EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODESULFURIZATION OF DIBENZOTHIOPHENE AND HYDRODEOXYGENATION OF DIBENZOFURAN

By

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ABSTRACT

The effects of titanocene dichloride on dibenzothiophene hydrodesulfurization and dibenzofuran hydrodeoxygenation over three different kinds of catalysts were studied by using a Berty type gradientless reactor. The reaction rates and the rate constants were calculated by assuming a pseudo-first order reaction model. By comparing the reactant conversion and the rate constants, titanocene dichloride did not appear to have any effect on dibenzothiophene hydrodesulfurization either over NiMo/alumina or over CoMo/alumina but it increased the catalyst activity in the case of dibenzofuran hydrodeoxygenation over both NiMo/alumina and CoMo/alumina catalyst. No conversion was observed in all of the experimental runs which were done over plain alumina. The coke content of NiMo/alumina catalyst in the hydrodeoxygenation run was found to be lower while that of CoMo/alumina catalyst in both hydrodeoxygenation and hydrodesulfurization runs appeared to be higher with the addition of titanocene dichloride.

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INTRODUCTION

INTRODUCTION

Deactivation of hydroprocessing catalysts is one of the major problems in catalytic hydrotreatment processes. Coke formation is the primary mode of catalyst deactivation and determines the active catalyst life and the need for regeneration. Therefore, any means to reduce the coking rate will result in a reduction of the processing cost.

Chan, et al., (1982) found that the addition of bis-cyclopentadienyl titanium dichloride or titanocene dichloride to an SRC-II coal liquid reduced the coke formation and increased the catalyst activity in the hydrotreatment process. A later study by Tscheikuna and Seapan (1984) showed that the effects of titanocene dichloride on the catalyst activity and coke formation depended on the type of the hydrocarbon feedstock. They also observed the homogeneous reaction between titanocene dichloride and Tetralin resulted in the formation of an insoluble titanium compound.

Following those early observations the role of titanocene dichloride on hydrodesulfurization and hydrodeoxygenation of model compounds were studied in this project. Dibenzothiophene and dibenzofuran were chosen to represent sulfur and oxygen compounds, respectively, in coal liquid. Tetralin, a hydrogen donor solvent in coal liquefaction processes, was used as the solvent. The solvent was doctored with 100 ppm titanium as titanocene dichloride and hydrotreated in a Berty type gradientless reactor over three different kinds of catalysts: a NiMo/alumina (Shell 324), a CoMo/alumina (Shell 344), and plain alumina. The results were compared with the runs made without titanocene dichloride. The reaction rates and rate constants were calculated by assuming pseudo first order reaction. The titanium deposition on catalyst and catalyst coking, pore volume, and surface area were also measured and studied.

In this thesis, the effects of titanocene dichloride on hydrodesulfurization of dibenzothiophene are presented in Chapter II and the effects of titanocene dichloride on hydrodeoxygenation of dibenzofuran are presented in Chapter III. Chapter IV is the overall conclusions and recommendations. The raw data of product analysis are presented in Appendix A. The details of gas chromatographic calculation, precision of the gas chromatograph, catalyst analysis, and rate constant calculation technique are summarized in Appendices B, C, D, and E respectively.

The study showed that titanocene dichloride improved dibenzofuran hydrodeoxygenation while the dibenzothiophene hydrodesulfurization was not affected by titanocene dichloride.

CHAPTER II

EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODESULFURIZATION OF DIBENZOTHIOPHENE

EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODESULFURIZATION OF DIBENZOTHIOPHENE

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ABSTRACT

The effects of titanocene dichloride on dibenzothiophene hydrodesulfurization over three different kinds of catalysts, NiMo/alumina (Shell 324), CoMo/alumina (Shell 344), and plain alumina, were studied by using a Berty type gradientless reactor. The experiments were conducted at 250 C (482 F) and 10.4 MPa (1500 psig). The major products were biphenyl and cyclohexylbenzene. Pseudo-first order reaction was assumed to calculate the rates of reactions and reaction rate constants. Both Shell 324 and Shell 344 catalysts gave about the same rate of conversion but their selectivities were different. Plain alumina did not yield any conversion either on dibenzothiophene or on Tetralin. The addition of titanocene dichloride did not appear to have any effect on the ability of the catalyst to hydrodesulfurize dibenzothiophene.

EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODESULFURIZATION OF DIBENZOTHIOPHENE

INTRODUCTION

Catalytic hydrotreatment of coal liquids and petroleum feedstocks to remove sulfur is carried out to alleviate several problems. First of all, combustion of sulfur-containing fuels is a major cause of SO_x pollution of the atmosphere. Secondly, platinum-containing catalysts of the catalytic reformer unit can be poisoned by sulfur. Furthermore, sulfur compounds can react with organometallic compounds in feedstocks and form solid metal sulfides, which can accumulate in the reactors.

Although hydrodesulfurization is considered to be one of the most important reactions in hydrotreatment processes, the basic questions about the catalyst structure and the reaction mechanism are still unanswered. Many investigators have put emphasis on hydrodesulfurization of coal-derived liquids and of petroleum residua. In these feedstocks, the heterocyclic sulfur containing compounds are expected to be among the least reactive compounds. In order to understand the behavior of aromatic sulfur containing compounds, model compounds such as thiophene, benzothiophene, and dibenzothiophene are frequently chosen to represent the sulfur compounds in feedstocks. Kilanowski, et al., (1978) studied the reactivity of these three compounds at atmospheric pressure and concluded that at low pressures the reactivity did not decrease with an increase in number of rings, as it did at high pressures. The reason was suggested that more reactive compounds (e.g.,thiophene) have less surface coverage at low pressures. Claudine, et al., (1986) investigated reaction rates of phenothiazine, phenoxatin, thianthrene, thioxathene, and dibenzothiophene at high pressures They summarized that dibenzothiophene had the lowest rate of reaction, due to the difficulty of the adsortion and a transition state which would depend on the planar form of the molecule. Since we are studing the hydrotreatment at a high pressure 10.4 MPa (1500 psig), dibenzothiophene appears to be a better choice to represent the sulfur compounds in coal liquid feedstocks.

In recent years dibenzothiophene has received remarkable attention by many researchers (Broderick, et al., (1982); Charles, et al., (1983); Houalla, et al., (1978); Nagai, et al., (1983, 1986); Lee and Ollis (1984); Pecoraro, et al., (1981); Singhal, et al., (1981); Stevens, et al., (1981)). However, the catalyst structure and reactivity patterns are still unclear. Houalla, et al., (1978) presented an approximate reaction network for dibenzothiophene hydrodesulfurization (Figure 1). According to their work, dibenzothiophene C-S bond cleavage occurs before the ring hydrogenation and the main reaction is direct sulfur extrusion to give biphenyl and hydrogen sulfide. Many other investigators followed this reaction pattern to study the effects of process variables.

Recently, Nagai, et al., (1983, 1986) studied the poisoning effect of nitrogen compounds on dibenzothiophene using conditions nearly identical to those of Houalla, et al., (1978). They proved that biphenyl in dibenzothiophene solution was not hydrogenated to yield cyclohexylbenzene by observing no increase in cyclohexylbenzene after biphenyl was added to the feed (Figure 2). Therefore, they proposed a reaction scheme (Figure 3) slightly different from Houalla, et al., (1978).

Even though the current hydrodesulfurization processes achieve the desired sulfur level in the products, the process is expensive because hydrogen is consumed not only for sulfur removal but also for other undesired reactions such as hydrogenation of aromatics. In order to reduce the hydrogen consumption, every factor affecting the sulfur removal must be understood.

Nagai, et al., (1983, 1986) added nitrogen compounds to dibenzothiophene solution and found that the nitrogen compounds only retarded the hydrogenation of dibenzothiophene, but did not inhibit the fission of the C-S bond. Broderick, et al.,(1982) explained the phenomena by stating that the sites active for hydrogenolysis were different from those active for hydrogenation; hydrogenation sites for aromatic compounds were acidic, being poisoned by such bases as pyridine, quinoline, and acridine.

Lee and Ollis (1984) added benzofuran to a dibenzothiophene solution and observed a very strong inhibition by the oxygen compound on the conversion of dibenzothiophene. Nagai, et al., (1983) added various oxygen compounds, such as phenol, xanthene, and dibenzofuran, into a xylene solution containing dibenzothiophene and found that the desulfurization products diminished while the hydrogenated products increased slightly. Hydrogen sulfide affected dibenzothiophene hydrodesulfurization in a way similar to the oxygen compounds (Broderick, et al., 1982, Nagai, et al., 1983, 1986). In summary, nitrogen compounds poison the active sites of hydrogenation while oxygen and sulfur compounds poison the desulfurization sites of catalysts.

Houalla, et al., (1978) also tested and compared the selectivity of CoMo/alumina and NiMo/alumina catalysts on hydrodesulfurization of dibenzothiophene. According to their work, CoMo/alumina works better on the hydrogenolysis while NiMo/alumina performs better on the hydrogenation reactions. Nagai, et al., (1983, 1986) observed the same phenomena in their works. The yield of cyclohexylbenzene increased and that of biphenyl decreased when they used NiMo/alumina instread of CoMo/alumina in their hydrodesulfurization experiments.

Studies by Chan, et al., (1982) showed that the addition of titanocene dichloride to a SRC-II coal liquid reduced coke formation and increased the catalyst activity. The effect of titanocene dichloride on hydrodesulfurization was studied in this part. Dibenzothiophene was chosen to represent sulfur compounds in coal liquids. By assuming pseudo first order reaction, rates of reactions and reaction rate constants were calculated and compared. Coke content, pore volume, and surface area of the spent catalysts were also examined.

In our studies, a mixture of 5 wt% dibenzothiophene in Tetralin was doctored with 100 ppm of titanium as titanocene dichloride and hydrotreated in a Berty type reactor over three different catalysts: CoMo/alumina, NiMo/alumina , and plain alumina. The effects of titanocene dichloride on catalyst coking and hydrogenation activity were studied. The experiments were conducted at 250 C (482 F) and 10.4 MPa (1500 psig). Biphenyl and cyclohexylbenzene were the two major products of dibenzothiophene hydrodesulfurization. Dicyclohexyl was not found in this work. Trans- and cis- decalin were the predominant products of Tetralin hydrogenation reaction. Alkyl cyclohexanes and methyl indans which are often found at high temperature studies were not detected in this work.

EXPERIMENTAL SECTION

A process flow diagram of the reactor system is shown in Figure 4. The reactor used in these studies was the Berty type gradientless reactor. The reactor internals are shown in Figure 5. The operating conditions are summarized in Table II. The list of experimental runs is presented in

Table III.

The feed solvent, Tetralin, was used with and without doctoring with 100 ppm of titanium as titanocene dichloride. Dibenzothiophene was dissolved in the solvent to a concentration of 5 wt % and the mixture was hydrotreated at 10.4 MPa (1500 psig) and 250 C (482 F).

Liquid feed was continuously pumped into the reactor by a Milton Roy positive displacement pump. The liquid was mixed with the hydrogen gas feed at the bottom of the reactor. Without passing the catalyst, the mixture was forced to flow to the top of the reactor by the centrifugal force provided by the impeller. At the top of the reactor, the mixture was separated into two streams. The major stream flowed down through the catalyst basket while a minor stream flowed out of the reactor to the first separation cylinder. The major stream, after flowing through the catalyst basket, mixed with the fresh feedstock and was recirculated back to the top of the reactor.

After the liquid and gas products were separated, the exit gases were scrubbed with a sodium hydroxide solution before they were exhausted into the atmosphere. The exit gas flow rate was measured by a Brook Sho-Rate Model 1355 rotameter.

The temperature and stirrer speed were controlled by Autoclave Engineers temperature controller and Autoclave Engineers speed controller, respectively. A more detailed description of the reactor system is given by Williams

(1987) and Tscheikuna (1988).

Before each run, the catalyst was calcined with nitrogen gas at a pressure of 1.8 MPa (250 psig) and a temperature of 300 C (572 F) for one hour. The catalyst was allowed to cool down to 250 C (482 F) under nitrogen gas before it was sulfided with 5 % hydrogen sulfide in hydrogen mixture. The catalyst was heated at a rate of 120 C/h (216 F/h) from 250 C (482 F) to 360 C (680 F) and kept at 360 C (680 F) for two hours. Each run used 20 g of catalyst with properties listed in Table I. The duration of each experiment was 12 hours with liquid product samples taken every two hours.

ANALYSIS

The liquid samples were analyzed by a Hewlett Packard Model 5890 A Gas Chromatograph equipped with a 60 meters DB-1 capillary column and a thermal conductivity detector. The output of the detector was measured and recorded by a Hewlett Packard Integrator Model 3392 A. The concentrations of titanium in feedstocks and product samples were analyzed by a Perkin Elmer Model 503 Atomic Absorption Spectrometer.

CATALYST ANALYSIS

The catalyst from each run was extracted in a Soxhlet unit with tetrahydrofuran for 60 hours. The samples were then air dried for 48 hours. The catalyst samples were then analyzed for coke content, surface area, pore volume, and titanium distribution inside the pellets.

For coke content, the catalyst samples were weighed at room temperature before the carbonaceous material was burned off. Then, the catalyst samples were heated to 550 C (1022 F) for 60 hours. After that, the catalyst samples were cooled down to room temperature and reweighed. The difference in weights is considered to be the amount of coke. The surface area and pore volume were analyzed by an Autoscan 60 Porosimeter. The titanium distribution is measured by a Joel Model JFM-35 Scannig Electron Microscope equipped with an Energy Dispersive X-ray Analyzer (EDAX). The catalyst samples were analyzed for titanium deposition at the catalyst surface and at four different points of the cross section from center to edge of the pellets.

RESULTS

The nine experimental runs were conducted and were separated into three sets. The first set (S1, S2, and S3) was to observe the behavior of pure Tetralin solvent on CoMo/alumina, NiMo/alumina, and plain alumina catalysts. The second set (S4, S5, and S6) was to investigate the hydrodesulfurization of dibenzothiophene. The third set (S7, S8, and S9) was to study the effect of titanocene dichloride on dibenzothiophene hydrodesulfurization. One duplicate Run, S10, was conducted to observe the reproducibility of the experiment. Run S11 was conducted at 300 C to study the conversion of dibenzothiophene at a higher temperature.

The conversions of Tetralin and dibenzothiophene were calculated from the compositions analyzed by the gas chromatograph. The conversion of both Tetralin and dibenzothiophene of each run are presented and compared in Figures 6, 7, 8, 9, 10, and 11. Details of the calculation are given in Appendix E. Concentration of cyclohexylbenzene, and biphenyl are presented in Figures 12, 13, 14, 15, 16, and 17.

The overall coke contents of the catalyst samples were analyzed twice and are presented in Figure 20. Pore volume and surface area of the catalyst from each run are presented in Figures 21 and 22. A pseudo-first order reaction was assumed to calculate the rate constant for dibenzothiophene conversion. The results are shown in Table IV. Details of calculation are presented in Appendix E.

DISCUSSION

Table V shows the amount of Ti deposited on the surface of catalyst pellet. There was no titanium detected along the cross section of the catalyst pellet. This is similar to the observations of Lynch (1986) when he passed titanium porphyrin through Shell 324 (NiMo/alumina) catalyst in a microflow reactor and found that most of the titanium was deposited near the edge of the catalyst samples. This phenomena can be explained by the rapid reaction of titanocene dichloride with the catalyst, resulting in deposition of titanium on the outer surface of the catalyst.

Runs S4, S5, and S6 are reference runs for hydrodesulfurization on different catalysts. The hydrodesulfurization activity and the amount of coke formed on the catalysts of Runs S7, S8, and S9 which were with titanocene dichloride are compared to Runs S4, S5, and S6.

A CoMo/alumina catalyst was used to treat the undoctorated and doctorated feeds under the identical operating condition in Run S4 and S7 , respectively. The analyses of liquid samples showed that the conversion of dibenzothiophene in Run S7 was slightly lower than that from run S4 (Figures 6 and 23).

The coke formation from Run S7 was higher than that from Run S4 (Figure 20). The pore volume and surface area of the spent catalysts varied inversely with the amount of coke deposited on catalysts.

The conversion of Tetralin in these two runs are compared with the conversion of pure Tetralin (Run S1) in Figure 9. The conversion of Tetralin decreases when dibenzothiopene is added to Tetralin, but the addition of titanocene dichloride to the solution does not retard the conversion of the solvent any further. Furthermore, the conversion of Tetralin appears to be slightly increased with the addition of titanocene dichloride. The effects of titanocene dichloride on Tetralin hydrogenation were studied thoroughly in another part of the project by Tscheikuna (1988) at a higher temperature (350 C).

Runs S5 and S8 were conducted to study the effects of titanocene dichloride on dibenzothiophene hydrodesulfurization with the NiMo/alumina catalyst. Figure 7 shows the conversion of dibenzothiophene in Run S5 and Run S8. The conversion of dibenzothiophene from Run S8 is much lower than that from Run S5 in the first 8 hours of the experiment. However, the conversions of dibenzothiophene in these two runs approach each other; the difference becomes small after 8 hours of experiment. Formation of both biphenyl and cyclohexylbenzene in these two runs were similar to the conversion of dibenzothiophene, as shown in Figures 12, 13, 15, and 16.

The conversion of pure Tetralin from Run S2, using NiMo/alumina instead of CoMo/alumina in Run S1, was compared to the conversion of Tetralin mixtures from Runs S5 and S8 in Figure 10. Run S5 gave conversion of Tetralin slightly higher than that by run S8. However, they were about 9 to 11 percent lower than that from Run S2. Therefore, the hydrogenation of Tetralin should be inhibited by dibenzothiophene rather than by titanocene dichloride.

The coke formation of catalysts from Runs S2, S5, and S8 were nearly equal. The pore volume and surface area of the spent catalysts from these three runs were almost identical.

Runs S3, S6, and S9 were done with plain alumina catalyst to observe the effect of alumina support on dibenzothiophene reactions. However, the conversions of dibenzothiophene and Tetralin from these three runs were too low to indicate any effect of titanocene dichloride on either dibenzothiophene hydrodesulfurization or Tetralin hydrogenation (Figures 8, 11, and 23). The Tetralin conversions of runs S3 and S6 appeared as slightly lower than zero. This is probably due to the errors in Gas Chromatographic analysis.

The activity of CoMo/alumina catalyst from Run S4 was compared with that of NiMo/alumina from Run S5. According to our experiments, both NiMo/alumina and CoMo/alumina yield similar products and resulted in nearly equal conversions of dibenzothiophene. However, the fraction of products from these two catalysts were different. The ratio of biphenyl to cyclohexylbenzene given by CoMo/alumina was about six times higher than the ratio given by NiMo/alumina. This is primarily due to the fact that nickel is a better hydrogenation catalyst than cobalt. The observation is in agreement with those of Houalla, et al.,(1978) and Nagai, et al., (1983,1986).

Coke formation from Run S4 was lower than that from Run S5. Since the conversion of Tetralin from Run S4 was much lower than Run S5, the higher coke formation was believed to be the result of Tetralin hydrogenation reaction.

Run S4 was also compared to run S10, the duplicate run, to study the experimental error. However, due to operational problems its results turned out to be completely out of sequence with any of the observations mentioned above. Therefore the results of run S10 are considered as incorrect. Run S11 was conducted at 300 C over CoMo/alumina catalyst. Dibenzothiophene appeared to be completely converted.

CONCLUSION

Addition of titanocene dichloride slightly reduces the rate of hydrodesulfurization of dibenzothiophene. This can be the result of titanium deposition on the external surface of the catalyst which blocks the surface pores, reducing the diffusion of reactants into the catalyst pellet. Since dibenzothiophene molecules are larger than Tetralin molecules, their diffusion is reduced more than that of Tetralin.

Dibenzothiophene reduces the rate of Tetralin hydrogenation on both NiMo/alumina and CoMo/alumina catalysts, however it does not change the selectivity of formation of trans- and cis-decalins.

Addition of titanocene dichloride to a Tetralin-dibenzothiophene mixture does not affect the Tetralin hydrogenation rate for both CoMo/alumina and NiMo/alumina catalysts.

Titanocene dichloride has no effect on the coking of the NiMo/alumina catalyst but increases the coking of CoMo/alumina catalyst.

The surface area and pore volume of the spent catalysts vary inversely with the amount of coke on the catalyst.

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TABLE I

PROPERTIES OF CATALYST

	Shell 324	Shell 344	Alumina*
Chemical composition wt%			
Co	-	2.4	-
Ni	2.7	-	-
Mo	13.2	9.8	-
Physical Properties :			
Geometry	1.6 mm extrudate	1.6 mm extrudate	2.0 mm extrudate
Surface area, m^2/g	202	238	248
Pore Volume, cm^3/g	.51	.59	.75

* Alumina 005-2E Test No. 21006 Akzo Chemic.

TABLE II

OPERATING CONDITION

Catalyst weight:	20 g
Pressure:	10.4 MPa (1500 psig)
Hydrogen Flowrate:	0.024 m^3/h (400 cm^3/min)
Feedstock Flowrate:	3.0E-05 m^3/h (30 cm^3/h)
Sampling Intervals:	every 2 h
Run Duration:	12 h
Magnedrive Speed:	1500 rpm

TABLE III

LIST OF DIBENZOTHIOPHENE EXPERIMENTAL RUNS

Run No.	Feed	Catalyst
S1	Tetralin	CoMo
S2	Tetralin	NiMo
S3	Tetralin	Alumina
S4	Tetralin + DBT	CoMo
S5	Tetralin + DBT	NiMo
S6	Tetralin + DBT	Alumina
S7	Tetralin + DBT + Ti	CoMo
S8	Tetralin + DBT + Ti	NiMo
S9	Tetralin + DBT + Ti	Alumina
S10	Tetralin + DBT	CoMo
S11	Tetralin + DBT*	CoMo

* Run S11 was made at 300 C

TABLE IV

RATE CONSTANTS
(Unit: $m^3/(kg\ cat)\ (s)$)

		Shell 344		
		Tet.	Tet+DBT	Tet+DBT+Ti
Tetralin	(k1)	2.19E-08	1.03E-08	1.17E-08
	(k2)	6.95E-09	3.68E-09	4.38E-09
DBT	(k3)		8.48E-08	8.46E-08
	(k4)		4.09E-07	3.55E-07

		Shell 324		
		Tet.	Tet+DBT	Tet+DBT+Ti
Tetralin	(k1)	1.40E-07	6.52E-08	6.19E-08
	(k2)	3.22E-08	1.55E-08	1.51E-08
DBT	(k3)		3.86E-07	2.13E-07
	(k4)		3.14E-07	1.74E-07

		Shell 344	
		Tet+DBT	Duplicate
Tetralin	(k1)	1.03E-08	-
	(k2)	3.68E-09	-
DBT	(k3)	8.48E-08	6.68E-08
	(k4)	4.09E-07	6.25E-07

TABLE V

PERCENT TITANIUM ON CATALYST SURFACE

Run No.	Catalyst	% titanium*
S7	CoMo/alumina	4.25
S8	NiMo/alumina	3.02
S9	Plain alumina	7.06

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* Percent titanium was approximated from percent area of titanium which was analyzed by Electron Scaning Microscope

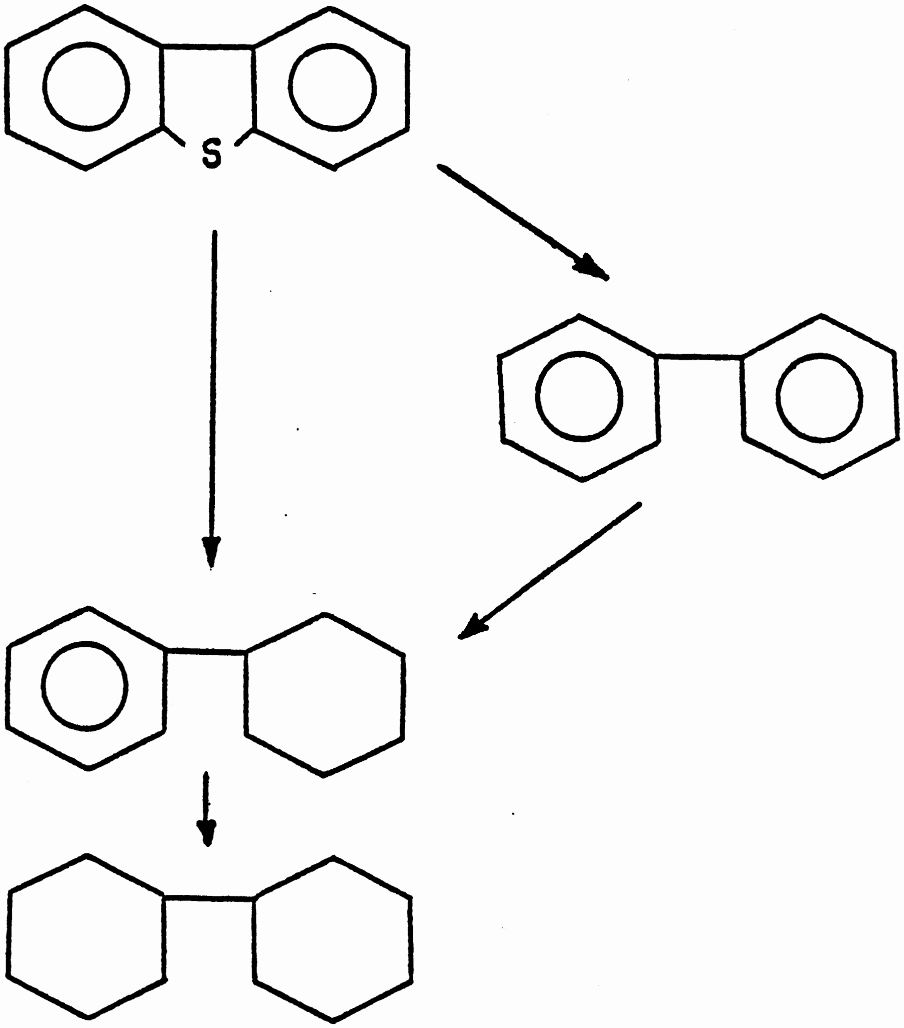

Figure I. Reaction Net-work of Dibenzothiophene by Houalla, et al., (1978)

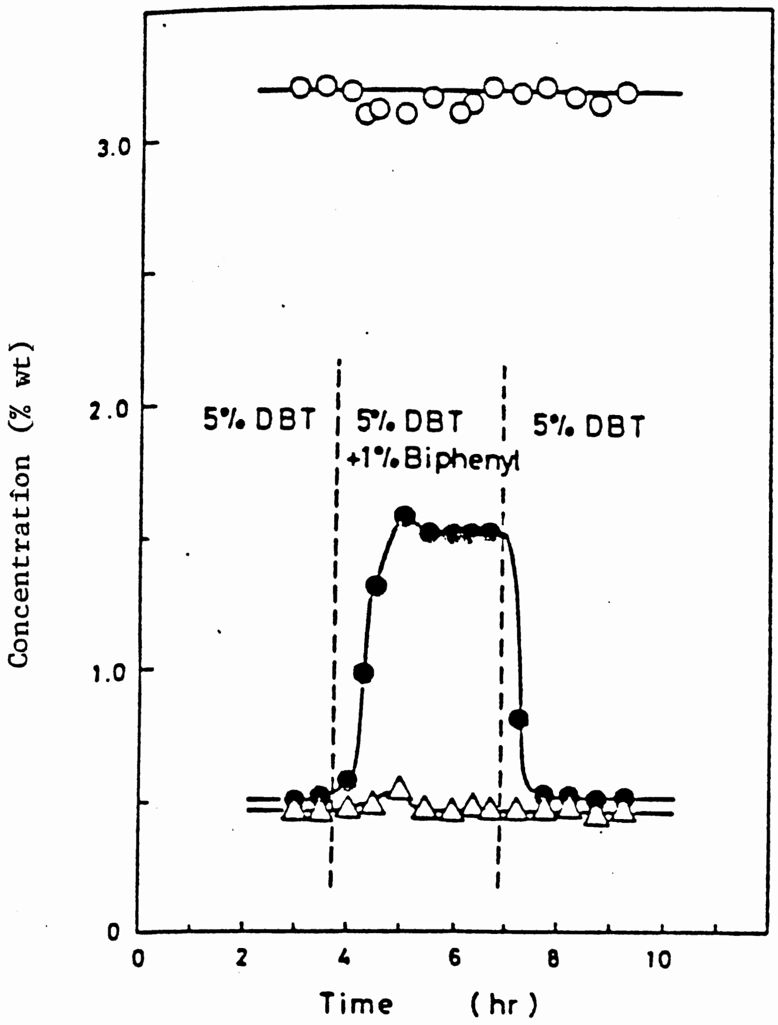

Figure 2. Effect of Addition of Biphenyl on the Formation of Cyclohexylbenzene in Hydrogenation of Dibenzothiophene

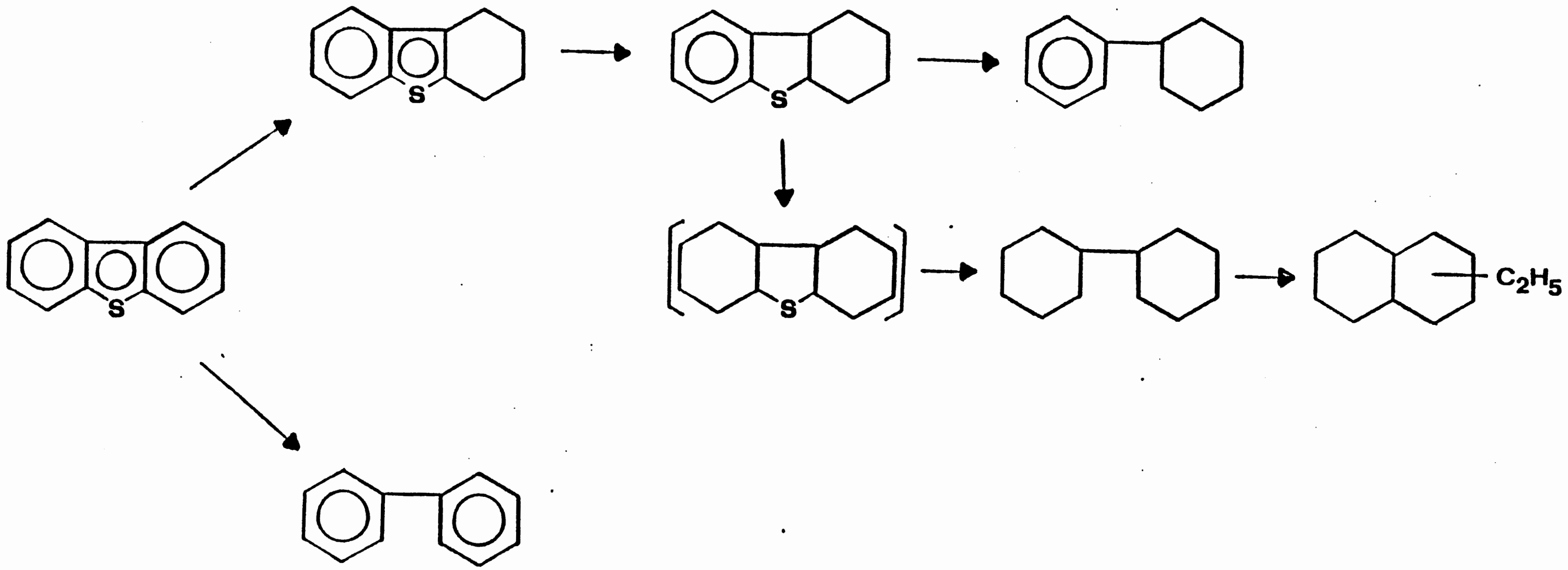

Figure 3. Reaction Network of Dibenzothiophene by Nagai, et al., (1983)

