

DOE/PC/90045--T10

Quarterly
~~ANNUAL~~ REPORT

Report Period

~~October 1, 1990~~ to September 30, 1991

July 1, 1991

30/91

RECEIVED
USDOE/PETC
91 NOV 18 AM 11:18
ALLOCATION & ASSISTANCE DIV.

FOR

CATALYSTS AND PROCESS DEVELOPMENT FOR
SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

Submitted to

United States Department of Energy
Pittsburgh Energy Technology Center

Cynthia -
This is
the tech.
gtrly 10-20-91

November 6, 1991

by

Rayford G. Anthony and Aydin Akgerman
Kinetics, Catalysis and Reaction Engineering Laboratory
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3122

UNDER DOE CONTRACT NO. DE-AC22-90PC90045

(Texas A&M Research Foundation Project No. 6722)

ds **MASTER**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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

DOE CONTRACT NO. 90PC90045

TEXAS A&M RESEARCH FOUNDATION PROJECT NO. 6722

Annual Report

Report Period: 10/01/90 to 9/30/91

PROJECT OBJECTIVES

The objectives of this project are to develop a new catalyst, the kinetics for this catalyst, 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 a biomass. This hydrogen-lean synthesis gas could 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 YEAR

The goals for this year were to recruit and organize the project team, complete the literature and patent searches, complete the management plan and other reporting requirements, complete the revision and upgrading of existing bench scale units for the project, and synthesize, characterize and evaluate the catalytic activity of zirconia prepared (1) by co-precipitation of zirconyl nitrate with ammonium hydroxide and (2) by preparing a hydrous zirconium oxide using the modified sol gel method developed at the Sandia National Laboratories followed by calcination. The same preparation procedure would be used to prepare supports for impregnation with thorium nitrate, a potassium salt and a sodium salt. The synthesis of new crystalline zirconates were to be attempted with the objective of producing new compositions of matter which might have higher activities and selectivities than zirconia. Substantial progress on reactor and kinetic models for slurry and trickle bed reactors was to be achieved.

SUMMARY OF ACCOMPLISHMENTS FOR THE YEAR

This section presents a summary of the accomplishments for the year. Details are given in the manuscript prepared for the DOE contractors meeting, Sept. 1991. This manuscript is included in this report in the appendix.

Recruitment of the Research Team

The research team was recruited and consists of Mr. Walter Postula, a Ph. D. student, Mr. Z. Feng, a Ph.D. student, Dr. C. Erkey, a Post-Doctoral Research Associate, Dr. C. V. Philip, an Associate Research Scientist and the two co-principal investigators, Professors R. G. Anthony and A. Akgerman. Mr. Postula received his B. S. degree in Chemical Engineering from Texas A&M University in May, 1990 and began graduate school in September, 1990. He passed the Departmental Qualifying Examination for admission to the Ph. D. program in January, 1991. Mr. Feng completed the requirements for the M.S. degree January, 1991. His thesis was supervised by Professor Anthony, and was on the use of hydrous titanium oxide, hydrous Ti-Si oxide, and hydrous zirconium oxide as supports for nickel, molybdenum, platinum, and

palladium for the dehydrogenation and aromatization of propane. Mr. Feng passed the Qualifying Examination required by the Chemical Engineering Department for admission to the Ph. D. program in May, 1990. Dr. Erkey received the Ph.D. degree from Texas A&M University in 1989, and has been working with Dr. Akgerman on measurement of diffusivities in Fischer-Tropsch liquids. He also directed Professor Akgerman's group when Professor Akgerman was on Sabbatical in the Fall of '89. Dr. C. V. Philip, Associate Research Scientist, received his Ph. D. in Chemistry in 1972, and has been working with Professor Anthony on coal liquefaction and catalyst projects since 1976.

Literature Search

A patent and literature search was completed, and as of this writing no new articles have been found that were not included in the review of the state of the art published in the proposal. However, from this review we have determined a need to conduct baseline experiments with a zirconia catalyst prepared by precipitation of zirconyl nitrate using ammonium hydroxide and impregnated with sodium hydroxide. The procedures published by Maehashi et al. (1984), Maruya et al. (1988, 1989) Oneshi et al. (1988) will be used.

Table 1 illustrates a first step at organizing this information into a condensed summary. A senior undergraduate student, Mr. Mike Fuchi compiled this table for us. The table illustrates the limited amount of work which has been performed on isobutylene synthesis since the work of Pichler and Ziesecke (1949). No U.S. patents have been issued on isobutylene synthesis from synthesis gas in the last ten years. A close examination of Table 1 shows that in recent years high selectivities of isobutylene from synthesis gas have been obtained at low pressures and at pressures up to 21 atmospheres when using zirconium dioxide as the catalyst. The production rate of isobutylene at 21 atmospheres is 1000 times the production rate at 0.2 atmospheres. There appears to be some loss in selectivity to isobutylene at the higher pressure. Isobutylene production rates at 50 atmospheres should be even greater than those at 21 atmospheres.

The mechanism for isobutylene synthesis is unknown, but the active sites appears to be different from the sites for producing alcohols and linear hydrocarbons. Maruya et al. (1989) report the following postulates: (1) methanol may be formed from a methoxy species, (2) there is no evidence for decomposition of CO to C(s) and O(s), (3) formaldehyde is formed with no

induction time, (4) hydrocarbons are formed with no induction time, (5) $\text{CH}_x\text{O}_y(\text{s})$ is a possible intermediate in hydrocarbon formation, and (6) they present data to eliminate formation of hydrocarbons by aldol condensation.

Reporting Requirements

All of the reports, management plan, monthlies, cost plan and status and quarterlies have been filed.

Bench Scale Reactor Systems

Two bench scale reactor systems are being used in the project. The first one was an existing unit, which has been modified to conduct catalytic activity tests. A new gc and a Carle refinery gc were installed on-line. With this unit on-line analysis of the total reactor effluent can be achieved. This unit is referred to as BR#1. The second unit is a CDS 900 reactor system manufactured by Chemical Data Systems. (Chemical Data Systems was purchased from Autoclave Engineers in 1990, and the unit is call AE BTRS 900 by Autoclave Engineers. We will continue to use the designation CDS 900.) The unit uses a tubular reactor with controls and on-line analysis of the reactor products. All products in the reactor effluent are analyzed on-line, but 1-butene and isobutene elute simultaneously. Therefore, an off-line analysis is conducted to determine the ratio of 1-butene to isobutene. The composition of isobutylene and 1-butene are then calculated from this additional information.

Catalysts Synthesis and Characterization

Several batches of zirconia were prepared by precipitation of zirconyl nitrate with ammonium hydroxide at different pH for the precipitation. The active catalysts were prepared by calcining at 500 °C for 4 hours. The catalysts evaluated were predominately monoclinic zirconia, and the activity test were conducted in BR#1 prior to installation of the Carle Refinery gc for hydrocarbon, CO, CO₂ and H₂ on-line analysis. Therefore, all of the analysis were conducted off-line for this series of experiments. The results obtained with this unit compared favorably with data reported by UOP for a zirconia prepared by co-precipitation of zirconium chloride with ammonium hydroxide. The catalysts were referred to as C1.

A zirconia was prepared from hydrous zirconium oxide by calcination at 600 °C. The activity and product distributions for this catalysts were different than those obtained for catalysts C1. The results of these experiments are reported in the manuscript submitted to the DOE

Contractors meeting, September 1991.

A new zirconate was synthesized with a first reflection of the XRD pattern at 1.2 nm. This material appears to be a new composition of matter, because no Raman spectra or XRD patterns have been found in the literature, patent literature, or data bases, which match the spectra and pattern obtained for the new material. Activity testing is planned for the coming year.

Kinetic and Reactor Modelling

Two approaches are being used for developing kinetic models for these reactions. The first is the classical approach of using macrokinetic models and the second is the use of microkinetic models. For the first approach experimental data from activity testing and kinetic experiments are used. For the second approach, a detailed kinetic mechanism composed of many elementary steps is used. Published adsorption data and theoretical calculations are used to obtain the first approximation of the specific rates of the individual reactions. Judiciously planned experiments are then used to refine the model. The latter approach should increase our understanding of the probable mechanisms occurring in the selective synthesis of isobutylene, and lead to a macrokinetic model. This macrokinetic model should incorporate more detail and could be a better predictor of the reactor and catalyst performance than a macrokinetic model developed by the first approach which is all empirical.

Development of the programs for modelling the trickle bed reactors is proceeding in a satisfactory manner. Preliminary results on the modelling effort are presented in the Appendix.

GOALS FOR THE SECOND YEAR

The goals for the coming year are to continue the synthesis, characterization and evaluation of catalytic activity for new catalyst preparations, file necessary reports, continue and essentially complete the kinetic model, and essentially complete the programs for the trickle bed and slurry reactors. For the fixed bed gas phase reactors plug flow is being assumed and SimuSolve is being used for model development and parameter estimation.

During the first quarter of the second year the following activities are planned.

1. Prepare a zirconia from $K_{0.3}ZrO$ which is to be synthesized using procedure developed by R. G. Dosch at the Sandia Laboratories. Make at least 50 grams. Take the potassium zirconium oxide and ion exchange with HCl at a pH of 3. Do at least three

exchanges with filtering and washing (after an acetone rinse pull air through the filter 5 minutes before reslurring in water) between each exchange. Then take 20 grams and ion exchange with ammonium hydroxide at pH of 10 three times with filtering and air drying (5 min.) in between. Do not use water in any of the rinses, use acetone only. After the final ammonium hydroxide exchange, i.e. the pH stays at 10 for 10 minutes on reslurring, calcine at 600 °C for 4 hours. This is the catalyst to be placed into the reactor. XRD and surface areas need to be determined on a sample after calcination and after reaction. A potassium analysis using the AA is also needed. TGA and DTA analysis on catalysts samples used before and after reaction are also to be conducted.

Take the other 20 grams and adjust the potassium level to a pH of 0.4 wt% by ion exchange. Calcine for 4 h at 600 °C, etc.. Do all rinses with acetone. Final pH prior to calcination should be about 10. Addition of ammonium hydroxide may be required to maintain a pH of 10.

Activity testing: Do the test at a temperature, pressure and residence time (space velocity) to obtain 20% conversion of CO. This will be the base case. Then do a matrix of residence time 50% less and 50% greater, and temperatures 25 ° higher and 25 °C lower than the base case.

Kinetics: Use Simusolve to obtain a rate equation for CO disappearance, hydrogen disappearance and CO+H₂ disappearance. This needs to be done for the experiments conducted in August.

2. Obtain data on zirconia at low temperatures for the purpose of producing methanol. Kinetic data in the low temperature region are needed by Dr. Can Erkey for the microkinetic model development. Three or four space velocities and three temperatures are to be used. The three temperatures will be done only at the base case velocity.
3. Prepare the ppt. zirconia. In the hydrous form add sodium hydroxide to obtain 0.1, 0.3 and 0.5 wt% sodium. Final pH should be about 10. Calcine at 600 °C.

Activity testing: see above comments.

Kinetics: See above.

4. Dr. Philip has prepared a zirconia catalyst impregnated with thorium nitrate and then calcined. This catalyst will be evaluated in the CDS 900 unit.

5. Reproduce the synthesis of the 1.2 nm d_0 spacing zirconate, and prepare at least a 100 g batch of the same.
6. Take 20 g and remove the sodium by ion exchange with HCl to a level of less than 0.5 wt%. Then adjust the pH to 10 with ammonium hydroxide. Three NH_4OH treatments may be required. See above comments. Calcine at 600 °C for 4 hours and then get surface areas, AA, and XRD analysis. The sample which is prepared will be used for catalytic activity testing.
7. Continue the development of the microkinetic model.
8. Other experiments will be planned based on the results of the experiments conducted above and the model development.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE 1. CATALYSTS AND PROCESS CONDITIONS FOR ISOBUTYLENE SYNTHESIS

<u>Source</u>	<u>Temperature</u>	<u>Pressure</u>	<u>C₄ Yield</u> <u>mole %</u>	<u>i-C₄H₈ Selectivity</u>	<u>WHSV</u>	<u>Feed Ratios</u>	<u>Catalyst</u>
1	200 °C	0.68 atm	0.087%	—	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
1	250 °C	0.68 atm	0.088%	—	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
1	300 °C	0.68 atm	1.05%	—	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
1	350 °C	0.68 atm	11.11%	97.1%	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
1	400 °C	0.68 atm	12.23%	88.4%	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
1	450 °C	0.68 atm	5.38%	56.8%	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
1	400 °C	10.0 atm	7.42%	—	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
1	400 °C	21.0 atm	5.98%	96.4%	2300 1/hr	CO-H ₂ (1:3)	ZrO ₂
<u>Residence Time</u>							
2	425 °C	35 atm	4.6%	—	0.237 min	CO-H ₂ (1:1)	ZrO ₂
2	425 °C	35 atm	4.1%	—	0.158 min	CO-H ₂ (1:1)	ZrO ₂
2	425 °C	35 atm	3.4 %	—	0.119 min	CO-H ₂ (1:1)	ZrO ₂
2	425 °C	35 atm	5.9%	—	0.237 min	CO-H ₂ (1:1)	ZrO ₂
2	400 °C	35 atm	3.5%	—	0.246 min	CO-H ₂ (1:1)	ZrO ₂
2	375 °C	35 atm	1.7%	—	0.256 min	CO-H ₂ (1:1)	ZrO ₂
2	350 °C	35 atm	0.6%	—	0.266 min	CO-H ₂ (1:1)	ZrO ₂
<u>C₄ Yield</u> <u>weight %</u>							
3	240 °C	1.5 MPa	24%	<u>i-n ratio</u> 6.8	<u>W/F (g cat hr/mol)</u> 7.0	CO-H ₂ (2:3)	HY + 2% Ru
3	240 °C	1.5 MPa	22%	10	7.0	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	240 °C	1.5 MPa	31%	6.5	14	CO-H ₂ (2:3)	HY + 2% Ru & HY + 2% Pt
3	240 °C	1.5 MPa	17%	7.5	7.0	CO-H ₂ (2:3)	HY + 0.5% Ru + 2% Pt
3	240 °C	1.5 MPa	31%	9.3	7.0	CO-H ₂ (2:3)	HY + 1% Ru + 2% Pt
3	240 °C	1.5 MPa	1.6%	0.2	7.0	CO-H ₂ (2:3)	HY + 4% Ru + 2% Pt
3	240 °C	1.5 MPa	18%	0.3	7.0	CO-H ₂ (2:3)	HY + 8% Ru + 2% Pt
3	240 °C	0.2 MPa	20%	1.7	12.5	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	240 °C	0.8 MPa	23%	3.7	12.5	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	240 °C	1.5 MPa	19%	5.2	12.5	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	240 °C	2.1 MPa	13%	2.5	12.5	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	240 °C	5.1 MPa	8%	1.5	12.5	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt

