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ORGANIC COOLANT RECLAMATION
THIRD QUARTERLY PROGRESS REPORT

June 15, 1959 - September 15, 1959

Contract AT(11-1)-705
United States Atomic Energy Commission

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October 15, 1959

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FOREWARD

This is the Third Quarterly Progress Report on Contract AT(11-1)-705, Organic Coolant Reclamation. The research reported has been done by the Monsanto Chemical Company, Research and Engineering Division, Special Projects Department, Everett Station, Boston 49, Massachusetts. The Monsanto Project Director is R. J. Wineman. The Technical Representative for the United States Atomic Energy Commission is Mr. Don E. Reardon of the Chicago Operations Office. The period of research reported is June 15, 1959 to September 15, 1959.

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ABSTRACT

In the third quarter of research on organic coolant reclamation, reaction conditions which show promise as reclamation procedures have been found in two major areas of investigation. In the study of hydrocracking of polyphenyls, ten catalysts have shown activity. One of these, a platinum on alumina, gives a very clean reaction with high conversions per pass and high yields in the model systems under study. The redistribution reaction in the model case of benzene and p-terphenyl gave reproducible results with high enough conversion to be of interest for reclamation.

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SECTION I.

INTRODUCTION

This research program was initiated to find a way to lower the coolant costs of the organic moderated reactor. To date, a number of model chemical systems have been examined to determine which might function as a practical coolant reclamation method.

In this Third Quarterly Progress Report, the status of the work is given in the two areas of principal investigation: hydrocracking and the redistribution reaction. In both areas reaction conditions have been found which appear promising as bases for coolant reclamation.

SECTION II.

VAPOR PHASE CATALYTIC HYDROCRACKING STUDIES (D. A. Scola)

INTRODUCTION

Vapor phase catalytic hydrocracking studies on model compounds such as biphenyl, terphenyls and p-quaterphenyl are being made in an effort to cleave the carbon-carbon bond between phenyl rings. Catalysts which can bring about this conversion will be used with spent coolants in an effort to produce lower boiling, more soluble, less viscous polyphenyls or alkyl substituted polyphenyls.

CONCLUSIONS

Hydrogenolysis of the carbon-carbon bond between phenyl rings can be accomplished.

Experiments with various catalysts on biphenyl and terphenyls at high temperatures have shown that catalysts having both hydrogenation-dehydrogenation and acid activity are responsible for this type of reaction.

Ten catalysts have exhibited activity for hydrocracking of polyphenyls. Seven are nickel on active supports (alumina, kieselguhr); two are platinum on alumina; one is a cobalt-molybdena-alumina. The active catalysts are:

Girdler T-310	} Nickel Catalysts
Girdler T-312	
Girdler T-316	
Girdler G-52	
Nicomo 1 (Davidson Hydrodesulfurization catalyst)	
Nicomo 2 (Davidson Hydrodesulfurization catalyst)	
Girdler T-680	
Houdry Platinum on Alumina	
1% Platinum on Activated Alumina	
Girdler G-35B (Co-Mo-Al)	

In preliminary runs conversions and yields per pass with the platinum alumina catalyst were significantly higher than those obtained with the other catalysts tested. Furthermore, these yields and conversions (25-60%) are in the range for a practical reclamation process.

Increasing the temperature from 450°C to 550°C increases the hydrocracking activity of 1% platinum on activated alumina. Cracking does not occur in the absence of hydrogen with this catalyst at 550°C and with longer contact times. A comparison of the hydrocracking activity of 1% platinum on activated alumina with activated alumina containing no active metal shows that platinum is essential for this reaction.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of the hydrocracking of biphenyl and m-terphenyl with various nickel catalysts at atmospheric pressure. Runs 47 and 49 (Table 1) show that Nicomo 1 and 2 hydrodesulfurization catalysts are ineffective in causing a hydrocracking reaction. No liquid products were isolated. However, the same catalysts have shown hydrocracking and isomerization activity with m-terphenyl (Table 2, runs 48, 50, 51, 52).