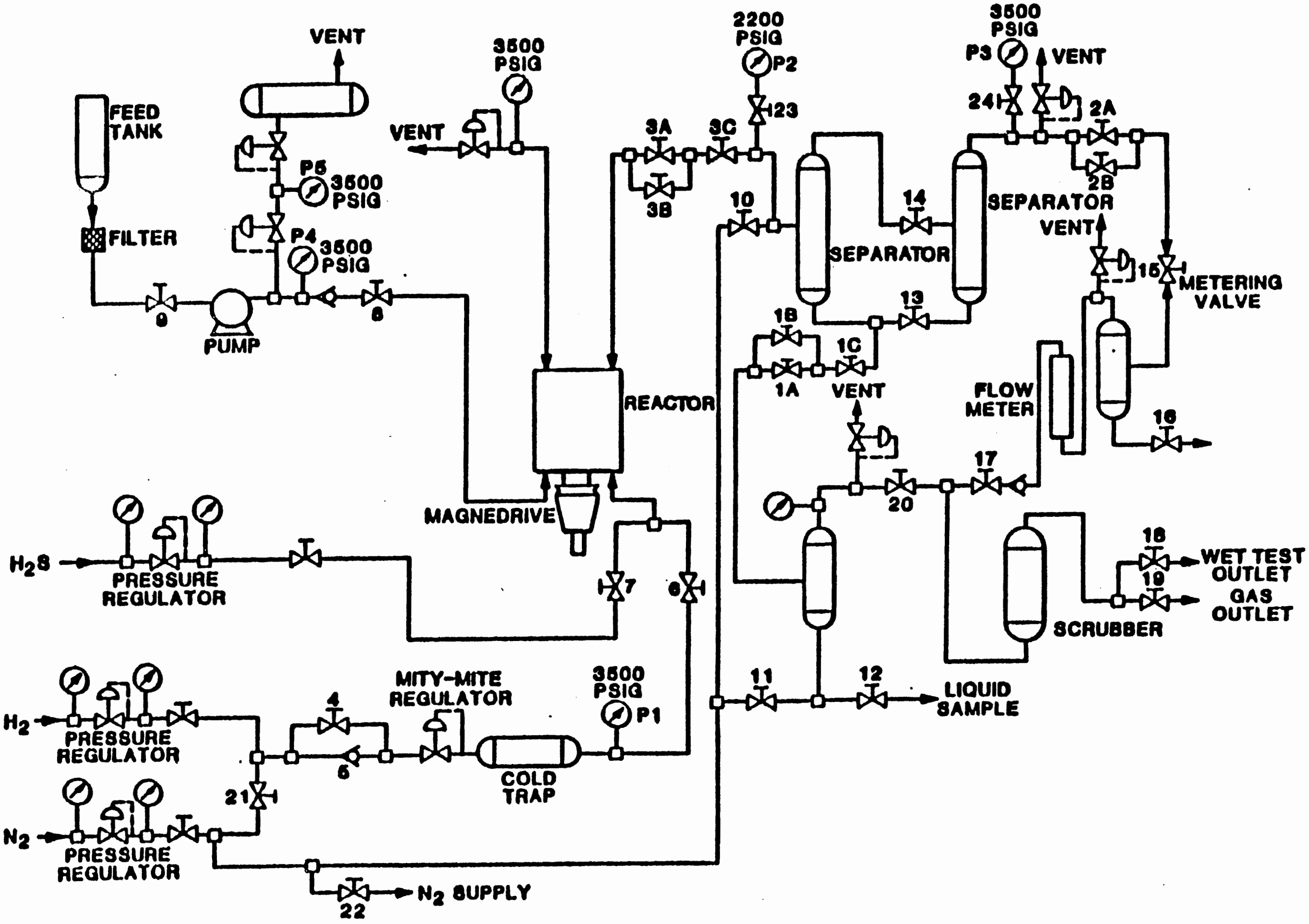

Figure 4 - Process Flow Diagram of Reactor System

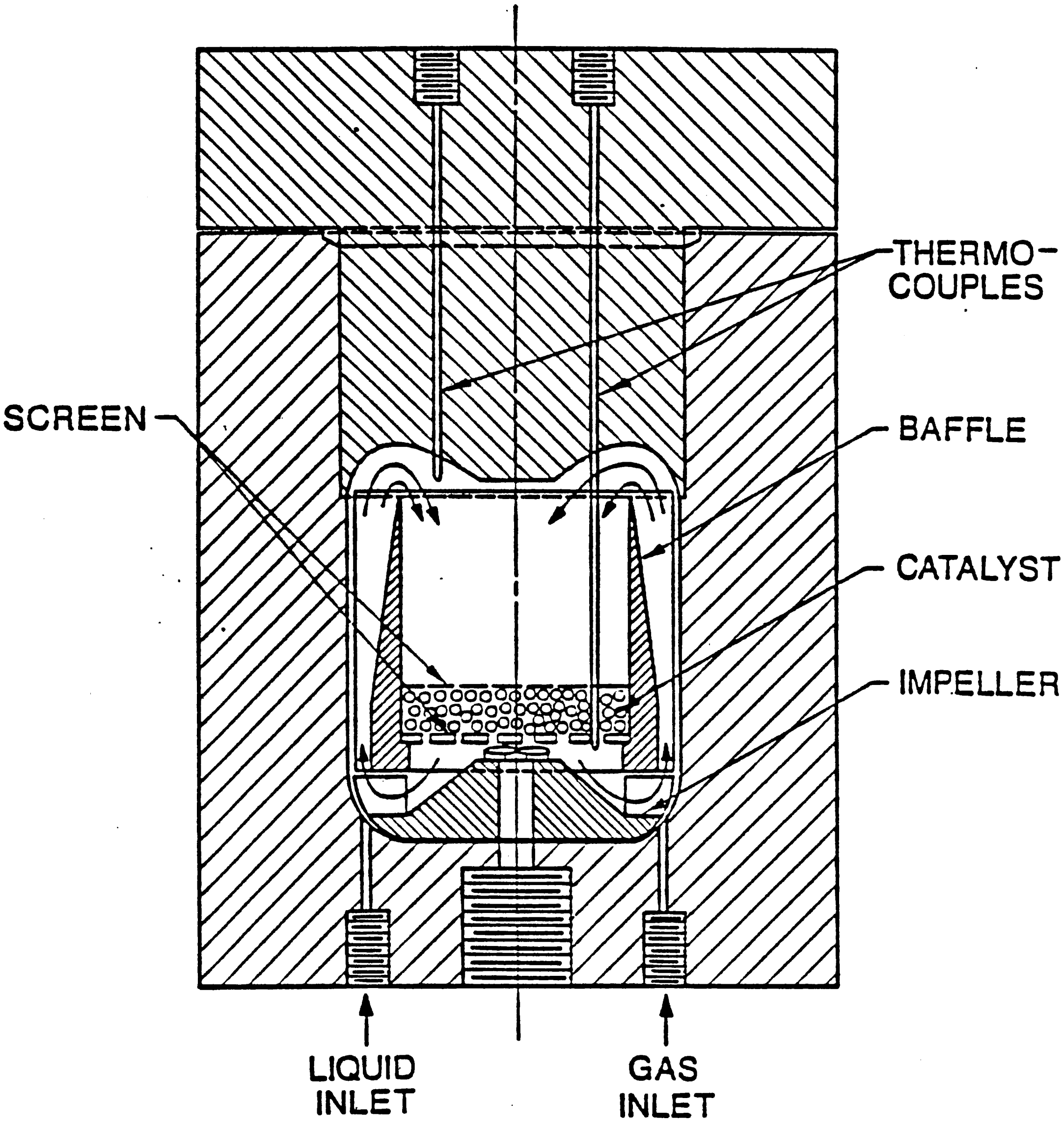

Figure 5. Internals of Berty Reactor

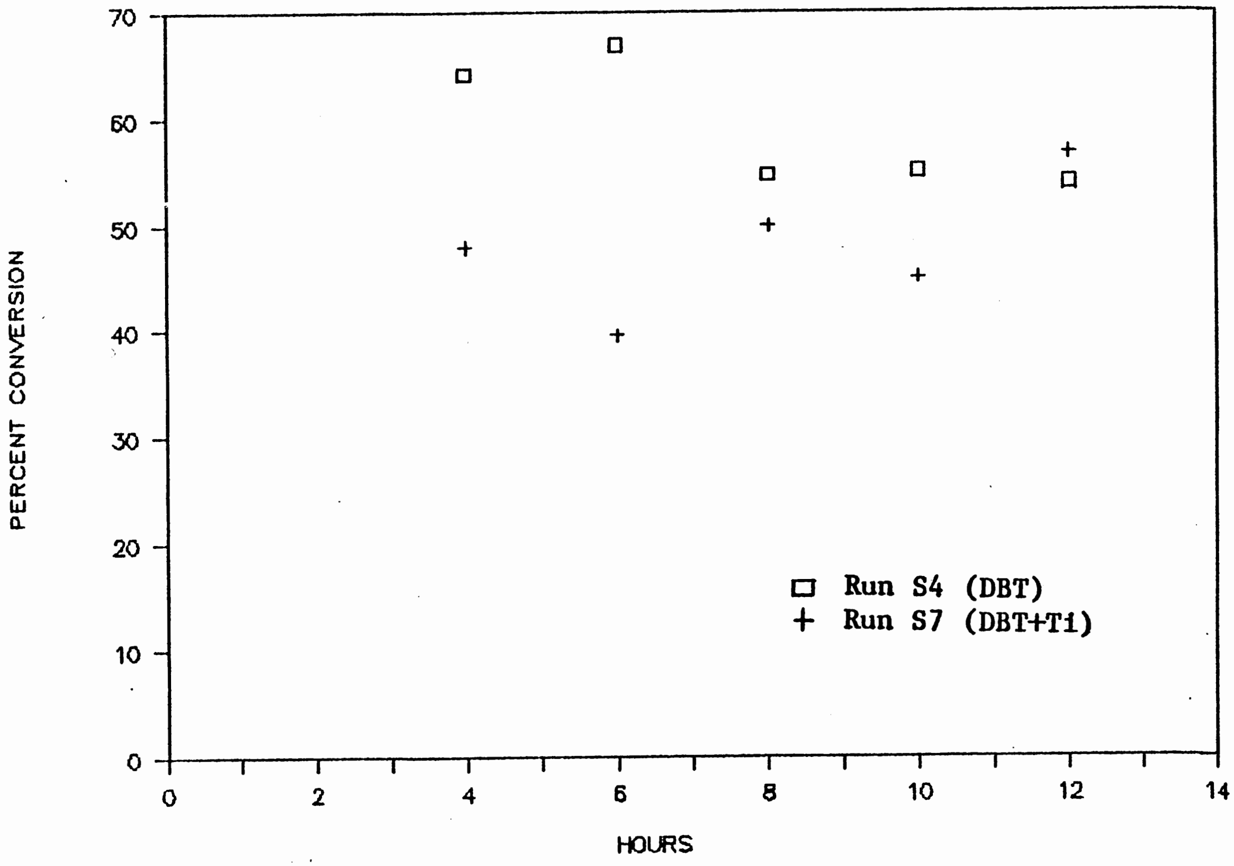

Figure 6. Effect of Titanocene Dichloride on the Conversion of Dibenzothiophene over the CoMo/alumina Catalyst

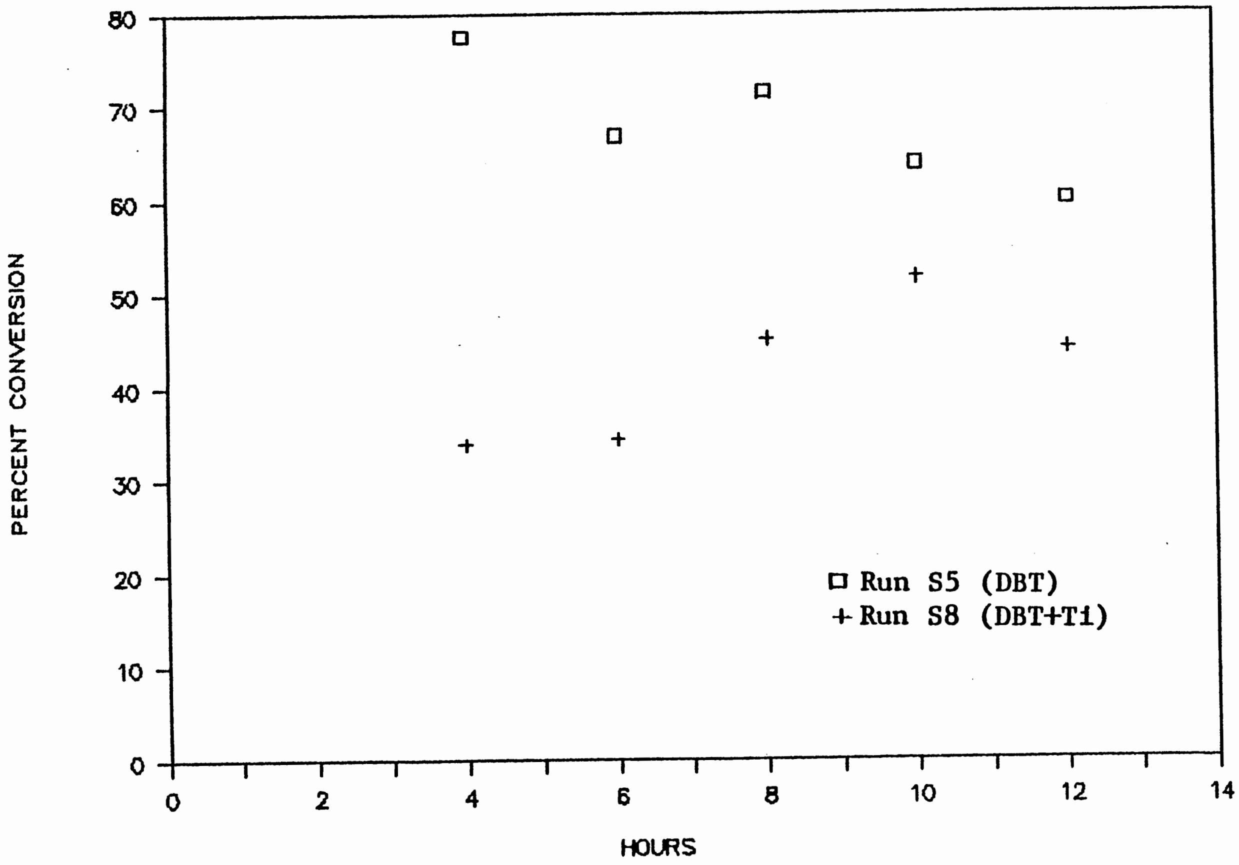

Figure 7. Effect of Titanocene Dichloride on the Conversion of Dibenzothiophene over the NiMo/alumina Catalyst

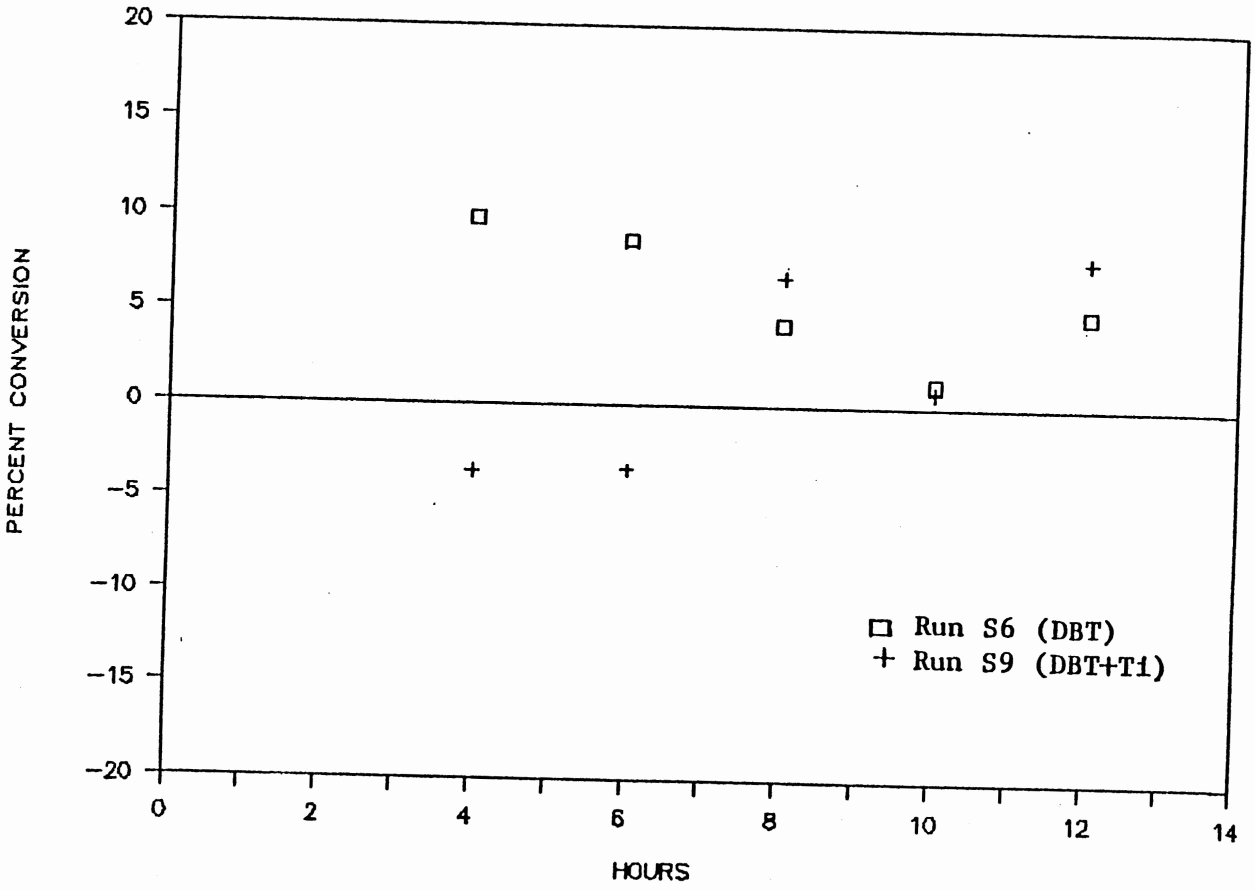

Figure 8. Effect of Titanocene Dichloride on the Conversion of Dibenzothiophene over Alumina

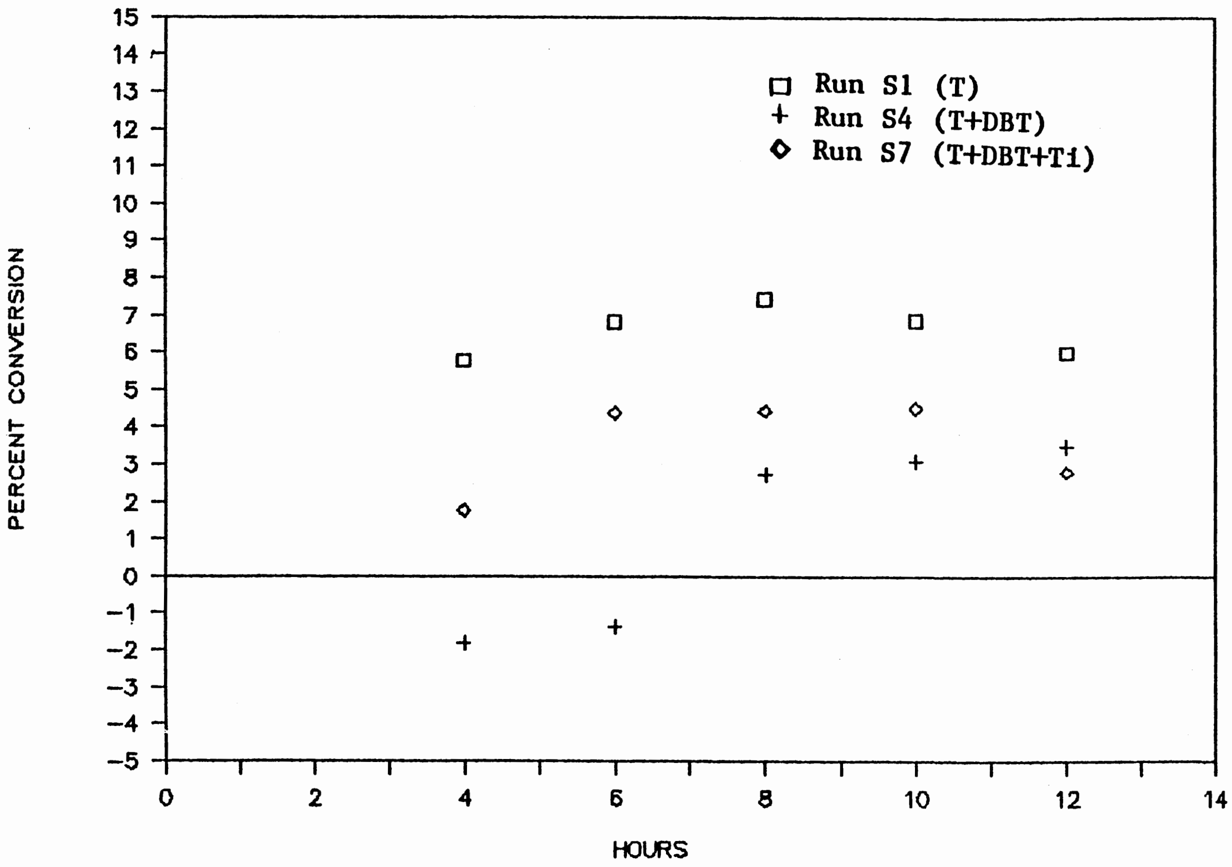

Figure 9. Effect of Titanocene Dichloride on the Conversion of Tetralin over the CoMo/alumina Catalyst

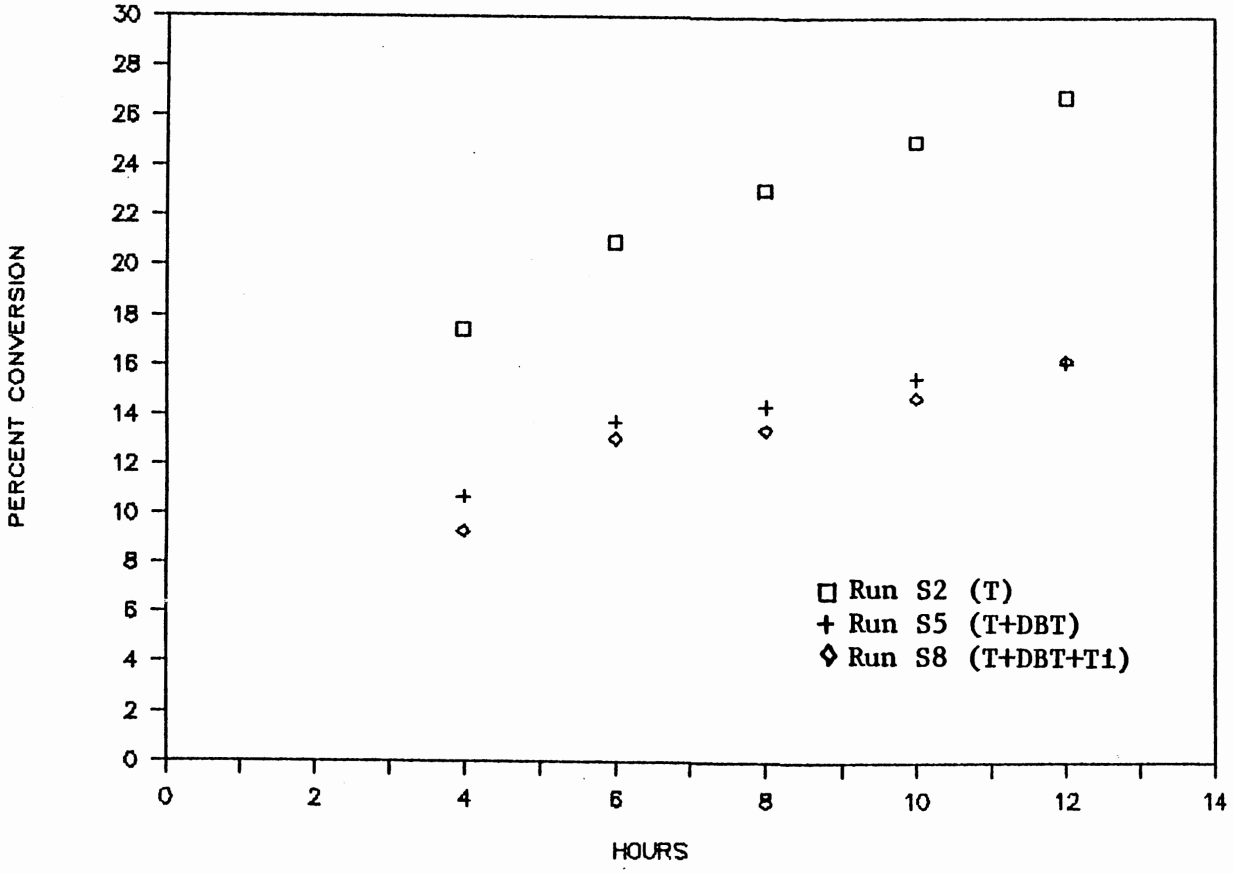

Figure 10. Effect of Titanocene Dichloride on the Conversion of Tetralin over the NiMo/alumina Catalyst

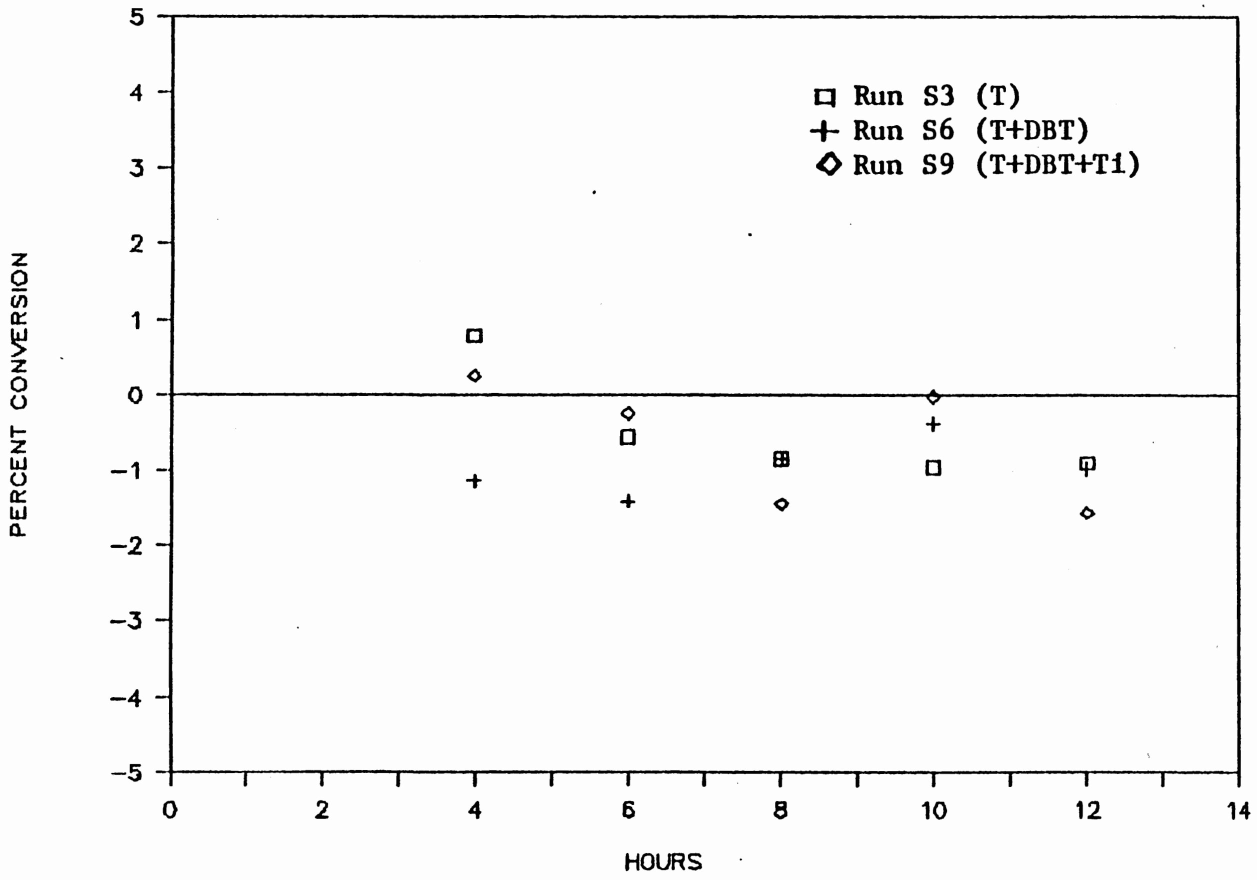

Figure 11. Effect of Titanocene Dichloride on the Conversion of Tetralin over Alumina

