



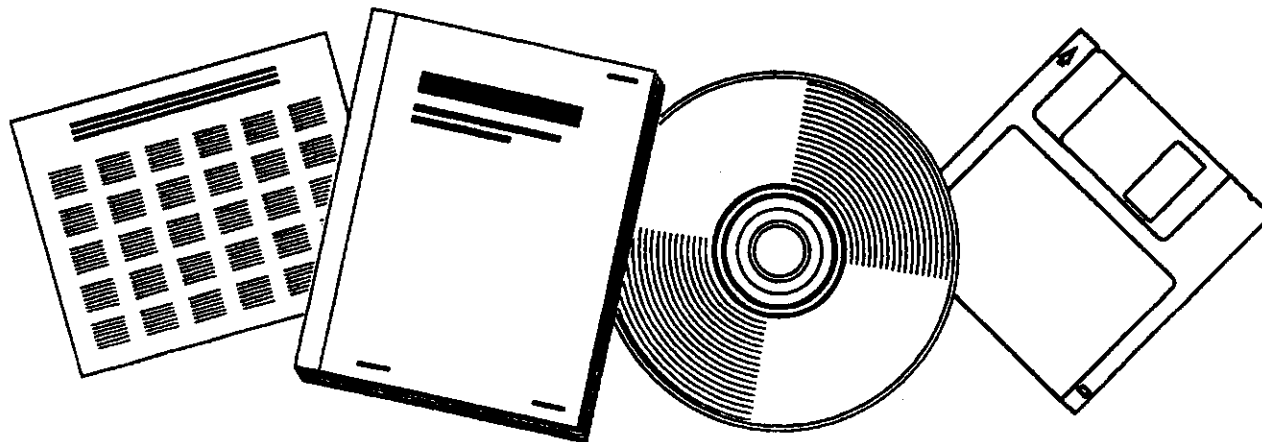
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**CHEMISTRY AND CATALYSIS OF COAL
LIQUEFACTION; CATALYTIC AND THERMAL
UPGRADING OF COAL LIQUIDS; AND
HYDROGENATION OF CO TO PRODUCE FUELS.
VOLUME 9. FINAL REPORT**

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CATALYTIC AND THERMAL UPGRADING OF COAL LIQUIDS:
AND HYDROGENATION OF CO TO PRODUCE FUELS

FINAL REPORT

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Volume IX

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ABSTRACT

The hydrogenation of carbon monoxide to produce low-molecular-weight olefins (C_2-C_4) has been investigated over unsupported iron-manganese catalysts. It was found that a catalyst with approximately 2 parts of manganese per 100 parts of iron was effective in modifying the activity and selectivity of unsupported iron catalysts for the production of C_2-C_4 olefinic hydrocarbons.

The highly exothermic nature of the carbon monoxide hydrogenation reactions can result in significant temperature excursions in the fixed-bed reactor. At a carbon monoxide conversion level of 10 percent, the observed temperature rise in the catalyst zone was 15 K. At higher conversion levels, a severe hot spot developed in the bed. The initial objective of this study was to investigate the influence of the catalyst loading and reactor operating modes on the activity and selectivity of iron-manganese catalysts for carbon monoxide hydrogenation. The following modes were studied: (1) conventional dense-bed reactor, (2) dense bed trickle flow reactor, (3) dense bed pseudo slurry reactor, (4) diluted bed reactor, (5) diluted bed trickle flow reactor and (6) diluted bed pseudo slurry reactor.

The standard operating conditions were as follows: reactor temperature 593K (220°C), reactor inlet pressure 2.76 MPa (400 psig), reactant gas space velocity $1.0 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and a H_2/CO ratio of 2. Mobil #1

base stock MCP-151 without additives and n-hexadecane were used as heat transfer media in the trickle flow and pseudo slurry reactor operations.

The heat transfer liquid was pumped through the reactor at a fixed rate of $0.103 \text{ cm}^3 \text{ s}^{-1}$. Both MCP-151 and n-hexadecane suppressed the observed temperature rise and led to a nearly isothermal temperature profile throughout the catalyst bed. Lower carbon monoxide conversion levels were observed at similar average catalyst bed temperatures when the heat transfer media was introduced into the reactor, especially for the diluted bed pseudo slurry reactor. n-Hexadecane was selected as the standard heat transfer medium as it indicated an advantage for the production of $\text{C}_2\text{-C}_4$ olefinic hydrocarbons.

