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INVESTIGATION OF MECHANISMS OF HYDROGEN TRANSFER IN COAL HYDROGENATION

Quarterly Progress Report
for January-March, 1977

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REA

Quarterly Technical Progress Report
for January-March, 1977

(Phase I, Stage 2)

ABSTRACT

In the study of hydrogen-transfer reactions, experimentation with the dibenzyl/tetralin system in a nitrogen atmosphere is complete. Data are being reduced to a form to develop a kinetic model of the reaction. Dibenzyl was converted quantitatively to toluene. As a side reaction, much of the tetralin was rearranged to methyl indane. The conversion rate of dibenzyl did not appear to be affected by the type of donor solvent, namely dimethyl tetralin, octahydrophenanthrene, and even decalin. In addition, the conversion rate of dibenzyl was the same when an inert solvent, mesitylene, was used with a hydrogen atmosphere. Experimentation with tagged compounds is under way, but analytical data are not yet available.

OBJECTIVE AND SCOPE OF WORK

The overall objective of this study is to develop an understanding of the mechanism of hydrogen transfer to coal during coal liquefaction. This is being done using both tagged and untagged compounds as donors and acceptors. The tagged compounds include those containing stable (^{13}C and deuterium) or radioactive (^{14}C and tritium) isotopes. In addition, it includes those compounds having functionality that allows for isolation by extraction, for example, tetrahydroquinoline. Experimentation is being done at conditions consistent with processes currently being developed to liquefy coal.

The project is divided into two 18-month phases, the first covering the study of model compounds and the second consisting of the application of these results to the study of coal and coal-derived liquids. The first stage (six months) of Phase I consisted of preparatory work and experimentation. It was completed and reported in the Semi-annual Technical Progress Report issued in January 1977.

Two research areas are being covered concurrently in Stage 2. The primary area consists of in-depth experimentation of selected acceptors with a series of donors (with and without tags). Sufficient experimentation is being carried out with each acceptor to develop a kinetic model of the transfer reaction. The second area consists of background or scrambling reactions which may interface with the above results. A schedule of experimentation for this stage was given in the previous Semi-annual Report and is included herein with minor modifications as Figure 1.

The following is a summary of the planned tasks to be covered in Stage 2. (Some changes of the original plan have been included as a result of observations from the preliminary experiments of Stage 1.)

a. Perform experiments for selected hydrogen-transfer reactions using both tagged and untagged model compounds having similar characteristics to those present in coal liquefaction. Emphasis will be placed upon experimentation at conditions typical for coal liquefaction. Runs will be made with nitrogen or hydrogen (selected runs with deuterium) to separate the role of dissolved hydrogen. Catalytic runs will also be made using finely divided catalyst with a high degree of agitation.

b. Perform necessary analytical work.

c. Reduce the data and interpret the results to explain hydrogen transfer kinetics and mechanisms.

d. Submit a comprehensive report of the Phase I program.

SUMMARY OF PROGRESS TO DATE

The project is essentially progressing on schedule. Experimentation with the acceptor dibenzyl has been completed with the untagged donor solvents. A limited number of analyses remain to be completed but should be available within 1-2 weeks. The reduction of data to a form necessary for establishing a reaction model of the dibenzyl/tetralin system is nearing completion. Experimentation with deuterium-tagged donor solvent is under way; however, it is about two weeks behind schedule. The primary delay is that of scheduling mass spectroscopic analyses to coincide with filament replacements. Delays occur between the analyses of groups of samples. The preparation of ^{13}C-tagged octahydrophenanthrene and dimethyl tetralin is nearing completion under the direction of Professor Eisenbraun. Experiments with these donors will be scheduled when they become available, presumably by June 1. This latter date will not affect the overall schedule in that experimentation will progress with the use of deuterated solvents and the remaining acceptors.

A copy of the program schedule is included as Figure 2. Reference is again made to Figure 1 for further details.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Stage 2. Model Compounds Experimentation

A. Experimental Procedure

The donor/acceptor experiments are being done in a 300-cc batch, stirred autoclave reactor. The unit also has a 300-cc heated feed tank to provide for injection of reactants at elevated temperatures under pressure. In most runs, 75 grams of donor is charged to the reactor and rapidly heated to the desired temperature (60-80 minutes were needed). At this temperature, a 75-gram charge of donor and

acceptor is injected using nitrogen at 10.3 MPa (1500 psig). The injected liquid is typically heated to 275-300°C. At the time of injection, reactor temperature drops 5-10°C, but it recovers within three minutes. Provision is included to periodically take samples from the reactor during the run.

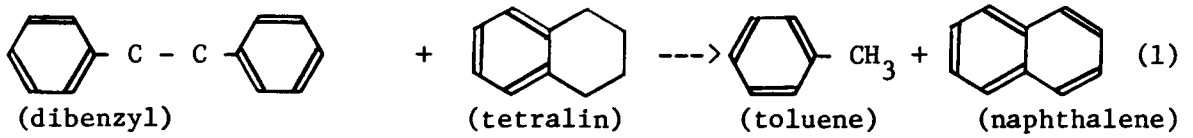
In most of the donor/acceptor reactions, the reactor samples are analyzed using a high-resolution capillary GLC with a 100-foot SCOT column. Selected samples are also analyzed using a medium-resolution GC with interfacing to a DuPont 21-491 mass spectrometer. The analysis of tagged compounds is now under way using a CEC-103 low-voltage mass spectrometer. It is noted that low-voltage mass spectra are normally obtained only when a sufficient number of samples exist. The Isotron must be replaced frequently when operating under these conditions.

For reference, a listing of the experiments carried out in the above reactor is included in the Appendix as Tables I and II.

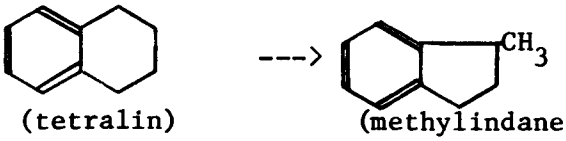
B. Experimental Results

The major portion of our experimental effort this quarter has been devoted to various reactions with the dibenzyl acceptor. Preliminary screening studies reported in the previous quarter strongly suggested that this compound was ideal for evaluating donor characteristics, reaction products and reaction kinetics. The reactivity of dibenzyl has been studied in the 400-475°C range in tetralin, mesitylene, 2,6-dimethyltetralin, sym-octahydrophenanthrene and D_4-tetralin under both nitrogen and hydrogen environments. Although some analyses remain to be completed, major reaction paths can be deduced.

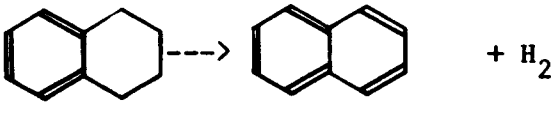
Dibenzyl/Tetralin System. In good donor solvents such as tetralins, the cracking of dibenzyl proceeds nearly quantitatively to toluene. The following is a summary of this reaction and the remaining reactions being evaluated in developing a mechanism for the dibenzyl/tetralin system (these reactions are intentionally not balanced):



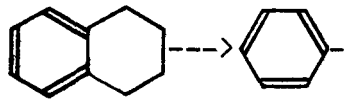
(dibenzyl) (tetralin) (toluene) (naphthalene) (1)



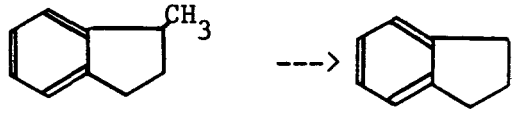
(tetralin) (methylindane) (2)



(3)



(4)



(indane)

(5)

dicyclic ---> cracked products (6)

compounds other than toluene and indane.

As shown in Figure 3, a wide range of dibenzyl conversions is observed over the temperature range of 400°-475°C. These runs were made in a nitrogen atmosphere with a feed dibenzyl concentration of 10 wt.%. The concentrations of the remaining reactants and products are shown graphically in Figures 4 through 9. It is noted that in a nitrogen atmosphere and in the absence of donor solvent (1,3,5-trimethyl benzene [mesitylene] was used), only trace levels of dibenzyl and toluene cracking were observed.

To observe the effect of concentration, a series of experiments was made using various ratios of dibenzyl and tetralin in a nitrogen atmosphere. The results plotted in Figure 10 strongly indicate that conversion is independent of dibenzyl concentration as long as the minimum hydrogen requirements for bond stabilization can be met by the solvent.

Dibenzyl/Decalin System. Completely saturated cyclic compounds have generally been regarded as non-donor solvents. Assuming that decalin would function as an "inert" solvent, dibenzyl thermal stability experiments were performed in a nitrogen atmosphere with the surprising result that conversion followed essentially the same curve as shown for tetralin (see Figure 11). Careful GC-MS studies of a 450°C run with pure decalin revealed that small levels of dehydrogenation to tetralin occurred. At similar conditions but with dibenzyl present, the dehydrogenation to tetralin increased.

The fact that dibenzyl was cleanly converted to toluene in the decalin system is useful evidence to indicate that low concentrations of hydrogen donors can be consumed if generated in-situ. Although the donor ability of decalin was quite unexpected, similar extrapolation to more complex, alkylated, cycloparaffins should not be made at this time. The presence of alkyl groups on decalins may well inhibit thermal dehydrogenation at 450°C. Selected experiments on this point are currently being conducted.

Dibenzyl/2,6-Dimethyl Tetralin System. 2,6-Dimethyltetralin can be prepared by the catalytic hydrogenation of the corresponding naphthalene. This donor solvent is being used for selected experiments in an attempt to determine the effect that alkyl groups have on the hydrogen-transfer process and the stability and fate of solvent.

The thermal stability of 2,6-dimethyltetralin was determined by heating in an inert solvent (mesitylene) with a 1500 psig unit pressure (nitrogen). The reactor temperature was increased incrementally between 300° and 475°C. No evidence of thermal cracking or dehydrogenation was observed up through 450°C. Rapid dehydrogenation to 2,6-dimethylnaphthalene together with traces of demethylation to 2-methylnaphthalene occurred between 450° and 463°C. We are determining if contraction to a tri-substituted indane had occurred. If so, it was not nearly so extensive a side reaction as that of similar tetralin reactions (see the January 1977 report).

When 2,6-dimethyltetralin was reacted with dibenzyl at 450°C, a conversion path nearly identical to tetralin was observed (see Figure 11). It appears that the methyl groups on the donor solvent do not affect hydrogen transfer rates.

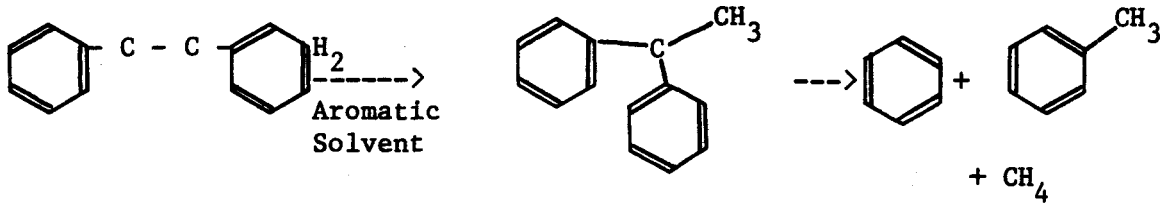
Dibenzyl/Octahydrophenanthrene System. Limited experiments have been done with sym-octahydrophenanthrene as a donor solvent. Although this solvent is stable at 400°C, some structural alterations appear at 450°C. The nature of the skeletal changes and possible catalyzing effect by acceptors, as reported earlier for tetralin (January 1977 report), are currently being studied.

As seen in Figure 11, this donor solvent will convert dibenzyl to toluene at essentially the same rate as tetralin or dimethyltetralin. This indicates that, at least with the dibenzyl system, conversion is independent of the concentration of "transferable hydrogens" in the solvent. (Theor. H_T = 8 for octahydrophenanthrene vs. 4 for tetralins.)

Dibenzyl/Hydrogen System. A series of runs were made with 10% dibenzyl in mesitylene with a hydrogen atmosphere (1500 psig). As shown in Figures 11 and 12, the conversion of dibenzyl was essentially the same as that in previous experiments with donor solvents. The family of curves illustrated in Figure 12 strongly indicate that dibenzyl cracking-hydrogen abstraction are concomitant processes controlled by the temperature of the reaction. (It is again noted that dibenzyl was essentially stable in mesitylene with a nitrogen environment.)

Although the conversion curves for dibenzyl were nearly identical in either a hydrogen donor, or H_2(g) environment, the products from the latter were much more complex (Figure 13). The non-donor aromatic solvent, mesitylene, reacted with benzene, toluene and xylene cracking products to form a variety of high molecular weight polymers. This side-reaction also increased with temperature.

The apparent increase in free radical concentration from solvent molecules in a hydrogen atmosphere (vs. a nitrogen environment) coupled with C-C bond formation preferred over C-H was an unexpected observation. GC-MS evidence for the rearrangement of dibenzyl (1,2-diphenyl ethane) to the 1,1-diphenyl ethane isomer was obtained. This rearrangement has not been observed in good donor solvents. In addition, this rearrangement could partially explain large amounts of methane being evolved from the H_2/dibenzyl experiments together with large amounts of benzene. The postulated reaction path is shown below:



As shown in Figure 11, there appeared to be no synergistic effect when both hydrogen atmosphere and tetralin were used. However, the hydrogen atmosphere did promote much more secondary cracking to methane, ethane and benzene. In addition, the degradation of tetralin to indane was enhanced.

