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**CATALYST AND PROCESS DEVELOPMENT FOR
SYNTHESIS GAS CONVERSION TO ISOBUTYLENE**

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CATALYST AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

DOE CONTRACT NO. 90PC90045

TEXAS A&M RESEARCH FOUNDATION PROJECT NO. 6722

Quarterly Report

Report Period: 01/01/93 to 3/31/93

PROJECT OBJECTIVES

The objectives of this project are to develop a new catalyst, the kinetics for this catalyst, reactor models for trickle bed, slurry and fixed bed reactors, and simulate the performance of fixed bed trickle flow reactors, slurry flow reactors, and fixed bed gas phase reactors for conversion of a hydrogen lean synthesis gas to isobutylene.

JUSTIFICATION FOR THE PROJECT

Isobutylene is a key reactant in the synthesis of methyl tertiary butyl ether (MTBE) and of isooctanes. MTBE and isooctanes are high octane fuels used to blend with low octane gasolines to raise the octane number required for modern automobiles. The production of these two key octane boosters is limited by the supply of isobutylene. MTBE when used as an octane enhancer also decreases the amount of pollutants emitted from the exhaust of an automobile engine.

Hydrogen-rich synthesis gas has been converted to isobutylene using a zirconia based catalyst. However, the productivity and yields are low, and the ability of the catalyst to convert a hydrogen-lean synthesis gas to isobutylene with high productivity and yields, and without excessive deactivation is unknown.

PROPOSED PROCESS

A hydrogen-lean synthesis gas with a ratio of H_2/CO of 0.5 to 1.0 is produced from the gasification of coal, lignite, or biomass. This hydrogen-lean synthesis gas can be processed in a "shift reactor" with steam to convert the hydrogen-lean synthesis gas to a hydrogen-rich synthesis gas. But, this processing step is inefficient and consumes considerable energy. If the hydrogen-lean synthesis gas could be converted directly to isobutylene, a significant increase in

process efficiency will be the result. We envision a reactor system and catalyst that will selectively and efficiently convert hydrogen-lean synthesis gas to isobutylene. The catalyst, based on past work published in the literature, will most likely be zirconia or thoria based, and will contain components to promote the water-gas shift reaction and increase the selectivity of isobutylene.

GOALS FOR THE QUARTER

Prepare a cerium zirconia by the precipitation method, and obtain surface area and XRD patterns for catalysts prepared in October. Synthesize zirconium oxides by sol-gel method, and then wash with various acids, including HCl, H₂SO₄, HNO₃, silicic acid, etc. The purpose of these experiments is to compare effects of different acid treatment on the activity of catalysts. Continue the trickle bed experiments, prepare a precipitated cerium-zirconia catalyst, evaluate the effect of acid treatment on the catalyst prepared by the sol gel method, and continue the synthesis and attempted pillaring of a layered zirconate.

Continue trickle bed reactor experiments at 396°C; Investigate the effects of space velocity, oil flow rate and CO/H₂ ratio on CO conversions and selectivities; Investigate the effect of using 0.5% H₂S in decalin. Evaluate the performance of the ceria/zirconia catalysts.

ACCOMPLISHMENTS FOR THE QUARTER

Filing of necessary reports

The quarterly report for the period of October 1, 1992 to December 31, 1992 was filed and approved. Monthly reports for December, 1992, January and February, 1993 were also filed.

Experimental Program

The six main accomplishments for the quarter are the following: (1) activity testing with the 7% (wt.) Ce-ZrO₂, (2) activity testing the same catalyst with CO from an aluminum cylinder, (3) preparation of ZrO₂ by heating zirconyl nitrate, (4) preparation of an active zirconia prepared by a modified sol gel procedure and evaluation of the catalytic activity of a commercial zirconia and the catalysts prepared by the sol gel procedure, (5) determining the effect of separator temperatures and oil flow rate on the performance of a trickle bed reactor, and (6) calculation of the equilibrium composition of the C₂ to C₅ olefins, and initiation of the development of a macrokinetic model. The details of each of these accomplishments are discussed below.

Experiments over 7% (wt) Ce-ZrO₂

Runs C7A through C7J were conducted over the 7 wt.% Ce-ZrO₂. The catalyst was pretreated for 18 hours at 400 °C under flowing nitrogen (100 cm³/min). Tables 1 and 2 contain the conversions and hydrocarbon distributions for these runs. The conversion obtained on this catalyst was the highest of any tested thus far in BR#1 (figure 1). A conversion of ~51% was achieved at 450 °C and 120 second space time (run C7I). Methane production rate was somewhat lower than other high conversion catalysts (figure 2) while isobutylene production remained about the same (figure 3). Total hydrocarbon production increased slightly (figure 4). The ratio of isobutane to isobutylene increased with increasing space time and temperature. Methane was still the dominant product formed at all conditions (28-60 wt%). The cerium catalyst produced more C₂ and C₃ hydrocarbons than previous catalysts which would account for the increase in total hydrocarbon production even though methane production rate was lower. The percentage of C₅+ in the total hydrocarbons was lower on average (5-27%) than found for other catalysts. The trend of decreasing dimethyl ether with space time and temperature was also found for this catalyst. The increase in methane with temperature was expected. A shift in product distribution (toward methane) occurred after returning to 400 °C from higher temperatures. This behavior was found previously in the 1.6% Na, 10.3% Ti, ZrO₂ (HT) catalyst. It seems that only the product distribution is changed while the conversion remains relatively constant. 5) An aluminum CO cylinder was ordered to try and eliminate any contamination because of iron carbonyls.

Experiments over 7% (wt.) Ce-ZrO₂ using Aluminum CO Cylinder

Runs ACOC7A-ACOC7C were performed using the aluminum CO cylinder. The aluminum CO cylinder was used in order to eliminate any catalyst poisoning effect because of iron carbonyls. The reactor was packed with fresh catalyst from the same 7 wt.% cerium batch that was used in the catalyst studies described above. The catalyst was pretreated under flowing nitrogen (100 cm³/min) at 400 °C for 15 hours and 35 minutes. The results are shown in tables 3 and 4. Figures 5-8 compare these runs to runs using CO from a iron cylinder (runs C7A-C7J). The conversion is higher using CO from the aluminum cylinder, but the increase in conversion was seen only as an increase in methane production (figure 2) while isobutylene production rate remained the same (figure 3). Total hydrocarbon production rate was higher because of the increase in methane production. This result was not expected because Dr. Ekerdt, at the

University of Texas at Austin, attributed methane formation to carbonyls poisoning the catalyst. His hypothesis may be based on work performed at much lower conversions, however. Because methane is the favored product at higher temperatures, perhaps the only way to decrease methane production is to reduced reaction temperature. This may lead to increased oxygenate production. Hopefully, the experiments with 1.0% H₂S/H₂ mixture will give reduced methane while not severely reducing catalyst activity.

Preparation of ZrO₂ by Heating Zirconyl Nitrate

A zirconia sample was prepared by heating zirconyl nitrate {ZrO(NO₃)₂·xH₂O} powder. A paper¹ described preparing a tetragonal zirconia powder by this method. Also, other authors² prepared tetragonal zirconia by heating Zr(SO₄)₂·4H₂O. This sample was mesoporous ($r_p=80$ Å) and had a surface area 90 m²/g. The details of the sample preparation (from the reference) is as follows: Zirconyl nitrate powder was placed in an oven and heated to 100 °C to drive off NO₂ gas. When the brown gas ceased to be visible the powder was heated to 500 °C for 1½ hours to yield crystalline tetragonal ZrO₂. In our preparation the powder remained at 100 °C for 2 hours (could not see gas evolving inside muffle furnace). Then the temperature was raised to 500 °C and left there for 7 hours. The sample was weighed after being at 500 °C for 4 hours. The weight loss was less than what was expected so the sample was calcined for an additional 3 hours. Very little (<0.005 g) loss in weight was observed with additional calcining. This weight loss could be the result of material lost during transfer. The final weight of the sample indicates that the x in the formula for zirconyl nitrate is 5. The sample prepared in our lab has a surface area of 37 m²/g and a bimodal pore size distribution with pores of 30-40 Å and 150-200 Å. Samples that are calcined for shorter times may give higher surface area zirconia. The bulk density of this sample is 1.66 g/cm³, which is in between that obtained for catalysts prepared by the hydrothermal and precipitation methods. The XRD pattern will be obtained by next month.

This sample was prepared with the hope of obtaining a catalyst with larger pores. The

¹Evans, P.A., Stevens, R., and Binner, J.G.P., "Quantitative X-ray Diffraction Analysis of Polymorphic Mixes of Pure Zirconia," *Br. Ceram. Trans. J.* 83(2), 39-43 (1984).

²Platero, E.E., and Mentrui, M.P., "Preparation and characterization of catalytic zirconia with temperature-resistant surface area," *Mater. Lett.* 14, 318-321 (1992).

precipitation method usually gives a catalyst with a single maximum in pore diameter at 30-40 Å. The hydrothermal method results in zirconia with pores in the 150 Å range. Catalysts prepared by the hydrothermal method showed a very high selectivity for iso-C₄ compounds, but lower activity than catalysts prepared by precipitation. Preparing zirconia by heating zirconyl nitrate may be a bridge between the precipitation and hydrothermal methods, but catalyst testing is required.

Preparation of ZrO₂ by Modified Sol Gel Procedure

Zirconium oxide was synthesized by modified sol-gel method as follows:

- a. Dissolve tetramethylammonium hydroxide (CH₃)₄NOH in methanol to get 10 wt% methanol solution of TMAOH.
- b. Slowly add zirconium isopropoxide Zr(OC₃H₇)₄ into the TMAOH solution to get a clear soluble intermediate. Add acetone if necessary.
- c. Hydrolyze the intermediate by adding into acetone-water solution. Continuously stir the slurry.
- d. Filter in absence of acetone or water wash, and dry in vacuum overnight.
- e. Calcine the catalyst at 500 °C for 4 hours. About 25 grams of catalysts were recovered after calcination. This catalyst is referred to ZrO₂ (sol-gel).

Chemicals used in the synthesis are listed in Table 5.

ZrO₂ (sol-gel) was evaluated using the CDS bench unit, and showed promising results as illustrated in Table 5. Compared with the commercial ZrO₂ produced by Harshaw, ZrO₂ (sol-gel) shows a much higher percentage of i-C₄H₈ in C₄ hydrocarbons. The weight fraction of C₄ in hydrocarbons is also higher. However, the activity of the precipitated zirconia is still greater than that of the zirconia prepared by the sol gel method. This is the most active sol-gel catalyst synthesized so far.