A complete process variable investigation was conducted in the diluted bed reactor and in the diluted bed pseudo slurry reactor using n-hexadecane as the heat transfer liquid. The process variables investigated were reaction temperature, reactor pressure, H_2/CO ratio and reactant gas space velocity. In the range of operating variables investigated the following observations were made:

- Temperature - increased reactor temperature resulted in increased olefin and carbon dioxide selectivity.
- Reactor Pressure - increased reactor pressure resulted in higher $\text{C}_2\text{-C}_4$ selectivity and in reduced olefin selectivity (decline in $\text{C}_2\text{-C}_4$ olefin/paraffin ratio).
- H_2/CO Ratio - increased H_2/CO ratio resulted in greater $\text{C}_2\text{-C}_4$ selectivity and in reduced $\text{C}_2\text{-C}_4$ olefin selectivity.

- H_2/CO Space Velocity - increased reactant gas space velocity resulted in higher C_2-C_4 hydrocarbon selectivity and in reduced carbon dioxide selectivity.

The Hydrogenation of Carbon Monoxide over Iron-Manganese Catalysts

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Alex G. Oblad

Introduction

The catalytic hydrogenation of carbon monoxide to produce a variety of hydrocarbons, commonly known as the Fischer-Tropsch synthesis, is a well-established process for the indirect production of liquid fuels and chemical feedstocks from hydrogen deficient materials such as coal.^{1,2} Although this process was first introduced some fifty years ago, it has only been infrequently carried out on a commercial scale because of the abundant supply of relatively inexpensive petroleum feedstocks that served as the principal source of liquid fuels and petrochemical raw materials. The 1973 OPEC oil embargo, and the concomitant escalation in the price of crude petroleum resulted in a considerable increase in the price of motor fuels and oil-based raw materials such as paraffins, olefins, BTX, alcohols, etc. These political and economic factors revived interest in the Fischer-Tropsch process as an alternative domestic source of liquid fuels and chemical feedstocks.

The majority of the earlier Fischer-Tropsch investigations focused on the production of methane, gasoline-boiling-range hydrocarbons, or oxygenated hydrocarbons, and little attention was paid to the production of low-molecular-weight olefins, such as ethylene, propylene, and butylene. However, these olefinic hydrocarbons are important feedstocks for the petrochemical industry and their

production from an alternative fossil energy resource, such as coal, could significantly alleviate the dependence upon imported petroleum.

Yang and coworkers³⁻⁵ used a bench-scale fixed-bed reactor to test the activity and selectivity of a variety of metal catalysts for the hydrogenation of carbon monoxide. The most promising catalyst system for the production of low molecular weight olefins was determined to be manganese promoted iron. This conclusion confirmed the observation of Kolbel, et al.⁶ that manganese promoted iron catalysts were selective for the synthesis of low molecular weight olefins. A complete process variable investigation for the hydrogenation of carbon monoxide over a series of coprecipitated iron-manganese catalysts was carried out by Tsai.^{7,8} The manganese/iron atomic ratio of the catalysts tested ranged from zero up to six. The presence of a small amount of manganese (2.2 Mn/100 Fe) had a significant influence upon the olefin selectivity of the catalyst; however, at higher manganese/iron atomic ratios (> 70 Mn/100 Fe) the olefin/paraffin ratio decreased significantly. The activity of the manganese/iron catalysts for the hydrogenation of carbon monoxide was insensitive to the presence of manganese at low manganese/iron ratios (< 20 Mn/100 Fe); however, at higher manganese concentrations (> 100 Mn/100 Fe) there was a significant decrease in activity.⁷

The hydrogenation of carbon monoxide over suitable catalysts and at the appropriate process operating conditions can produce a broad spectrum of hydrocarbon products ranging from methane to wax and including oxygenated species such as alcohols.⁹ The highly exothermic nature of the carbon monoxide hydrogenation reaction has led to the development of a number of different types of reactors designed to

efficiently remove the heat of reaction. The first commercial Fischer-Tropsch process units were fixed-bed reactors.² Subsequent developments included fluidized and entrained bed reactors and slurry reactors. Slurry reactors have been reported to be effective for the removal of the heat of reaction for high single-pass conversions of carbon monoxide with low hydrogen-to-carbon monoxide ratio feedstocks for the production of C₂-C₄ olefinic hydrocarbons.¹⁰

The objective of this investigation was to determine the activity and selectivity of coprecipitated iron-manganese catalysts for the hydrogenation of carbon monoxide to produce low molecular weight hydrocarbons in a reactor through which a suitable heat transfer liquid was circulated.