C. Deuterium Studies (Tetralin)

Experimentation to prepare reasonable quantities of D_{4-8}-tetralin has been performed using 9 MPa (1300 psig) D_2, a commercial NiW catalyst, Nalco Sphericat 550, and 350°C (662°F). This preparation was deemed necessary in view of the inability to purchase large volumes of the labeled solvent at reasonable cost. At the above conditions, deuterium was incorporated to the D_4-D_5 level. Upon distillation a solvent of about 92% D_4-tetralin and 8% naphthalene was obtained. NMR studies indicated that the deuterium was randomly distributed.

The above solvent is being used for some initial experiments to determine the extent of scrambling that can be expected using a steel reactor. Experiments are also being carried out to enrich the deuterium level of the solvent by second-stage exchange at lower temperatures with either fresh catalyst or more selective catalysts (Pd/C). The results of these experiments are not complete at this time due to instrument delays in obtaining low-voltage mass spectra.

D. Experimentation with Dibenzyl Ether

The previous quarterly report (January 1977) indicated that dibenzyl ether reacted with tetralin at a much faster rate than dibenzyl. Based on these screening studies, we suggested that this compound be used as the second acceptor for kinetic and mechanistic model development. Ether bonds are likely constituents of low rank coals and an understanding of their reactivity with donor solvents is deemed very necessary.

Since screening experiments showed that dibenzyl ether was completely converted in tetralin within one hour at 400°C, we chose to study the temperature range of 300-400°C. Figure 14 shows typical conversion curves at 325°, 350°, 375° and 400°C. Reaction does occur to a slight extent at 300°C but reproducibility of data was poor.

A study of the various products from dibenzyl ether cleavage indicates that the following consecutive reactions were taking place:

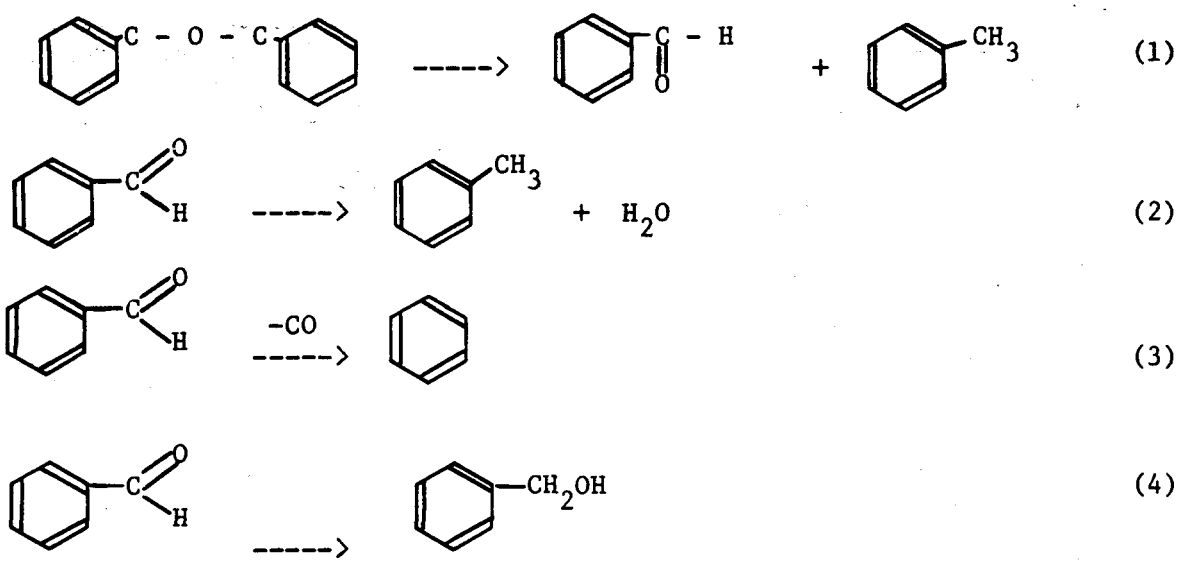


Figure 15 illustrates how the major products vary at 375°C over a three-hour period. These curves indicate that reaction (1) prevails for the first hour after which the concentration of benzaldehyde remains constant. The linearity of benzene formation is an indication of a first-order reaction in (3) although it is quite slow. Conversely, reaction (2) is also probably first order and at a similar rate since benzaldehyde concentration is essentially constant in the 2-3 hour period.

Studies will soon be done with benzaldehyde and tetralin to better distinguish the rates of Equations (2) and (3). Experimentation will also be done with dimethyltetralin and octahydrophenanthrene as donor solvents to determine if rates and reaction paths are affected by donor strength. The kinetic calculations will then be done in a manner analogous to that used for dibenzyl.

One important conclusion from these particular studies is that carbonylic functional groups formed during coal liquefaction have reasonable stability but can also function as hydrogen acceptors. Since no evidence of benzyl alcohol has yet been found, reaction (4) either does not occur or is a short-lived intermediate in the dehydration step (2).

E. Experimentation with Dibenzyl Sulfide

Because dibenzyl ether reacted so readily with tetralin at 400°C, we chose to evaluate the effect of substituting sulfur for the oxygen in the same basic system. Furthermore, since preliminary screening experiments showed that dibenzothiophene was completely inert to tetralin up to 475°C, dibenzyl sulfide offers a comparison between aromatic and non-aromatic C-S-C bond cleavage. The reaction proceeded very rapidly in tetralin with 50% completion at 350°C and 100% completion after reaching 400°C in a span of 30 minutes. A study of the intermediates and products of this reaction revealed large quantities of stilbene and the expulsion of H_2S. The stilbene appeared to react further with

tetralin to form dibenzyl and eventually toluene. Since this reaction proceeds very fast at 400°C, future studies will utilize temperatures in the range of 300-375°C to monitor intermediates more accurately. The isolation of stilbene as a major intermediate is of particular significance to the question of desulfurizing (organic S) coals with donor solvents. It's quite obvious that non-aromatic sulfur bonds are readily cleaved at low temperatures.

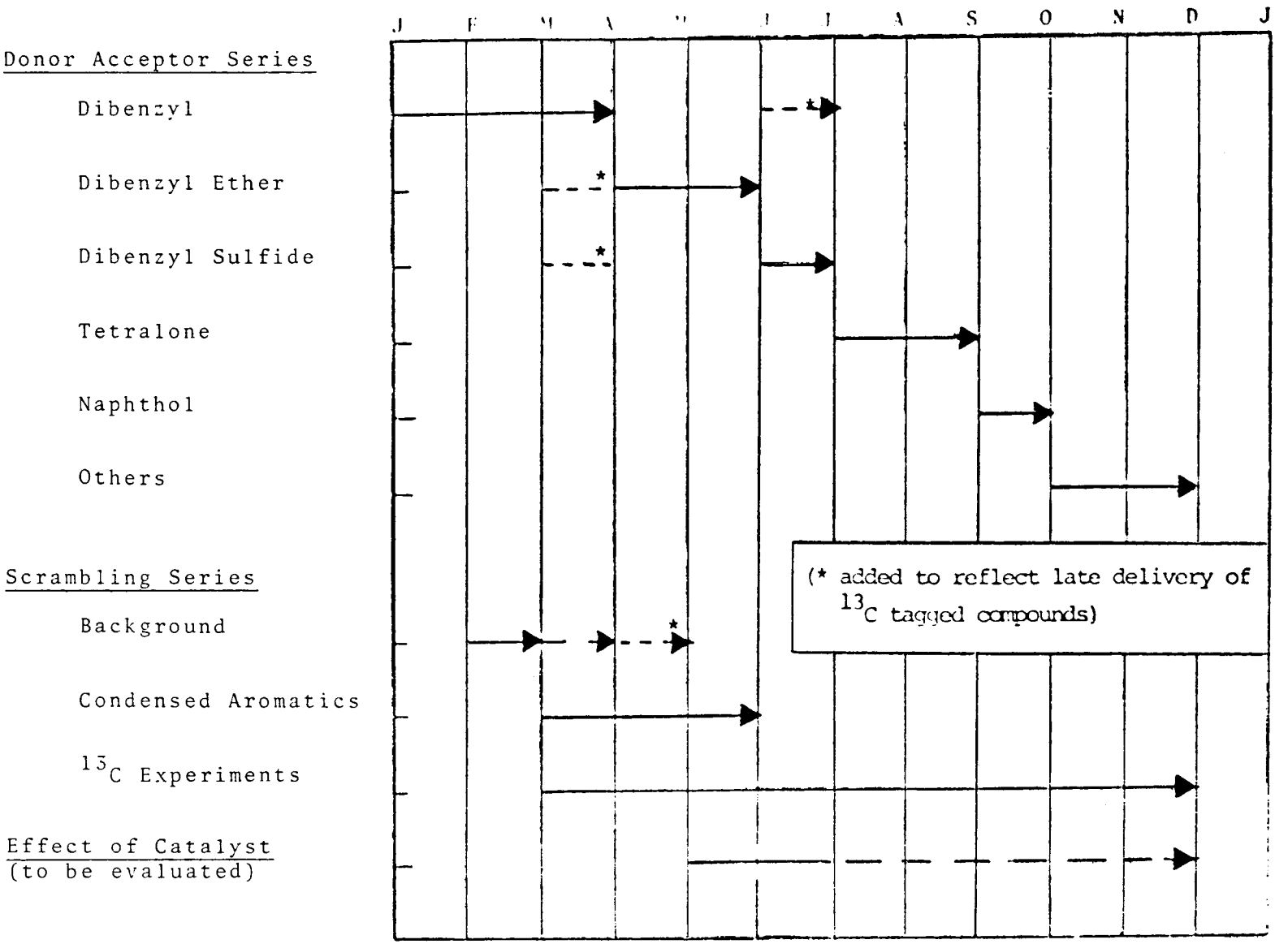
F. Synthesis of Labeled Donor Solvents

All steps for the synthesis of ^{13}C-labeled 2,6-dimethyl tetralin and sym-octahydrophenanthrene have been established. Since 1 kg quantities of each compound at the 10% ^{13}C enrichment level are being prepared, current efforts are directed at the repetitive aspects of each step in order to prepare the total quantities needed. Since overall yields of the octahydrophenanthrene derivative are better, this solvent may be completed within the next 4-5 weeks. Upon completion of these syntheses, a separate report on the chemistry involved will be prepared.

DCC:DMJ:WPC

Figure 1

Planned Experiments: Stage 2



NOTE: The above schedule is that of experimentation; additional time may be necessary to complete analysis.