Trickle Bed Reactor Experiments

Experiments conducted in the trickle bed reactor indicated that mass transfer resistances were occurring in regard to the propagation of the hydrocarbon chain. A greater amount of propylene is produced in the trickle bed than with the fixed bed gas phase reactor. The separator temperatures and oil flow rates were shown to have minor effects on the product distribution. Figures 9 through 12 illustrate the effects of the oil flow rate and the separator temperature on

the product distribution.

Equilibrium Calculations and Macrokinetic Model

The equilibria product distribution gives us an indication of the thermodynamic barrier of achieving high selectivity of a given product. The equilibrium distribution of C₂ to C₅ olefins at T = 700 K and P = 70 atm has been calculated using the following data and equations.

1. $10 \text{ CO} + 5 \text{ H}_2 \rightarrow \text{i-C}_5\text{H}_{10} + 5 \text{ CO}_2$ $x_1, \Delta G_1^0 = -6.73, K_1=126.230$
2. $8 \text{ CO} + 4 \text{ H}_2 \rightarrow \text{i-C}_4\text{H}_8 + 4 \text{ CO}_2$ $x_2, \Delta G_2^0 = -5.29, K_2=44.8315$
3. $6 \text{ CO} + 3 \text{ H}_2 \rightarrow \text{C}_3\text{H}_6 + 3 \text{ CO}_2$ $x_3, \Delta G_3^0 = -3.72, K_3=14.5016$
4. $4 \text{ CO} + 2 \text{ H}_2 \rightarrow \text{C}_2\text{H}_4 + 2 \text{ CO}_2$ $x_4, \Delta G_4^0 = -0.2, K_4=1.15463$

where x_j is the conversion of CO for by reaction j.

When one considers the magnitude of Gibbs energy for C₅, the effect of pressure, and the fact that the mechanism for chain growth is similar, except for C₄, for the hydrocarbons, the cause of low selectivities for the butenes is readily apparent. However, it is well recognized that production of hydrocarbons from synthesis gas has a yield based on CO of 50% when CO₂ is produced, i.e. half of the CO consumed is converted to hydrocarbons.

The above data were combined with the following equations and the set were solved for the equilibrium compositions.

$$n_{\text{CO}} = n_{\text{CO}}^0(1-x_1-x_2-x_3-x_4)$$

$$n_{\text{H}_2} = n_{\text{H}_2}^0 \left(1 - \frac{x_1+x_2+x_3+x_4}{2} \right) = n_{\text{CO}}^0 \left(1 - \frac{x_1+x_2+x_3+x_4}{2} \right)$$

$$n_{\text{CO}_2} = n_{\text{CO}}^0 \left(\frac{x_1+x_2+x_3+x_4}{2} \right)$$

and

Therefore,

$$n_{C_1} = n_{CO}^0 \frac{x_1}{10}$$

$$n_{C_2} = n_{CO}^0 \frac{x_2}{8}$$

$$n_{C_3} = n_{CO}^0 \frac{x_3}{6}$$

$$n_{C_4} = n_{CO}^0 \frac{x_4}{4}$$

$$n_T = n_{CO}^0 \left(2 - \frac{9x_1}{10} - \frac{7x_2}{8} - \frac{5x_3}{6} - \frac{3x_4}{4} \right)$$

$$K_1 = \frac{\left(2 - \frac{9x_1}{10} - \frac{7x_2}{8} - \frac{5x_3}{6} - \frac{3x_4}{4} \right)^9}{P} \frac{\left(\frac{x_1}{10} \right) \left(\frac{x_1 + x_2 + x_3 + x_4}{2} \right)^5}{(1 - x_1 - x_2 - x_3 - x_4)^{10} \left(1 - \frac{x_1 + x_2 + x_3 + x_4}{2} \right)^5}$$

$$K_2 = \frac{\left(2 - \frac{9x_1}{10} - \frac{7x_2}{8} - \frac{5x_3}{6} - \frac{3x_4}{4} \right)^7}{P} \frac{\left(\frac{x_2}{8} \right) \left(\frac{x_1 + x_2 + x_3 + x_4}{2} \right)^4}{(1 - x_1 - x_2 - x_3 - x_4)^8 \left(1 - \frac{x_1 + x_2 + x_3 + x_4}{2} \right)^4}$$

$$K_3 = \frac{\left(2 - \frac{9x_1}{10} - \frac{7x_2}{8} - \frac{5x_3}{6} - \frac{3x_4}{4} \right)^5}{P} \frac{\left(\frac{x_3}{6} \right) \left(\frac{x_1 + x_2 + x_3 + x_4}{2} \right)^3}{(1 - x_1 - x_2 - x_3 - x_4)^6 \left(1 - \frac{x_1 + x_2 + x_3 + x_4}{2} \right)^3}$$

The equilibrium conversions of CO by each reaction are: $x_1 = 51.31\%$, $x_2 = 30.45\%$, $x_3 = 15.43\%$, and $x_4 = 1.710\%$, and the total CO equilibrium conversion is 98.9%. Thermodynamically the conversion of CO to hydrocarbons is very favorable. A problem with the zirconia catalyst is the low activity. Equilibrium composition of the olefins is as follows.

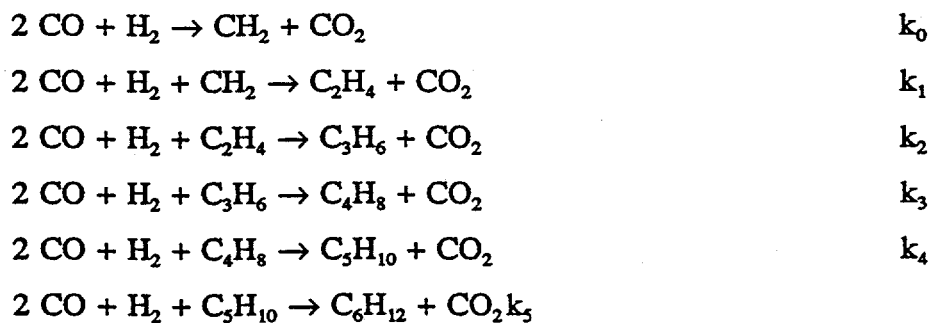
$$K_4 = \frac{\left(2 - \frac{9x_1}{10} - \frac{7x_2}{8} - \frac{5x_3}{6} - \frac{3x_4}{4}\right)^3}{P} \frac{\left(\frac{x_4}{4}\right) \left(\frac{x_1+x_2+x_3+x_4}{2}\right)^2}{(1-x_1-x_2-x_3-x_4)^4 \left(1 - \frac{x_1+x_2+x_3+x_4}{2}\right)^2}$$

| Component | Ethylene | Propylene | Isobutylene | Isopentene |
|-----------|----------|-----------|-------------|------------|
| Mole, % | 3.582 | 21.45 | 31.89 | 42.99 |
| Weight, % | 1.729 | 15.60 | 30.79 | 51.89 |

From the equilibrium calculation, the formation of C_5^+ hydrocarbons is thermodynamically favorable. This is consistent with our experimental results.

Macrokinetic model

Previous work indicated that C_4 hydrocarbons are formed via a series of consecutive reactions. These reactions can be represented as:



Assuming that $k_1 = k_2 = k_3 = \dots = k$, and $k_0 = 2k$, we obtain the distribution of C_n intermediate specie as follows

$$P_{C_n} = \frac{k_0}{k} \left[1 - e^{-k\tau} \sum_{i=1}^n \frac{(k\tau)^{i-1}}{(i-1)!} \right]$$

where $n = 1$ to 6 . This model does not account for the increase in the C_4 content observed experimentally. However, the trends are in the correct direction and adjustment of the

rate constants such that k_3 is twice or three times k_j , j equal to other reactions will result in producing a distribution similar to the experimental results.

Figure 13 is a plot of the normalized molar fractions of intermediate species as a function of dimensionless time $k\tau$ defined as

$$\tau = \int_0^t p_{CO}^a p_{H_2}^b dt$$

Figure 13 also indicates that the percentage of C_4 in hydrocarbons increases with space time, which is what we observed in our experiments (Figure 14).

SIGNIFICANT ACCOMPLISHMENTS AND CONCLUSIONS

Work has continued on examining different methods of preparing zirconia to obtain a more active and selective catalyst for synthesis of isobutylene from hydrogen lean synthesis gas. The equilibrium calculation illustrates the difficulty of obtaining a high concentration of isobutylene relative to the C_5^+ and methane production. Methane was shown in the previous quarterly to be the most favorable product. Within the hydrocarbon distribution the alkanes are the next most favorable products. Examination of the olefin equilibrium distribution shows that isopentene is the most favorable product. Since the mechanism for producing the hydrocarbons, with the exception of the C_4 s, appears to be approximately the same, the difficulty of stopping the reaction at isobutylene is apparent. In general, a lower temperature with a more active catalyst is needed to produce less methane, have higher conversions, and to decrease the pressure. By decreasing the pressure, less C_5^+ should be produced.

However, we have found several catalyst that have relatively high activities, and demonstrated the importance of the method of preparation on producing an active catalyst

GOALS FOR THE NEXT QUARTER

Continue the macrokinetic modelling and examine new catalyst formulation, which might result in producing higher active catalyst.

