentration should be controlled as required to hold bed temperatures below 245°C (475°F). Initial addition of sulphiding agents to the charge oil should be on the low side (0.5-1.0 wt% S), since excessive sulphur injection might hamper temperature control. The reactor temperature increase due to presulphiding should be limited to 15-25°C (25-50°F). During presulphiding operation, hydrogen sulphide removal from the recycle gas by amine treatment or any other method should cease until the catalyst has been fully presulphided.

If the hydrogen partial pressure at the reactor outlet goes below 10 barg (150 psig) a continuous hydrogen make-up and purge should be maintained. This will hold pressure and ensure a reasonably constant hydrogen concentration in the recycle gas, as the hydrocarbons generated from the decomposition of the sulphiding agent will be expelled from the system. It is important to monitor the H<sub>2</sub>S concentration in the purge gas after breakthrough in order to calculate the amount of sulphur on the catalyst.

#### **H<sub>2</sub>S breakthrough**

Continue to sulphide the catalyst until a copious breakthrough of H<sub>2</sub>S is observed. In the early stages of sulphiding, the H<sub>2</sub>S in the recycle gas will remain low, typically

30-160 ppm vol H<sub>2</sub>S. When breakthrough occurs, H<sub>2</sub>S concentrations will rise rapidly. Most refiners wait until the concentration reaches 3000+ ppm vol H<sub>2</sub>S in the recycle gas before acknowledging breakthrough. The concentration of H<sub>2</sub>S in the recycle gas can be measured by a device such as a Drager tube. The H<sub>2</sub>S in the recycle gas should be checked at least once every hour prior to breakthrough.

Once breakthrough has been reached, a preliminary sulphur balance should be performed. Approximately one half of the stoichiometric sulphur should have passed over the catalyst before breakthrough. This is especially important for once-through treat gas units where premature H<sub>2</sub>S breakthrough might not be easily recognised. (On units with gas recycle, the refiner also has the option of stopping the sulphiding agent injection for 30-60 minutes and monitoring H<sub>2</sub>S concentration. A rapidly decreasing H<sub>2</sub>S concentration indicates premature breakthrough. Sulphur injection should be restarted immediately especially if the H<sub>2</sub>S level drops below 1000 ppm vol.)

### **Second-stage sulphiding**

A second stage of sulphiding is required to ensure complete sulphiding. After determining the quantity of sulphiding agent already used (see above) and the amount remaining, restart sulphiding injection at previous levels. Raise the reactor temperature to 345°C (650°F) at 15°C/hr (25°F/hr), then hold for 1 hour. Maintain the reactor outlet H<sub>2</sub>S concentration at 1000 ppm minimum. If the H<sub>2</sub>S level falls below 1000 ppm, keep the reactor temperature constant until 1000 ppm H<sub>2</sub>S is re-established. Continue sulphur injection until at least the stoichiometric quantity of sulphur has been passed over the catalyst.

### **Feed in at start-of-run conditions**

When presulphiding is complete, remove H<sub>2</sub>S from the recycle gas by placing the

recycle gas scrubber in service (if available), or reduce H<sub>2</sub>S level below 1 vol % by purging with hydrogen.

Adjust reactor pressure and feed rate to normal conditions and temperature to 25°C (50°F) below the anticipated start of run temperature. It is also recommended to not increase reactor temperatures until feed and product analysis has been evaluated. This will prevent the highly active catalyst from being operated at a higher temperature than necessary which will increase the relative coke make. If the anticipated start-of-run temperature is higher than 345°C (650°F), do not exceed 345°C (650°F) for 2 days. Then increase reactor temperature by 15°C/day (25°F/day) to desired start-of-run temperature.

**Note:** if the normal feed stock contains cracked material, condition the catalyst with virgin feed stock for 3 days. Then begin gradually increasing the amount of cracked material in the feed stock until normal level is reached.

Figure 3 is an example of time-temperature profile for presulphiding.