Figure 2

Program Schedule for Hydrogen Transfer Project

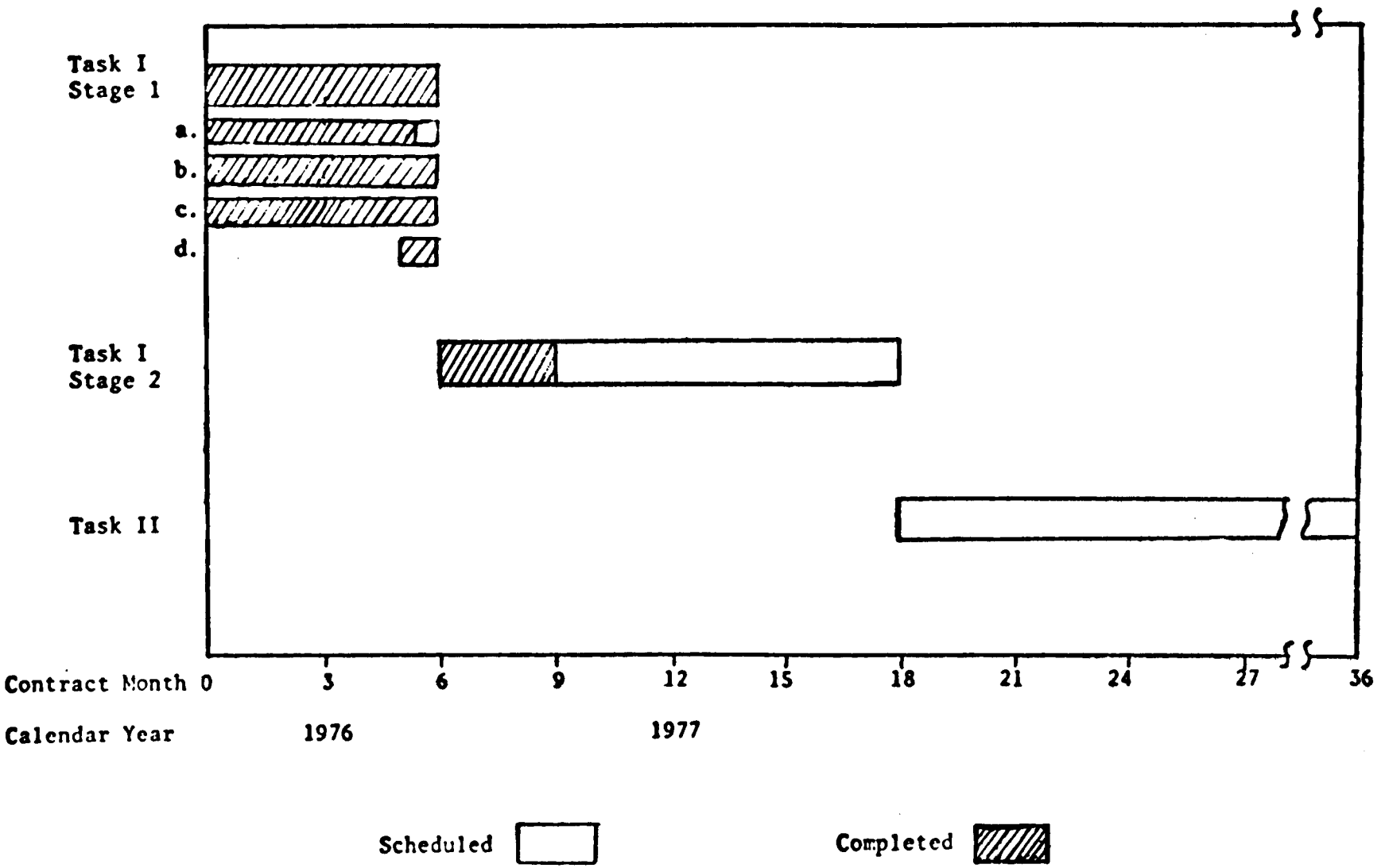


Figure 3

DIBENZYL CONCENTRATION

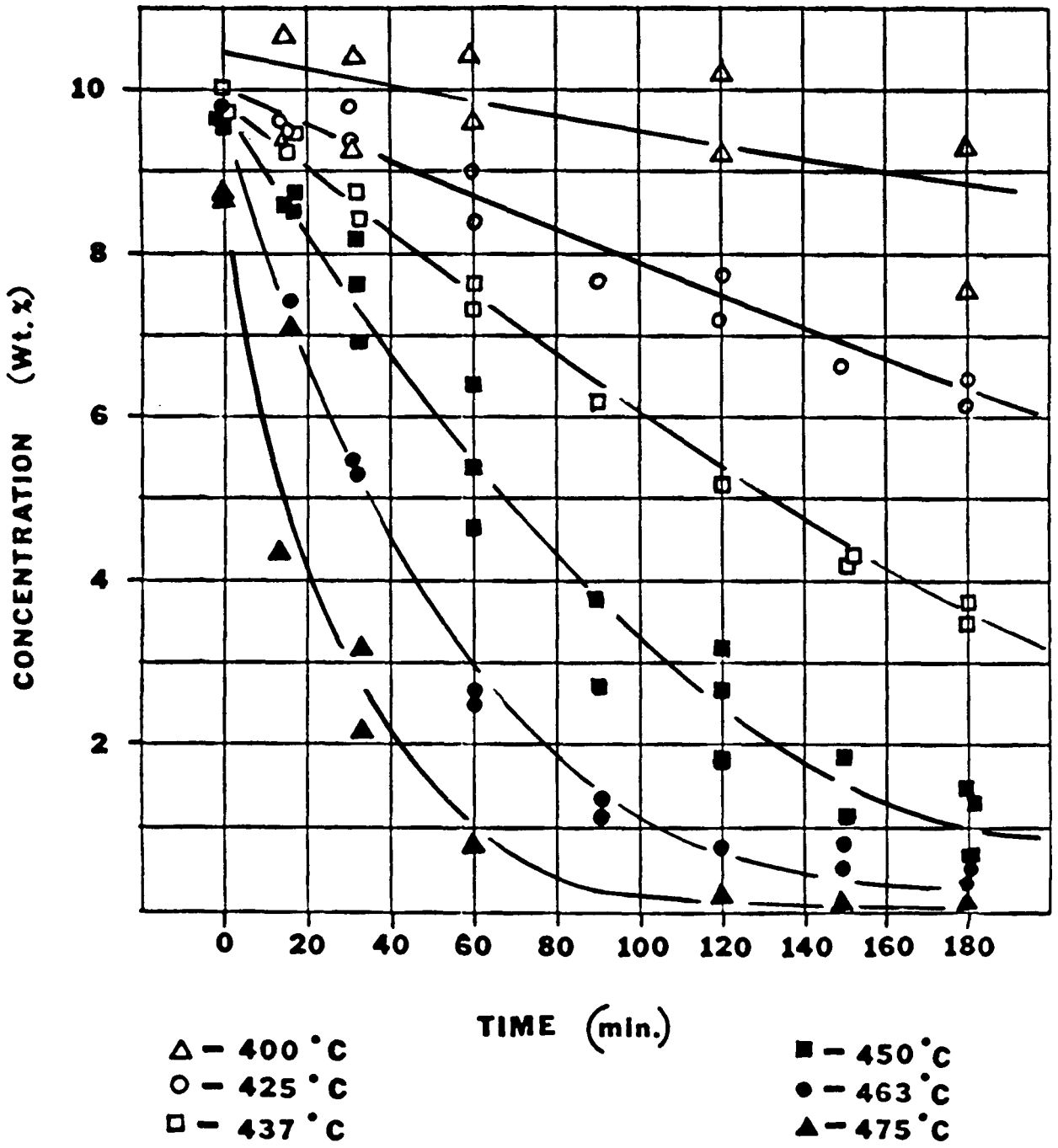


Figure 4

TOLUENE CONCENTRATION

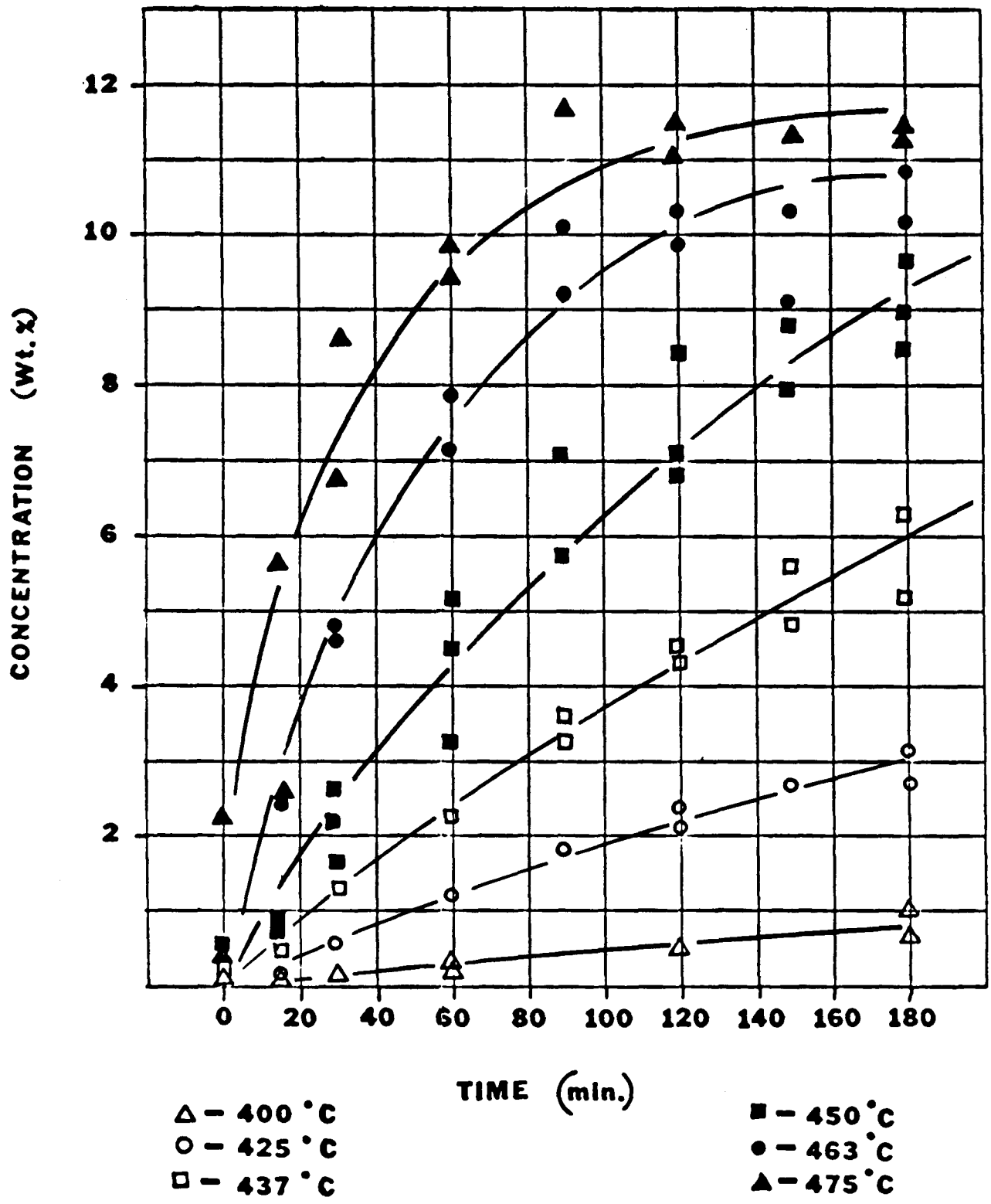


Figure 5

TETRALIN CONCENTRATION

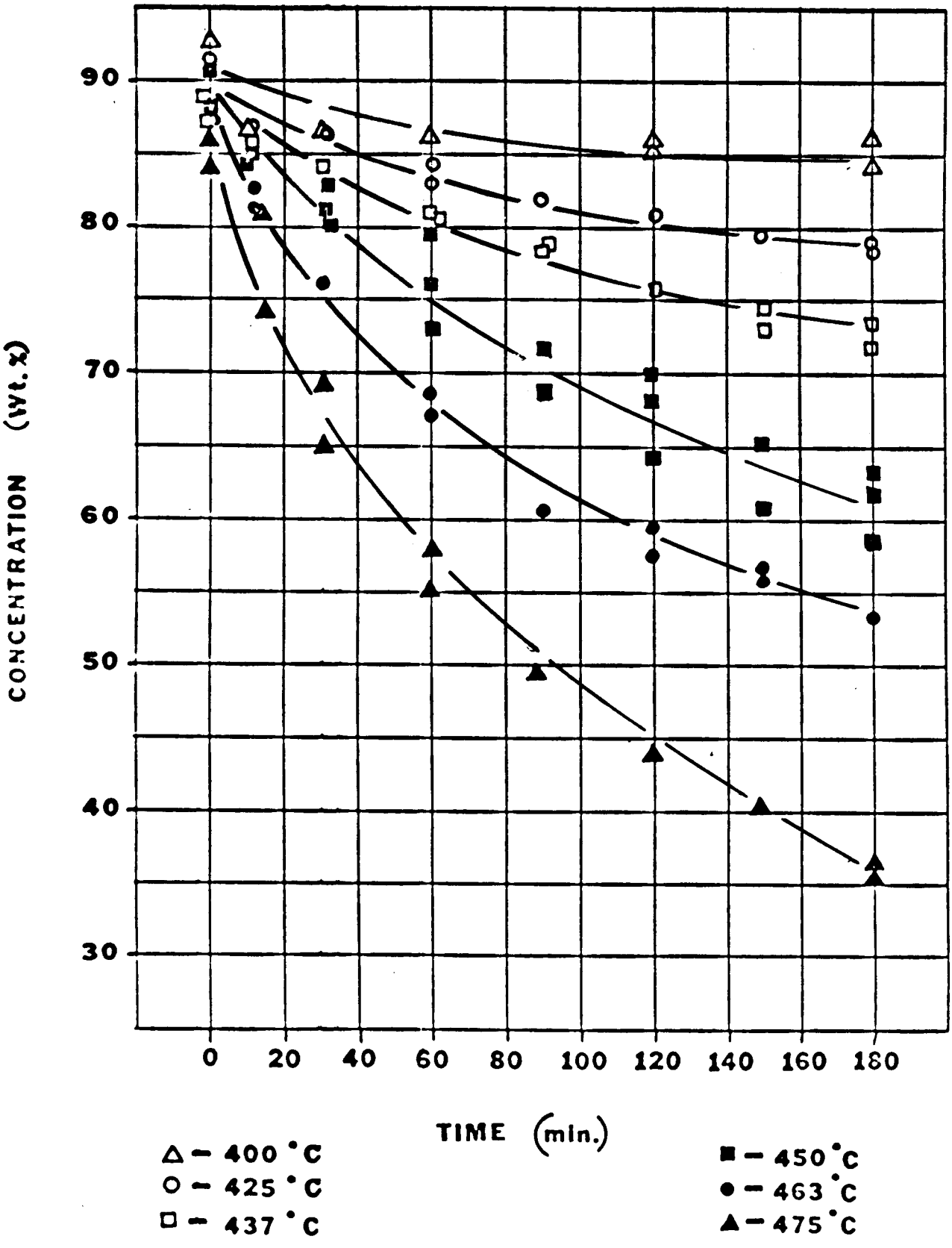