Table 1 - Run Results for 7.0 wt.% Ce on ZrO₂

| Run | T (°C) | P (atm) | CO/H ₂ Ratio | Space Time (sec) | CO/CO Conversion (%) | Isoynthesis Profile wt. mol. | Branched/Linear C ₄ wt. mol. | i-C ₃ H ₈ /CH ₄ wt. mol. | i-C ₃ H ₈ /C ₅ ⁺ wt. | i-C ₃ H ₈ /All C ₄ 's wt. mol. | i-C ₃ H ₈ /i-C ₃ H ₁₀ wt. |
|-----|--------|---------|-------------------------|------------------|----------------------|------------------------------|---|---|--|---|---|
| C7A | 400 | 50 | 1/1 | 30 | 13.14 0.57* | 1.746 1.065 0.072 0.043 | 1.716 1.717 0.106 0.107 | 0.616 0.176 0.015 0.004 | 0.717 0.053 | 0.558 0.561 0.009 0.009 | 7.62 |
| C7B | 400 | 50 | 1/1 | 60 | 19.98 0.04 | 1.891 1.156 0.103 0.049 | 1.852 1.848 0.078 0.076 | 0.509 0.145 0.002 0.000 | 0.572 0.012 | 0.517 0.520 0.008 0.008 | 3.89 |
| C7C | 400 | 50 | 1/1 | 90 | 26.68 0.61 | 2.107 1.262 0.126 0.085 | 1.965 1.952 0.097 0.095 | 0.367 0.105 0.022 0.006 | 0.472 0.014 | 0.425 0.429 0.008 0.008 | 1.78 |
| C7D | 400 | 50 | 1/1 | 120 | 30.61 0.11 | 2.562 1.528 0.060 0.030 | 2.073 2.054 0.014 0.013 | 0.341 0.098 0.004 0.001 | 0.406 0.016 | 0.386 0.390 0.005 0.005 | 1.33 |
| C7E | 400 | 50 | 1/1 | 150 | 35.31 0.45 | 2.673 1.598 0.028 0.021 | 2.200 2.176 0.019 0.019 | 0.286 0.082 0.010 0.003 | 0.365 0.014 | 0.332 0.337 0.008 0.008 | 0.93 |
| C7F | 425 | 50 | 1/1 | 90 | 35.81 0.35 | 2.826 1.665 0.123 0.077 | 2.439 2.409 0.029 0.029 | 0.209 0.060 0.007 0.002 | 0.366 0.012 | 0.248 0.253 0.005 0.005 | 0.54 |
| C7G | 425 | 50 | 1/1 | 120 | 40.77 0.52 | 2.179 1.276 0.157 0.091 | 2.515 2.485 0.016 0.016 | 0.120 0.034 0.008 0.002 | 0.318 0.011 | 0.186 0.190 0.004 0.004 | 0.35 |
| C7H | 450 | 50 | 1/1 | 90 | 44.58 0.41 | 1.671 0.972 0.127 0.075 | 2.674 2.647 0.061 0.059 | 0.057 0.016 0.003 0.001 | 0.281 0.013 | 0.118 0.122 0.001 0.001 | 0.19 |
| C7I | 450 | 50 | 1/1 | 120 | 51.23 0.26 | 0.935 0.542 0.039 0.022 | 2.403 2.386 0.028 0.027 | 0.021 0.006 0.000 0.000 | 0.253 0.004 | 0.078 0.080 0.001 0.001 | 0.12 |
| C7J | 400 | 50 | 1/1 | 90 | 24.77 0.17 | 1.517 0.889 0.088 0.052 | 2.415 2.395 0.028 0.028 | 0.113 0.032 0.005 0.001 | 0.571 0.001 | 0.357 0.362 0.003 0.003 | 1.02 |

* The number below each result indicates the estimated error in that result.

Table 2- Hydrocarbon Distributions (wt.) for 7 wt.% Ce on ZrO₂ (ppt.)

| Run | C7A | C7B | C7C | C7D | C7E | C7F | C7G | C7H | C7I | C7J |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Methane | 0.278 | 0.295 | 0.328 | 0.326 | 0.337 | 0.369 | 0.432 | 0.506 | 0.605 | 0.580 |
| Ethane | 0.067 | 0.059 | 0.060 | 0.048 | 0.046 | 0.050 | 0.068 | 0.085 | 0.113 | 0.071 |
| Ethylene | 0.029 | 0.024 | 0.019 | 0.018 | 0.017 | 0.017 | 0.013 | 0.011 | 0.006 | 0.010 |
| Propane | 0.042 | 0.041 | 0.032 | 0.025 | 0.027 | 0.029 | 0.037 | 0.044 | 0.055 | 0.032 |
| Propylene | 0.038 | 0.029 | 0.023 | 0.021 | 0.018 | 0.014 | 0.010 | 0.007 | 0.004 | 0.009 |
| Iso-butane | 0.023 | 0.039 | 0.067 | 0.083 | 0.103 | 0.143 | 0.148 | 0.149 | 0.105 | 0.065 |
| n-Butane | 0.015 | 0.014 | 0.016 | 0.016 | 0.018 | 0.028 | 0.032 | 0.037 | 0.034 | 0.014 |
| 1-butene | 0.024 | 0.021 | 0.019 | 0.018 | 0.017 | 0.016 | 0.012 | 0.008 | 0.004 | 0.010 |
| Iso-butylene | 0.171 | 0.150 | 0.120 | 0.111 | 0.096 | 0.077 | 0.052 | 0.029 | 0.013 | 0.066 |
| trans-2-butene | 0.044 | 0.040 | 0.036 | 0.035 | 0.033 | 0.028 | 0.021 | 0.013 | 0.007 | 0.017 |
| cis-2-butene | 0.030 | 0.028 | 0.025 | 0.024 | 0.023 | 0.020 | 0.015 | 0.009 | 0.005 | 0.013 |
| C5+'s | 0.239 | 0.262 | 0.255 | 0.274 | 0.264 | 0.211 | 0.162 | 0.103 | 0.051 | 0.115 |
| DME/HC | 0.023 | 0.016 | 0.016 | 0.013 | 0.011 | 0.007 | 0.003 | 0.001 | 0.001 | 0.020 |

Table 3 - Run Results for 7.0 wt.% Ce on ZrO₂ (Aluminum CO Cylinder)

| Run | T (°C) | P (atm) | CO/H ₂ Ratio | Space Time (sec) | CO ₂ /CO Conversion (%) | Isosynthesis Profile wt. mol. | Branched/linear r C4 wt. mol. | i-C ₄ H ₁₀ / CH ₄ wt. mol. | i-C ₄ H ₁₀ / C ₅ * wt. | i-C ₄ H ₁₀ / All C ₄ 's wt. mol. | i-C ₄ H ₁₀ / i-C ₄ H ₁₀ wt. |
|------------|-----------|------------|----------------------------|------------------------|--|-------------------------------------|--|---|---|---|---|
| ACC C7A | 400 | 50 | 1/1 | 60 | 23.12 0.31* | 1.108 0.684 0.072 0.045 | 1.618 1.616 0.065 0.065 | 0.271 0.078 0.011 0.003 | 0.371 0.021 | 0.495 0.498 0.009 0.009 | 4.02 |
| ACC C7B | 400 | 50 | 1/1 | 90 | 29.23 0.20 | 1.418 0.839 0.044 0.027 | 1.892 1.880 0.028 0.027 | 0.191 0.054 0.008 0.002 | 0.387 0.025 | 0.435 0.439 0.011 0.010 | 1.99 |
| ACC C7C | 400 | 50 | 1/1 | 120 | 33.96 0.34 | 1.567 0.919 0.073 0.047 | 1.966 1.950 0.004 0.004 | 0.158 0.045 0.012 0.003 | 0.389 0.002 | 0.373 0.377 0.009 0.009 | 1.29 |

* The number below each result indicates the estimated error in that result.

Table 4 - Hydrocarbon Distributions (wt.) for 7 wt.% Ce on ZrO₂ (ppt.)
(Aluminum CO Cylinder)

| Run | ACOC7A | ACOC7B | ACOC7C |
|----------------|--------|--------|--------|
| Methane | 0.361 | 0.447 | 0.477 |
| Ethane | 0.073 | 0.074 | 0.071 |
| Ethylene | 0.021 | 0.014 | 0.014 |
| Propane | 0.059 | 0.034 | 0.030 |
| Propylene | 0.025 | 0.016 | 0.014 |
| Iso-butane | 0.024 | 0.043 | 0.058 |
| n-Butane | 0.012 | 0.011 | 0.013 |
| 1-butene | 0.015 | 0.013 | 0.013 |
| Iso-butylene | 0.098 | 0.085 | 0.075 |
| trans-2-butene | 0.028 | 0.025 | 0.025 |
| cis-2-butene | 0.020 | 0.018 | 0.017 |
| C5+'s | 0.264 | 0.220 | 0.193 |
| DME/HC | 0.007 | 0.011 | 0.008 |

Table 5. Chemicals and their amounts in the synthesis of ZrO_2 (sol-gel)

| Chemical | Molar amount | M.W. | Purity | Weight, g | Volume, cc |
|-----------------|--------------|--------|--------------------|-----------|------------|
| $Zr(OC_3H_7)_4$ | 0.1 | 327.58 | 70% in isopropanol | 46.7971 | 44.82 |
| TMAOH | 0.03 | 91.15 | 25% in MeOH | 10.938 | - |
| CH_3OH | | 32.04 | 99.8% | 19.1415 | 24.17 |
| acetone | | 58.8 | 99.8% | | 80 |
| water | | | | | 8 |

Table 6. Comparison of the activities of commercial ZrO₂, ZrO₂ (sol-gel) and precipitated zirconia

| | commercial ZrO ₂ | ZrO ₂ (sol-gel) | ZrO ₂ (ppt) |
|--|-----------------------------|----------------------------|------------------------|
| Surface area, m ² /g | 50 | 27 | 50 |
| Temperature, °C | 450 | 450 | 450 |
| Pressure, atm | 70 | 70 | 70 |
| Space time, sec | 80 | 80 | 80 |
| CO conversion, % | 11.8 | 17.0 | 31.6 |
| Hydrocarbon distribution, wt% | | | |
| CH ₄ | 11.8 | 22.5 | 24.3 |
| C ₂ H ₄ | 1.52 | 1.01 | 2.08 |
| C ₂ H ₆ | 2.08 | 2.70 | 4.25 |
| C ₃ H ₈ | 1.23 | 1.30 | 3.26 |
| C ₃ H ₆ | 1.68 | 0.839 | 1.43 |
| C ₄ 's | 9.01 | 15.63 | 22.6 |
| C ₅ ⁺ | 72.68 | 56.02 | 42.08 |
| C ₄ hydrocarbon distribution, wt% | | | |
| i-C ₄ H ₁₀ | 30.1 | 25.2 | 39.5 |
| i-C ₄ H ₈ | 47.6 | 63.9 | 29.8 |
| n-C ₄ H ₁₀ | 6.14 | 2.48 | 10.4 |
| 1-C ₄ H ₈ | 3.26 | 2.98 | 4.79 |
| trans-C ₄ H ₈ | 7.23 | 2.07 | 8.86 |
| cis-C ₄ H ₈ | 5.66 | 3.36 | 6.66 |