EXPERIMENTAL APPARATUS AND METHODS

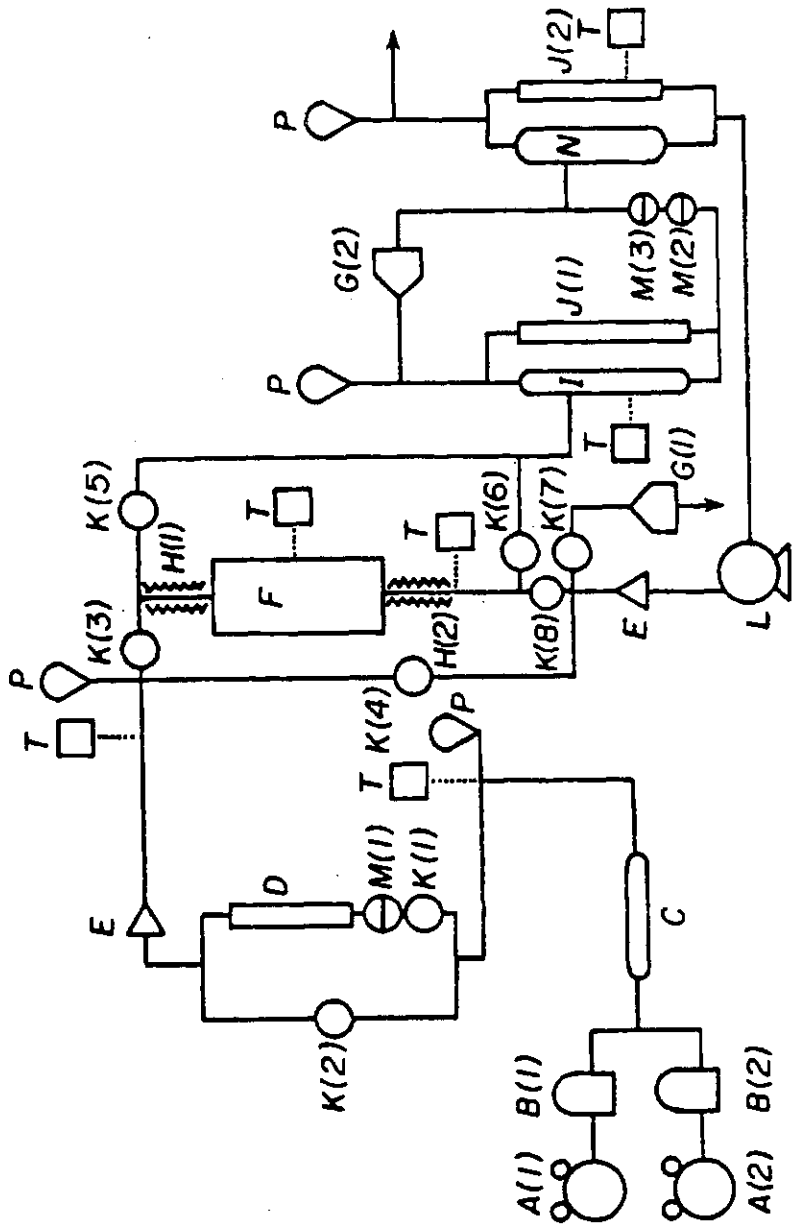
3.1 Experimental Apparatus

A schematic of the high pressure reaction system used in this investigation is presented in Figure 9. This system was designed to permit both downflow and upflow operation. Upstream reactant gas pressures were adjusted by the high pressure regulators (A) on the control panel. The flow rates of carbon monoxide and hydrogen were controlled by a Union Carbide FM-4550 Mass Flowcontroller (B) with a working pressure range between atmospheric pressure and 10 MPa. The blended carbon monoxide-hydrogen stream was purified with 6-8 mesh Alfa activated charcoal pellets in a 6HD-500 Hoke sampling cylinder (C). The activated charcoal was pretreated and regenerated periodically in flowing hydrogen at 423 K and ambient pressure for four hours. Stainless steel screen with fibreglass wool and Swagelok gas filters were installed in both the inlet and outlet lines to the purifier to avoid the transfer charcoal fines into the reactor with the reactant gas stream. The combined carbon monoxide/hydrogen flow-rate was also monitored with a high pressure Hoke rotameter (D). A by-pass was used to protect the flow meter when the system was operated at high pressure. A Milroyal DB-1-30R metering pump (L) with a maximum pumping rate of 0.3028 liters per hour was used to circulate the heat transfer liquid through the system during the

Figure 9

The Reactor System Flowchart for
Carbon Monoxide Hydrogenation.

- A. Inline Pressure Regulator
- B. Mass Flow Controller
- C. Activated Charcoal Purifier
- D. Rotameter
- E. Check Valve
- F. Reactor
- G. Grove Loader Back Pressure Regulator
- H. Heat Transfer Liquid Preheater
- I. High Pressure Gas-Liquid Separator
- J. Jerguson Liquid [Level] Indicator
- K. Block Valve
- L. Heat Transfer Liquid Circulation Pump
- M. Metering Valve
- N. Low Pressure Gas-Liquid Separator
- T. Thermocouple
- P. Pressure Indicator



trickle flow and pseudo slurry operations. Heavy duty Brisket heating tapes were wrapped around the tubing to preheat the reactant stream to a specified reactor inlet temperature. The heat tapes were controlled by a series 49 Love temperature controller. The reactor was heated by a hinge type furnace with the inside diameter of 7.62 cm. The furnace was made of two 45.72 cm-long semicylindrical units with a maximum power of 1700 watts. The furnace temperature was controlled by a series 522 Love temperature