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FOR

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: 10/1/92 to 12/31/92

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

The goals for the quarter include: 1) Conduct experiments using a trickle bed reactor to determine the effect of reactor type on the product distribution. 2) Use spherical pellets of silica as a support for zirconia for the purpose of increasing surface area and performance of the catalysts. 3) Conduct exploratory experiments to determine the effect of super critical drying of the catalyst on the catalyst surface area and performance. 4) Prepare a ceria/zirconia catalyst by the precipitation method, since doping of zirconia with ceria was reported by ¹Maruya, et al. (1988) to increase the activity of the zirconia.

ACCOMPLISHMENTS FOR THE QUARTER

Filing of necessary reports

The quarterly report for the period of July 1, 1992 to September 30, 1992 was filed and approved. Monthly reports for September, October, and November were also filed. A revised budget, management plan and other forms required on an annual basis were filed.

Experimental Program

Trickle Bed Reactor Experiments: Three large batches of zirconia and a commercial zirconia were evaluated using our reactor system, which can be operated as a fixed bed gas phase or as a trickle bed reactor. A difficulty with using the zirconia prepared in our laboratory was a fine powder was produced, and we had difficulty producing particles in the range of 300 - 420 μm . Therefore, excessive pressure drop occurred when operating in the trickle bed mode. However, scoping experiments were conducted with the zirconia prepared "in house," and decalin was determined to be the best oil to use for the trickle bed experiments. Linear hydrocarbons

¹Maruya, K., T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, and T. Onishi, *The CO-H₂ Reaction over ZrO₂ to Form Isobutene Selectively*, *Bull. Chem. Soc. Jpn.*, **61**, 667-671 (1988).

hydrocracked over the zirconia at the temperature of the isosynthesis.

A schematic diagram of the trickle bed reactor system is presented in Figure 1. The Feed gases are purified by flow through a guard bed which consists of activated carbon and molecular sieves with a particle size of 0.16 cm. Hydrogen and carbon monoxide flowrates are controlled with Brooks model 5850E mass flowmeters which have flow rate ranges of 0-1.5 slpm and 0-2 slpm, respectively. The flowmeters were calibrated by checking the controller set point versus the volumetric flowrate determined by bubble flow meter. The feed gas streams are combined at a predetermined H₂/CO ratio. To enhance mixing, the gases are passed through a bed of glass beads prior to the reactor. Decalin was fed to the unit using a Milton Roy pump. A relief valve, which is set at 10.6 MPa, is placed before the reactor to prevent uncontrolled pressure rises in the system. The reactor is a 316 SS tube 25 cm long, 0.96 cm ID, and 1.2 cm OD. It is mounted vertically in a bed of aluminum pellets. The reactor bed is divided into three sections. Prior to and after the 7 cm catalyst bed are 6 and 12 cm supporting sections filled with 0.2 cm diameter glass beads. The reactor is heated by heating the block and the temperature is controlled by Omega model 6100 temperature controller. A thermocouple inserted through the middle of the catalyst bed is used to measure the temperature of the bed. The reactor pressure is maintained with a Grove model 91W back pressure regulator. The reactor effluent passes through the back pressure regulator where the pressure is reduced to atmospheric pressure prior to the gas oil separator. The decalin collected at the bottom of the separator is recycled to the reactor. After the gas oil separator a sampling port is used to take gas samples for analysis. The gas is pass through a soap bubble meeter to measure the volumetric flowrate before it is vented to the hood. The decalin used in this study was obtained from Sigma Chemicals and exists as cis trans isomers of decahydronaphthalene with a minimum purity of 98% as determined by gas chromatography.

The performance of commercial zirconia at 453°C and 71 atm is presented in Figures 2-4 when operating the reactor as a gas phase fixed bed reactor. However, trickle bed experiments could not be conducted at 453 °C, because decalin, the solvent used in the trickle bed experiments, begins to decompose at ca. 430°C. Therefore, additional experiments were conducted at 396°C. A comparison of the performance of the catalysts when operating the reactor in the fixed and trickle bed modes at 396°C and 51 atm is presented in Figures 5 and

6. The selectivity for isobutylene and the C₄ components was higher when operating the reactor as a conventional gas phase fixed bed reactor than when operating the reactor as a trickle bed. The CO conversion was approximately the same for both modes of operation. The product distribution obtained with the trickle bed contains more C₃'s, less methane, less C₄'s, and less C₅+ than the product distribution obtained when operating in the gas phase fixed bed reactor mode. Even though problems were encountered with reactor plugging and catalyst deactivation when using the zirconia prepare in our laboratory, the trends observed using the "in house" catalysts were the same as those found when using the commercial catalysts.