Figure 6

METHYL INDANE CONCENTRATION

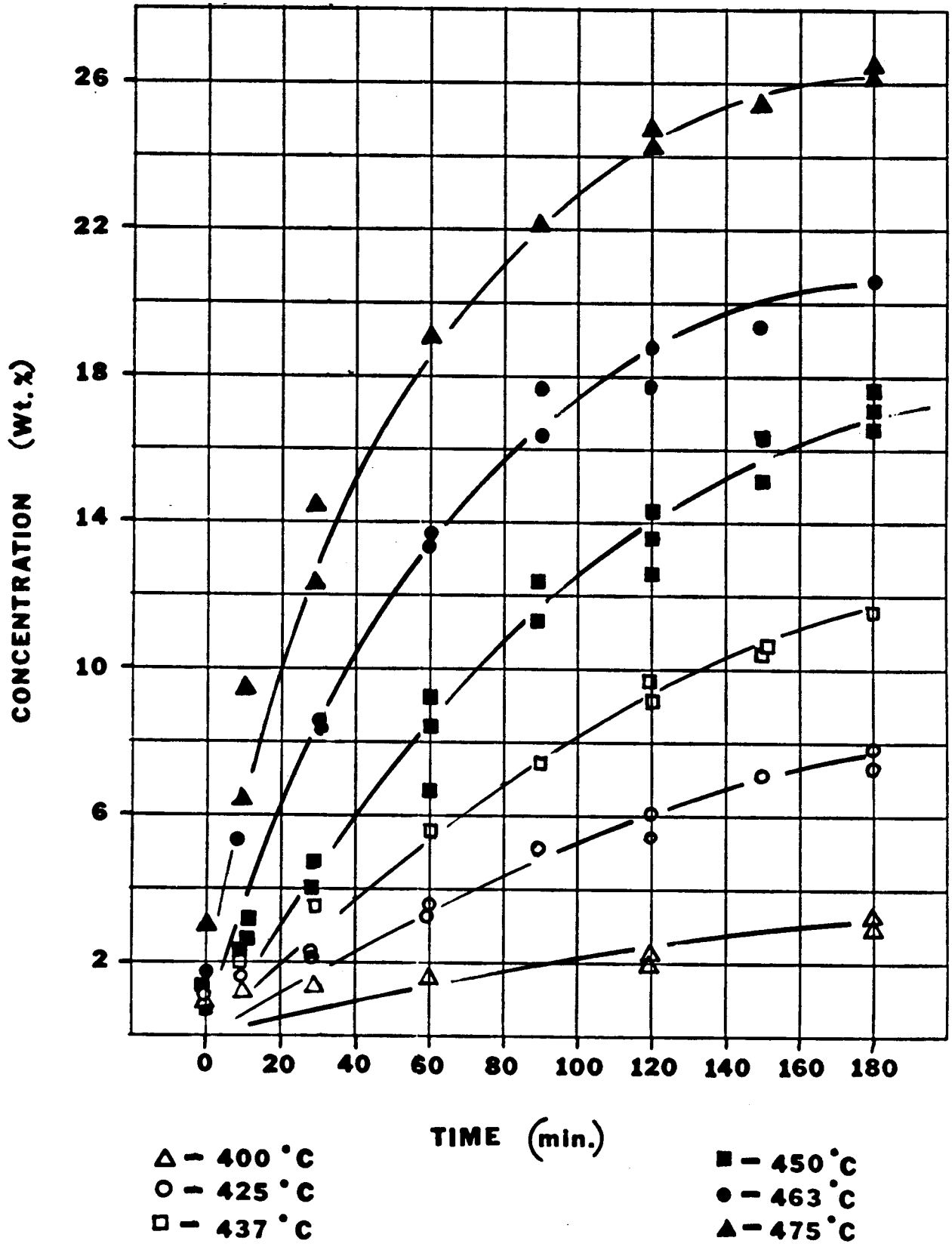


Figure 7

NAPHTHALENE CONCENTRATION

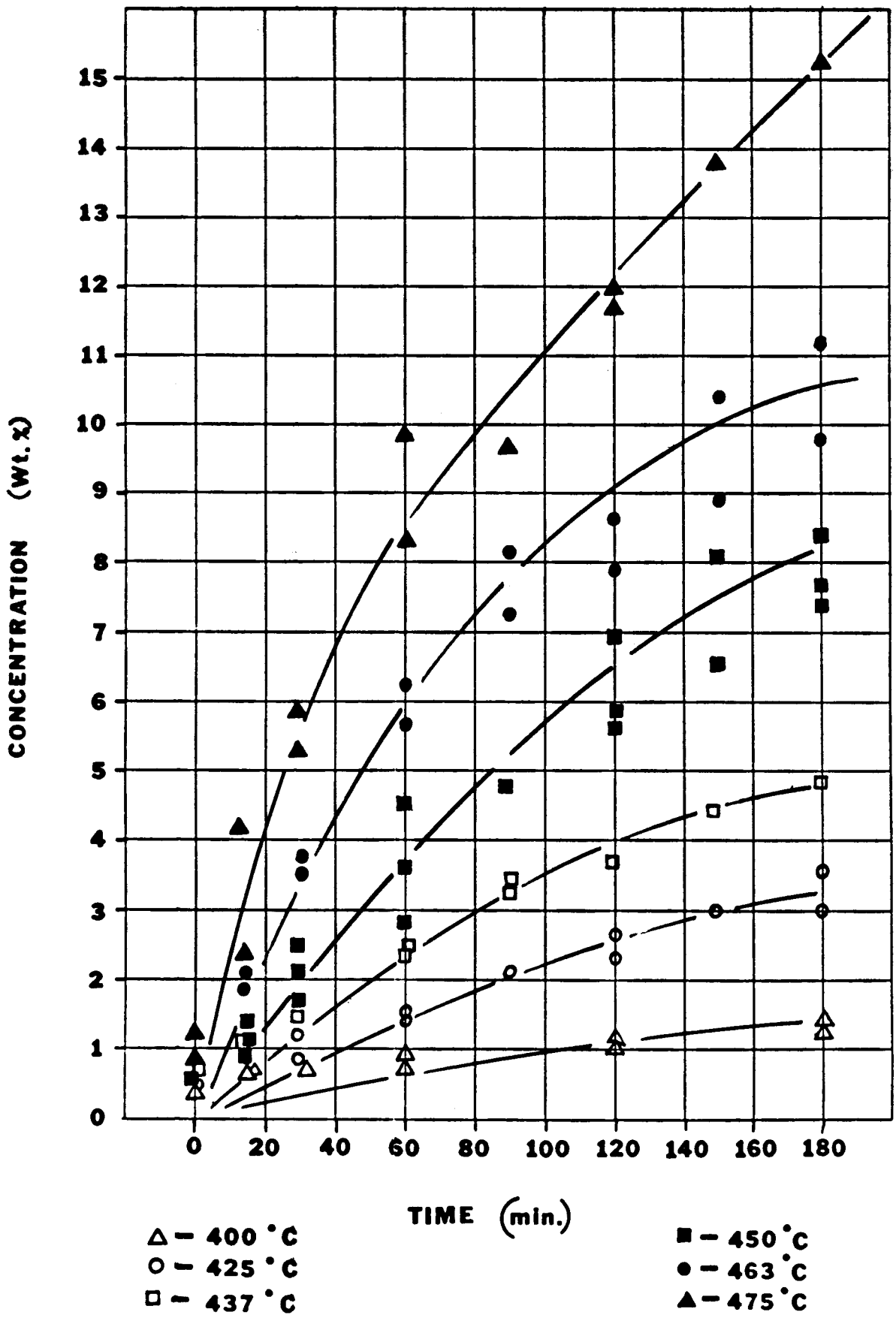


Figure 8

INDANE CONCENTRATION

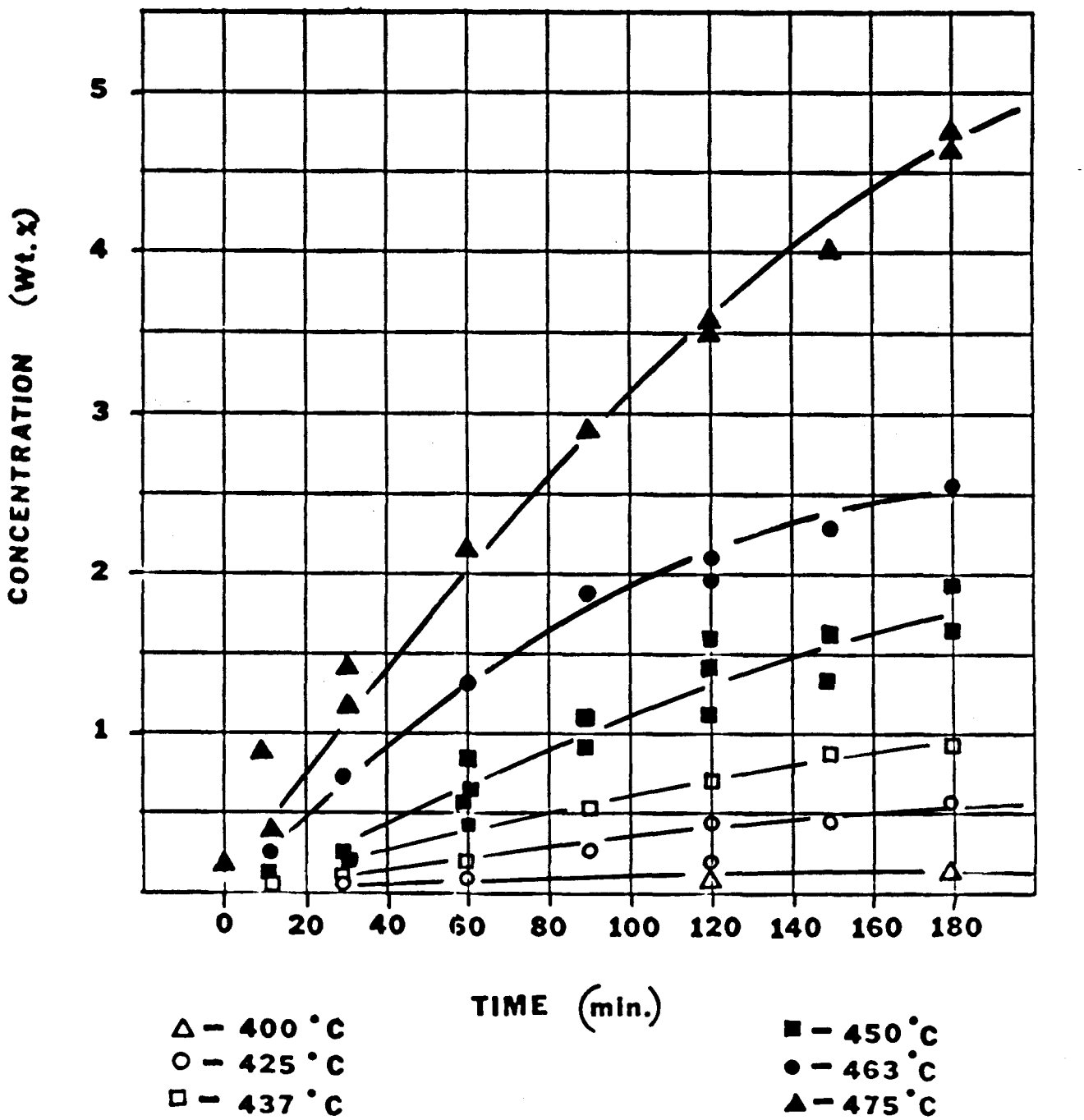


Figure 9

CONCENTRATION OF CRACKED PRODUCTS
(BENZENE + ET.-BENZENE +
XYLENES + LIGHT UNKNOWNS)