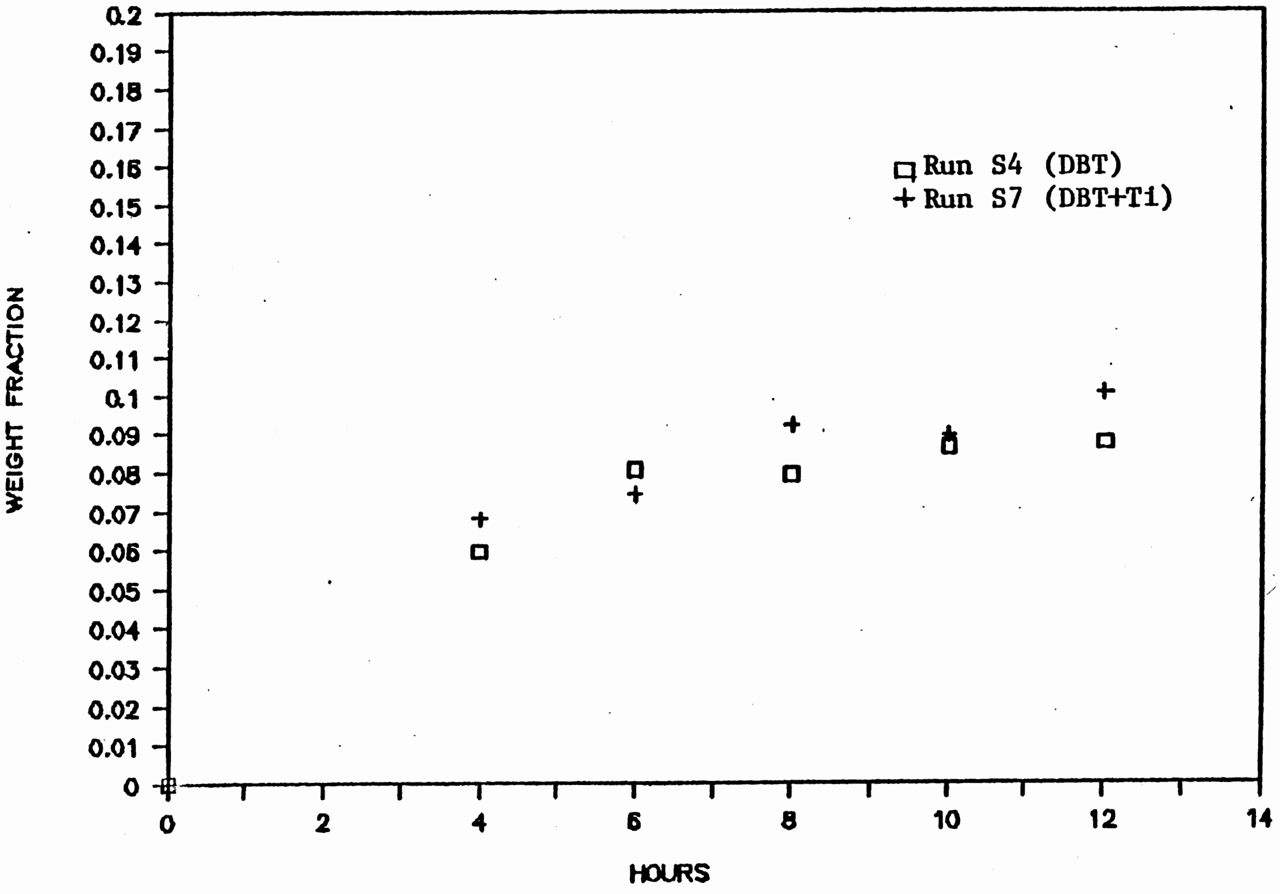

Figure 12. Weight Fraction of Cyclohexylbenzene over the CoMo/alumina Catalyst

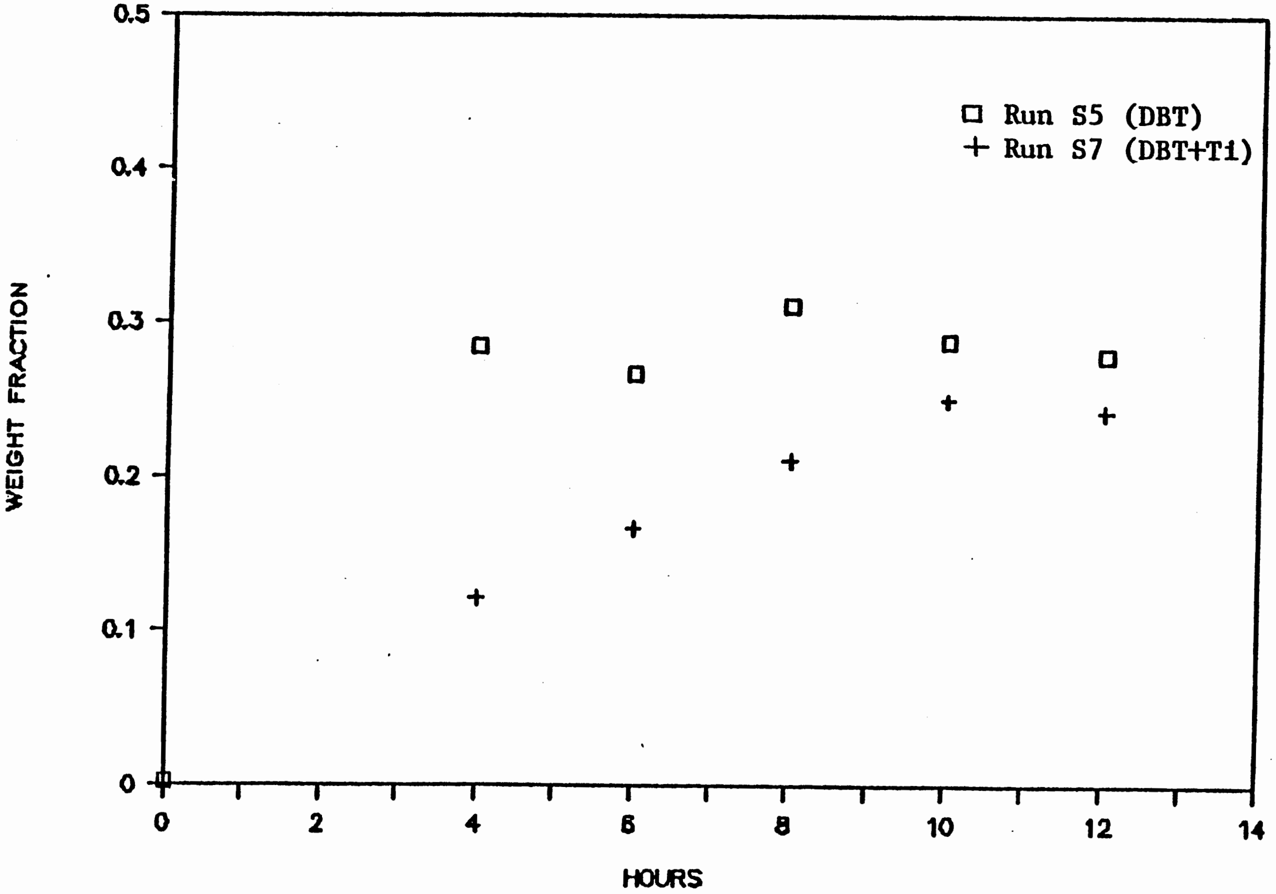

Figure 13. Weight Fraction of Cyclohexylbenzene over the NiMo/alumina Catalyst

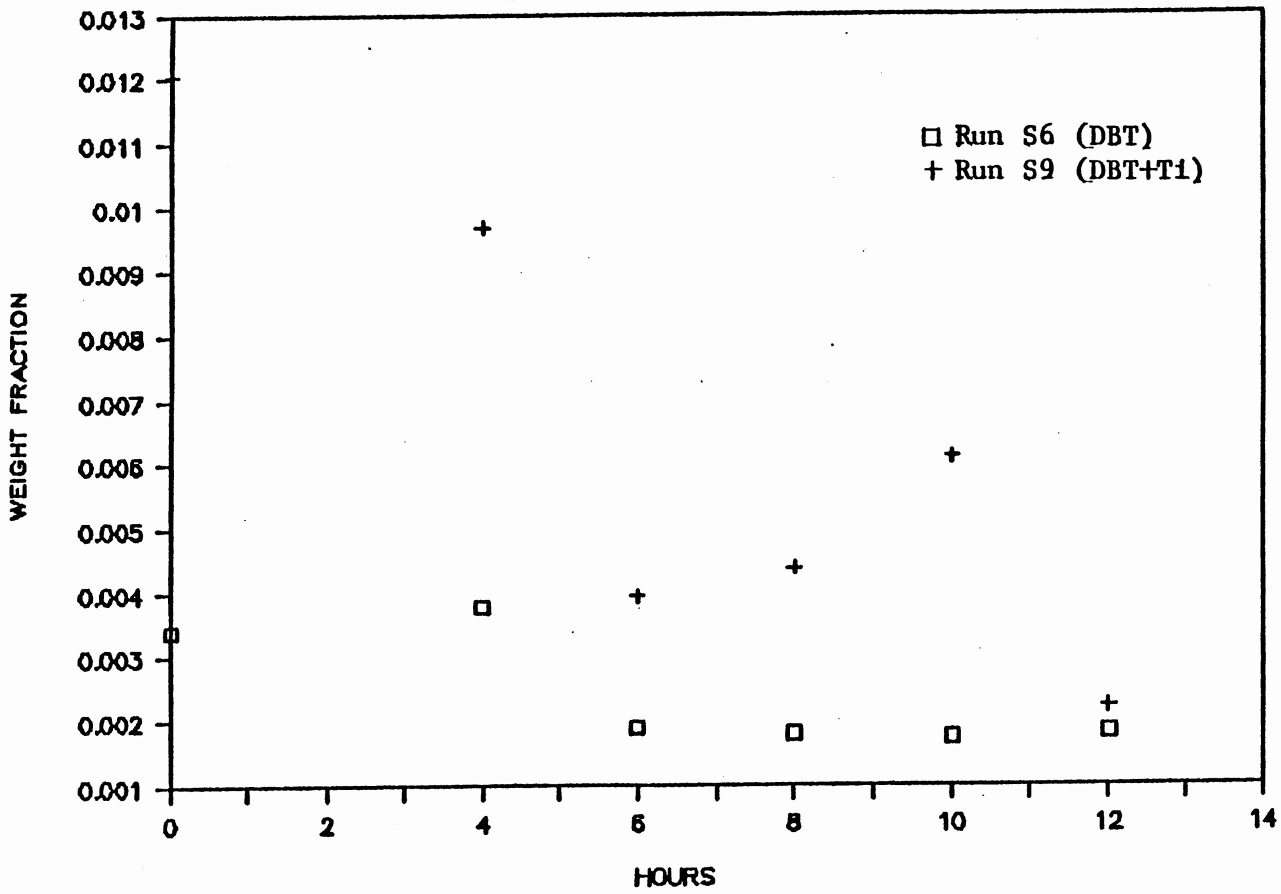

Figure 14. Weight Fraction of Cyclohexylbenzene over Alumina

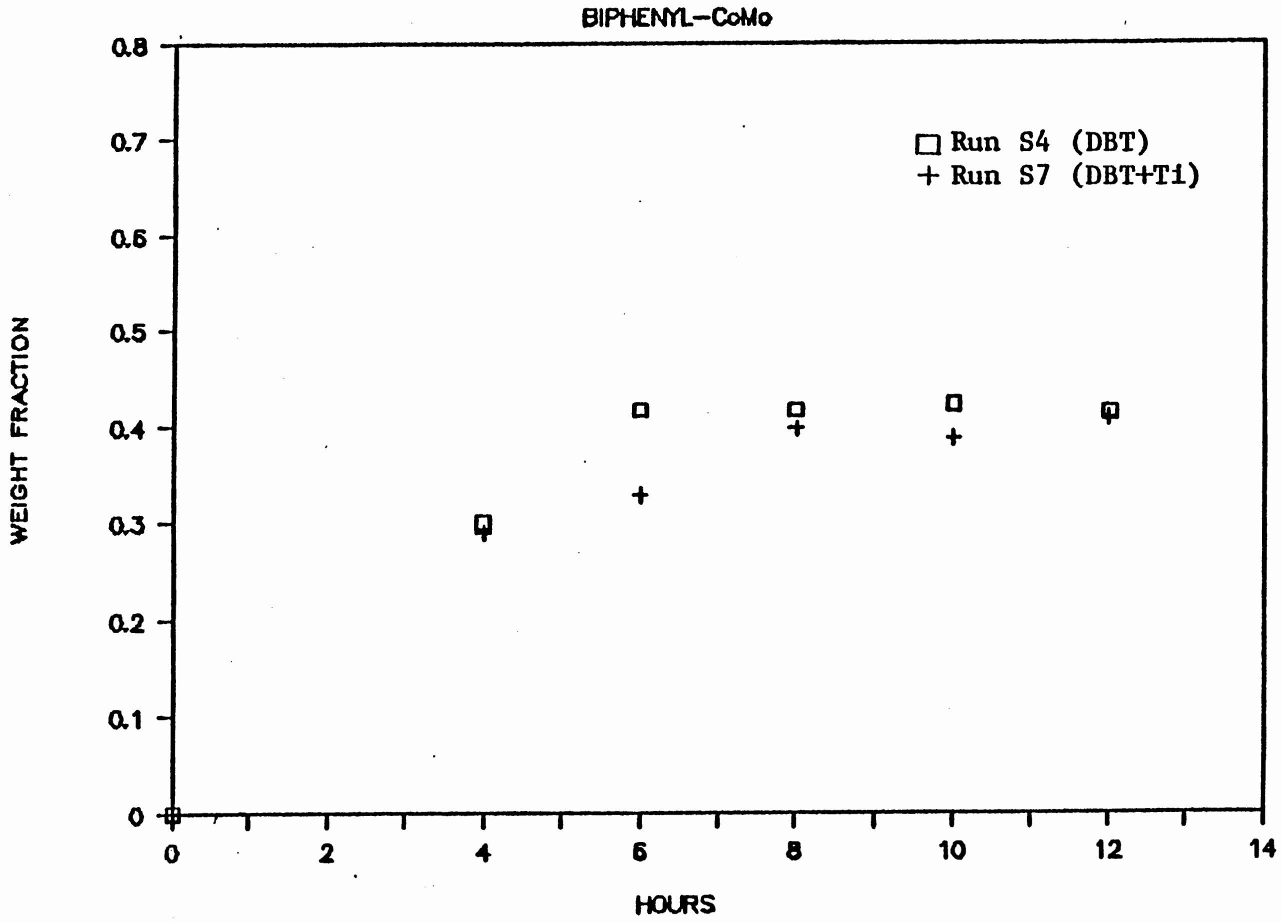

Figure 15. Weight Fraction of Biphenyl over the CoMo/alumina Catalyst.

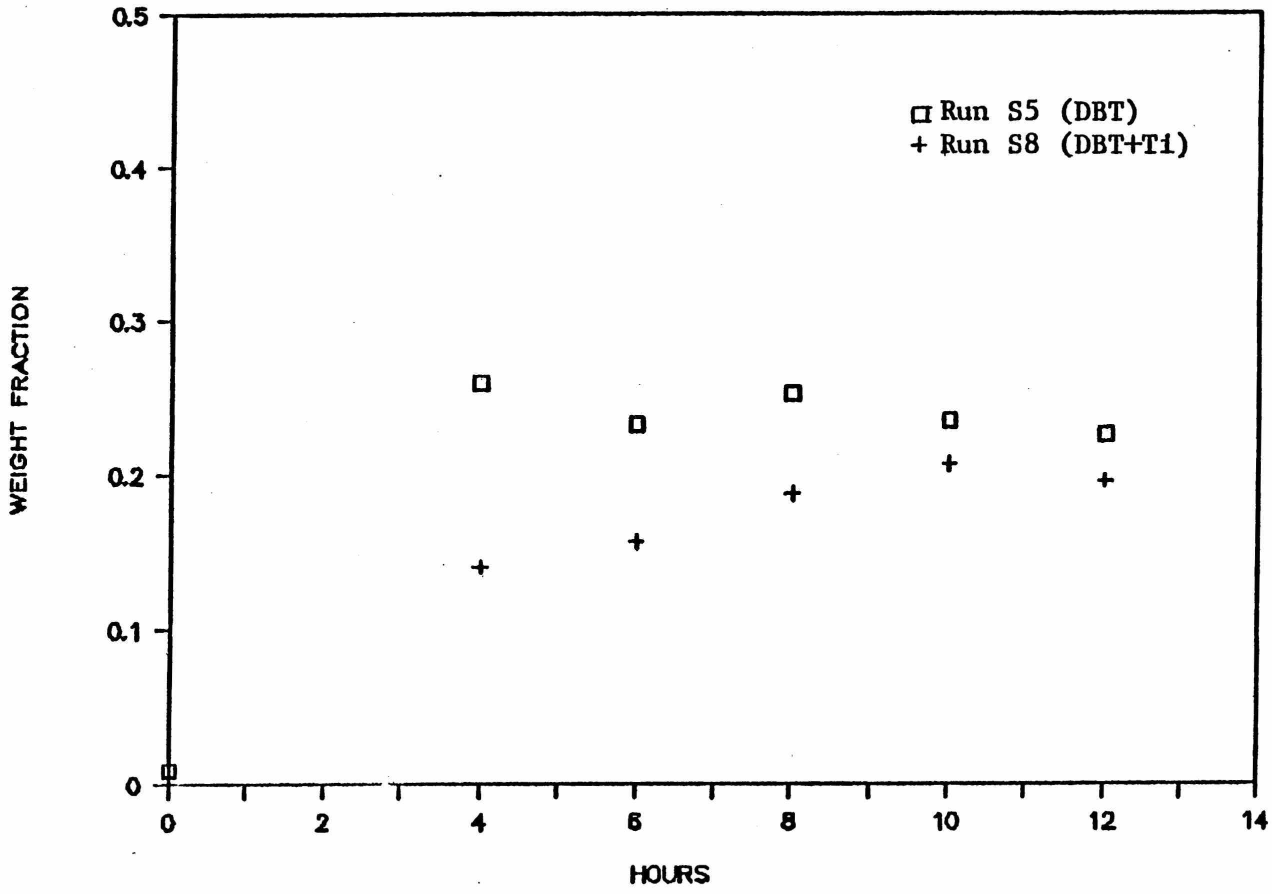

Figure 16. Weight Fraction of Biphenyl over the CoMo/alumina Catalyst.

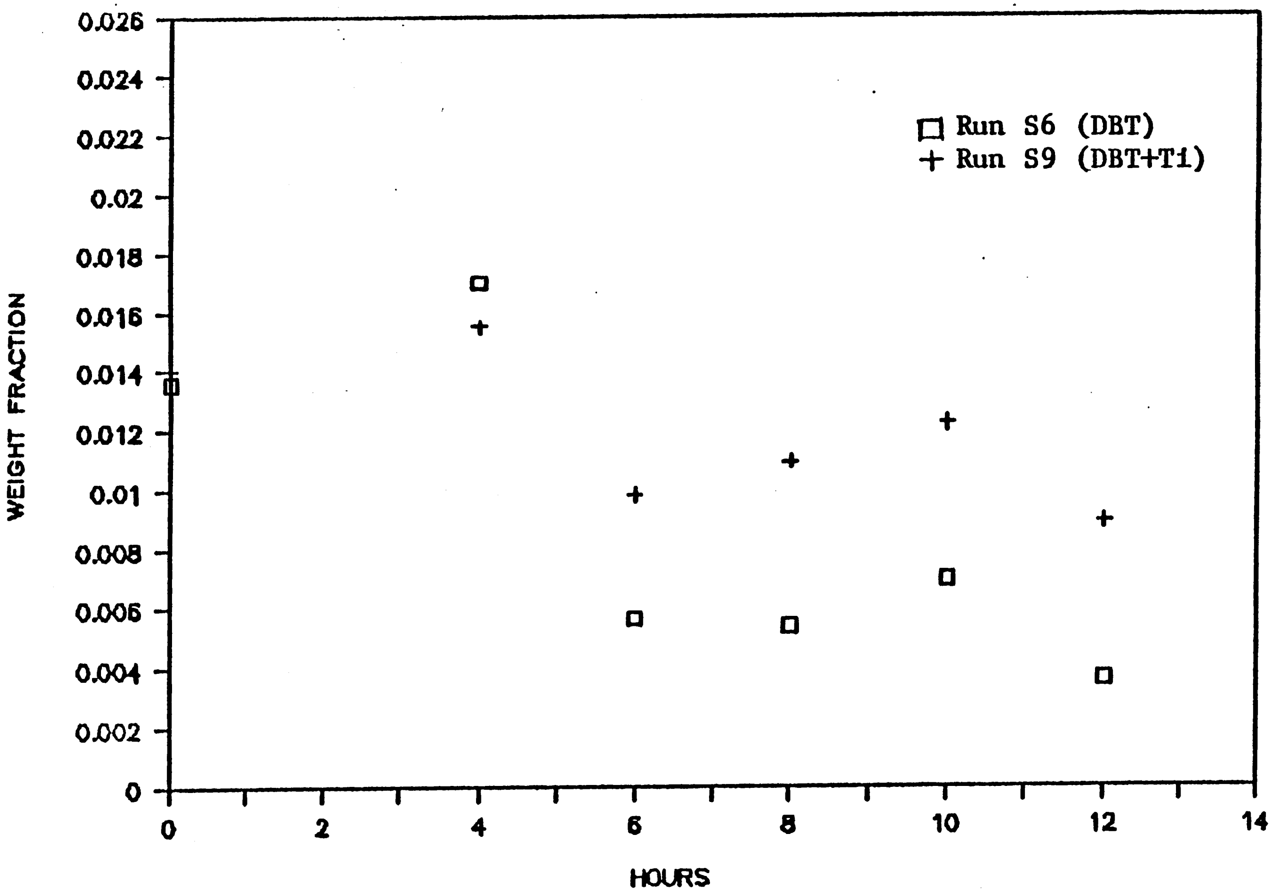

Figure 17. Weight Fraction of Biphenyl over the Plain Alumina

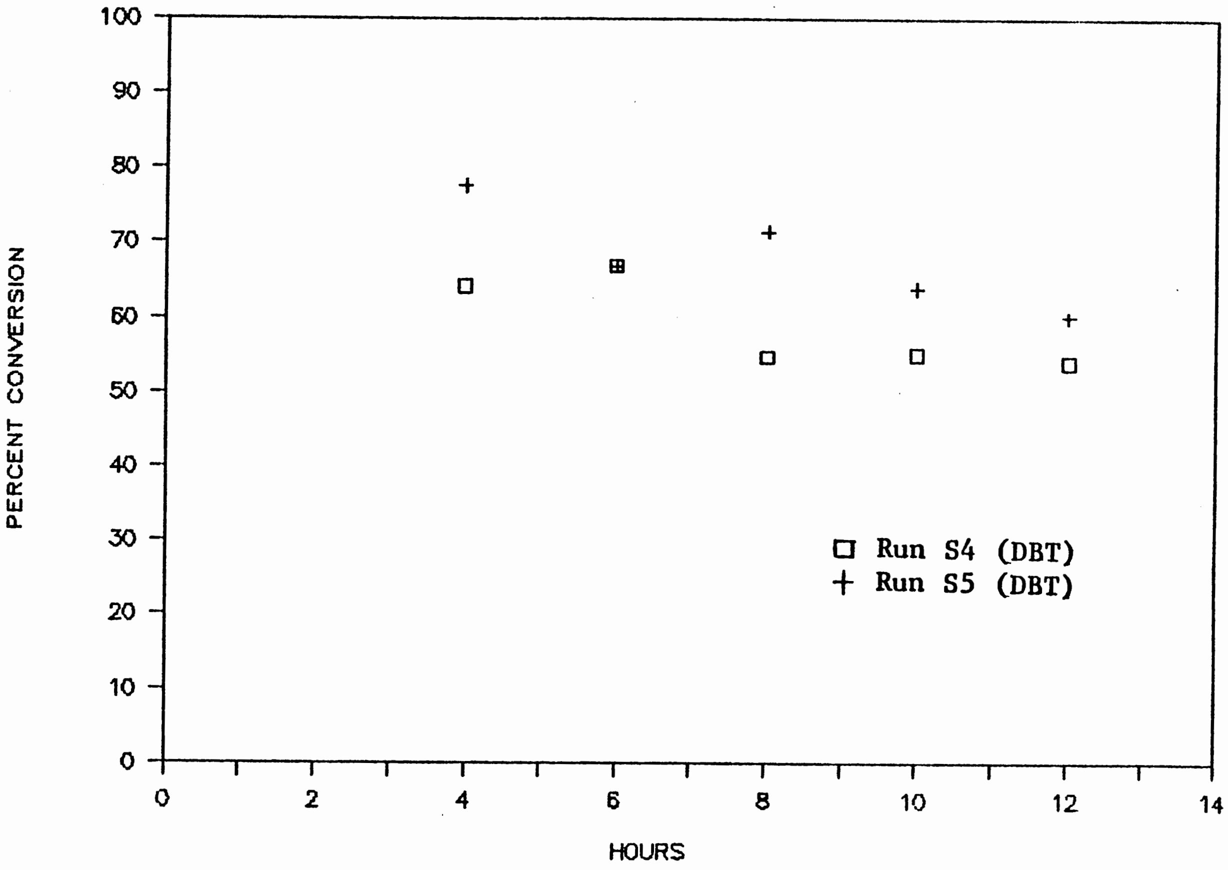

Figure 18. Catalyst Activity Comparison between the CoMo/alumina and the NiMo/alumina on Dibenzothiophene Conversion

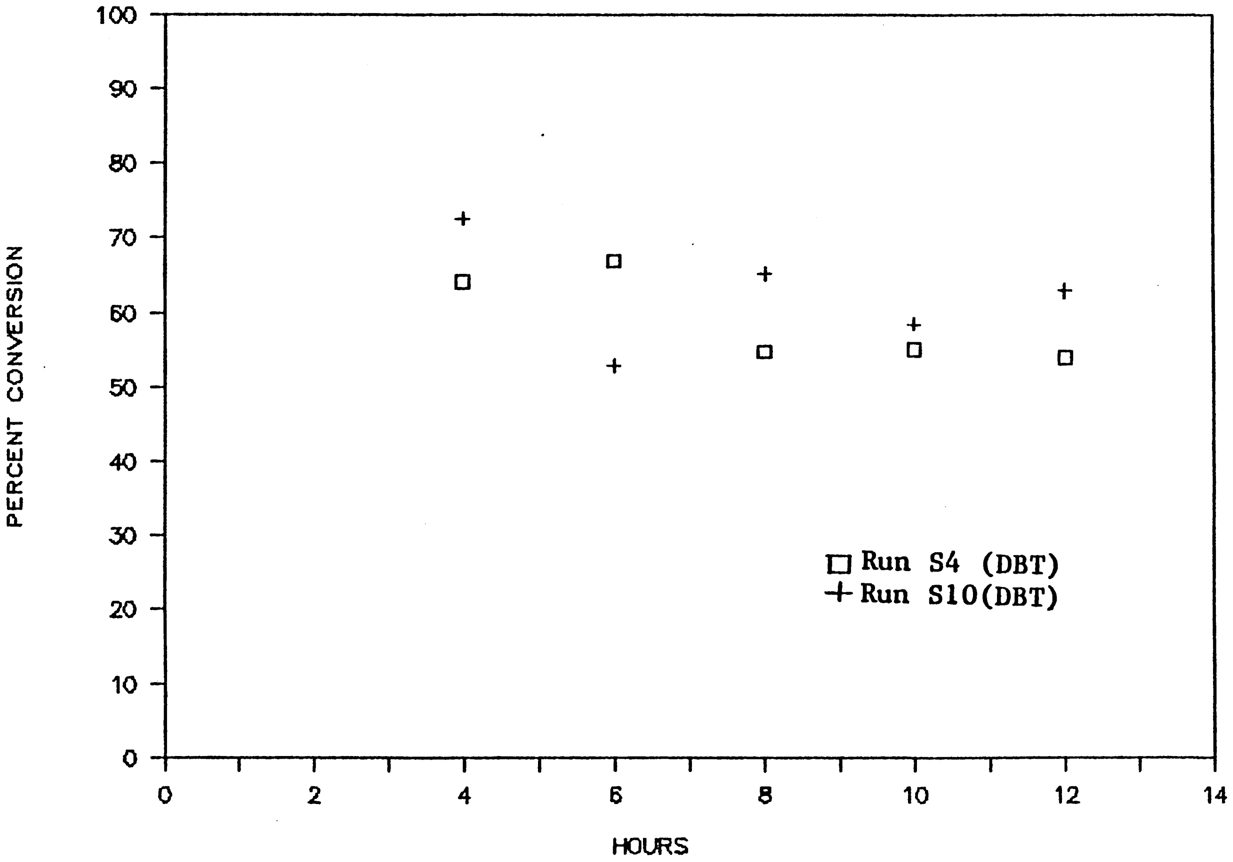

Figure 19. The Reproducibility of the System.