TABLE 1
HYDROCRACKING OF BIPHENYL WITH VARIOUS
CATALYSTS AT ATMOSPHERIC PRESSURE

Run No. Wt. in g.	Catalyst	Temp. °C	Con- tact Time sec.	Vol. H ₂ Vol. 00	Products	
					Solid	Liquid
47 5.12	Nicomo 1 Davidson Hydro- desulfurization cat. SMR-55-6381	450	16	1.7	2.4 g. biphenyl	none
49 5.13	Nicomo 2 Davidson Hydro- desulfurization cat. SMR-55-6381	465	18.7	2.6	4.99 g. biphenyl	none
53 6.46	Girdler T-680 Nickel (11%) on Kaolin	455	11.7	1.5	6.05g. biphenyl	benzene-97.6% toluene- 2.4%
54 5.39	Girdler T-316 50% NiO on Kieselguhr	445	17.2	2.8	0.60 g. biphenyl	none*
55 5.78	Girdler T-316	452	16.8	2.6	none	none*

* CH₄ and CO₂ gas identified as off-gases.

TABLE 2

HYDROCRACKING OF m-TERPHENYL WITH VARIOUS
CATALYSTS AT ATMOSPHERIC PRESSURE

Run No. Wt. in g.	Catalyst	Temp. °C	Con- tact Time sec.	Vol. H ₂ Vol. m-Ø ₃	Products	
					Solid	Liquid
48 6.20	Nicomo 1 Davidson Hydro- desulfurization cat. SMR 55-6381	480	21	4.2	2.30g. o-terphenyl- 7.8% m-terphenyl-67.3% p-terphenyl-24.6%	none
50 6.09	Nicomo 2 Davidson Hydro- desulfurization cat. SMR 55-6381	450	17.5	3.1	4.73g. o-terphenyl- 7.1% m-terphenyl-78.0% p-terphenyl-14.9%	none
51 5.82	Nicomo 2	565	18.3	3.2	3.67g. o-terphenyl- 5.6% m-terphenyl-71.6% p-terphenyl-22.4%	0.26 g. organic liquid
52 5.99	Nicomo 2	578	14.5	4.3	4.73g. o-terphenyl- 5.7% m-terphenyl-63.0% p-terphenyl-23.7%	benzene-99% toluene- 3%
56 5.79	Girdler T-680 Nickel (11%) on Kaolin	468	13.4	2.8	4.70g. biphenyl - 6.8% o-terphenyl- 7.8% m-terphenyl-60.0% p-terphenyl-29.0%	hexane- 74% benzene-20% toluene-5.1%
57 5.81	Girdler T-680	518	11.3	3.6	4.89g. biphenyl- 5.2% o-terphenyl- 5.0% m-terphenyl-61.7% p-terphenyl-27.4%	none
58 5.92	Girdler T-680	505	13.6	3.8 ≈10% by volume HBr	4.90g. biphenyl- 2.3% o-terphenyl- 9.4% m-terphenyl-66.6% p-terphenyl-18.2%	none
59 5.78	Girdler T-310 Nickel oxide on activated alumi- na (10-12% Nickel)	495	14.8	4.8	4.80g. biphenyl- 13.7% m-terphenyl-71.9% unknowns- 15.0%	none
60 5.80	Gridler T-310	508	14.5	4.4	4.31g. biphenyl- 12.9% m-terphenyl-65.9% unknowns- 21.0%	benzene-69.1% toluene-26.7% unknown- 4.1%
61 5.69	Girdler T-310	500	11.5	4.3 H ₂ mØ ₃ 1.4 iso- butane mØ ₃	4.79g. biphenyl- 6.8% m-terphenyl-76.6% unknowns- 17.0%	benzene-58.5% toluene-34.0% unknown- 6.0%

Girdler T-680 also exhibited isomerization activity and some hydrocracking activity (run 53, Table 1; runs 56, 57, 58, Table 2). Little or no benzene formed. These catalysts are dual-function catalysts. They possess both hydrogenation-dehydrogenation activity and acid activity. The acid activity is probably responsible for the isomerization of m-terphenyl to o- and p-terphenyl which has resulted. Girdler T-310 demonstrated cracking activity, but cracking occurred not only at the bond between phenyl rings but in the ring. Therefore, this catalyst and Girdler T-316 are not showing selective hydrocracking activity of the bonds between phenyl rings.

As was shown in a previous report (Second Quarterly Progress Report) Girdler T-316 has a destructive effect on biphenyl, m- and p-terphenyl at long contact times. It has been found that the gases produced by hydrocracking biphenyl with this catalyst (runs 54 and 55) were largely methane and carbon dioxide. The gases were trapped using liquid air and analyzed by vapor phase chromatography and infrared spectroscopy. Both analytical techniques showed the presence of methane and carbon dioxide with methane present in the greatest concentration.

