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RESEARCH AND DEVELOPMENT STUDY RELATED TO THE SYNTHESIS OF FORMALDEHYDE FROM CO_2 AND H_2

GARD Project 1416

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SYNTHESIS OF FORMALDEHYDE

Introduction

This report summarizes the activities of the General American Research Division during May through July 1967 on Contract NAS2-3889, Synthesis of Formaldehyde. The activities during this quarter were concerned with (1) oxidation of methane to formaldehyde by oxygen or air using gaseous nitrogen oxide catalyst in the presence of alkali tetraborates, (2) oxidation of methane to formaldehyde with ozonized air in the presence of metal salts and potassium tetraborate catalysts, and (3) experiments to determine the feasibility of separating the formaldehyde from other reaction products in the form of solid paraformaldehyde.

The highest formaldehyde yields obtained from the oxidation of methane using 0.2% by volume NO catalyst and reaction beds packed with porcelain Berl saddles coated with potassium tetraborate range up to nearly 3% of the methane with feed mixtures consisting of 5% CH_4 and 95% O_2 and approximately 2.25% with feed containing 20% CH_4 and 80% air. Both with oxygen-methane and air-methane mixtures, the formaldehyde yields decrease with an increase in the methane concentration. However, the total absolute amounts of formaldehyde produced reach their maxima with 60% methane - 40% oxygen and 35% methane - 65% air feed mixtures. Thus, with a single pass reactor containing a 40 cm^3 reaction bed, the formaldehyde production with air-methane feeds reaches 54 g/day using a space velocity of 7500 hr^{-1}.

The production of formaldehyde by the oxidation of methane with ozonized oxygen or air was investigated using metal salts and potassium tetraborate catalysts. With the metal salts catalyst, the formaldehyde yields were generally low, ranging from traces to 0.33% of the methane in feed. With the potassium tetraborate catalyst, the formaldehyde yields range up to approximately 1.3% of the methane. With a single pass reactor containing 40 cm^3 reaction bed, and the ozone concentration of 0.3% the formaldehyde production reached 23 g/day using a space velocity of 7500 hr^{-1}.

A preliminary investigation indicates that essentially all the formaldehyde can be condensed from the reaction product by cooling; however, it condenses together with water in the form of a liquid solution. Experiments with formaldehyde vapors obtained from heated paraformaldehyde showed the same results.

Experimental Activities

1. Oxidation of Methane Using Nitrogen Oxide Catalysts

The use of nitrogen oxides as homogeneous gas phase catalysts for the partial oxidation of methane to formaldehyde were investigated using single pass reactors having reaction zones packed with 6 mm porcelain Berl saddles coated with potassium tetraborate. Literature indicates that the expected yields of formaldehyde may reach up to approximately 2.8% of the methane in feed using single pass reactors and NO concentrations of 0.08 - 0.2% by volume. Both, oxygen - methane and air - methane feed mixtures were investigated to find the optimum experimental conditions not only giving the maximum formaldehyde yields based on methane in feed, but also the highest mass production of formaldehyde.

1.1 Oxygen - Methane Feed

The experiments with oxygen - methane feed were performed using a 23 mm I.D. Vycor tube which contained a 4" long heated reaction zone filled with porcelain Berl saddles coated with potassium tetraborate. The volume of the reaction zone was 40 cm^3. Metered amounts of oxygen and methane were premixed before entering the reaction tube. Nitric oxide was added to the oxygen stream in amounts giving approximately 0.2% NO by volume in the feed gas.

In a series of experiments, the dependence of formaldehyde yields on the feed gas composition has been investigated by using feed gases containing 5%, 53%, 66%, 80%, and 90% methane, the remainder being oxygen. Since oxygen - methane mixtures containing 5% - 53% methane are explosive, this composition range was not investigated. Runs were obtained at a temperature range of 540°C - 620°C and space velocities ranging from 2200 hr^{-1} to 3750 hr^{-1}. Under these conditions, the highest formaldehyde yields were obtained at 620°C and this was the highest temperature at which the reaction zone temperature could be safely maintained. A further increase in temperature, generally, caused a sudden increase in the formationof CO to concentrations reaching 50% of the product, with accompanying release of heat and a sudden rise of the reaction zone temperature to 700°C - 750°C.