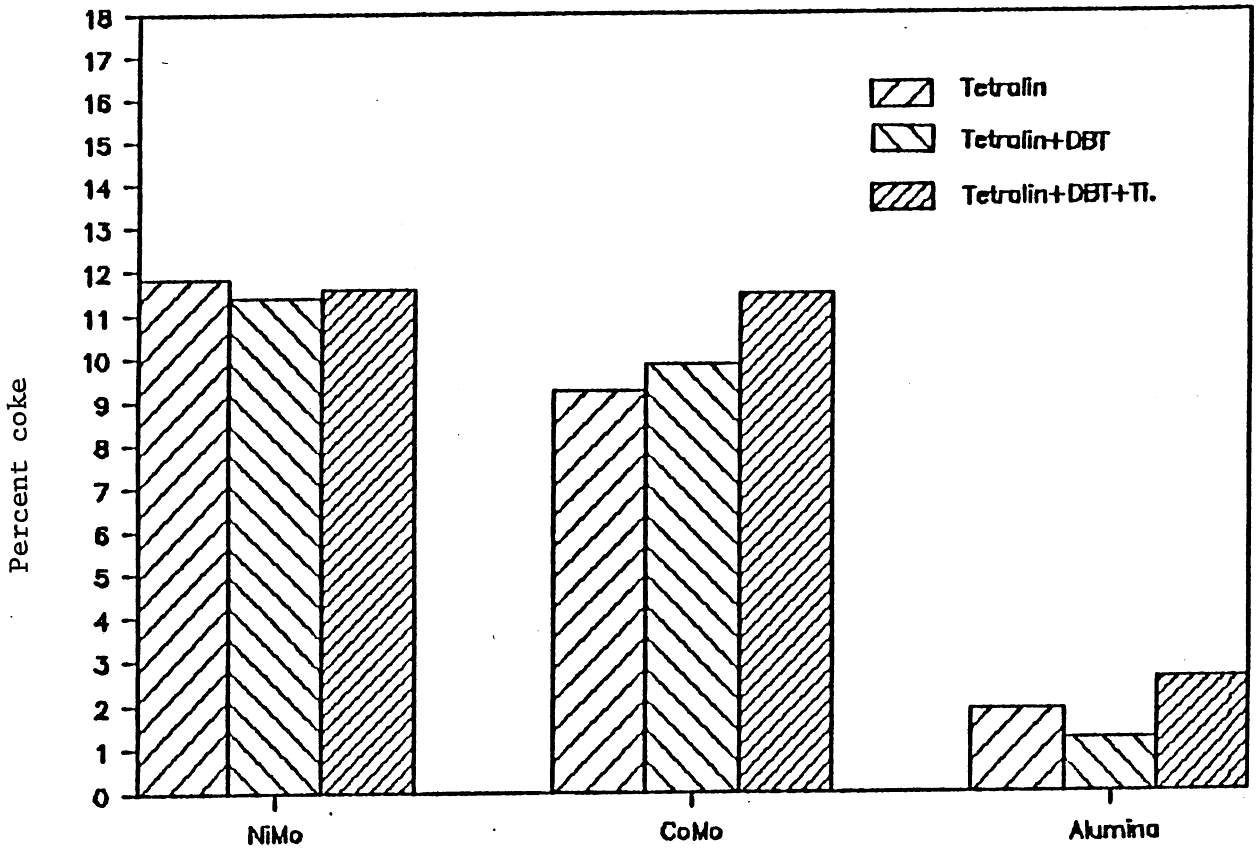

Figure 20. Coke Formation.

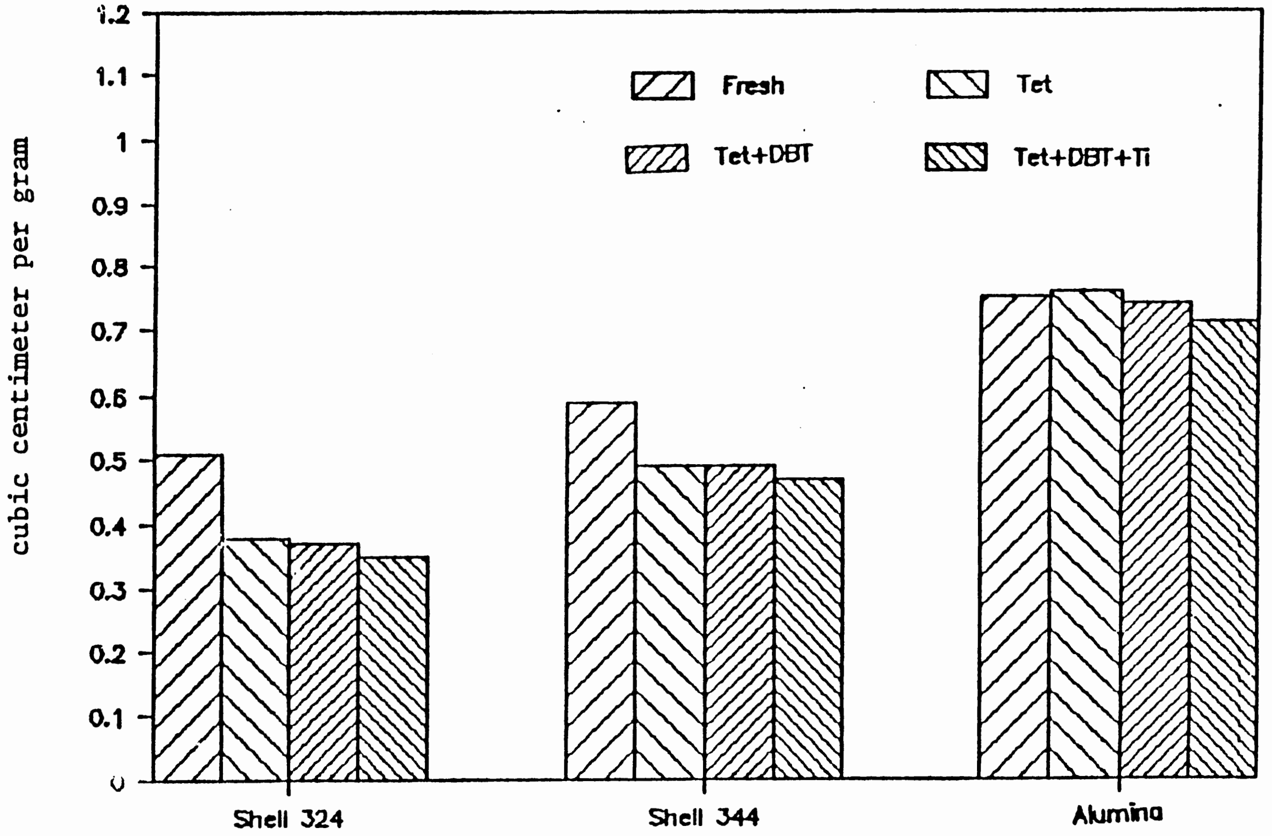

Figure 21. Pore Volume of the Spent Catalysts.

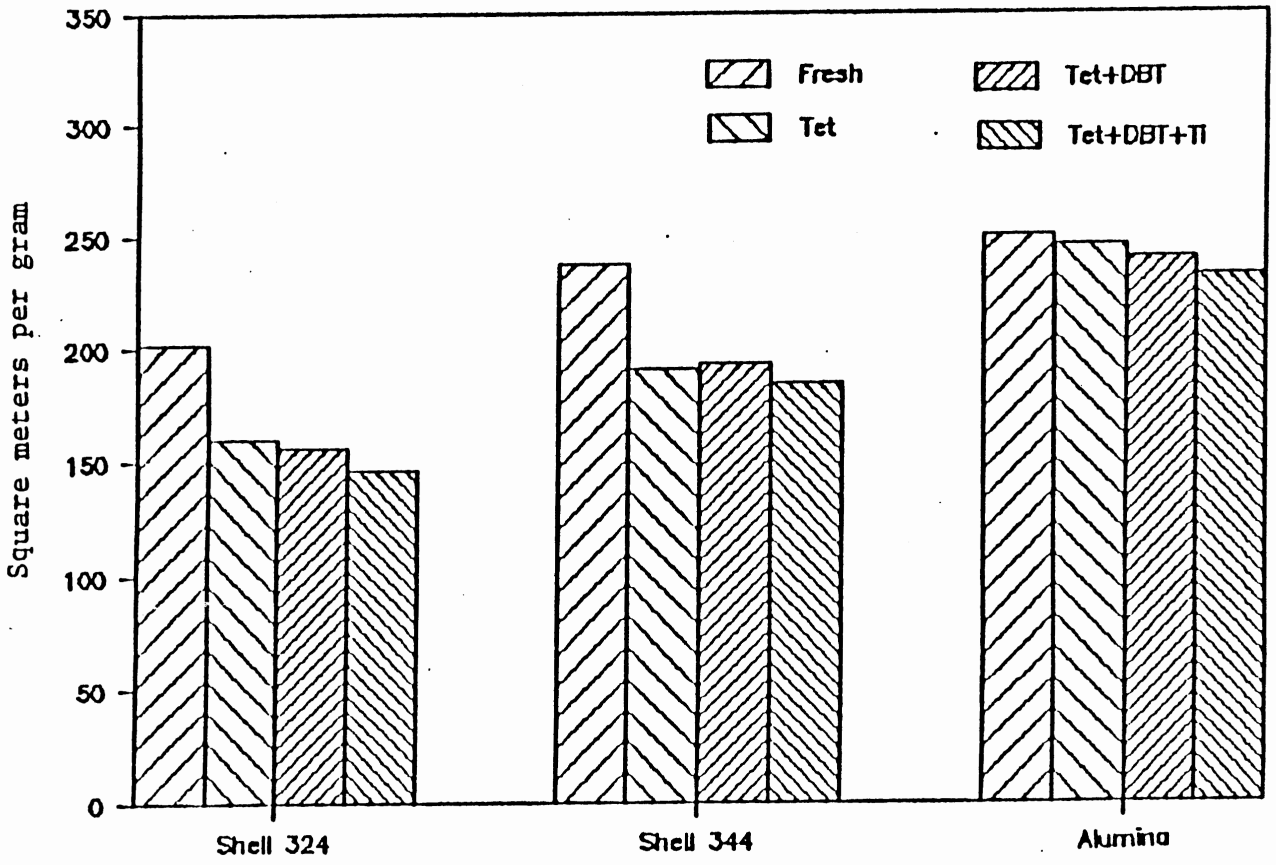

Figure 22. Surface Area of the Spent Catalysts.

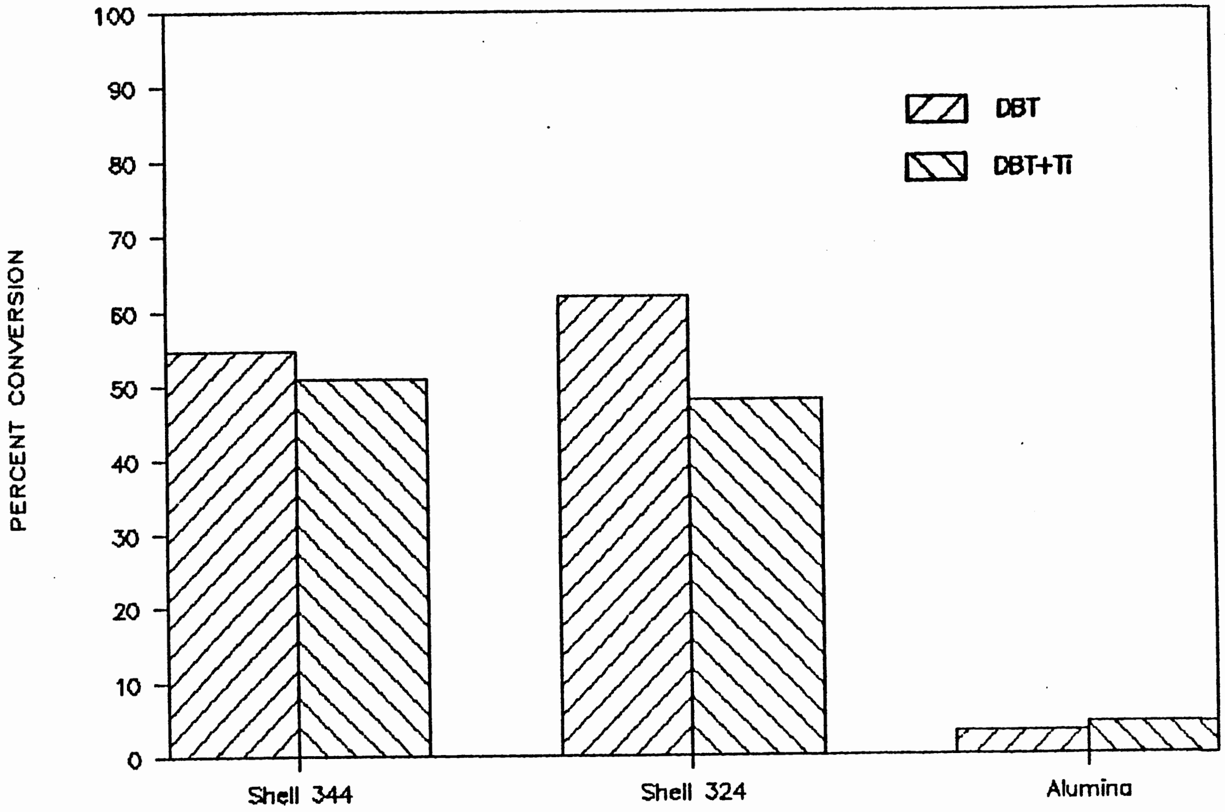

Figure 23. Effects of Titanocene Dichloride on Dibenzothiophene Conversions.

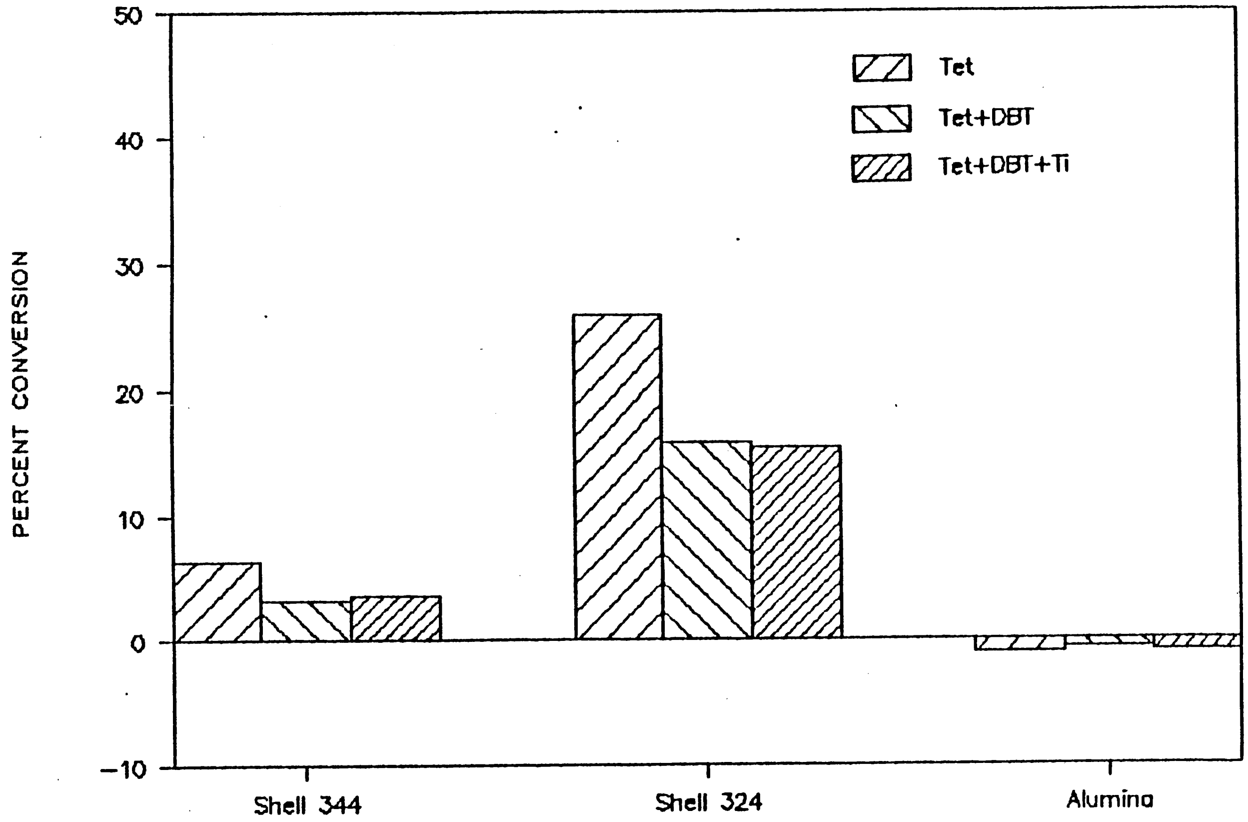

Figure 24. Effect of Titanocene Dichloride on Tetralin Conversions.

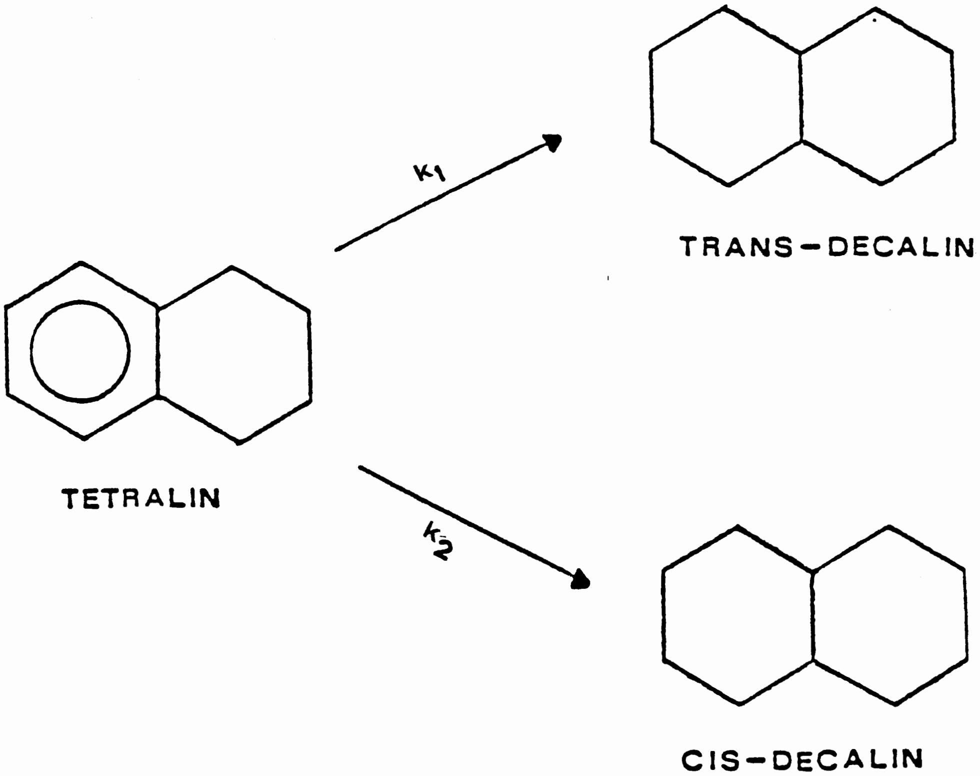

Figure 25. Simplified Tetralin Reaction Network

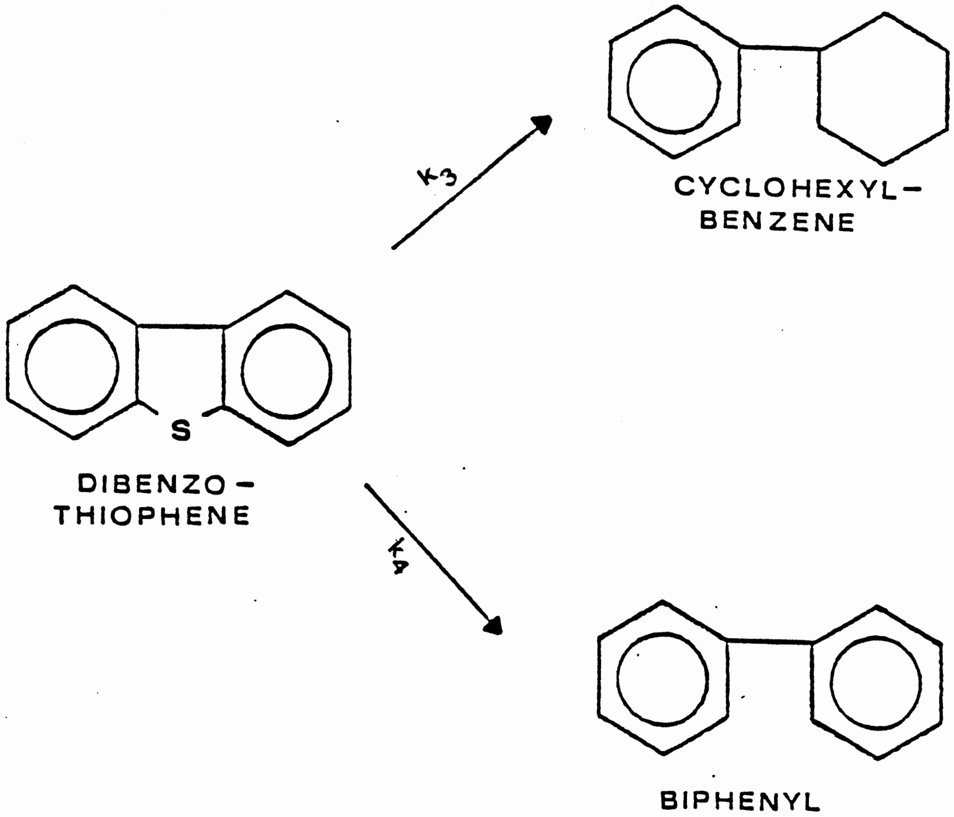

Figure 26. Simplified Dibenzothiophene Reaction Network

CHAPTER III

EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODEOXYGENATION OF DIBENZOFURAN

EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODEOXYGENATION OF DIBENZOFURAN

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ABSTRACT

The effects of titanocene dichloride on dibenzofuran hydrodeoxygenation over three different kinds of catalysts, NiMo/alumina (Shell 324), CoMo/alumina (Shell 344), and plain alumina were studied by using a Berty type gradientless reactor. The experiments were conducted at 275 C (527 F) and 10.4 MPa (1500 psig). Cyclohexane and dicyclohexyl were products of dibenzofuran hydrodeoxygenation under our experimental conditions. Trace amounts of cyclohexylbenzene were also detected. The addition of titanocene dichloride was found to improve the rate of dibenzofuran hydrodeoxygenation over both CoMo/alumina and NiMo/alumina catalysts. Titanocene dichloride was found to increase the coke content of CoMo/alumina catalyst but decreased the coking of NiMo/alumina catalyst. The selectivity of either trans- to cis- decalins or cyclohexane to dicyclohexyl was not sinificantly changed by titanocene dichloride for both CoMo/alumina and NiMo/alumina catalysts.

EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODEOXYGENATION OF DIBENZOFURAN

INTRODUCTION

Due to the continual increase in rate of energy consumption and the inevitable depletion of petroleum resources, utilization of other sources of energy must be investigated to prevent the impending energy crisis.

Coal, the most abundant fossil fuel in the United States, seems to have the highest potential to substitute crude oils. Unfortunately, it also happens to be a source of environmental pollution due to high contents of nitrogen, sulfur and oxygen.

In order to remove nitrogen, sulfur, and oxygen from coal-derived liquids, catalytic hydrotreatment at high pressures and high temperatures on NiMo/alumina, NiW/alumina or CoMo/alumina catalysts was utilized. The cost of the upgrading of coal liquids depends strongly on the life and activity of the catalyst. Any means to increase catalyst activity and reduce the rate of deactivation can favorably change the economics of the process.

Studies by Chan, et al., (1982) showed that addition of titanocene dichloride to a SRC II coal liquid reduced coke formation and increased the catalyst activity. The effect of titanocene dichloride on hydrodeoxygenation is studied in this part. The scope of this project is limited to hydrodeoxygenation only.

Although the oxygen removing process, hydrodeoxygenation, is one of the major reactions in hydrotreatment processes, very little is understood about the catalyst structure and the reaction mechanisms. The hydrodeoxygenation reaction results in the formation of water which is considered to deactivate the hydrodesulfurization activity of CoMo/alumina catalysts.

Petrakis, et al., (1983) analyzed a heavy distillate from an SRC-II coal liquid and found that the oxygen compounds in the liquid were phenols, aryl ethers, and benzofurans. Dibenzofuran was found to be a major oxygen containing compound in California Petroleum by Snyder (1970).

Badilla, et al.,(1979) had examined the hydroprocessing of a mixture of dibenzothiophene, dibenzofuran, quinoline and phenanthrene and found that dibenzofuran was the least reactive compound in the group. The results agreed with those of Rollmann, et al., (1977) who reported that the activity of dibenzofuran was lower than that of quinoline and benzothiophene. It is also believed that the rate of oxygen removal from the heterocyclic oxygen containing compounds like furan, benzofuran, and dibenzofuran decreases with increasing number of aromatic rings (Krishnamurthy, et al., 1981)

In an early work, Hall and Cawley (1939) studied the hydrodeoxygenation of dibenzofuran on MoS_2 catalyst and proposed two different machanisms at two different temperatures. Biphenyl was the product of dibenzofuran hydrodeoxygenation at higher temperatures while cyclohexylbenzene was produced at lower temperatures. So far, the products and mechanism of dibenzofuran given by Krishnamurthy, et al.,(1980) (Figure 1) seem to be the most comprehensive reaction network. His experiments were conducted in the temperature range of 616 to 649 K and 6.89 to 13.78 MPa hydrogen pressure. Carbon disulfide was added to the feed to maintain a H_2S partial pressure during the reactions. The conclusion was drawn that the removal of oxygen from dibenzofuran could be proceeded by indirect oxygen extrusion without hydrogenation of the adjacent benzene rings as well as by forming an intermediate hydrogenated product such as 1,2,3,4 tetrahydrodibenzofuran before the oxygen was removed.

Vito La Vopa and Satterfield (1987) investigated the hydrodeoxygenation of dibenzofuran on sulfided NiMo/alumina catalyst from 350 to 390 C and 7.0 MPa. They found that the major products were single-ring hydrocarbons, cyclohexane predominating. The reaction network is shown in Figure 2. The major pathway was through saturation of one ring of dibenzofuran, forming tetrahydrodibenzofuran, hexahydrodibenzofuran and then 2-cyclohexylphenol. Single-ring products were believed to form from this pathway. The catalyst in the oxide form had lower activity than in the sulfide form and the major products were the double ring compounds. They also observed that the reaction of dibenzofuran hydrodeoxygenation was first order.

In this project dibenzofuran was chosen to represent the oxygen compounds in crude oil due to its low activity in hydrodeoxygenation reaction. One hundred parts per million of titanium as titanocene dichloride was added to the mixture and hydrotreated in a Berty type gradientless reactor to study the effects of titanocene dichloride on hydrodeoxygenation of dibenzofuran.

Three different catalysts, NiMo/alumina, CoMo/alumina, and plain alumina were used and the results are compared in this study. Most investigators studied hydrodeoxygenation on NiMo/alumina rather than on CoMo/alumina due to the significantly higher conversion yields by NiMo/alumina.

The experiments were made at 275 C (527 F) and 10.4 MPa (1500 psig). Cyclohexane and dicyclohexyl were the predominant product from dibenzofuran hydrodeoxygenation. Trace amounts of cyclohexylbenzene were also detected.

EXPERIMENTAL SECTION

The process flow diagram of the reactor system is shown in Figure 3. The reactor used in these studies was the Berty type gradientless reactor. The reactor internal is shown in Figure 4. The operating conditions are summarized in Table I.

Before the operating temperature was set, two trial runs were conducted at 250 C (482 F) and 300 C (572 F) to find the proper temperature for our study. At 250 C (run O11), the conversion of dibenzofuran over CoMo/alumina catalyst appeared to be too low while its conversion over NiMo/alumina at 300 C (run O12) appeared to be too high.

The feed solvent, Tetralin, was used with and without doctoring with 100 ppm of titanium as titanocene dichloride. Dibenzofuran was dissolved in the solvent to a concentration of 10 wt % and hydrotreated in the reactor at 10.4 MPa(1500 psig) and 275 C (527 F).

Liquid feed was continuously pumped into the reactor by a Milton Roy positive displacement pump to mix with hydrogen gas feed at the bottom of the reactor. Without passing through the catalyst, the mixture was forced to flow to the top of the reactor by the centrifugal force provided by the impeller. At the top of the reactor, the mixture was separated into two streams. The major portion of the fluid flowed down through the catalyst basket while a minor fraction flowed out of the reactor to the first separation cylinder. The major stream, after flowing through the catalyst basket, mixed with the fresh feedstocks and was recycled into the catalyst basket.

After the liquid and gas products were separated, the exit gases were scrubbed with a sodium hydroxide solution before they were exhausted into the atmosphere. The exit gas flow rate was measured by a Brooks Sho-Rate Model 1355 rotameter.

The temperature and stirrer speed were controlled by

Autoclave Engineers temperature controller and Autoclave Engineers speed controller, respectively. A more detailed description of the reactor system is given by Williams (1987) and Tscheikuna (1988).

Before each run, the catalyst was calcined with nitrogen gas at a pressure of 1.8 MPa (250 psig) and the temperature of 300 C (572 F) for 1 h. The catalyst was allowed to cool down to 250 C (482 F) under nitrogen gas before it was sulfided with 5 % hydrogen sulfide in hydrogen mixture. The catalyst was heated at a rate of 120 C/h (216 F/h) from 250 C (482 F) to 360 C (680 F) and kept at 360 C (680 F) for two hours. Each run used 20 g of catalyst with properties reported in Table II. The duration of each experiment was 12 hours with liquid product samples taken every two hours.

ANALYSIS

The liquid samples were analyzed by a Hewlett Packard Model 5890 A Gas Chromatograph equipped with a 60 m DB-1 capillary column and a thermal conductivity detector. The output of the detector was measured and recorded by a Hewlett Packard Model 3392 A Integrator. The concentration of titanium in the feedstocks and product samples were analyzed by a Perkin Elmer Model 503 Atomic Absorption Spectometer.

CATALYST ANALYSIS

The catalyst from each run was extracted in a Soxhlet unit with tetrahydrofuran for 60 hours. The samples were then air dried for 48 hours. Then the catalyst samples were analyzed for coke content, surface area, pore volume, and titanium distribution inside the pellets.

For coke content, the catalyst samples were weighed at room temperature before the carbonaceous material was burned off. Then, the catalyst samples were heated to 550 C (1022 F) for 60 hours to burn off the carbonaceous matter. After that, the catalyst samples were cooled down to room temperature and reweighed. The difference in weights is considered to be the amount of coke. The surface area and pore volume of each catalyst sample was analyzed by an Autoscan 60 Porosimeter. The titanium distribution is measured by a Joel Model JFM-35 Scanning Electron Microscope equipped with an Energy Dispersive X-ray Analyzer (EDAX). The catalyst samples were analyzed for titanium deposition at the catalyst surface and at four different points of the cross section from center to edge of the pellets.

RESULTS AND DISCUSSION

Nine experimental runs with one duplicate run were conducted over three different kinds of catalysts: NiMo/alumina (Shell 324), CoMo/alumina (Shell 344), and plain alumina. The list of experimental runs is given in

Table III.

Dibenzofuran was chosen to represent a hard-to-react oxygen compound in coal liquids. The conversion of dibenzofuran was taken as an indicator of hydrodeoxygenation. Figure 5 shows the comparison of dibenzofuran conversion on three different catalysts before and after titanocene dichloride was added to the feedstocks. The NiMo/alumina catalyst was approximately twice as active as the CoMo/alumina catalyst. Titanocene dichloride was found to increase the activities of both CoMo/alumina and NiMo/alumina catalysts on hydrodeoxygenation as shown in Figure 5. This is also presented by rate constants and rate of reaction which were calculated on the assumption that the reaction was first order (Table IV). Cyclohexane was the product which appeared to be significantly increased with the addition of titanocene dichloride (Figure 11).