For the convenience of the reader the relationship between space times used in this study and space velocities used by other investigators is presented in Table 1.

Table 1. Relationship of Space Time to Space Velocity for Experiments*

$$\text{Space Velocity, } h^{-1} = \frac{1}{\tau} * \frac{P(\text{atm})}{1\text{atm}} * \frac{273}{T}$$

T °C	T K	Pressure, atm.	Space Time τ , seconds	Space Velocity h ⁻¹
404	677	76	71	1154
429	702	76	68	1568
453	726	71	58	1657
453	726	71	113	850
453	726	71	204	471
396	669	51	89	842
396	669	51	89	842

*Space time is represented by the symbol τ .

Silica Pellets Coated with Zirconia: Spherical silica 3 mm pellets were coated with coated with ZrO(NO₃)₂ and then hydrolyzed by using NH₄OH. After drying the pellets were crushed and sieved to form particles less than 250 μ m. The resulting catalyst was 5% zirconia on silica. The implicit assumption in this method of preparation is that the Zr⁺⁴ was distributed uniformly throughout the porous structure of the silica pellets, so that crushing and sieving had no effect

on the activity of the catalyst. In any event, the silica served partially as a diluent, and partially in a mode to increase the availability of zirconia. The activity of the catalyst when compared with a non supported zirconia is illustrated in Table 2.

Table 2. A Comparison of the Activity of Supported and Unsupported Zirconia (Temperature 450°C, Pressure 70 atm, Space time 80 sec, CO+H₂ flowrate 200 sccm)

	Zirconia on Silica	ZrO ₂ (ppt. unsupported)
CO rxn rate (g/kg-cat/hr)	133	32.6
HC formation rate (g/kg-cat/hr)	36.1	11.1
i-C ₄ H ₈ in C ₄ 's, wt%	27.7	29.4
i-C ₄ H ₁₀ in C ₄ 's, wt%	15.0	41.0

CO reaction rate and hydrocarbon formation rate for coated silica far exceed those for precipitated zirconium oxide at the same feed rates and space time. However, the conversion of CO is substantially less for the supported zirconia than for the unsupported zirconia. Isobutane in the C₄s is substantially less for the supported zirconia than for the unsupported zirconia.

Another advantage of using coated silica gels is the suppression of C₅⁺ formation as shown in Figure 7. An explanation for this could be the slow diffusion of high molecular weight hydrocarbons out of the pores. A potential advantage of using supported zirconia is the ability to distribute the rate of heat generation throughout the reactor.

Hydrocarbon Distributions
Coated Silica Gels. 70 atm, 450 C

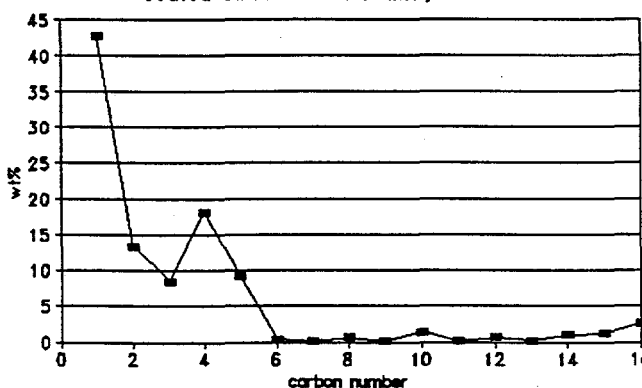


Figure 7. Hydrocarbon distribution for zirconia on Silica

These experiments illustrate that supported zirconia could be used to distribute the zirconia throughout the reactor. A possible design would be the use of supported pellets in the upper one

third of the reactor to distribute the heat load, followed by supported or unsupported catalyst with increasing amount of zirconia.

Supercritical drying of catalysts: Supercritical drying of a catalysts will in some instances allow the removal of condensable vapor from a solid without the collapse of the solid matrix. Hence, a high surface area material is produced. Our initial experiments to super critically dry zirconia have not produced high surface area zirconia, but instead have produced very low surface area material. Some of the catalysts prepared are listed in Table 3.

Table 3. Results of supercritical drying preparations.