<u>Source</u>	<u>Temperature</u>	<u>Pressure</u>	<u>C₄ Yield</u> <u>weight %</u>	<u>i-C₄H₈ Selectivity</u>	<u>W/F</u> <u>g cat hr/mol</u>	<u>Feed Ratios</u>	<u>Catalyst</u>
3	240 °C	1.5 MPa	22%	10.0	7.0	CO-H ₂ (2:3)	HY+2%Ru+2%Pt
3	240°C	1.5 MPa	21%	3.6	18.0	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	240°C	1.5 MPa	18%	1.4	33.0	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	270 °C	1.5 MPa	11%	1.1	12.5	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	290 °C	5.1 MPa	6%	0.1	12.5	CO-H ₂ (2:3)	HY + 2% Ru + 2% Pt
3	240 °C	1.5 MPa	23%	1.7	12.5	CO-H ₂ (2:3)	SiO ₂ ,Al ₂ O ₃ + 2% Ru + 2% Pt
3	240 °C	1.5 MPa	—	—	12.5	CO-H ₂ (2:3)	HM + 2% Ru + 2% Pt
3	240 °C	1.5 MPa	24%	1.2	12.5	CO-H ₂ (2:3)	CaY + 2% Ru + 2% Pt
			<u>C₄ Yield</u> <u>mmol/g cat hr</u>				
4	240°C	1.5 MPa	2.05	7.1	12.5	CO-H ₂ (2:3)	DAH _Y + 2% Pt + 0.1% 1-octene
4	240 °C	1.5 MPa	0.012	3.4	12.5	CO-H ₂ (2:3)	DAH _Y + 2% Ru
4	240 °C	1.5 MPa	0.77	3.7	12.5	CO-H ₂ (2:3)	DAH _Y + 2% Ru +0.1% 1-octene
4	240°C	1.5 MPa	0.54	3.8	12.5	CO-H ₂ (2:3)	DAH _Y + 2%Ru+2%Pt
4	240 °C	1.5 MPa	1.27	4.6	12.5	CO-H ₂ (2:3)	DAH _Y + 2% Ru + 2% Pt + 0.1% 1-octene
4	240 °C	1.5 MPa	1.05	10.4	12.5	CO-H ₂ (2:3)	DAH _Y + 0.1% 1-octene
4	240 °C	1.5 MPa	1.24	5.9	12.5	CO-H ₂ (2:3)	DAH _Y + 2% Ru + 2% Pt+0.1% 1-undecene
4	300 °C	1.5 MPa	1.34	1.6	12.5	CO-H ₂ (2:3)	DAH _Y + 2% Ru + 2% Pt + 0.1% 1-undecene
4	240 °C	1.5 MPa	0.23	3.8	12.5	CO-H ₂ (2:3)	DAH _Y +2%Ru+2%Pt
4	300 °C	1.5 MPa	0.39	1.3	12.5	CO-H ₂ (2:3)	DAH _Y + 2% Ru + 2% Pt

<u>Source</u>	<u>Temperature</u>	<u>Pressure</u>	<u>g C₃/m³ Feed</u>	<u>i-C₃ Selectivity Total i-C₃</u>	<u>% i-C₃H₈ of i-C₃(Total)</u>	<u>Feed Ratios</u>	<u>Catalyst</u>
5	450 °C	150 atm	18.2	88%	—	CO-H ₂ (1.2:1)	ThO ₂
5	450 °C	150 atm	11.0	82%	—	CO-H ₂ (1.2:1)	ZrO ₂
5	450 °C	150 atm	1.6	81%	—	CO-H ₂ (1.2:1)	CeO ₂
5	450 °C	150 atm	4.7	59%	—	CO-H ₂ (1.2:1)	Al ₂ O ₃
5	400 °C	150 atm	8.4	87%	—	CO-H ₂ (1.2:1)	ThO ₂
5	450 °C	0 atm	—	—	—	CO-H ₂ (49:41)	ThO ₂
5	450 °C	6 atm	—	—	—	CO-H ₂ (43:48)	ThO ₂
5	450 °C	30 atm	5.7	92%	30%	CO-H ₂ (49:41)	ThO ₂
5	450 °C	75 atm	—	—	—	CO-H ₂ (49:41)	ThO ₂
5	450 °C	150 atm	18.6	88%	24%	CO-H ₂ (49:41)	ThO ₂
5	450 °C	300 atm	27.5	85%	4%	CO-H ₂ (49:41)	ThO ₂
5	450 °C	300 atm	30.6	84%	7%	CO-H ₂ (45:45)	ThO ₂
5	450 °C	300 atm	23.9	90%	5%	CO-H ₂ (41:49)	ThO ₂
5	450 °C	600 atm	50.0	90%	2%	CO-H ₂ (40:50)	ThO ₂
5	450 °C	1000 atm	36.7	90%	—	CO-H ₂ (44:47)	ThO ₂
5	450 °C	300 atm	25.9	88%	8%	CO-H ₂ (1:1)	ThO ₂
5	475 °C	300 atm	31.1	88%	5%	CO-H ₂ (1:1)	ThO ₂
5	450 °C	300 atm	43.0	87%	10%	CO-H ₂ (1:1)	ThO ₂ + 10% Al ₂ O ₃
5	475 °C	300 atm	60.2	83%	3%	CO-H ₂ (1:1)	ThO ₂ + 10% Al ₂ O ₃
5	450 °C	300 atm	53.3	89%	4%	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃
5	450 °C	600 atm	62.2	94%	2%	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃
5	450 °C	1000 atm	63.9	86%	5%	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃
5	425 °C	300 atm	30.7	87%	46%	CO-H ₂ (1:1)	ThO ₂ + 40% Al ₂ O ₃
5	450 °C	300 atm	41.6	85%	18%	CO-H ₂ (1:1)	ThO ₂ + 40% Al ₂ O ₃
5	475 °C	300 atm	48.6	88%	6%	CO-H ₂ (1:1)	ThO ₂ + 40% Al ₂ O ₃
5	450 °C	300 atm	33.3	84%	5%	CO-H ₂ (1:1)	ThO ₂ + 29% Al ₂ O ₃
5	400 °C	300 atm	21.0	81%	11%	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃
5	450 °C	300 atm	69.5	87%	8%	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃
5	475 °C	300 atm	77.0	90%	2%	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃
5	450 °C	600 atm	67.9	91%	6%	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃

Source	Temperature	Pressure	g C ₄ /m ³ Feed	i-C ₄ Selectivity (Total)	% i-C ₄ H ₁₀ of i-C ₄	Feed Ratios	Catalyst
5	425 °C	300 atm	26.2	67%	—	CO-H ₂ (1:1)	ThO ₂ + 20% Al ₂ O ₃
5	450 °C	300 atm	26.0	90%	—	CO-H ₂ (49:41)	ThO ₂
5	450 °C	300 atm	13.0	92%	—	CO-H ₂ (49:41)	ThO ₂ + 0.6% K ₂ CO ₃
5	450 °C	300 atm	70.0	87%	8%	CO-H ₂ (49:41)	ThO ₂ + 20% Al ₂ O ₃
5	450 °C	300 atm	77.0	87%	8%	CO-H ₂ (49:41)	ThO ₂ + 20% Al ₂ O ₃ + 0.2% K ₂ CO ₃
5	450 °C	300 atm	95.0	90%	5%	CO-H ₂ (49:41)	ThO ₂ + 20% Al ₂ O ₃ + 0.6% K ₂ CO ₃
5	450 °C	300 atm	16.0	63%	—	CO-H ₂ (49:41)	Al ₂ O ₃
5	450 °C	300 atm	3.0	67%	—	CO-H ₂ (49:41)	Al ₂ O ₃ + 3% K ₂ CO ₃
5	450 °C	300 atm	2.5	76%	6%	CO-H ₂ (41:49)	ZnO
5	450 °C	300 atm	36.4	87%	3%	CO-H ₂ (40:50)	ThO ₂ + 25% ZnO
5	425 °C	150 atm	12.9	90%	—	CO-H ₂ (48:42)	ThO ₂ + 25% ZnO
5	450 °C	150 atm	18.2	88%	11%	CO-H ₂ (48:42)	ThO ₂ + 25% ZnO
5	450 °C	150 atm	25.2	89%	—	CO-H ₂ (48:42)	ThO ₂ + 13% ZnO
5	450 °C	300 atm	22.4	86%	—	CO-H ₂ (48:42)	ThO ₂ + 25% ZnO
5	425 °C	150 atm	5.9	64%	—	CO-H ₂ (49:41)	ZnO + 39% Al ₂ O ₃
5	450 °C	150 atm	22.2	88%	6%	CO-H ₂ (49:41)	ZnO + 39% Al ₂ O ₃
5	450 °C	300 atm	30.8	86%	3%	CO-H ₂ (41:49)	ZnO + 39% Al ₂ O ₃
5	450 °C	300 atm	28.6	84%	14%	CO-H ₂ (41:49)	ZnO + 56% Al ₂ O ₃
5	450 °C	300 atm	36.4	87%	—	CO-H ₂ (51:39)	ThO ₂ + 11% Al ₂ O ₃ + 30% ZnO
5	450 °C	300 atm	37.2	92%	—	CO-H ₂ (56:39)	Cr ₂ O ₃
5	500 °C	300 atm	—	—	—	CO-H ₂	Al ₂ O ₃ + 10% Cr ₂ O ₃
5	400 °C	150 atm	8.5	—	—	CO-H ₂ (48:42)	H ₃ PO ₄
5	450 °C	300 atm	19.4	89%	—	CO-H ₂	ThO ₂ + 0.25% Fe

<u>Source</u>	<u>Temperature</u>	<u>Pressure</u>	<u>g C₄/m³ Feed</u>	<u>i-C₄ Selectivity</u>	<u>% i-C₄H₁₀ of i-C₄</u>	<u>Feed Ratios</u>	<u>Catalyst</u>
5	450 °C	300 atm	24.0	94%	—	CO-H ₂	ThO ₂ +1.25% Fe
5	425 °C	300 atm	78.7	87%	11%	CO-H ₂ (50:50)	ThO ₂ +20% Al ₂ O ₃
5	375 °C	300 atm	11.0	88%	54%	CO-H ₂ (50:50)	ThO ₂ +20% Al ₂ O ₃
6	475 °C	300 atm	78.7	87%	11%	CO-H ₂	ThO ₂ +20% Al ₂ O ₃
<u>Feed ml/min</u>							
7	643 K	69 kPa	—	57%	93%	N ₂ DME (91-0.01)	ZrO ₂
7	643 K	69 kPa	—	74%	93%	N ₂ DME (91-0.43)	ZrO ₂
7	643 K	69 kPa	—	77%	100%	N ₂ DME (91-0.7)	ZrO ₂
7	643 K	69 kPa	—	92%	100%	N ₂ DME (91-6.2)	ZrO ₂
7	643 K	69 kPa	—	97%	100%	N ₂ CO-H ₂ (18-36-36)	ZrO ₂
7	643 K	69 kPa	—	92%	100%	N ₂ CO-H ₂ DME (18-36-36-0.23)	ZrO ₂
7	643 K	69 kPa	—	95%	98%	N ₂ CO-H ₂ DME (18-36-36-0.7)	ZrO ₂
7	643 K	69 kPa	—	97%	100%	N ₂ CO-H ₂ DME (18-36-36-4.4)	ZrO ₂
7	643 K	69 kPa	—	97%	100%	N ₂ CO-H ₂ DME (18-36-36-6.1)	ZrO ₂
<u>C₄ Yield mmol/min</u>							
7	643 K	69 kPa	2.7	97%	100%	N ₂ CO-H ₂ C ₂ H ₄ (20-40-40-1)	ZrO ₂
7	643 K	69 kPa	6.0	85%	99%	N ₂ CO-H ₂ (20-40-40)	ZrO ₂
7	633 K	69 kPa	2.1	97%	100%	N ₂ CO-H ₂ C ₂ H ₆ (20-40-40-1)	ZrO ₂
7	633 K	69 kPa	2.4	36%	97%	N ₂ CO-H ₂ (20-40-40)	ZrO ₂
7	643 K	69 kPa	0.1	—	—	N ₂ CO-H ₂ C ₂ H ₅ OC ₂ H ₅ (20-40-40-0.96)	ZrO ₂
7	643 K	69 kPa	9.2	97%	100%	N ₂ CO-H ₂ CH ₃ CHO ZrO ₂ (20-40-40-0.01)	

<u>Source</u>	<u>Temperature</u>	<u>Pressure</u>	<u>C₄ Yield mmol/min</u>	<u>i-C₄ Selectivity</u>	<u>% i-C₄H₈ of i-C₄</u>	<u>Feed ml/min</u>	<u>Catalyst</u>
7	643 K	69 kPa	4.4	98%	99%	N ₂ ,CO-H ₂ , CH ₃ CH(OCH ₃) ₂ (20-40-40-0.02)	ZrO ₂
7	643 K	69 kPa	0.4	42%	57%	N ₂ ,CO-H ₂ , CH ₃ CH ₂ CHO (20-40-40-0.003)	ZrO ₂
7	643 K	69 kPa	0.4	—	—	N ₂ ,CO-H ₂ , CH ₃ COCH ₃ , (20-40-40-0.03)	ZrO ₂
			<u>C₄ Yield μmol/min</u>			<u>Feed Ratios 35 ml/min</u>	
8	523 K	69 kPa	0.23	29%	98%	H ₂ ,CO (3:1)	ZrO ₂
8	573 K	69 kPa	5.3	91%	100%	H ₂ ,CO (3:1)	ZrO ₂
8	623 K	69 kPa	129	98%	99%	H ₂ ,CO (3:1)	ZrO ₂
8	673 K	69 kPa	220	92%	95%	H ₂ ,CO (3:1)	ZrO ₂
8	723 K	69 kPa	151	68%	84%	H ₂ ,CO (3:1)	ZrO ₂
8	673 K	71 kPa	0.6	—	—	H ₂ ,CO (3:1)	Zr
8	673 K	71 kPa	1.4	—	—	H ₂ ,CO (3:1)	ZrH
8	673 K	84 kPa	280	—	—	H ₂ ,CO (3:1)	ZrO ₂
8	673 K	71 kPa	79	—	—	H ₂ ,CO (3:1)	ZrO ₂ + 13% NaOH
8	673 K	84 kPa	152	—	—	H ₂ ,CO (3:1)	ZrO ₂ + 10% CaO
8	623 K	67 kPa	8.7	—	—	H ₂ ,CO (3:1)	ZrO ₂ + 10% Al ₂ O ₃
8	623 K	67 kPa	2	—	—	H ₂ ,CO (3:1)	ZrO ₂ + 10% SiO ₂
8	623 K	84 kPa	150	—	—	H ₂ ,CO (3:1)	ZrO ₂ + 1% Sc ₂ O ₃
8	623 K	84 kPa	274	—	—	H ₂ ,Co (3:1)	ZrO ₂ + 1% Y ₂ O ₃
8	623 K	84 kPa	278	—	—	H ₂ ,CO (3:1)	ZrO ₂ + 10% CeO ₂
8	623 K	84 kPa	282	—	—	H ₂ ,CO (3:1)	ZrO ₂ + 1% Nd ₂ O ₃
8	623 K	84 kPa	189	—	—	H ₂ ,CO (3:1)	ZrO ₂ +5% Nd ₂ O ₃
8	623 K	84 kPa	263	—	—	H ₂ ,CO (3:1)	ZrO ₂ +1% Sm ₂ O ₃
8	623 K	84 kPa	37	—	—	H ₂ ,CO (3:1)	ZrO ₂ +10%Nb ₂ O ₃

SOURCES

1. Maehashi, Tatsuichi; Maruya, Ken-ichi; Domen, Kazunari; Aika, Ken-ichi; Onishi, Takaharu; "Selective Formation of Iso-Butene from Carbon Monoxide and Hydrogen over Zirconium Oxide Catalyst", Chemistry Letters, 1984, p. 747-748.
2. Tseng, Shiaw C.; Jackson, Nancy B.; Ekerdt, John G.; "Isosynthesis Reactions of CO/H₂ over Zirconium Dioxide", Journal of Catalysis, Vol. 109, 1988, p. 284-297.
3. Tatsumi, T.; Shul, Y. G.; Sugiura, T.; Tominaga, H.; "Selective Synthesis of Isoalkanes from Synthesis Gas over Zeolite-Supported Ru-Pt Catalyst", Applied Catalysis, Vol. 21, 1986, p. 119-131.
4. Shul, Yong-Gong; Arai, Yukari; Tatsumi, Takashi; Tominaga, Hiro-o; "Reaction Mechanism for Selective Synthesis of Gasoline-Range Isoalkanes from Syngas over RuPtHY Zeolites", Bulletin of the Chemical Society of Japan, Volume 60, 1987, p. 2335-2341.
5. Pichler, Helmut; Ziesecke, Karl-Heinz; "The Isosynthesis" , Brennstoff-Chemie, Vol. 30, 1949, p. 1-39.
6. Storch, Henry; Golumbic, Norma; Anderson, Robert; The Fischer-Tropsch and Related Synthesis, Wiley and Sons, New York, p. 125-139, 454-463.
7. Maruya, Ken-ichi; Fujisawa, Takeshi; Takasawa, Akihiro; Domen, Kazunari; Onishi, Takaharu; "Effect of Additives on Selective Formation of Isobutene from the CO-H₂ Reaction over ZrO₂", Bulletin of the Chemical Society of Japan, Vol. 62, 1989, p. 11-16.
8. Maruya, Ken-ichi; Maehashi, Tatsuichi; Haraoka, Takashi; Narui, Shinichiro; Asakawa, Yukihiko; Onishi, Takaharu; "The CO-H₂ Reaction over ZrO₂ to Form Isobutene Selectively", Bulletin of Chemical Society of Japan, Vol. 61, 1988, p. 667-671.

