IDO-16877
May 1963

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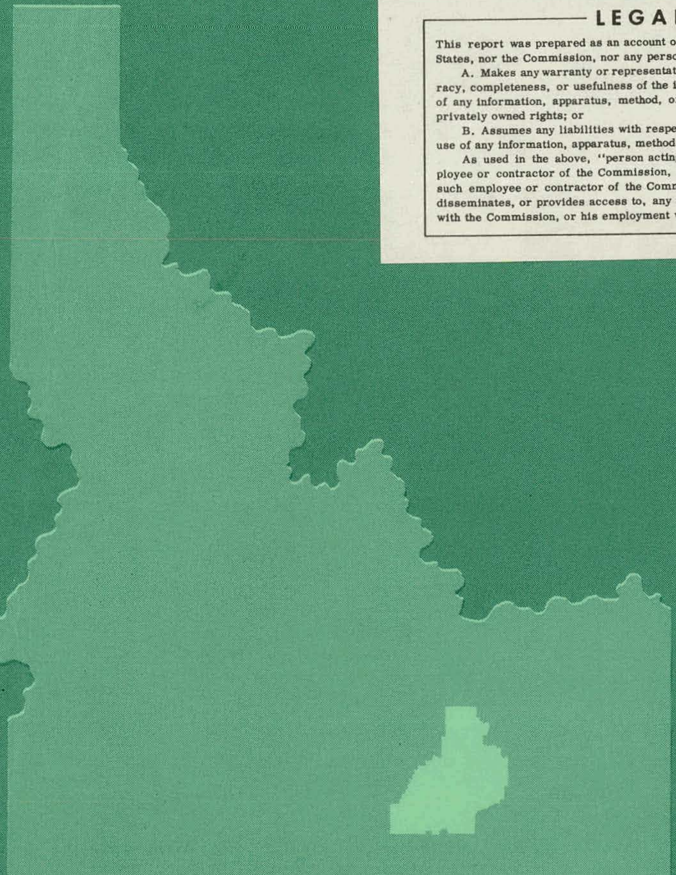

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NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

PRICE $ .75

Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

Printed in USA

EOCR

IDO-16877
AEC Research and Development Report
Reactor Technology
TID-4500 (19th Ed.)
Issued: May 20, 1963

CATALYTIC HYDROCRACKING OF HIGH BOILER IN NUCLEAR REACTOR COOLANT

by

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Idaho Operations Office
U. S. ATOMIC ENERGY COMMISSION

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CATALYTIC HYDROCRACKING OF HIGH BOILER IN NUCLEAR REACTOR COOLANT

SUMMARY

Selective hydrocracking of total coolant was found to be an efficient and economic method for reconstitution of high boiler in the coolant to usable product. Such a process could eliminate the expense of vacuum distillation and disposal of high boilers produced in a nuclear reactor power plant. The selective conversion was possible since polyphenyls were found to be more susceptible towards hydrocracking as the phenyl chain length increased. Both cobalt molybdate on alumina and nickel oxide on alumina (50 to 80 square meters per gram) were found to be efficient catalysts at conditions of 900°F and 1000 psig with the latter giving more selective conversion to terphenyls.

Continuous flow hydrocracking tests on OMRE Core II coolant (containing 23 percent high boiler) resulted in 90 to 100 percent conversion of high boiler at product recoveries of 85 to 95 weight percent. Average molecular weights of the products (biphenyl and heavier) were in the range 205 to 225 compared to 270 for Core II coolant. High boiler in Core III-A coolant which contained mainly first-generation polymers (hexaphenyls) was slightly more refractory toward hydrocracking than Core II high boiler, and conversion decreased slightly with increasing on-stream time. However, at optimum conditions for processing coolant, coke formation on the catalyst for Core III-A coolant was about one-third that for Core II coolant. Products from hydrocracked OMRE coolant samples were found to be stable to electron irradiation at 650°F and dosages on the order of 10^9 to 10^{10} rads, and pyrolysis threshold temperatures were between 750 and 825°F in 48-hour tests.

A proposal has been outlined for utilization of the process in the Coolant Technology Loop at the EOCR at the National Reactor Testing Station. A conservative cost estimate was made for a 1000-megawatt-per-day (thermal) reactor producing 25,000 pounds per day of high boiler (minimum value). Total manufacturing cost was 7 cents per pound compared to the present cost of fresh terphenyl coolant (Santowax OMP) of 17 cents per pound.

On the assumption that the cost of fresh coolant would ultimately be reduced to 10 cents per pound, a payout for the above estimate was 3.7 years.

CATALYTIC HYDROCRACKING OF HIGH BOILER IN NUCLEAR REACTOR COOLANT

CONTENTS

FIGURES

TABLES

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CATALYTIC HYDROCRACKING OF HIGH BOILER IN NUCLEAR REACTOR COOLANT

I. INTRODUCTION

This report is the third of a series of reports on reclamation of damaged terphenyl coolant by catalytic hydrocracking techniques. The initial report [1] described an extensive catalyst-screening program for selective hydrocracking of polyphenyls using pure compounds as charge stocks. The second [2] reported and discussed data for hydrocracking high boiler stocks which had been obtained from Atomics International (OMRE Core II and Core III-A). The importance of removing and/or reclaiming high boiler produced in organic-cooled and -moderated reactors was discussed in these reports. Also, development of efficient catalysts and process conditions was accomplished. A preliminary survey using laboratory data indicated that high boiler could be converted economically to usable, stable coolant. In general, the advantages which can be realized from such a process are as follows:

(1) Reduction of coolant make-up requirements
(2) Elimination of waste disposal
(3) Removal of film-forming material
(4) Overall reduction of operating costs

Previous data indicated that polyphenyls become less refractory toward hydrocracking with increasing number of phenyl rings as shown in the series, benzene/biphenyl/terphenyl/high boiler. This suggested the possibility of processing the total coolant through the hydrocracking unit with selective hydrocracking of the high boiler and a minimum amount of terphenyl conversion. This method would further economize the process since an expensive vacuum distillation system could be eliminated. Should a reactor be operated at low high-boiler concentration (say from 5 to 10 weight percent) two alternatives are possible. The first is processing a side stream directly to the hydrocracker. The other is utilizing a vacuum flash drum which returns a fraction of the terphenyls to the coolant loop, and the remainder with the high boiler is fed to the hydrocracker. Light ends produced in the hydrocracking step are to be separated in an existing degassing system. A simplified flow sheet of a coolant hydrocracking process is shown in Figure 1.

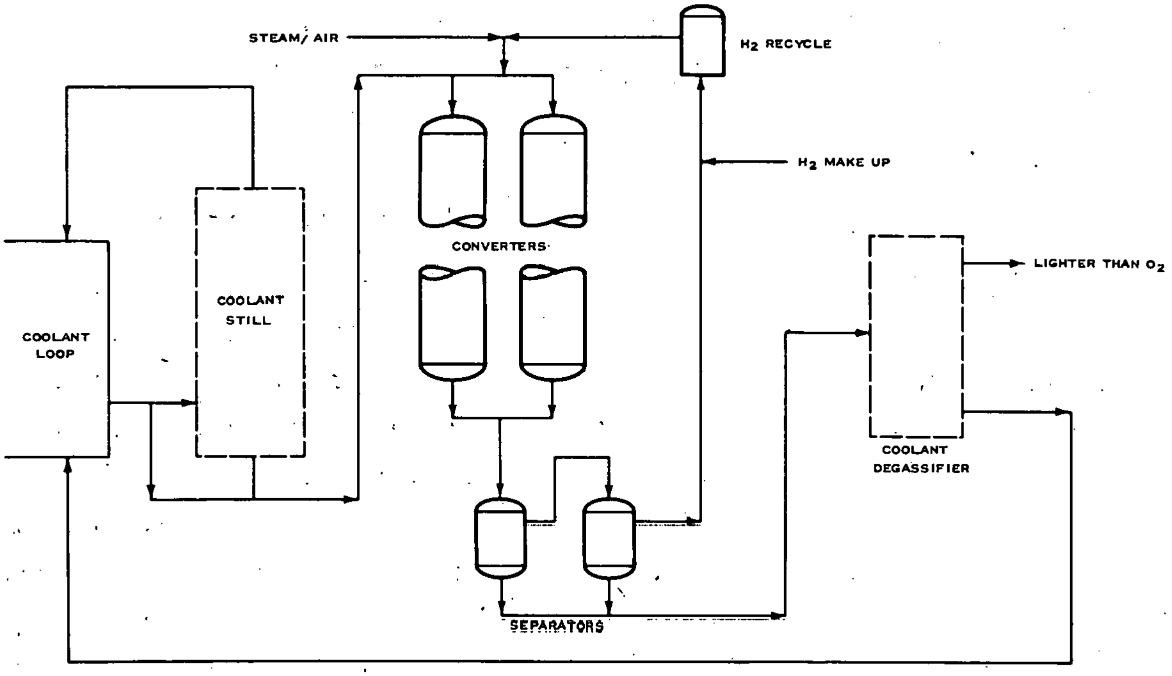


Fig. 1 Simplified flow sheet for coolant hydrocracking.

This report summarizes experimental work which was designed to demonstrate the above proposal as a method of coolant reclamation. Core II coolant samples were available from the OMRE. Core III-A high boiler also was available and was used for making synthetic blends, which represented coolant containing first-generation polymer (hexaphenyls).

II. APPARATUS, MATERIALS, PROCEDURE

A. Hydrocracking Techniques

The equipment used in this research was the same as previously described[3]. Briefly the essential parts of the hydrocracking apparatus consisted of two pressurized, continuous-downflow reactors and associated control and sampling devices. All tests were carried out at 1000 pounds per square inch and at temperatures of 850 to 950°F. Hydrogen flow rates were normally 25 moles per mole of high boiler charged, and total liquid charge rates varied from 0.5 to 4.0 volumes per volume of catalyst per hour. Run procedure was similar to that previously described[4].

B. Materials

Experimental work was limited to three catalysts which were found to be effective in hydrocracking high boiler. These are listed along with their properties in the following tabulation:

Catalyst	Composition (Wt%)	Surface Area (M^2/g)
$CoMoO_4$-Al_2O_3 (G-67)	4.0 Co, 14.0 Mo	57
NiO-Al_2O_3 (G-71)	1.3 Ni	79
Pt-Al_2O_3 (G-66)	1.0 Pt	80

The first two catalysts were used in most of the tests. Catalyst samples were regenerated between runs in air, and $CoMoO_4$-Al_2O_3 (G-67) was regenerated more than 20 times with no apparent loss in activity or selectivity.

Charge stocks used in coolant hydrocracking were as follows:

OMRE Core II coolant (22.5% HB in coolant)
Synthetic Core II coolant (23.6% HB in terphenyls)
Synthetic Core III-A coolant (5 to 30% in terphenyls)
Synthetic coolant (10 to 30% Core II HB in DOM*)
Synthetic coolant (10 to 30% Core III-A HB in DOM*)

Properties of Core II coolant are listed in the left hand column of Table I, and the other charge stock properties are given in appropriate tables along with hydrocracking data. The first three feedstocks listed were charged to the hydrocracker in 40 to 50 percent p-xylene solution. DOM* charge stocks contained no solvent.

---

* Monsanto Chemical Co. eutectic mixture of biphenyl, o-terphenyl, and m-terphenyl.