Batch #	Wash	Drying Method	Surface Area (m ² /g)
15	EtOH	Air, Aspirator	28
16A	EtOH	Air, No Aspirator	1.9
16B	EtOH	SC CO ₂	8.2
17A	water	Air (Vacuum pump), oven	24
17B	acetone	Air, No aspirator	28
17C	acetone	SC CO ₂	10.4

All of the catalysts were calcined by the usual method of heating from room temperature to 500 °C under nitrogen (heating rate ~3.1 °C/min) and then holding at 500 °C for 2 ½ hours. All the samples had pore sizes in the 30-40 Å range. The super critically dried sample (17C) also had pores in the 100-500 Å range. The smaller pores seem to be a characteristic of zirconia prepared by precipitation. A catalyst prepared previously by the hydrothermal method (ID# 20723-ZRTITH-24-L2) had pores in the 150 Å range and had a surface area of ~53 m²/g. None of the catalysts in Table 3 have very high surface areas. A reason for the low surface areas of the SC dried samples could be that neither one was completely dry when it was removed from the extractor tube. Drying in a slurry type system may be a better alternative, because there does seem to be some difference in pore size distribution with drying procedure. The low surface areas for air drying with ethanol and acetone was not expected. Further work is required in

developing this technique to produce high surface area zirconia.

Preparation of a precipitated ceria/zirconia catalyst: A precipitated Ce_2O_3/ZrO_2 [7 wt. % Ce] was prepared for evaluation for catalyst activity² in January, 1993. The crystal structure of cerium is face centered cubic, which is also the same as thorium, which improved the catalysts activity when used with zirconia. The electronic structures of the two are different with cerium being $[Xe]4f^35d^06s^2$ and thorium being $[Rn]6d^27s^2$. Cerium can have a valence of a +3 or a +4, whereas thorium only has a valence of a +4. However, doping of zirconia with ceria has been reported to increase the activity and selectivity of the zirconia. The procedure for preparing the ceria/zirconia is as follows:

The solutions used in the preparation are given in Table 4.

Table 4. Solutions used in 7% Ce zirconia preparation.

Solution	pH
65.0005 g $ZrO(NO_3)_2 \cdot 8H_2O$ + 5.1674 g $Ce(NO_3)_3 \cdot 6H_2O$ in ~1200 ml water [†] { ~15/1 Zr/Ce molar ratio }	1.78
~93 ml of NH_4OH stock solution (28-30 wt. %) in 1860 ml water	10.55

[†]All of the water used in the preparation is deionized-distilled water.

The zirconyl nitrate/cerium nitrate solution was poured into the ammonium hydroxide solution, which was in a beaker sitting on a stirrer plate. The usual voluminous precipitate formed and the solution with precipitate had a pH of 9.80. Then HNO_3 was added to decrease the pH to 6.00 and stirring was continued for thirty minutes. Stirring was discontinued and the precipitate was allowed to sit in this solution for 16 hr. and 40 min. This was done, because ³Mercera et. al. (1991) stated that they achieved a more stable, higher surface area zirconia

²Maruya, K., T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, and T. Onishi, *The CO-H₂ Reaction over ZrO₂ to Form Isobutene Selectively*, *Bull. Chem. Soc. Jpn.*, **61**, 667-671 (1988).

³Mercera, P.D.L., J.G. van Ommen, E. B. M. Doesburg, A. J. Burggraaf, and J. R. H. Ross, *Zirconia as a support for catalysts: Influence of additives on the thermal stability of the porous texture of monoclinic zirconia*, *Applied Catalysis*, **71** (1991) 363-391.