[COMMENT by RGA: Table 1 was prepared January, 1991. No additions to the Table have been made since its initial tabulation. Additional references of importance are found in the manuscript submitted to the DOE Contractors meeting, September, 1991, which is included in the Appendix of this report.]

APPENDIX

CATALYST AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

by

Rayford G. Anthony and Aydin Akgerman

Project Team and Contributors to This Report
Dr. C. V. Philip, Associate Research Scientist
Dr. Can Erkey, Post Doctoral Research Associate
Z. (Jeffrey) Feng, Ph. D. Student
Walter Postula, Ph. D. Student

DOE Contract No. DE-AC22-90PC90045
Texas A&M Research Foundation Project No. 6722

OBJECTIVES

The objectives of the project are: (1) To synthesize new catalysts; (2) To develop kinetic and reactor models for fixed bed trickle flow, slurry flow, and fixed bed gas phase reactors; and (3) to simulate and optimized the performance of these reactors for conversion of hydrogen lean synthesis gas to isobutylene. To accomplish the stated objectives of the project, five major tasks have been defined. The first two are short term and consist of performing a thorough review of the literature, including the patent literature to identify the proven catalysts for isobutylene synthesis, and to begin the modification of existing bench scale equipment to perform the evaluation of catalysts and development of kinetic data. A preliminary literature search was conducted in the preparation of the proposal, however, this area was revisited to insure that no important work reported in the literature was overlooked. The other three tasks are on synthesis, characterization and activity testing of potential catalysts, development of kinetic models for the respective catalysts, and optimization of the reactor configuration to maximize production of isobutylene. This report highlights the accomplishments with primary emphases on establishing base line results.

BACKGROUND

Earlier work on isobutylene and isobutane synthesis employed thoria based catalysts. Later isoalkenes were produced when zirconia was used at lower pressures and temperatures of 623 to 673 K. These difficultly reducible oxide catalysts such as ThO_2 (Pichler and Ziesecke,

1950a&b) and Dy_2O_3 , (Kieffer et al. 1983) were used under very severe conditions. A CdO catalysts combined with acid supports was used under mild conditions. Recently (Maruya, et al., 1988 and Onishi et al., 1988) have reported the use of ZrO_2 at mild conditions, and methoxide species and formate ions have been observed on the surface of the ZrO_2 catalysts. The mechanisms for formation of the branched alkanes has been postulated to be different than the mechanism for formation of linear alkanes.

It is believed (Vedage et al. 1985) that linear products are produced by CO insertion into an alkoxide instead of an aldol-like condensation scheme in which a formyl species reacts with an enolate (RCH_2-HCHO) at the carbon next to the carbonyl carbon. Mazanec (1986) proposed a CO insertion scheme involving a bound aldehyde to produce a cyclic acyl which has a two valence structures and the carbonyl carbon in one has carbenic character. Subsequent 1,2 shifts of hydrogen or R can lead to linear or branched products. Condensations reactions between eta-enolates and alkoxides were proposed to account for deviations from the Shulz-Flory distribution. Tseng et al. (1988) and Jackson and Ekerdt (1990) present the results of a comprehensive study and detailed discussion of proposed mechanisms on isosynthesis using zirconia. The formation of C_4 s is postulated to be by addition and condensation reactions (Maruya, et al. 1988, 1989; Tseng et al., 1988; Jackson and Ekerdt, 1990).

Pichler and Ziesecke (1950a&b) performed much of the pioneering work on conversion of synthesis gas to isoalkanes with high yields to isobutane and isobutylene. Severe conditions (300 atm. and 673 K) were used for this synthesis. Zirconia was found by Pichler and Ziesecke to be the second most active catalysts for the isosynthesis reaction. Maruya, et al. (1989) producing a C_4 fraction with 99+ % isobutylene, but the carbon C_4 selectivities were in the range of 77 to 85% . The latter value was obtained when zirconia was impregnated with NaOH.

CATALYSTS SYNTHESIS AND CHARACTERIZATION

Synthesis: Three types of synthesis procedures are to be used in the project. They are the precipitation from inorganic salts, such as zirconyl chloride or zirconyl nitrate with ammonium hydroxide or a hydroxide from group 1 of the periodic table. These materials will be referred to as preparation method 1, i.e. Cat. #1. For example data presented herein will be on catalysts prepared by precipitation of zirconyl nitrate with ammonium hydroxide. The catalysts are labeled CAT 1, batch 1,2,3 or 4. Catalysts prepared by the Sandia procedure (Dosch et al.,

1990a & b and Stephens et al., 1985) developed by Dosch for hydrous metal oxides will be referred to a CAT. 2. Data are presented herein for Cat. 2. Method 3 consists of using the method developed by Anthony and Dosch (1990) for the preparation of a new series of titanates. Zirconium will be used instead of titanium in the preparation. No data will be reported in this paper on Cat. No. 3.

Characterization: Differentiation between cubic zirconia and tetragonal zirconia by use of XRD has been reported to be very difficult and impossible. Cubic zirconia is normally formed at temperatures above 1200 °C except in the presence of alkali or alkaline salts. The cubic form can then be stabilized at lower temperatures. Inspection of XRD powder patterns suggests that one should be able to distinguish between the cubic and tetragonal forms. However, this is very difficult to accomplish except for highly crystalline zirconia. Figures 1 through 3 illustrate XRD spectra of Cat. #1 Batch #1. Shortly after calcination, the zirconia appeared to be cubic, but was most probably composed of tetragonal and very small crystallites of monoclinic zirconia. Figures 2 and 3 illustrate XRD diffraction pattern and a Raman spectra after 6 months, and the Raman spectra clearly shows the presence of the monoclinic and tetragonal phases. The monoclinic phase based on Raman spectroscopy appears to be the dominant phase. The XRD pattern might lead one to believe otherwise. Using the same procedure as in Batch #1, Cat. No. 1, three additional batches were prepared and they all were monoclinic based on the XRD pattern. Activity data reported herein for Cat. 1 is for batches 3 and 4, because they were initially only monoclinic.

Figure 4 illustrates the titration curve for hydrous sodium zirconium oxide prepared by Dosch's method. The sodium content was decreased to a small level using HCl exchange, and then calcined at 500 °C for 4 hours. The zirconia formed by this method should be more acidic than the zirconia prepared according to procedure #1. The sodium can be removed by ion exchanging with ammonium hydroxide/chloride solution at a high pH and then calcined. Zirconia synthesized with this method will be more basic than when using HCl to remove the sodium. However, the catalyst #2 activity reported herein is for the HCl exchanged catalysts. After calcination Catalyst #2 appeared to be monoclinic. Jackson and Ekerdt (1990) have reported that the catalytic activity does not appear to be a function of the particular phase.

BENCH SCALE UNITS AND PROCEDURES USED IN EVALUATING THE CATALYSTS ACTIVITIES

Bench-Scale Unit #1: A schematic diagram of BSU1 is shown in Figure 5. The feeds CO and H₂ are metered with mass flow meter-controllers, pass through a mixer, into a preheater contained in the oven I, and into a 3/8" reactor. The effluent from the reactor is passed through a back-pressure regulator, a liquid gas separator (L), and to a three-way valve which can be turned to vent the product gases into a hood, or pass the product gases through a gc sample loop to a bubble meter and then vent into a hood. A nitrogen purge line is also connected to the reactor. Molecular sieve (5A) dryers are on each of the feed lines for removal of residual moisture from the feed gases, and a charcoal filter is on the CO line to remove carbonyls. For this report the gc column is picric acid on Carbopak. Propylene, the C₄s and higher molecular weight hydrocarbons are separated on this column. The gc is equipped with FID and TCD detectors. A gas sampling port is also located at M for collecting samples for off-line analysis on a Carle gc equipped with several columns and switching valves. Hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane, propylene, each of the butylenes, butadiene, isobutane and n-butane and C₅⁺ hydrocarbons are obtained. The oxygenates, methanol, dimethyl ether, and water, are determined off-line by using a Gow-Mac gc equipped with a Poropak Q column. In the reactor thermocouples are located at the beginning and end of the bed. Some product is condensed in the trap L. These were high boiling hydrocarbons which eluted on a gc with a macropore silica column over the temperature range of 160 to 200 °C. Twenty four to forty eight hours of operation were required to detect the formation of these high molecular weight products. They are estimated to account for less than 1 %(w) of the hydrocarbon product produced.

Bench-Scale Unit No. 2: Bench unit No. 2 used in this work is a CDS 900 totally automated reactor-gc system. A schematic diagram is presented in Figure 6. (This unit is currently manufactured by Autoclave Engineers and called an AE MSBTR 900.) Nitrogen purge lines are not shown on this diagram. All of the lines from the reactor are heated to 180 °C, and no condensate is collected prior to analysis using the on-line gc. The on-line gc uses a palladium transfer tube for hydrogen analysis, a mole sieve for methane and CO; a Poropak Q for analysis of CO₂, methanol, water, dimethyl ether, ethane, ethylene, propane, propylene, isobutane, butane,

total butylenes, and other oxygenates using a TCD detector; and a macrobore silicon column with 5% methyl phenyl coating and a FID detector for determining the composition of the hydrocarbons produced. Isobutylene composition is determined by off-line analysis using the Carle gc described above. Since the analysis with the Carle yields some of the same information as the on-line analysis, the results are compared to determine if sample is lost in the process of sampling and analyzing off-line. The C_5^+ fraction from the Carle is usually 1 to 5% less than the C_5^+ fraction from the on line analysis.

A schematic of the reactor and ovens are shown in Figure 7. The reactor oven is maintained at a temperature of 180 °C, and the separate furnaces on the reactor tube are used to control reaction temperature. Liquid CO_2 can be fed to the heat exchanger located on the reactor tube to quench the reaction products. However, no CO_2 quenching was done in this study. A thermowell is located down the center of the 1/2" i.d. reactor tube, and used to measure the temperature profile with nitrogen flowing through the system and during the reaction. Figures 8 and 9 illustrate measured temperature profiles with and without reaction, and Figure 9 illustrated the simulation of the temperature profile from a reactor model for the unit. The catalyst is located in the isothermal portion of the reactor, i.e. between 20 to 25 cm. All three reactor heaters were maintained at the same temperature for this study, but a larger isothermal region should be the result by increasing the reactor heater temperatures at the top and bottom of the reactor.

For both systems the catalysts was loaded and purged with nitrogen at 400 °C for 4 hours prior to conducting the activity studies. Catalytic activity data reported herein for the precipitated catalysts, Cat. #1 batches 3 and 4, were obtained in the BTU1, and catalytic activity data reported for Cat. #2 were obtained using the AE MSBTR 900.

CATALYSTS EVALUATION

Figure 10 illustrates the activity and effect of pressure on CO conversion for zirconia using preparations 1&2. Preparation #2 is designated by the (\$ Feng @ 425). The space time, τ , is defined as the bulk volume of the catalysts divided by the volumetric feed rate calculated at reaction conditions. The actual residence time is greater than the space time because of the decrease in the number of moles with reaction. However, at low conversions space time is a close approximation to residence time, which is dependent on the extent of reaction. Figure 10

illustrates that pressure does not have a significant effect on conversion at equal space times for a 1:3 or a 1:1 CO:H₂ ratio. Similarly results were obtained by Pichler and Ziesecke (1950 a&b) for thoria catalysts. The data also seems to suggest that Cat. #2 is not as active as Cat. #1. Figures 11 and 12 illustrate the expected trend for change in conversion with space time at 95 atm. and 400 °C. Space times of 90 seconds are required to obtain 20% CO conversion. Figure 13 illustrates the expected increase in conversion with increasing temperature for the two catalysts. The trends are the same indicating essentially the same reaction mechanism and activation energy.

Figure 14 illustrates the long term activity of catalyst #2. There appears to be an increase in activity with time on stream. All of the previous data were reported after approximately two hours on stream. However, based on the results from Figure 14 longer times at a fixed set of conditions may be required to reach a true steady state in relation to CO conversion. The amount of isobutylene in the C₄ fraction did not change with time on stream. Reaction stoichiometry appears to correspond primarily to that for the formation of olefins, alkanes and carbon dioxide.

The usage ratio of hydrogen to carbon monoxide was 0.53 ± 0.01 , and with the exception of methane formation the hydrocarbon distribution appears to be predominately olefins.

In order to gain some insight into the type of reactions occurring several ratios were calculated, and are presented Table 1. Table 1 illustrates the average values obtained for the isosynthesis profile, the branched to linear C₄s and the isobutylene selectivity within the C₄ fraction. The isosynthesis profile was defined by Jackson and Ekerdt as the ratio of C₄s to (ethane + propane). Jackson and Ekerdt used a molar ratio, but the data presented in Table 1 are weight ratios. Data reported by Jackson and Ekerdt and data obtained for Catalysts #1 and #2, respectively are presented. The isosynthesis profile is a measure of the relative importance of the condensation reactions. The data shown in Table 1 did not appear to show any trends because of the large error bands on the experimental points. Further work on refining the analytical and sampling procedures is required to determine if a trend exists with a variation in temperature, pressure, space time and CO:H₂ ratio. Ratios and the profile obtained in this study are comparable with the values reported by Jackson and Ekerdt (1990).

Figures 16, 17 and 18 illustrate the effect of pressure, space time, and CO:H₂ ratio on the molar ratio of isobutylene to methane and the weight ratio of isobutylene to C₅⁺ for Cat. #1. For

a 1:3 CO:H₂ ratio the isobutylene to C₅⁺ decreases as the pressure is increased, but the molar ratio of isobutylene to methane is essentially constant at 0.3. These conditions correspond to CO conversions less than 5%. However, at 95 atm and a 2:1 CO:H₂ ratio, the isobutylene to methane molar ratio varies from 0.5 to 0.75 as the CO conversion is increased with an increase in residence time.

Figure 19 shows a comparison of catalysts preparation procedures. An increase in the weight ratio of isobutylene to C₅⁺ catalysts show the same increasing trend with increasing temperature. Figure 20 shows a comparison of the weight ratio of isobutylene to methane for Catalysts #1 and #2. For Catalyst #2 a decrease in the ratio is observed with increasing temperature. For Catalysts #1, a trend with increasing temperature is not observed. Obviously more data are needed to fully substantiate these results, since only two points at comparable space time were measure for each catalyst.