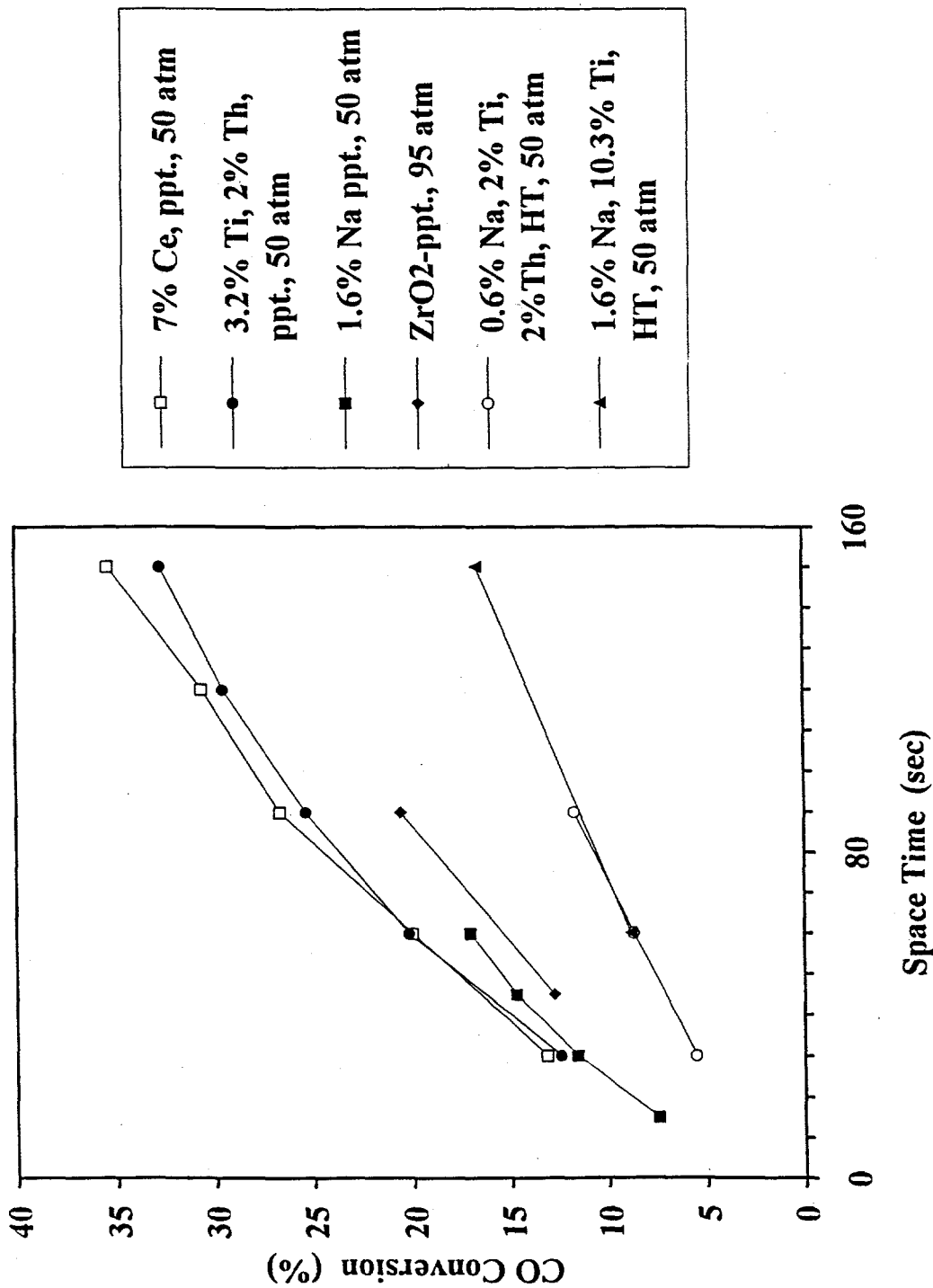


Figure 1. Changes in Conversion with Space Time at 400 °C and 1/1 CO/H₂ Ratio.

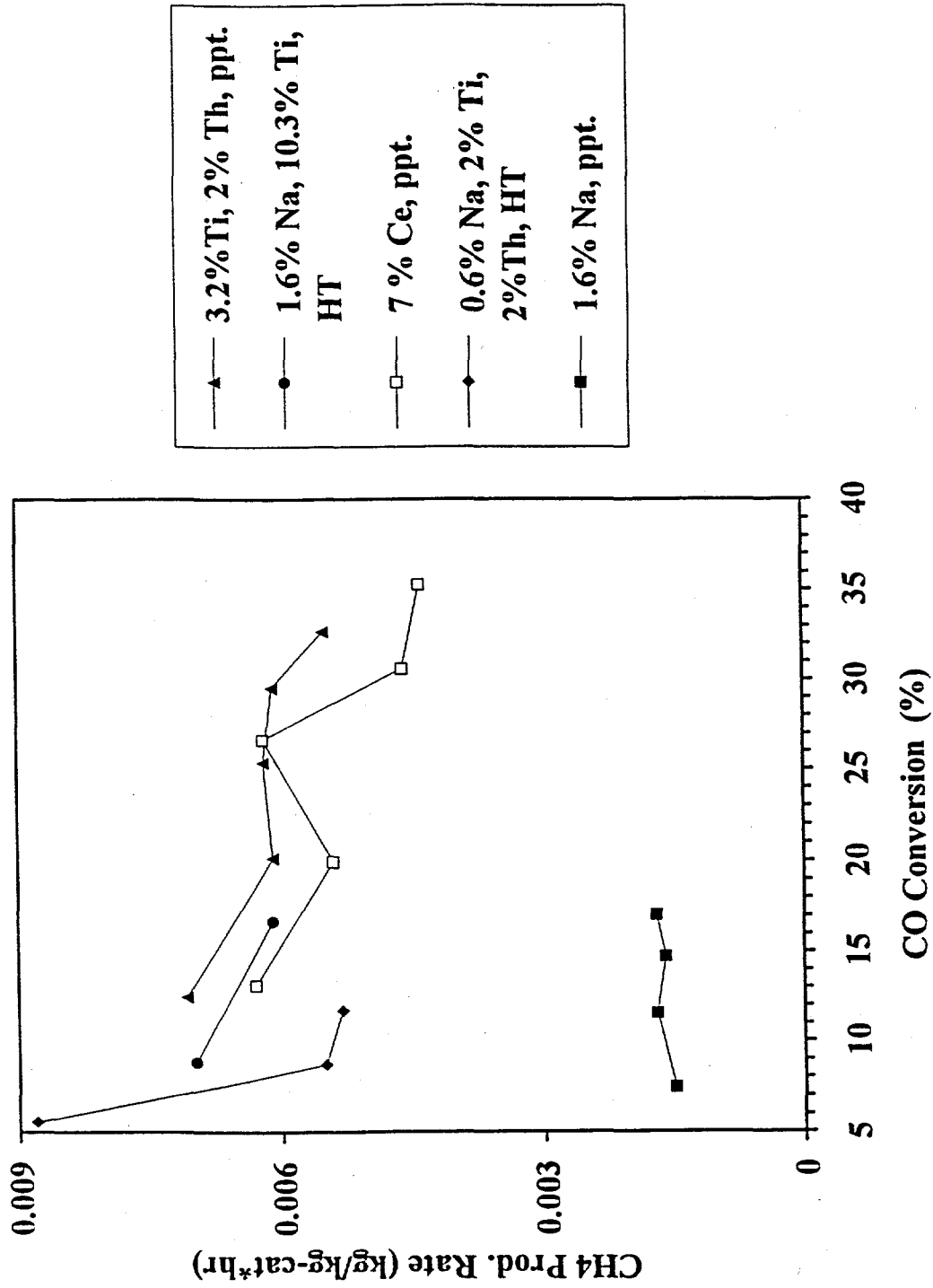


Figure 2. Methane Production Rate at 400 °C, 50 atm, and 1/1 CO/H₂ Ratio.

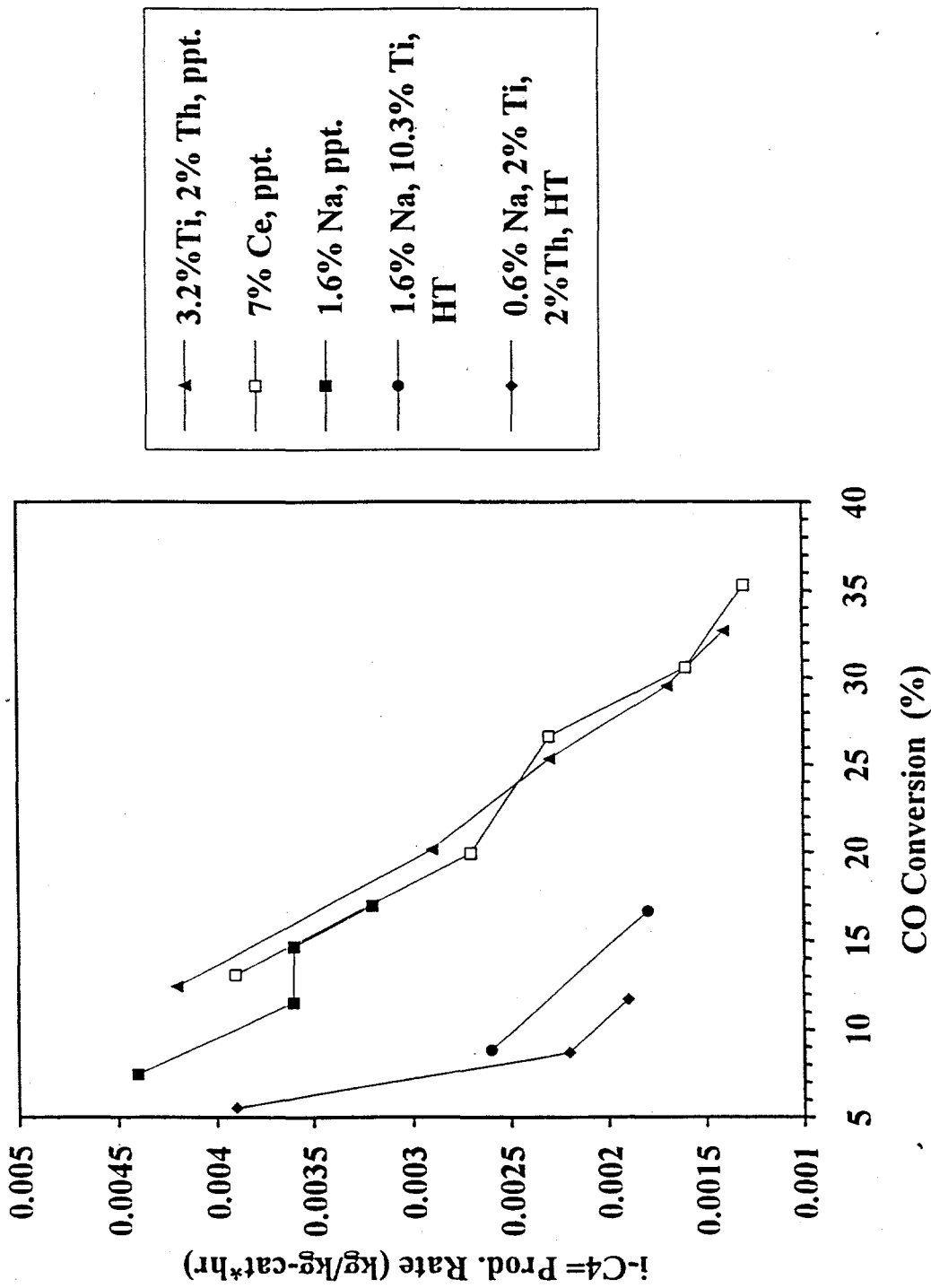


Figure 3. Isobutylene Production Rate at 400 °C, 50 atm, and 1/1 CO/H₂ Ratio.