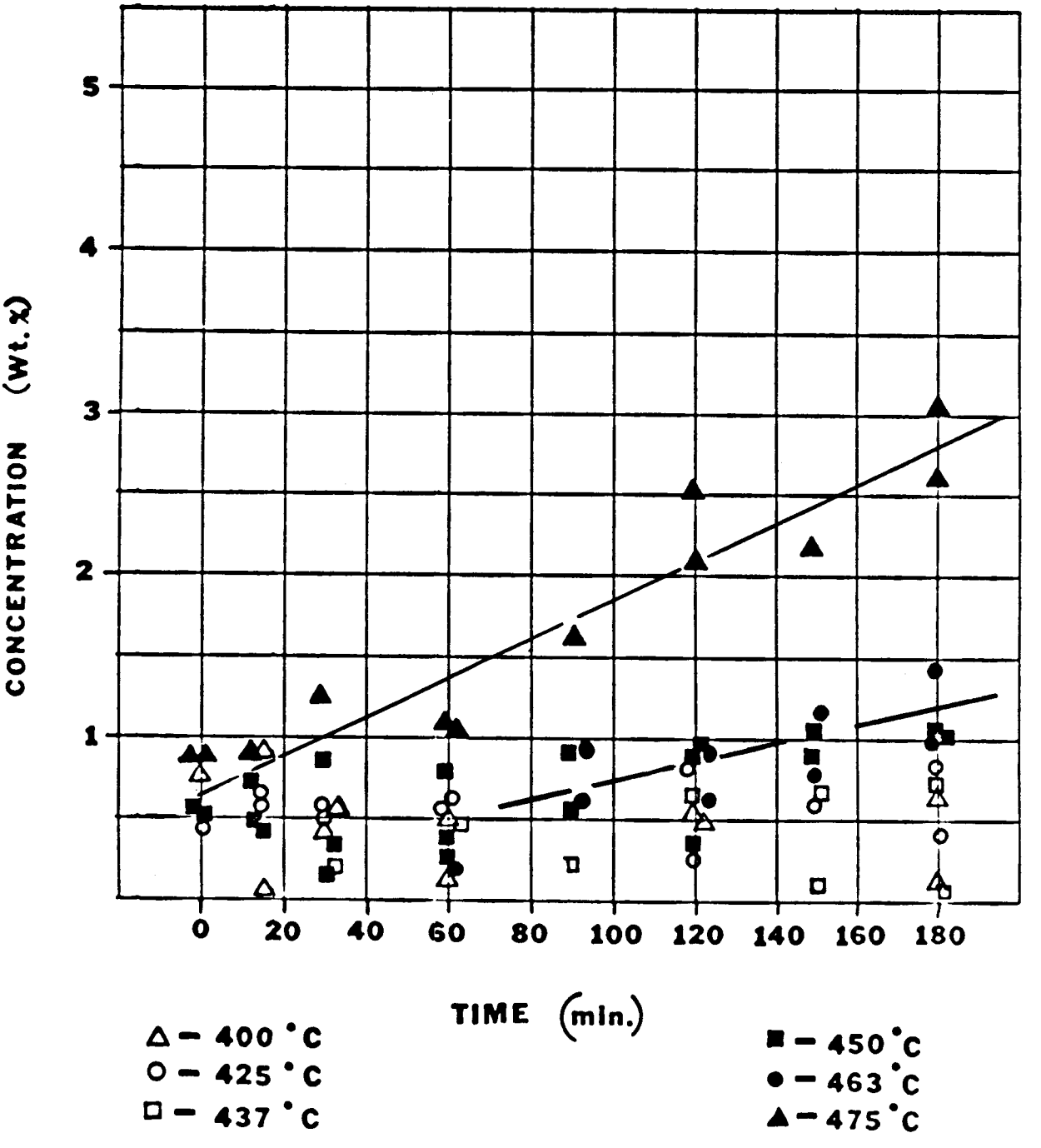


Figure 10

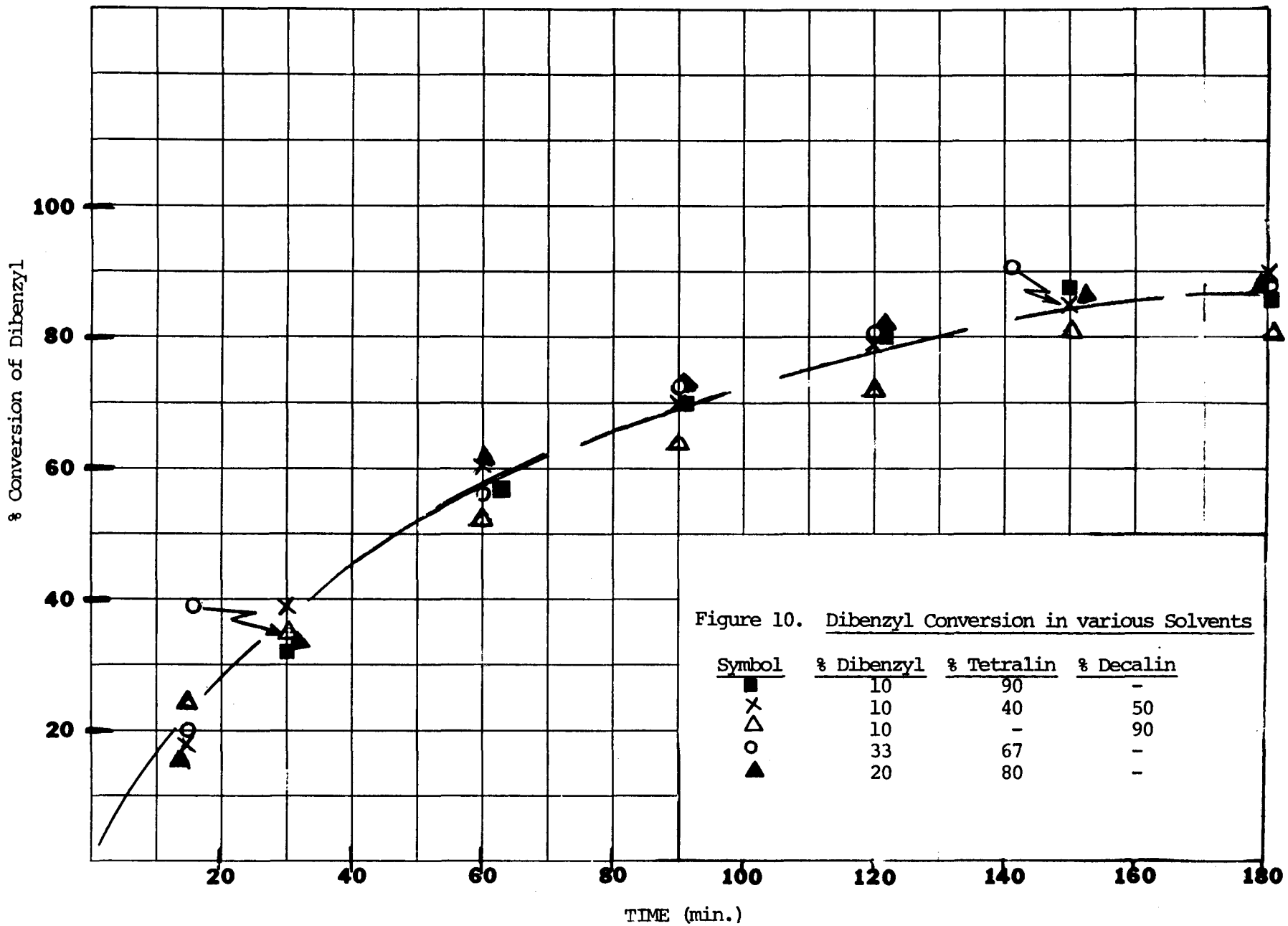


Figure 10. Dibenzyl Conversion in various Solvents

Symbol	% Dibenzyl	% Tetralin	% Decalin
■	10	90	-
×	10	40	50
△	10	-	90
○	33	67	-
▲	20	80	-