Several experiments have been run to attempt to promote hydrogenolysis of the bond between phenyl rings by the use of potential sources of hydrogen atoms. In these runs the free radical hydrogen atom donors, hydrogen bromide and isobutane, were used in addition to hydrogen.

Hydrogen bromide, in addition to hydrogen, was used in run 58 (Table 2, Girdler T-680 catalyst). A comparison of this run with runs 56 and 57 (hydrogen present, hydrogen bromide absent) indicates that hydrogen bromide has little or no effect on the course of the reaction or on the reaction product. This preliminary run was not sufficiently conclusive to rule out the use of hydrogen bromide in other experiments.

Isobutane was used in run 61 as a source of more easily available hydrogen, in addition to hydrogen gas, in an effort to bring about the hydrocracking reaction. A comparison of this run (61) with runs 59 and 60 shows that isobutane does not alter the course of the reaction. The product composition was essentially the same in all three runs.

Additional experiments with hydrogen bromide and isobutane are warranted before any definite conclusions can be drawn. However, the results indicate that this hydrocracking reaction does not occur by a free radical mechanism. The results with dual-function catalysts do indicate that hydrogenolysis of this carbon-carbon bond between phenyl rings occurs by means of a carbonium ion mechanism. More research in both areas will serve to strengthen these postulates.

Girdler G-35B (Cobalt-Molybdena-Alumina) was also screened for its potential use as a catalyst. The results of these runs are shown in Table 3. The solid and liquid product composition of runs 85 and 86 show that isomerization of m-terphenyl to o- and p-terphenyl is the major reaction occurring. It is accompanied by hydrocracking and a small amount of ring rupture. The melting points of the solids obtained from runs 85 and 86 indicate that a definite mixture prevails in each case.

TABLE 3

HYDROCRACKING OF POLYPHENYLS WITH GIRDLER G-35B
CATALYST AT ATMOSPHERIC PRESSURE

Run No.	Wt. in g. (Ø) _n	Con- tact Time sec.	Vol. H ₂ Vol. (Ø) _n	Temp. °C	Products	
					Solid	Liquid
83 7.94 ØØ		9.5	2.5	556	7.8 g. biphenyl	0.05 g. benzene-97% toluene- 2.6%
84 7.96 ØØ		9.3	3.8	580	7.23 g. biphenyl	0.1 g. benzene-97% toluene- 2.6%
85 7.93 mØ ₃		11.0	5.4	575	5.66 g. biphenyl- 10.7% o-terphenyl- 2.8% m-terphenyl-59.5% p-terphenyl-27.0% m.p. 61-150°C	0.1 g. benzene-95% toluene- 4.2% unknown- 0.7%
86 7.80 mØ ₃		10.5	3.7	559	6.38 g. biphenyl- 3.0% o-terphenyl- 5.5% m-terphenyl-73.0% p-terphenyl-19.4% m.p. 61-152°C	0.13 g. benzene-94.5% toluene- 4.8% unknown- 0.7%

One percent platinum on activated alumina selectively causes hydrogenolysis of the carbon-carbon bond between rings in polyphenyl systems. The data shown in Tables 4, 5 and 6 show the role of the catalyst in this reaction.

The equations below give the probable course of the reactions. Biphenyl hydrocracks to give benzene only. The terphenyls can be reduced to biphenyl and benzene or benzene only.

Finally, p-quaterphenyl can hydrocrack to p-terphenyl and benzene, biphenyl or benzene only. Secondary hydrocracking reactions of the biphenyl and terphenyl produced would increase the amount of benzene formed. p-Terphenyl (traces), biphenyl, and benzene were among the products of reaction 3. The basis for percentage yield calculations was therefore chosen arbitrarily. These points were recognized and the calculations shown are reported for comparative purposes only. Future work using larger amounts of starting materials and changing other variables will inevitably alter the data.