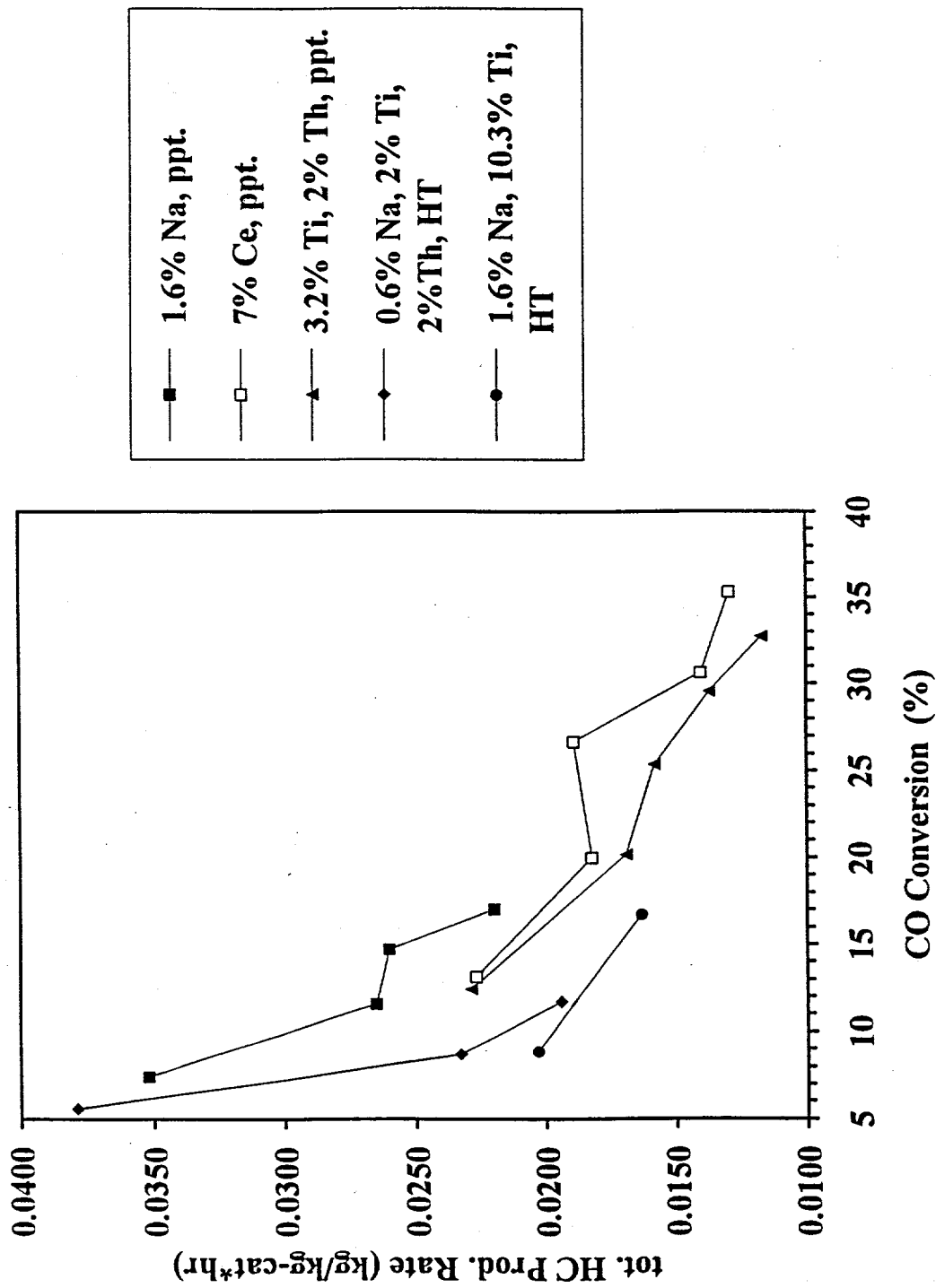


Figure 4. Total Hydrocarbon Production Rate at 400 °C, 50 atm, and 1/1 CO/H₂ Ratio.

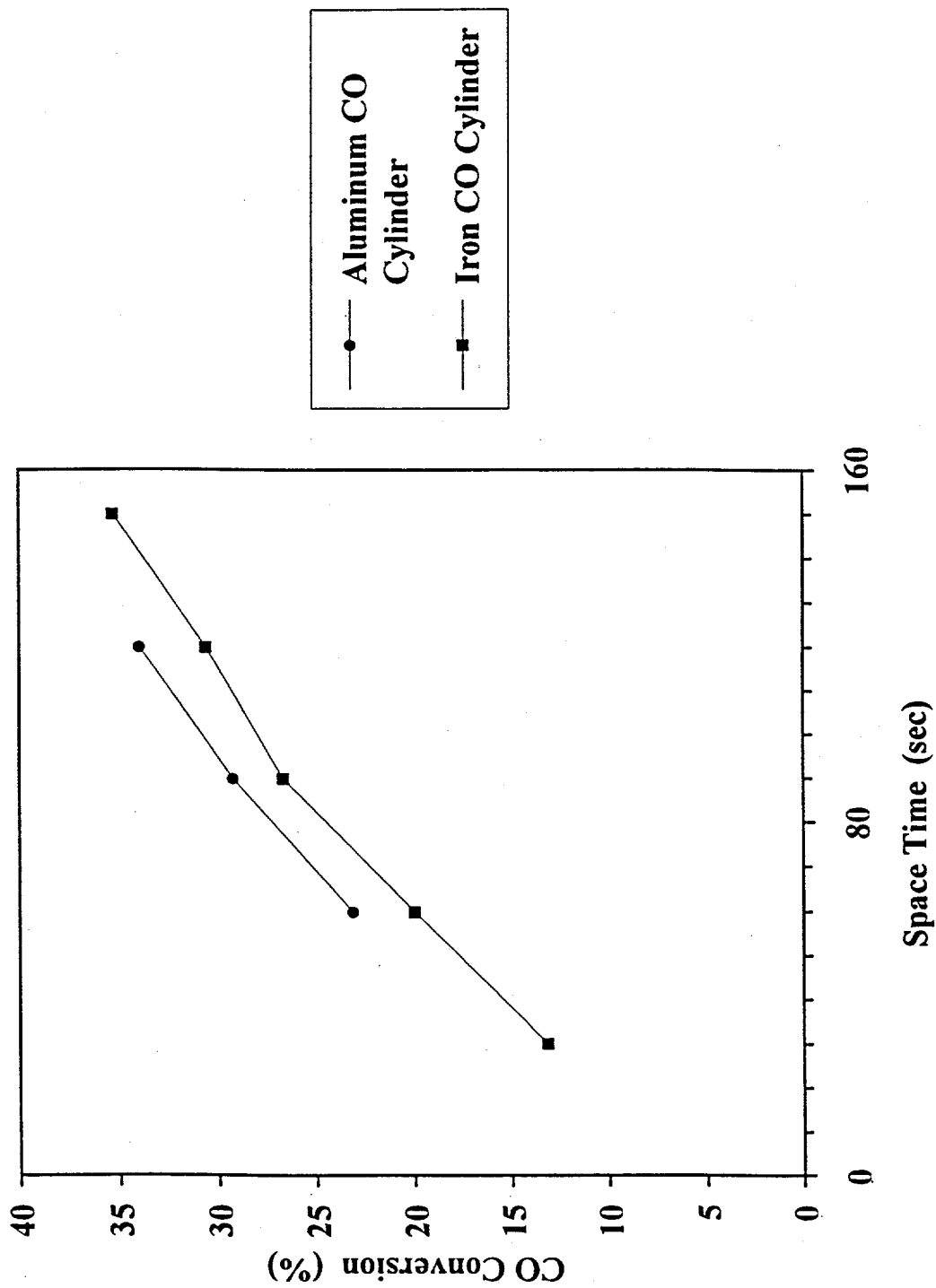


Figure 5. Changes in Conversion with Space Time and CO Cylinder at 400 °C, 50 atm, and 1/1 CO/H₂ Ratio over 7 wt.% Ce-ZrO₂ (ppt.).