In the case of NiMo/alumina catalyst, coke content was found to be dropped when titanocene dichloride was added to the feed. (Figure 7). Pore volume and surface area of the spent catalysts were found to have increased with the addition of titanocene dichloride as shown in Figures 8, and 9.

In the case of CoMo/alumina catalyst, the catalyst from doped run was found to have higher coke content and lower pore volume and surface area. This leads to a conclusion that, in case of CoMo/alumina, even though titanocene dichloride increaces the amount of coke formation on catalyst, it does not retard the hydrodeoxygenation. In other words, the amount of coke which was increased by titanocene dichloride did not deposit on the hydrodeoxygenation sites of the catalyst. Pore volume and surface area of the spent catalyst were found to have decreased with the increaced coke.

The conversion of Tetralin was found to be inhibited by dibenzofuran in both CoMo/alumina and NiMo/alumina catalysts. This indicates that the hydrogenation of dibenzofuran shares the same catalyst sites as Tetralin hydrogenation. The degree of conversion does not change any further when titanocene dichloride is added. This indicates that titanocene dichloride does not affect the hydrogenation of Tetralin (Figure 6).

The NiMo/alumina catalyst yields Tetralin conversions about twice as high as the CoMo/alumina catalyst. These results indicate that a nickel promotor has a strong effect on hydrogenation enhanchment of catalyst. The reason that the conversion of dibenzofuran on CoMo/alumina is not as high as the conversion on NiMo/alumina catalyst can be explained by the pathway of dibenzofuran hydrodeoxygenation. The first stage of dibenzofuran hydrodeoxygenation is to form intermediate hydrogenated compounds such as tetrahydrodibenzofuran, hexahydrodibenzofuran or o-phenyl-phenol before the oxygen atom is cleft. The hydrogenation sites of CoMo/alumina catalyst are not as reactive as those of NiMo/alumina catalyst.

All the titanium which deposited on catalyst was found at the surface of the catalyst pellet. This is similar to the Lynch (1986) studies when he passed titanium porphyrin through Shell 324 (NiMo/alumina) in the microflow reactor and found that most of the titanium deposited near the edge of the catalyst samples. This phenomena can be explained by the high reactivity of the organic compound of titanocene dichloride with the catalyst resulting in deposition of titanium on the outer surface of the catalyst.

Addition of titanocene dichloride reduces the rate of hydrodeoxygenation of dibenzofuran in case of plain alumina (Figures 5, 6, 15, and 21). This rate reducing effect is more pronounced with dibenzofuran than it is with Tetralin.

The selectivity of either trans- to cis-decalins or cyclhexane to dicyclohexyl is unaffected by titanocene dichloride for both NiMo/alumina or CoMo/alumina catalysts. For plain alumina, the conversions of dibenzofuran and Tetralin from the doped run were too low to indicate the effect of titanocene dichloride on the selectivity of either cyclohexane to dicyclohexyl or trans- to cis-decalins

The effect of titanocene dichloride on dibenzofuran hydrodeoxygenation is found to be very interesting because titanocene dichloride increases the activities of both

CoMo/alumina and NiMo/alumina catalysts and decreases the coking rate of NiMo/alumina catalyst. Therefore, it could provide a means to reduce the processing cost of hydrotreatment.

CONCLUSION

This study indicates that titanocene dichloride increases the rate of dibenzofuran hydrodeoxygenation over both CoMo/alumina and NiMo/alumina catalysts.

Titanocene dichloride reduces the amount of coke on NiMo/alumina catalyst but increases the coking of CoMo/alumina.

Addition of titanocene dichloride to a Tetralin-dibenzofuran mixture does not affect the Tetralin hydrogenation rate.

Shell 324 (NiMo/alumina) gives about twice higher conversion for dibenzofuran than Shell 344 (CoMo/alumina).

The selectivity of either trans- to cis-decalins or cyclohexane to dicyclohexyl is unaffected by titanocene dichloride for both NiMo/alumina and CoMo/alumina catalysts.

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TABLE I

OPERATING CONDITION

Catalyst weight:	20 g
Pressure:	10.4 MPa (1500 psig)
Hydrogen Flowrate:	0.024 m^3/h (400 cm^3/min)
Feedstock Flowrate:	3.0E-05 m^3/h (30 cm^3/h)
Sampling Intervals:	every 2 h
Run Duration:	12 h
Magnedrive Speed:	1500 rpm

TABLE II

PROPERTIES OF CATALYST

	Shell 324	Shell 344	Alumina*
Chemical composition wt%			
Co	-	2.4	-
Ni	2.7	-	-
Mo	13.2	9.8	-
Physical Properties :			
Geometry	1.6 mm extrudate	1.6 mm extrudate	2.0 mm extrudate
Surface area, m^2/g	202	238	248
Pore Volume, cm^3/g	.51	.59	.75

* Alumina 005-2E Test No. 21006 Akzo Chemic.

TABLE III

LIST OF DIBENZOFURAN EXPERIMENTAL RUNS

Run No.	Feed	Catalyst
O1	Tetralin	CoMo
O2	Tetralin	NiMo
O3	Tetralin	Alumina
O4	Tetralin + DBF	CoMo
O5	Tetralin + DBF	NiMo
O6	Tetralin + DBF	Alumina
O7	Tetralin + DBF + Ti	CoMo
O8	Tetralin + DBF + Ti	NiMo
O9	Tetralin + DBF + Ti	Alumina
O10	Tetralin + DBF	CoMo
O11	Tetralin + DBF*	CoMo
O12	Tetralin + DBF**	NiMo

* Run O11 was made at 250 C

** Run O12 was made at 300 C

TABLE IV

RATE CONSTANTS
(Unit: $m^3/(kg\ cat)\ (s)$)

		Shell 344		
		Tet.	Tet+DBF	Tet+DBF+Ti
Tetralin	(k1)	3.76E-08	2.83E-08	2.49E-08
	(k2)	1.24E-08	9.82E-09	8.70E-09
Dibenzofuran	(k3)		1.18E-07	1.35E-07
	(k4)		8.63E-09	9.03E-09

		Shell 324		
		Tet.	Tet+DBF	Tet+DBF+Ti
Tetralin	(k1)	3.62E-07	2.64E-07	2.91E-07
	(k2)	9.53E-08	6.30E-08	7.29E-08
Dibenzofuran	(k3)		2.85E-07	3.67E-07
	(k4)		1.12E-07	1.16E-07

		Shell 324	
		Tet+DBF	Duplicate
Tetralin	(k1)	2.64E-07	2.51E-07
	(k2)	6.30E-08	6.05E-08
Dibenzofuran	(k3)	2.85E-07	2.89E-07
	(k4)	1.12E-07	1.20E-07

TABLE V

PERCENT TITANIUM ON CATALYST SURFACE

Run No.	Catalyst	% titanium*
07	CoMo/alumina	0.6
08	NiMo/alumina	6.7
09	Plain alumina	5.4

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* Percent titanium was approximated from percent area of titanium which was analyzed by EDAX attachment to the Scaning Electron Microscope

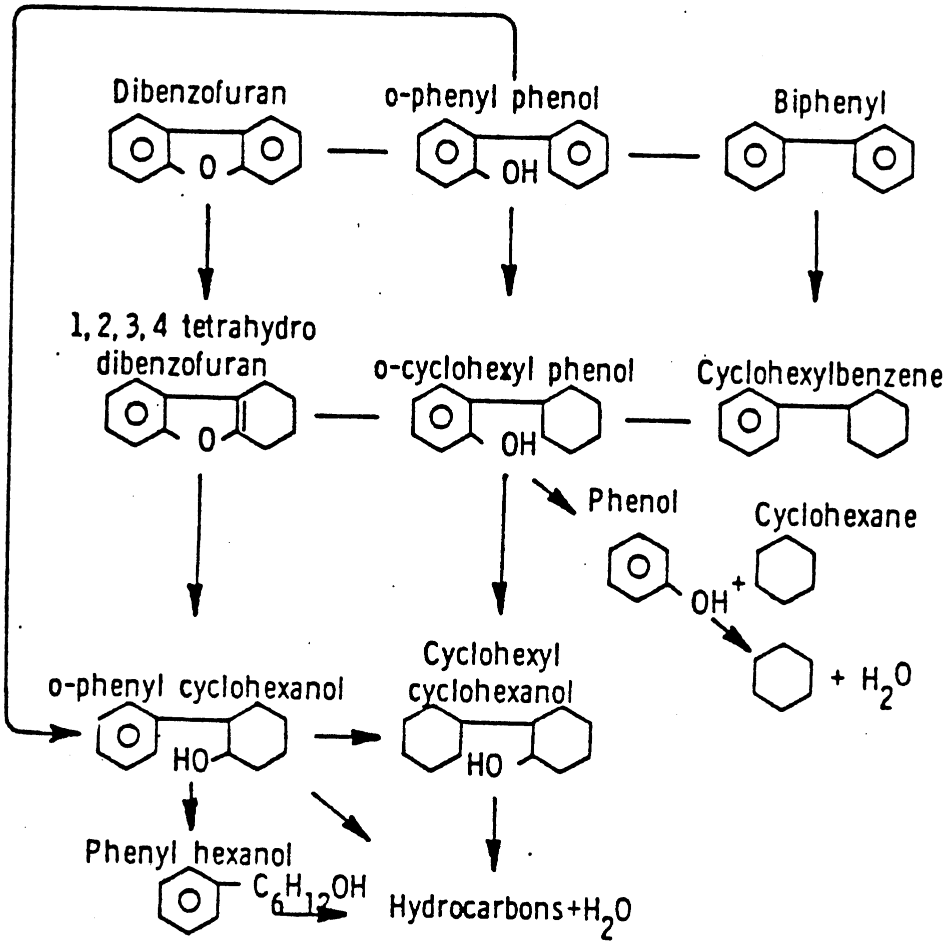

Figure 1. Reaction Network of Dibenzofuran by Krishnamurthy, et al., (1980)

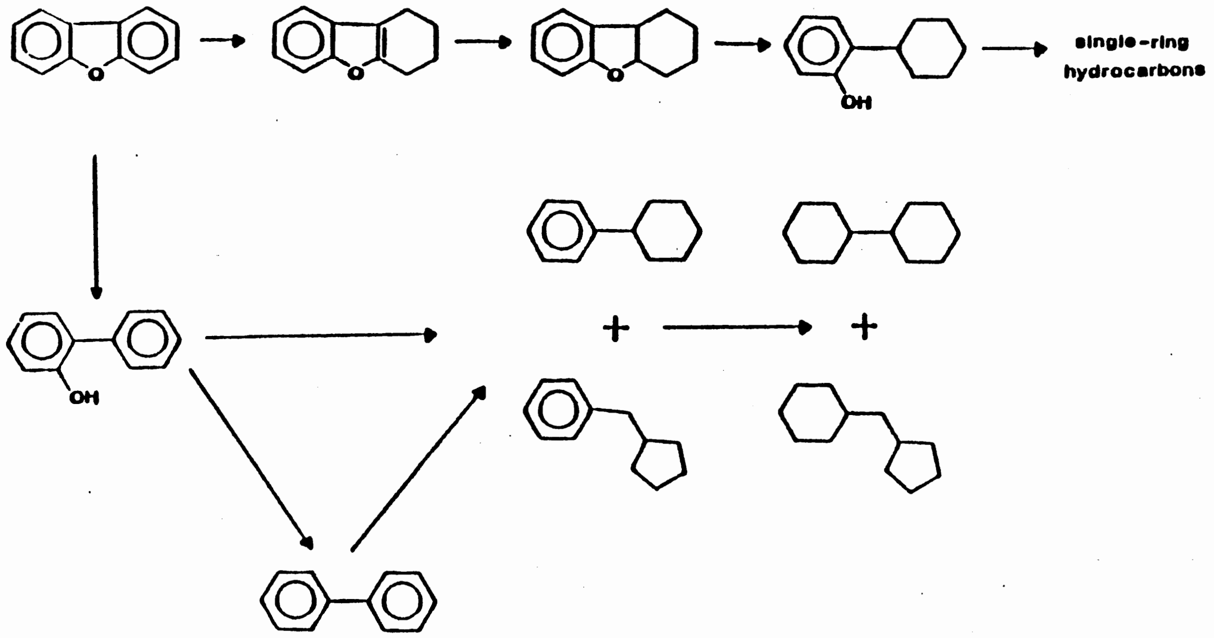

Figure 2. Reaction Network of Dibenzofuran by La Vopa, et al., (1986)

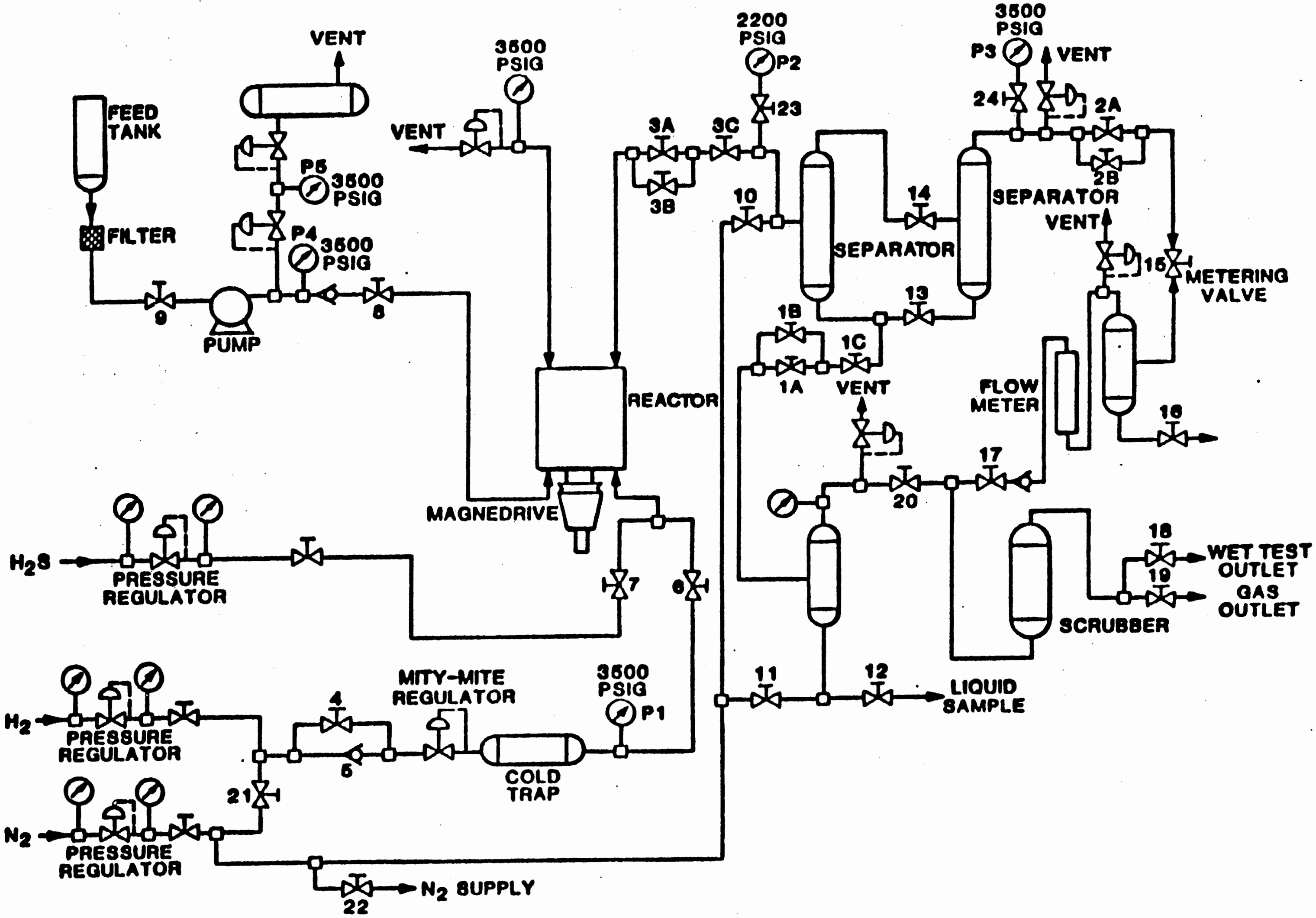

Figure 3. Process Flow Diagram of Reactor System

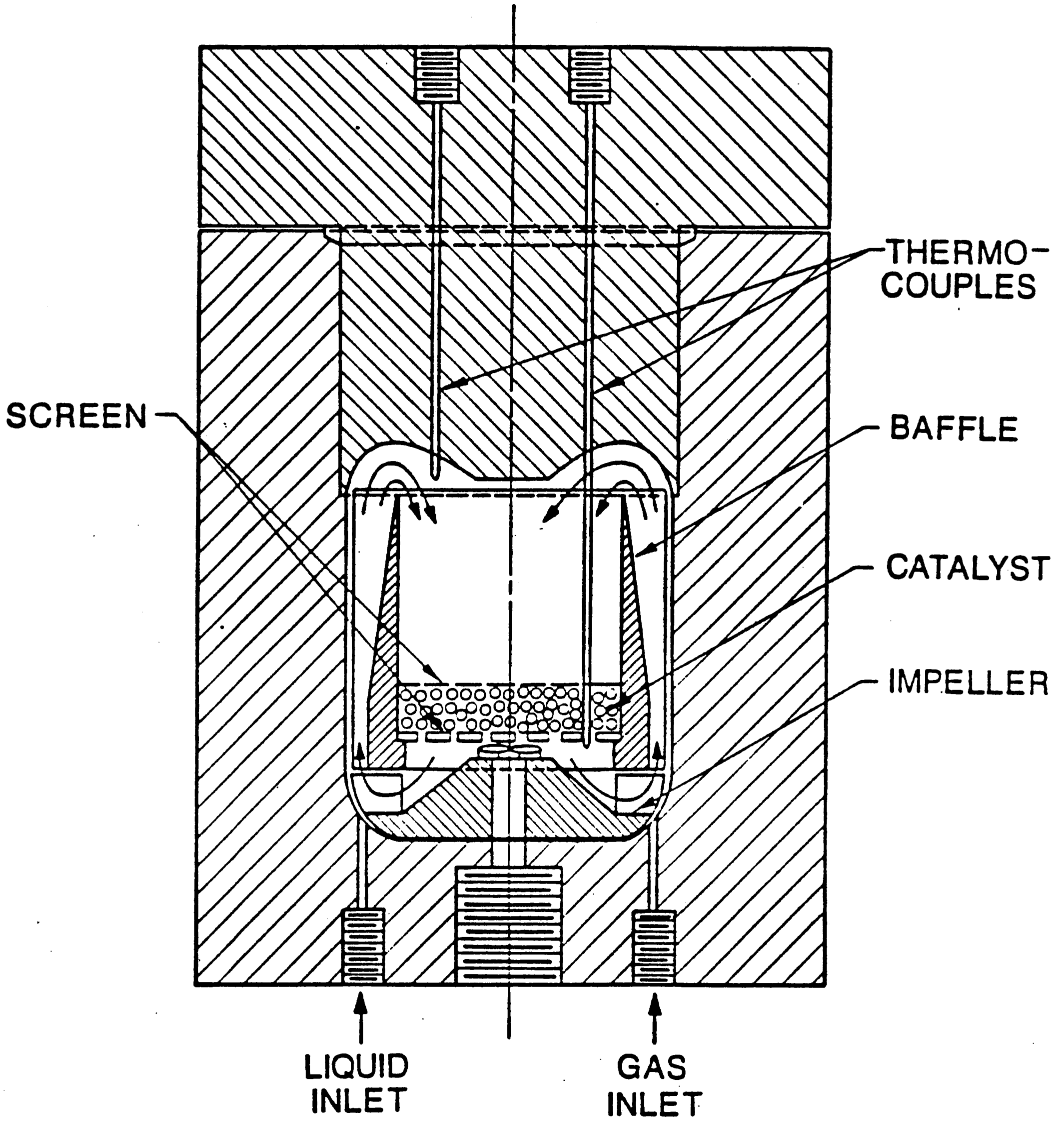

Figure 4. Internals of Berty Reactor

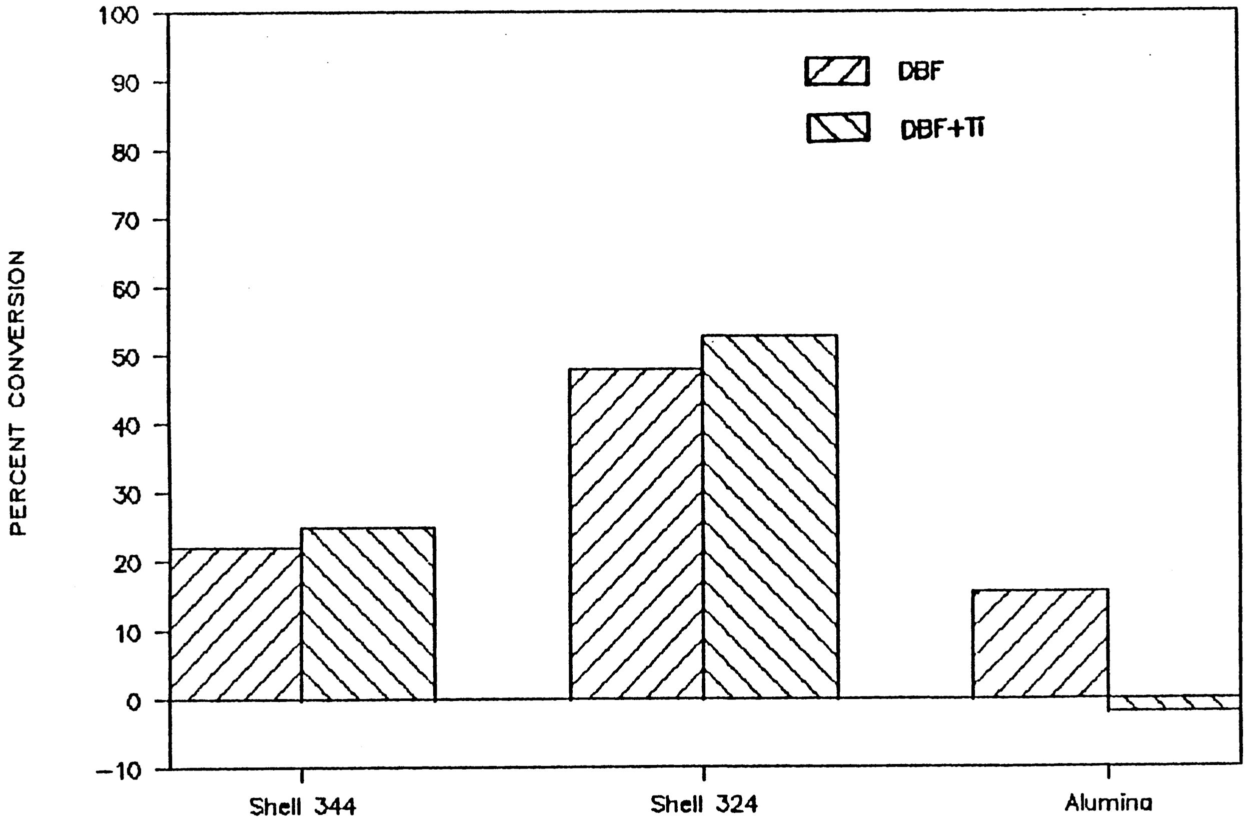

Figure 5. Effects of Titanocene Dichloride on Dibenzofuran Conversions.

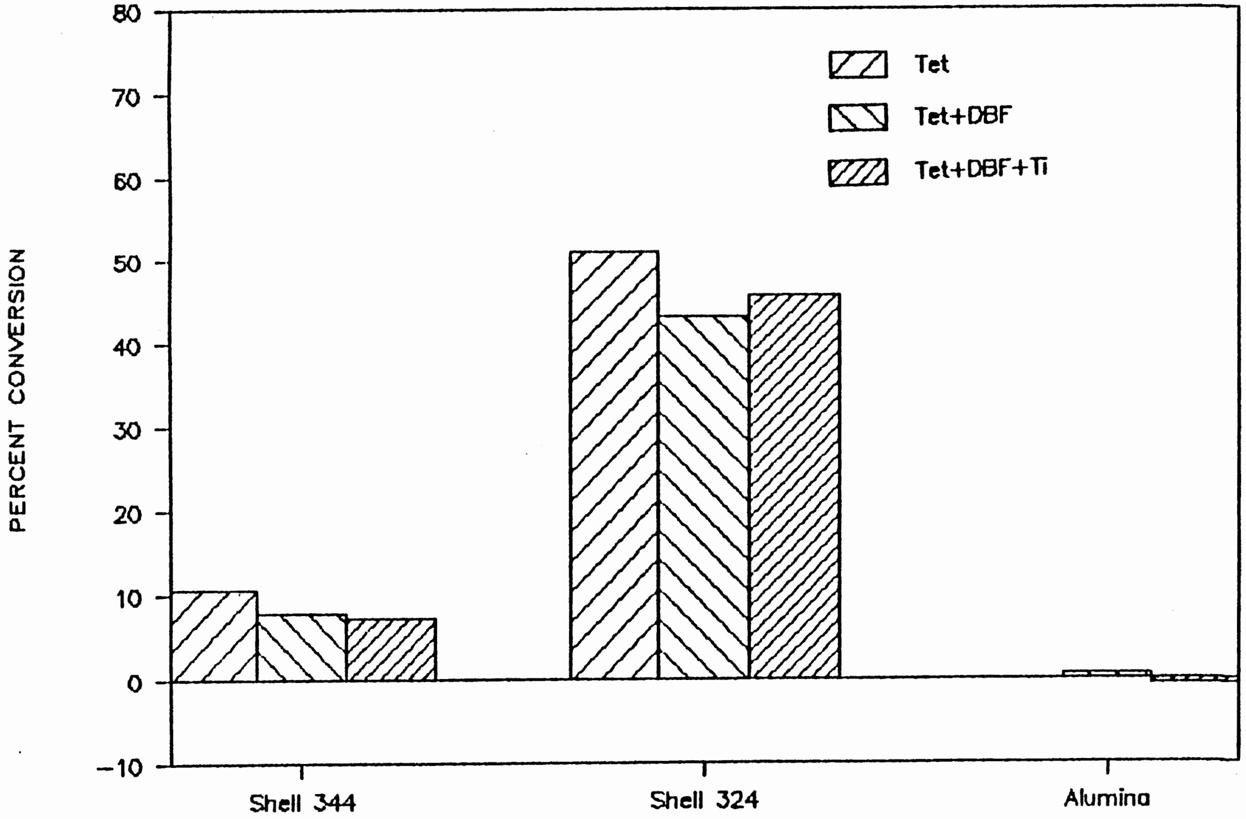

Figure 6. Effects of Titanocene Dichloride on Tetralin Conversions.

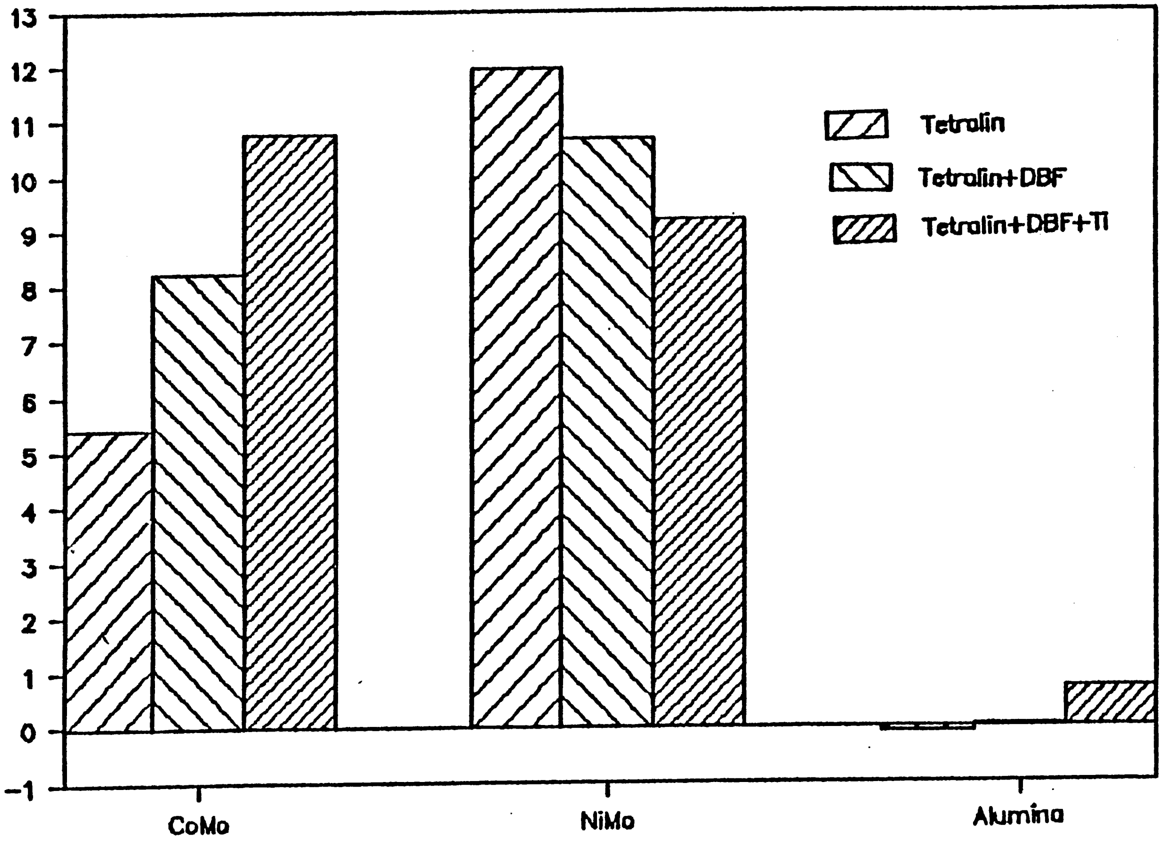

Figure 7. Coke Formation

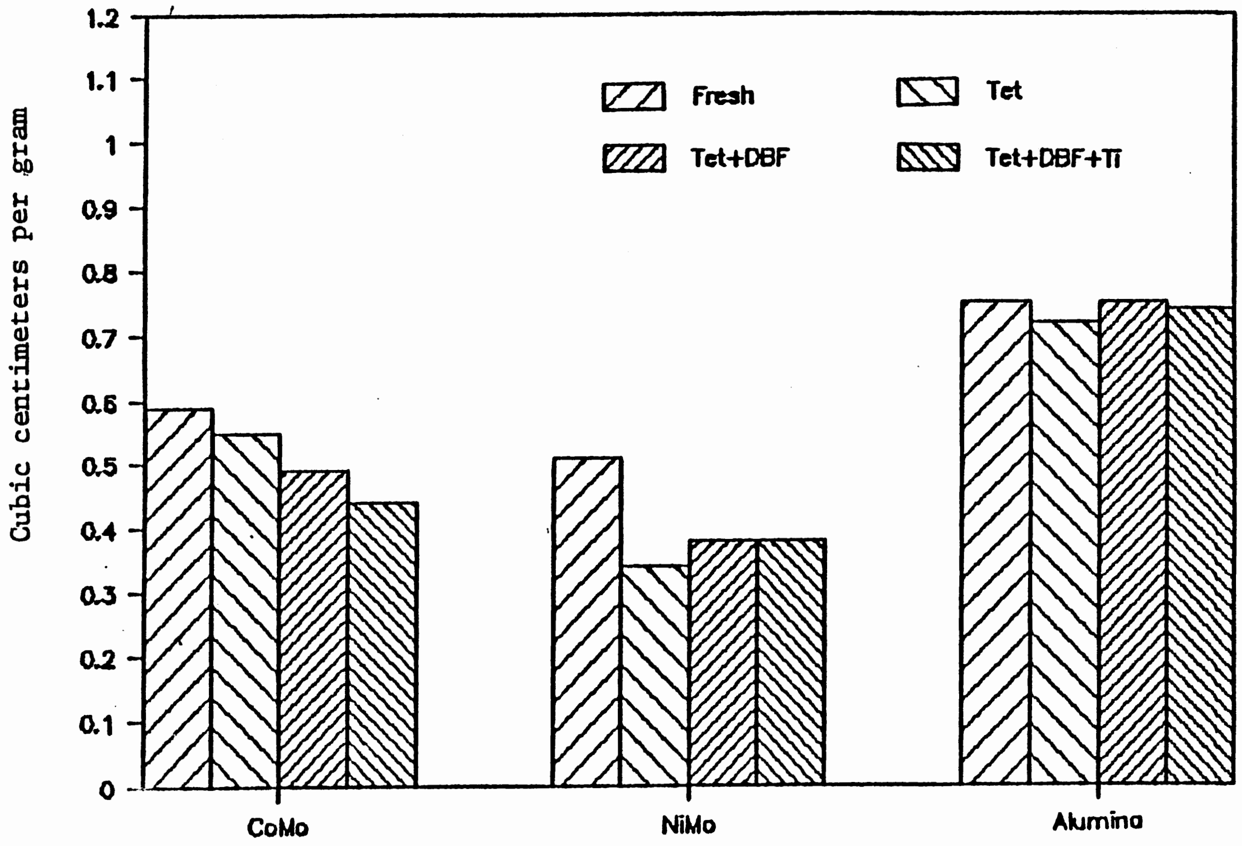

Figure 8. Pore Volume of the Spent Catalysts.