MACRO AND MICRO KINETIC MODELS

Macrokinetic models: Two approaches are being used to develop kinetic models for isobutylene synthesis from hydrogen lean synthesis gas. The first is to examine surface response models over comparable ranges of conversion and the parameter $kRT\tau$. Maruya et al. (1988) report a second order dependence on carbon monoxide and a first order dependence for hydrogen at pressures of 69 kPa (0.69) atmospheres. We considered these results and the possibility of reaction orders of first order CO and first order hydrogen, and second order hydrogen and first order CO. Utilizing the data from our experiments, a range of values for $kRT\tau$ which would give reasonable conversions were determined. The equations for these three cases at low conversion, which corresponds to only a small change in volumetric flow rate due to the decreasing stoichiometry of the reaction, are presented as follows.

Second Order CO and First Order H₂:

$$k R T \tau = \frac{2}{P_A^0 P_B^0 (2-\beta)} \left[\frac{x}{1-x} - \frac{\beta}{2-\beta} \log_e \frac{1-0.5\beta x}{1-x} \right] \quad \beta \neq 2$$

(1)

$$k R T \tau = \frac{2 x - x^2}{2 p_A^0 p_B^0 (1-x^2)} \quad \beta=2$$

(2)

$\beta = p_A^0/p_B^0$, the ratio of the initial partial pressures of A and B, where A = CO and B = H₂.

The stoichiometry, which was used, is for the reaction to produce olefins and CO₂.

First Order CO and Second Order H₂:

$$k R T \tau = \frac{2}{(p_B^0)^2 (\beta-2)} \left[\frac{\beta/2 x}{1-\beta/2} - \frac{2}{\beta-2} \log_e \frac{1-x}{1-\beta/2 x} \right] \quad \beta \neq 2$$

(3)

For $\beta = 2$

$$k R T \tau = \frac{2 x - x^2}{2 (p_A^0)^2 (1-x)^2}$$

(4)

First Order CO and First Order H₂:

$$k R T \tau = \frac{2}{p_B^0 (2-\beta)} \log_e \frac{1 - 0.5 \beta x}{1 - x} \quad \beta \neq 2$$

(5)

For $\beta = 2$

$$k R T \tau = \frac{x}{p_B^0 (1-x)} \quad \beta=2$$

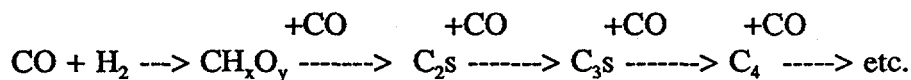
(6)

The left hand side of Equations (1) through (6) is a function of temperature and space time, and has the units of reciprocal atm. to the first or second power. The right hand side of these

equations is a function of conversion, pressure and the feed composition. The unit on the right hand side are also reciprocal atm.

Figures 20, 21, and 22 illustrate plots of these equation for the different orders and feed compositions. The most interesting feature of these graphs are the low conversion predicted for first order hydrogen and first order carbon monoxide. The second interesting feature is the shifting of the curves for CO:H₂ feeds of 1:3 and 2:1 for the two reaction orders shown. The conversions obtained in this study appear to be representative of Equations 1 through 4. Additional work is required to discriminate between these equations.

The approach represented above could be the first step in a series, parallel reaction sequence of the following type.



With the exception of the formation of CH_xO_y and the C₂s, condensation reactions would also occur in addition to CO insertion. This macro reaction sequence needs further refining to account for branching reactions.

Micro Kinetic Model: A micro kinetic sequence is being developed based on elementary steps. The mechanisms presented by Tseng et al. (1988), Maruya et al. (1988 and 1989) and Jackson and Ekerdt (1990) are being used in development of the microkinetic model. In addition, the bond energies of each elementary step are calculated using the Bond Order Conservation Theory of Schustorovich. This approach is the group contribution method which involves the use of heats of chemisorption of atoms of O, H, and C on metal surfaces to calculate the heats of chemisorption of molecular species. The heats of chemisorption of O and H on zirconia were estimated using literature data. The values for C were extrapolated based on the periodic table. These heats of chemisorption of individual atoms when combined with gas phase dissociation energies enables one to calculate the activation energies. A total of 68 equations have been postulated to occur. The theory has been developed for metals, and we are extending the method to the metal oxides.

The results of the initial calculations are encouraging because the activation energies which have been calculated suggest reaction pathways which have been proposed by others

(Jackson and Ekerdt, 1990). Table 2 list the reaction sequences and activation energies calculated to date. Many additional steps are required to complete the model for isobutylene synthesis.

REACTOR MODELS

Substantial progress has been made in developing a reactor model for the trickle bed reactor for isobutylene synthesis from synthesis gas. As a first approximation a molecular second order reaction is being used to develop the basic algorithm. Further work will be required when a kinetic rate equations have been developed. Figures 23 through 26 show the dimensionless equations and boundary conditions and some typical results obtained for the proposed model. Gas and liquid concentration profiles are calculated, and a profiles of the concentration of reactants and products within the pores are also illustrated. Resistance to diffusion of the reactants and products are illustrated in Figure 26. If no resistance to diffusion existed the concentrations would be uniform throughout the catalyst pellet.

SUMMARY OF ACCOMPLISHMENTS AND FUTURE PLANS

The bench scale reactor systems have been successfully operated for a period of approximately one month with substantial amount of data obtained. The data reported above are for Batches 3 and 4 of catalysts preparation Cat. #1. Data were also obtained on a catalyst prepared by catalyst preparation #2. Batches 2 and 3 for preparation of Cat. 1 were chosen because the XRD patterns and Raman spectra indicated they were predominately monoclinic, and unlike the result obtained for batch #1, the XRD pattern did not change after the first calcination. Cat. 2 was used to illustrate the performance of the AE MSBTR 900 for this system. Experiments are planned for the AE MSBTR 900 reactor system using preparation, Cat. #1, to produce the zirconia. The objective of these experiments is to verify that the same or nearly the same results are obtained when using either reactor system. The experimental procedures used to obtain the data presented herein needs to be refined. Our gc-ms is being repaired so the type (olefins, alkanes, oxygenates) of the higher molecular weight compounds can be determined.

Several methods of preparing the zirconia will be investigated to determine the effect of calcination and drying on the catalysts activity. Methods to be used are supercritical extraction, coating of pre-engineered supports. Removing the sodium or potassium from the hydrous zirconium oxide by ion exchanging with ammonium hydroxide or ammonium chloride, followed

by filtering, drying and calcination. We also plan to evaluate catalysts prepared by using Cat. prep. #3. It is well known that the method of preparation can greatly affect the catalytic activity. For example, the mixed oxides of MgO-TiO₂ (10% MgO) and TiO₂-SnO₂ when calcined in vacuum have high basicities, (Tanabe, 1970 and 1981). Recent work reported at the 12th North American Catalysts Society Meeting in Lexington, KN (May, 1991) showed the effect on zirconia surface area by using supercritical extraction to prepare the zirconia. We plan to make significant progress in the synthesis of isobutylene in the next year.

LITERATURE CITED

- Anthony, R. G. and Dosch, R. G., "Catalysts and Preparation of New Titanates," in Preparation of Catalysts V, Ed. Poncelet, G. P. A. Jacobs, P. Grange and B. Delmon, Elsevier Science Publishers B. V., Amsterdam, pages 637-646 (1990).
- Dosch, R.G., Stephens, H. P., and Stohl, F. V., SAND89-2400, Sandia National Laboratories, 1990a.
- Dosch, R. G., Stephens, H. P., and Stohl, F. V., SAND8902400, Sandia National Laboratories, 1990b.
- Holland, C. D. and R. G. Anthony, Fundamentals of Chemical Reaction Engineering, Prentice-Hall Inc., Engelhard, NJ (1989).
- Kieffer, R., G. Cherry, and R. E. Bacha, "Carbon Monoxide-Hydrogen Reactions. Mechanism of Isobutane Formation in Isosynthesis," Mol. Chem., 2(1), 11- 23 (1983).
- Jackson, N. B. and Ekerdt, J. G., "The Surface Characteristics Required for Isosynthesis over Zirconium Dioxide and Modified Zirconium Dioxide," J. of Catal. 126, 31-45 (1990).
- Mazanec, T. J., "On the Mechanism of Higher Alcohol Formation Over Metal Oxide Catalysts" J. Catal. 98, 115 (1986).
- Maruya, 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).
- Maruya, K., T. Fujisawa, A. Takasawa, K. Domen and T. Onishi, "Effect of Additives on Selective Formation of Isobutene from the CO-H₂ Reaction over ZrO₂," Bull. Chem. Soc. Jpn., 62, 11-16 (1989).
- Onishi, T., Maruya, K-I, Domen, K., Abe, H., and Kondo, J., "The Mechanism of CO Hydrogenation Over Zirconium Oxide Studied by FT-IR," Catalysis: Theory to Practice,

- Vol. 2 (M. J. Phillips and M. Ternan, Editors), Proceedings of the 9th International Congress on Catalysis, Calgary, (1988).
- Pichler, H., and Ziesecke, K-H., "Über die bei der Isosynthese entstehenden sauerstoffhaltigen Verbindungen, unter besonderer Berücksichtigung der Alkole," *Brennst. Chem.*, **31**, 360 (1950a).
- Pichler, H., and Ziesecke, K-H., "The Isosynthesis," *Bur. Mines Bull.*, 488 (1950b).
- Stephens, H. P., Dosch, R. G., and Stohl, F. V., *Ind. & Engr. Che., Prod. Res & Dev.*, **24**, 15 (1985).
- Tanabe, K., *Solid Acids and Bases*, Academic Press, New York (1970).
- Tanabe, K., "Solid Acid and Base Catalysts," vol 2, pp. 231-273 in *Catalysis-Science and Technology*, Ed. J. R. Anderson and M. Boudart, Pub. Springer-Verlag, Berlin (1981)
- Tseng, S. C., N. Jackson, and J. G. Ekerdt, "Isosynthesis Reactions of Carbon Monoxide/Hydrogen Over Zirconium Dioxide," *J. Catal.* **109**(2), 284-297 (1988),
- Vedage, G. A., P. G. Himerfarb, G. W. Simmons, and K. Klier, in "Solid State Chemistry in Catalysis" Eds. R. K. Grasselli and J. F. Bradzil, ACS Symposium Series No. 279 (1985).

Table 1. Isosynthesis Characteristics of Different Catalysts

Item	Catalyst #1	Catalyst #2	J&E ¹
Isosynthesis Profile ²	4.55±1.28	2.29±0.79	2.30
Branched/ Linear C ₄	2.71±0.67	2.97±0.33	0.18
i-C ₄ H ₈ / All C ₄ 's	0.63±0.06	0.37±0.15	0.84

¹ N.B. Jackson and J.G. Ekerdt (1990). 425°C, 35 atm, 1:1 H₂/CO

² Defined as (total weight of C₄ hydrocarbons / total weight of C₂'s and C₃'s)

All the ratios are calculated on weight basis.

Table 2 Microkinetic Reaction Parameters

Reaction	E_A^f (kcal/mol)	E_A^r (kcal/mol)
(1) $H_2 + 2Zr \rightleftharpoons 2ZrH$	15	-7
(2) $ZrH + ZrO \rightleftharpoons ZrOH + Zr$	45	26
(3) $CO + Zr \rightleftharpoons ZrCO$	-32	
(4) $ZrCO + Zr \rightleftharpoons ZrC + ZrO$	25	-32
(5) $ZrC + ZrH \rightleftharpoons ZrCH + Zr$	39	5
(6) $ZrCH + ZrH \rightleftharpoons ZrCH_2 + Zr$	18	23
(7) $ZrCH_2 + ZrH \rightleftharpoons ZrCH_3 + Zr$	5	33
(8) $ZrCH_3 + ZrH \rightleftharpoons CH_4 + 2Zr$		
(9) $ZrCH_3 + ZrH \rightleftharpoons ZrCH_4 + Zr$	1	34
(10) $ZrCO + ZrH \rightleftharpoons ZrOCH + Zr$	13	19
(11) $ZrOCH + Zr \rightleftharpoons ZrCH + ZrO$	31	51
(12) $ZrOCH + ZrH \rightleftharpoons ZrOCH_2$	33	3
(13) $ZrOCH_2 + Zr \rightleftharpoons ZrCH_2 + ZrO$	4	-24
(14) $ZrOCH_2 + ZrH \rightleftharpoons ZrOCH_3 + Zr$	-4	23
(15) $ZrOCH_3 + ZrH \rightleftharpoons ZrCH_3OH + Zr$		
(16) $ZrCH_3OH + Zr \rightleftharpoons ZrCH_3 + ZrOH$		
(17) $ZrOCH_3 + ZrH \rightleftharpoons CH_3OH + 2Zr$		
(18) $ZrCH_3OH + Zr \rightleftharpoons ZrCH_3 + ZrOH$		
(19) $ZrCO + ZrOH \rightleftharpoons ZrOOCH + Zr$	17	18
(20) $ZrOOCH + Zr \rightleftharpoons ZrOCH + ZrO$	13	45
(21) $ZrOOCH + ZrH \rightleftharpoons ZrHCOOH + Zr$		
(22) $ZrOOCH + Zr \rightleftharpoons ZrO_2C + ZrH$	21	-13

XRD of Batch #1 - 4 Days after Preparation

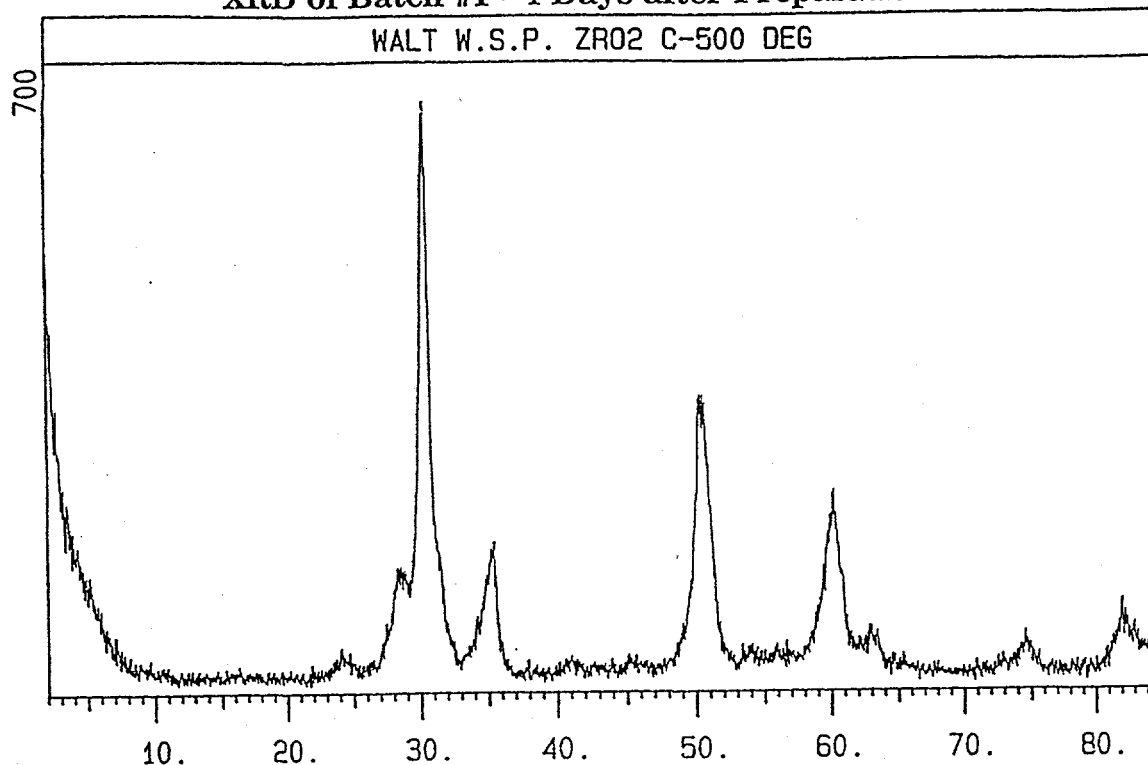


Figure 1. Catalyst #1, Batch #1 -- XRD Pattern Indicates Formation of Cubic or Tetragonal Zirconia.