TABLE I

HYDROCRACKING OMRE CORE II COOLANT OVER COBALT MOLYBDATE-ON-ALUMINA CATALYST

Run number	OMRE Core II Coolant	11434-4		1194-20	11194-22		1194-19		11434-6		11434-7	11434-8	
Avg. temperature, °F		850		900	900		930		900		900	910	
Vol. charge/vol. catalyst/hour		1.0		1.0	0.97		0.96		0.75		0.80	1.9(5)	
Run length, hours		6		4	6		6		3		12	3	
Hours sampled		2-4	5-6	2-4	2-4	5-6	2-4	5-6	1-2	2-3	0-12	1-2	2-3
High boiler conversion, Wt. %(1)		40	78	87	91	96	87	76	100	96	100	100	100
Reclaimed coolant yield, Wt. %(2)		97	94	95	91	95	77	78	85	87	87	80	88
Coke yield, wt. % of catalyst		62		7.9	7.7		10.5		7.7		11.5	6.8	
<u>Product Analysis</u>													
Sublimate, wt. % (3)	77.5	85	94	97	98	99	97	97	100	99	100	100	100
Avg. molecular weight	270	245	235	225	221	223	207	206	214	219	224	218	224
C/H atomic ratio	1.32	1.22	1.20	1.22	1.20	1.22	1.18	1.18	1.09	1.08	1.18	1.18	1.20
<u>Yields, wt. % of coolant charged</u>													
Low boilers (4)		1	4	2	9	2	19	18	15	11	10	18	10
Alkylbiphenyls	0.2	2	1	2	4	3	8	7	7	6	3	3	3
Alkylterphenyls	1.2	8	7	8	7	6	6	6	9	8	7	8	6
Biphenyl	0.5	4	2	6	8	5	11	9	10	7	7	7	5
o-terphenyl	20.5	18	22	22	20	23	15	18	17	19	20	16	20
m-terphenyl	37.3	32	39	38	32	39	24	27	25	29	36	32	38
p-terphenyl	15.0	16	15	12	13	13	7	6	13	13	12	10	13
Triphenylene	2.6	2	2	2	2	2	2	2	2	2	2	3	2
Quaterphenyls	0.2	1	1	1	0	2	1	2	0	2	1	1	1
High boiler	22.5	14	5	3	2	1	3	1	0	1	0	0	0
Coke		2	2	3	3	3	4	4	2	2	2	2	2

Run Conditions: 1000 psig, 25 moles H_2/mole coolant, 50 wt. % coolant in p-xylene

(1) Disappearance of high boiler.
(2) Total product yield including unconverted high boiler.
(3) Sublimable product at 240 C, 0.20 mm., and 30 minutes.
(4) Products boiling lower than biphenyl and including mechanical losses.
(5) 40 wt. % coolant in solvent.

Definitions of various terms used in this report are summarized in the Glossary (Section VI).

III. RESULTS AND DISCUSSION

A. Initial Experiments on Core II Coolant

Preliminary data on coolant hydrocracking were obtained using OMRE Core II coolant and synthetic coolant prepared by adding OMRE Core II high boiler to terphenyls. This series was limited to two of the more promising catalysts, $CoMoO_4$-Al_2O_3 (G-67) and NiO-Al_2O_3 (G-71). Reaction conditions were 850 to 930°F, 1000 psig, 0.8 to 2.5 volumes charge per volume of catalyst, 40 to 50 weight percent coolant in p-xylene, 25 moles hydrogen per mole high boiler, and run lengths of 2, 4, 6, and 15 hours. These early runs were quite promising in that yellow, solid products were obtained with high conversion of the 23 weight percent high boiler in the coolant charged.

1. Cobalt Molybdate Catalysts

Data from seven Core II coolant hydrocracking runs are summarized in Table I. Run length varied from 3 to 12 hours in this series, and conversions of high boiler varied from 78 to 100 percent. At the highest temperature (930°F average) overcracking occurred, and temperature rises in the catalyst bed of 100°F were observed. This naturally led to low product yield (78 weight percent), higher coke yield, and a net loss of terphenyls. At 900°F high conversion was obtained with a product yield of 95 percent and a net gain in terphenyl content (Run 11194-22). At the lowest temperature conversion dropped to 78 percent, but slightly better selectivity to terphenyls was shown. In this series of tests product molecular weights generally were in the 210 to 230 range compared to 270 for Core II coolant containing 23 weight percent high boiler. These data indicated that a coolant hydrocracking process might be feasible in that the high boiler was selectively converted in the presence of terphenyl. These results were consistent with previous hydrocracking data on the series of benzene/biphenyl/terphenyl. Run time was extended to a 12-hour test at 900°F, 1000 psig, and 0.8 Vl/Vc/hr. Although the shorter runs indicated that these conditions were too severe, they were maintained throughout because activity was expected to drop off during the longer test. Apparently good conversion was obtained throughout, as all products were pale yellow in color. The composite samples were batched together for analysis. Overall product yield was 87 percent at 100 percent conversion of high boiler. Molecular weight of the reclaimed coolant (biphenyl and heavier) was 224, and its composition was as follows:

Component	Composition (Wt%) Reclaimed Coolant	Composition (Wt%) Core II Coolant
Alkylbiphenyls	3	0.2
Alkylterphenyls	10	1.2
Biphenyl	8	0.5
O-terphenyl	21	20.5
M-terphenyl	40	37.3
P-terphenyl	14	15.0
Triphenylene	3	2.6
Quaterphenyl	1	0.2
High boilers	0	22.5

2. Nickel-Alumina Catalyst

Several Core II hydrocracking runs were made over NiO-Al_2O_3 catalyst (G-71) at high conversion. A synthetic coolant was used in most of these tests since the original supply of Core II coolant (23 percent high boiler) was nearly exhausted. The blend was made by mixing the terphenyl isomers with Core II high boiler (545 molecular weight) to give a sample which was quite similar to the actual coolant. Properties of these samples are listed in Table II along with

TABLE II

COOLANT HYDROCRACKING RUNS USING NiO-Al_2O_3 CATALYSTS

Run number, 11434-		16		17		20	23				
Run length, hours		5		6		12	15(6)				
Hours sampled		4-5		2-4	5-6	11-12	3-4	5-6	6-7	9-10	14-15(7)
High boiler conversion, wt. %(1)		100		100	95	95	90	100	100	87	90
Reclaimed coolant yield, wt. %(2)	Core II	83	Synthetic	82	87	84	91	87	88	94	91
Coke yield, Wt. % of catalyst		6.9		6.9		7.8	24.4				
Product Analysis	Coolant		Coolant								
Sublimate, wt. %(3)		100		100	99	100	89	100	100	97	98
Avg. molecular weight	270	237		221	232	227	224	221	229	229	231
C/H atomic ratio	1.32	1.26		1.19	1.28	1.24	1.22	1.21	1.22	1.22	1.23
Yields, Wt. % of coolant charged											
Low boilers(4)		14.7		15.3	10.1	14.7	6.9	10.9	9.9	4.4	6.6
Alkylbiphenyls	0.2	0.5			0.3	0.3	0.4	0.4		0.3	1.0
Alkylterphenyls	1.2	0.5			0.5	1.6	1.2	1.1		0.5	0.9
Biphenyl	0.5	3.5			3.4	2.1	2.0	2.2		1.5	2.0
o-Terphenyl	20.5	25.0	21.5		23.9	23.0	25.0	24.5		26.6	25.9
m-Terphenyl	37.3	38.2	39.1	(82.2)(5)	40.4	44.0	41.7	41.3	(88.0)(5)	41.4	42.1
p-Terphenyl	15.0	14.3	15.8		17.0	11.3	17.3	14.4		18.6	16.0
Triphenylene	2.6	0.2			0.7	0.2	0.3	0.3		0.3	0.3
Quaterphenyls	0.2	0.6			0.0	1.1	1.3	1.1		1.3	0.9
High boiler	22.5	0.0	23.6	0.0	1.2	0.0	1.8	1.7	0.0	3.0	2.2
Coke		2.5		2.5	2.5	1.8	2.1	2.1	2.1	2.1	2.1

Reaction Conditions: 900 F
1000 psig
1.0 volume charge per volume catalyst per hour (V/V/Hr.)
40 weight per cent coolant in p-xylene
25 moles hydrogen per mole coolant

(1) Disappearance of high boiler.
(2) Total product yield including unconverted high boiler.
(3) Sublimable product at 240 C, 0.2 mm, and 30 minutes.
(4) Product boiling lower than biphenyl.
(5) Complete analysis was not run.
(6) Fifteen hour run was not continuous.
(7) First 14 hours were at 2.0 V/V/Hr., last hour at 1.0 V/V/Hr.

data from four hydrocracking runs over NiO-Al_2O_3 catalyst. In general, NiO-Al_2O_3 gave slightly lower product yields than $CoMoO_4$-Al_2O_3. Inspection data on the products indicated that this was possibly due to higher activity for cracking the carbon-carbon bonds between rings. Analyses of the atmospheric distillate fractions showed more benzene in runs over NiO-Al_2O_3. However, this greater selectivity gave higher yields of terphenyls, and alkylpolyphenyl yields were considerably lower than for runs using $CoMoO_4$-Al_2O_3. Yield data for the two catalysts for the sixth hour on stream at 100 percent conversion are shown in the following tabulation:

Yields (Wt% of Coolant Charged)	$CoMoO_4$-Al_2O_3	NiO-Al_2O_3
Lighter than biphenyl	9	14
Alkylbiphenyl, alkylterphenyls	9	1
Biphenyl	6	3
Terphenyls	71	78
Triphenylene	2	1
Quaterphenyls	1	1
Coke	2	2

Other runs using NiO-Al_2O_3 were with the synthetic coolant rather than the actual Core II coolant and may not be directly comparable to data reported for $CoMoO_4$-Al_2O_3. Three runs of 6, 12, and 15 hours are summarized in detail in Table II. The two longer runs showed some loss in activity with increasing on-stream time. Surprisingly there was very little change in conversion when the charge rate was altered in the range of 1.0 to 2.0 volumes charge per volume catalyst per hour. In the 12-hour run it was of interest to follow the changes in product composition by comparison of chromatograms of total reactor effluents. Figures 2, 3, 4, and 5 show these changes for the 0- to 2-, 4- to 6-, 7- to 8-, and 11- to 12-hour products respectively. The major changes were in biphenyl and an unidentified component (probably an alkylterphenyl) which eluted between o-terphenyl and m-terphenyl. The 15-hour run shown in Table II was actually made in five different segments with the oil-saturated catalyst shut in overnight between runs. This probably led to a higher coke yield, but the overall run demonstrated that good catalyst activity could be maintained even after a coke buildup of 25 weight percent of catalyst. The last hour on stream still gave 90 percent conversion of high boiler and a reclaimed coolant with an average molecular weight of 231. An increase in total charge rate had very little effect on conversion or

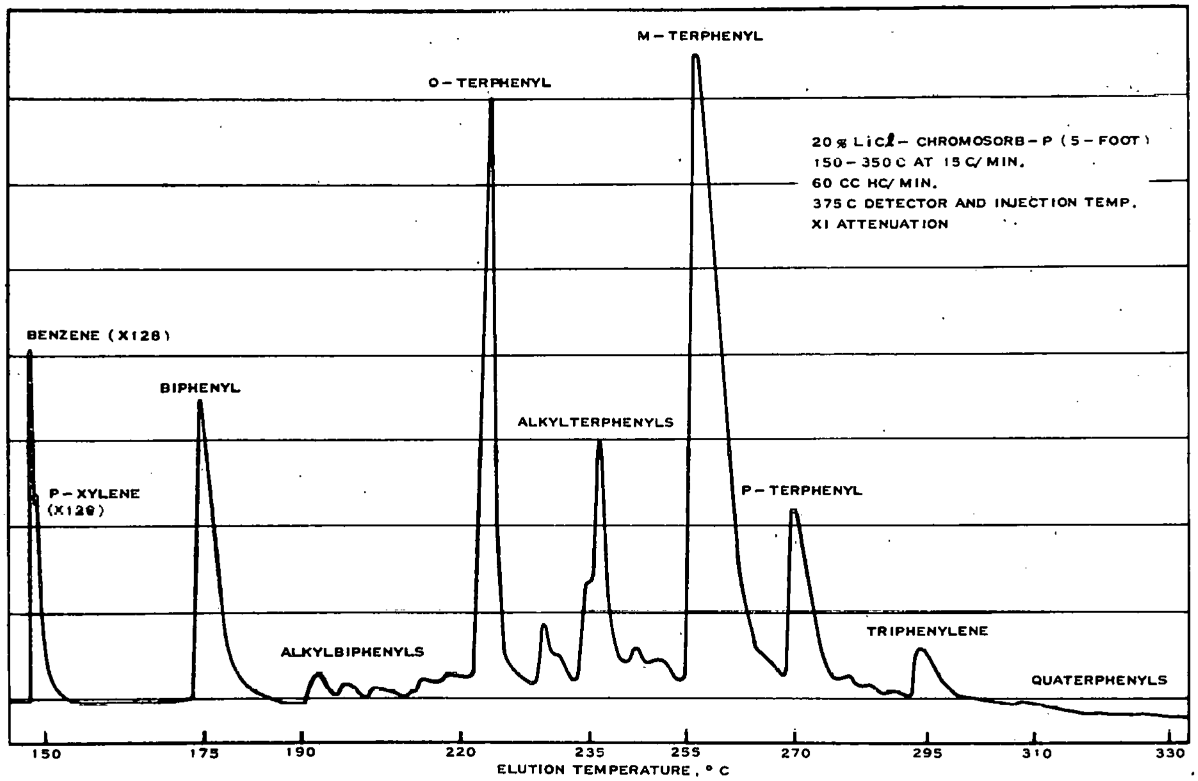


Fig. 2 Product from hydrocracking used coolant over NiO - Al_2O_3 catalyst (0 to 2 hr).