The highest formaldehyde yield obtained was 2.35 - 3.4% (median 2.9%), based on methane in the feed, using feed gas consisting of 5% methane and 95% oxygen, at 620°C and space velocities of 2250 - 3750 hr^{-1}. At the same temperature and space velocities, an increase in methane concentration decreases the formaldehyde yields nearly linearly so that with feed gas containing 53% methane, the formaldehyde yield drops to 1.3 - 1.5%; with 90% methane, the yields of formaldehyde are only 0.7%.

Based on the formaldehyde yield data, the absolute amounts of formaldehyde produced using various methane concentrations in the feed gas were calculated. Figure 1 illustrates the formaldehyde yields and the formaldehyde production in one day. It is seen that the maximum production of formaldehyde is obtained with feed gas containing about 60% of methane; the production decreases going both to lower and to higher methane concentrations. Thus, using the reactor described above and space velocity of 3750 hr^{-1} at 620°C approximately 33 g of formaldehyde can be produced per day.

1.2 Air - Methane Feed

Partial oxidation of methane to formaldehyde by air was investigated using a gaseous nitrogen oxide catalyst and a reaction bed packed with porcelain Berl saddles which were coated with potassium tetraborate. In previous experiments all the reaction gases were premixed before entering the reactor and then were passed through the hot reaction zone. This arrangement made the control of the reaction bed temperature difficult; therefore, the reactor was modified to provide a more satisfactory control of the reaction temperature.

In this new arrangement, the feed gas of desired composition is prepared by premixing metered amounts of air and methane. This mixture is then preheated by passing it through the upper portion of the reaction tube which is packed with alumina pellets and heated by an electric heater surrounding this portion of the reaction tube. To the preheated air - methane mixture, NO is added in measured proportions through a side-arm located below the preheater zone. The hot reaction mixture now passes through a 40 cm^3 reaction