TABLE 4

HYDROCRACKING OF POLYPHENYLS AT 560-595°C WITH
1% PLATINUM ON ACTIVATED ALUMINA AT ATMOSPHERIC PRESSURE

Run No.	Con- tact Wt. in g. (Ø)n	Time sec.	Vol. H ₂ Vol. (Ø)n	% Con- ver- sion per pass	% Yield per pass	Products	
						Solid	Liquid
62	10.2	2.5	40	37	5.14g	biphenyl-94%	benzene-99%
8.08					5.14g	unknown- 6%	traces toluene
63	10.3	2.8	27	35	6.08g	biphenyl-97%	benzene-99%
8.02					6.08g	unknown- 3%	traces toluene
64	11.5	4.1	55	55	4.18g	biphenyl-27.6%	benzene-99%
6.28					4.18g	m-terphenyl- 64.8%	traces toluene

TABLE 4

(Continued)

Run No.	Wt. in g. ($\emptyset$) _n	Con-tact Time sec.	Vol. H ₂ Vol. ($\emptyset$) _n	% Conversion per pass	% Yield per pass	Products		
						Solid		Liquid
65	6.18	11.5	4.7	45	48	4.79g	biphenyl -22.3%	0.96g benzene-99%
m- $\emptyset$ ₃						4.79g	m-terphenyl-71.6%	0.90g traces toluene
66	6.06	10.5	2.9	44	38	4.57g	biphenyl -13.4%	0.81g benzene-99%
p- $\emptyset$ ₃						4.57g	p-terphenyl-75.0%	0.81g traces toluene
67	6.13	11.7	4.7	30	35	5.12g	biphenyl -14.3%	0.72g benzene-99%
p- $\emptyset$ ₃						5.12g	p-terphenyl-75.0%	0.72g traces toluene
68	3.07	12.1	7.2	66	69	1.50g	biphenyl -25.3%	0.54g benzene-99%
p- $\emptyset$ ₄						1.50g	p- $\emptyset$ ₄ -70.0%	0.54g traces toluene
69	5.98	12.0	5.6	Incom- plete	62	3.92g	Incomplete	0.94g benzene-99%
p- $\emptyset$ ₄						3.92g		0.94g traces toluene

$$* \% \text{ Conversion/pass} = \frac{\text{moles of starting material reacted}}{\text{moles of starting material}} \times 100$$

$$** \% \text{ Yield/pass} = \frac{\text{moles product (benzene)}}{\text{moles starting material}} \times 100$$

The temperature of each run in Table 4, exclusive of runs 68 and 69, was about 560°C. Runs 68 and 69 were done at 595°C so that the boiling point of p-quaterphenyl would be exceeded in each case. The temperature of each run in Table 5 was about 450°C. A comparison of the data in both tables shows clearly that a high temperature favors the hydrocracking reaction with this catalyst at atmospheric pressure.

TABLE 5

HYDROCRACKING OF POLYPHENYLS AT 450°C WITH 1% PLATINUM
ON ACTIVATED ALUMINA AT ATMOSPHERIC PRESSURE

Run No. Wt. in g. (Ø) _n	Con- tact Time sec.	Vol. H ₂ Vol. (Ø) _n	% Con- ver- sion per pass	% Yield per pass	Products	
					Solid	Liquid
70 8.10 ØØ	10.4	2.4	2.2	6.9	7.92g biphenyl-97.9% unknown- 2.0%	0.28g benzene-99% traces toluene
71 8.07 ØØ	10.3	2.3	2.1	5.2	7.90g biphenyl-	0.21g benzene-99% traces toluene
72 5.98 m-Ø ₃	12.3	4.9	7.2	7.9	5.56g biphenyl - 3.4% m-terphenyl-92.5%	0.16g benzene-99% traces toluene
73 6.07 m-Ø ₃	11.1	3.1	8.4	4.8	5.16g biphenyl - 3.4% m-terphenyl-92.5%	0.10g benzene-99% traces toluene

The dependence on the presence of hydrogen for this reaction is illustrated by the data in Table 6. Biphenyl and m-terphenyl with 1% platinum on activated alumina at 550°C and in the absence of hydrogen were not cracked to lower-boiling components. Unchanged biphenyl and m-terphenyl were recovered and no benzene was formed. A comparison of these data with Table 4 shows clearly the expected requirement for hydrogen in this hydrocracking reaction.