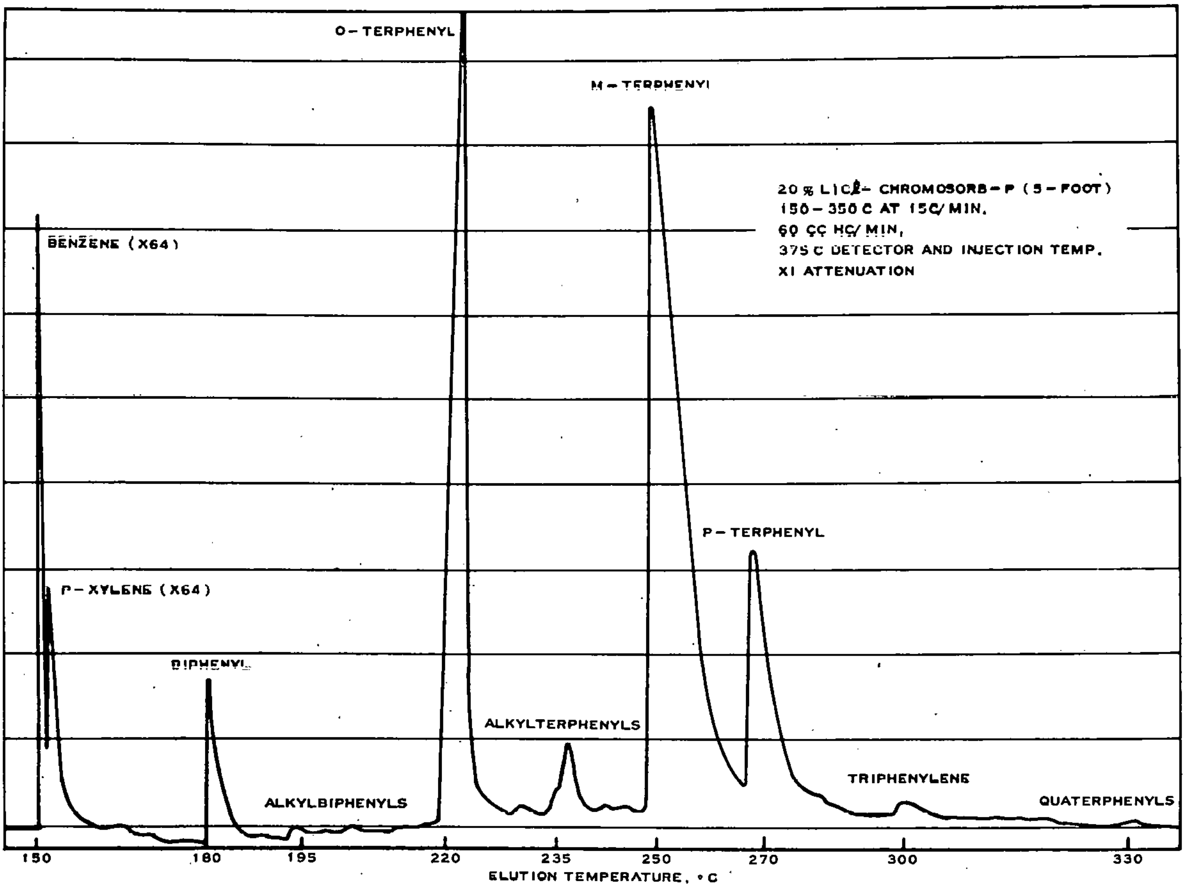


Fig. 3 Product from hydrocracking used coolant over NiO - Al_2O_3 catalyst (4 to 6 hr).

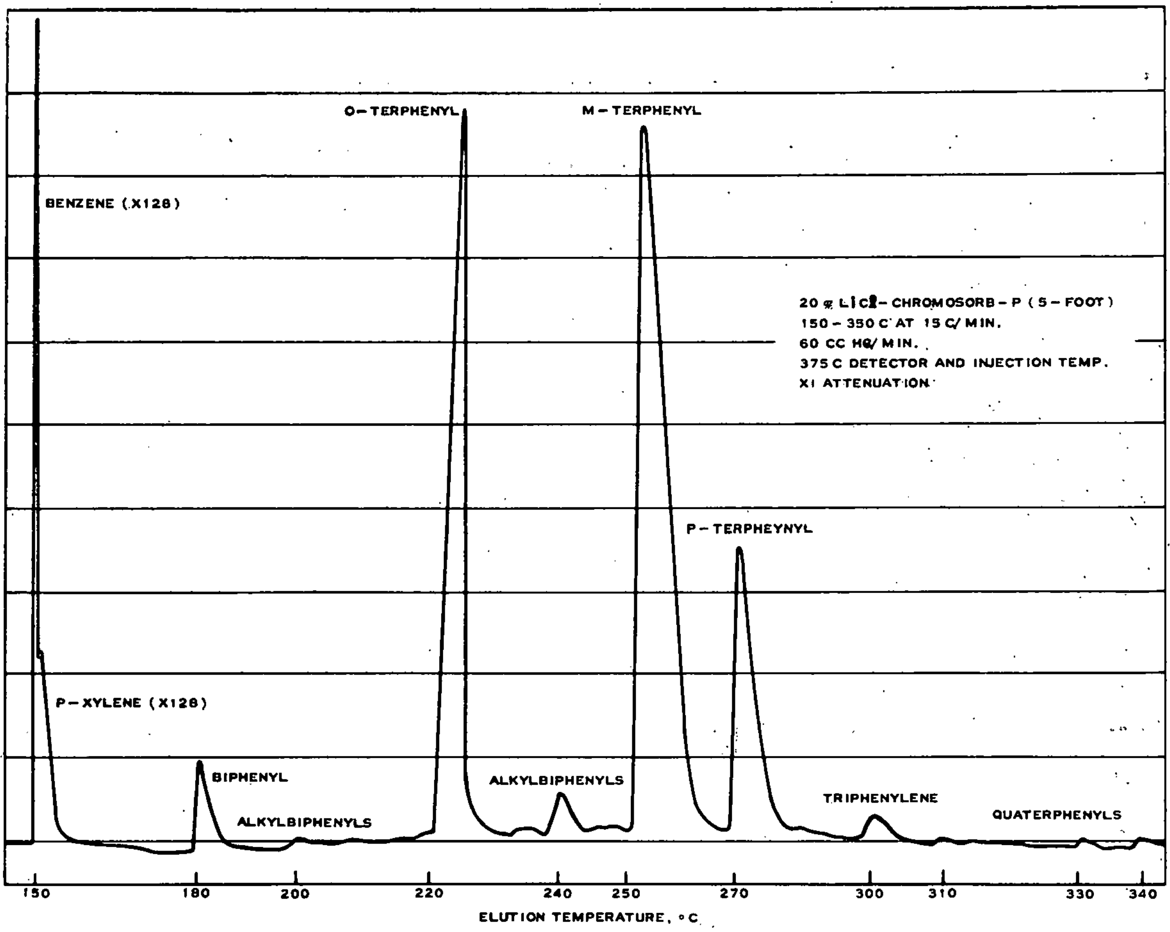


Fig. 4 Product from hydrocracking used coolant over NiO - Al_2O_3 catalyst (7 to 8 hr).

product yields. Conversions varied from 87 to 100 percent during the run, and coolant yields were 87 to 94 weight percent.

B. Coolant Type

The above preliminary work on coolant hydrocracking was carried out on Core II coolant since it was the only material then available in sufficient quantities. This material, however, is not typical of the high boilers which would be present in terphenyl coolants under conditions now being proposed in organic reactor technology. These conditions include low high-boiler concentration and elimination of higher-molecular-weight ends from the high boiler. Thus the nature of high boiler present in the coolant loop would closely approach first-generation polymer (or hexaphenyls). Previous reports [5, 6] have shown that the highly damaged material (Core II high boiler) can be economically reconstituted to a usable, radiolytically stable coolant. When OMRE Core III-A high boiler became available it was of interest to compare its reactivity towards hydrocracking with

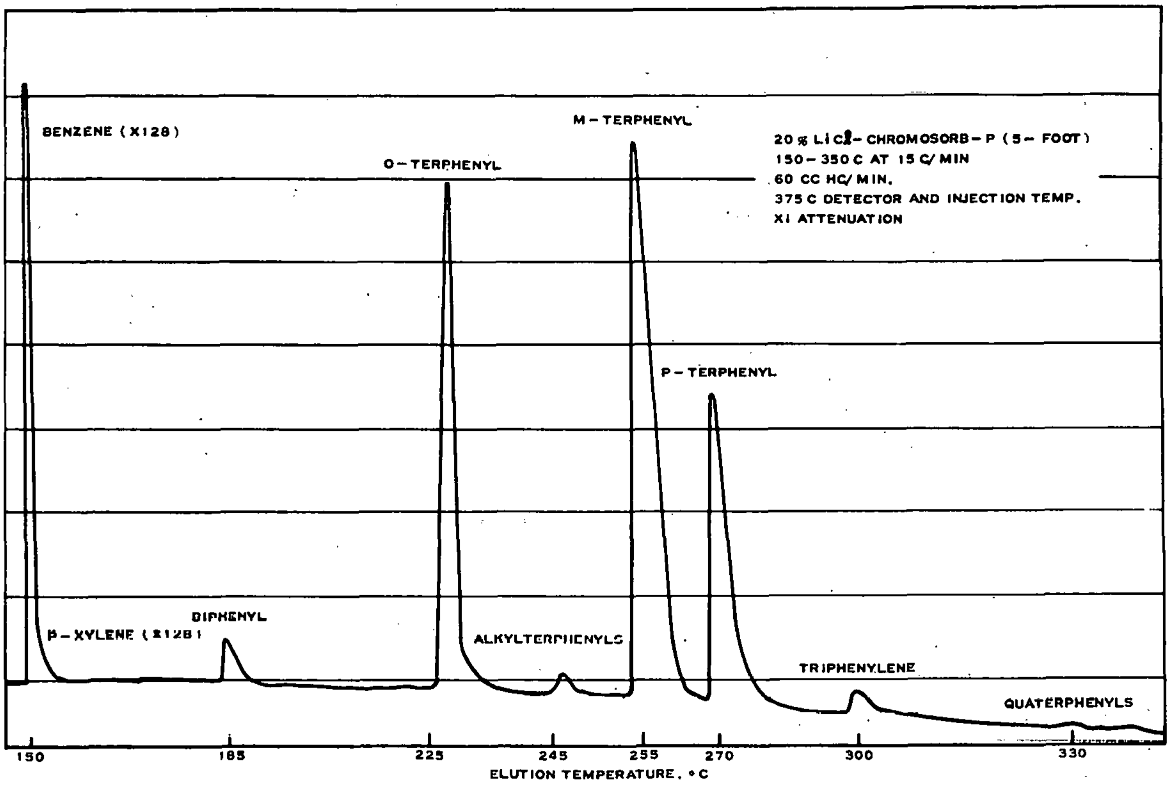
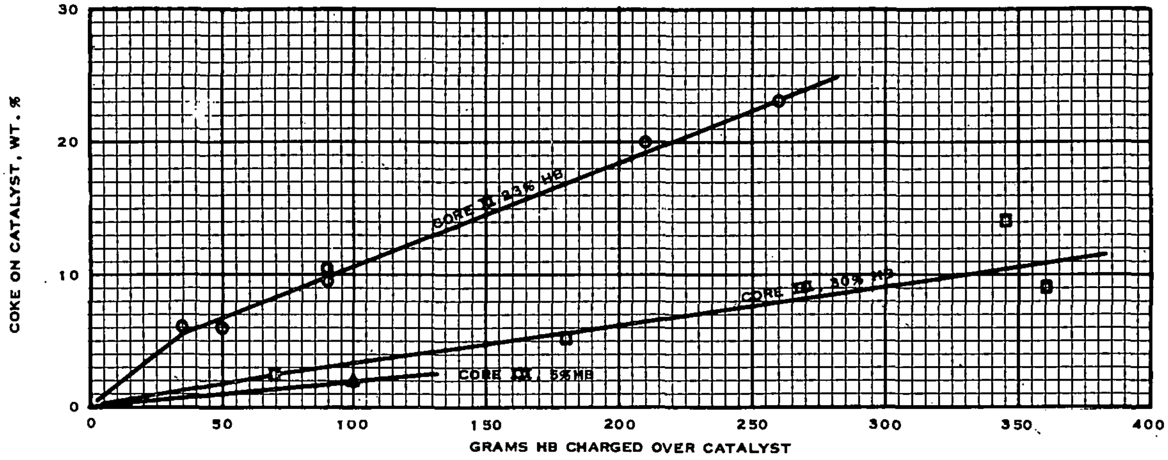