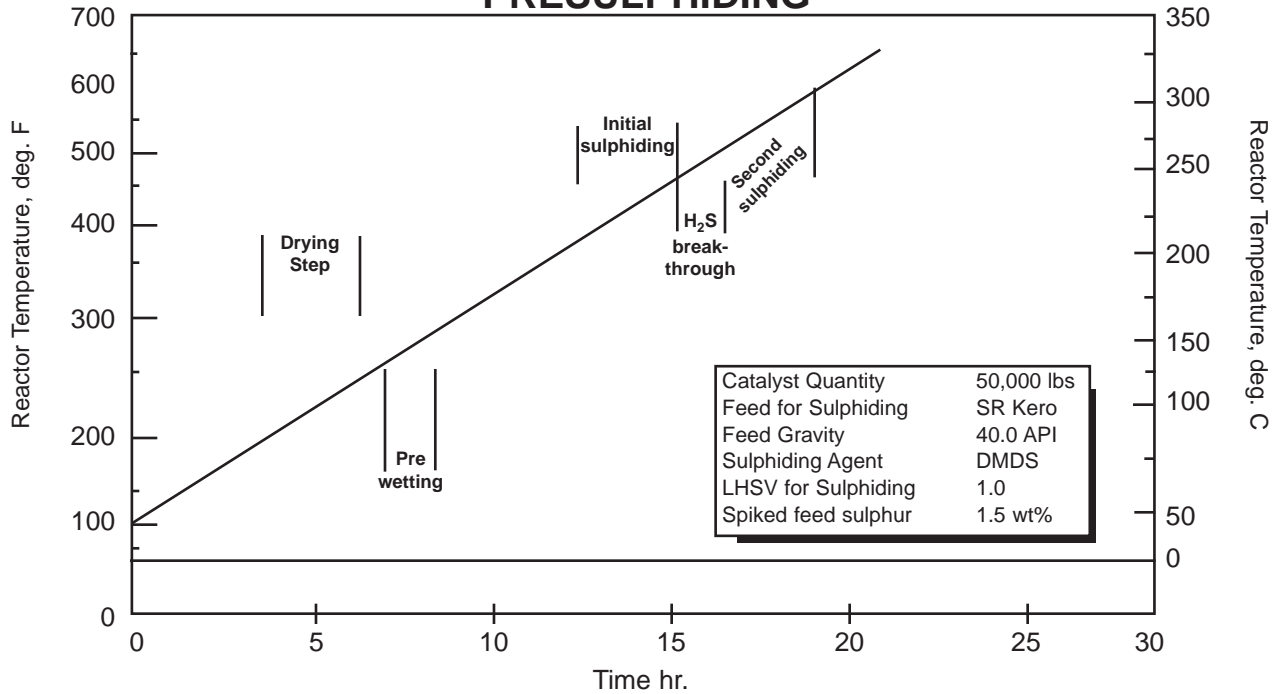
### **IV. Alternative Commercial Presulphiding Procedure (Gas Phase)**

1. After the catalyst is loaded, purge the system thoroughly with inert gas. Adjust the reactor pressure to 15-35 barg (200-500 psig) with dry hydrogen. Establish maximum once-through hydrogen rate and heat to 180°C (300°F) at 25°C/hr (50°F/hr). Maintain maximum cooling on condensers to remove as much water as possible in the separator. Drain water from the separator as needed. Maintain hydrogen purge at 180°C (350°F) for at least 1 hour and until no more than 4 liters/hr (1 gallon/hr) water is taken out at the separator.

2. Establish once-through or recycle treat gas rate at 300-400 Nm<sup>3</sup>/hr/m<sup>3</sup> of cat-



Figure 3  
**TIME-TEMPERATURE PROFILE FOR  
 PRESULPHIDING**



alyst (300-400 SCF/hr/ft<sup>3</sup> of catalyst). The concentration of H<sub>2</sub>S in the hydrogen-rich treat gas should be between 2-3 mole %. The H<sub>2</sub>S should be added to the unit at the completion of the drying step while the reactor temperature is 180°C (300°F). Increase reactor temperature to 205°C (400°F). Care should be taken not to exceed 245°C (475°F) anywhere in the catalyst bed during initial sulphiding. Depending upon gas sulphur concentration and resultant exotherm, reactor temperatures could reach into an undesirable 315°-370°C (600°-700°F) range. In this high range, coking and promoter metal oxide reduction will occur before sulphiding is complete. The H<sub>2</sub>S concentration should be controlled as required to hold bed temperatures below 246°C (475°F). Additions of H<sub>2</sub>S to the treat gas should be on the low side (1 mole %) initially, since excessive H<sub>2</sub>S injection might hamper temperature control. During presulphiding operation, hydrogen sulphide removal, from the recycle gas by amine treatment

or any other method should cease until the catalyst has been fully presulphided.