TABLE 6

CRACKING OF POLYPHENYLS AT 550°C WITH 1% PLATINUM ON
ACTIVATED ALUMINA AT ATMOSPHERIC PRESSURE*

Run No. Wt. in g. (Ø) _n	Contact Time sec.	Solid Product
80 7.79 ØØ	16.6	7.01 g. biphenyl recovered
81 7.87 ØØ	18.5	7.78 g. biphenyl recovered
82 8.16 mØ ₃	15.0	7.6 g. m-terphenyl recovered

*Hydrogen absent in these runs

Hydrocracking studies were made using activated alumina containing no active metal as the catalyst. The data shown in Table 7 illustrate the fact that although alumina caused hydrocracking to a small degree, the reaction is not selective since ring rupture has occurred. Furthermore, the conversions and yields, compared with those of Table 4 in which the comparable reaction conditions were used, are extremely small.

TABLE 7
HYDROCRACKING OF POLYPHENYLS WITH ACTIVATED ALUMINA
AT ATMOSPHERIC PRESSURE

Run No. Wt. in g. (Ø) _n	Temp. °C	Con- tact Time, sec.	Vol. H ₂ Vol. (Ø) _n	Products	
				Solid	Liquid
74 8.23 ØØ	552	9.5	2.3	8.0 g. biphenyl	benzene- 92.0% cyclohexane-6.7% toluene -1.1%
75 7.99 ØØ	557	10.1	2.3	7.90g. biphenyl	benzene -92.0% cyclohexane-6.7% toluene -1.1%
76 5.97 m-Ø ₃	555	10.8	3.9	5.9 g. m-terphenyl-97% biphenyl -0.9%	benzene-93.7% toluene- 6.3%
77 6.00 m-Ø ₃	555	10.8	3.9	5.9 g. m-terphenyl-96% biphenyl -1.0%	benzene-94% toluene- 6%
78 5.84 p-Ø ₃	560	10.5	3.4	2.59 g. solid (analysis incom- plete) m.p. 211-216°C	0.06 g. organic liquid
79 9.70 p-Ø ₃	558	12.1	7.6	11.2* g. solid (analysis in- complete) m.p. 211-214°C	benzene-97.5% toluene- 2.5%

* Some solid from run 78 included.

To summarize, the data on Tables 4 and 5 show that an increase in temperature increases the effectiveness of the catalyst. This results in a greater yield of product. The data in Table 4 and 6 show that hydrogen is necessary for reaction to occur; in its absence, no cracking occurs. Finally, the data of Table 4 and 7 show clearly that alumina alone is not nearly as effective as a hydrocracking catalyst as platinum on alumina.

EXPERIMENTAL

In addition to the horizontal flow system (see First Quarterly Progress Report, pp 6-7), a vertical flow system was constructed to increase the efficiency of catalyst screening. A typical run using the horizontal flow system is described in the Second Quarterly Progress Report. A typical run using the vertical flow system (see First Quarterly Progress Report, pp 12-13) will be described briefly. In each experiment, the preheater and furnace temperatures were recorded using chromel-alumel thermocouples attached to a Brown Elektronik Multipoint Recorder.

The reaction tube is charged with the desired amount of catalyst calculated to give a certain contact time. The portion of the tube containing no catalyst is filled with inert material such as porcelain chips and the apparatus is assembled as shown in Figures 3 and 4 (First Quarterly Progress Report). A sample of biphenyl or other polyphenyl is placed in the pressure equalizer addition funnel (wrapped with electrical heating tape) and the sample is melted and added dropwise after treatment of the catalyst as described below.

The system is flushed out with nitrogen and the catalyst is brought to the desired temperature in the presence of nitrogen. The catalyst is "activated" or reduced by passing hydrogen over it for about one hour or until there appears to be no more hydrogen uptake as shown by the exit flowmeter or by absence of water formation. At this point, the sample is melted and added dropwise to the reactor tube at a definite dropping rate. After addition of the sample is completed, the system is allowed to operate for one-half hour and is then allowed to cool to room temperature in the presence of a stream of nitrogen. The weight of products collected in each receiver is determined and the solid and liquid products are analyzed quantitatively by vapor phase chromatography and infrared spectroscopy where applicable.

FUTURE PLANS

1. Continued catalyst screening is planned for the hydrocracking reaction.
2. Platinized porcelain will be used for the hydrocracking reaction to compare with other variables studied and discussed in this report.
3. An apparatus for a pressurized flow system for hydrocracking studies will be designed.
4. Hydrocracking studies on spent coolant high boiler fractions using proven active catalysts will be started.
5. Investigation of hydrocracking at elevated temperatures (600-800°C) with and without catalysts is planned.