FIGURE 11

DIBENZYL REACTIONS AT 450° C WITH VARIOUS SOLVENTS

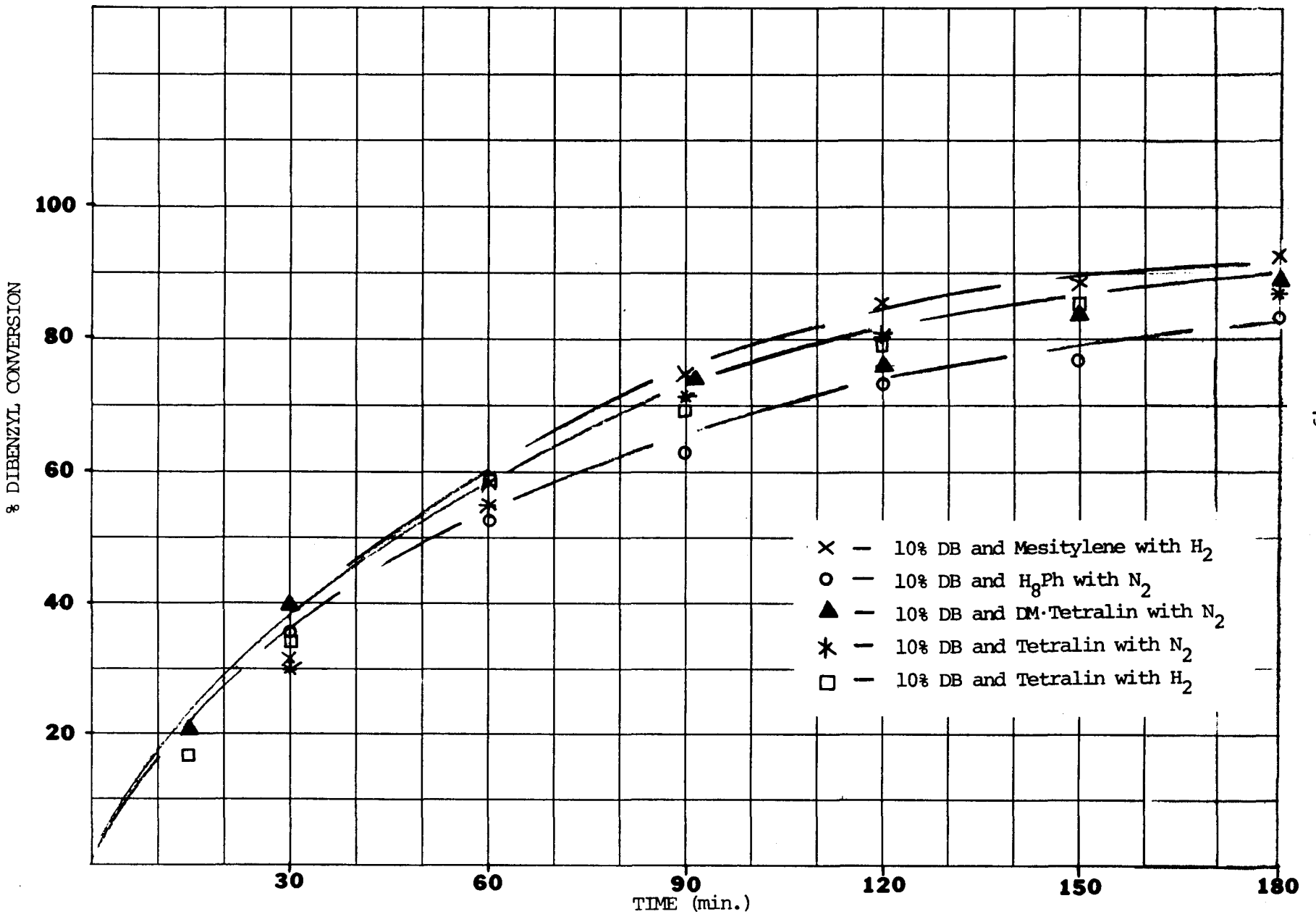


FIGURE 12

DIBENZYL REACTIONS IN MESITYLENE WITH A HYDROGEN ATMOSPHERE

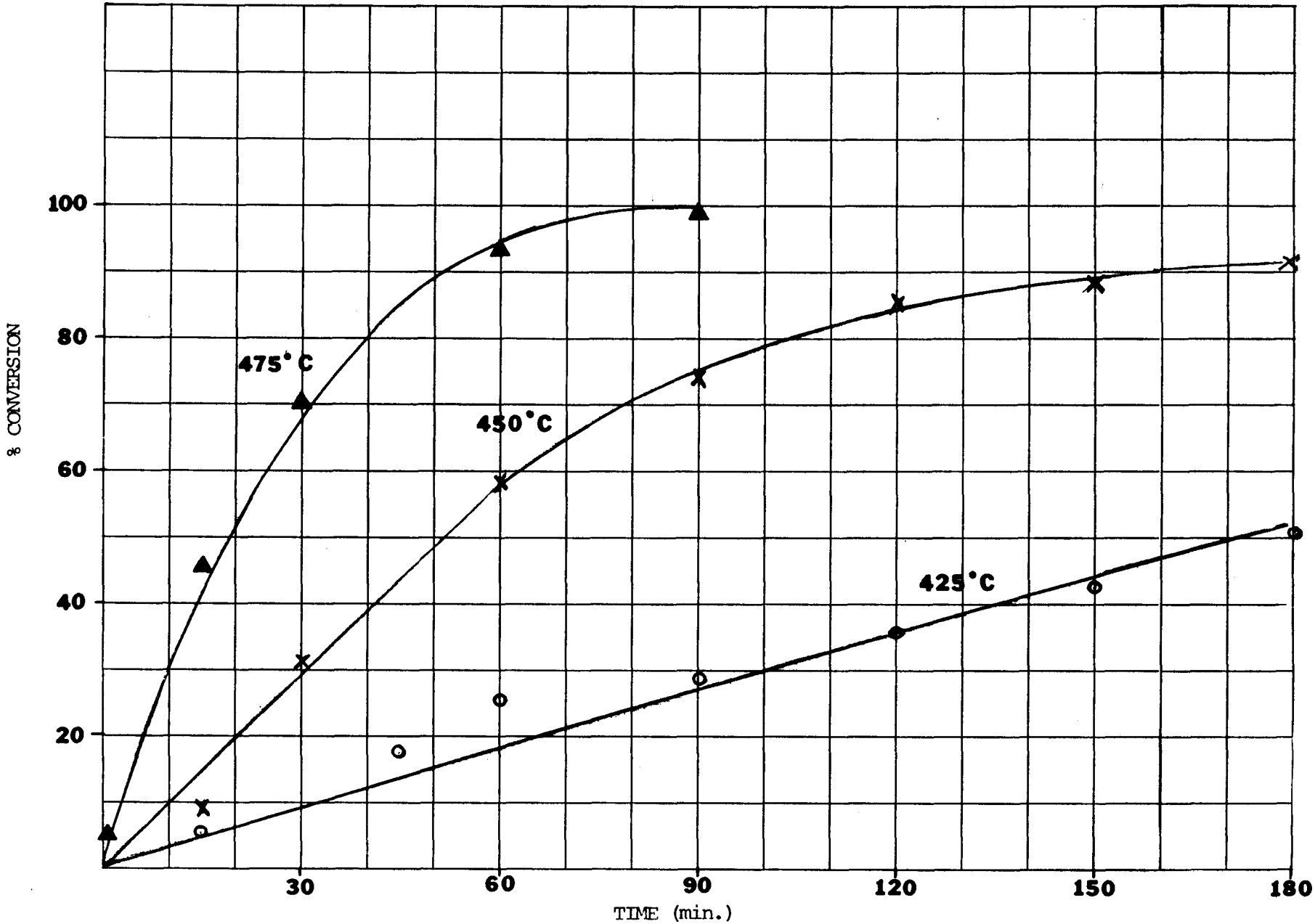


FIGURE 13

DIBENZYL PRODUCTS: REACTION IN MESITYLENE WITH HYDROGEN ATMOSPHERE

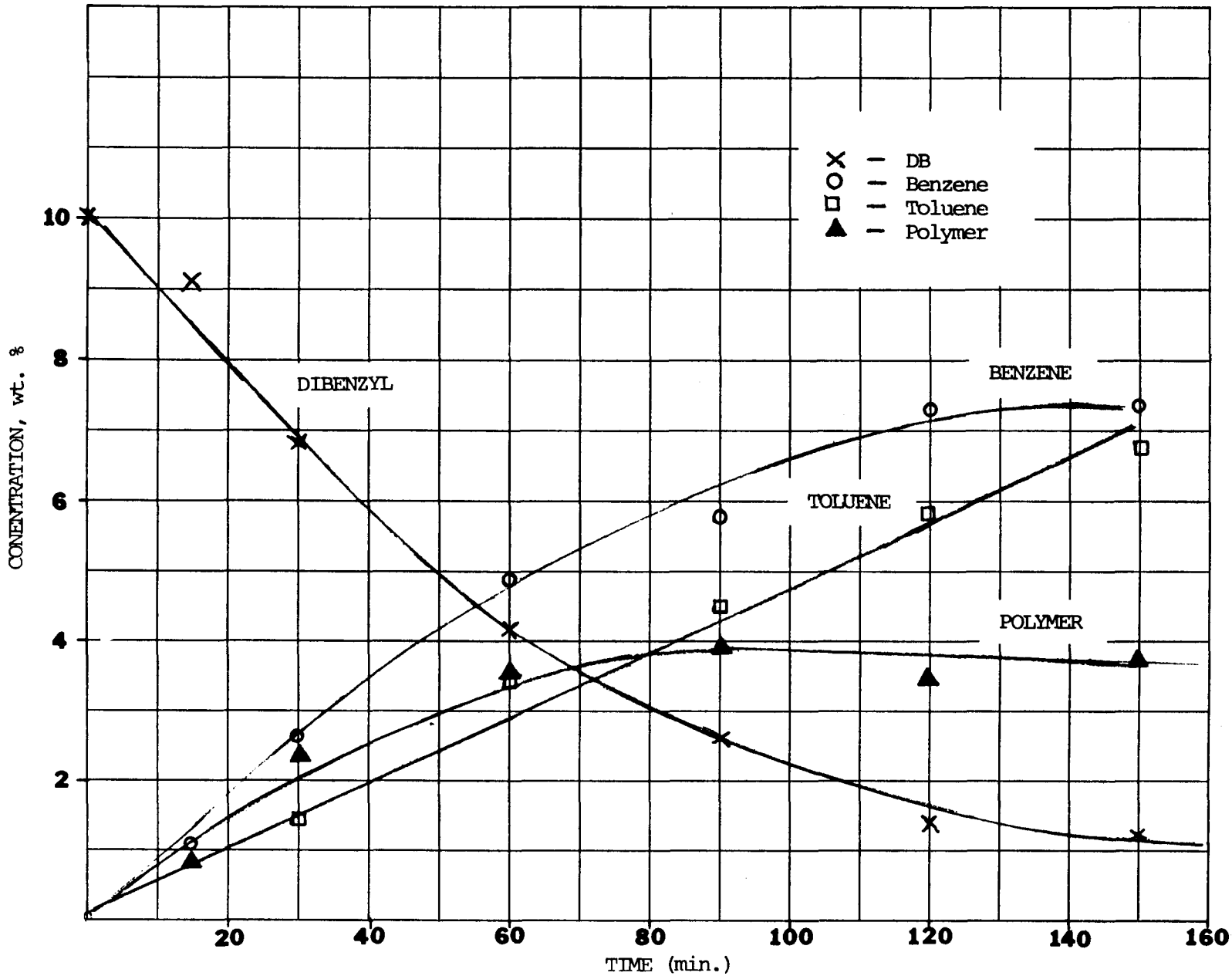


FIGURE 14

DIBENZYL ETHER REACTIONS IN TETRALIN WITH A NITROGEN ATMOSPHERE

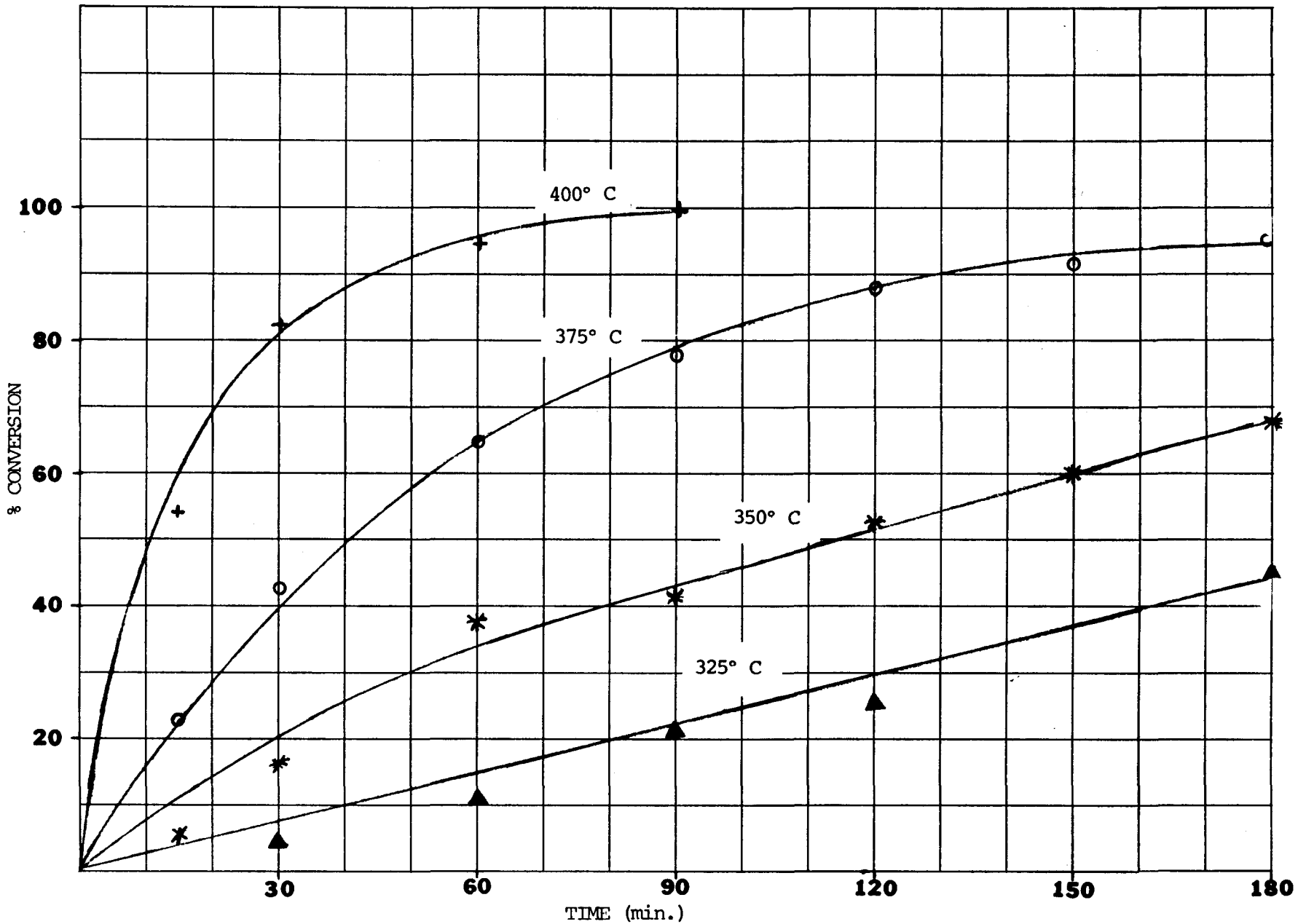
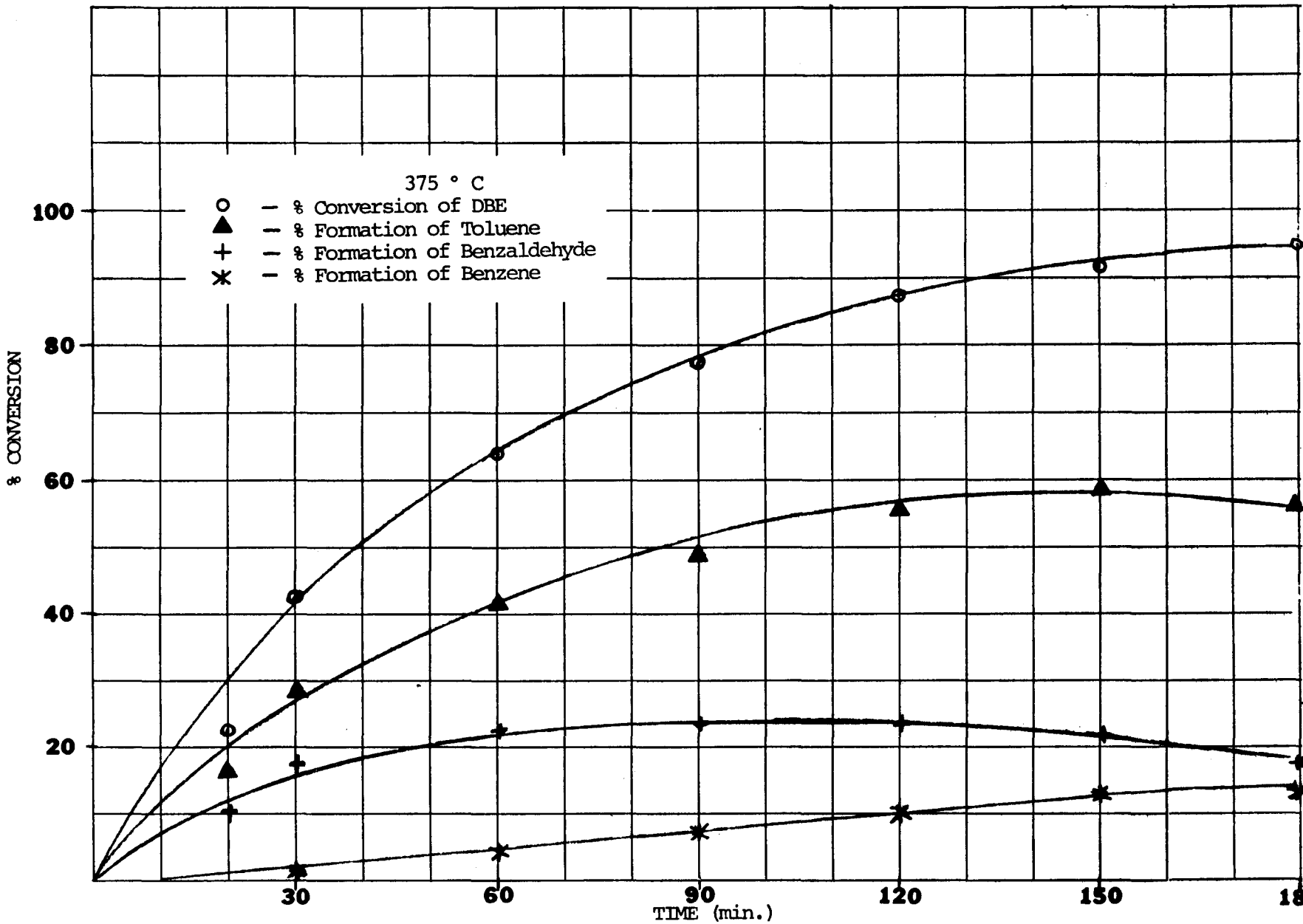