Fig. 5 Product from hydrocracking used coolant over NiO - Al_2O_3 catalyst (11 to 12 hr).

that of high boiler from OMRE Core II. Synthetic coolants (5 to 30 weight percent high boiler) were prepared by dissolving Core III-A high boiler (as received from OMRE Core III-A distillation operation) in a mixture of the isomeric terphenyls. The results of these tests are given below and in the following sections.

One of the more important aspects in comparison of Core II and Core III-A high boiler lies in the coke formation tendencies. This factor controls on-stream cycle length in a hydrocracking process and also the eventual life of the catalyst. As expected, Core III-A high boiler (30 percent HB in terphenyl) gave much lower coking rates than Core II high boiler (23 percent HB in terphenyl). Data are compared in Figure 6, and it is indicated that for a given amount of high boiler charged over the catalyst, the coking rate is about three times higher for the coolant containing the higher molecular weight high boiler from Core II. The molecular weights of the high boilers used in these experiments were 450 for Core III-A and 545 for Core II. These data make the coolant hydrocracking



RUN CONDITIONS: 900F, 1000 PSIG, 1.0 – 3.0 LHSV, 40% COOLANT IN P–XYLENE

Fig. 6 Coke yields in hydrocracking core II and III coolants.

technique look attractive economically since on-stream cycle time can be increased by at least three times over that used in straight high-boiler hydrocracking.

In a brief study of the effect of charge rate, it was indicated that in hydrocracking coolants, Core II high boiler was slightly less refractory than Core III-A. In this series of tests reaction temperature, pressure, and hydrogen recycle ratios were held constant. High-boiler conversion is plotted as a function of charge rate in Figure 7. This difference in conversion is about 5 to 20 percent at the optimum charge rate of about 0.2 to 0.4 gram high boiler per gram catalyst per hour. However, it has been found that an increase in conversion from 80 to 100 percent is not of great advantage since product yields decreased from 95 to 100 percent down to 90 percent at the higher conversion. Also, it is not essential to have 100 percent conversion since favorable changes occurred in the unconverted high-boiler fraction at conversion levels as low as 25 percent. Since reactivity toward hydrocracking increases with increasing phenyl chain length, the assumption can be made that the unconverted high boiler (defined as material boiling above triphenylene) contains the lower-molecular-weight polyphenyls.

C. Long Runs on Core III-A Coolant

Three long hydrocracking runs were made on synthetic Core III-A coolant samples. In addition to studying the effect of on-stream time on activity changes, these experiments were designed to observe effects of charge rate and high-boiler concentration in the coolant (5 to 30 weight percent). The coolants were

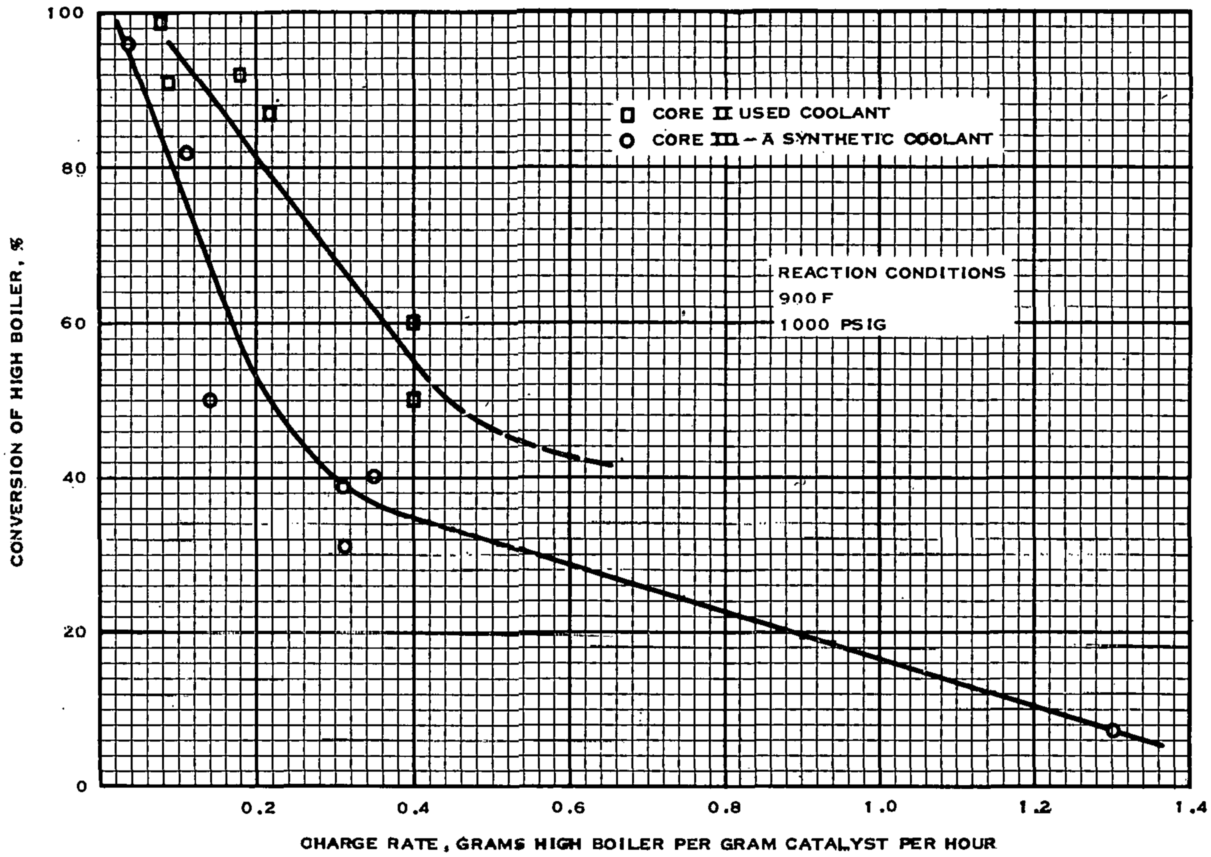


Fig. 7 Effect of space velocity on high-boiler conversion in hydrocracking used coolants.

prepared by dissolving a mixture of Core III-A high boiler and terphenyls (2:4:1 ratio of ortho/meta/para) in p-xylene to give a 40 weight percent solution of coolant as charge to the hydrocracker. Run lengths up to 40 hours were made on each sample at total charge rates of 1.0, 2.0, and 3.0 volumes per volume of catalyst per hour. Temperature, pressure, and hydrogen flow rate were held constant at 900°F, 1000 psig, and 10:1 moles per mole of coolant. Low surface cobalt molybdate on alumina (G-67) was used in all these tests. The catalyst sample had been regenerated between each long run in air at 900°F (1050°F maximum). In each run activity changes were followed by periodic sampling and subsequent analysis.

Typical data from these runs are summarized in Table III. The data shown were from samples after at least 20 volumes of charge per volume catalyst had passed through the hydrocracker. A considerable difference was shown in doubling the charge rate from 1.0 to 2.0 volumes per volume of catalyst per hour. However, product samples were light yellow in both runs with the exception

TABLE III

HYDROCRACKING SYNTHETIC CORE III COOLANT OVER COBALT MOLYBDATE-ALUMINA AT 900°F AND 1000 PSIG

Run No.(2)	30% HB(1) Charge	11675-6	11675-7	5% HB Charge	1175-8
Vol. charge/vol. catalyst/hr.		1.0	2.0		3.0
Total run time, hours		39	30		24
Wt. % HB in coolant		30	30		5.0
Product recovery, wt. %		90	99		99
Conversion of HB, wt. %(3)		92	52		26
Coke yields, wt. % of coolant charged		1.0	0.46		0.07
wt. % of HB charged		3.3	1.5		1.4
wt. % of catalyst		14.3	10.5		1.8
Product Analysis					
Avg. molecular weight	296	228	243	255	228
C/H atomic ratio	1.32	1.16	1.22		
Sublimate, wt. %(4)	70	97	85	95	96.5
Composition, wt. %					
Alkylbiphenyls		3.4	1.1		0.1
Alkylterphenyls		8.1	3.4		1.5
Biphenyl		6.5	3.7		1.3
o-Terphenyl	20.0	21.2	20.3	27.1	29.0
m-Terphenyl	40.6	38.2	40.4	54.3	51.2
p-Terphenyl	10.8	16.4	15.3	13.6	12.9
Triphenylene	0.4	1.3	0.3		0.4
Quaterphenyls		2.1	0.9		0.0
Residue	28.2	2.8	14.6	5.0	3.6
Net Yields, wt. % of HB converted					
Lighter than biphenyl + coke		13	8		
Alkyls		32	25		
Biphenyl		26	27		
Terphenyls		17	34		
Triphenylene + quaterphenyls		12	6		

(1) Prepared by dissolving Core III-A high boiler in terphenyls.
(2) Data were obtained from samples after at least 20 volumes of charge per volume of catalyst had been pumped through the hydrocracker.
(3) Based on disappearance of high boiler.
(4) Sublimable product at 240 C, 0.2 mm., 30 minutes.

of two of three hourly samples from each run. Analyses of the products in each case indicated a gain in total terphenyl content. Based on product recoveries, product properties, and net yields, operation at the higher charge rate is favored for a coolant containing 30 weight percent high boiler. For example, the net yield data show that high boiler converted to terphenyls was doubled in doubling the charge rate. During the majority of the run at the lower charge rate there was no increase in net yield of terphenyl (based on high boiler converted). The net yields of all products for the run at 2.0 volumes charge per volume of catalyst per hour are plotted in Figure 8, and the yields (based on coolant charged) of the terphenyls and alkylated species are summarized in Figure 9. These plots also include data from the 3.0 charge rate run for coolant containing 5.0 weight percent high boiler. Yields were plotted against volume of coolant charged which equilizes the different run times and charge rates used in the three runs. Terphenyl content of the product increased with on-stream time and high-boiler conversion decreased. All runs on Core III-A coolant showed declines in conversion as shown in Figure 10. Hydrocracking data on Core II coolant did not show these declines in activity in 12-hour tests over $CoMoO_4$-Al_2O_3 and the 15-hour run on NiO-Al_2O_3. This was further evidence of the greater resistance of the lower-molecular-weight polyphenyls toward hydrocracking.