SECTION III
REDISTRIBUTION REACTION STUDIES
(J. S. Adams)

INTRODUCTION

The redistribution reaction of benzene and higher polyphenyls to produce lower molecular weight polyphenyls is a potential reclamation method for high boiler residue. In work reported previously (Second Quarterly Progress Report), lack of reproducible results prevented our drawing any conclusions on this method. In this quarter, satisfactory operation was achieved.

Experimental work has been done on the redistribution reaction using the conversion of benzene and m-terphenyl to biphenyl as a model. Reaction conditions best suited for this conversion have been investigated. In addition, the reactant ratio of benzene to m-terphenyl was varied to determine what effect, if any, the use of a smaller benzene-to-terphenyl ratio has on the conversion products. Finally, some exploratory work was done with pure m-terphenyl in the presence of a small amount of trans-decalin (which acted as a hydrogen donor and free radical initiator) to determine the effects of thermally cracking this system under conditions favorable for a redistribution reaction.

CONCLUSIONS

A particularly favorable temperature and contact time for the redistribution reaction between m-terphenyl and benzene over porcelain berl saddles to produce biphenyl are 800°C and 15 seconds, respectively. Lower temperatures and longer contact times at these temperatures failed to produce appreciable quantities of biphenyl while temperatures higher than 800°C brought about excessive carbonization of the reaction products.

Runs were made on mixtures of benzene and m-terphenyl in which the weight percent of m-terphenyl was varied between 10 and 50 in 10 weight percent increments. Carbonization increased as the weight percent terphenyl was increased and only very slight changes were noted in the production of biphenyl.

When molten m-terphenyl and trans-decalin, in a 97.5 to 2.5 weight percent ratio, was passed over porcelain berl saddles at 800°C and 15 seconds contact time, much carbonization was noted. However, benzene and biphenyl were both formed in appreciable quantities. Additional quantitative data will be obtained on this reaction.

RESULTS AND DISCUSSION

Data presented in Tables 8 and 9 are compilations of runs made at 800°C and 15 seconds contact time. Two factors were studied in this series of experiments:

- (1) the effect of carbon disulfide (0.5 wt. percent) on the production of biphenyl, and

- (2) the contribution of the pyrolysis reaction of pure benzene to the overall yield of biphenyl produced via the redistribution reaction.

Runs 6989 (with carbon disulfide) and 6982 (without carbon disulfide) show less than a one percent difference in conversion to biphenyl. Runs on the pyrolysis of benzene alone (for example, 6995, in the presence of carbon disulfide and 6978, in carbon disulfide's absence) show that the redistribution reaction accounts for from 25-38% of the biphenyl produced. The presence of carbon disulfide seems to enhance the pyrolysis reaction of benzene to a greater degree than it does the redistribution reaction between benzene and m-terphenyl.

TABLE 8

REDISTRIBUTION REACTION BETWEEN m-TERPHENYL AND BENZENE
(800°C, 15 seconds contact time; 3 grams m-terphenyl,
27 grams benzene)

<u>Exp. No.</u>	<u>Wt. % ØØ produced</u>
6989 (CS ₂)	19.5
6993 (CS ₂)	19.2
6973 (CS ₂)	19.3
6982	18.7
6987	17.9

TABLE 9

PYROLYSIS OF BENZENE TO BIPHENYL
(800°C, 15 seconds contact time;
27 grams benzene)

<u>Exp. No.</u>	<u>Wt. % ØØ formed</u>
6995 (CS ₂)	14.5
6967 (CS ₂)	14.2
6978	11.7
6985	11.9

Runs in which the weight percent of m-terphenyl in the m-terphenyl benzene reaction mixture was increased from 10 to 50 percent are presented in Table 10. Runs 4367 and 4369 were familiarization runs. Run 4367 had about an 18-second contact time, and three times the usual amount of starting materials was used. The yield of biphenyl produced in this run compares favorably with that formed in previous experiments run under similar conditions of temperature and contact time. Run 4369 showed a rather low biphenyl production but a known instrument difficulty was responsible.