FIGURE 15

DIBENZYL ETHER PRODUCTS: REACTIONS IN TETRALIN WITH NITROGEN ATMOSPHERE



APPENDIX

TABLE I

SUMMARY OF EXPERIMENTS: HYDROGEN TRANSFER STUDIES
(Screening Runs)

Run No.	Time Hrs.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
76- 1	3	425	Tetralin	47.6	Tetralin	47.6		
76- 2	3	475	Tetralin	121.6				
76- 3	3	475	Tetralin	75	Tetralin	60	Phenanthrene	15
76- 4	3	475	Tetralin	75	Tetralin	60	Dibenzylfuran	15
76- 5	3	475	Tetralin	75	Tetralin	60	Dibenzylthiophene	15
76- 6	3	475	Tetralin	75	Tetralin	60	Dibenzyl-ether	15
76- 7	3	475	Tetralin	75	Tetralin	60	N-ethyl carbazole	15
76- 8	3	475	Tetralin	75	Tetralin	60	Dibenzyl	15
76- 9	3	475	Tetralin	75	Tetralin	60	Hexadecyl ether	15
76-10	3	475	Tetralin	75	Tetralin	60	Dodecyl ether	15
76-11	3	475	Tetralin	75	Tetralin	60	Dodecyl sulfide	15
76-12	3	475	Tetralin	75	Tetralin	60	Tetralone	15
76-13	3	400	Tetralin	120	-	-	-	-
			Dibenzyl	30	-	-	-	-
76-14	3	400	Dibenzyl ether	150	-	-	-	-
76-15	3	400	Tetralin	125.5	-	-	-	-
			Tetralone	31.8	-	-	-	-
76-16	3	400	Tetralin (Plugged)	120	-	-	-	-
			Hydroxylquinolin	30	-	-	-	-

GS&TC
DCC:ill
4/6/77

TABLE II - (CONTINUED)

Run No.	Time Hrs.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77-25	3 3/4	400	Mesitylene	135	-	-	-	-
		425	DiMethyl-Tetralin	15	-	-	-	-
		437						
		450	(1/2 hour at each temperature)					
		463						
		475						
77-26	3	400	Tetralin	135	-	-	-	-
			Stilbene	15				
77-27	3	450	Tetralin	135	-	-	-	-
			Stilbene	15	-	-	-	-
77-28	3	450	Tetralin	75	Dimethyl Tetralin	60	Dibenzyl	15
77-29	3	450	Mesitylene	75	H_8P	60	Dibenzyl	15
77-30	3	400	Mesitylene	135	-	-	-	-
			Octahydrophenanthrene	15				
77-31	3	450	Tetralin	70	Tetralin	56	Dibenzyl	14
77-32	3	400	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-33	3	375	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-34	3	350	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-35	3	325	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-36	3	300	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-37	3	425	Mesitylene	75	Mesitylene	60	Dibenzyl	1[illegible]
77-38	3	450	Mesitylene	75	Mesitylene	60	Dibenzyl	1[illegible]
77-39	3	475	Mesitylene	75	Mesitylene	60	Dibenzyl	15
77-40	3	450	Tetralin	113	Tetralin	22.2	Dibenzyl	14.8
77-41	1 1/2	400	Mesitylene	100	D_4 Tetralin	50	-	-
	1 1/2	450	Mesitylene	100	D_4 Tetralin	50	-	-

GS&TC
DCC:ill
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TABLE II

SUMMARY OF EXPERIMENTS: HYDROGEN TRANSFER STUDIES

Run No.	Time Hrs.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77- 1	2	400	Tetralin	150	-	-	-	-
77- 2	3	400	Tetralin	120	-	-	-	-
			2,6 Di Tert Butyl-4 Methylphenol	30	-	-	-	-
77- 3	3	400	Tetralin	120	-	-	-	-
			4 Methyl 1 Tetralone	30	-	-	-	-
77- 4	3	400	Tetralin	120	-	-	-	-
			Benzyl Sulfide	30	-	-	-	-
77- 5	3	400	Tetralin	135	-	-	-	-
			Dibenzyl	15	-	-	-	-
77- 6	3	400	Tetralin	75	Tetralin	60	Dibenzyl	15
77- 7	3	425	Tetralin	75	Tetralin	60	Dibenzyl	15
77- 8	3	450	Tetralin	75	Tetralin	60	Dibenzyl	15
77- 9	3	475	Tetralin	75	Tetralin	60	Dibenzyl	15
77-10	3	400	Tetralin	75	Purified Tetralin	60	Dibenzyl	15
77-11	3	425	Tetralin	75	Tetralin	60	Dibenzyl	15
77-12	3	450	Tetralin	75	Tetralin	60	Dibenzyl	15
77-13	3	475	Tetralin	75	Tetralin	60	Dibenzyl	15
77-14	3	437	Tetralin	75	Tetralin	60	Dibenzyl	15
77-15	3	463	Tetralin	75	Tetralin	60	Dibenzyl	15
77-16	3	437	Tetralin	75	Tetralin	60	Dibenzyl	1
77-17	3	463	Tetralin	75	Tetralin	60	Dibenzyl	15
77-18	3	450	Decalin	150	-	-	-	-
77-19	3	450	Decalin	75	Decalin	-	Dibenzyl	30
77-20	3	450	Decalin	75	Tetralin	75		
77-21	3	450	Decalin	75	Tetralin	60	Dibenzyl	15
77-22	3	450	Tetralin	75	Tetralin	75	Dibenzyl	30
77-23	3	450	Tetralin	50	Tetralin	50	Dibenzyl	50
77-24	1	450	Mesitylene (Incomplete)	144	-	-	-	-
			Dibenzyl	16				

Run No. HT-77-1

Run Conditions:

Temperature 400 °C

Charge	Reactor	Feed Tank
Dibenzyl		
Tetralin	150g	
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)				0	30	60	90	120		

Component	Wt %									
Benzene								1.27		
Toluene										
Ethyl Benzene										
Indane										
Dec. &/or M-Ind.						1.17		1.75		
Tetralin						98.37		96.63		
Naphthalene						0.46		0.62		
Dibenzyl										

Unknowns:

Light										
Medium										
Heavy										

Run No. HT-77-5

Run Conditions:

Temperature 400 °C

Charge	Reactor	Feed Tank
Dibenzyl	15g.	
Tetralin	135g	
Decalin		
MST		

Sample:	F	1	3	4	5	6	7	8	9	11 ~~10~~
Time (Min)					0	30	60	90	120	180

Component	Wt %									
Benzene	1.25	0.11								
Toluene	0.75	0.29								
Ethyl Benzene										
Indane										
Dec. &/or M-Ind.		0.87					1.52			
Tetralin	78.76	89.75	89.37				87.52			
Naphthalene		0.48								
Dibenzyl	18.81	9.02								

Unknowns:

Light		0.34								
Medium										
Heavy	0.16									

Run No. HT-77-6

Run Conditions:

Temperature 400 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene	0.43	0.41	0.46	0.11		0.50		0.19		
Toluene		0.13	0.21	0.33		0.55		1.09		
Ethyl Benzene										
Indane						0.11		0.17		
Dec. &/or M-Ind.	0.99	1.02	1.17	1.52		2.10		2.78		
Tetralin	93.12	97.16	97.79	96.41		85.47		80.54		
Naphthalene	0.40	0.71		0.76		1.53		1.36		
Dibenzyl	5.22	10.66	10.26	11.42		10.25		7.56		

Unknowns:

Light										
Medium										
Heavy		0.18								

Run No. HT-77-7

Run Conditions:

Temperature 425 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene	0.42	0.62	0.57	0.58		0.85		0.76		
Toluene		0.30	0.59	1.20		2.12		3.24		
Ethyl Benzene										
Indane				0.20		0.38		0.54		
Dec. &/or M-Ind.	1.05	1.47	2.07	3.32		5.49		7.30		
Tetralin	92.80	87.56	86.13	84.27		80.80		78.10		
Naphthalene	0.91	0.58	0.84	1.38		2.34		3.05		
Dibenzyl	5.31	9.47	9.81	9.05		7.87		6.12		

Unknowns:

Light										
Medium										
Heavy						0.16		0.19		

Run No. HT-77-8

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene		0.52	0.26							
Toluene	0.70	0.73	1.62					2.45		
Ethyl Benzene										
Indane		0.13						1.64		
Dec. &/or M-Ind.	1.21	2.37						16.48		
Tetralin	91.33	84.46						63.34		
Naphthalene	0.47	0.96	1.72					7.70		
Dibenzyl	6.05	8.68						1.54		

Unknowns:

Light										
Medium								0.35		
Heavy	0.24	0.14						0.49		

Run No. HT-77-9

Run Conditions:

Temperature 475 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene			1.37	0.19		0.26		0.35		
Toluene	2.22	2.64	6.88	9.43		11.02		11.40		
Ethyl Benzene	0.80			0.55		1.25		1.93		
Indane	0.23	0.49	1.22	2.18		3.57		4.75		
Dec. &/or M-Ind.	3.24	6.04	12.36	19.06		24.80		26.50		
Tetralin	84.09	81.19	69.19	58.25		49.11		36.15		
Naphthalene	1.33	2.49	5.31	8.36		12.00		15.24		
Dibenzyl	8.19	7.09	3.10	0.87		0.18		0.13		

Unknowns:

Light				0.32		0.95		[illegible]		
Medium			0.23	0.13		0.63		0.35		
Heavy		0.12	0.32	0.72		1.21		1.7[illegible]		

Run No. HT-77-10

Run Conditions:

Temperature 400 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene	0.81	0.91	0.55	0.54		0.49		0.77		
Toluene	0.24	0.17	0.23	0.31		0.32		0.66		
Ethyl Benzene										
Indane	0.17					0.15		0.17		
Dec. &/or M-Ind.	1.95	1.82	1.74	1.59		2.25		2.78		
Tetralin	87.26	87.60	87.35	84.13		86.34		84.94		
Naphthalene	1.07	0.61	0.67	0.82		1.06		1.36		
Dibenzyl	6.42	9.90	9.39	11.61		9.32		9.31		

Unknowns:

Light										
Medium										
Heavy										

Run No. H7-77-11

Run Conditions:

Temperature 425 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		
Component	**Wt %**									
Benzene										
Toluene		0.30	0.64	1.38	1.87	2.29	2.58	2.65		
Ethyl Benzene										
Indane			0.12	0.23	0.32	0.41	0.49	0.54		
Dec. &/or M-Ind.		1.55	2.27	3.72	4.92	6.06	7.00	7.73		
Tetralin		87.10	86.14	83.98	82.84	81.07	79.95	78.32		
Naphthalene		0.76	1.07	1.65	2.10	2.64	3.01	3.50		
Dibenzyl		9.59	9.24	8.47	7.82	7.04	6.62	6.57		
Unknowns:										
Light		0.70	0.52	0.57		0.32	0.69	0.45		
Medium										
Heavy					0.13	0.16	0.30	0.24		

Run No. HT-17-1

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene	0.11							illegible		
Toluene	0.16	0.73	illegible	illegible	illegible	illegible	illegible	8.48		
Ethyl Benzene					illegible	0.21	illegible	illegible		
Indane		illegible	illegible	illegible	0.98	1.21	1.41	1.61		
Dec. &/or M-Ind.	1.21	2.54	4.83	8.41	illegible	illegible	illegible	illegible		
Tetralin	illegible	illegible	illegible	76.77	72.40	illegible	65.36	illegible		
Naphthalene	illegible	1.04	2.01	illegible	illegible	illegible	illegible	illegible		
Dibenzyl	illegible	illegible	illegible	illegible	illegible	illegible	illegible	1.29		

Unknowns:

Light	illegible	illegible	illegible	illegible	illegible	illegible	0.75	illegible		
Medium										
Heavy	illegible		illegible	0.19	illegible	illegible	illegible	illegible		

Run No. HT-77-13

Run Conditions:

Temperature 475 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene			0.10	0.14	0.31	0.25	0.27	0.31		
Toluene	0.37	5.71	8.71	9.82	11.79	11.54	11.26	11.24		
Ethyl Benzene		0.14	0.30	0.68	0.89	1.20	1.50	1.79		
Indane	0.12	0.89	1.95	2.18	2.84	3.46	4.05	4.58		
Dec. &/or M-Ind.	2.93	9.70	14.23	19.08	22.15	24.16	25.48	26.11		
Tetralin	86.81	71.27	65.42	55.14	49.88	44.89	40.64	37.59		
Naphthalene	0.86	4.09	5.98	9.98	9.90	11.93	13.80	15.12		
Dibenzyl	8.61	9.95	2.20	0.79	0.31	0.21	0.18	0.14		

Unknowns:

Light	0.80	0.59	0.63	0.32	0.56	0.[illegible]	0.37	0.47		
Medium				0.13	0.50	0.60	0.80	0.88		
Heavy		0.17	0.98	1.74	0.97	1.[illegible]5	1.64	1.74		