controller. Pressure gauges were located at the inlet and the outlet of the reactor to measure the pressure drop across the catalyst bed. The reactor effluent was depressurized by a series 91-W Grove back pressure regulator (G) at the outlet of the reactor. A glass condenser immersed in an ice bath was used to condense water and any heavy hydrocarbon products in the reactor effluent. When operating in the trickle flow and pseudo slurry modes, the heat transfer liquid and product gas were first separated in the high pressure separator fabricated from a 6HD-500 Hoke sampling cylinder (I). The gas stream from the high pressure separator (I) was depressurized by a 91-W Grove back pressure regulator and passed into the low pressure separator (N). The low pressure separator (N) that was fabricated from a 4HD-1000 Hoke sampling cylinder was usually operated at ambient pressure to separate heavy gas from the heat transfer liquid. The flow rate of the heat transfer liquid from the high pressure separator to the low pressure separator was controlled by a combination of two series 22 Whitey micrometering valves (M). Heavy duty Brisket heating tapes were used to raise the temperature of both gas-liquid separators slightly above 373 K to vaporize product water and heavier hydrocarbon

products from the heat transfer liquid. The liquid levels in both separators were monitored with Jerguson high pressure, liquid level indicators (J) installed in parallel with the gas-liquid separators. The flow rate of the effluent gas stream was measured with a wet test meter.

The reactor assembly (side view) is presented in Figure 10. The reactor was fabricated from a 45.7 centimeter-long, 316 stainless steel tube with an outside diameter of 2.54 centimeters and a wall thickness of 0.241 centimeter. A 2.54 centimeter-thick aluminum shield was placed around the reactor tube. A piece of stainless steel tubing with 1.91 centimeter outside diameter was used as a spacer at the bottom of the reactor to adjust the position of the catalyst bed. A screen disk with an opening of 300 micrometers was placed on the spacer to hold all the catalyst pellets and inert reactor packing particles. A stainless steel tube with 0.32 centimeter outside diameter was inserted along the axis of the reactor as a thermocouple well. Temperatures at different positions inside the reactor were measured by a movable 91.44 centimeter-long, 0.102 centimeter-sheath diameter, J-type thermocouple.