XRD of Batch #1 - 6 Months after Preparation

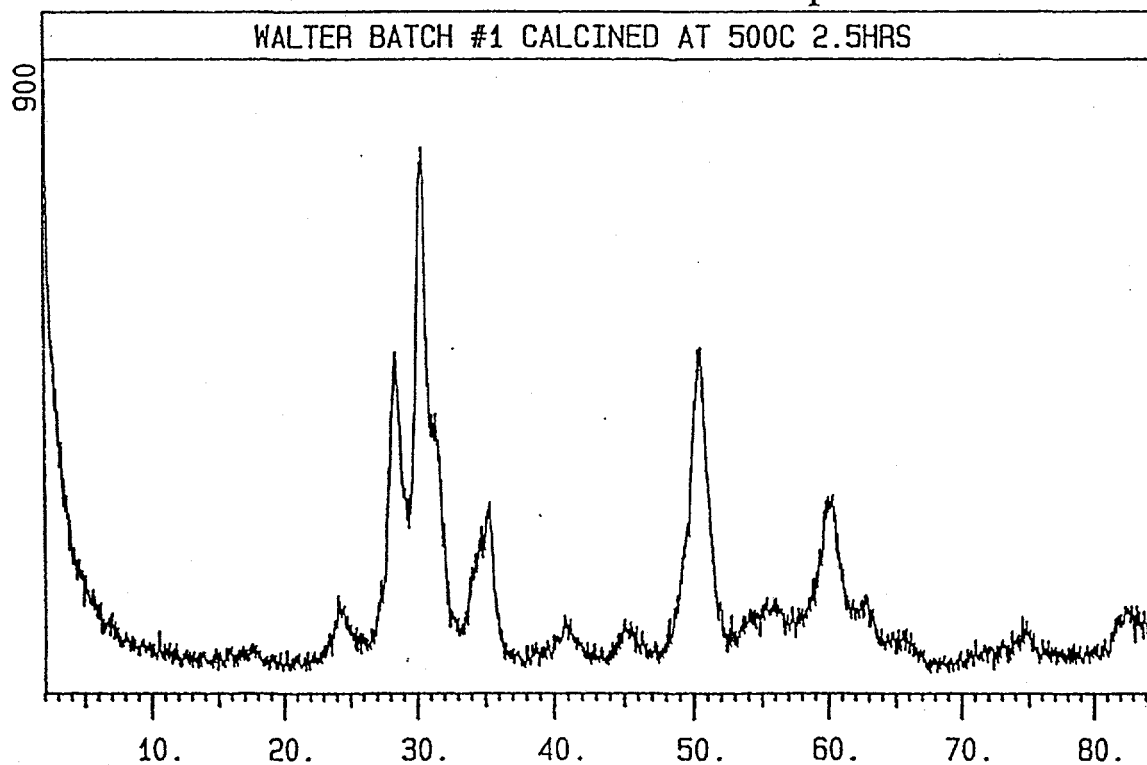


Figure 2. Catalyst #1, Batch #1 -- After Setting in Desiccator For Six Months.

Raman Spectra of Batch #1 - 6 Months after Preparation

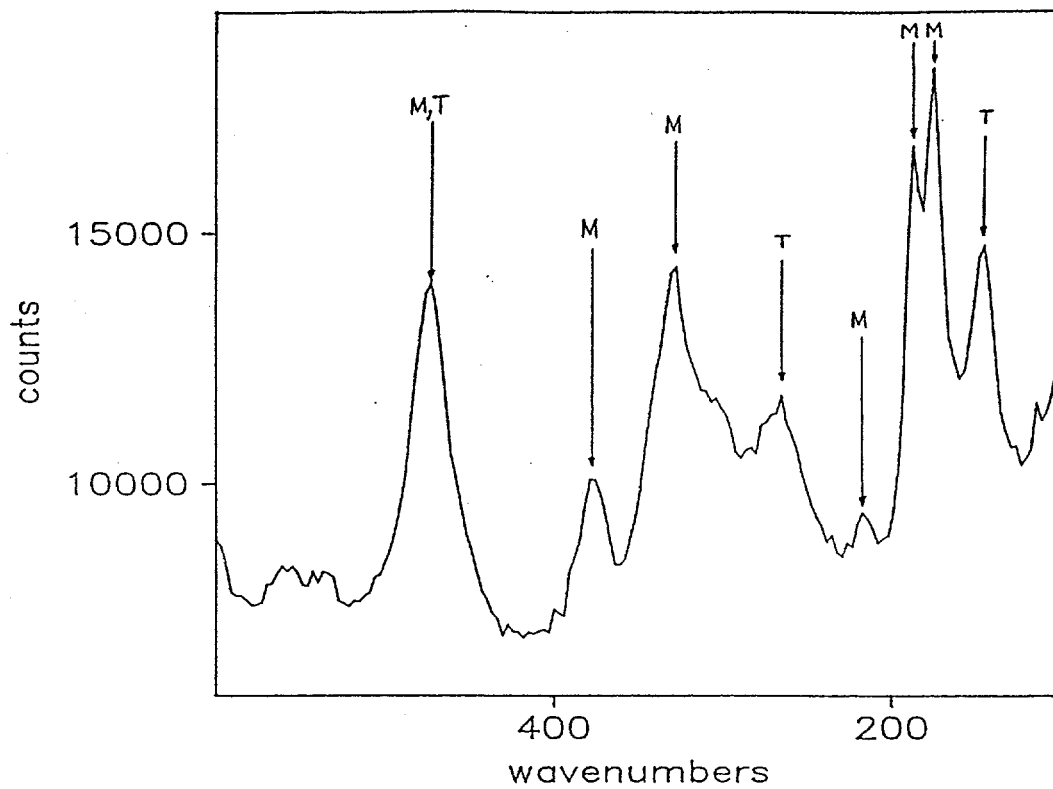


Figure 3. Catalyst #1, Batch #1 -- Raman Spectra Indicates Presence of Monoclinic and Tetragonal Zirconia.

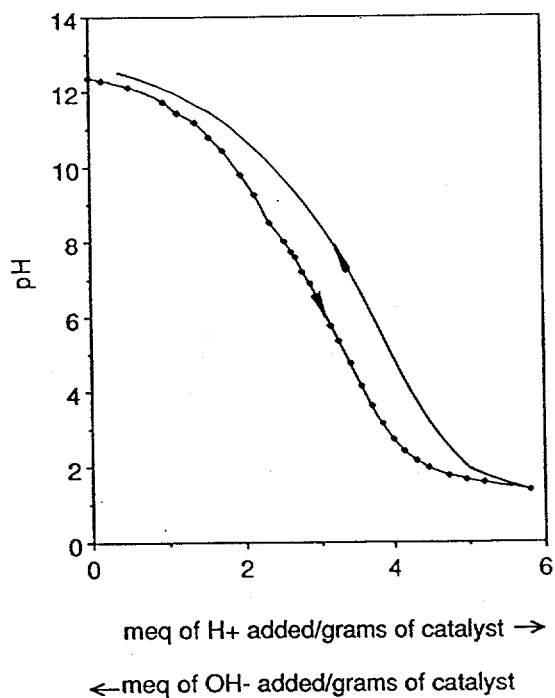


Figure 4. Titration Curve for Hydrous Sodium Zirconium Oxide.

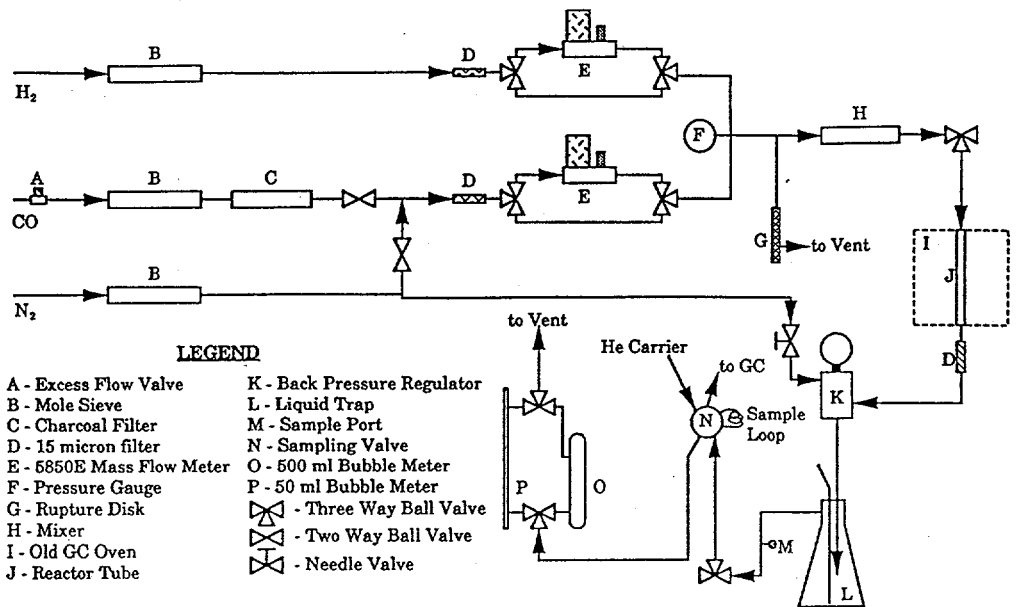


Figure 5. Schematic Diagram of Bench Top Reactor System #1.

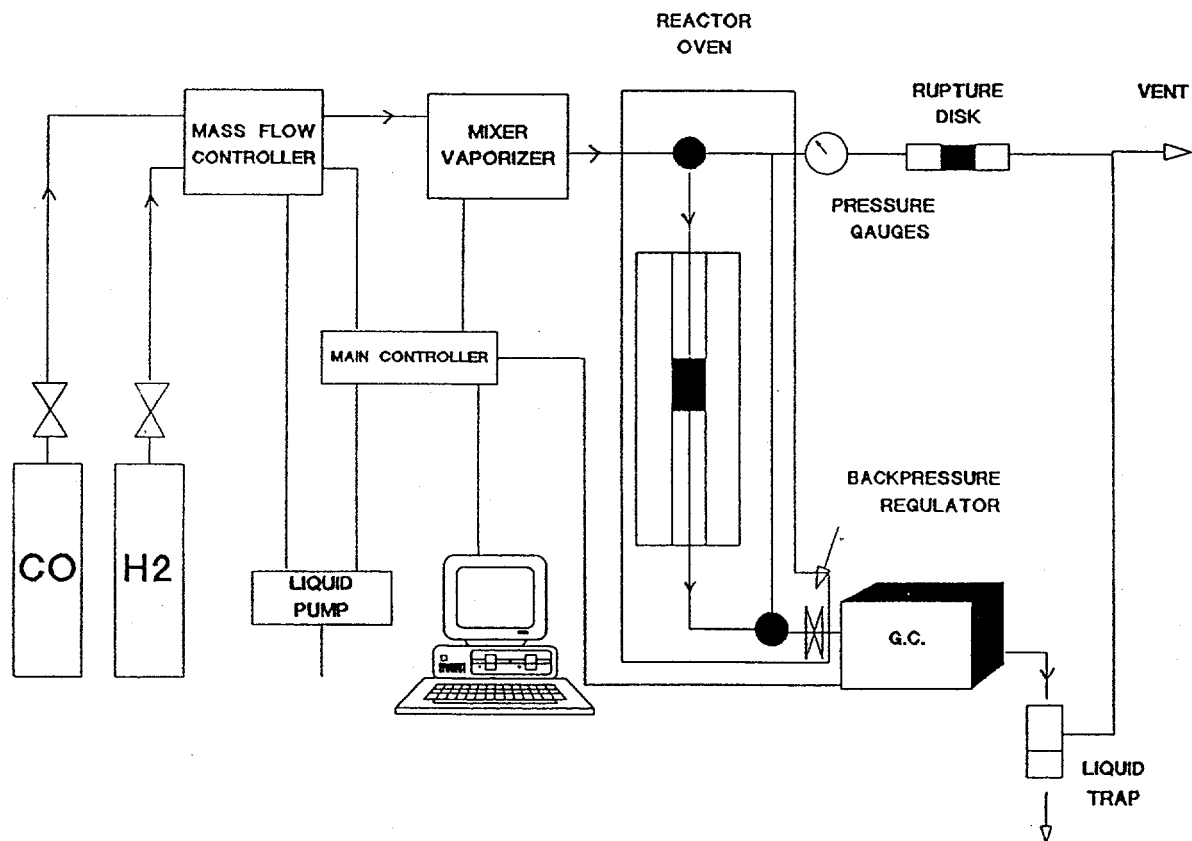


Figure 6. Schematic Diagram of AE MSBTR 900 (Formerly CDS 900) Reactor System

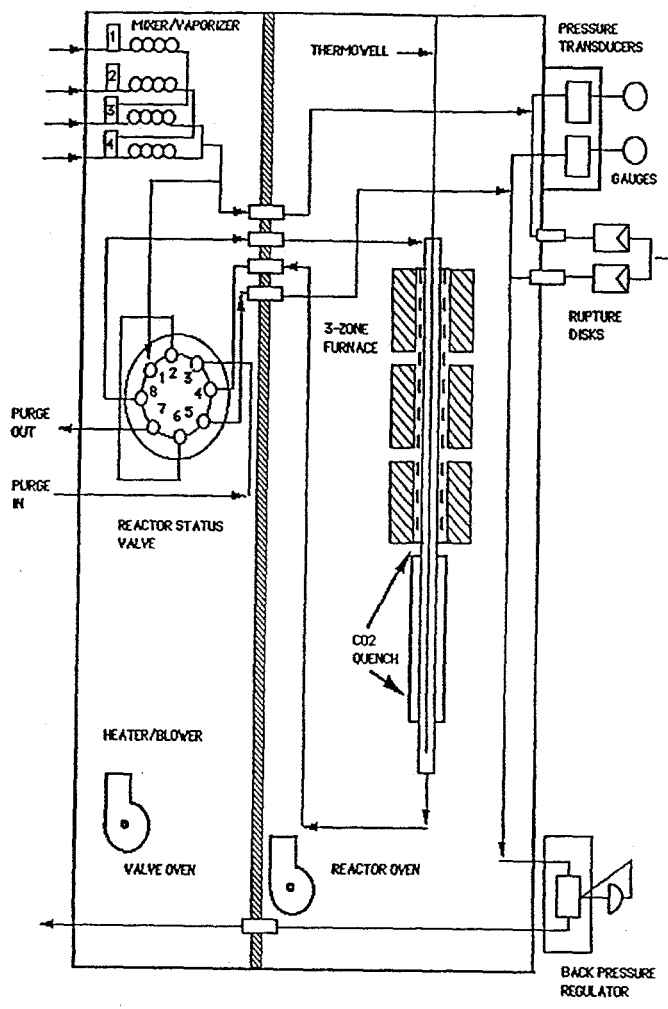


Figure 7. Reactor, Reactor Oven and Switching Valve Oven for AE MSBTR 900

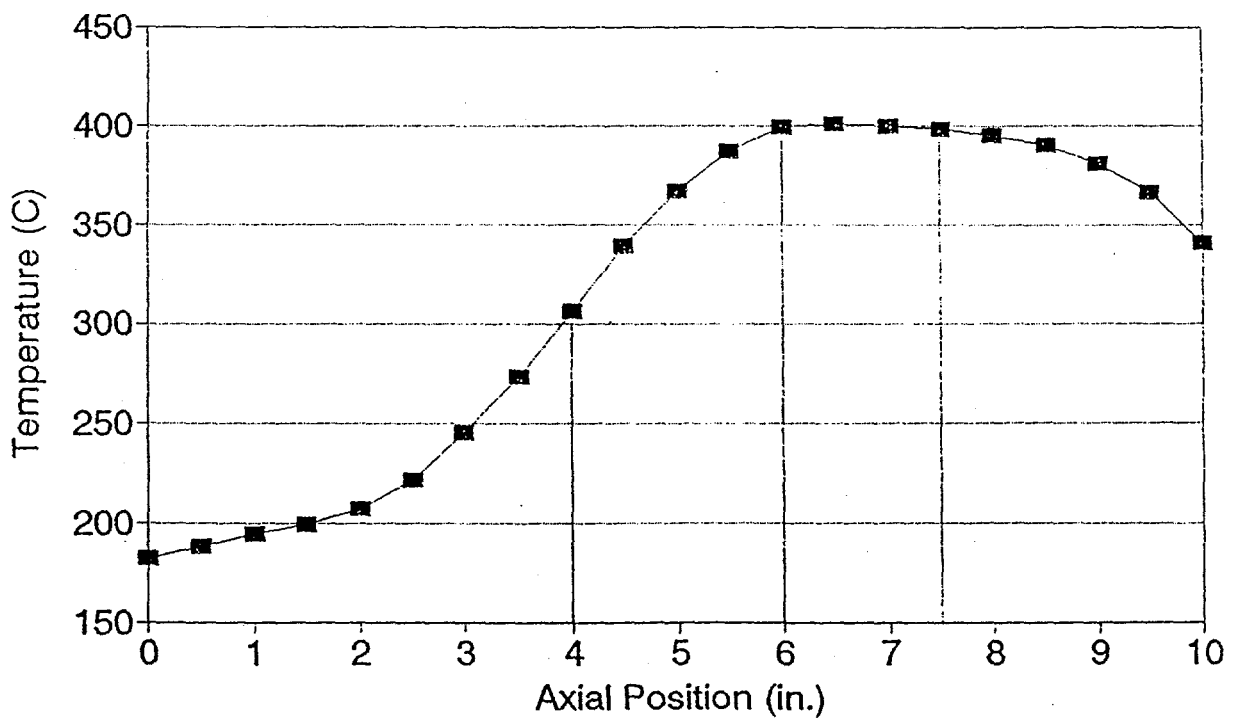


Figure 8. Typical Temperature Profile in the Reactor

Simulation of Temperature Profiles for CDS reactor system
(N₂ Flow, Heating Jacket Temp = 410 C, Oven temp = 180 C)