Runs in which the weight percent of m-terphenyl employed in the reaction mixture was increased in increments of 10 weight percent to a maximum of 50 weight percent show only small variations in weight percent of biphenyl produced. The data in Table 10 also reveal the increased amount of carbonization evident with increasing m-terphenyl content in the reaction mixture.

Included also in Table 10 are two runs (4380 and 4381A) in which molten m-terphenyl (97.5 wt. %) and trans-decalin (2.5 wt. %) were passed over porcelain berl saddles under a nitrogen atmosphere at 800°C and approximately 15 seconds contact time. Because of some clogging of the reaction tube, it is difficult to draw conclusions regarding the quantitative yield of lower boiling materials in these reactions. However, considerable amounts of benzene and biphenyl were produced in both reactions together with extensive carbonization. It would appear that if the redistribution reaction goes through a free radical mechanism the presence of a free radical initiator and hydrogen donor (such as decalin, tetralin, etc.) should enhance the production of lower boiling materials (biphenyl or benzene in the case of the model reaction currently under study). Reactions to check this theory quantitatively will be carried out with m-terphenyl both in the presence and absence of benzene.

TABLE 10

REDISTRIBUTION REACTION BETWEEN m-TERPHENYL AND BENZENE-
EFFECT OF REACTANT RATIO (800°C, 15 seconds contact time)

Starting Materials						
Exp. No.	Wt. m- $\phi\phi\phi$ g.	Wt. ϕ H g.	Wt. % m- $\phi\phi\phi$	Total wt. Recovered (g.)	Analysis, Wt. % $\phi\phi$	m- $\phi\phi\phi$
4367	10.0	90.0	10.0	P=86.4 T= 5.3 C= 0.7	19.9	5.3
4369	3.0	26.9	10.0	P=24.8 T= 1.7 C= 0.14	14.6	3.1
4370	6.0	24.0	20.0	P=26.7 T= 1.3 C= 0.01	18.2	7.8
4371	6.0	24.0	20.0	P=24.9 T= 1.7 C= 0.1	16.2	6.2
4372	9.0	21.0	30.0	P=25.7 T= 1.0 C= 0.4	19.1	9.3

TABLE 10
(Continued)

Starting Materials				Total wt. Recovered (g.)	Analysis, Wt. %	
Exp. No.	Wt. m- 000 g.	Wt. ØH g.	Wt. % m- 000		00	m- 000
4373	9.0	21.0	30.0	P=23.8 T= 2.4 C= 0.08	20.6	11.3
4374	12.0	18.0	40.0	P=23.7 T= 2.2 C= 0.25	23.9	15.3
4375	12.0	18.0	40.0	P=23.5 T= 1.9 C= 0.27	20.5	12.5
4378	15.0	15.0	50.0	P=23.0 T= 1.3 C= 0.63	21.0	10.4
4381C	15.0	15.0	50.0	P=23.3 T= 0.81 C= 0.66	21.5	9.1
4382	15.0	15.0	50.0	P=23.8 T= 0.25 C= 0.42	18.3	9.5
4383	12.0	18.0	40.0	P=23.8 T= 0.93 C= 0.41	17.0	7.96
4383A	4.8	7.25	40.0	P= 8.06 T= 0.26 C= 0.09	18.6	7.0
4380	20.0	0.0	97.5*	-	18.9**	3.1
4381A	10.0	0.0	97.5*	-	13.7**	8.4

* 2.5 wt. % trans-decalin added.

** Represents weight percent of material found before clogging of reaction tube took place.

Definitions:

P - product found in receiver and analyzed for biphenyl and m-terphenyl

T - material carried over to trap; nearly pure benzene

C - carbon found in reaction tube, analyzed by oxidation to carbon dioxide; subsequently trapped in ascarite weighing tubes

FUTURE PLANS

The effect of free radical initiators and hydrogen donors on the system m-terphenyl-benzene and m-terphenyl alone under the conditions found favorable to the redistribution reaction will be investigated. Some of the promoters to be studied will be tetralin, decalin, and platinized quartz fibers (replacing the porcelain berl saddles as reaction tube packing).

The use of hydrogen and benzene in forming lower molecular weight polyphenyls will be studied. This will be extended to pure thermal hydrogenations.

After establishment of optimum reaction conditions for the model system benzene-m-terphenyl, the system benzene-p-quaterphenyl will be investigated under these conditions as a logical extension to the much more empirical condition to be encountered with the OMR radiolytic tars.