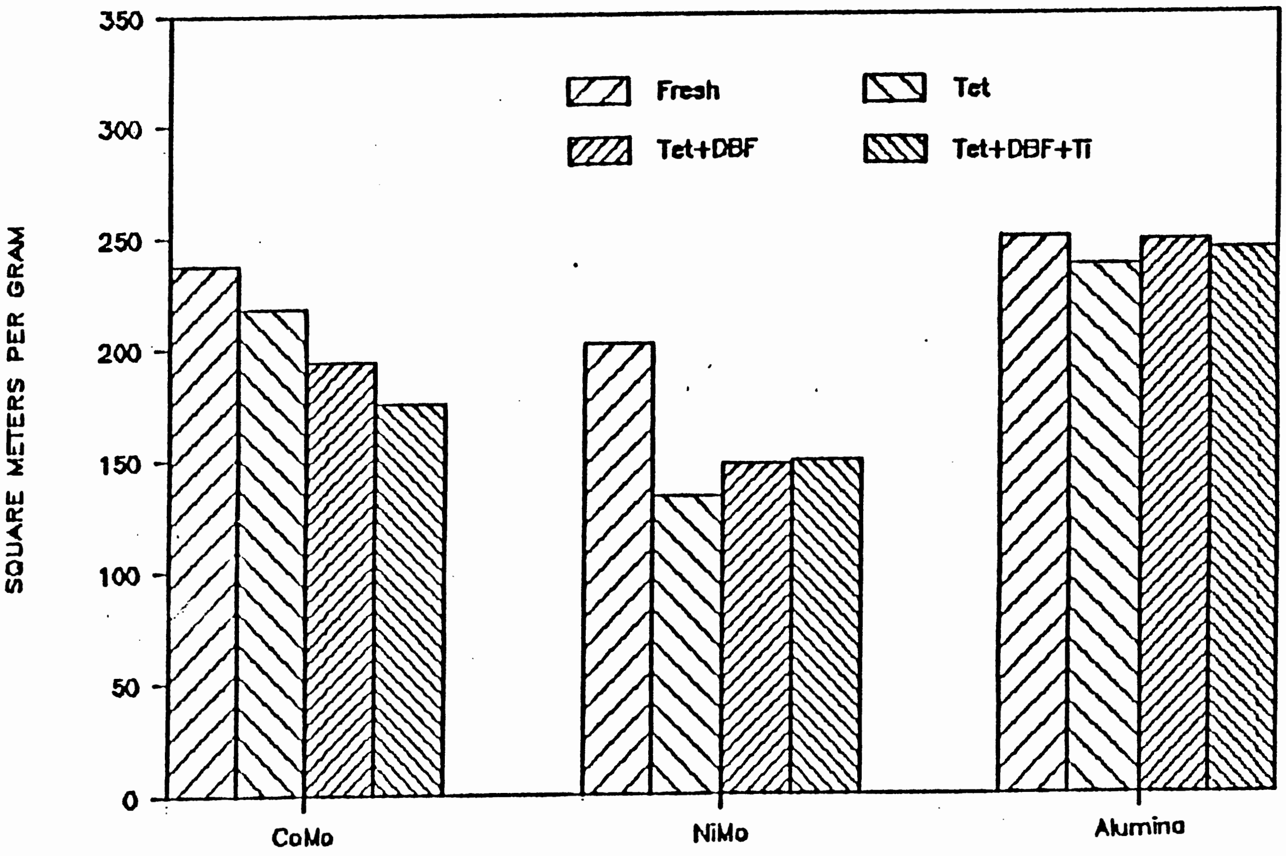

Figure 9. Surface Area of the Spent Catalysts.

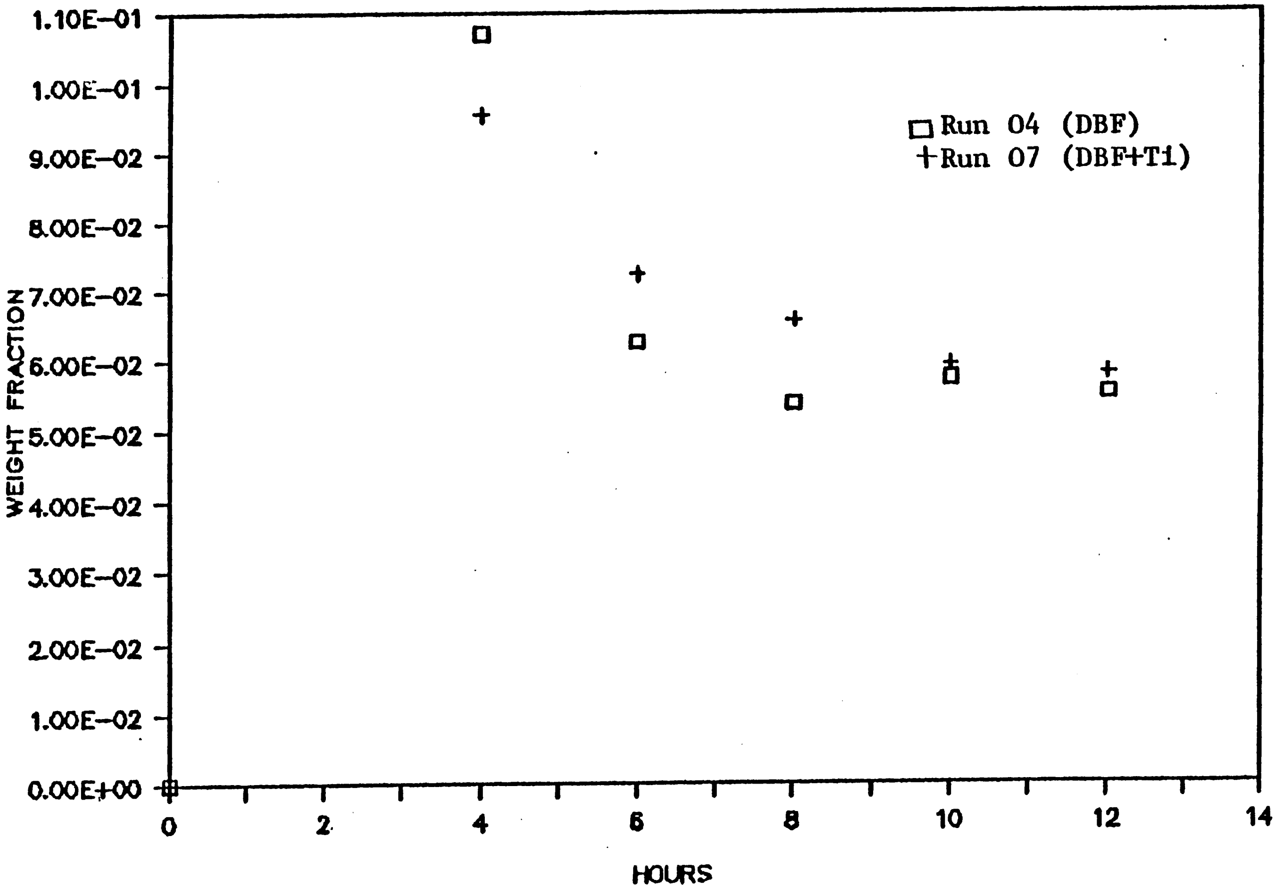

Figure 10. Weight Fraction of Cyclohexane over the CoMo/alumina Catalyst.

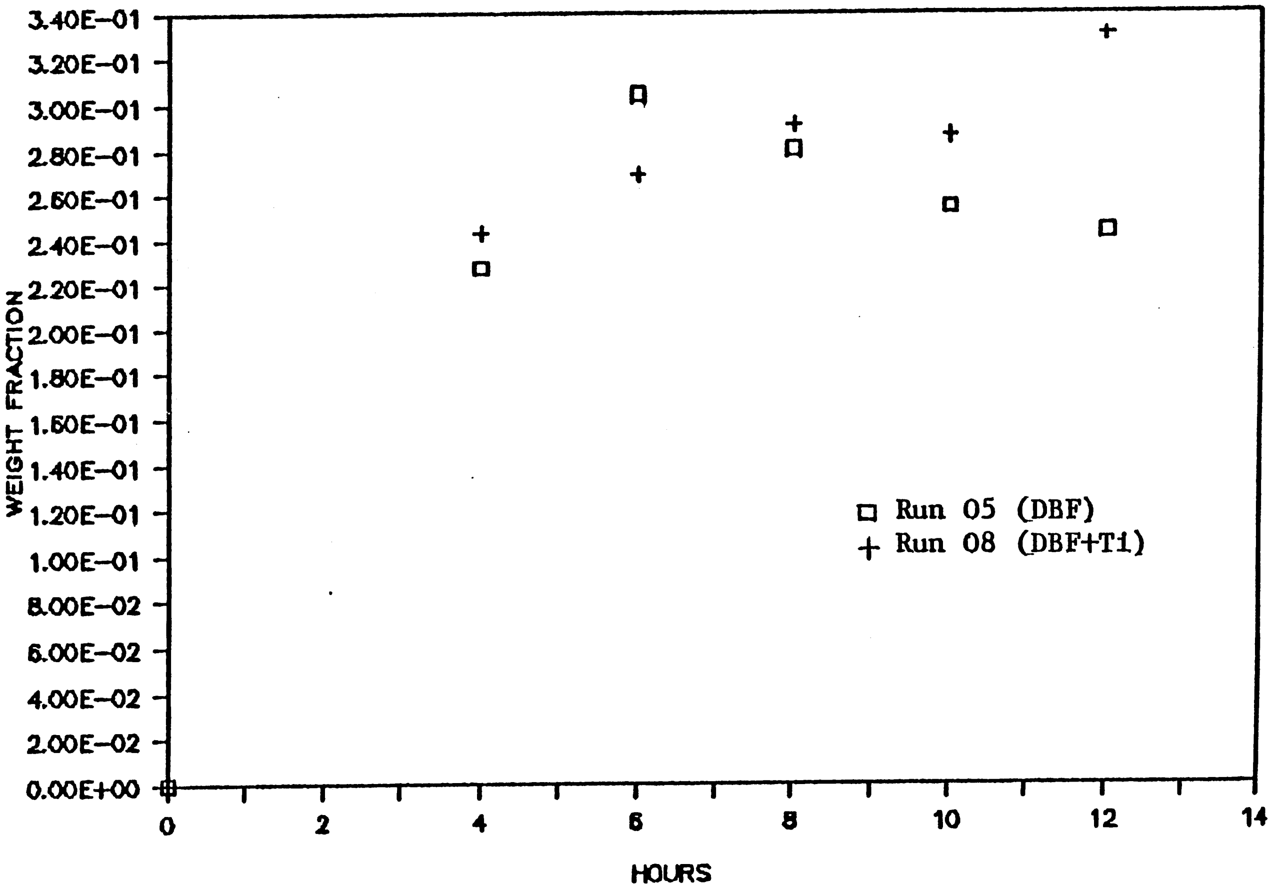

Figure 11. Weight Fraction of Cyclohexane over the NiMo/alumina Catalyst.

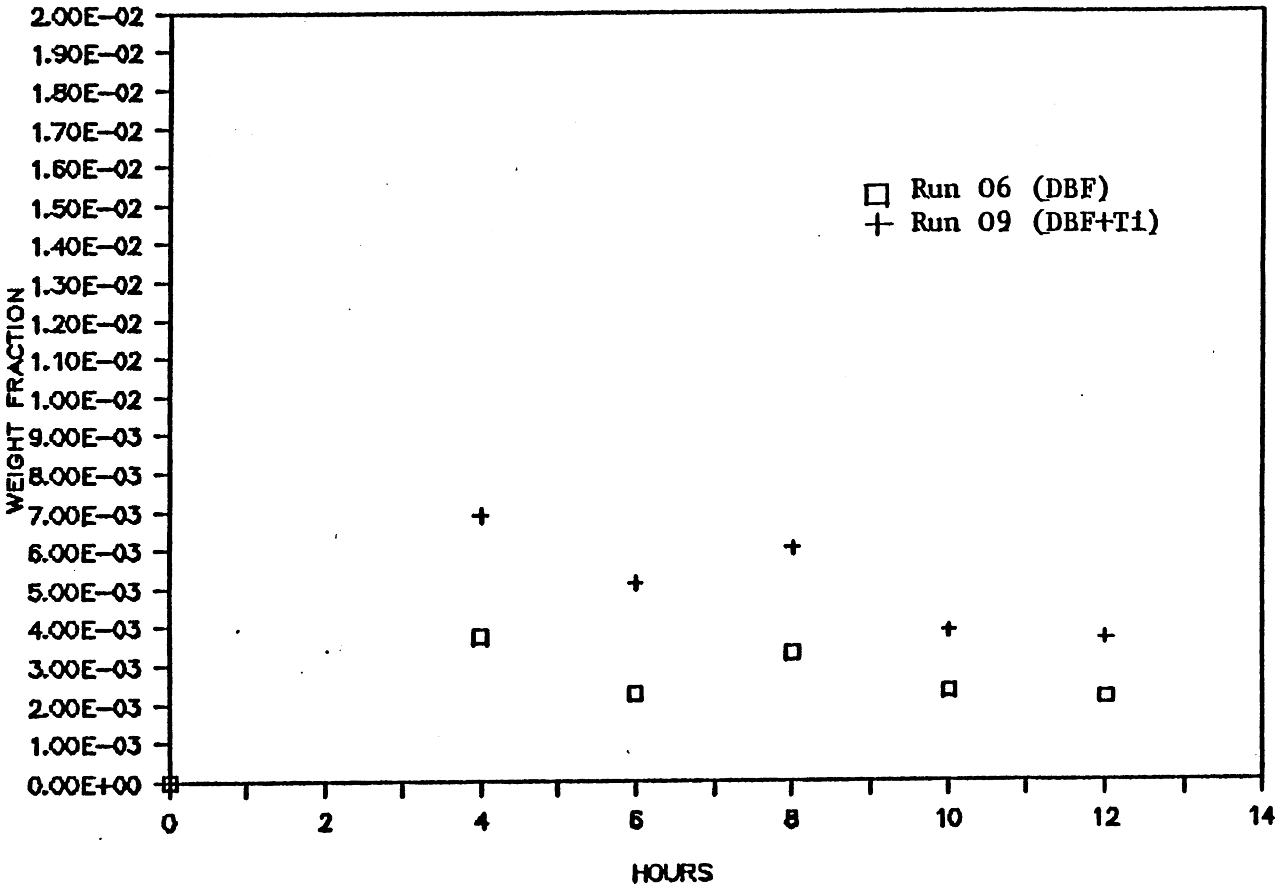

Figure 12. Weight Fraction of Cyclohexane over Alumina

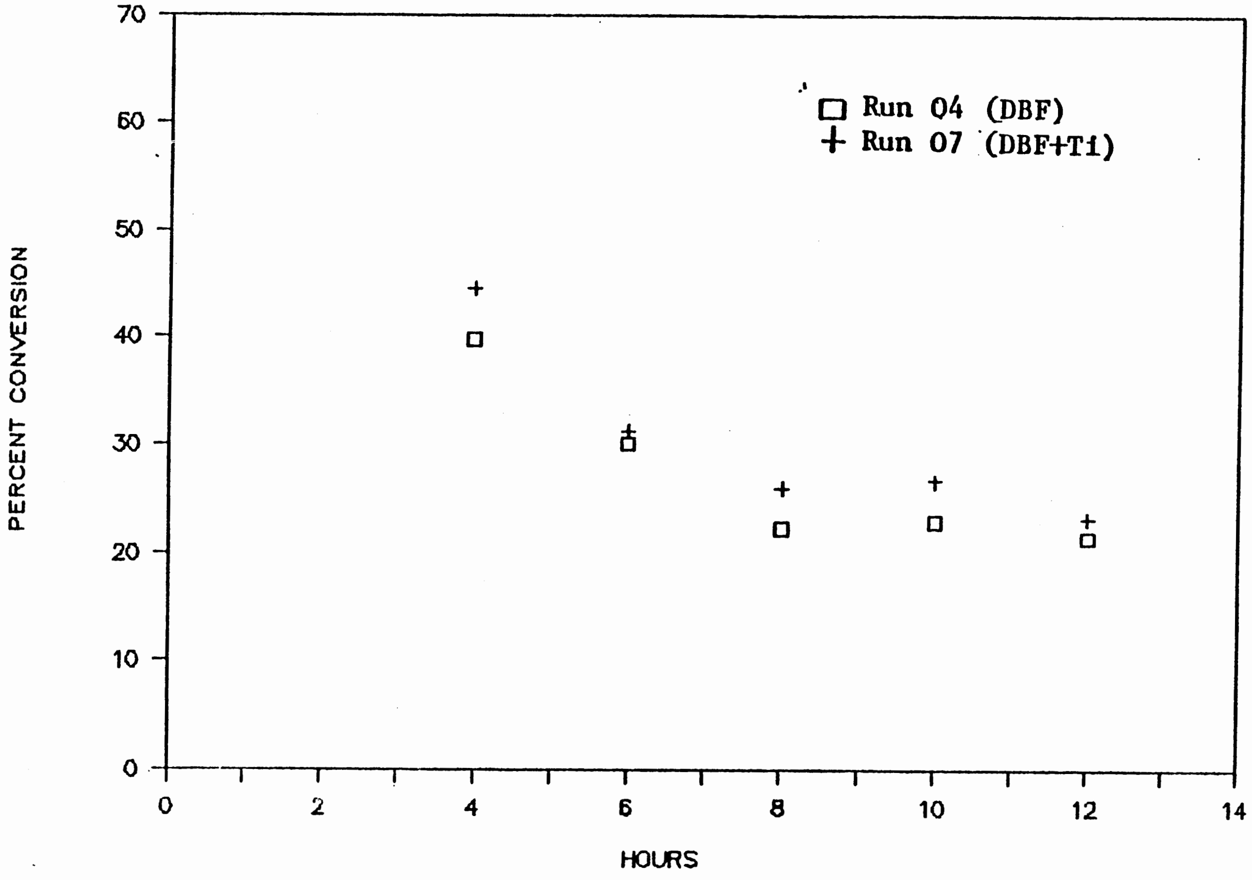

Figure 13. Effect of Titanocene Dichloride on the Conversion of Dibenzofuran over the CoMo/alumina Catalyst.

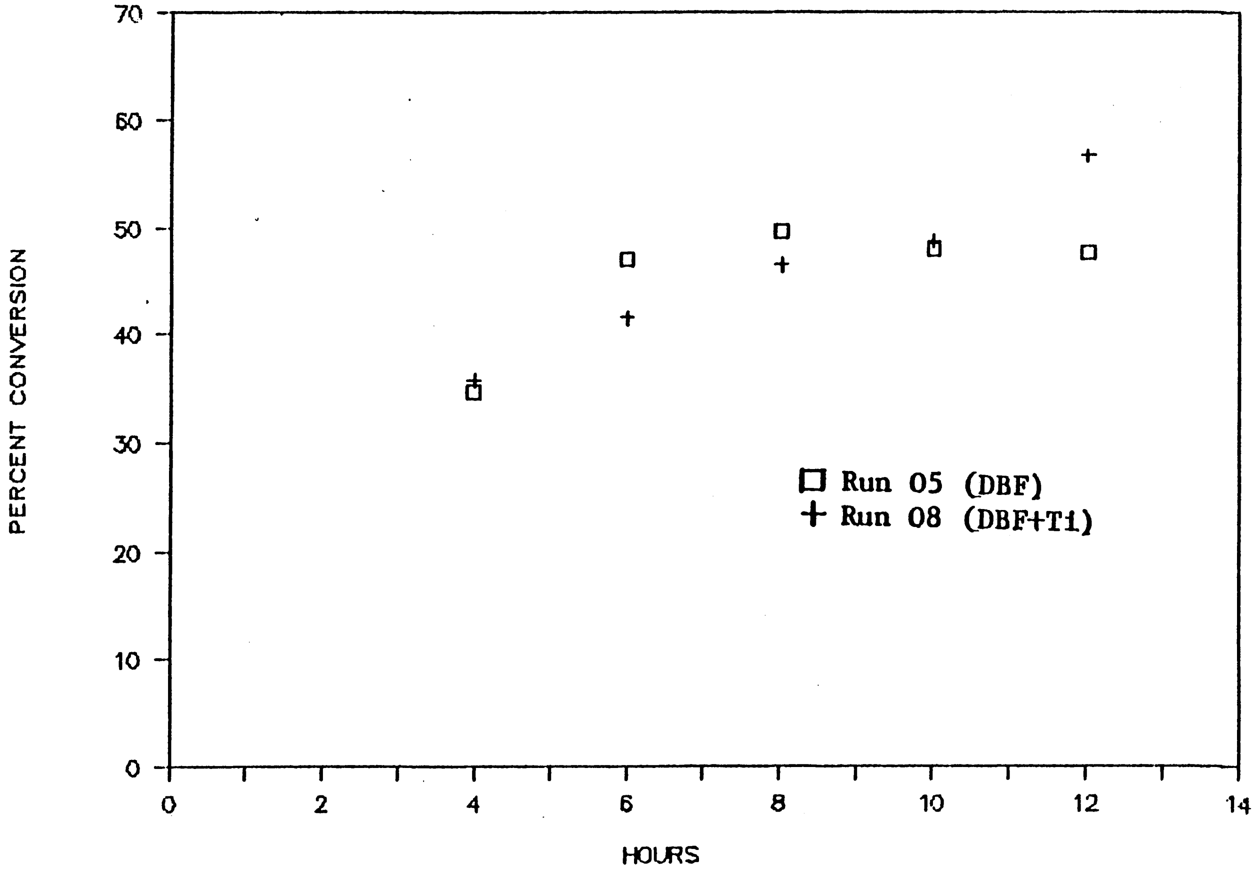

Figure 14. Effect of titanocene Dichloride on the Conversion of Dibenzofuran over the NiMo/alumina Catalyst.

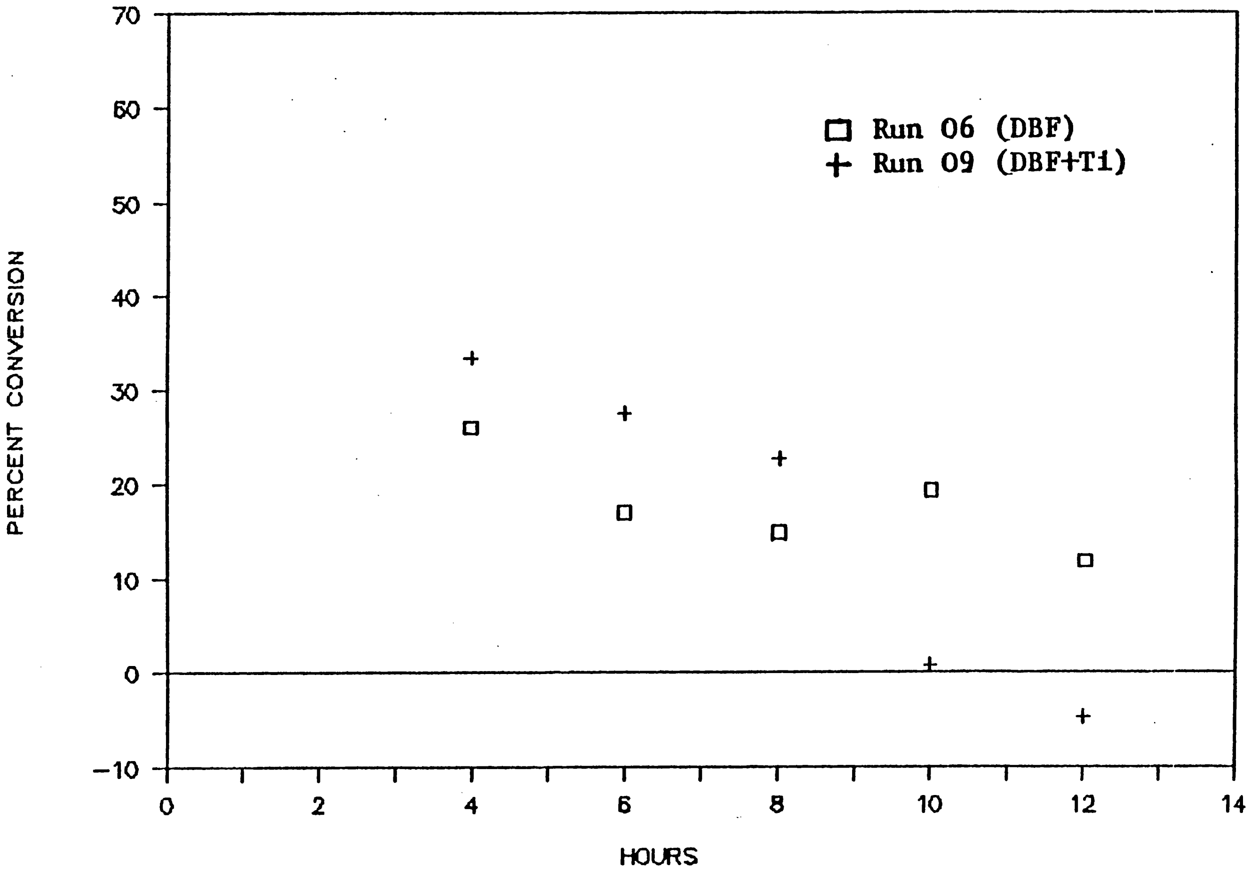

Figure 15. Effect of Titanocene Dichloride on the Conversion of Dibenzofuran over Plain Alumina

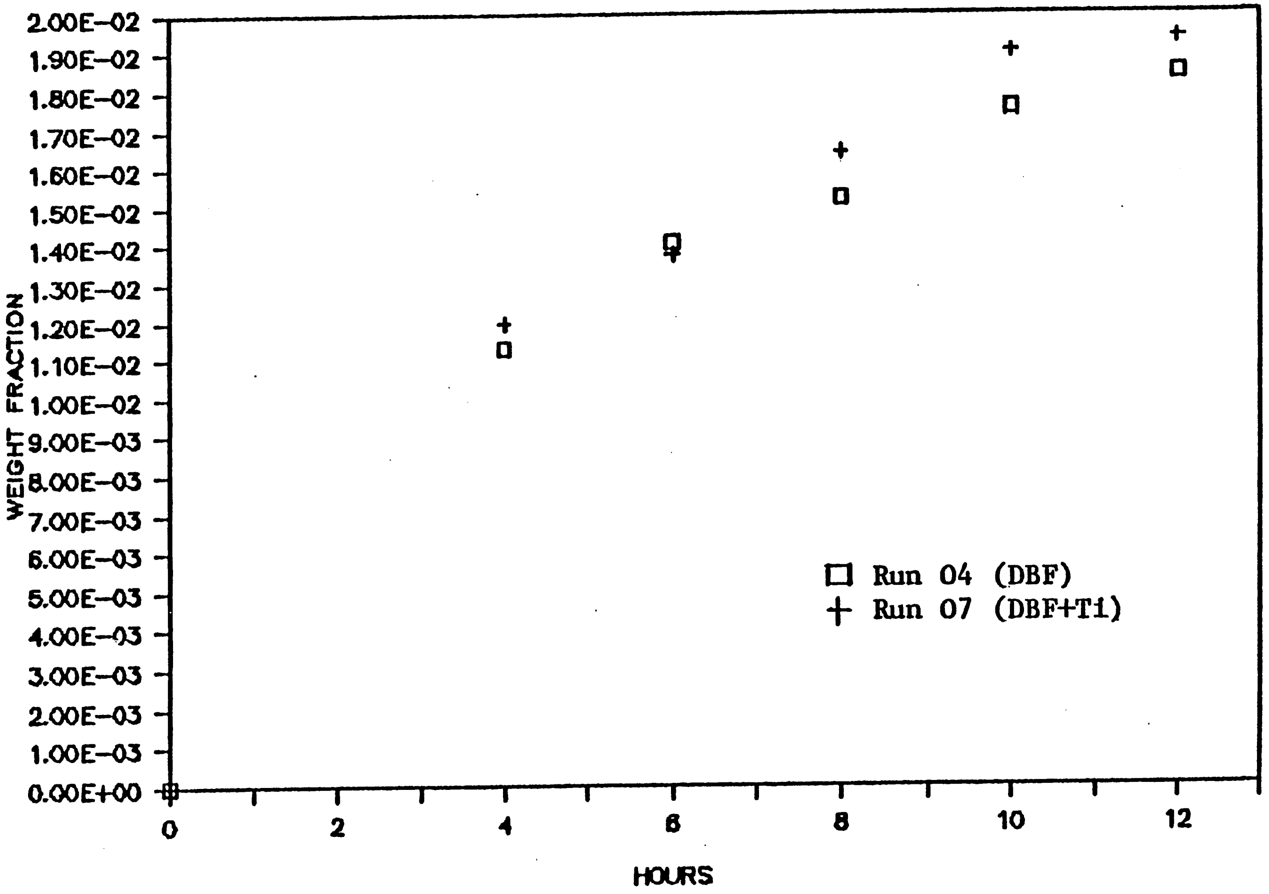

Figure 16. Weight Fraction of Dicyclohexyl over the CoMo/alumina Catalyst.