Molecular weights of the products (biphenyl and heavier) increased with increasing on-stream time, but changes were not nearly as pronounced as the changes in conversion might indicate. This indicated that structural changes had occurred in the "unconverted residue" fraction of the hydrocracked product. Average molecular weight values of the products (biphenyl and heavier) are plotted in Figure 11 for the three long runs on Core III-A coolant. After charging 60 volumes over the catalyst, conversion of high boiler was reduced to 41 percent in the run at 2.0 volumes per volume catalyst per hour. However, molecular weight reduction from 295 for the feed to 255 for the product was observed. Also, the light yellow color of the total product (compared to the brown color of the charge) indicated that high boiling and high-molecular-weight material had either been removed (by coke formation on the catalyst) or converted to material in the 250 to 350 molecular weight range.

Further evidence of structural changes was found in a run with coolant containing 5.0 percent high boiler. In this test (Run 11675-8) good yields (99 percent and low coke formation (0.07 percent of coolant charged) were observed. However, conversions of high boiler to terphenyls and lighter products were quite low and lined out at about 26 percent. Since the charge rate with respect to high boiler was actually lower than in Run 11675-6 (0.06 compared to 0.12 volume high boiler per volume catalyst per hour), this lower activity must be attributed to a dilution effect. The conversion value may be misleading since it is defined as material converted to product lower boiling than quaterphenyl. Analysis of the kettle residues from vacuum distillation of biphenyl and heavier products indicated changes in the material defined as high boiler (or unconverted residue).

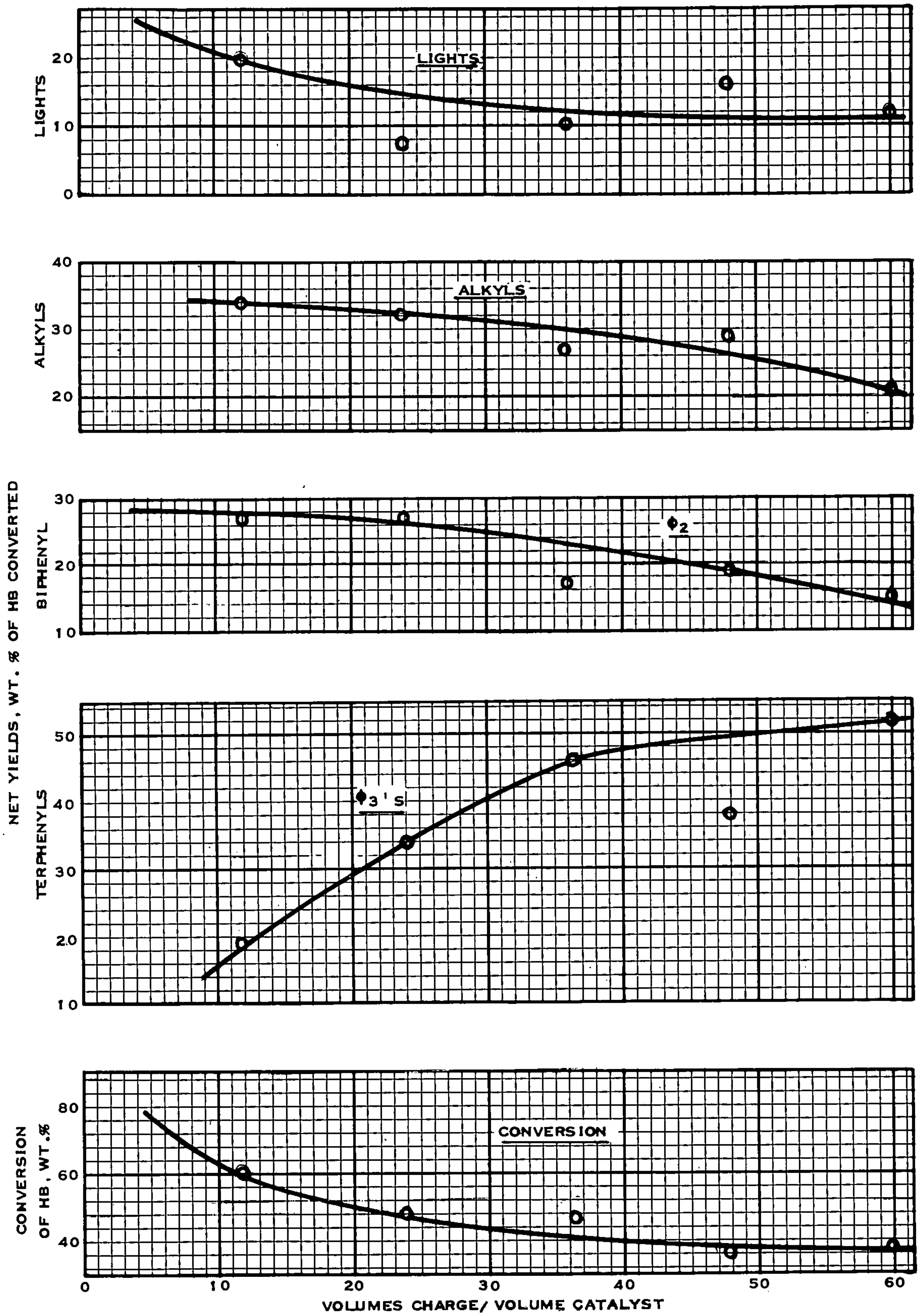


Fig. 8 Net yields in hydrocracking core III coolant over cobalt molybdate-alumina catalyst.

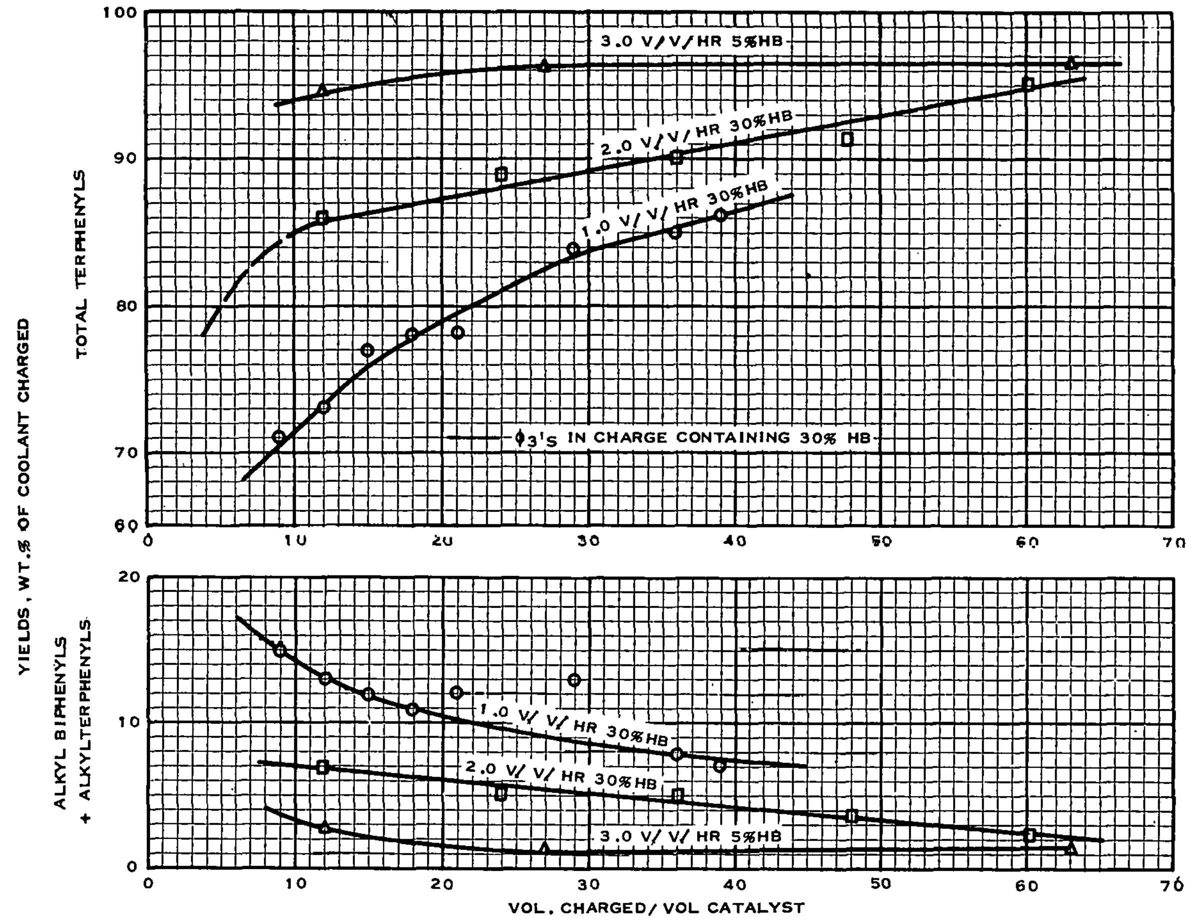


Fig. 9 Yield pattern in hydrocracking synthetic core III coolant.

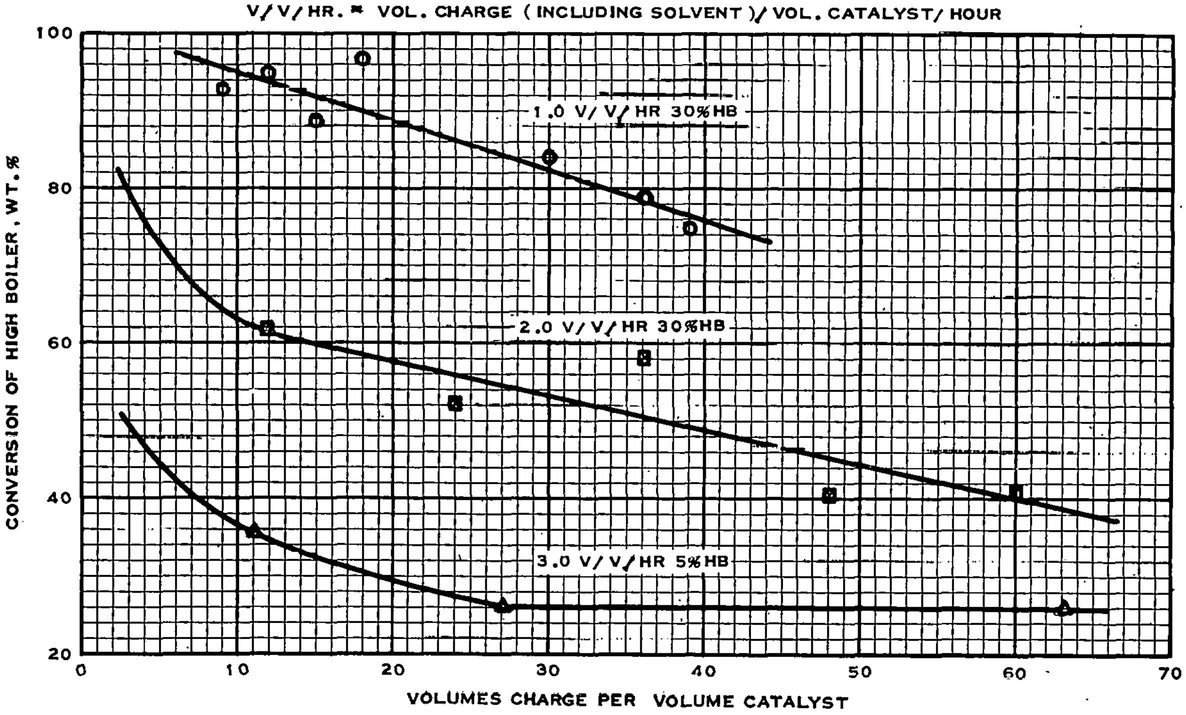


Fig. 10 Effect of on-stream time on conversion during coolant hydrocracking over cobalt molybdate catalyst.