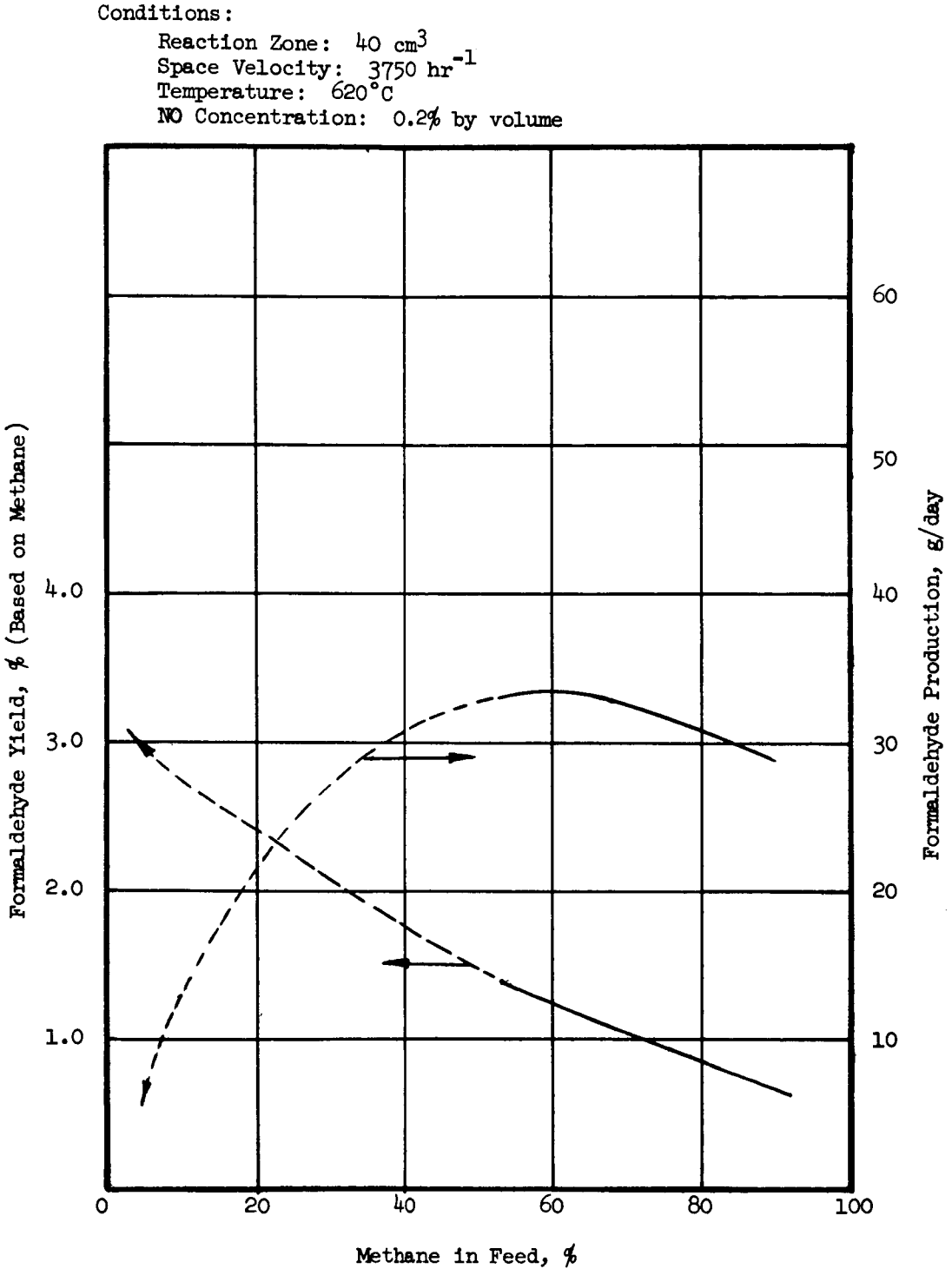

Figure 1 FORMALDEHYDE YIELDS AND PRODUCTION USING OXYGEN - METHANE FEED GAS

zone packed with 6 mm porcelain Berl saddles coated with potassium tetraborate. A second independently controlled heater surrounding the reaction zone maintains a constant temperature in the reaction zone. This arrangement not only allows close temperature control of the reaction zone but also provides a well-controlled reaction contact time.

In a series of experiments, the dependence of formaldehyde yields on the feed gas composition, reaction temperature, and space velocities was investigated. In all of these runs, the nitric oxide concentration was 0.2% by volume. Data were obtained using feed gas containing 20%, 30%, 40%, and 50% methane in the temperature range of 594°C - 705°C and space velocities ranging from 2250 up to 7500 hr^{-1}. The explosive range of air - methane mixtures lies between 5% and 14% methane; therefore, compositions below 20% methane were not investigated.

Figure 2 summarizes the experimental data obtained with air - methane gas feeds. Here, the formaldehyde yields based on the methane in feed gas are expressed as functions of temperature, composition, and space velocity. Whenever several runs were obtained under the same conditions, an average result was plotted in Figure 2. It is seen that the formaldehyde yields depend on the space velocities at temperatures 594°C and 621°C; however, at 650°C and higher temperatures, formaldehyde yields appear to be independent of space velocities in the range investigated. Generally, the yields of formaldehyde decrease with an increase in methane concentration of the feed gas. These results indicate that the yields of formaldehyde do not increase when temperatures higher than 650°C are used.