Run No. HT-77-19

Run Conditions:

Temperature 437 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		
Component	**Wt %**									
Benzene	0.27									
Toluene	0.10	0.65	1.30	2.43	3.62	4.55	5.57	6.27		
Ethyl Benzene		0.62				0.10	0.13	0.16		
Indane		0.13	0.23	0.39	0.56	0.70	0.84	0.95		
Dec. &/or M-Ind.	1.27	2.19	3.50	5.41	7.43	8.99	10.36	11.45		
Tetralin	87.78	86.17	84.76	81.52	79.55	76.58	73.72	71.77		
Naphthalene	0.54	1.00	1.51	2.31	3.15	3.78	4.40	4.72		
Dibenzyl	10.03	9.23	8.47	7.30	6.17	5.15	4.14	3.52		
Unknowns:										
Light			0.23	0.51	0.35	0.53	0.55	0.52		
Medium										
Heavy				0.19	0.19	0.23	0.23	0.23		

Run No. HT-[illegible]-5

Run Conditions:

Temperature [illegible] °C

Charge	Reactor	Feed Tank
Dibenzyl		15[illegible]
Tetralin	75[illegible]	6[illegible]
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		

Component	Wt %									
Benzene	[illegible]				0.10	0.12	0.11	[illegible]		
Toluene	[illegible]	[illegible]	[illegible]	[illegible]	1.49	1.42	1.08	[illegible]		
Ethyl Benzene				0.24	[illegible]	0.61	0.61	0.85		
Indane		[illegible]	[illegible]	1.30	1.86	[illegible]	2.25	2.56		
Dec. &/or M-Ind.	[illegible]	[illegible]	[illegible]	[illegible]	17.51	18.65	[illegible]	[illegible]		
Tetralin	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	57.11	[illegible]	[illegible]		
Naphthalene	0.57	[illegible]	[illegible]	0.7	8.25	8.71	[illegible]	[illegible]		
Dibenzyl	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		

Unknowns:

Light										
Medium					[illegible]	0.12	[illegible]	[illegible]		
Heavy		[illegible]	0.19	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		

Run No. HT-77-16

Run Conditions:

Temperature 457 °C

Charge	Reactor	Feed Tank
Dibenzyl		15[illegible]
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	[illegible]	60	[illegible]	120	180	[illegible]		

Component	Wt %									
Benzene										
Toluene		0.69	1.22	2.30	3.24	4.[illegible]	4.81	5.[illegible]		
Ethyl Benzene							[illegible]	[illegible]		
Indane		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
Dec. &/or M-Ind.	1.25	[illegible]	3.46	5.60	7.59	[illegible]	10.55	11.07		
Tetralin	[illegible]	[illegible]	[illegible]	[illegible]	79.10	76.61	[illegible]	73.14		
Naphthalene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.58	4.37	4.[illegible]		
Dibenzyl	[illegible]	[illegible]	8.85	1.66	[illegible]	5.[illegible]	[illegible]	[illegible]		

Unknowns:

Light										
Medium										
Heavy				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		

Run No. HT-77-17

Run Conditions:

Temperature 463 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	5	15	30	60	90	120	150	180		

Component	Wt %									
Benzene					0.12	0.14	0.15	0.18		
Toluene	0.37	2.31	4.81	7.98	10.13	10.40	10.32	10.91		
Ethyl Benzene				0.29	0.400	0.52	0.63	0.78		
Indane		0.33	0.71	1.28	1.72	1.98	2.24	2.55		
Dec. 6/or M-Ind.	1.91	4.69	8.37	13.29	16.98	17.88	19.21	20.54		
Tetralin	86.92	83.01	76.35	67.91	61.68	59.17	56.43	53.37		
Naphthalene	0.74	1.90	3.63	5.80	7.19	7.97	8.99	9.81		
Dibenzyl	9.73	7.49	5.34	2.61	1.29	0.95	0.71	0.46		

Unknowns:

Light	0.33	0.27	0.62	0.40	0.91	0.26	0.48	0.52		
Medium						0.10	0.12	0.13		
Heavy			0.18	0.49	0.59	0.63	0.71	0.74		

Run No. HT-77-18

THERMAL STABILITY OF DECALIN

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		
Tetralin		
Decalin	150g	
MST		

Tetralin not resolved from Decalin

Sample:	1	2	3	4	5	6	7	8	9	10 11
Time (Min)			0	1	15	30	60	90	120	180

Component	Wt %									
Benzene										
Toluene		0.10				1.52	2.14		3.25	4.19
Ethyl Benzene										
Indane										
Dec. &/or M-Ind.		99.08				92.14	89.78		84.14	79.09
Tetralin										
Naphthalene		0.48				0.72	0.75		1.01	1.40
Dibenzyl										

Unknowns:

Light		0.34				1.23	1.25		2.14	2.42
Medium						3.94	5.33		7.86	9.43
Heavy						1.17	0.74		1.60	2.94

Run No. HT-77-19

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		30g
Tetralin		
Decalin	75g	45g
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene										
Toluene	0.55	4.98	8.46	12.89	16.15	17.99	20.96	19.58		
Ethyl Benzene										
Indane	0.78	2.29	2.86	3.37	3.58	3.60	3.64	3.83		
Dec. &/or M-Ind.	78.38	73.07	68.09	62.27	58.83	57.28	55.51	55.56		
Tetralin										
Naphthalene		0.18	0.24	0.52	0.67	0.87	1.13	1.39		
Dibenzyl	19.42	14.50	12.32	9.96	7.08	5.42	3.72	3.57		

Unknowns:

Light		1.20	1.93	2.74	2.98	3.30	3.53	3.10		
Medium	0.67	2.45	3.81	5.29	6.33	6.98	7.74	8.12		
Heavy	0.21	1.39	2.19	3.46	4.39	4.57	4.26	4.86		

Run No. HT-77-20

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		
Tetralin		75g
Decalin	75g	
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		
Component	**Wt %**									
Benzene										
Toluene	0.32	0.41	0.48	0.79	1.04	1.28	1.42	1.82		
Ethyl Benzene										
Indane	0.50	0.73	0.91	0.72	1.53	1.81	2.04	2.38		
Dec. &/or M-Ind.	48.06	48.21	48.58	49.76	50.16	50.75	50.84	51.58		
Tetralin	49.92	48.81	48.55	45.69	43.92	41.62	40.09	37.75		
Naphthalene	0.27	0.55	0.78	1.13	1.57	2.08	2.63	3.15		
Dibenzyl										
Unknowns:										
Light	0.61	0.93	0.38	0.79	1.25	1.02	1.10	0.96		
Medium	0.18	0.25	0.32	0.57	0.79	1.02	1.32	1.62		
Heavy	0.14	0.10			0.23	0.43	0.57	0.73		

Run No. AT-77-21

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin		60g
Decalin	75g	
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene		0.11	0.19	0.35	0.48	0.59	0.80	0.91		
Toluene	0.38	2.59	4.56	7.22	8.56	9.47	11.04	11.58		
Ethyl Benzene		0.12	0.22	0.39	0.52	0.63	0.80	0.92		
Indene	0.53	1.25	0.93	1.08	1.21	1.32	1.45	1.48		
Dec. &/or M-Ind.	48.58	49.09	49.67	49.48	48.95	48.94	48.59	48.54		
Tetralin	40.39	36.93	33.91	29.77	27.32	25.51	23.10	21.86		
Naphthalene	0.46	1.70	2.56	4.13	5.26	6.13	6.78	7.49		
Dibenzyl	9.37	7.69	5.71	3.65	2.74	1.95	1.21	0.85		

Unknowns:

Light			0.47	0.88	0.98	0.89	1.32	0.84		
Medium	0.17	0.38	1.30	2.24	2.67	3.08	3.48	3.89		
Heavy	0.11	0.14	0.48	0.81	1.31	1.47	1.93	1.63		

Run No. AT-77-22

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		30g
Tetralin	75g	45g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene										
Toluene		3.48	7.58	13.74	15.96	17.79	17.50	18.31		
Ethyl Benzene										
Indane		0.41	0.77	1.32	1.66	1.96	2.10	2.25		
Dec. &/or M-Ind.	1.25	4.75	7.81	12.07	14.77	16.42	17.15	17.55		
Tetralin	69.13	72.44	67.16	57.96	52.64	48.05	46.06	44.62		
Naphthalene	10.55	2.60	4.52	7.01	9.31	10.58	12.02	12.38		
Dibenzyl	16.94	15.71	11.09	5.98	4.40	2.67	2.18	1.70		

Unknowns:

Light		0.23	0.54	0.93	0.90	0.71	0.79	0.99		
Medium			0.15	0.34	0.48	0.75	0.91	0.95		
Heavy	2.13	0.39	0.37	0.64	0.38	1.06	1.28	1.25		

Run No. HT-77-23

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		50g
Tetralin	50g	50g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	CHARGE TANK FEED 9	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene		0.10	0.16	0.28	0.34	0.38	0.41	0.47		
Toluene	0.46	5.66	10.87	18.67	23.35	25.10	26.78	29.28	0.10	
Ethyl Benzene	0.29	0.15	0.28	0.54	0.76	0.90	1.04	1.20		
Indene		0.46	0.78	1.26	1.61	1.81	1.98	2.13		
Dec. &/or M-Ind.	1.21	4.41	6.58	9.70	11.87	12.96	13.66	14.14	0.45	
Tetralin	64.72	58.75	54.53	44.57	39.92	35.75	34.13	31.97	50.62	
Naphthalene	0.57	3.29	5.26	8.98	11.81	14.01	15.04	14.80	0.20	
Dibenzyl	32.43	25.61	20.63	13.67	8.49	6.43	4.57	3.14	48.13	

Unknowns:

Light		0.86		0.69	0.25	0.34	0.20	0.67		
Medium						0.12	0.13	0.14		
Heavy	0.32	0.70	0.90	1.63	1.60	2.20	2.06	2.05	0.50	

Run No. HT-77-24

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl	16g	
Tetralin		
Decalin		
MST	144 g	

Sample:	1	2	3	4	MST check purity 8F	8O	7	8	9	10
Time (Min)		0		2						

Component	Wt %									
Benzene					0.13					
Toluene	0.14			0.74		0.23				
Ethyl Benzene										
Indane										
Dec. &/or M-Ind.										
Tetralin	0.58	0.60		0.79		0.78				
Naphthalene										
Dibenzyl	9.07	9.17		9.12		8.30				
MST	90.21	90.23		88.44	99.87	90.70				

Unknowns:

Light										
Medium				0.10						
Heavy				0.81						

Run No. HT-77-31

Run Conditions:

Temperature 450 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	09	10
Time (Min)	0	15	30	60	90	120	150	180		

Component	Wt %									
Benzene	0.57	0.46	0.78	0.55	0.67	0.47	0.10	0.13		
Toluene	0.89	0.92	2.59	5.06	7.01	8.45	8.80	9.72	1.13	
Ethyl Benzene				0.13	0.22	0.31	0.39	0.50		
Indane		0.21	0.43	0.87	1.21	1.47	1.69	1.91		
Dec. &/or M-Ind.	1.28	2.71	5.09	9.39	12.44	14.66	16.48	17.79	12.11	
Tetralin	86.57	84.98	80.43	73.63	68.44	64.27	61.12	58.43	86.94	
Naphthalene	0.68	1.46	2.52	4.59	5.96	7.02	8.21	8.47	0.61	
Dibenzyl	9.65	8.65	6.94	4.67	2.78	1.85	1.22	0.72	9.7	

Unknowns:

Light							0.38	0.50		
Medium		0.85	0.88	0.91	0.93	0.95		1.24		
Heavy	0.55	0.27	0.33	0.21	0.34	0.56	0.65	0.60	0.90	

Run No. HT-76-8

Run Conditions:

Temperature 475 °C

Charge	Reactor	Feed Tank
Dibenzyl		15g
Tetralin	75g	60g
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	10
Time (Min)	0	10	40	70	100	130	160	275		

Component	Wt %									
Benzene								0.19		
Toluene								8.98		
Ethyl Benzene								0.94		
Indene								3.02		
Dec. 6/or M-Ind.								22.65		
Tetralin								49.49		
Naphthalene								12.90		
Dibenzyl								0.27		

Unknowns:

Light										
Medium								0.30		
Heavy								1.31		

Run No. HT-76-13

Run Conditions:

Temperature 400 °C

Charge	Reactor	Feed Tank
Dibenzyl	30g	
Tetralin	120g	
Decalin		
MST		

Sample:	1	2	3	4	5	6	7	8	9	11 ~~10~~
Time (Min)					0	30	60	90	120	180

Component	Wt %									
Benzene										
Toluene							19.67		27.26	15.31
Ethyl Benzene										
Indane										
Dec. &/or M-Ind.			0.89		1.29					
Tetralin			77.30		80.74		77.31		71.65	82.70
Naphthalene			0.76		0.19		0.18		0.36	0.10
Dibenzyl			19.64		16.77		2.11		0.26	0.40

Unknowns:

Light										
Medium										
Heavy			1.91		0.99		0.73		0.46	1.24