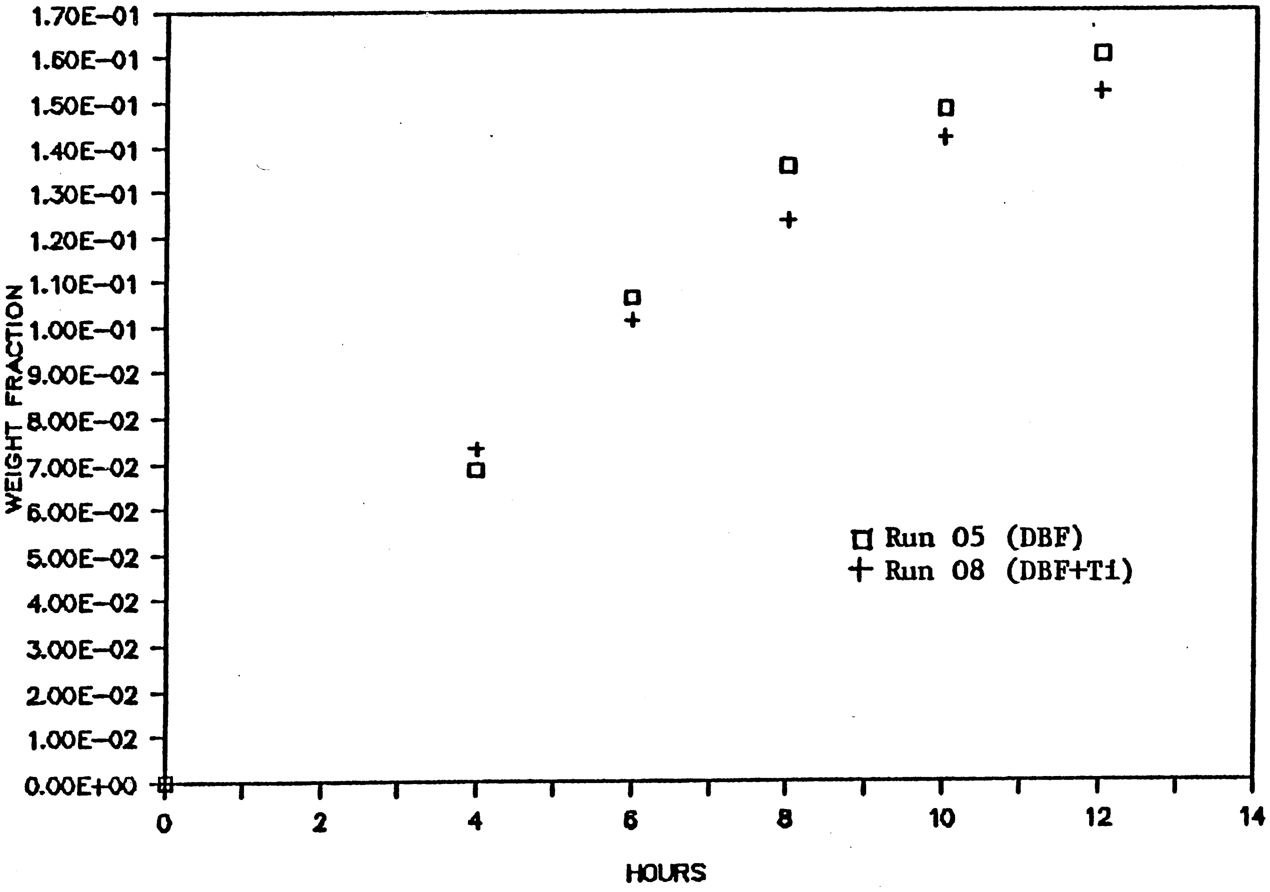

Figure 17. Weight Fraction of Dicyclohexyl over the NiMo/alumina Catalyst

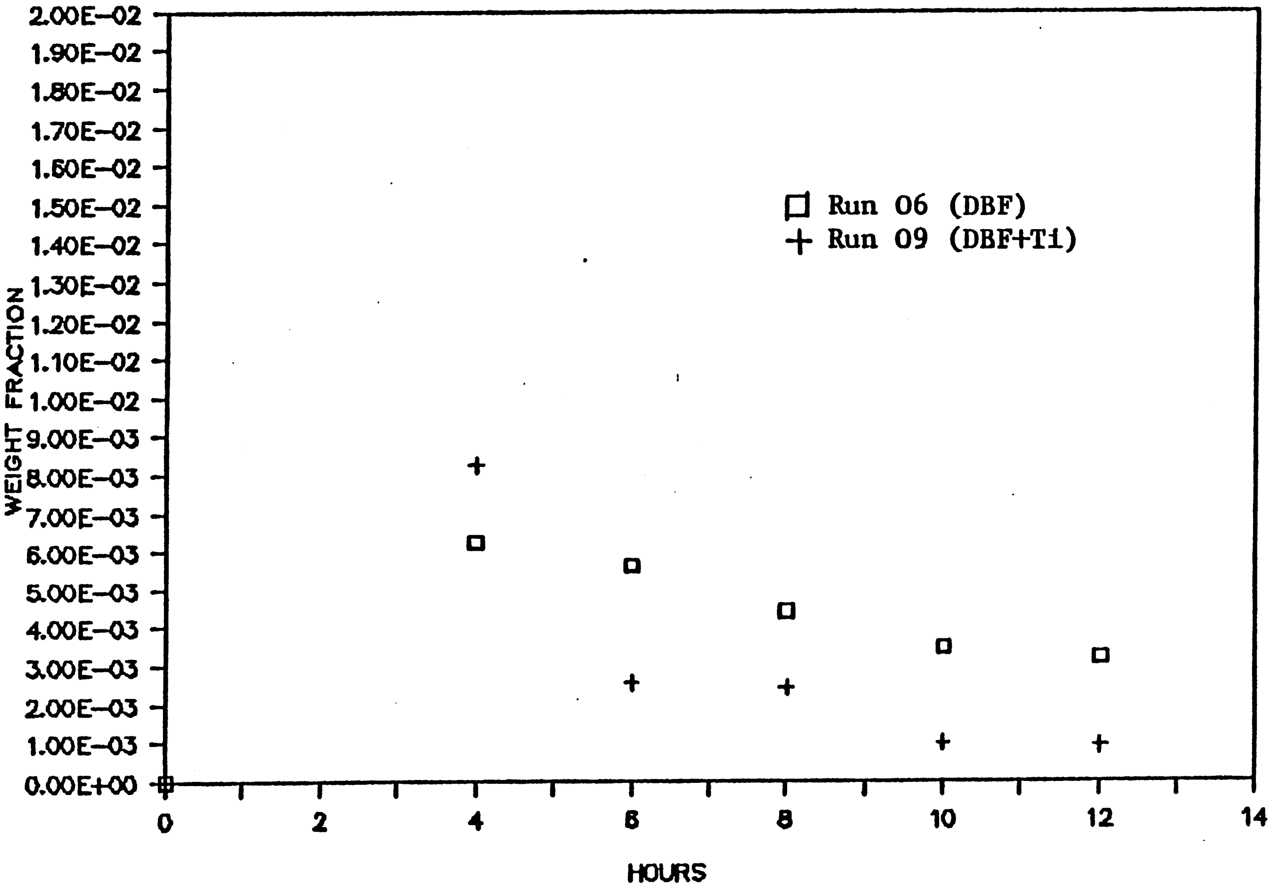

Figure 18. Weight Fraction of Dicyclohexyl over Alumina

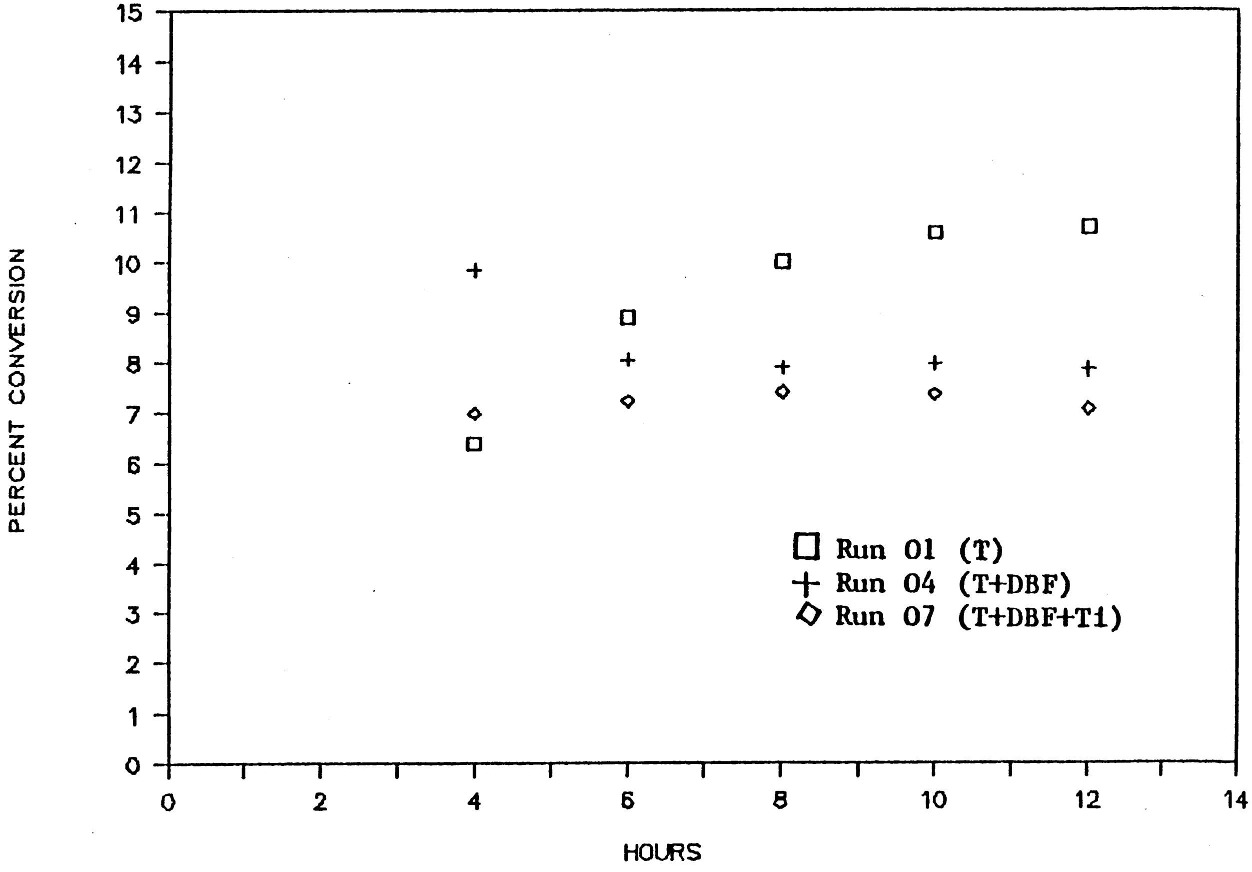

Figure 19. Effect of Titanocene Dichloride on the Conversion of Tetralin over the CoMo/alumina Catalyst

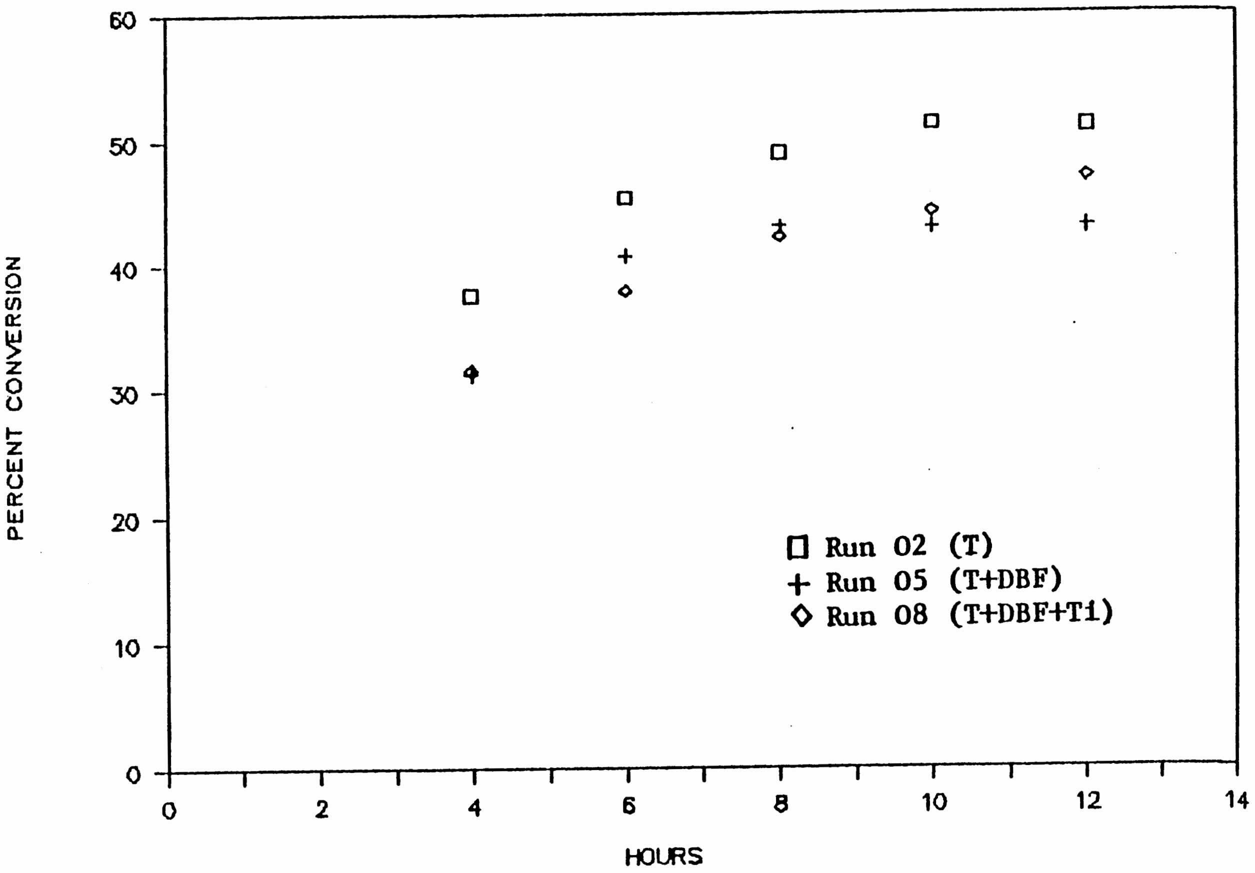

Figure 20. Effect of Titanocene Dichloride on the Conversion of Tetralin over NiMo/alumina Catalyst.

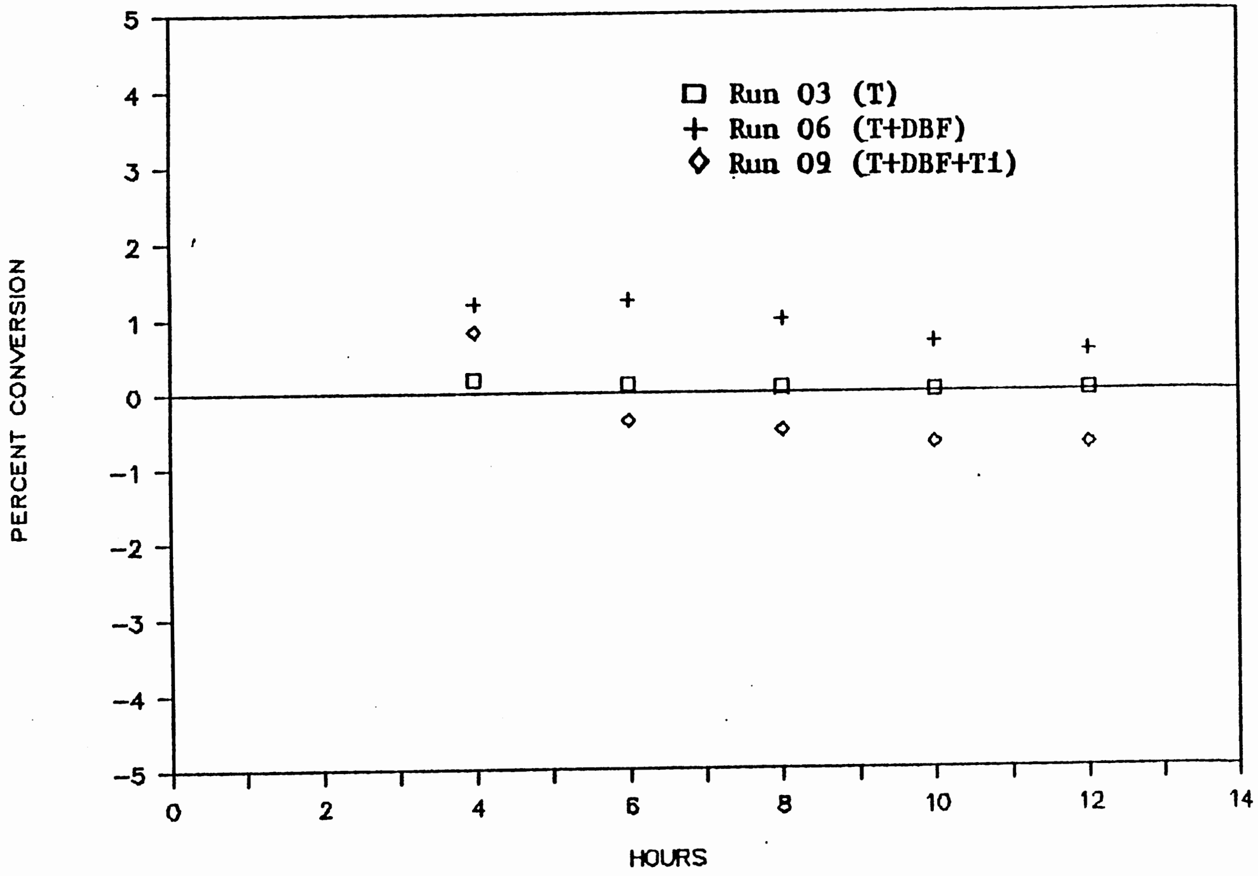

Figure 21. Effect of Titanocene Dichloride on the Conversion of Tetralin over Alumina

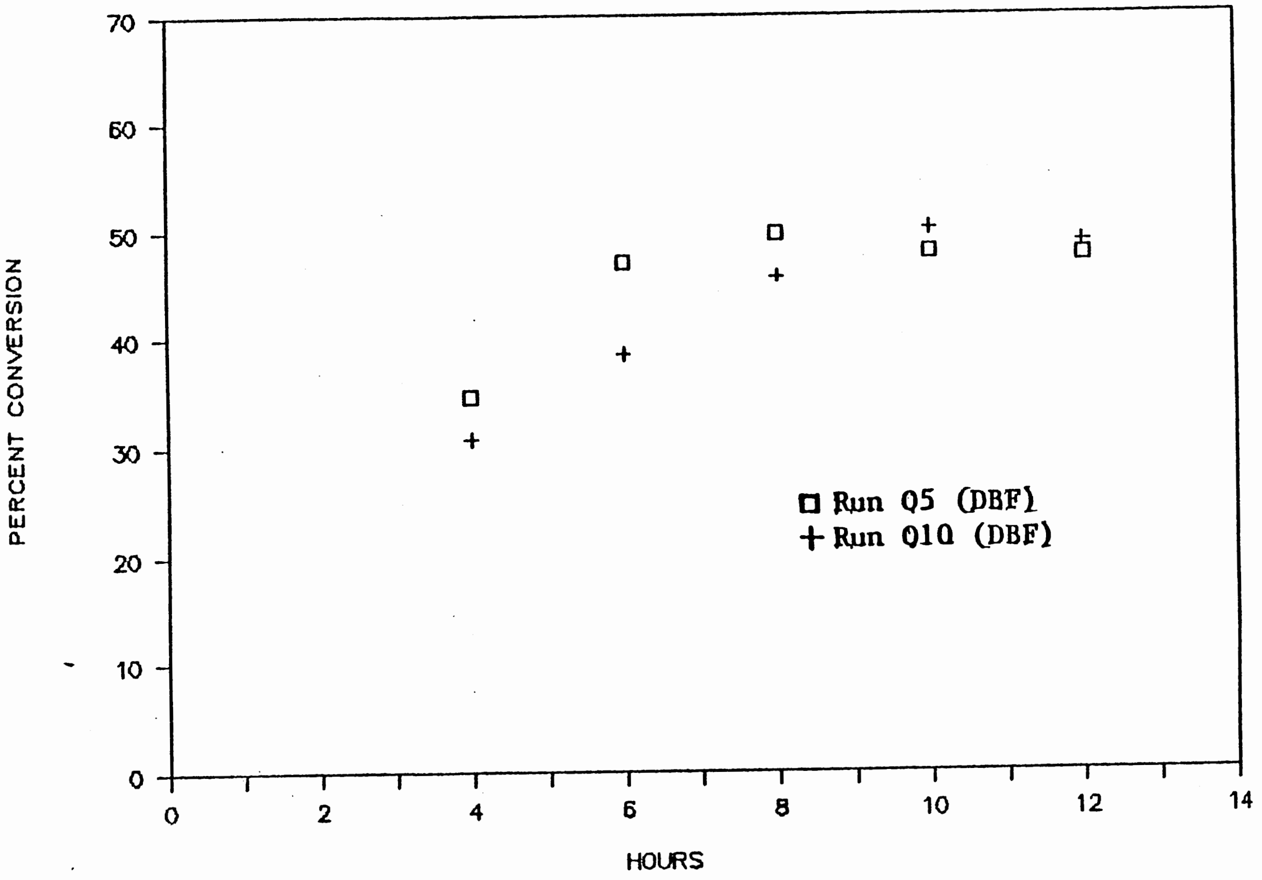

Figure 22. The Reproducibility of the System.

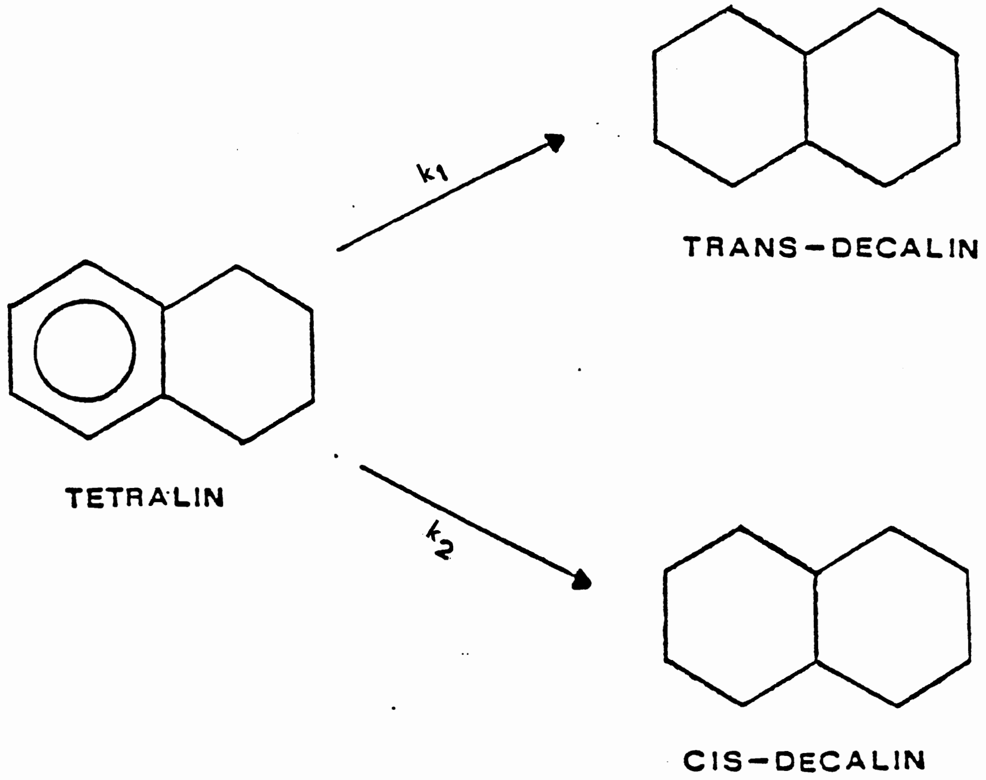

Figure 23. Simplified Tetralin Reaction Network

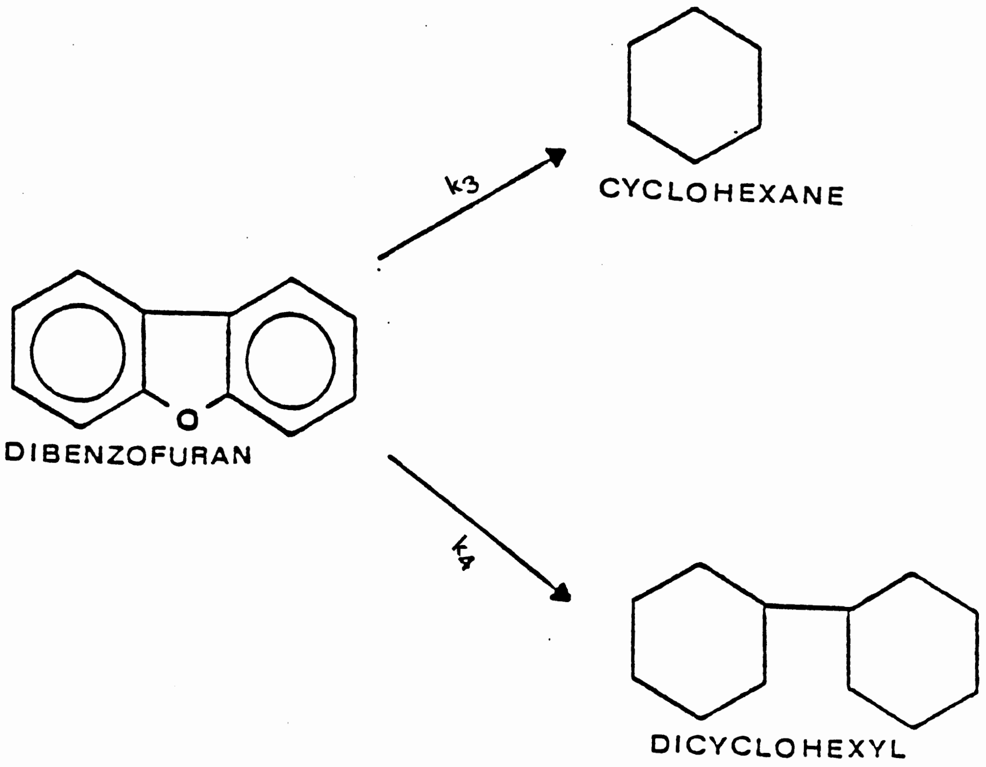

Figure 24. Simplified Dibenzofuran Reaction Network

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The following conclusions are drawn from the experimental results:

1. Addition of titanocene dichloride improved the rate of dibenzofuran hydrodeoxygenation over both NiMo/alumina (Shell 324) and CoMo/alumina (Shell 344).

2. The rate of dibenzothiophene hydrodesulfurization slightly decreases with the addition of titanocene dichloride.

3. The amount of coke content was increaced with the addition of titanocene dichloride in case of CoMo/alumina for both hydrodeoxygenation and hydrodesulfurization experiments. For NiMo/alumina, the amount of coke stayed unchanged in case of hydrodesulfurization but for hydrodexygenation it appeared to be reduced by the addition of titanocene dichloride.

4. The catalyst pore volume and surface area varied inversely with the coke content in the catalyst.

5. In the hydrodeoxygenation experiments, NiMo/alumina yielded dibenzofuran conversions twice as high as CoMo/alumina.

6. In the hydrodesulfurization experiment, both CoMo/alumina and NiMo/alumina gave about the same dibenzothiophene conversion but the fractions of products were different. Biphenyl to cyclohexylbenzene ratio from CoMo/alumina was about six times as high as the ratio from NiMo/alumina.

7. NiMo/alumina could hydrogenate Tetralin much better than CoMo/alumina.

RECOMMENDATIONS

1. In order to magnify the effects of titanium on catalyst activities other titanium compounds which have higher solubilities should be used because 100 ppm of titanium seem to be too low for titanium to penetrate into the large surface area of catalyst pellets.

2. The performance of the regenerated catalyst from this experiment should be investigated because Lynch (1986), by comparing the activities of regenerated catalysts, evidenced a higher conversion of dibenzothiophene over titanium deposited catalyst.