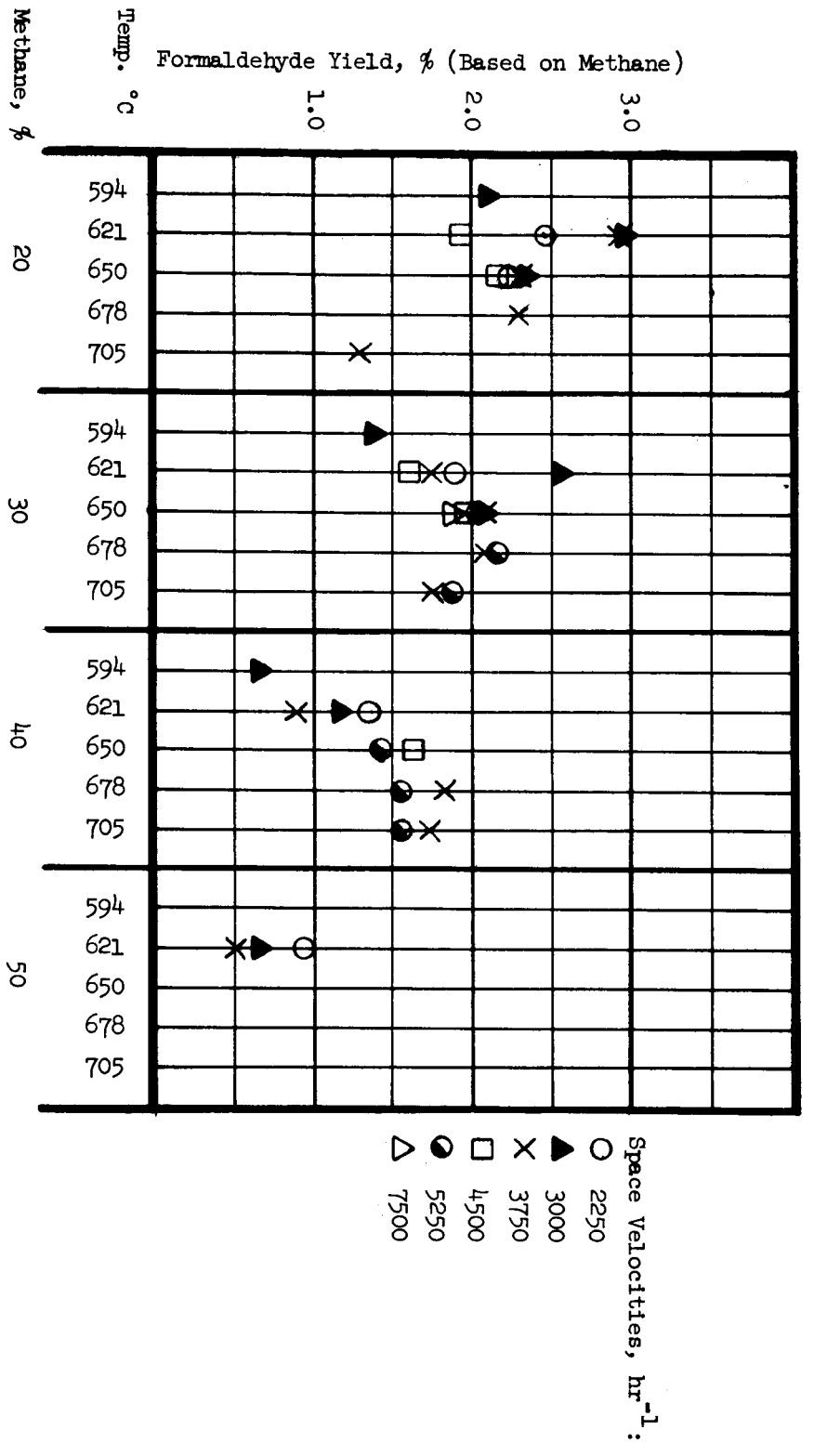

Figure 2 SUMMARY OF EXPERIMENTAL DATA WITH AIR - METHANE MIXTURES

From the experimental yields obtained with air - methane mixtures, the absolute amounts of formaldehyde produced in this system have been calculated for various methane concentrations at 650°C. Figure 3 shows formaldehyde yields and formaldehyde production in one day (24 hours) for the highest space velocity investigated so far (7500 hr^{-1}). The maximum rate of formaldehyde is achieved with approximately 35% methane in the feed gas. Using this reactor with a 40 cm^3 reaction zone, up to 53 - 54 g. of formaldehyde can be produced per 24 hours at the reaction temperature of 650°C and space velocity of 7500 hr^{-1}.

2. Oxidation of Methane Using Ozonized Oxygen

Tests on the use of ozonized oxygen or ozonized air for the oxidation of methane to formaldehyde were conducted using reaction beds packed either with metal salts or porcelain Berl saddles coated with potassium tetraborate. In these experiments, oxygen or air was passed through an ozonator; then the ozonized oxygen or air was premixed with measured amounts of methane and the mixture passed through a 23 mm I.D. Vycor glass reactor containing a heated reaction zone packed with solid particles. The concentration of ozone was determined by a standard iodometric titration method. Feed gas composition, ozone concentration, reaction temperature, and space velocity were varied during the experimentation; in general, the testing pattern was designed to optimize the absolute production of formaldehyde, while keeping the O_3 levels as low as possible.