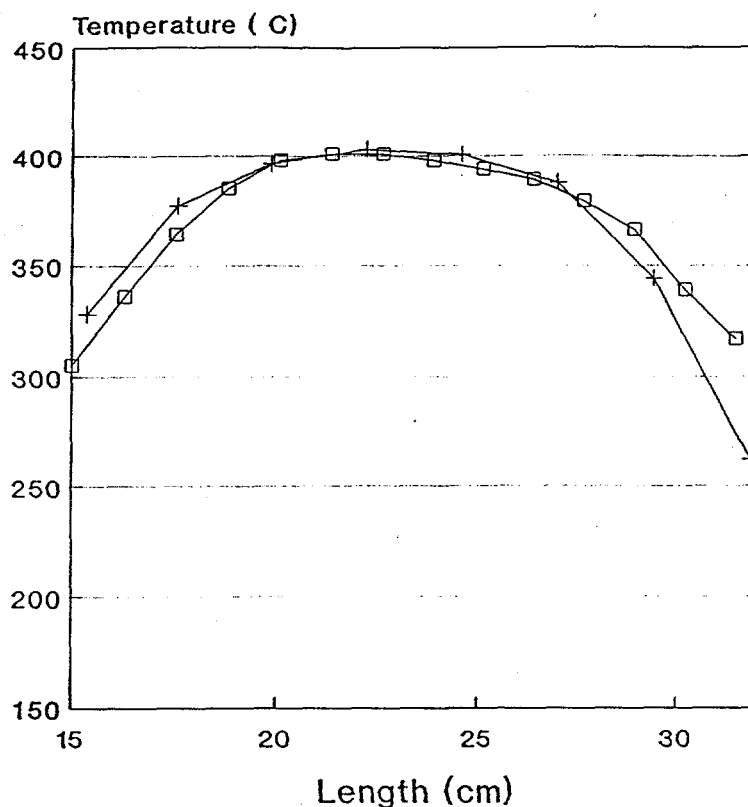


Figure 9. Actual and Calculated (Simulated) Reactor Profile for AE MSBTR 900

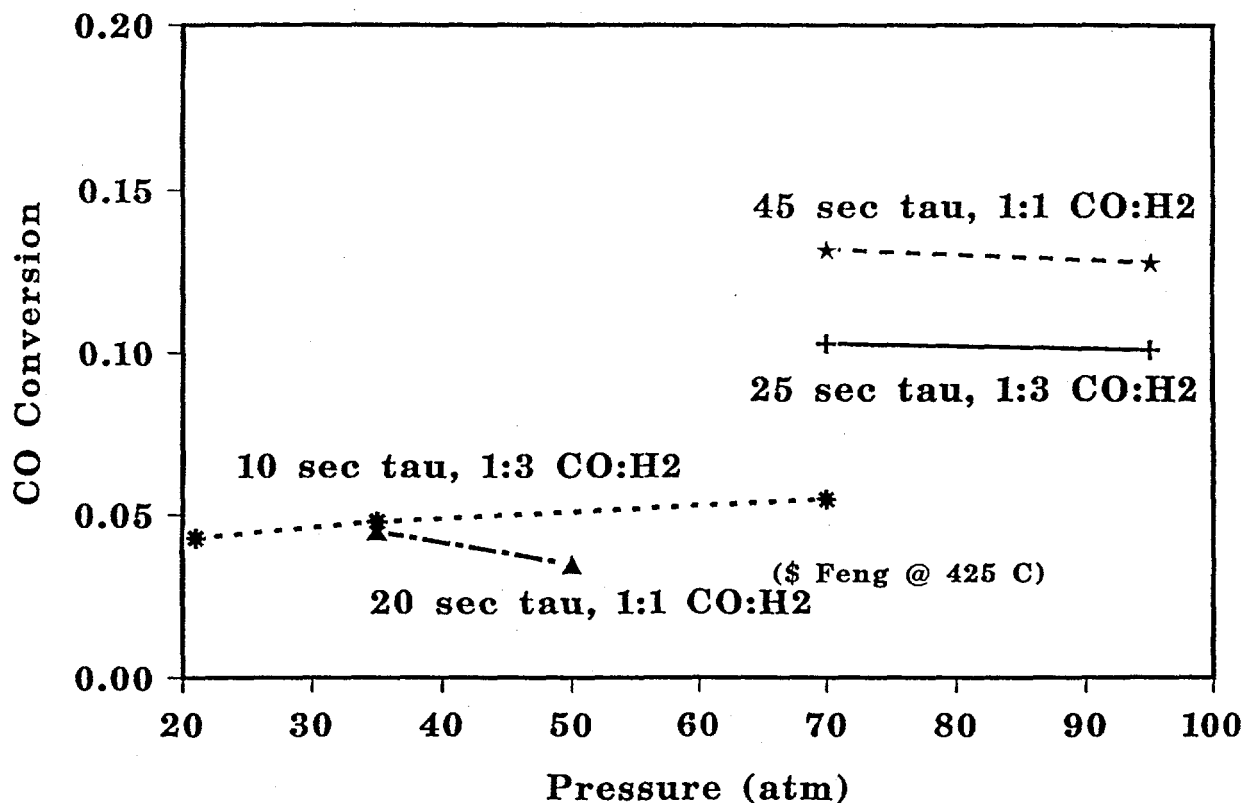


Figure 10. Activities and Effect of Pressure on Activity for Catalysts #1 and #2. (Cat. 2 is indicated by the (\$ Feng @ 425 °C).).

CO:H2 Ratio at 95 atm & 400 C

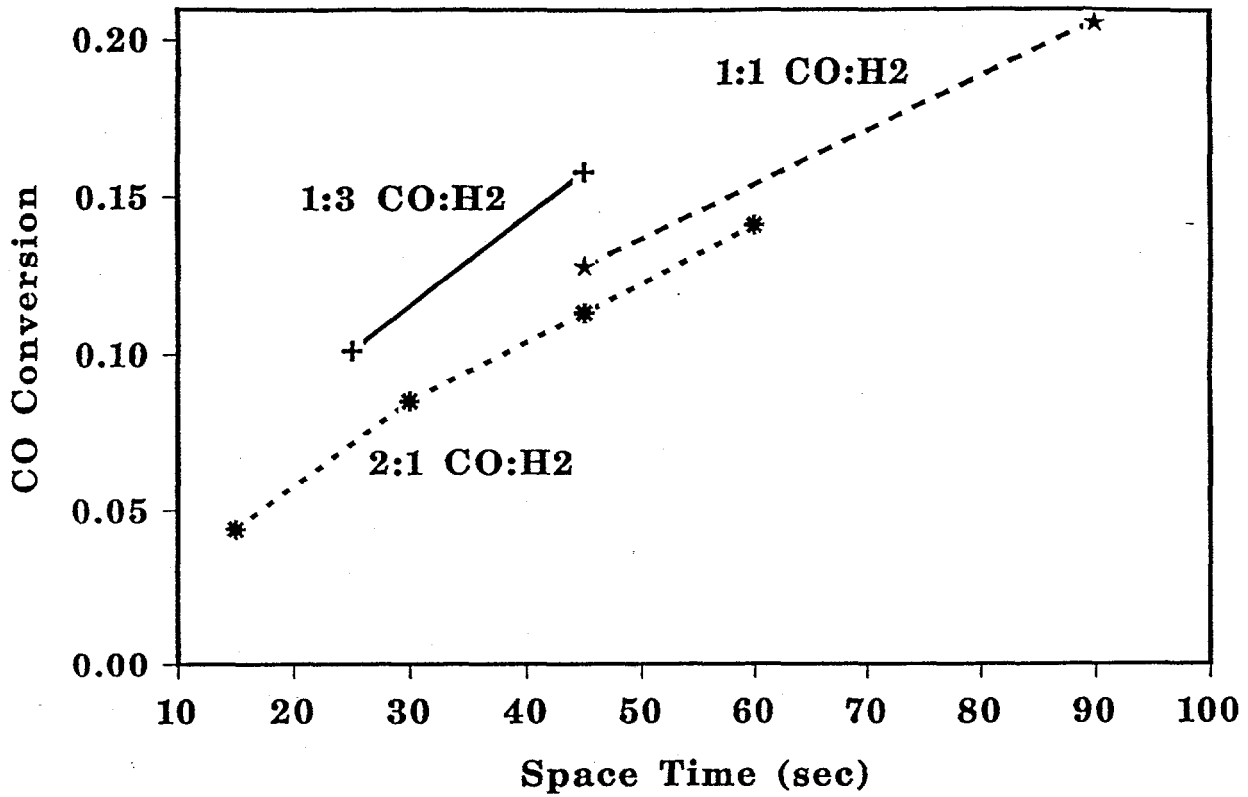


Figure 11. Activity as a Function of Space Time and Feed Ratios for Cat. #1.

CO/H2 1:1, 50 atm, 425 C

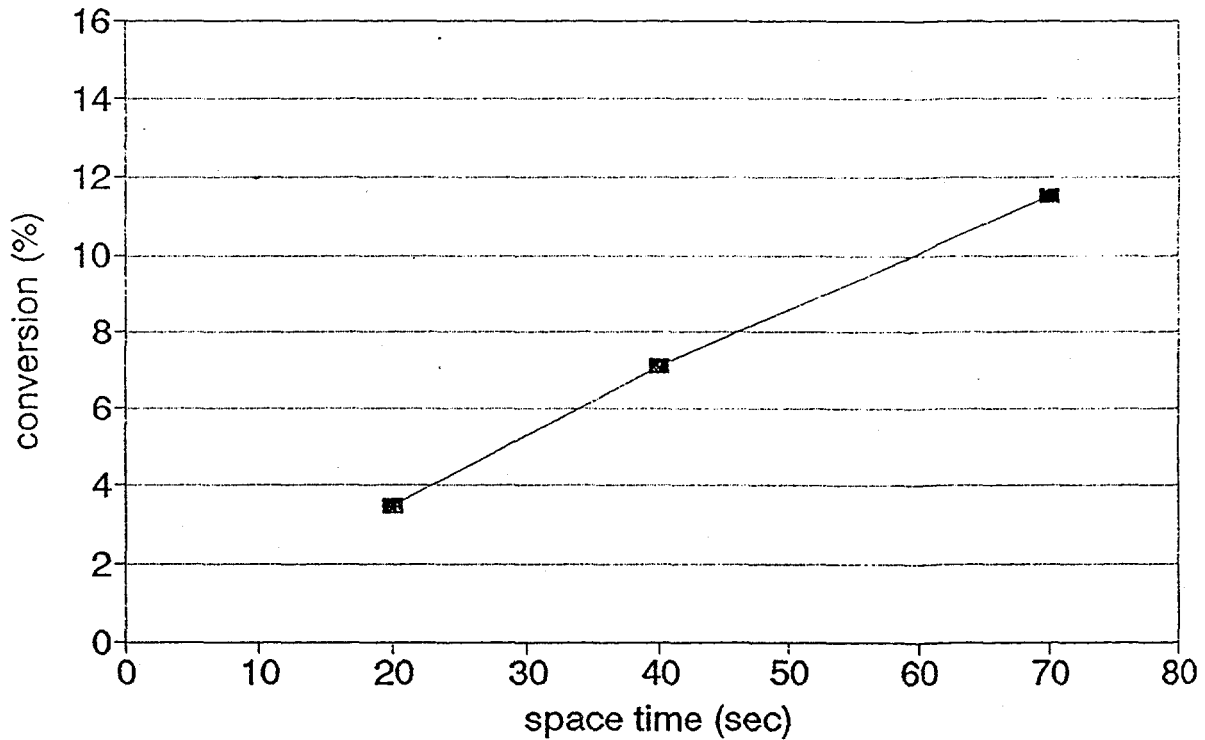


Figure 12. Activity of Catalyst #2.