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APPENDIX A

PRODUCT CONCENTRATION DISTRIBUTION

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S1

(Feed: Tetralin, carbon disulfide)
(250 C; Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.22	0.10	98.70	0.50
4	1.67	5.24	92.84	0.25
6	1.90	6.08	91.85	0.18
8	2.01	6.57	91.27	0.15
10	1.91	6.12	91.81	0.15
12	1.76	5.44	92.63	0.17

Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.49	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S2

(Feed: Tetralin, carbon disulfide)
(250 C; Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.24	0.18	98.85	0.51
4	3.35	14.31	82.04	0.30
6	4.00	17.20	78.68	0.12
8	4.39	18.93	76.59	0.09
10	4.71	20.47	74.75	0.07
12	5.02	21.86	73.06	0.06
Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.23	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S3

(Feed: Tetralin, carbon disulfide)
(250 C; Plain alumina)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.24	0.22	98.53	0.49
4	0.67	1.49	97.32	0.52
6	0.38	0.55	98.57	0.51
8	0.30	0.33	98.86	0.51
10	0.27	0.26	98.96	0.51
12	0.28	0.31	98.90	0.51
Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.51	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S4

(Feed: Tetralin, Dibenzothiophene)
(250 C; Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.24	0.23	93.80	0.50
4	0.93	2.42	93.30	0.50
6	1.08	3.06	92.81	0.32
8	1.10	3.06	90.87	0.28
10	1.15	3.22	90.61	0.26
12	1.21	3.41	90.31	0.25

Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.00	0.00	0.00	5.23
4	0.00	0.17	0.86	1.83
6	0.00	0.27	1.40	1.69
8	0.00	0.37	1.95	2.36
10	0.00	0.41	2.01	2.34
12	0.00	0.42	1.99	2.40

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S5

(Feed: Tetralin, Dibenzothiophene)
(250 C; Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.31	0.15	93.11	0.61
4	3.04	12.79	81.10	0.29
6	3.23	13.58	79.20	0.21
8	3.36	14.16	78.60	0.16
10	3.35	14.08	78.07	0.15
12	3.35	14.09	77.75	0.15
Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.00	0.00	0.00	5.81
4	0.00	0.79	0.72	1.27
6	0.00	1.01	0.88	1.90
8	0.00	1.16	0.94	1.63
10	0.00	1.25	1.02	2.08
12	0.00	1.30	1.05	2.31

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S6

(Feed: Tetralin, Dibenzothiophene)
(250 C; Plain alumina)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.24	0.22	93.15	0.50
4	0.27	0.27	93.64	0.51
6	0.23	0.14	93.85	0.50
8	0.22	0.14	93.59	0.50
10	0.22	0.15	93.37	0.50
12	0.21	0.11	93.67	0.50
Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.00	0.02	0.08	5.79
4	0.00	0.02	0.09	5.19
6	0.00	0.01	0.03	5.25
8	0.00	0.01	0.03	5.52
10	0.00	0.01	0.04	5.71
12	0.00	0.01	0.02	5.48

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S7

(Feed: Tetralin, Dibenzothiophene,)
(Titanocenedichloride)
(250 C; Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.21	0.11	94.34	0.54
4	0.99	2.72	91.87	0.59
6	1.15	3.24	90.41	0.37
8	1.26	3.56	90.22	0.29
10	1.14	3.05	90.47	0.30
12	1.15	3.08	91.28	0.30
Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.00	0.00	0.03	4.77
4	0.00	0.26	1.11	2.46
6	0.00	0.36	1.58	2.89
8	0.00	0.43	1.86	2.39
10	0.00	0.45	1.95	2.63
12	0.00	0.42	1.71	2.05

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S8

(Feed: Tetralin, Dibenzothiophene,)
(Titanocenedichloride)
(250 C; Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.20	0.11	93.86	0.53
4	2.10	7.97	84.89	0.44
6	2.70	10.41	81.76	0.20
8	2.80	11.16	81.22	0.17
10	3.00	12.38	79.96	0.11
12	3.10	12.64	79.04	0.11

Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.00	0.00	0.03	5.25
4	0.00	0.57	0.66	3.46
6	0.00	0.85	0.80	3.45
8	0.00	1.01	0.90	2.88
10	0.00	1.16	0.96	2.53
12	0.00	1.27	1.03	2.95

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S9

(Feed: Tetralin, Dibenzothiophene,)
(Titanocenedichloride)
(250 C; Plain alumina)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.33	0.65	93.51	0.52
4	0.33	0.53	93.44	0.54
6	0.26	0.29	93.82	0.53
8	0.24	0.25	94.42	0.53
10	0.27	0.35	93.68	0.55
12	0.25	0.25	94.47	0.53
Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.00	0.06	0.07	4.85
4	0.00	0.05	0.08	5.03
6	0.00	0.02	0.05	5.02
8	0.00	0.02	0.05	4.50
10	0.00	0.03	0.06	4.82
12	0.00	0.01	0.04	4.45

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S10

(Feed: Tetralin, Dibenzothiophene)
(250 C; Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.31	0.16	94.07	0.62
4	0.81	1.71	94.57	0.61
6	0.81	1.71	93.30	0.49
8	0.82	1.74	93.68	0.46
10	0.81	1.69	93.20	0.42
12	0.81	1.67	93.36	0.45

Time,h	Carbon Disulfide	Cyclohexyl-Benzene	Biphenyl	Dibenzo-Thiophene
Feed	0.00	0.00	0.00	4.84
4	0.00	0.11	0.90	1.29
6	0.00	0.14	1.28	2.26
8	0.00	0.16	1.48	1.66
10	0.00	0.18	1.71	1.99
12	0.00	0.19	1.75	1.77

GAS CHROMATOGRAPHIC ANALYSIS OF RUN S11

(Feed: Tetralin, Dibenzothiophene)
(300 C; Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.34	0.18	94.09	0.57
4	4.5	12.07	79.92	0.28
6	4.64	12.68	78.19	0.21
8	5.01	14.11	77.42	0.17
10	5.72	15.88	76.64	0.16
12	6.14	16.96	73.29	0.15
Time,h	**Carbon Disulfide**	**Cyclohexyl-Benzene**	**Biphenyl**	**Dibenzo-Thiophene**
Feed	0.00	0.00	0.00	4.82
4	0.00	1.21	1.63	0.40
6	0.00	1.44	2.29	0.55
8	0.00	1.27	1.78	0.24
10	0.00	1.42	0.19	0.00
12	0.00	1.55	1.90	0.00

GAS CHROMATOGRAPHIC ANALYSIS OF RUN 01

(Feed: Tetralin, Carbon Disulfide)
(275 C; Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.72	1.91	96.36	0.52
4	2.34	6.96	90.39	0.31
6	2.95	9.00	87.86	0.20
8	3.25	9.88	86.72	0.14
10	3.40	10.32	86.15	0.14
12	3.45	10.40	86.01	0.13

Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.49	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O2

(Feed: Tetralin, Carbon Disulfide)
(275 C; Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.25	0.12	98.61	0.54
4	8.25	30.78	60.78	0.19
6	9.78	37.17	52.97	0.08
8	10.52	39.93	49.49	0.05
10	10.97	41.83	47.16	0.04
12	11.00	41.60	47.37	0.04

Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.48	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00

GAS CHROMATOGRAPHIC ANALYSIS OF RUN 03

(Feed: Tetralin, Carbon Disulfide)
(275 C; Plain alumina)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.25	0.12	98.58	0.54
4	0.30	0.26	98.91	0.53
6	0.28	0.21	98.98	0.53
8	0.27	0.18	99.02	0.53
10	0.26	0.15	99.06	0.53
12	0.26	0.15	99.06	0.53
Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.51	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O4

(Feed: Tetralin, Carbon Disulfide,)
(Dibenzofuran; 275 C; Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.24	0.25	88.57	0.48
4	2.43	7.76	82.44	0.25
6	2.12	6.36	83.51	0.17
8	2.11	6.15	82.99	0.17
10	2.15	6.19	82.96	0.17
12	2.12	6.11	82.92	0.17
Time,h	**Carbon Disulfide**	**Cyclo-Hexane**	**Dicyclo-Hexyl**	**Dibenzo-Furan**
Feed	0.39	0.00	0.00	10.07
4	0.00	0.76	0.08	6.26
6	0.00	0.49	0.11	7.22
8	0.00	0.46	0.13	7.96
10	0.00	0.49	0.15	7.90
12	0.00	0.48	0.16	8.04

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O5

(Feed: Tetralin, Carbon Disulfide,)
(Dibenzofuran; 275 C; Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.23	0.12	88.29	0.48
4	5.89	23.51	60.77	0.19
6	7.45	30.88	52.26	0.09
8	7.84	32.80	50.36	0.05
10	7.81	32.77	50.34	0.05
12	7.82	32.79	50.23	0.04
Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.55	0.00	0.00	10.38
4	0.00	2.19	0.66	6.78
6	0.00	2.84	0.99	5.49
8	0.00	2.51	1.21	5.23
10	0.00	2.30	1.34	5.40
12	0.00	2.22	1.46	5.43

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O6

(Feed: Tetralin, Carbon disulfide,)
(Dibenzofuran; 275 C)
(Plain alumina)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.23	0.13	88.20	0.48
4	0.47	1.04	90.00	0.49
6	0.47	1.08	89.08	0.48
8	0.42	0.87	89.15	0.48
10	0.37	0.64	89.88	0.48
12	0.34	0.53	89.29	0.48

Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.59	0.00	0.00	10.38
4	0.00	0.03	0.05	7.93
6	0.00	0.02	0.05	8.81
8	0.00	0.03	0.04	9.01
10	0.00	0.02	0.03	8.59
12	0.00	0.02	0.03	9.32

GAS CHROMATOGRAPHIC ANALYSIS OF RUN 07

(Feed: Tetralin, Carbon Disulfide,)
(Titanocene Dichloride,)
(Dibenzofuran; 275 C)
(Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.28	0.34	88.27	0.49
4	1.87	5.60	85.44	0.40
6	1.97	5.81	84.00	0.21
8	2.03	5.91	83.35	0.18
10	2.03	5.88	83.50	0.17
12	1.98	5.62	83.45	0.17

Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.26	0.00	0.00	10.37
4	0.00	0.64	0.08	5.98
6	0.00	0.58	0.11	7.31
8	0.00	0.56	0.14	7.82
10	0.00	0.50	0.16	7.76
12	0.00	0.51	0.17	8.10

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O8

(Feed: Tetralin, Carbon Disulfide,)
(Titanocene Dichloride,)
(Dibenzofuran; 275 C)
(Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.47	1.14	87.02	0.46
4	6.19	24.25	59.66	0.20
6	7.36	29.00	53.96	0.10
8	8.12	32.24	50.16	0.06
10	8.53	33.73	48.43	0.06
12	8.98	36.06	46.23	0.05
Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.57	0.00	0.00	10.34
4	0.00	2.36	0.71	6.64
6	0.00	2.58	0.97	6.03
8	0.00	2.74	1.16	5.51
10	0.00	2.65	1.31	5.29
12	0.00	2.87	1.32	4.49

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O9

(Feed: Tetralin, Carbon Disulfide,)
(Titanocene Dichloride,)
(Dibenzofuran; 275 C)
(Plain alumina)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.40	0.83	87.41	0.47
4	0.59	1.45	90.19	0.51
6	0.36	0.56	90.80	0.48
8	0.32	0.47	90.45	0.48
10	0.28	0.32	88.58	0.48
12	0.27	0.30	88.09	0.48
Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.58	0.00	0.00	10.32
4	0.00	0.05	0.06	7.15
6	0.00	0.04	0.02	7.74
8	0.00	0.05	0.02	8.21
10	0.00	0.04	0.01	10.30
12	0.00	0.04	0.01	10.81

GAS CHROMATOGRAPHIC ANALYSIS OF RUN 010

(Feed: Tetralin, Carbon Disulfide,)
(Dibenzofuran; 275 C; Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.45	1.17	87.11	0.47
4	4.27	17.21	69.49	0.15
6	6.18	25.72	58.74	0.07
8	7.28	30.24	53.37	0.05
10	7.91	32.90	50.19	0.05
12	8.06	33.29	49.60	0.04

Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.69	0.00	0.00	10.10
4	0.00	1.28	0.55	7.07
6	0.00	2.12	0.94	6.22
8	0.00	2.34	1.23	5.49
10	0.00	2.51	1.41	5.04
12	0.00	2.31	1.53	5.16

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O11

(Feed: Tetralin, Carbon Disulfide,)
(Titanocene Dichloride,)
(Dibenzofuran; 250 C)
(Shell 344)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.19	0.09	89.11	0.51
4	1.32	4.18	87.75	0.52
6	1.26	3.93	85.68	0.52
8	1.21	3.52	86.15	0.25
10	1.08	3.04	86.52	0.26
12	1.18	3.44	86.69	0.24

Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.11	0.00	0.00	10.09
4	0.00	0.15	0.08	6.15
6	0.00	0.13	0.04	8.57
8	0.00	0.08	0.09	8.78
10	0.00	0.06	0.09	9.01
12	0.00	0.16	0.09	8.35

GAS CHROMATOGRAPHIC ANALYSIS OF RUN O12

(Feed: Tetralin, Carbon Disulfide,)
(Titanocene Dichloride,)
(Dibenzofuran; 300 C)
(Shell 324)

Time,h	Cis-Decalin	Trans-Decalin	Tetralin	Naphthalene
Feed	0.20	0.10	90.49	0.48
4	11.15	46.18	40.20	0.22
6	12.49	50.43	34.75	0.10
8	12.55	48.98	35.37	0.07
10	12.34	47.83	36.60	0.05
12	12.13	47.44	37.20	0.05

Time,h	Carbon Disulfide	Cyclo-Hexane	Dicyclo-Hexyl	Dibenzo-Furan
Feed	0.31	0.00	0.00	8.73
4	0.00	5.01	0.48	1.77
6	0.00	4.21	0.69	1.54
8	0.00	3.93	0.88	2.14
10	0.00	3.61	0.90	2.29
12	0.00	3.74	0.84	2.34

APPENDIX B

GAS CHROMATOGRAPHIC CALCULATION

The liquid samples from every run were analyzed by a Hewlett Packard Model 5890 A Gas Chromatograph with a 60 meters DB-1 capillary column and a thermal conductivity detector. The concentrations of compounds in the liquid samples were calculated from the response areas recorded by a Hewlett Packard Integrator Model 3392 A.

$$\text{Concentration of compound A} = F \times \frac{(\text{Area compound A})}{(\text{Area compound I})} \times \text{Concentration of I}$$

where : F = Response factor of compound A.

I = Internal standard compound.

The response factors were calculated by

$$\text{Response factor of compound A} = \frac{(\text{Concentration of A})}{(\text{Concentration of I})} \times \frac{(\text{Area of compound I})}{(\text{Area of compound A})}$$

The internal standard is an arbitrary compound that is added to the sample with a well defined weight. In our study, normal-hexadecane was chosen to be the internal standard.

Example: The objective is to calculate the concentrations of compounds in run S10 at fourth hour. The response area and the concentration of the internal standard are 11.972 and 12.43 wt%. respectively.

Solution

Compound	Area	F	Conc.	Conc. (normalized)
Trans-decalin	1.455	1.04	1.785	1.71
Cis-decalin	0.691	1.04	0.848	0.81
Tetralin	82.637	1.01	98.468	94.57
Naphthalene	0.474	1.14	0.637	0.61
Cyclohexylbenzene	0.082	1.16	0.112	0.11
Biphenyl	0.653	1.21	0.932	0.90
Dibenzothiophene	0.362	3.14	1.341	1.29
	Total		104.125	100.00

The total percent concentration can be slightly under or over 100 due to the errors in the gas chromatography. The fourth column shows the concentrations of compounds after normalization.

The concentrations of liquid samples of runs O1 to O12 in hydrodeoxygenation part were calculated by the same means. The response factors of the known compounds were shown as following:

Carbon disulfide	1.44
Cyclohexane	1.04
Trans-decalin	1.04
Cis-decalin	1.04
Tetralin	1.01
Naphthalene	1.14
Cyclohexylbenzene	1.16
Dicyclohexyl	0.85
Biphenyl	1.21

Dibenzothiophene	3.14*
Dibenzofuran	1.24-1.40**

* The response factor of dibenzothiophene changed to 3.35 after run S6.

** The response factor of dibenzofuran also depends on its concentration and can vary from 1.24 to 1.40 by the variation of concentration from 10 to 5 wt%.

APPENDIX C

PRECISION OF GAS CHROMATOGRAPH

THE PRECISION OF THE GAS CHROMATOGRAPH

Injection No.	Trans-Decalin	Cis-Decalin	Tetralin	Naphthalene
1	0.12	0.24	94.09	0.54
2	0.11	0.24	94.17	0.54
3	0.11	0.24	94.49	0.54
4	0.11	0.24	94.01	0.54
5	0.12	0.24	94.36	0.54
6	0.11	0.24	94.34	0.54
7	0.11	0.24	94.53	0.54
8	0.11	0.24	93.91	0.54
Average	0.11	0.24	94.22	0.54
Standard Diviation	0.00	0.00	0.21	0.00

Note: Feed is 5 %wt dibenzothiophene in Tetralin

THE PRECISION OF THE GAS CHROMATOGRAPH

Injection No.	Cyclohexyl Benzene	Biphenyl	Dibenzo-Thiophene	Carbon-Disulfide
1	0	0	5.02	0
2	0	0	4.94	0
3	0	0	4.62	0
4	0	0	5.09	0
5	0	0	4.74	0
6	0	0	4.76	0
7	0	0	4.58	0
8	0	0	5.19	0
Average	0	0	4.885	0
Standard Diviation	0.00	0.00	0.21	0.00

Note: Feed is 5 %wt dibenzothiophene in Tetralin

APPENDIX D

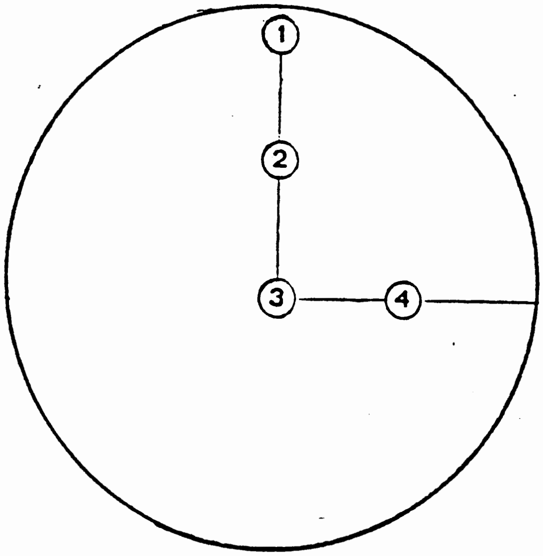
CATALYST ANALYSIS

PERCENT COKE CONTENT

Analysis No.	1	2	average	STD
S1	9.14	9.29	9.22	0.08
S2	12.30	11.32	11.81	0.49
S3	1.99	1.72	1.86	0.13
S4	9.95	9.74	9.84	0.10
S5	11.66	11.10	11.38	0.28
S6	1.41	1.00	1.20	0.20
S7	11.49	11.47	11.48	0.01
S8	11.71	11.46	11.58	0.13
S9	2.91	2.29	2.60	0.31
S10	9.44	9.26	9.35	0.09

PERCENT COKE CONTENT

Analysis No.	1	2	average	STD
O1	4.74	6.08	5.41	0.67
O2	12.21	11.70	11.95	0.26
O3	-0.07	-0.13	-0.10	0.03
O4	8.17	8.30	8.24	0.06
O5	11.04	10.30	10.67	0.37
O6	0.05	-0.03	0.01	0.04
O7	11.18	10.35	10.76	0.42
O8	8.86	9.49	9.18	0.31
O9	1.00	0.39	0.69	0.30
O10	13.85	13.11	13.48	0.37



Positions in Catalyst Basket.

CATALYST COKING ANALYSIS

WT.% COKE

Run No.	Position	First	Second	Third	Average	STD
S1	No.1	19.67	19.33	19.85	19.62	0.21
	No.2	15.42	20.25	18.31	17.99	1.98
	No.3	13.82	15.88	21.79	17.16	3.38
	No.4	15.91	16.73	18.07	16.90	0.89
S2	No.1	22.34	25.94	25.25	24.51	1.56
	No.2	22.87	26.34	--	24.60	1.74
	No.3	24.35	25.28	25.32	24.99	0.45
	No.4	24.42	15.89	24.18	21.50	3.97
S3	No.1	0.22	0.73	0.89	0.61	0.28
	No.2	0.04	0.88	0.40	0.44	0.34
	No.3	0.05	0.89	0.99	0.64	0.42
	No.4	-0.13	1.28	0.73	0.62	0.58
S4	No.1	20.82	19.52	17.96	19.43	1.17
	No.2	12.79	19.74	21.60	18.04	3.79
	No.3	17.38	21.27	21.34	20.00	1.85
	No.4	17.47	14.36	18.09	16.64	1.63
S5	No.1	13.00	--	--	13.00	--
	No.2	19.28	--	--	19.28	--
	No.3	16.48	--	--	16.48	--
	No.4	23.85	--	--	23.85	--

Note: Single pellet analysis.

CATALYST COKING ANALYSIS

WT.% COKE

Run No.	Position	First	Second	Third	Average	STD
S6	No.1	-0.29	0.50	1.10	0.44	0.57
	No.2	-0.44	0.41	0.18	0.05	0.36
	No.3	0.28	0.89	0.71	0.63	0.26
	No.4	-0.61	0.85	0.72	0.32	0.66
S7	No.1	17.96	17.20	19.69	18.28	1.05
	No.2	15.84	21.69	22.24	19.92	2.90
	No.3	21.15	15.42	3.63	13.40	7.29
	No.4	19.71	20.14	20.16	20.01	0.21
S8	No.1	18.84	18.56	18.56	18.65	0.13
	No.2	3.05	22.25	22.50	15.93	9.11
	No.3	20.64	20.31	19.41	20.12	0.52
	No.4	21.72	21.87	22.80	22.13	0.48
S9	No.1	0.19	0.84	0.97	0.67	0.34
	No.2	1.39	1.88	1.58	1.62	0.20
	No.3	0.12	1.33	--	0.73	0.61
	No.4	0.40	1.04	1.32	0.92	0.39
S10	No.1	9.49	--	--	9.49	--
	No.2	13.18	--	--	13.18	--
	No.3	12.98	--	--	12.98	--
	No.4	18.33	--	--	18.33	--

Note: Single pellet analysis.

CATALYST COKING ANALYSIS

WT.% COKE

Run No.	Position	First	Second	Third	Average	STD
01	No.1	6.80	13.86	14.40	11.69	3.47
	No.2	14.04	13.40	16.08	14.51	1.14
	No.3	14.00	15.46	13.22	14.23	0.93
	No.4	8.57	15.52	6.16	10.08	3.97
02	No.1	20.83	22.44	--	21.64	0.81
	No.2	18.19	21.04	--	19.61	1.42
	No.3	20.24	21.75	--	21.00	0.76
	No.4	20.46	20.81	--	20.64	0.18
03	No.1	-0.53	-0.84	-0.88	-0.75	0.16
	No.2	-0.48	-1.03	-0.86	-0.79	0.23
	No.3	-0.46	-1.45	-6.15	-2.68	2.48
	No.4	0.18	-0.91	-1.00	-0.58	0.54
04	No.1	14.29	13.90	16.64	14.94	1.21
	No.2	16.09	18.62	14.93	16.55	1.54
	No.3	13.51	12.91	--	13.21	0.30
	No.4	13.38	18.52	15.76	15.89	2.10
05	No.1	18.87	21.30	20.97	20.38	1.08
	No.2	19.68	20.05	21.11	20.28	0.61
	No.3	21.39	19.41	19.69	20.16	0.88
	No.4	19.88	23.22	19.16	20.75	1.77

Note: Single pellet analysis.

CATALYST COKING ANALYSIS

WT.% COKE

Run No.	Position	First	Second	Third	Average	STD
O6	No.1	0.20	-0.73	-1.04	-0.53	0.53
	No.2	0.17	-0.62	-0.35	-0.27	0.33
	No.3	0.29	-1.16	-0.59	-0.49	0.60
	No.4	0.64	-0.43	-0.63	-0.14	0.55
O7	No.1	8.22	--	--	8.22	--
	No.2	7.22	--	--	7.22	--
	No.3	5.71	--	--	5.71	--
	No.4	5.40	--	--	5.40	--
O8	No.1	19.39	20.60	20.81	20.27	0.63
	No.2	16.43	21.01	21.15	19.53	2.19
	No.3	19.05	16.15	16.86	17.35	1.23
	No.4	17.84	18.25	19.71	18.60	0.80
O9	No.1	0.10	-0.91	-0.48	-0.43	0.41
	No.2	0.00	-0.27	-0.26	-0.17	0.12
	No.3	-0.27	-0.46	--	-0.36	0.10
	No.4	0.53	-1.04	-0.58	-0.36	0.66
O10	No.1	21.62	21.68	20.09	21.13	0.73
	No.2	23.45	22.11	21.66	22.41	0.76
	No.3	23.02	21.11	22.34	22.16	0.79
	No.4	23.94	21.72	21.68	22.45	1.06

Note: Single pellet analysis.

PORE VOLUME AND SURFACE AREA OF CATALYSTS

Catalyst	Pore Vol. (cm^3/gm)	Surf. area (m^2/gm)
Shell 344 (Fresh)	0.59	238
Shell 324 (Fresh)	0.51	202
Plain alumina (Fresh)	0.75	248
S1	0.49	191
S2	0.38	160
S3	0.76	246
S4	0.49	193
S5	0.37	156
S6	0.74	241
S7	0.47	185
S8	0.35	146
S9	0.71	233
S10	0.48	192

PORE VOLUME AND SURFACE AREA OF CATALYSTS

Catalyst	Pore Vol. (cm^3/gm)	Surf. area (m^2/gm)
Shell 344 (Fresh)	0.59	238
Shell 324 (Fresh)	0.51	202
Plain alumina (Fresh)	0.75	248
O1	0.55	218
O2	0.34	133
O3	0.72	237
O4	0.49	194
O5	0.38	148
O6	0.75	248
O7	0.44	176
O8	0.38	149
O9	0.74	244
O10	0.28	109

APPENDIX E

KINETIC CALCULATION

KINETIC CALCULATION

The conversion of reactants are needed to relate the composition of product stream to that of the feed. Since the weight of liquid products changes during the hydrogenation, the weight percent of products need to be adjusted to get the correct amount of the product generated from feed. Tetralin does not crack under these conditions and its evaporative losses are negligible. Therefore a factor, f, is defined from Tetralin and products of Tetralin.

$$f = \frac{\left(\frac{\%\ \text{naphthalene}}{128} + \frac{\%\ \text{Tetralin}}{132} + \frac{\%\ \text{decalins}}{138}\right)_{\text{feed}}}{\left(\frac{\%\ \text{naphthalene}}{128} + \frac{\%\ \text{Tetralin}}{132} + \frac{\%\ \text{decalins}}{138}\right)_{\text{product}}}$$

Any value of weight percent in product stream should be multiplied by f to give the correct amount of that product generated from feed. Thus the percent conversion of Tetralin and dibenzothiophene may be calculated from:

$$\begin{array}{l}\%\ \text{conversion} \\ \text{of Tetralin}\end{array} = \frac{\begin{array}{c}(\%\ \text{tetralin}) \\ \text{in feed}\end{array} - \begin{array}{c}(\%\ \text{tetralin}) \\ \text{in product}\end{array} f}{(\%\ \text{tetralin in feed})} \times 100$$

$$\begin{array}{l}\%\ \text{conversion} \\ \text{of DBT}\end{array} = \frac{\begin{array}{c}(\%\ \text{DBT in}) \\ \text{feed}\end{array} - \begin{array}{c}(\%\ \text{DBT in}) \\ \text{product}\end{array} f}{(\%\ \text{DBT in feed})} \times 100$$

where: DBT = dibenzothiophene

Furthermore, selectivities may be calculated from the following relations.

$$\text{Selectivity of decalins} = \frac{(\%\ \text{trans-decalin in products})}{(\%\ \text{cis-decalin in products})}$$

$$\begin{array}{l}\text{Selectivity of direct}\\ \text{sulfur extrusion}\\ \text{versus ring saturation}\end{array} = \frac{(\%\ \text{biphenyl in products})}{(\%\ \text{cyclohexylbenzene in products})}$$

The reaction rates may be calculated from the following relation.

$$r_A = \frac{(Q) \times (d)}{w} \left(W_A\text{,feed} - W_A\text{,prod} \times f \right)$$

where:

r_A = rate of conversion of A, in kg of A reacted/(kg cat.) (s)

Q = volumetric flow rate of feed, m^3/s

d = density of feed, kg/m^3

w = weight of catalyst

W_A ,feed = weight fraction of A in feed

W_A ,prod = weight fraction of A in products

f = feed to product material balance factor

Assuming a pseudo-first order reaction, the rate constants may be calculated from:

$$k_A = \frac{r_A}{C_A\text{,out}}$$

$$\text{or } k_A = \frac{r_A}{(W_A\text{,prod}) \times (d\text{,prod})}$$

where: C_A,out is the concentration of A, in kg/m^3

d,prod is the density of product stream in kg/m^3

Our measurements indicated that the density of product is within 1% of the density of feed (0.977 for dibenzothiophene and 0.98 for dibenzofuran), therefore one may assume d,feed = d,prod. Thus the rate constants may be calculated from

$$k_A = \frac{(Q) \times (W_A,\text{feed} - (W_A,\text{prod}) \times f)}{w \times W_A,\text{prod}}$$

where k_A is the reaction rate constant in m^3/(kg cat)(s).

Summation of k1 + k2 may be calculated directly from tetralin data. If one neglects the isomerization of cis- and trans-decalins, the ratio of trans-decalin to cis-decalin will be equal to k1/k2. Thus individual rate constants, k1 and k2 can be calculated. Similarly dibenzothiophene concentrations will give k3 + k4, and the ratio of biphenyl to cyclohexylbenzene will give k3/k4. Thus rate constants k3 and k4 can be calculated. The rate constants for dibenzofuran can also be calculated similarly except for the ratio of cyclohexane to dicyclohexyl. If cyclohexane is the only product compound that evaporated, the cyclohexane to dicyclohexyl ratio can to be calculated from

$$\frac{\text{cyclohexane}}{\text{dicyclohexyl}} = \frac{(\%\ \text{DBF,feed}) - (\%\ \text{DBF,prod} + \%\ \text{DCX,prod})\ f}{(\%\ \text{DCX,prod})\ f}$$

where:

% DBF,feed = weight percent dibenzofuran in feed

% DBF,prod = weight percent dibenzofuran in product

% DCX,prod = weight percent dicyclohexyl in product

f = feed to product material balance factor

VITA 2

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Master of Science

Thesis: EFFECTS OF TITANOCENE DICHLORIDE ON HYDRODESULFURIZATION OF DIBENZOTHIOPHENE AND OF HYDRODEOXYGENATION OF DIBENZOFURAN

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