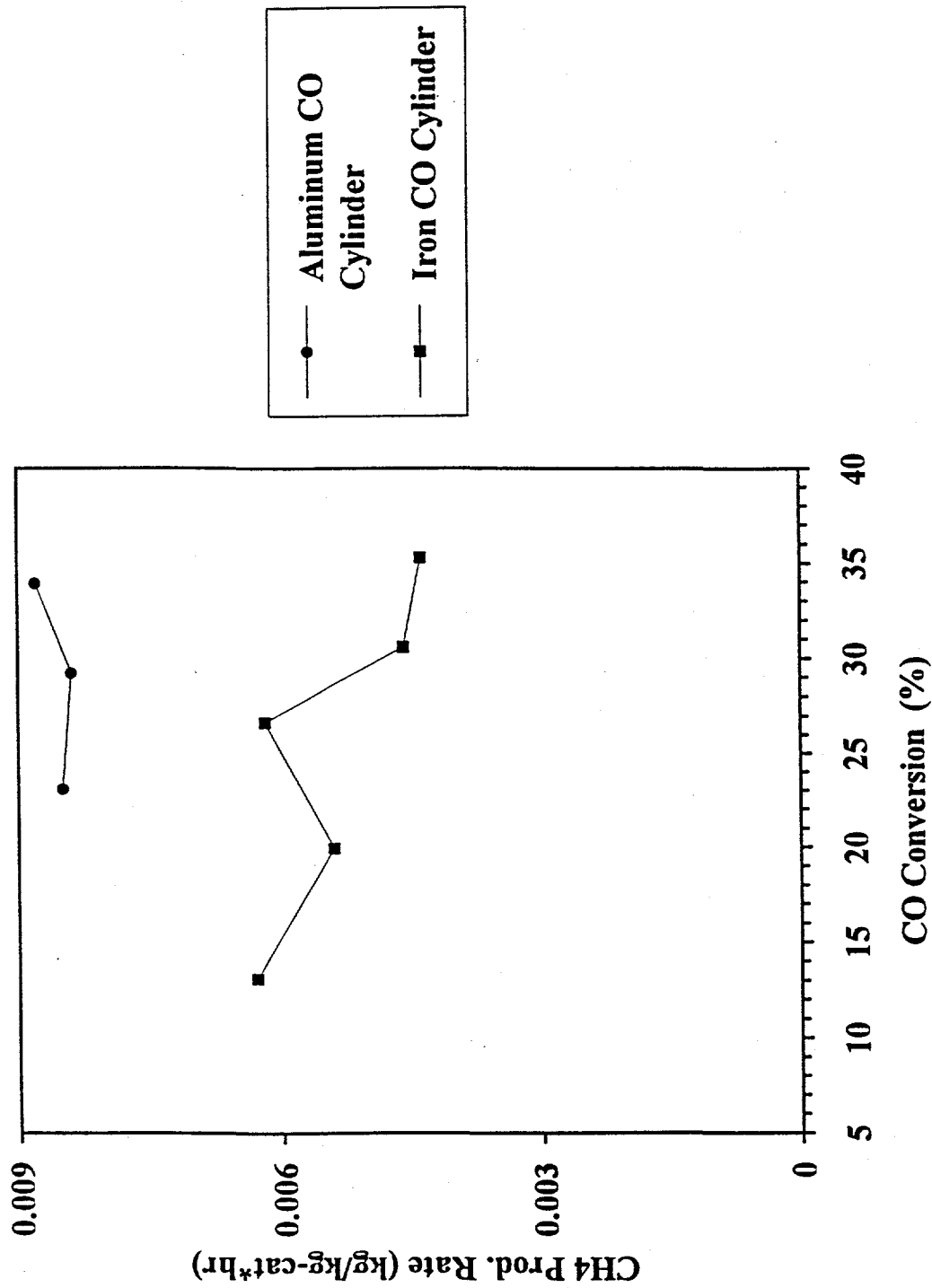


Figure 6. Changes in Methane Production Rate with Conversion and CO Cylinder at 400 °C, 50 atm, and 1/1 CO/H₂ Ratio over 7 wt.% Ce-ZrO₂ (ppt.).

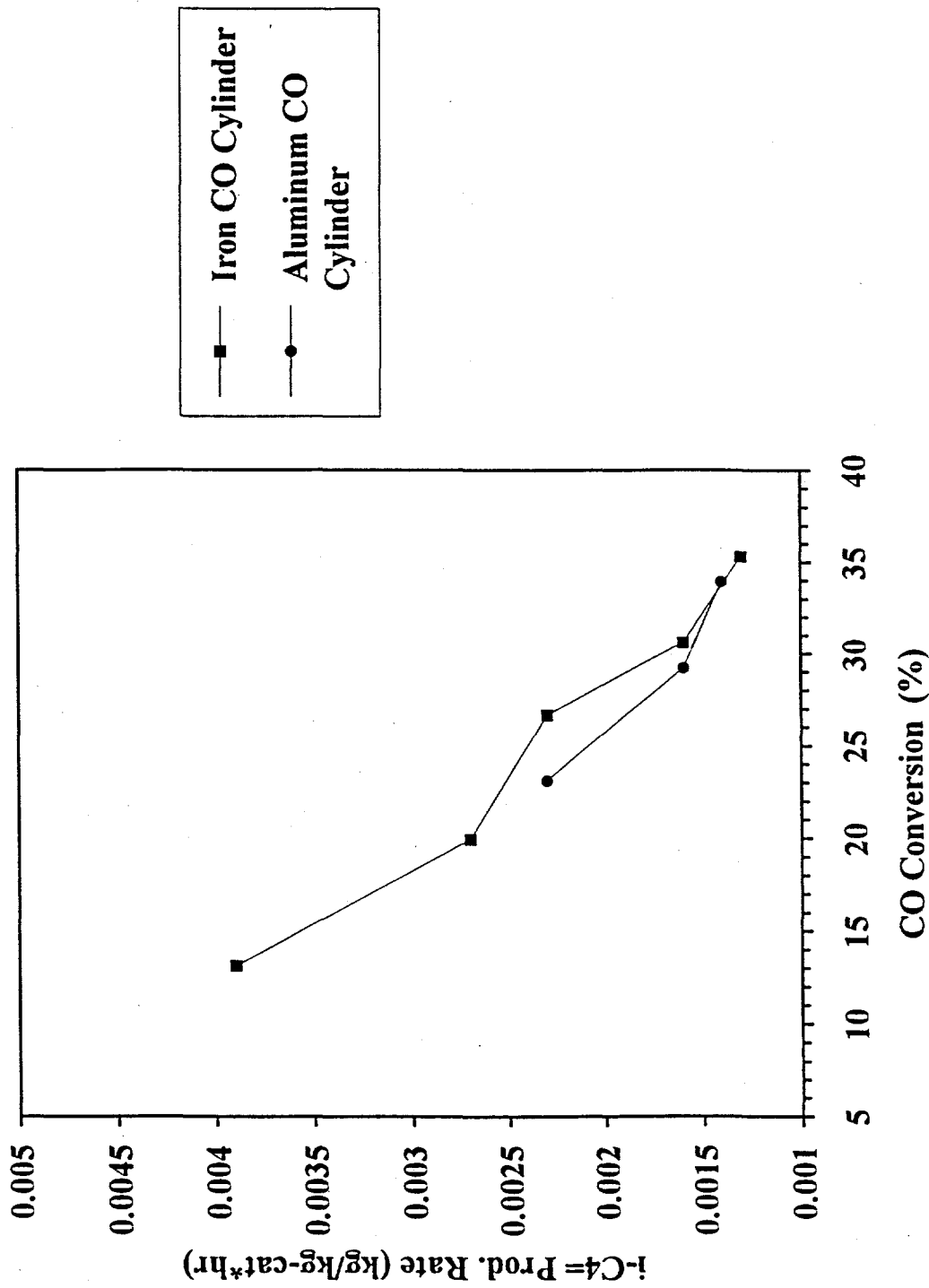


Figure 7. Changes in Isobutylene Production Rate with Conversion and CO Cylinder at 400 °C, 50 atm, and 1/1 CO/H₂ Ratio over 7 wt.% Ce-ZrO₂ (ppt.).

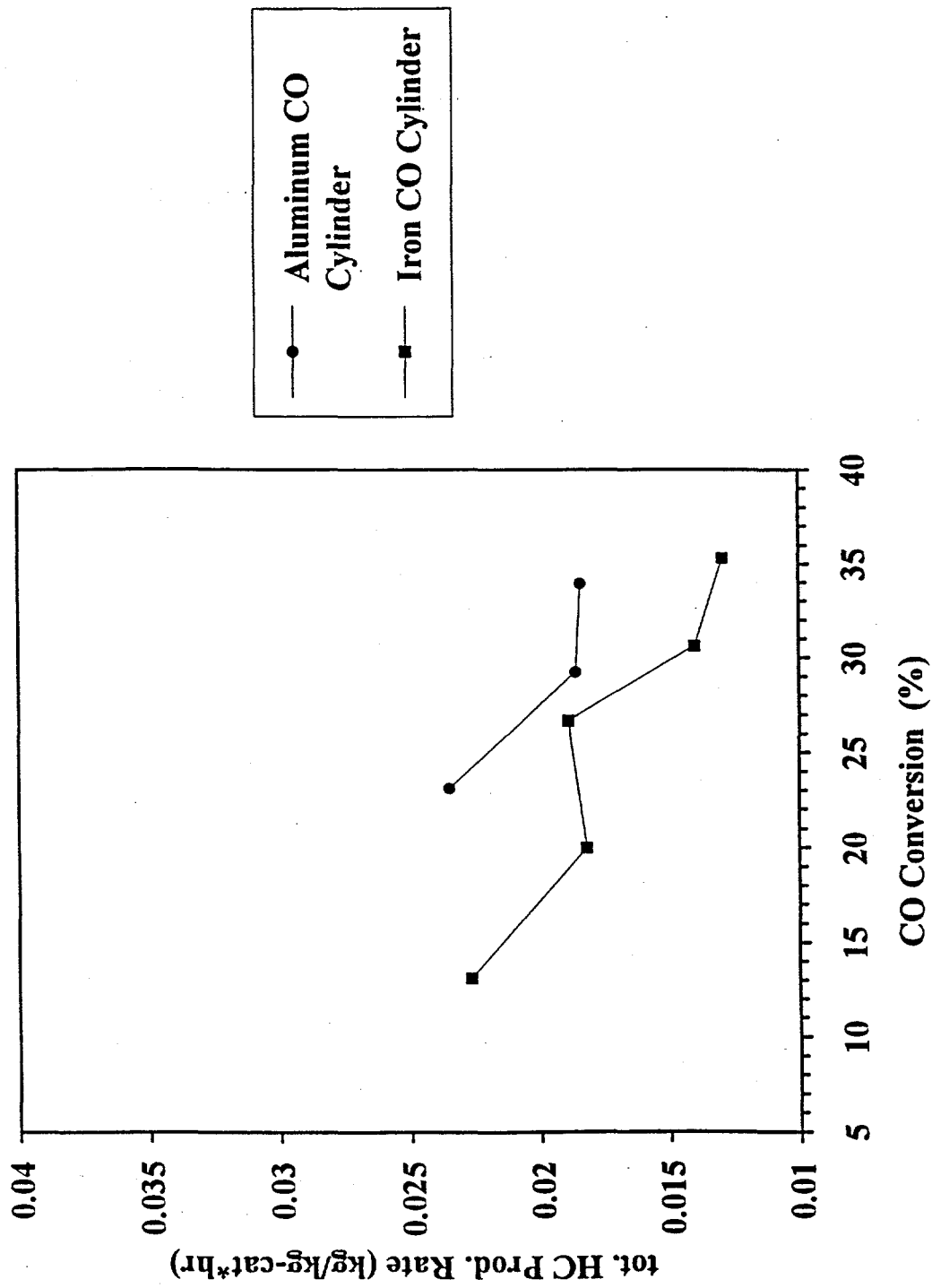


Figure 8. Changes in Total Hydrocarbon Production Rate with Conversion and CO Cylinder at 400 °C, 50 atm, and 1/1 CO/H₂ Ratio over 7 wt.% Ce-ZrO₂ (ppt.).