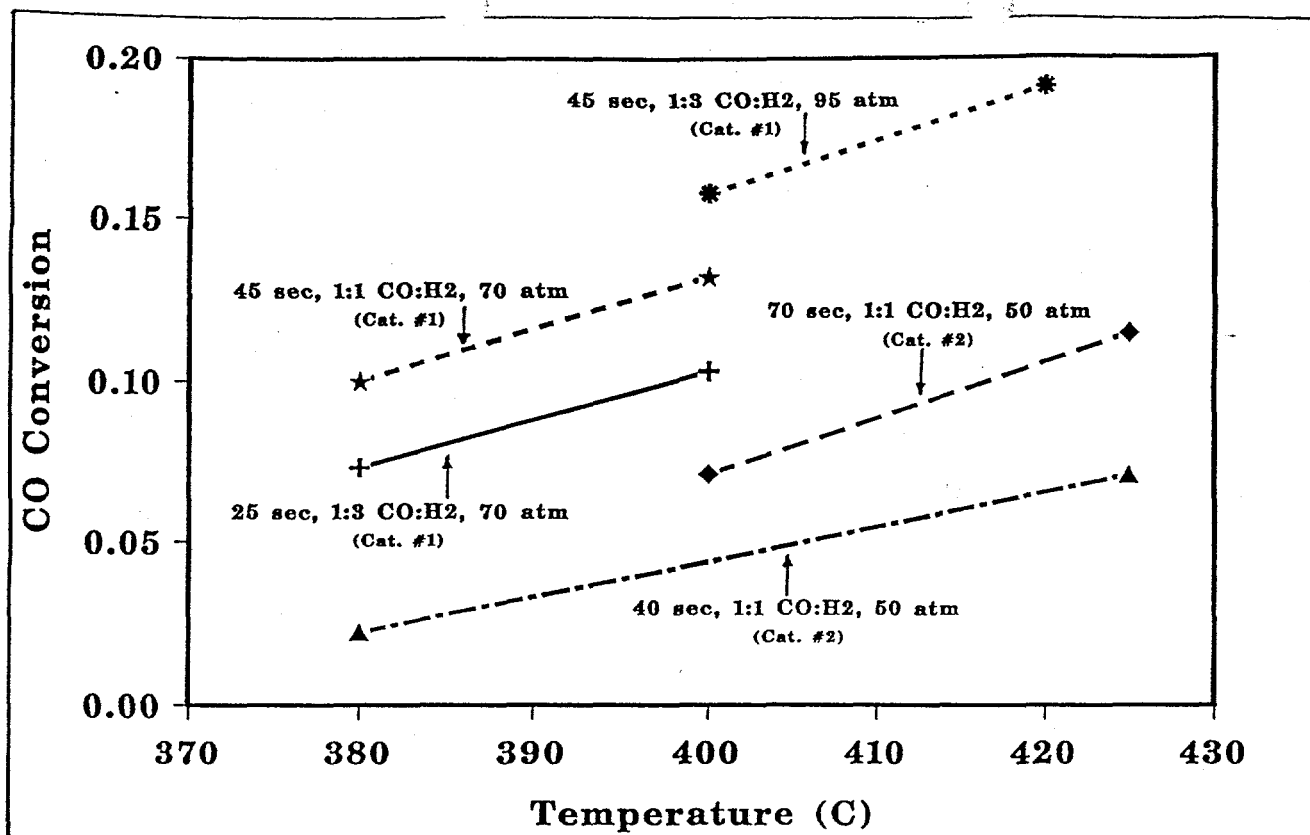


Figure 13. Comparison of Activities of Catalyst 1 and 2. Trends with respect to temperature are the same.

CO/H₂ 1:1, 35 atm, 425 C, 20 sec

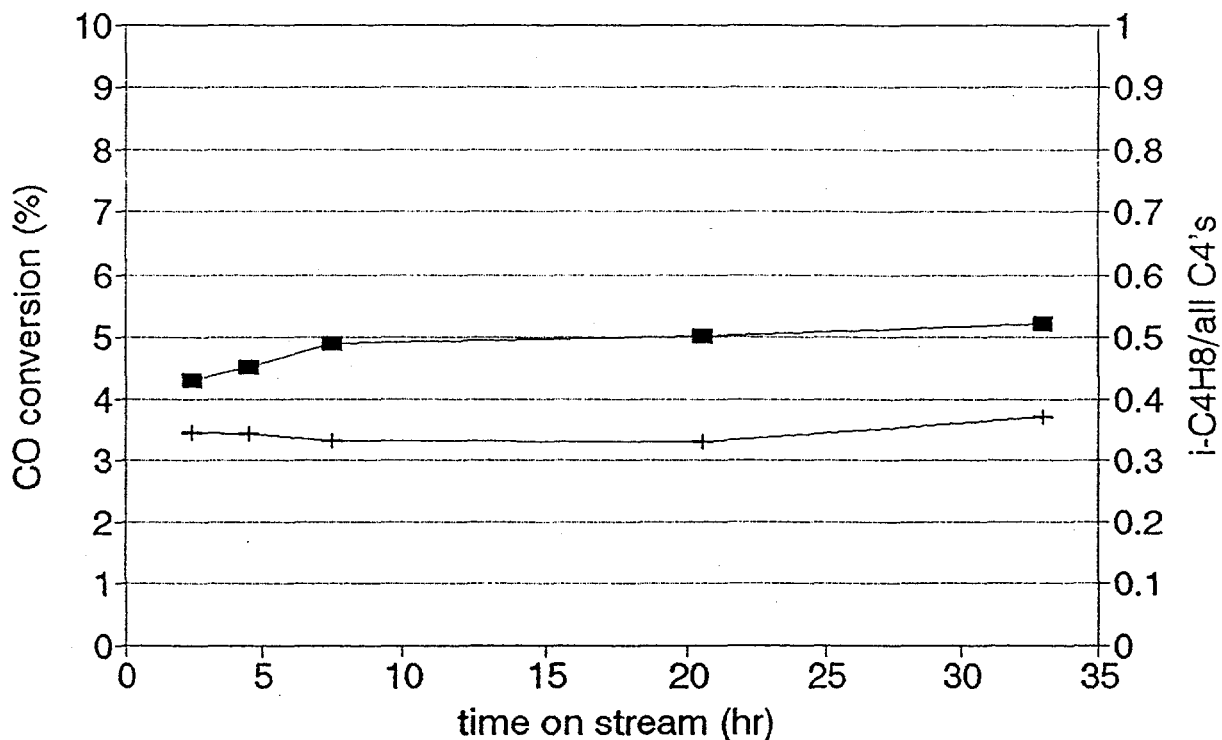
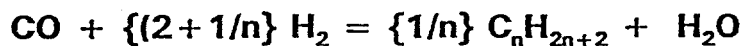
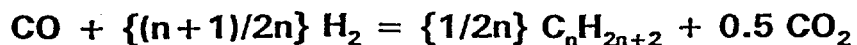


Figure 14. Selectivity and Conversions for Cat. 2 with Time on Stream.

ALKANES



OLEFINS

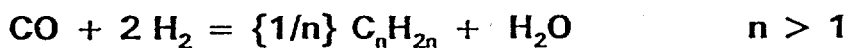
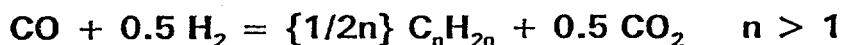


Figure 15. Potential Reaction Stoichiometry For Formation of Hydrocarbons.

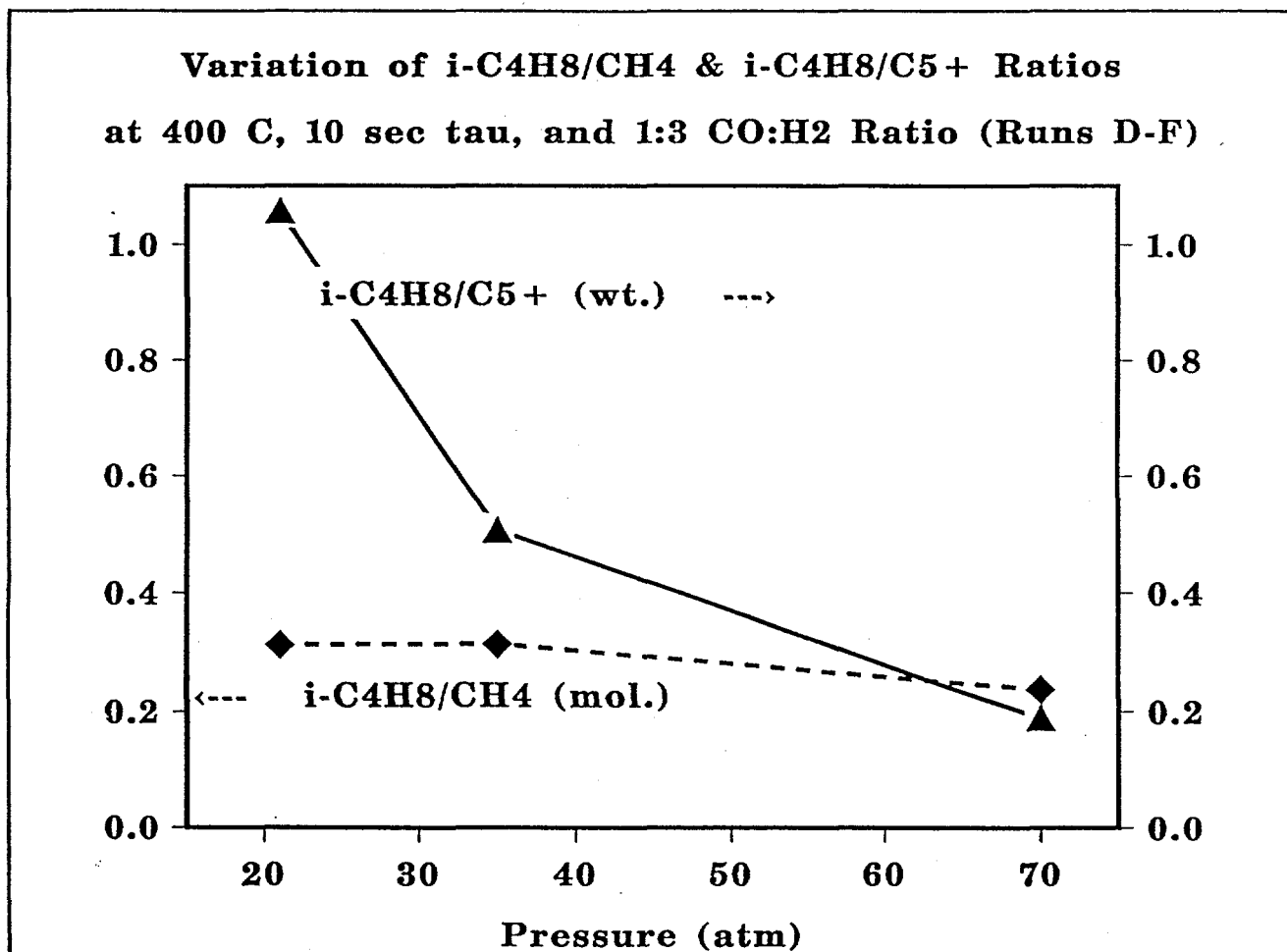


Figure 16. Effect of Pressure on Selectivities for Catalyst #1.

400 C, 95 atm, and 2:1 CO:H2 Ratio

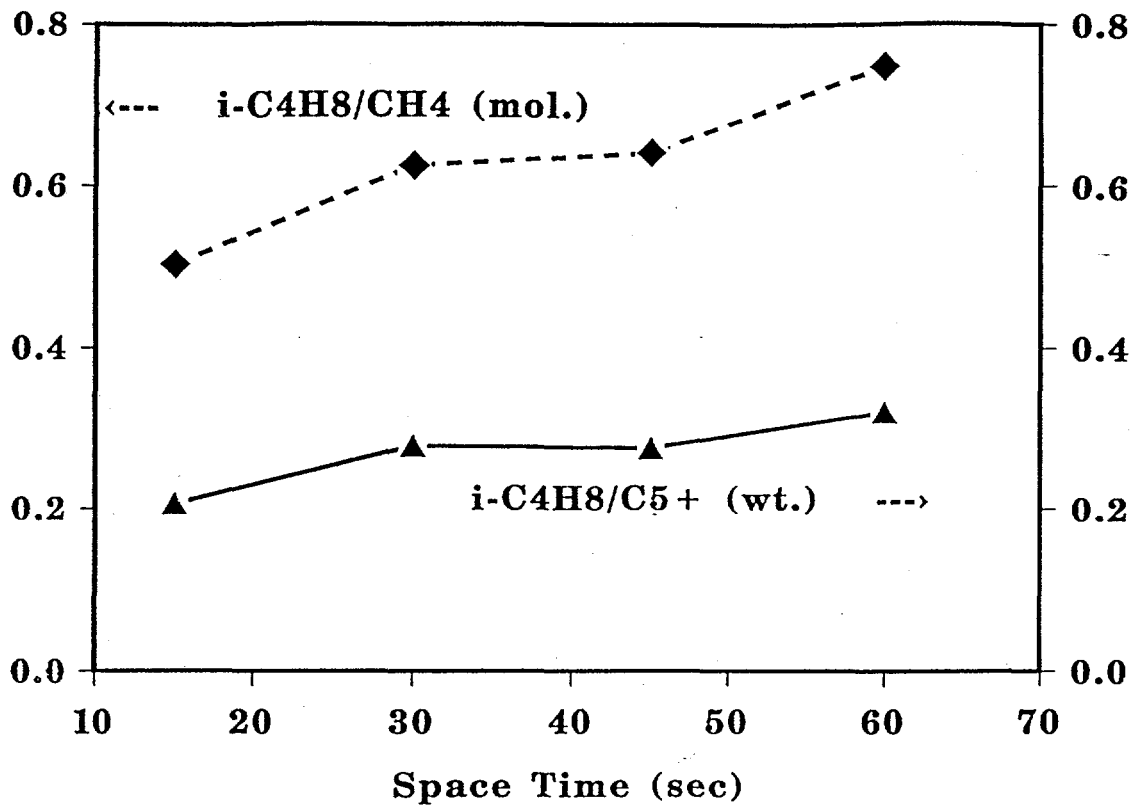


Figure 17. Selectivities For Catalyst #1.

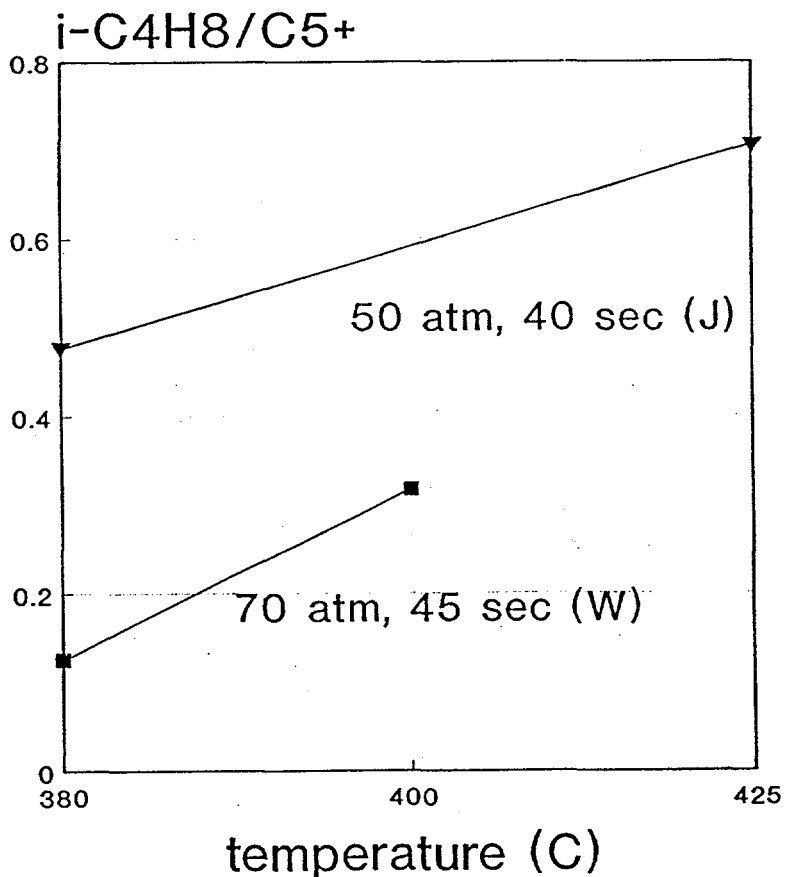


Figure 18. Weight Ratio of Isobutylene to C₅⁺ Increases with Temperature For Cat. 1 and 2.