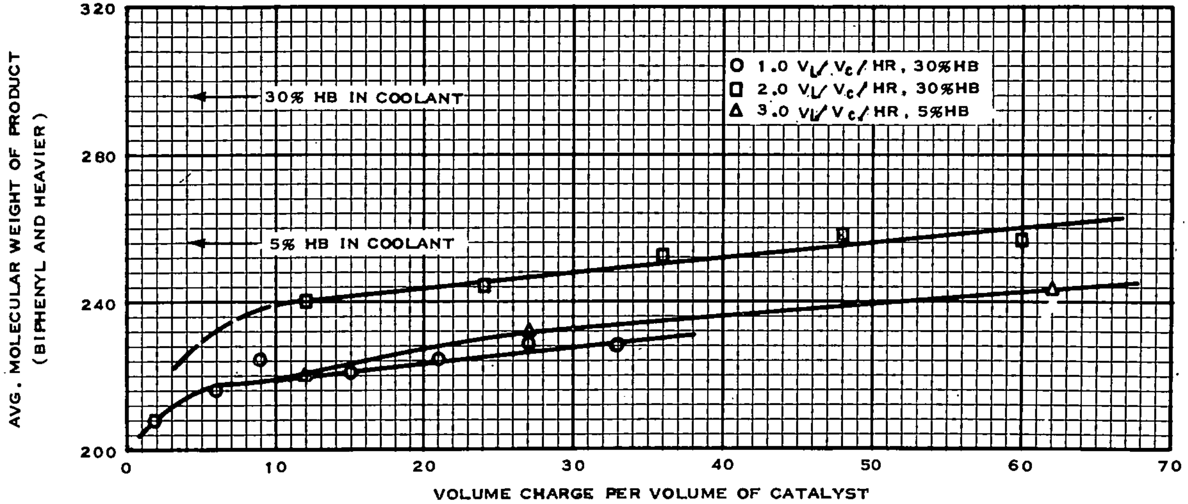


Fig. 11 Core III-A coolant hydrocracking molecular weight data.

These changes were indicated from molecular weight and carbon/hydrogen analyses. The distillations were carried out at 3.5 to 4.5 mm Hg to an end point of 750°F (corrected to 760 mm Hg) with the kettle temperatures held below 600°F to prevent any thermal decomposition. Properties of these residues from three segments of the run are compared with Core III-A high boiler in the following tabulation:

	Sublimate (Wt%) (at 240°C, 0.2 mm)	Avg. Molecular Weight	C/H Ratio
Core III-A high boiler	9.2	450	1.35
Product residue (3 to 6 hr)	6.3	335	1.28
Product residue (9 to 12 hr)	6.1	400	1.29
Product residue (20 to 24 hr)	5.6	370	1.27

These data indicated components in the quaterphenyl-quinquephenyl range, and the molecular weight/carbon-hydrogen correlation indicated some alkylated species.

Coke formation data from the above runs along with previous shorter runs (6 and 12 hours) were employed to establish overall and "steady state" coke-formation rates. These data are summarized in the following tabulation:

Overall Coke Yields	1.0 V/V/hr*	2.0 V/V/hr*
Wt% of coolant charged	1.03 (40 hr)	0.46 (30 hr)
Wt% of catalyst	14.3	10.5

---

* Volume charge (including solvent) per volume catalyst per hour.

"Steady State" Coking Rates	1.0 V/V/hr	2.0 V/V/hr
Wt% of coolant charged	0.30	0.17
Rate, (wt% of catalyst per day)	2.8	2.4

Thus on-stream cycle length in excess of 10 days has been indicated. However, in actual practice this will be determined by product quality and stability of the hydrocracker effluent.

D. Solvent-Free Hydrocracking Tests

Most of the hydrocracking experiments on total coolants were carried out using a solution in low-boiling aromatic solvents such as toluene or p-xylene. This was found necessary to keep coolant in a fluid state at the low pumping rates used with the bench scale apparatus (0.5 to 3.0 milliliters per minute). Plant scale operation would undoubtedly be on charge stock without solvent. There were indications in the preliminary tests that solvent contributed to lower product yields. This was caused by losses in handling hot products and in reaction of the solvent in the hydrocracker to give light hydrocarbons. In an attempt to demonstrate solvent-free operation, DOM* was employed as a simulated coolant. Utilization of this material, which is fluid at room temperature, resulted in synthetic coolant samples which could be handled readily in the laboratory scale equipment. An extensive series of runs was made in which coolants containing either Core II or Core III-A high boiler in DOM were hydrocracked. Three catalyst compositions were also investigated in this series: cobalt molybdate-alumina (G-67), nickel oxide-alumina (G-71), and platinum-alumina (G-66).

Typical data are summarized in Table IV for solvent-free runs on a coolant containing 30 weight percent Core II high boiler dissolved in DOM. Charge rates were varied at constant temperature (900°F) and pressure (1000 psig) which gave high-boiler conversions varying from 22 to 93 percent over the cobalt molybdate catalyst. The platinum catalyst appeared to be less active when considering conversion and product molecular weight. Some of the lower activity may have been due to the competing hydrogenation reactions. Examination of the yield and molecular weight data at low conversion (11 percent) showed loss of terphenyls and gain in the alkylated species with no change in molecular weight values. This along with the lowered C/H ratio indicated ring saturation. Since no increase in biphenyl content was found, it may be assumed that little or no cracking occurred at the carbon-carbon bond between phenyl groups. Cobalt molybdate catalyst produced a yield pattern which might be predicted from previous coolant hydrocracking tests. On the basis of high boiler charged per

TABLE IV

COOLANT HYDROCRACKING IN SOLVENT-FREE SYSTEM USING 30 PERCENT CORE II HIGH BOILER IN DOM(1)

Catalyst		$CoMoO_4$-Al_2O_3			Pt-Al_2O_3	
Vol. charge/vol. cat./hr.		1.1	0.54	0.30	1.0	0.5
Run length, hours		5	6	6	7	5
Hours samples		4-5	5-6	2-3	3-5	5-6
Product yield, wt. %(2)		95	99	94	97	95
Conversion of HB, wt. %		22	38	93	11	29
Product analysis	Charge					
Sublimate, wt. %(3)		77	83	98	75	79
Molecular weight, avg.	245	219	233	212	245	240
C/H ratio	1.26	1.22	1.22	-	1.16	1.16
Yields, wt. % of charge (4)						
Lighter than biphenyl		3.3	0.3	4.1	1.9	3.4
Alkylbiphenyls, alkylterphenyls		1.9	2.9	5.7	9.4	11.2
Biphenyl	19.0	21.3	23.6	25.5	19.8	18.3
o-terphenyl	36.4	33.3	36.5	42.2	28.6	30.2
m-terphenyl	14.9	13.7	14.4	14.7	11.2	10.6
p-terphenyl	1.5	1.5	1.2	1.3	0.6	1.2
Triphenylene	0.7	1.2	1.4	1.8	2.4	3.9
Quaterphenyls		0.2	0.4	0.5	0.0	0.0
High boilers	27.5	21.4	17.1	2.0	24.5	19.6
Coke(5)		2.2	2.2	2.2	1.6	1.6

Run Conditions: 1000 psig, 900 F

(1) Monsanto biphenyl, o-terphenyl, m-terphenyl eutectic mixture.
(2) Yield of biphenyl and heavier product.
(3) Sublimable product at 240 C, 0.2 mm., and 30 minutes.
(4) Based on chromatographic analysis of sublimate.
(5) Coke yields are averaged for complete runs since catalyst was not regenerated between runs.

unit time, conversion was essentially the same as that obtained from a xylene-coolant charge stock. However, yield in the solvent-free runs was higher (94 compared to 88 to 90 weight percent).

Results from typical tests on a DOM coolant containing Core III-A high boiler (30 weight percent) are summarized in Table V. Both nickel oxide-alumina and cobalt molybdate-alumina were used in this series, and the former appeared to be more active and more selective, which was consistent with initial results in total coolant hydrocracking tests. In all runs excellent product recoveries were obtained, and additional tests on a charge consisting of 10 percent high boiler gave similar results. In general, conversions at similar conditions were lower for Core III-A than for Core II high boiler.

TABLE V

COOLANT HYDROCRACKING IN SOLVENT-FREE SYSTEM USING 30 PERCENT CORE III-A HIGH BOILER IN DOM(1)

Catalyst		$CoMoO_4-Al_2O_3$		$NiO-Al_2O_3$		
Vol. charge/vol. cat./hr.		0.98	0.50	4.3	1.1	0.66
Run length, hours		5	5	4	6	4
Hours sampled		4-5	4-5	3-4	5-6	2-3
Product yield, wt. %(2)		99	96	100	98	99
Conversion of HB, wt. %		20	50	7	16	74
Product analysis	Charge					
Sublimate, wt. %(3)		77	85	74	76	93
Molecular weight, avg.	249	235	222	-	234	218
C/H ratio	1.26	1.23	1.16	-	1.22	1.18
Yields, wt. % of charge(4)						
Lighter than biphenyl		0.7	3.7	0.0	2.0	0.1
Alkylbiphenyls, alkylterphenyls		1.5	2.5	1.0	0.8	1.3
Biphenyl	18.8	23.4	25.4	19.7	21.0	28.8
o-terphenyl	38.0	35.6	36.9	36.0	34.4	39.0
m-terphenyl	14.0	13.7	14.3	15.0	16.0	19.4
p-terphenyl	0.9	1.2	1.5	1.1	1.4	2.5
Triphenylene		0.7	1.0	0.2	0.2	0.5
Quaterphenyl		0.0	0.0	0.4	0.2	0.8
High boilers	28.3	22.6	14.1	26.3	23.7	7.3
Coke(5)		0.6	0.6	0.3	0.3	0.3

Run Conditions: 1000 psig, 900 F

(1) Monsanto biphenyl, o-terphenyl, m-terphenyl eutectic.
(2) Yield of biphenyl and heavier product.
(3) Sublimable product at 240 C, 0.2 mm., and 30 minutes.
(4) Based on chromatographic analysis of sublimate.
(5) Coke yield are averaged for complete runs since catalyst was not regenerated between runs.

Due to the high concentration of biphenyl in DOM, analytical data obtained for comparison of catalysts gave some scattered values. In order to magnify these data for better comparison of the three catalysts tested, some runs were selected in which net yields were calculated for various components found in the hydrocracked products. Net yield values were based on high boiler converted and are essentially equivalent to selectivity. In Table VI net yield values are shown for runs on both simulated Core II and Core III-A coolants and the three catalysts tested. Since conversion of both biphenyl and terphenyls (in the DOM) occurred in some runs, the net yield values will not necessarily total to 100. An extreme example is shown for the run on platinum-alumina at 29 percent conversion in which the net yield of alkylated species was 142 percent. This

TABLE VI

PRODUCT NET YIELDS(1) IN HYDROCRACKING SOLVENT-FREE, SYNTHETIC COOLANT USING DOM

Feed, 30 % HB(2) in DOM	Catalyst	Conversion of HB, Wt. %	Net Yields, Wt. % of HB Converted Lights(3) + Coke	Alkyls	Biphenyl	Terphenyls
Core II	$CoMoO_4$-Al_2O_3	38	3	28	44	4
Core II	$CoMoO_4$-Al_2O_3	93	16	22	25	21
Core II	Pt-Al_2O_3	29	43	142	0	0
Core III-A	$CoMoO_4$-Al_2O_3	20	12	26	81	0
Core III-A	$CoMoO_4$-Al_2O_3	50	26	18	47	13
Core III-A	NiO-Al_2O_3	7	0	50	45	0
Core III-A	NiO-Al_2O_3	74	1	6	47	40

(1) Net yields $= \frac{\text{change in concentration of coolant components}}{\text{change in concentration of high boiler}} \times 100$

(2) Upon correction for terphenyls in high boiler, this value becomes 28.3 wt. %

(3) Lights include material boiling below biphenyl plus mechanical losses

value probably was obtained from ring saturation of a terphenyl followed by cracking of the ring to yield alkyl biphenyls. In the same run biphenyl net yield was a negative value (shown as zero) due to loss of biphenyl by the above mechanism to give alkylbenzenes. The end result was a high yield of lights (lower boiling than biphenyl) in addition to the excessive yield of alkylated biphenyls. Values in the table listed as zero indicate no net gain in that particular component. Thus catalysts can be compared by examination of these net yields. Obviously, platinum-alumina was quite inferior to the other two catalysts. Nickel oxide-alumina was more selective than cobalt molybdate-alumina and gave a net terphenyl yield of 40 percent at 74 percent conversion with only a 1.0 percent converted to low boiling product.