The dense and diluted bed packing arrangements are presented in Figure 11. The inert packing particles used in the reactor were Denstone 57 ceramic balls supplied by Norton Chemicals. The inert particles were cleaned by boiling in concentrated nitric acid for two hours and then they were rinsed with deionized water to remove impurities. The clean Denstone 57 particles were then dried at 423 K overnight in an oven before being used in the reactor. The catalyst pellets (20/32 mesh size) and the Denstone 57 ceramic particles were

Figure 10
Axial Cross Section of Reactor.

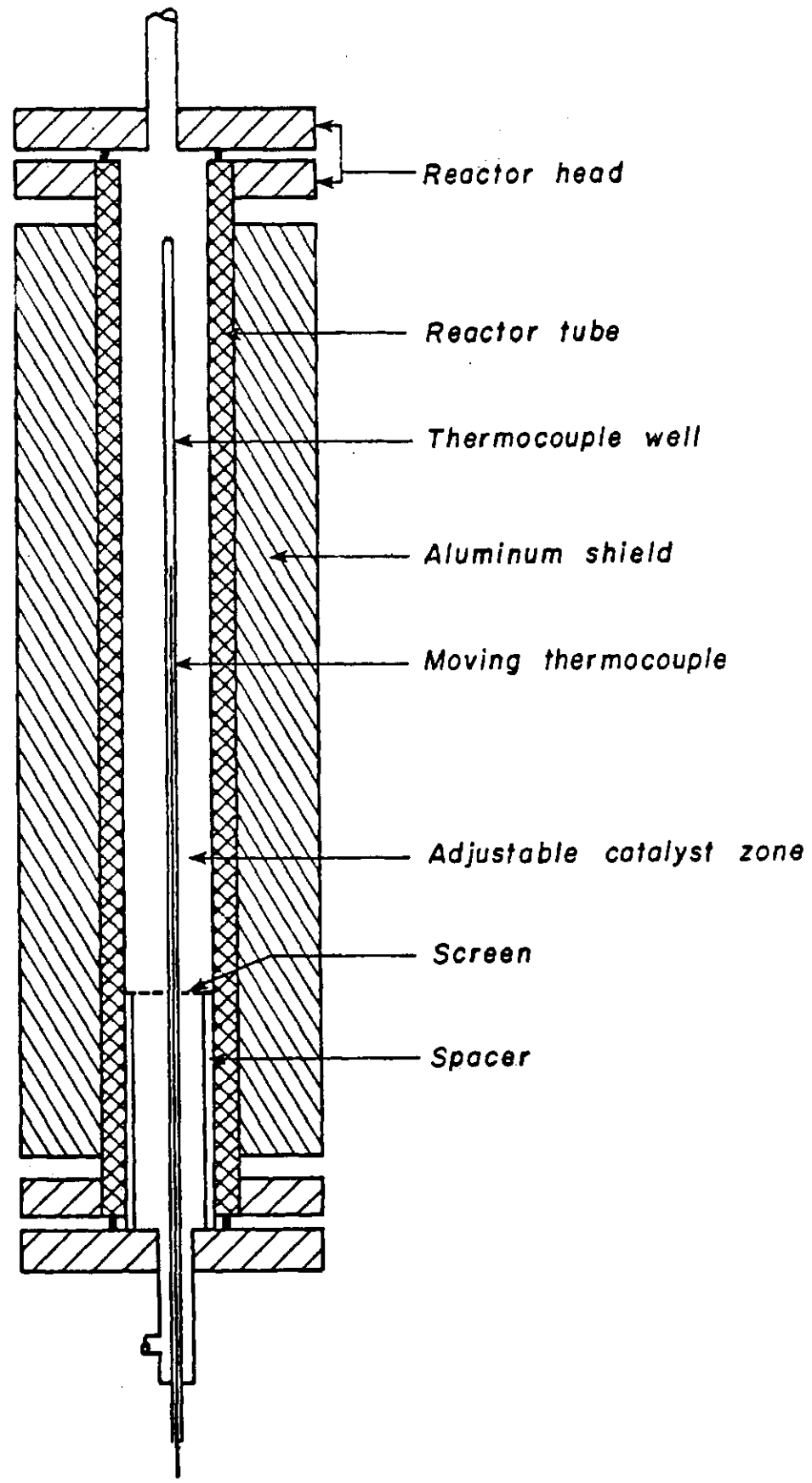
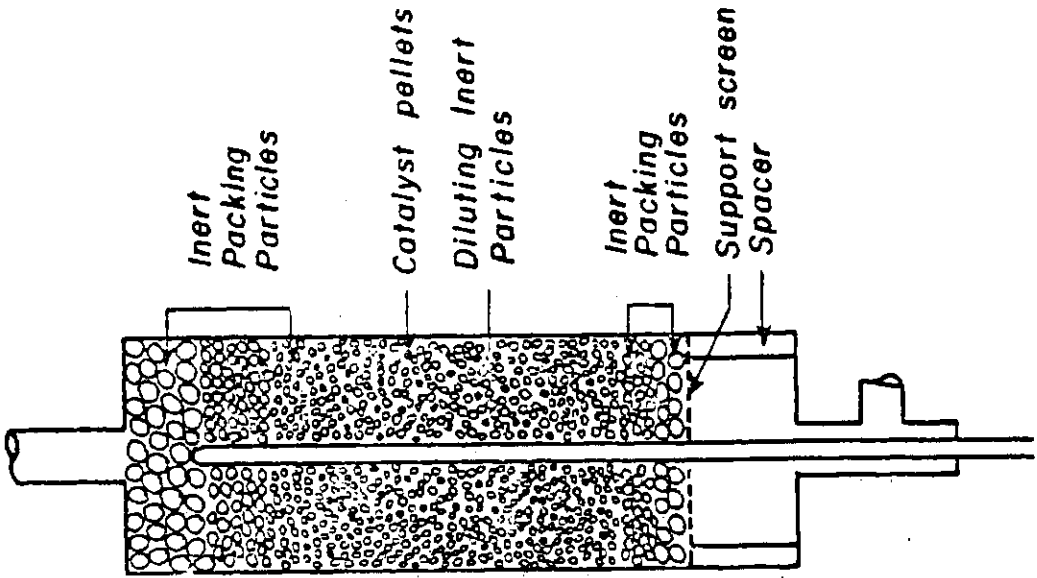
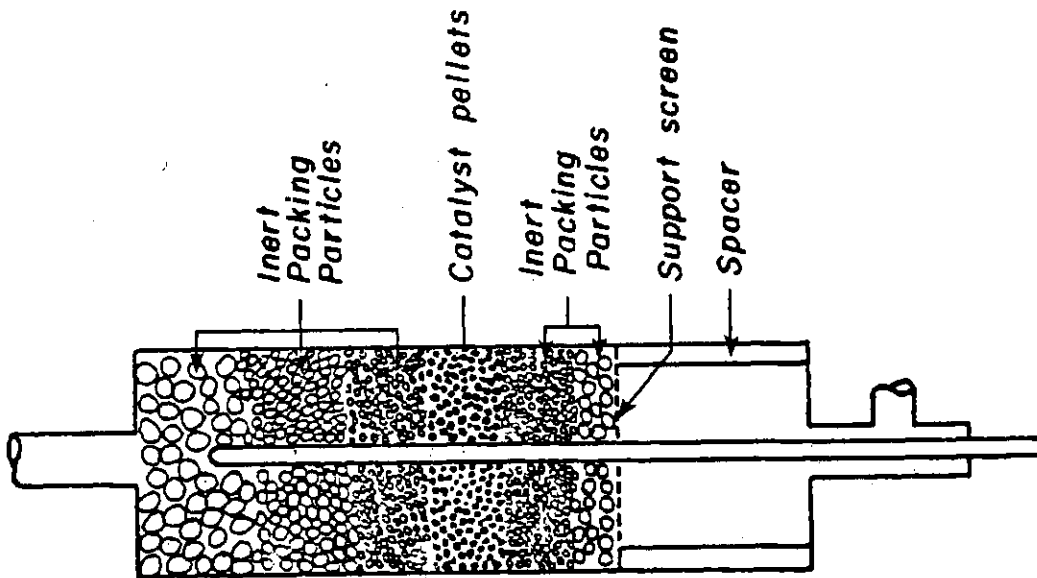


Figure 11

Dense Bed Catalyst Loading Mode and
Diluted Bed Catalyst Loading Mode.



DILUTED BED PACKING



DENSE BED PACKING