2.1 Metal Salts

Tests with metal salt catalyst were performed in both horizontal and vertical reactors. In the horizontal reactor, the catalyst

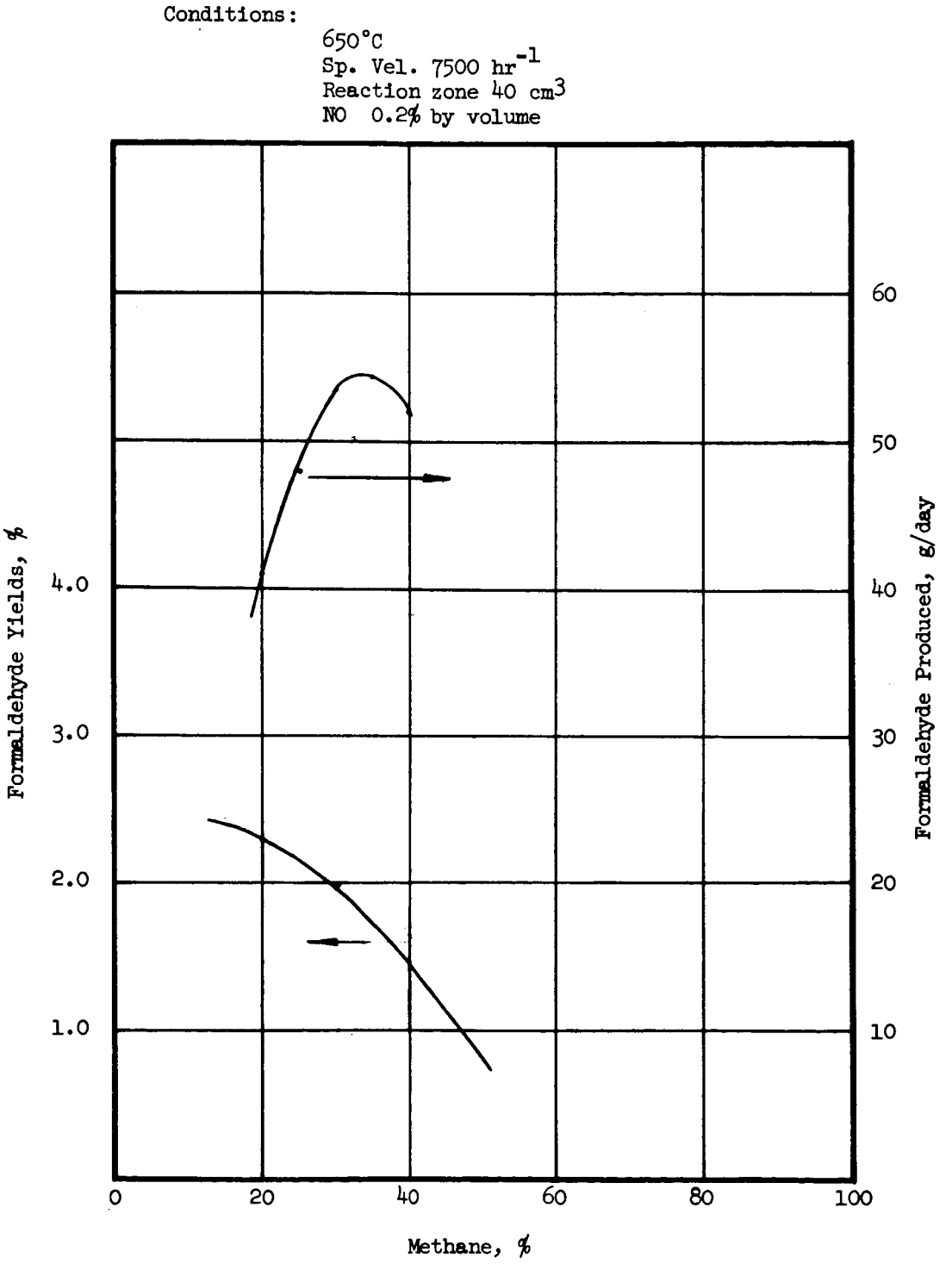

Figure 3 FORMALDEHYDE YIELDS AND TOTAL PRODUCTION AT 650°C

was in the form of extruded pellets. It was placed in a vitreous silica boat, 6 inches long, 1/2 inch wide, and 1/2 inch deep; the feed gas was passed over this heated boat containing the catalyst. Using this arrangement, the highest formaldehyde yields observed were 0.67% of the methane at 150°C, total flow rate of 1000 cc/min, and a feed gas containing 5% methane and 1% ozone in the oxygen. Higher methane concentrations resulted in a sharp decrease in the formaldehyde yield.

In vertical reactors, the reaction gases passed through a continuous bed of metal salt pellets instead of a layer of particles contained in a silica boat. Experiments were performed at reaction temperatures ranging from 150°C to 650°C, space velocities up to 12,000 hr^{-1}, and feed gas consisting of 53% CH_4 and 47% O_2 containing ozone in concentrations up to 1% of the total feed. The yields of formaldehyde were generally low, ranging from traces to 0.33% of the methane used.