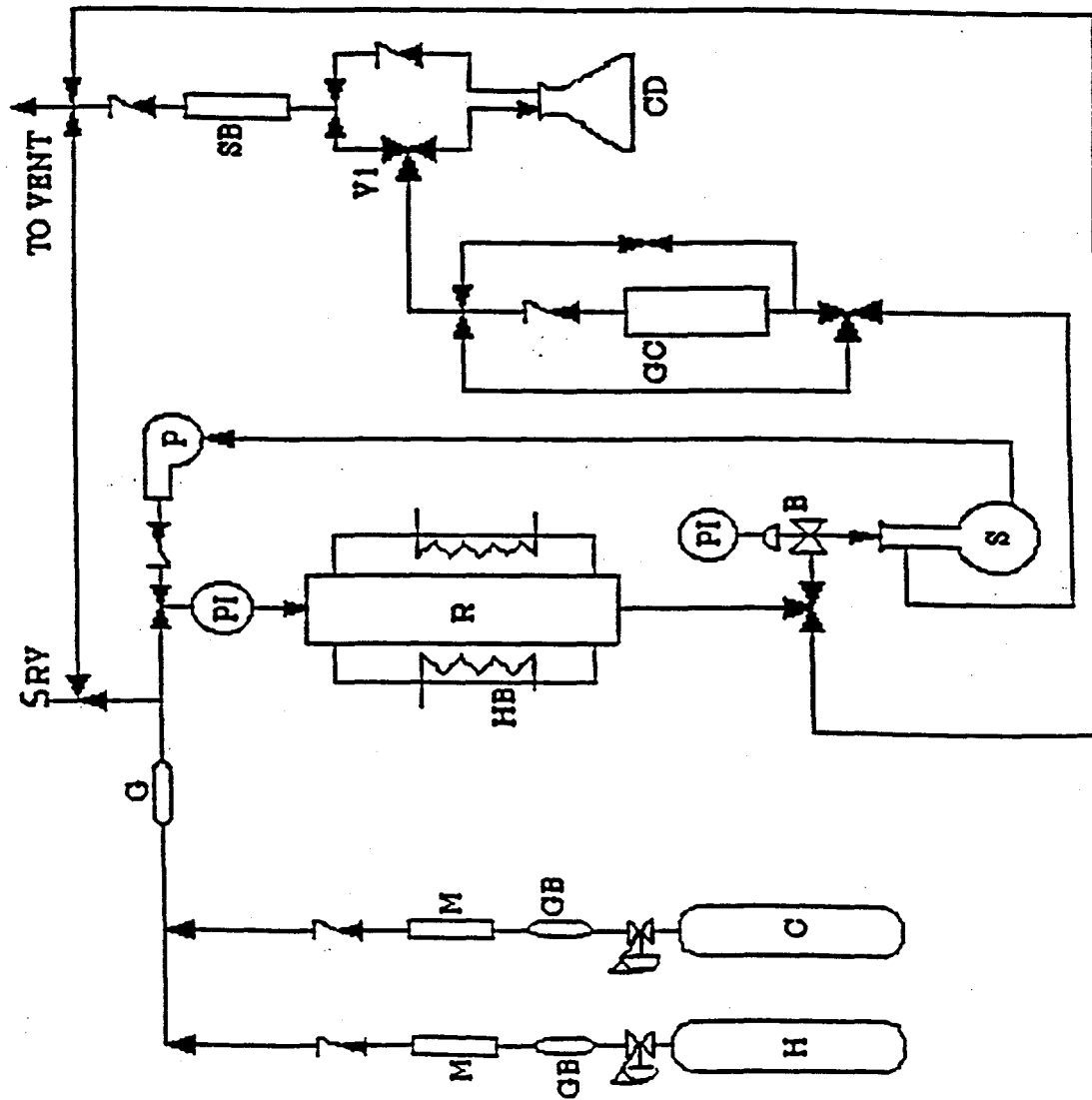
when the precipitate set in the original solution for an extended period of time. The precipitate was filtered (using vacuum pump), washed twice with water (~ 1000 ml each time), and dried in the oven at ~ 115 °C for 20 hr. and 45 min. Calcination was conducted as usual, except the final temperature was decreased from 500 to 450 °C. Also, the material was calcined in larger chunks (> 3 mm) instead of being ground into a powder (< 250 μm) before calcination. The average heating rate was about 3.16 °C/min. The catalyst has a yellowish color and a surface area of 103 m²/g. The higher surface area was expected because of the lower calcination temperature. The bulk density (2.28 g/cm³) was also slightly lower than normal for precipitated catalysts.

SIGNIFICANT ACCOMPLISHMENTS AND CONCLUSIONS

Major accomplishment was conducting the trickle bed reactor experiments. Several problems had to be resolved prior to obtaining good data. These involved evaluation of several solvents to determine which one would be best to use with the high temperatures used in the reaction. Linear and branched alkanes and cyclohexane hydrocracked at the reaction conditions. Decalin was found to be stable over the catalysts at the reaction temperatures. A major conclusion from the trickle bed reactor experiments is that methane production is slightly less, C₂ and C₃ productions is higher, and C₄s and C₅⁺ production is less than results obtained with a fixed bed gas phase reactor. Within the total C₄s, the isobutene selectivity is 30 to 40% less than that obtained with the fixed bed gas phase reactor.