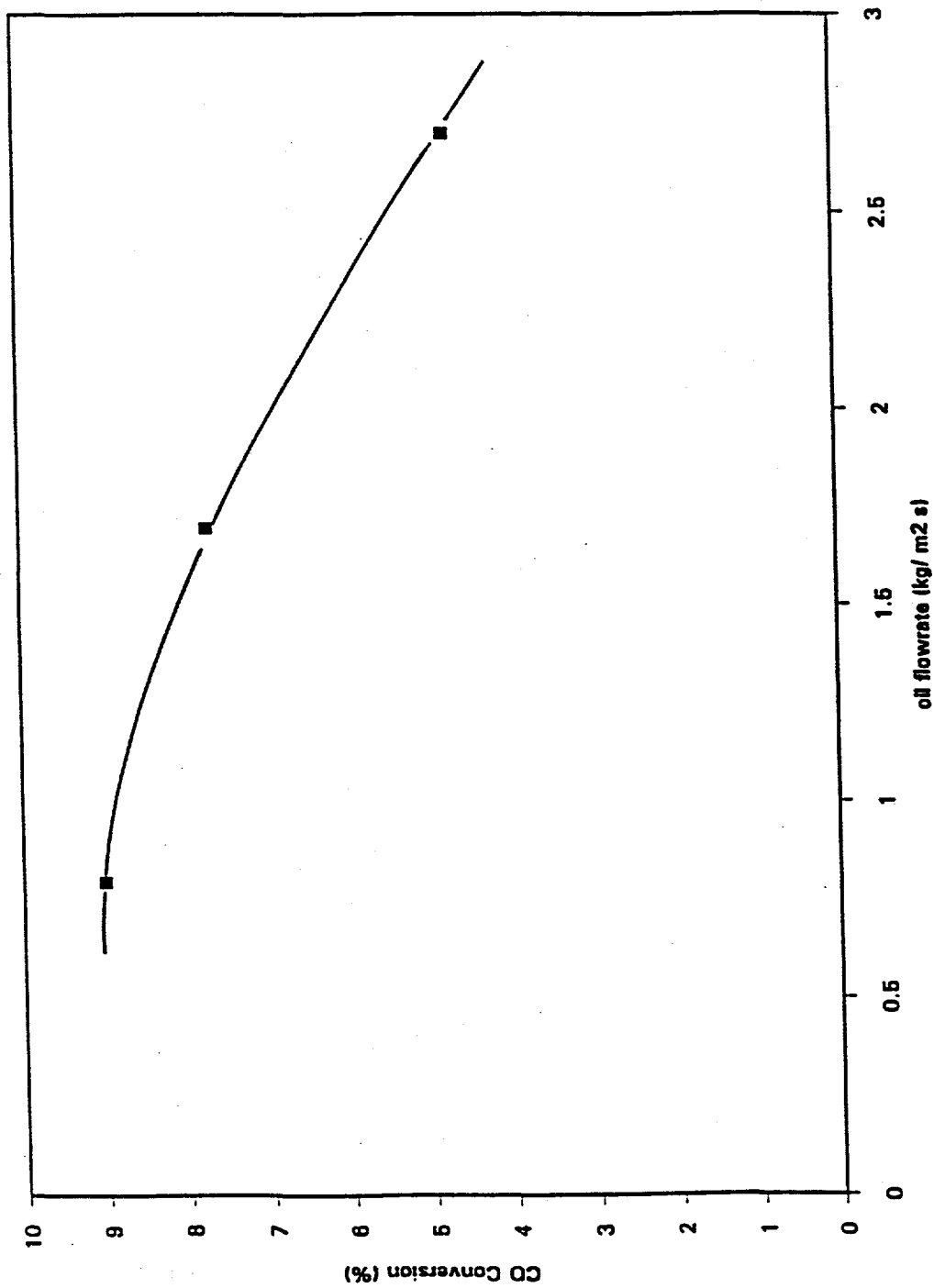


Figure 9. Effect of Oil Flowrate on CO Conversion.
Conditions: 396 C, 50 atm, CO/H₂=1.0

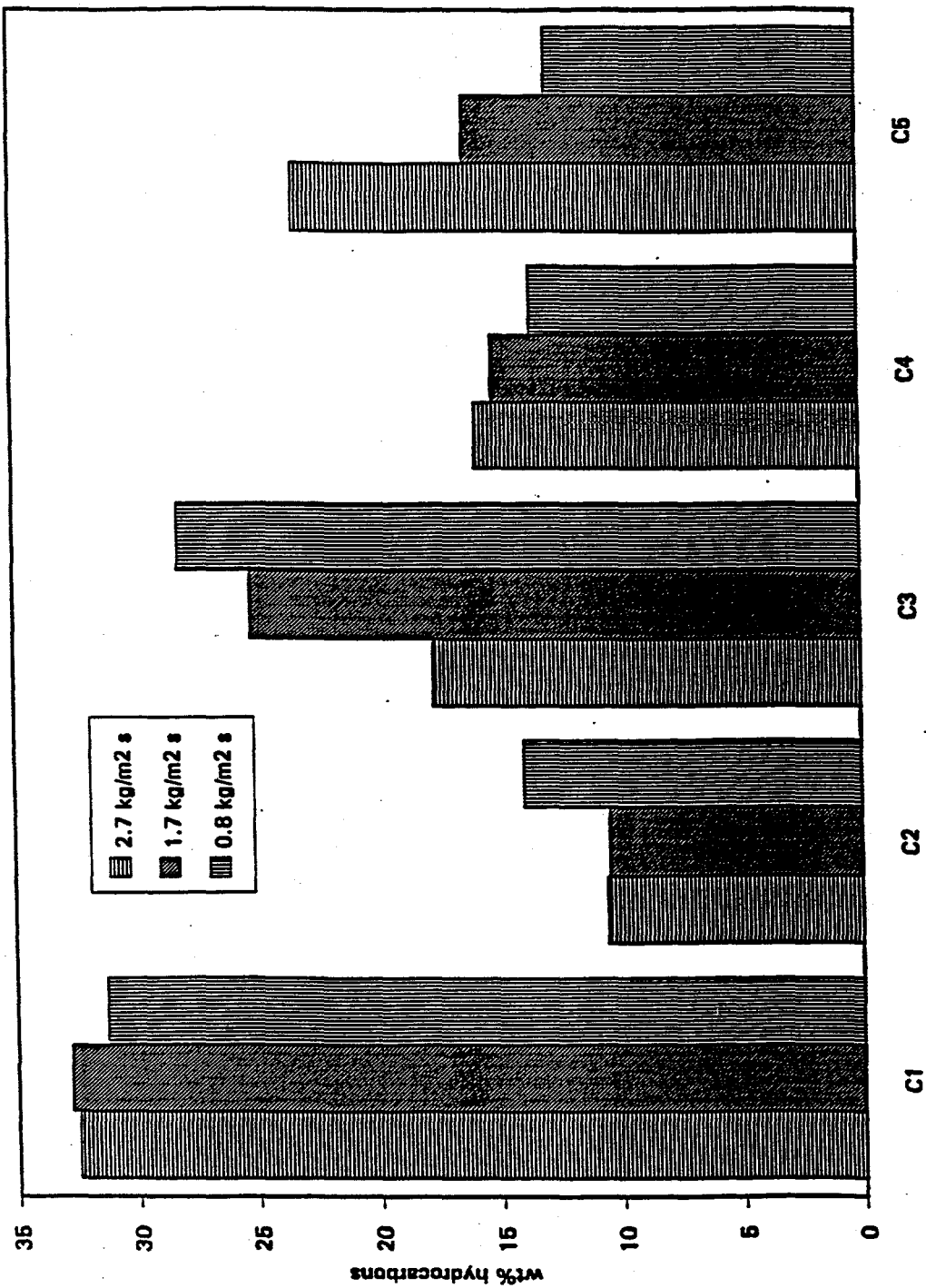


Figure 10. Variation of Hydrocarbon Distribution with Oil Flowrate.
 Conditions: 396 C, 50 atm, CO/H₂=1.0, Space Time=110s

**EFFECT OF OIL-GAS SEPARATOR TEMPERATURE ON HYDROCARBON
DISTRIBUTION IN TRICKLE BED REACTOR; CO CONVERSION: 10.0%
CONDITIONS: 396 C, 51 ATM, CO/H₂=1, SPACE TIME=89 s**

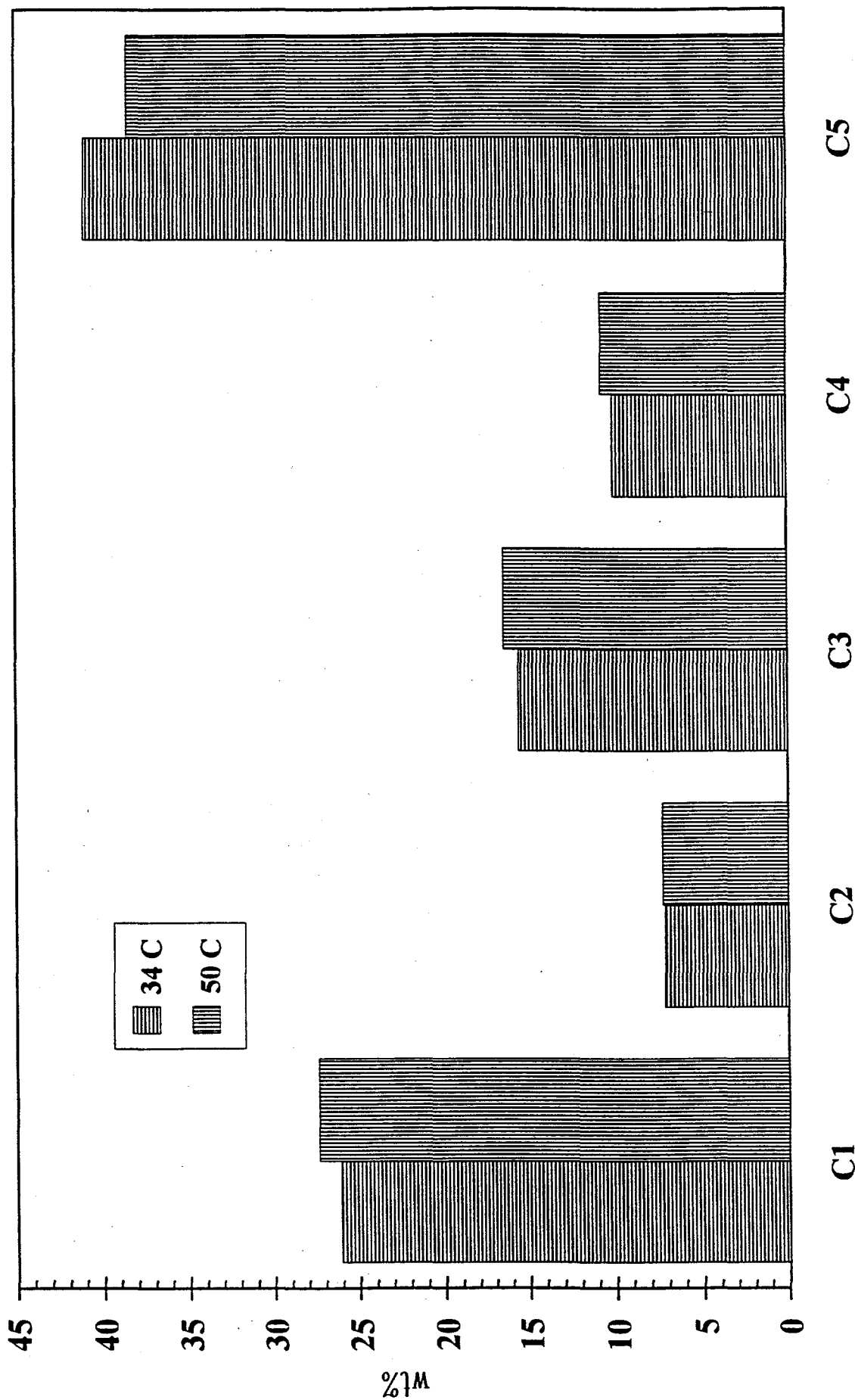


Figure 11

**EFFECT OF OIL-GAS SEPARATOR TEMPERATURE ON C4
DISTRIBUTION IN TRICKLE BED REACTOR
CONDITIONS: 396 C, 51 ATM, CO/H₂=1., SPACE TIME=89 s**