In separate experiments, it was determined that the metal salt catalyst destroys the ozone. When oxygen containing 1% ozone is passed through the bed, 85 - 90% of ozone is destroyed even at room temperature, while all the O_3 is decomposed at 205°C.

The general conclusion was that this catalyst is insufficiently active to produce significant formaldehyde yields.

2.2 Potassium Tetraborate

Partial oxidation of methane to formaldehyde by ozonized air in the presence of potassium tetraborate surfaces was investigated in a single

pass reactor. The heated reaction zone was packed with 40 cm^3 of 6 mm porcelain Berl saddles which were coated with potassium tetraborate. Air, ozonized to give ozone concentrations in the feed gas ranging from 0.1% to 0.8%, was premixed with methane and passed through the reaction bed with space velocities ranging up to 7500 hr^{-1}. Formaldehyde formation was investigated in the temperature range of 315°C - 705°C and feed gas mixtures containing from 17% to 40% methane.

The maximum formaldehyde production was obtained at temperatures of 650 - 705°C. At these temperatures, the yields of formaldehyde depend on the ozone concentration in the feed gas; for instance, with 30% methane and 0.1% O_3 in feed, the observed yields are approximately 0.4%; with 0.3% O_3, yields increase to 0.8%; and with 0.6% O_3 yields reach 1.1% of the methane in feed. However, the high ozone concentrations can be produced in the presently used ozonator only at low space velocities. At space velocities of approximately 7500 hr^{-1}, the ozone concentration conveniently achieved is in the neighborhood of 0.3%. Although this ozone concentration does not produce the highest formaldehyde yields, the total amounts of formaldehyde produced are higher than in experiments with higher O_3 concentrations but lower space velocities.

Under given conditions, the highest formaldehyde yields, were observed at low methane concentrations in the feed gas. Although an increase in the methane concentration decreases the formaldehyde yield, the absolute amounts of formaldehyde produced may remain the same or even increase. Figure 4 shows formaldehyde yields and total production as a function of methane concentration at a reaction temperature of 705°C, space velocity of 7500 hr^{-1}, and ozone concentration in feed 0.3%. With this reactor, a formaldehyde production reaching 21-23 g/day was achieved with 20% - 40% methane in feed gas.