GOALS FOR THE NEXT QUARTER

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 catalyst. Work on the development of the kinetic model for predicting the conversions and product distributions for the fixed bed reactor. Continue to conduct and explore possible new methods of preparation or catalyst which might enhance the activity of the zirconia, or replace the zirconia and still have an isosynthesis catalyst.



- B. Back Pressure Regulator
- C. Carbon Oxides Mixture
- CD. Condenser
- G. Glass Bead Bed
- GB. Guard Bed
- H. Hydrogen
- HB. Heating Block
- M. Mass Flow Controller
- P. Pump
- PI. Pressure Indicator
- R. Reactor
- RV. Relieve Valve
- S. Separator
- SB. Soap Bubble Meter
- VI. Three Way Valve

Figure 1. Experimental apparatus.

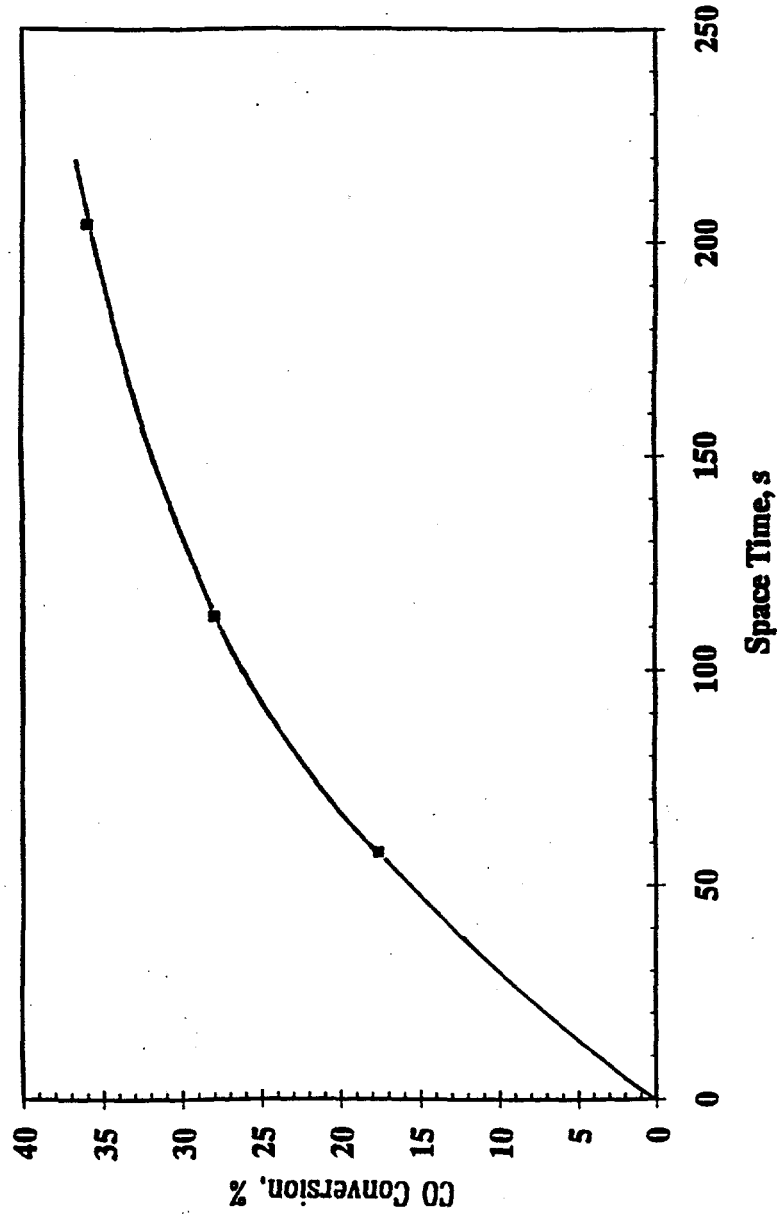


Figure 2. A demonstration of the activity of a commercial zirconia and operating in the fixed bed gas phase mode. (453°C, 71 atm., CO/H₂ feed ratio = 1).