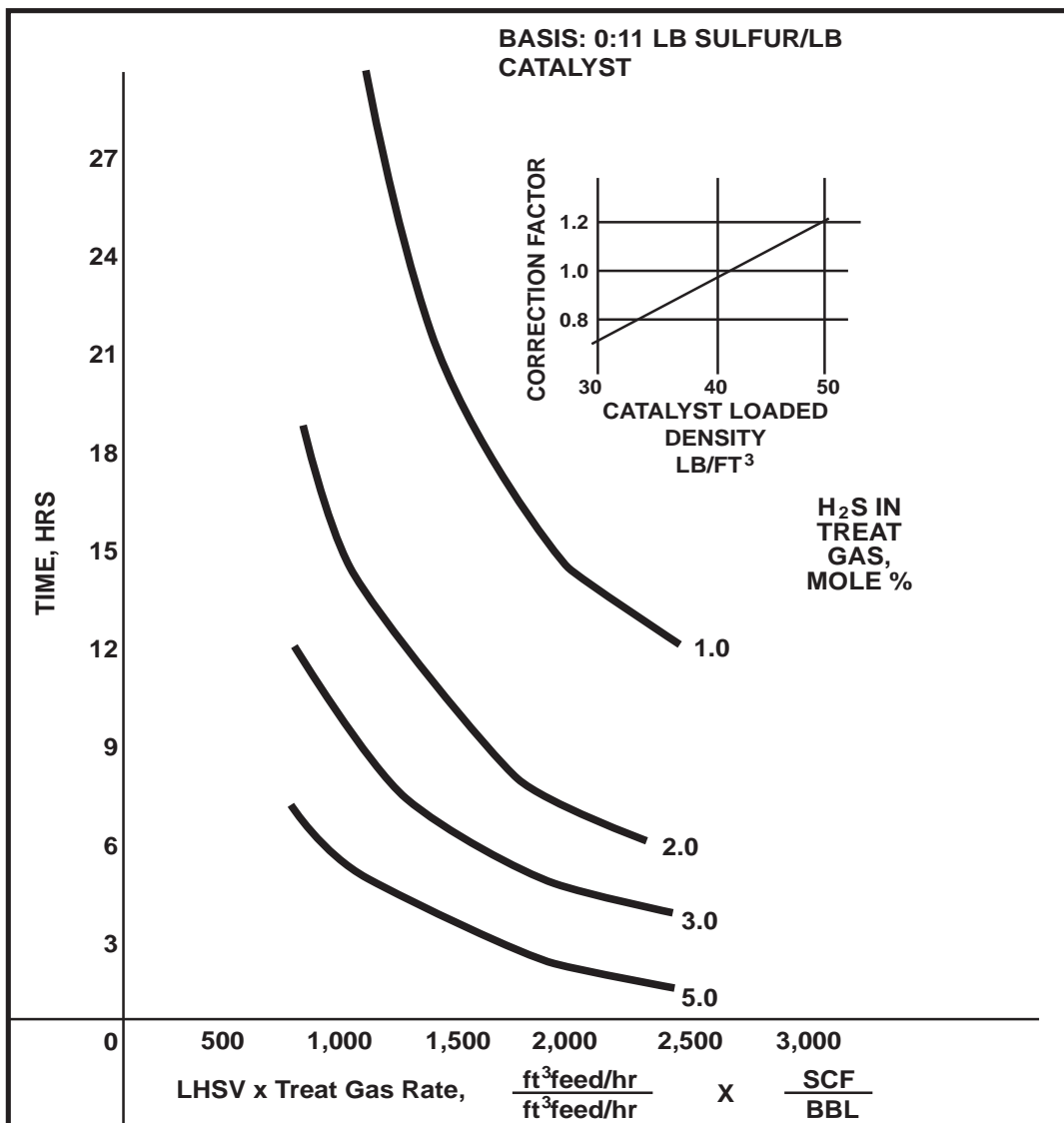
**3.** Continue to sulphide the catalyst until a copious breakthrough of H<sub>2</sub>S is observed. In the early stages of sulphiding, the H<sub>2</sub>S in the recycle gas will remain low, typically 30-160 ppm vol H<sub>2</sub>S. When breakthrough occurs, H<sub>2</sub>S concentrations will rise rapidly. Most refiners wait until the concentration reaches 3000+ ppm vol H<sub>2</sub>S in the recycle gas before acknowledging breakthrough. The concentration of H<sub>2</sub>S in the recycle can be measured by a device such as a Drager tube. The H<sub>2</sub>S in the recycle gas should be checked at least once every hour prior to breakthrough.