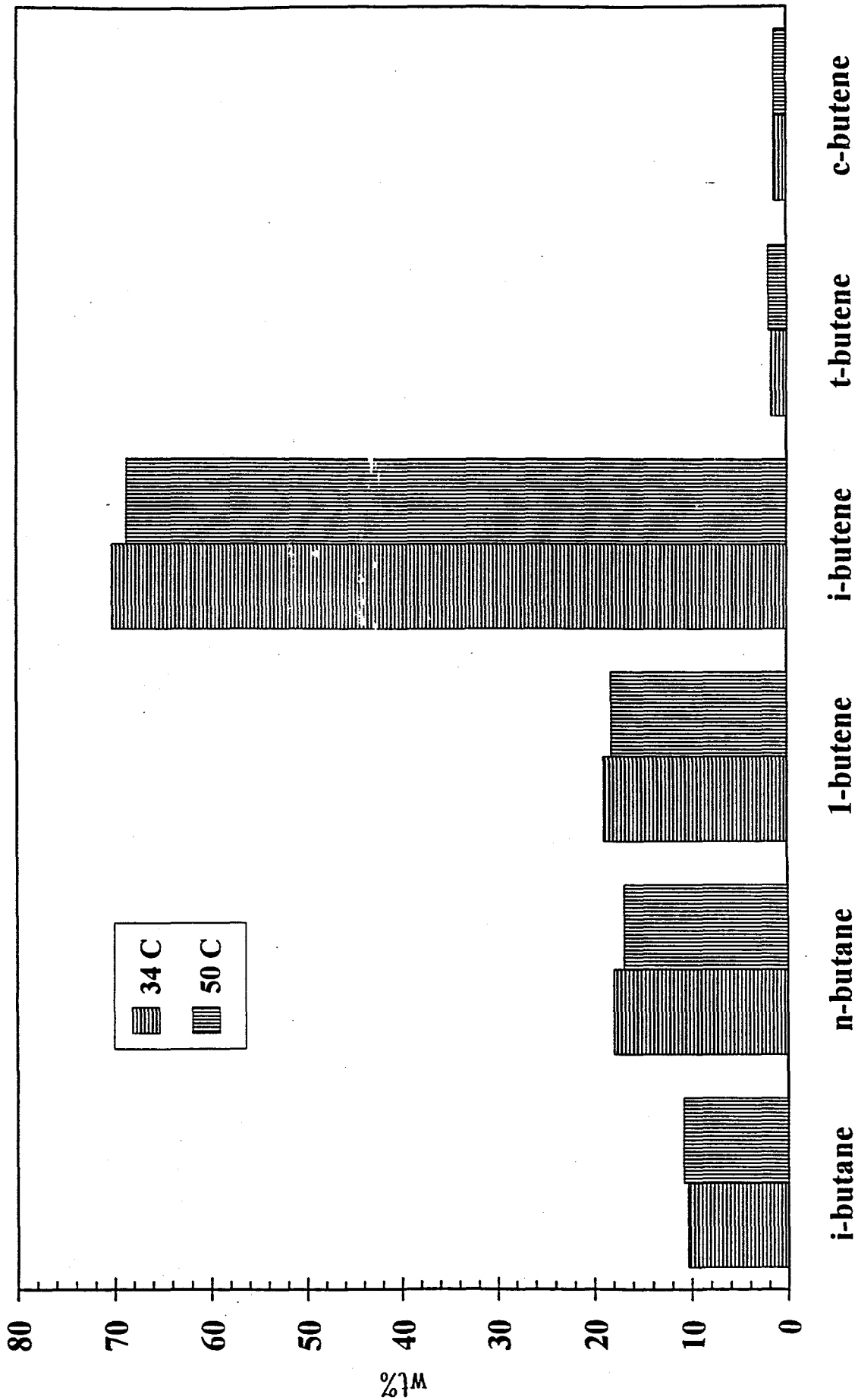


Figure 12

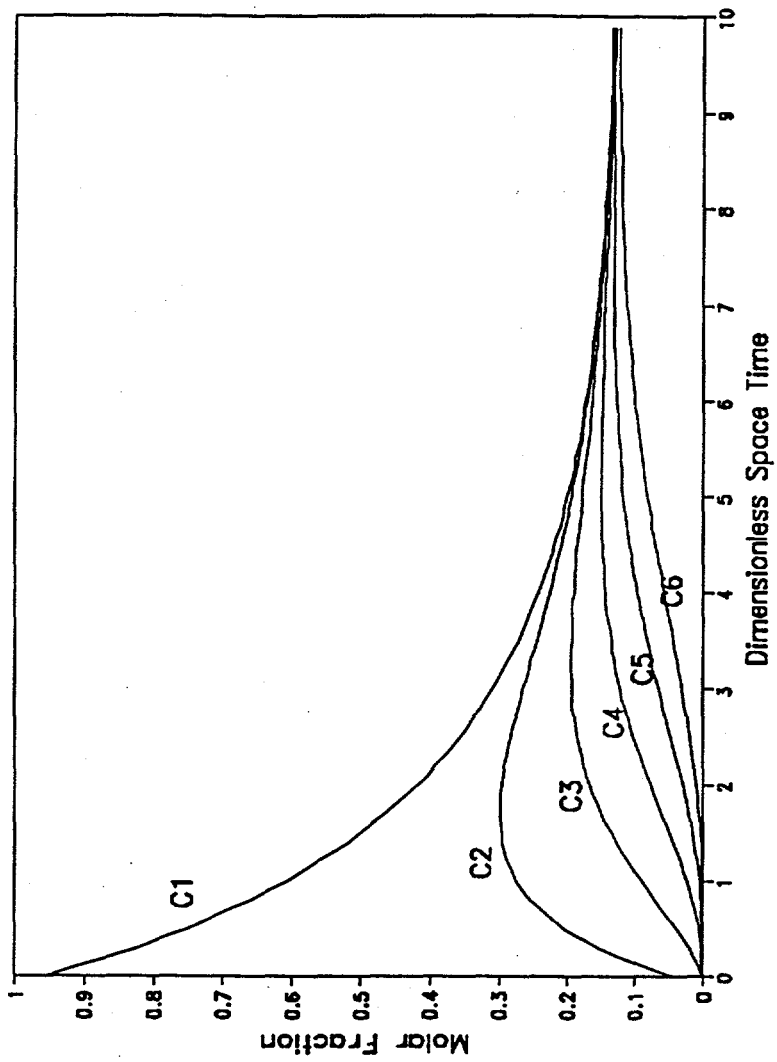


Figure 13. Distribution of C_1 to C_6 intermediate as a function of space time kt .

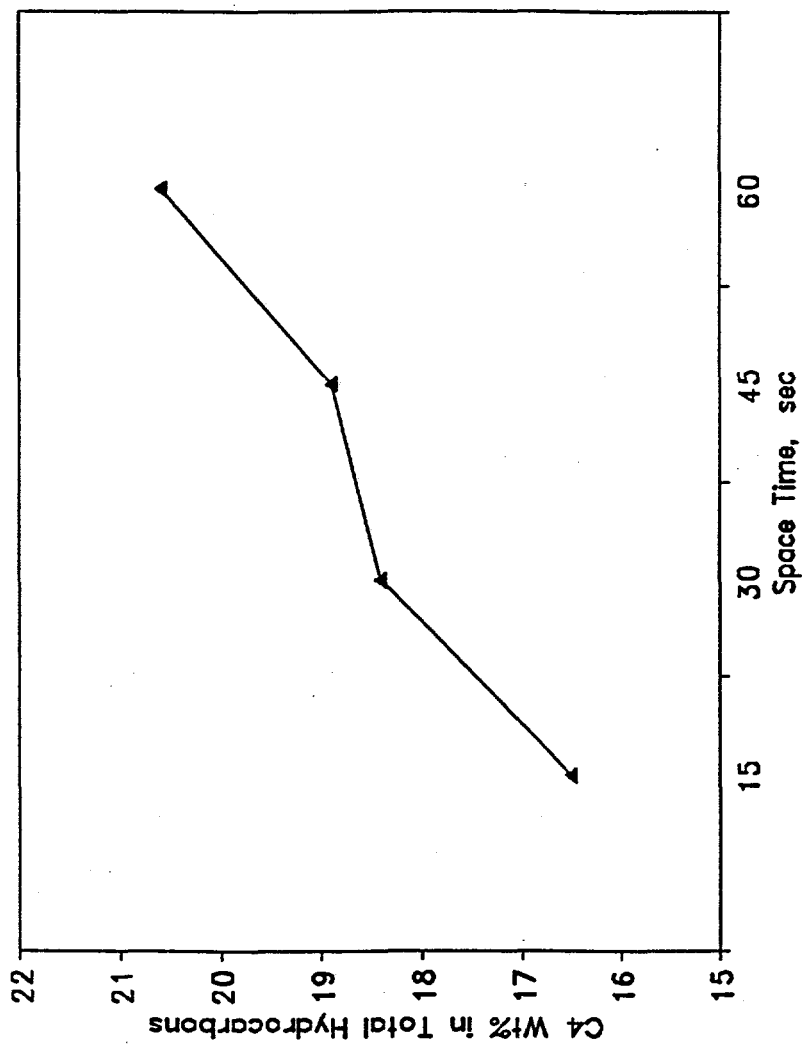


Figure 14. Illustration of the increase in C₄ content with space time. Catalyst: Na-ZrO₂(ppt), 400 °C, 50 atm.