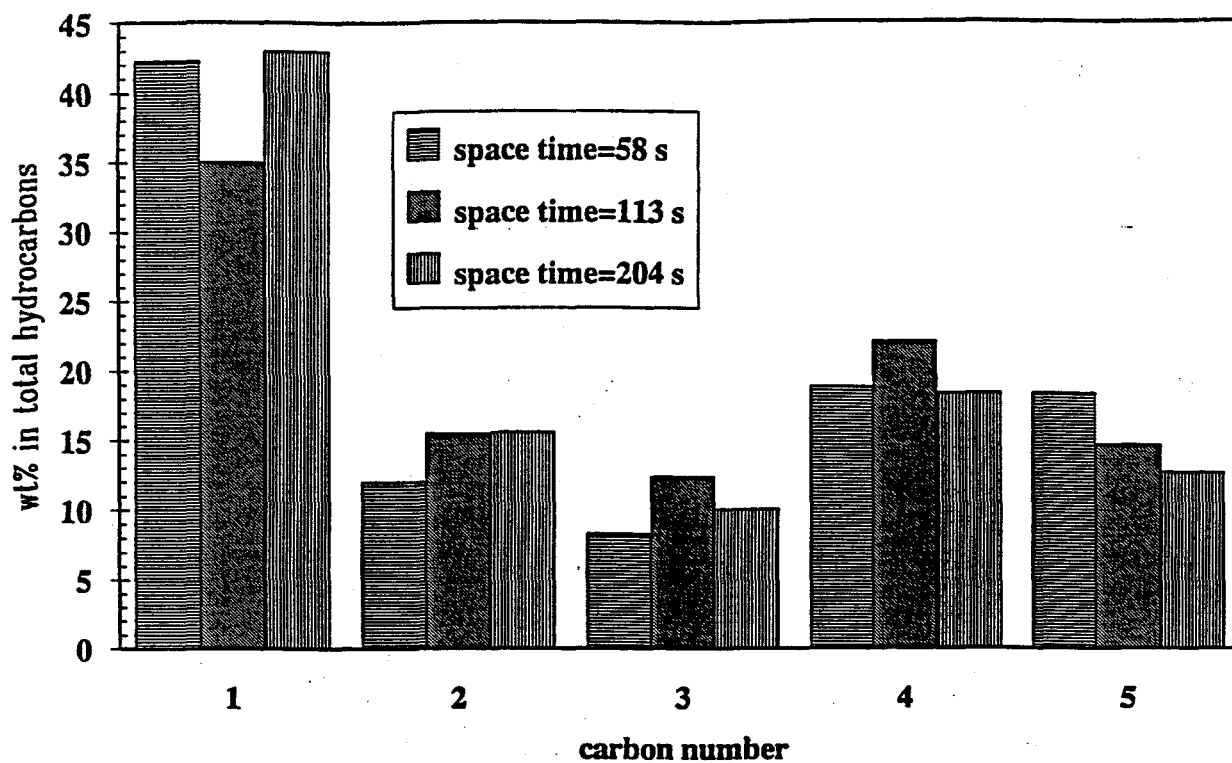


Figure 3. Selectivities obtained using a commercial zirconia and operating in the fixed bed gas phase mode. (453°C, 71 atm., CO/H₂ feed ratio = 1).