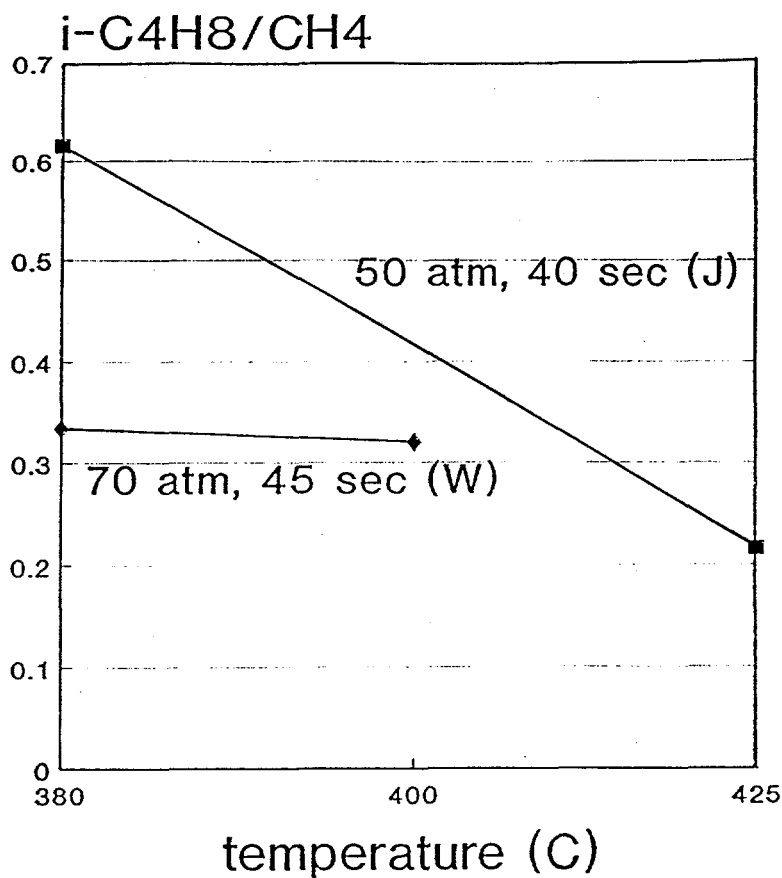


Figure 19. Weight Ratio of Isobutylene to Methane for Cat. 2 (J) and Cat. 1 (W).

Conversion @70 atm & 1:3 CO:H₂ Feed

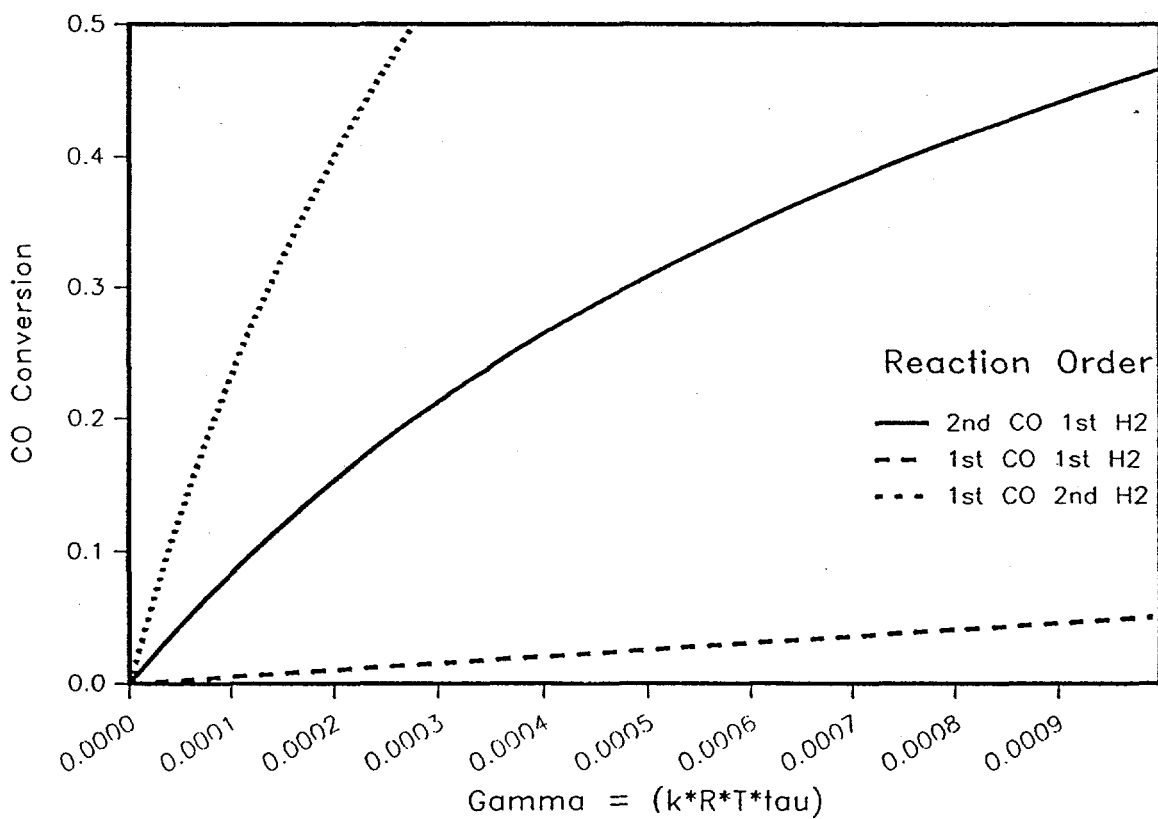


Figure 20. Calculated Conversions For Plug Flow Reactor With CO:H₂ Ratio of 1:3.

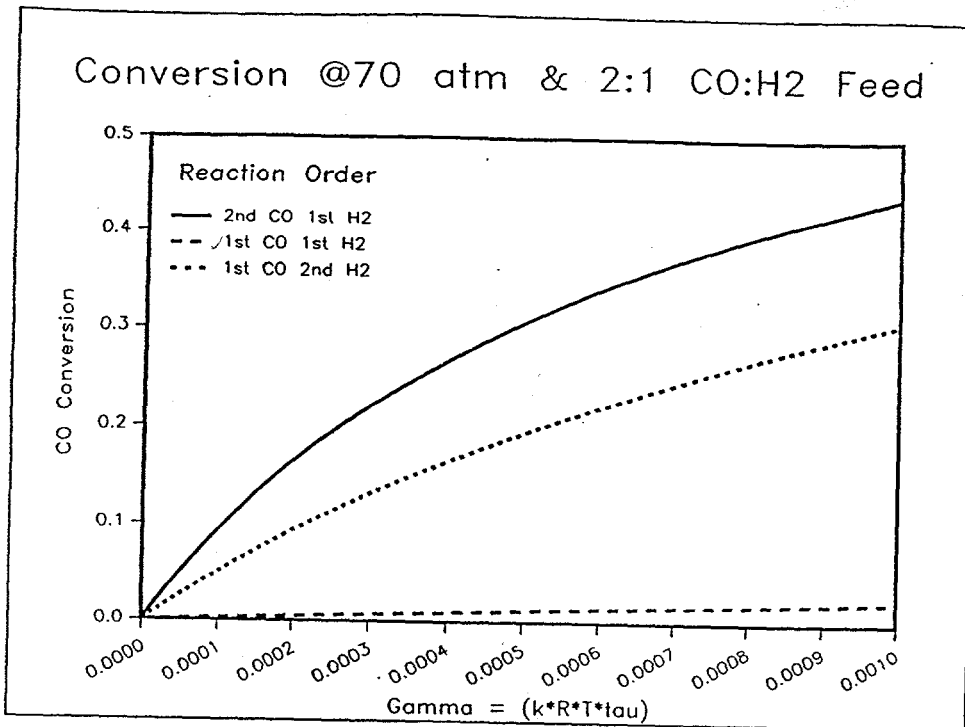


Figure 21. Calculated Conversions For Plug Flow Reactor With CO:H₂ Ratio of 2:1.

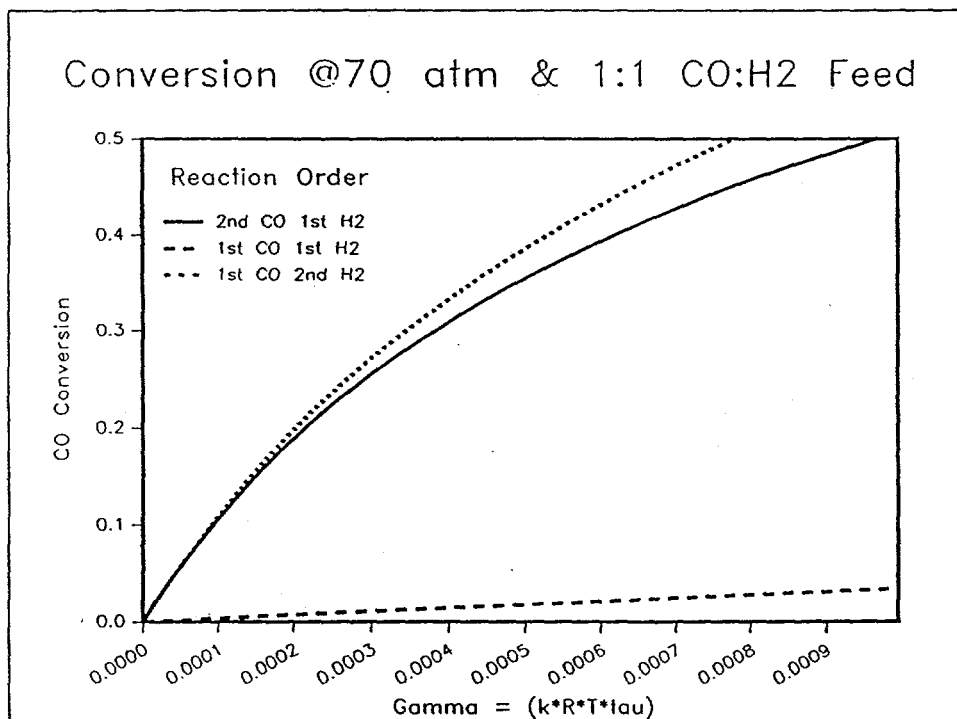


Figure 22. Calculated Conversions For Plug Flow Reactor With CO:H₂ Ratio of 1:1.

TRICKLE BED REACTOR MODEL

A two-dimensional three-phase isothermal trickle bed reactor with axial mixing, flux boundary conditions and a nonlinear reaction



The gas phase

$$\frac{\partial Y}{\partial Z} + F_L \cdot W^o \cdot \left(\frac{K}{H} \cdot Y - X \right) + (1-f) \cdot F_{gs} \cdot W^o \cdot \left(\frac{K}{H} \cdot Y - X_s \right) \Big|_{U=1} = 0$$

The liquid phase

$$\frac{\partial^2 X}{\partial Z^2} - P_{el} \cdot \frac{\partial X}{\partial Z} + P_{el} \cdot F_L \cdot \left(\frac{K}{H} \cdot Y - X \right) - f \cdot P_{el} \cdot F_{ls} \cdot (X - X_s) \Big|_{U=1} = 0$$

The solid phase

$$U \cdot \frac{\partial^2 X_s}{\partial U^2} + \frac{3}{2} \cdot \frac{\partial X_s}{\partial U} = \frac{1}{4} \cdot \mathcal{R}$$

with

$$\mathcal{R}_i = D_{fi} \cdot \prod_i X_{s,i}^{a_i} - D_{bi} \cdot \prod_i X_{s,i}^{b_i}$$

Where

X and Y are dimensionless concentration vectors.

With boundary condition

$$Y_i \Big|_{Z=0^+} = Y_i \Big|_{Z=0^-}$$

$$X_i \Big|_{Z=0^+} = X_i \Big|_{Z=0^-} - \frac{1}{P_{el}} \cdot \frac{\partial X_i}{\partial Z}$$

$$\frac{\partial X_i}{\partial Z} \Big|_{Z=1} = 0$$

$$\frac{\partial X_{s,i}}{\partial U} \Big|_{U=0} = \text{finite}$$

$$\frac{\partial X_{s,i}}{\partial U} \Big|_{U=1} = \frac{1}{2} \cdot f \cdot Sh_{l,i} \cdot (X_i - X_{s,i}) \Big|_{U=1} + \frac{1}{2} \cdot (1-f) \cdot Sh_{g,i} \cdot \left(\frac{K}{H_i} \cdot Y_i - X_{s,i} \right) \Big|_{U=1}$$

Figure 23. Trickle Bed Reactor Model In Dimensionless Variables.

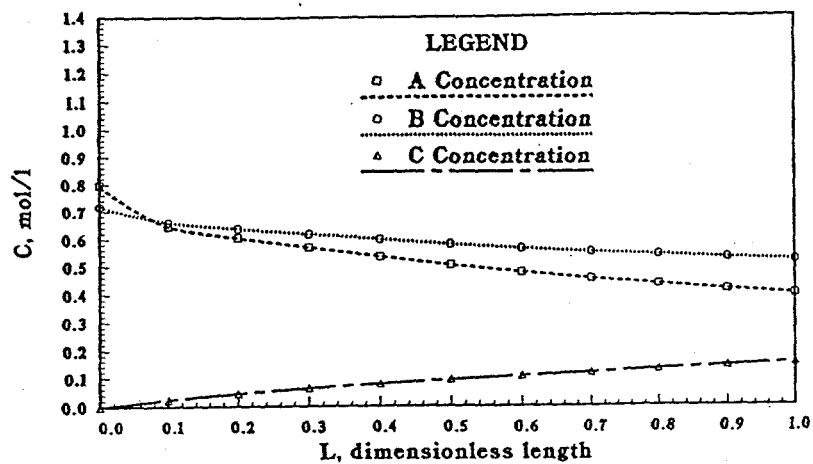


Figure 24. Calculated Gas Phase Profile For Model Presented in Figure 23.

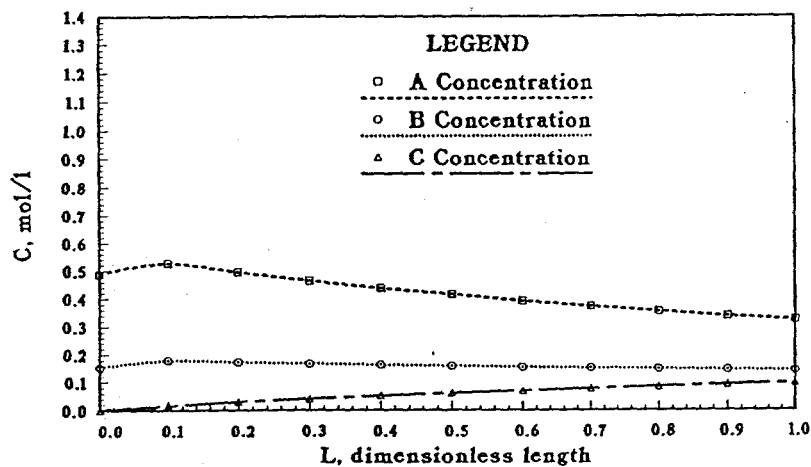


Figure 25. Calculated Liquid Phase Profile For Model Presented in Figure 23.

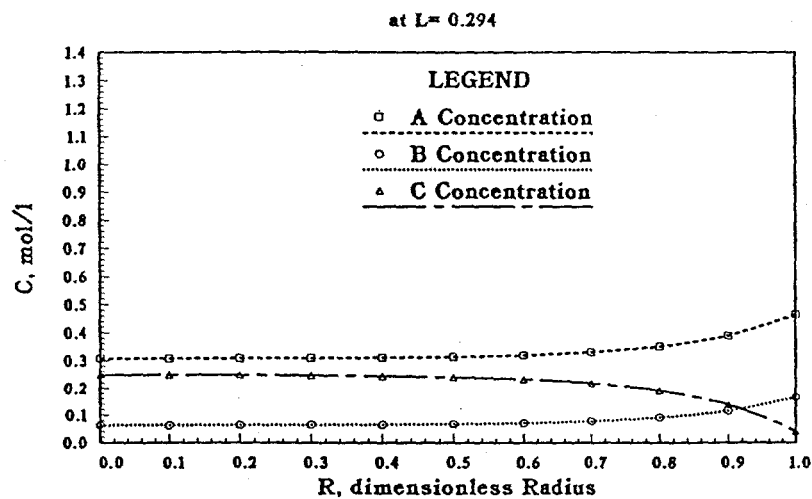


Figure 26. Calculated Solid Phase Profile For Model Presented in Figure 23 and Resistance to Pore Diffusion.