**4.** Once breakthrough has been reached, a preliminary sulphur balance should be performed. Approximately one half of the stoichiometric sulphur should have passed over the catalyst before breakthrough. This is especially important for once-through treat gas units where

premature H<sub>2</sub>S breakthrough might not be easily recognised. (On units with gas recycle, the refiner also has the option of stopping the sulphiding agent injection for 30-60 minutes and monitoring H<sub>2</sub>S concentration. A rapidly decreasing H<sub>2</sub>S concentration indicates premature breakthrough. Sulphur injection should be restarted immediately especially if the H<sub>2</sub>S level drops below 1000 ppm vol.

5. A second stage of sulphiding is required to assure complete sulphiding. This may be done by increasing the temperature to 345°C (650°F) at 15°C/hr (25°F/hr) and injecting sulphiding agent at the previous levels. Do not exceed the anticipated start of run temperature during the second sulphiding stage.

**Figure 4**  
**MINIMUM TIME FOR PRESULPHIDING WITH**  
**H<sub>2</sub>S IN RECYCLE GAS**



6. When the second breakthrough occurs, injection should be continued for 1 hour or until the stoichiometric amount of sulphur has been deposited on the catalyst. Figure 4, which does not account for time to raise temperatures or stabilise conditions, serves as a guide of the minimum time required to complete sulphiding. (Note: LHSV refers to normal feed rate. Treat gas rate is in units of SCF/B.) The time value must be adjusted by multiplying by the correction factor for catalyst loaded density.

7. When presulphiding is complete, remove H<sub>2</sub>S from the recycle gas by placing recycle gas scrubber in service (if available), or reduce H<sub>2</sub>S level below 1 vol % by purging with hydrogen.

**Note: Do not allow the recycle gas H<sub>2</sub>S level go below 1000 ppm when the catalyst bed temperature are above 245°C (475°F) otherwise the sulphur on the catalyst will be stripped off and metal reduction can occur.**

8. Reduce the reactor temperature to 232-260°C (450-500°F) prior to bringing in straight run feed. Establish initial liquid feed rate of at least 75% of design in order to provide adequate pre wetting and prevent flow maldistribution in the catalyst bed.

It is also recommended to not increase reactor temperatures until feed and product analysis has been evaluated. This will prevent the highly active catalyst from being operated at a higher temperature than necessary which will increase the relative coke make. If the anticipated start-of-run temperature is higher than 345°C (650°F), do not exceed 345°C (650°F) for 2 days. Then increase reactor temperature by 15°C/day (25°F/day) to desired start-of-run temperature.

**Note:** if the normal feed stock contains cracked material, condition the catalyst with virgin feed stock for 3 days. Then begin gradually increasing the amount of cracked material in the feed stock until normal level is reached.



## **ADDITIONAL INFORMATION**

All catalyst information supplied by CRITERION is considered accurate but is furnished with the express understanding that the customer receiving such information shall make its own assessments to determine suitability of such information for customer's particular purpose. All purchases of catalyst from CRITERION are subject to CRITERION's standard terms and conditions of sale (including CRITERION's product warranties) set forth in a sales proposal, sales contract, order acknowledgement, and/or bill of lading.

## **WORLDWIDE OFFICES:**

---

### **HOUSTON:**

#### **Criterion Catalyst Company L.P.**

16825 Northchase Drive, Suite 1000  
Houston, Texas 77060-6029  
Telephone: (1) 281- 874-2600  
Telefax: (1) 281- 874-2641  
(U.S.A., Mexico, Central America, South America and the Caribbean are serviced by the Houston Sales Office.)

### **CANADA:**

#### **Criterion Catalyst Canada, Inc.**

Suite 810, Centre 104  
5241 Calgary Trail Southbound  
Edmonton, Alberta T6H 5G8  
Canada  
Telephone: (1) 403-438-4188  
Telephone: (1) 780-438-4188 (effective 01/01/99)  
Telefax: (1) 403-438-3473  
Telefax: (1) 780-438-3473 (effective 01/01/99)

### **ENGLAND:**

#### **Criterion Catalyst Company Ltd.**

1650 Parkway  
The Solent Business Park,  
Whiteley, Fareham  
Hampshire, PO15 7AH  
England  
Telephone: (44) 1 489-881881  
Telefax: (44) 1 489-881882  
(Europe, Middle East, Africa, are serviced by the Fareham Sales Office.)

### **SINGAPORE:**

#### **Criterion Asia Pacific Pte Ltd**

298 Tiong Bahru Road  
#07-03/04/05 Tiong Bahru Plaza  
Singapore 168730  
Telephone: (65) 6276-3627  
Telefax: (65) 6276-7455  
(Japan, Korea, Taiwan, China, S.E. Asia Australia, New Zealand, India and Pakistan are serviced by the Singapore Sales Office.)