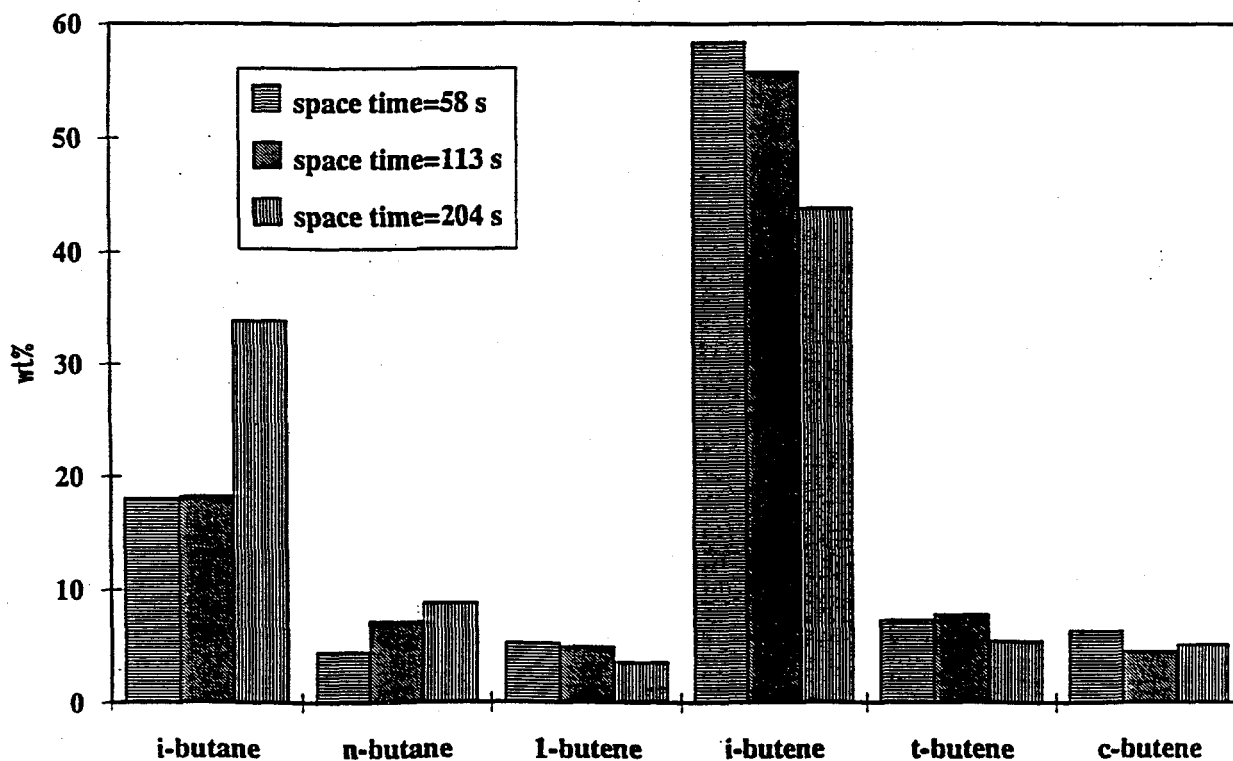


Figure 4. The C₄ distribution obtained when using a commercial zirconia and operating in the fixed bed gas phase mode. (453°C, 71 atm., CO/H₂ feed ratio = 1).