The investigations of hydrocracking a solvent-free coolant (synthetic) gave the following information:

(1) Product yields (recoveries) were about 5 percent higher than with a coolant dissolved in xylene for runs of 6 to 8 hours.

(2) Net yield data, based on high boiler converted, greatly magnified differences between the three catalysts which were shown to be almost equivalent in previous tests.

(3) Nickel oxide-alumina was found to be the most selective catalyst.

(4) Coke yields were lower from solvent-free stocks, possibly due to the higher partial pressure of hydrogen.

(5) Core III-A high boiler was found to be less susceptible to hydrocracking than Core II, high boiler.

(6) Conversions were similar at the same charge rate (based on volume high boiler per volume catalyst per hour).

E. Stability Evaluations

1. Radiolytic Stability Tests

Nine samples of reclaimed coolants were evaluated in radiolytic stability experiments. These samples were produced from hydrocracking tests on total OMRE Core II coolant (containing 23 percent high boiler) and were tested after removal of the solvent fraction (including product boiling below biphenyl). The experimental technique was described in previous reports [7]. Irradiation under a linear electron accelerator (Linac) was carried out at 650°F in 7- to 8-hour run times, and the samples received total dosages of 4.8 x 12.6 x 10^9 rads. Complete data from these tests are summarized in Table VII. As found in similar tests on coolants from hydrocracking high boiler, results [8] were very encouraging in that reclaimed coolant appeared to be slightly more stable than Santowax OMP at the chosen test conditions. Radiolytic gas was higher for the reclaimed samples and varied from 0.14 to 0.40 cc per watt-hour (or up to four times that produced from Santowax OMP). However, the higher value amounts only to 0.3 weight percent of the sample. Relative polymer values (relative to Santowax OMP) are not listed in the table since some of the samples contained some high boiler. One of these (Sample J, containing 9.4 percent high boiler) was the only coolant that gave a radiolyzed product of higher polymer content than the Santowax OMP control (34.9 compared to 33.4 percent) at a dosage of 1.3 x 10^{10} rads. All samples gave lower increases in molecular weight values than Santowax OMP. These reclaimed coolant samples contained less alkylated polyphenyls than the products from hydrocracking OMRE high boiler, varying from 1.0 up to 14 weight percent. The effect of alkyl concentration on radiolytic stability has been discussed previously [9]. At the conditions used the presence of alkyls contributed to lowering the polymer formation by radiolysis. Relative changes in alkyl and terphenyl concentration can be compared by examination of the analytical data in Table VII. A trend was shown which varied with dosage. For example, at 12.6 x 10^9 rads the average change in alkyl concentration was 19 percent compared to 25 percent change for terphenyls (total of the three isomers). At a lower dosage of 4.8 x 10^9 rads the changes were 32 and 10 percent respectively. Changes in biphenyl for both dosages were 30 to 34 percent. These

TABLE VII

RADIOLYTIC STABILITY OF RECLAIMED COOLANTS FROM HYDROCRACKING

(Electron irradiation at 650 F for 8 hours, total dosage of 1.26×10^{10} rads)(1)

	Santowax-OMP		Sample J		Sample K		Sample L		Sample M		Sample N		Sample O	
High Boiler, wt. %(2)	0.0	33.4	9.4	34.9	6.5	32.6	3.4	29.6	4.7	30.1	1.5	29.4	1.7	29.3
Radiolytic gas, cc/watt-hr.		0.06		0.11		0.14		0.29		0.26		0.22		0.07
Analytical Data														
Avg. molecular weight	230	269	243	276	233	270	229	258	220	254	227	261	226	265
C/H atomic ratio	1.29	1.28	2.24	1.22	1.26	1.27	1.18	1.22	1.18	1.22	1.19	1.22	1.20	1.26
Composition, wt. %(3)														
Alkylbiphenyls	0.0	0.0	0.3	0.3	0.1	0.2	2.4	1.5	5.6	2.6	0.7	0.6	0.9	0.9
Alkylterphenyls	0.0	0.2	0.5	0.5	0.4	0.5	6.3	4.6	8.5	5.7	3.4	2.3	3.7	2.9
Biphenyl	0.4	0.3	2.7	1.9	1.7	0.9	8.3	5.3	11.0	6.1	4.4	3.3	4.3	3.0
o-terphenyl	11.9	7.1	25.3	16.0	27.9	16.3	21.1	13.7	19.2	13.7	26.5	17.4	23.5	14.6
m-terphenyl	55.0	34.7	42.3	29.4	46.0	31.2	40.7	29.3	32.9	26.7	48.4	34.7	43.7	32.0
p-terphenyl	32.5	23.7	17.9	14.8	16.2	16.4	16.0	13.2	13.4	11.0	14.1	10.1	20.8	15.2
Triphenylene	0.2	0.6	1.2	2.1	0.9	1.8	1.6	2.5	3.5	2.7	1.0	2.2	1.4	1.9
Quaterphenyls	0.0	0.0	0.4	0.1	0.3	0.1	0.2	0.3	1.2	1.3	0.0	0.0	0.0	0.2
Residue	0.0	33.4	9.4	34.9	6.5	32.6	3.4	29.6	4.7	30.1	1.5	29.4	1.7	29.3

	Santowax-OMP		Sample F		Santowax-OMP		Sample F		Sample H	
High Boiler, wt. %(2)	0.0	23.8	0.0	21.0	0.0	17.1	0.0	15.5	1.0	14.6
Radiolytic gas, cc/watt-hr.		0.09		0.28		0.10		0.40		0.25
Analytical Data										
Avg. molecular weight	230	262	224	251	230	252	224	246	223	246
C/H atomic ratio	1.29	1.30	1.14	1.24	1.29	1.30	1.19	1.22	1.22	1.24
Composition, wt. %(3)										
Alkylbiphenyls	0.0	0.0	3.0	2.8			3.0	2.0	2.7	1.5
Alkylterphenyls	0.0	0.3	9.5	6.3			9.5	5.7	6.0	4.9
Biphenyl	0.4	0.2	8.0	5.4			8.0	5.8	5.6	3.7
o-terphenyl	11.9	6.2	21.3	15.2	(4)		21,3	20.1	24.7	21.5
m-terphenyl	55.0	41.7	39.5	31.6			39.57	36.3	41.5	37.7
p-terphenyl	32.5	27.2	13.5	11.5			13.5	11.2	13.7	12.0
Triphenylene	0.2	0.5	2.8	3.6			2.8	2.2	3.2	2.6
Quaterphenyls	0.0	0.4	1.4	1.1			1.4	1.2	2.6	1.5
Residue	0.0	23.8	0.0	21.0			0.0	15.5	1.0	14.6

Samples Description

Sample J - Hydrocracked Core II coolant over $NiO-Al_2O_3$ catalyst at 1.0 vol. per vol. catalyst per hour.
Sample K - Hydrocracked Core II coolant over $NiO-Al_2O_3$ catalyst at 2.0 vol. per vol. catalyst per hour.
Sample L - Total product from 12 hour hydrocracking run on synthetic Core II coolant over $NiO-Al_2O_3$ at 1.0 vol. per vol. catalyst per hour.
Sample M - Accumulated first hour products from hydrocracking Core II coolant over $CoMoO_4-Al_2O_3$ catalyst.
Sample N - Accumulated first hour products from hydrocracking Core II coolant over $NiO-Al_2O_3$ catalyst.
Sample O - Total product from 6 hour hydrocracking run on synthetic Core II coolant over $NiO-Al_2O_3$ at 2.0 LHSV.
Sample F - Hydrocracked Core II coolant from 12 hour run over $CoMoO_4-Al_2O_3$ at 0.8 vol. per vol. catalyst per hour.
Sample H - Hydrocracked Core II coolant from 6 hour run over $CoMoO_4-Al_2O_3$ at 1.0 vol. per vol. catalyst per hour.

(1) Data in right hand columns are after irradiation
(2) Residue remaining after micro-sublimation at 240 C, 0.2 mm. for 30 minutes
(3) Sublimates were analyzed by chromatographic analysis using 5-foot LiCl-on-Chromosorb P column programmed 150-350 C at 15 C per minute
(4) Data not available

results are not readily explainable. However, the results indicated that coolant produced by hydrocracking high boiler is relatively stable towards electron irradiation.

2. Thermal Stability Tests

Thermal stability evaluations were made on two reclaimed samples obtained by hydrocracking total coolant. Tests were run in mild-steel sample holders at temperatures of 600, 650, 750, and 825°F for 48-hour periods. Complete data are listed in Table VIII for these samples and Santowax OMP at the two higher temperatures (750 and 825°F). The lower temperatures were not shown

TABLE VIII

THERMAL STABILITY TESTS ON RECLAIMED COOLANTS

(48 hour tests at 750-825 F in mild steel test cells)

	Santowax-OMP			Sample F			Sample P		
Temperature	Before	750 F	825 F	Before	750 F	825 F	Before	750 F	825 F
High Boiler, wt. %(1)	0.0	0.6	6.0	0.0	7.2	38.3	0.0	6.8	30.7
Gas yield, cc/gram		0.5	0.5		6.8	16.4		10.3	16.2
Analytical Data									
Avg. molecular weight	230	232	236	224	227	280	218	222	279
C/H atomic ratio	1.29	1.28	1.28	1.18	1.24	1.36	1.18	1.24	1.35
Composition, wt. %									
Alkylbiphenyls(2)	0.0	0.0	0.0	3.0	3.2	2.8	4.3	4.3	3.5
Alkylterphenyls	0.0	0.0	0.0	9.5	3.7	1.3	10.3	3.5	1.5
Biphenyl	0.4	0.3	1.3	8.0	6.0	7.5	8.0	9.0	9.7
o-terphenyl	11.9	10.6	10.2	22.3	21.9	10.5	19.6	18.7	13.9
m-terphenyl	55.0	53.1	48.0	39.5	40.2	25.9	39.9	39.3	29.5
p-terphenyl	32.5	35.2	33.3	13.5	13.4	9.1	12.6	13.0	9.0
Triphenylene	0.2	0.2	0.3	2.8	3.2	3.1	4.0	4.3	2.0
Quaterphenyls	0.0	0.0	0.9	1.4	1.2	1.5	1.3	1.1	0.2
High Boilers	0.0	0.6	6.0	0.0	7.2	38.3	0.0	6.0	30.7

Sample Description
Sample F - Hydrocracked Core II coolant
Sample P - Hydrocracked Core II coolant

(1) Residue remaining after micro-sublimation at 240 C and 0.2 mm for 30 minutes

(2) Sublimates were analyzed by chromatography using 5-foot LiCl-on-Chromosorb P column programmed 150-350 C at 15 C per minute

in the table since no significant changes were observed. A summary of high boiler formation for these samples is shown in the following tabulation:

	High Boiler Content (Wt%)				
Sample	Original	650°F	700°F	750°F	825°F
Santowax OMP	0	-	-	0.6	6.0
Sample F	1.8	3.1	4.8	7.2	38
Sample P	0	-	-	6.8	31

The properties of the two coolant samples are shown in Table VIII. Fair stability was shown up to 750°F, but relatively poor stability at the highest temperature (825°F) when compared to Santowax OMP which gave only 6.0 percent high boiler. These data were in contrast to radiolytic stability measurements in which polymer formation was consistently less for the reclaimed coolant relative to Santowax OMP. Pyrolytic gas values are shown in the following tabulation:

	Gas Yields (cc per gram)			
Sample	650°F	700°F	750°F	825°F
Santowax OMP	-	-	0.5	1.0
Sample F	0.1	1.9	8.0	22
Sample P	-	-	10	16

Gas yields were quite high at 825°F and corresponding decreases in alkylpolyphenyls were observed, indicating considerable dealkylation. Referring to Table VIII it is shown that at 750°F loss of alkyl species occurred with essentially no net loss in terphenyl content. However at 825°F decreases in both components were found which indicated interaction to give higher-boiling compounds. Product characterization of the total radiolyzed products utilizing the carbon-hydrogen/ molecular weight correlation curve [10] indicated the samples to be more aromatic after radiolysis than before. Pyrolytic high-boiler formation and molecular weight data are plotted as a function of temperature for the complete temperature range studied in Figure 12.