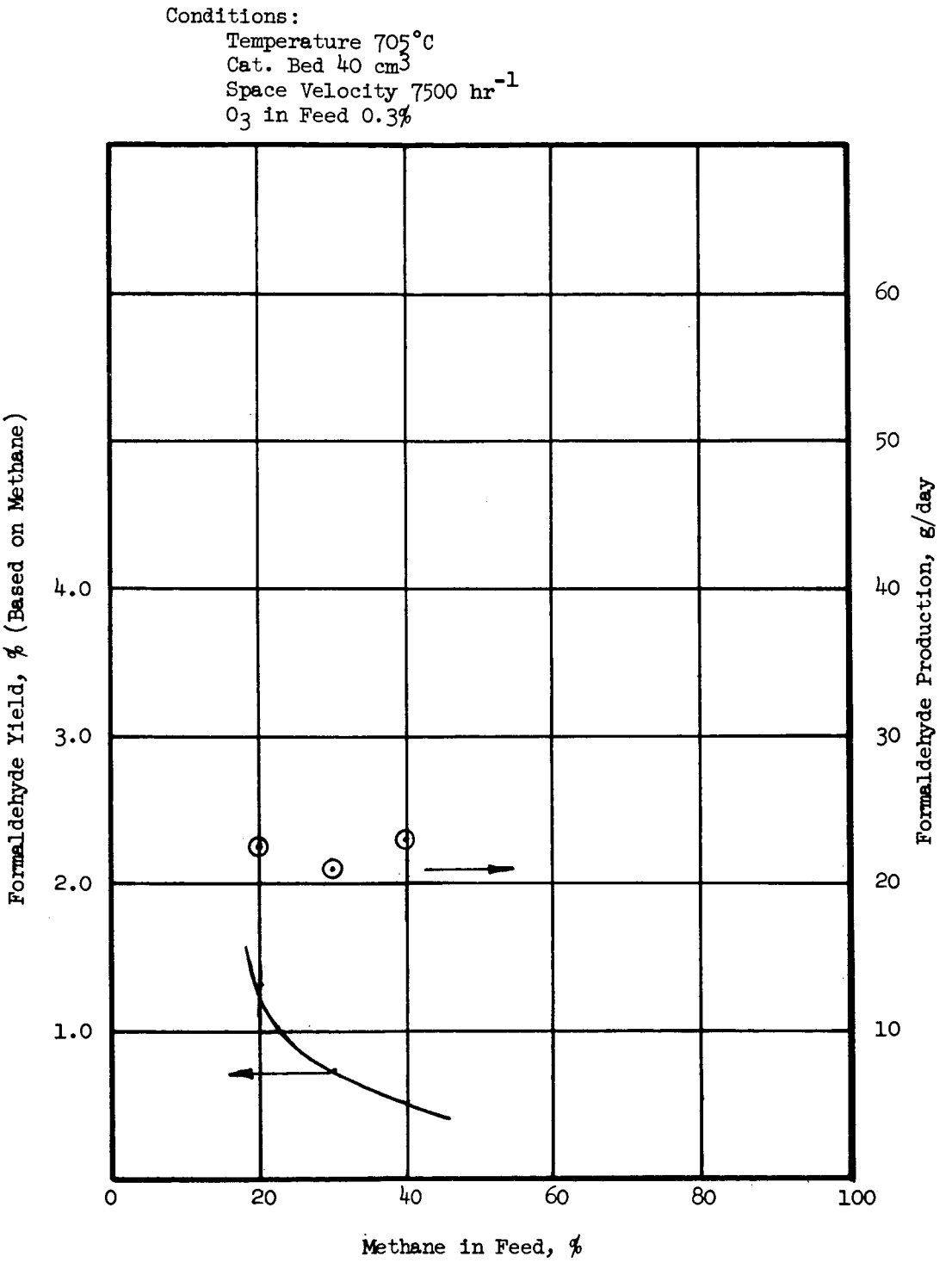

Figure 4 FORMALDEHYDE PRODUCTION USING OZONIZED AIR

When air is passed through the ozonator, some nitrogen oxides are formed. The analysis of these nitrogen oxides is difficult because ozone interferes. Nevertheless, it was established that the concentrations of nitrogen oxides are in the neighborhood of 100 ppm. This amount of nitrogen oxides has no significant effect on the formaldehyde yields. A run where air was passed through an ozonator was compared with another run in which oxygen alone was ozonized and then mixed with nitrogen and methane to obtain a feed composition identical to the first run. Although no nitrogen oxides were produced in the second run, the formaldehyde yields were the same in both runs.

3. Condensation of Formaldehyde

Preliminary experiments on the condensation and separation of formaldehyde from the reaction product were conducted to condense paraformaldehyde by cooling. A 3/8 inch diameter glass tube (12 turns in the form of a 1-1/4 inch diameter helical coil) was connected to the exit of the reactor producing formaldehyde. With air cooling, approximately 63% of the formaldehyde condensed in the coil; however, when a cooling tube containing dry ice-acetone was inserted into center of the helical coil, approximately 97% of formaldehyde was condensed. In both instances, however, water condenses with formaldehyde and the condensate is essentially an aqueous formaldehyde solution with but little solid paraformaldehyde being deposited on the walls.

Condensation experiments were repeated by passing dry air over heated and vaporized paraformaldehyde. The air became essentially saturated with formaldehyde vapor; however, on cooling it condensed primarily as a liquid solution.

These results indicated that cooling alone does not condense formaldehyde in the form of solid paraformaldehyde. Further investigation of the phenomena of paraformaldehyde condensation, the best conditions for it, and possible catalytic surfaces will be conducted.

Future Activities

The conversion of methane to formaldehyde using nitrogen oxide gaseous catalysts will be further studied in single pass systems with oxygen - methane mixtures and reaction beds packed with solid materials other than potassium tetraborate, i.e., related tetraborates and other alkaline salts. Recirculating systems will be investigated to obtain the maximum formaldehyde production.

Further experiments will be conducted with ozonized oxygen and ozonized air using the same alternate materials. Also, a recirculating system will be operated to determine the conditions for maximum formaldehyde production with ozone.

Experiments for the separation and purification of formaldehyde from the reaction gases in the form of solid paraformaldehyde will be continued. Different condensation temperatures and surfaces will be investigated both for vapors from solid paraformaldehyde and for the product gases from the experimental reactors.