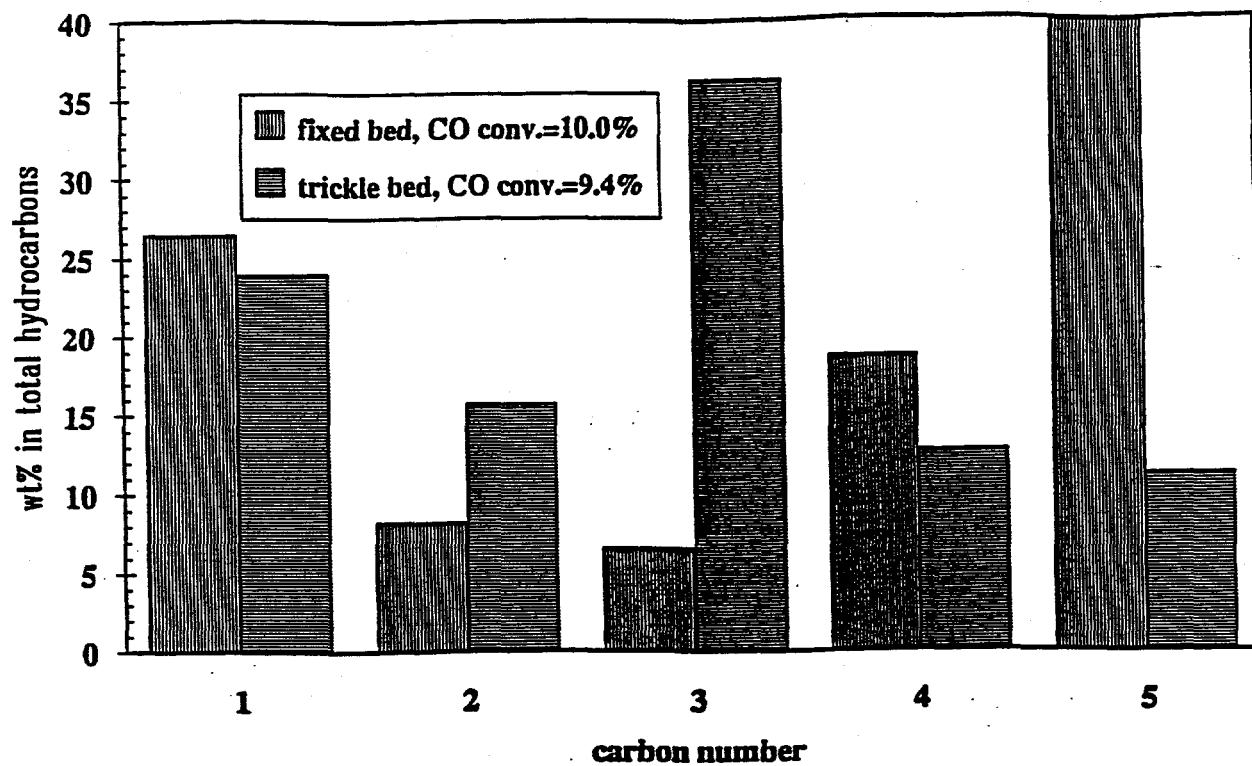


Figure 5. Selectivities obtained when using a commercial zirconia and operating in the fixed bed gas phase and trickle bed reactor modes. (396°C, 51 atm., CO/H₂ feed ratio = 1, τ = 89 s).

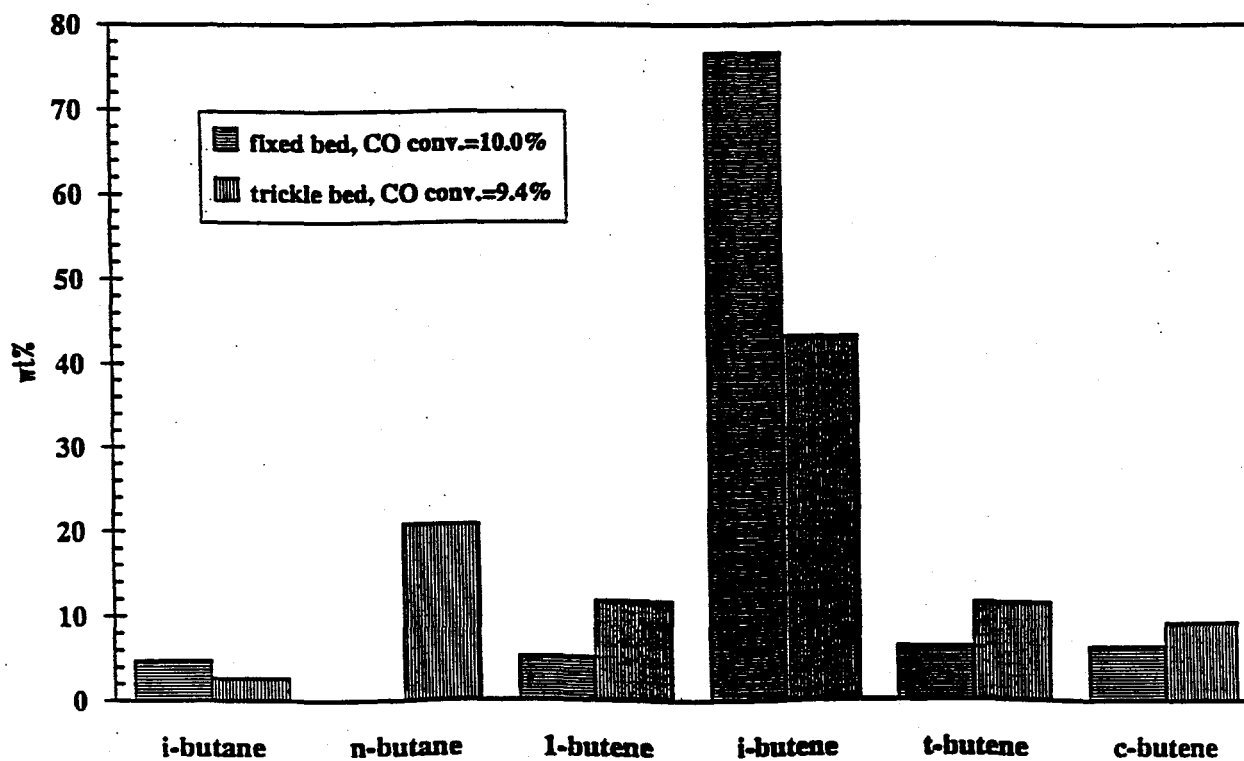


Figure 6. A demonstration of the C₄ distribution for a commercial zirconia operating in the fixed bed gas phase and trickle bed modes. (396°C, 51 atm., CO/H₂ feed ratio = 1, τ = 89 s).