The above results from stability evaluations of reclaimed coolants indicate good stability up to 750°F with a threshold value somewhere between 750 and 825°F. At 650°F no thermal high boiler is generated, and radiolytic damage occurs at a slower rate on reclaimed material than on terphenyls.

F. Economics of Coolant Hydrocracking

When initial experiments indicated that hydrocracking coolant was more feasible than hydrocracking neat high boiler, a preliminary economic study was carried out comparing the two processes. The former method of processing demonstrated several potential advantages including improved yields, lower investment, possible elimination of a distillation step, and lower catalyst requirements. The cost evaluation was made on available data from hydrocracking OMRE Core II coolant, and the premises for the calculations are listed in Table IX.

The calculation was made for a 1000-megawatt-per-day (thermal) reactor at a minimum high-boiler production rate of 25,000 pounds per day. The initial investment was estimated to be $885,000. Labor rates and utility rates were based on a midwestern location, and a seven-year amortization was assumed. On this basis, the direct manufacturing costs were estimated to be $354,000 per year, or 4.7 cents per pound of reclaimed coolant. The indirect costs including amortization were $172,000 per year, or 2.3 cents per pound. Thus, total manufacturing costs were 7.0 cents per pound of reclaimed coolant. On the assumption that fresh coolant cost would eventually be reduced to 10 cents per pound, the plant would show a gross income of $224,000, or $112,000 after taxes. With the $126,000 amortization credit, the amount applicable to payout was $238,000 per year. The initial $885,000 investment would be paid out in 3.7 years. For a comparable calculation on high-boiler hydrocracking for coolant reclamation, the plant payout was 5.0 years.

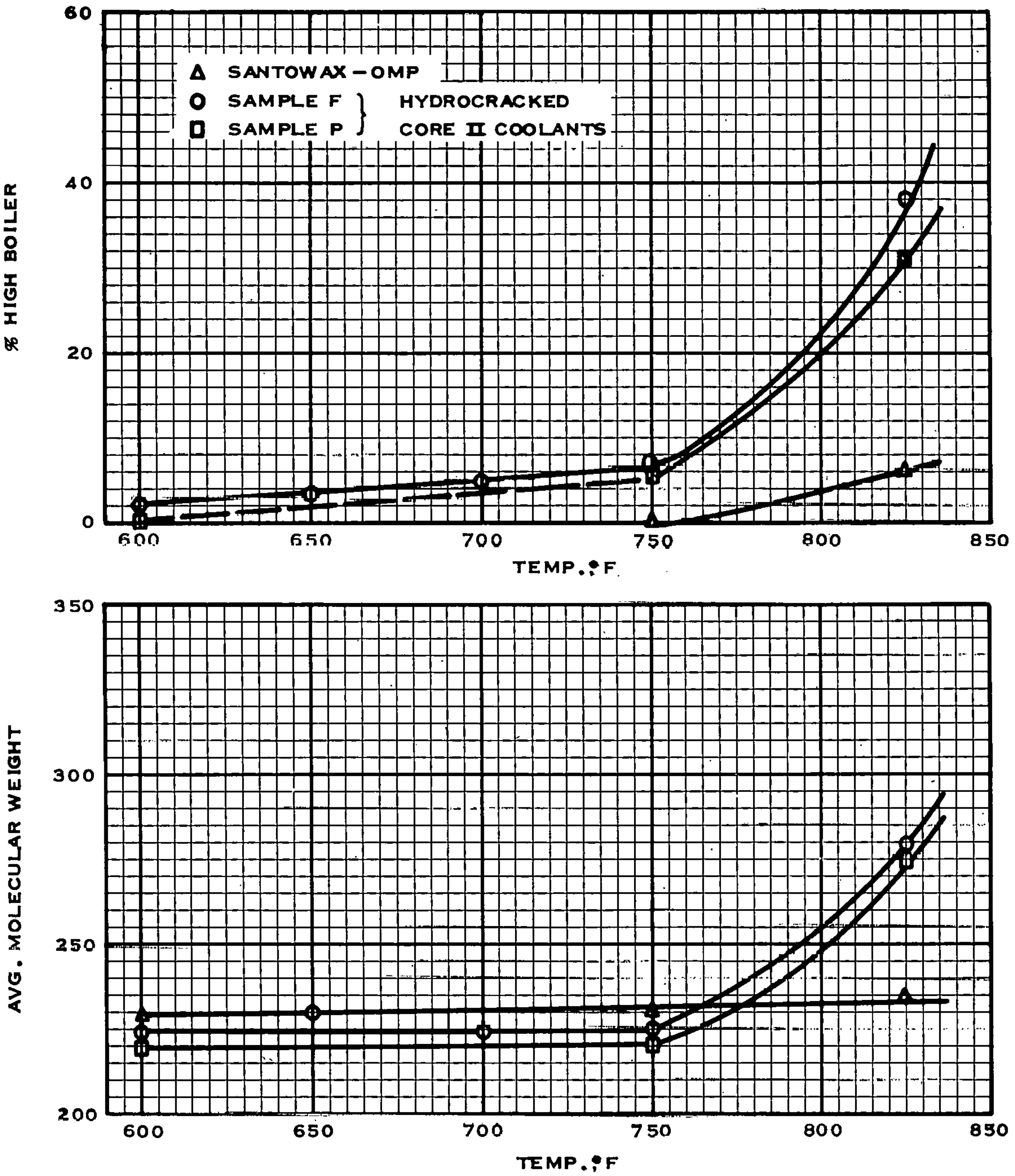


Fig. 12 Thermal stability experiments (48-hr tests).

The above estimate is definitely conservative. No credit was taken for reduced operating costs which would be realized with elimination of the expensive distillation step and high-boiler disposal. Using a more realistic coolant, for example, one containing first-generation high boiler, would result in higher product recoveries and much longer on-stream cycle times than were used for

TABLE IX

PREMISES IN ECONOMIC EVALUATION OF HYDROCRACKING TOTAL COOLANT

Feedstock	Coolant containing 30% HB (1)
Catalyst	$CoMoO_4$-Al_2O_3, low surface
Catalyst life, years	1
Cycle time, hours	100
Reactor temperature, °F	900
Reactor pressure, psig	1000
Charge rate, vol. HB/vol. catalyst/hr.	0.15
Recovery, pounds coolant/pound HB	82
Hydrogen recycle, moles/mole HB	25-100
Hydrogen consumption, SCF/bbl.	200
Cost of fresh coolant, cents/pound	10

(1) Data from hydrocracking Core II coolant

the calculations (90 percent recovery compared to 82 percent). Data on solvent-free coolant indicated that recoveries on the order of 98 to 99 percent are possible with nickel oxide-alumina catalyst. Of major importance is the high-boiler production rate. The value of 25 pounds per megawatt-day is admittedly low, and values of 100 pounds per megawatt-day have been observed in OMRE Core III operation.

IV. CONCLUSIONS

Although several phases of coolant hydrocracking need more investigation, sufficient data have been obtained to recommend this method as an economically feasible process for reclaiming coolant. Laboratory data are available for projecting the method into use in either pilot plant operation or actual experience on demonstrational nuclear power plants. Products from coolant hydrocracking have been shown to be stable towards electron irradiation and stable thermally up to 750°F. A potential additional benefit of a downflow, catalytic process in the presence of hydrogen lies in the removal of film-forming materials from the coolant such as particulate and soluble iron compounds, partially saturated aromatics, and oxygenated species [11].

One possible disadvantage of this process should be pointed out. Although biphenyl production decreases with run time, the net result would be a buildup of biphenyl concentration in the total coolant if the production rate exceeds the dimerization rate from radiolysis. Due to its relatively high vapor pressure, there would be a maximum allowable concentration of biphenyl in the coolant. A combination of hydrocracking and electron radiation data indicates that a build-up of alkylated polyphenyls would not occur due to dealkylation under pyrolysis and radiolysis. The exact equilibrium values and overall effects on nuclear powered reactors can best be determined in experimental loops.

The data presented in this report were used in preparation of a proposal for utilization of the coolant hydrocracking technique in loop experiments at the EOCR at the NRTS in Idaho. The proposal outlined a program for use in the coolant technology loop for removing coolant from the loop, converting the high boiler to usable material, and returning the product to the loop. The overall efficiency and economics of total coolant hydrocracking favor this method over high-boiler hydrocracking.

V. REFERENCES

1. L. E. Gardner, Evaluation of Catalysts for Selective Hydrocracking of Polyphenyls, IDO-16858 (April 25, 1963).
2. L. E. Gardner, Reclamation of Damaged Nuclear Reactor Coolant by Catalytic Hydrocracking, IDO-16853 (March 29, 1963).
3. L. E. Gardner, Evaluation of Catalysts for Selective Hydrocracking of Polyphenyls, IDO-16858, p 5 (April 25, 1963).
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10. Ibid, p 35.
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VI. GLOSSARY

High boiler: In coolant technology described as material boiling above p-terphenyl. In this research it has been arbitrarily defined as residue remaining after sublimation at 240°C, 0.20 mm Hg, and 30 minutes time.

Synthetic coolant: Coolant which was not obtained from OMRE reactor experience but was prepared by mixing OMRE high boiler with terphenyls.

Alkylbiphenyls: Components which eluted from the chromatographic column between biphenyl and o-terphenyl as shown in Figure 2. The first peak was believed to be 3, 3-dimethylbiphenyl.

Alkylterphenyls: Components which eluted from the chromatographic column between o-terphenyl and triphenylene (excluding m-terphenyl and p-terphenyl) as shown in Figures 2, 3, 4, and 5. One major component was always found in these chromatograms, but no identification has been made.

Lights: Any products from hydrocracking which were lower boiling than biphenyl.

Conversion: Disappearance of high boiler,

$$\%\ \text{Conversion} = \frac{\%\ \text{HB in coolant} - \%\ \text{HB in product}}{\%\ \text{HB in coolant}} \times 100$$

Product Recovery: Product includes biphenyl and heavier, or material remaining after distillation of solvent and products lower boiling than biphenyl.

Weight Percent Yield: Based on coolant charged,

$$\text{Wt\% yield} = \frac{\text{Wt of component}}{\text{Wt coolant charged}} \times 100$$

Net Yield: Based on high boiler in coolant converted,

$$\text{Wt\% net yield} = \frac{\text{Wt of component in effluent} - \text{wt of component in charge}}{\text{Wt of HB in charge} - \text{wt of HB in effluent}} \times 100$$

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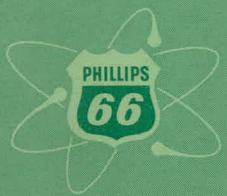

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