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ABSTRACT

The solvent distribution reclamation process using 5, 10, 15, 22, 30, 40, and 50 wt % Core II HB in Santowax-OMP has been accomplished. Cost evaluations show that spent coolant containing 20 wt % or more high boiler is economical to reclaim. The wiped-film distillation of Core II high boiler gave a 27% yield of reclaimed coolant; cost evaluations show this process to be economical. Catalytic hydrocracking process studies on 15.8% partially reduced high boiler have been completed. Processes giving 80% yield of hydrocracked product are economical. Preparation of several mono-alkyl polyphenyls for use in basic studies have been initiated. Cost comparisons of several technically feasible reclamation processes, presented in an earlier report, were reevaluated and are tabulated.

I. INTRODUCTION

The overall objectives of this program are (1) to develop a coolant reclamation process that is technically sound; (2) to evaluate by theoretical, experimental, and economic studies the relative practicality of reclamation processes (coolant management studies); and (3) to undertake a broad base research and development program in areas of coolant technology that will both complement present programs and will also contribute basic technology and knowledge to the organic coolant program.

The results of work in the following areas are described in this report: (1) solvent distribution reclamation studies; (2) wiped-film distillation of high boiler as a reclamation process; (3) catalytic hydrocracking of partially reduced high boiler for reconstituting high boiler; (4) evaluation of product from the reclamation processes; (5) preparation of mono-methyl and -ethyl terphenyl and other compounds for use in fundamental coolant studies; and (6) economic evaluation of various reclamation processes.

II. SUMMARY

Coolant reclamation studies were devoted to process development and product evaluation during this quarter. The solvent distribution process for reclaiming both OMRE Core I and OMRE Core II high boiler and spent coolant was extended to formulated spent coolant mixtures containing 5, 10, 30, 40, and 50 wt % high boiler. Fractionation of the high molecular weight fraction from the low molecular weight fraction (reclaimed coolant) was achieved in all cases. Cost calculations show that spent coolant containing 20 wt % or greater high boiler (HB) would be economical to reclaim. Economic evaluation shows that at these HB concentrations, the solvent distribution reclamation process gives a yearly profit of about \$750,000 and a per cent return on investment of 38 to 50%.

In addition, several blends of solvents were used to reclaim Core II high boiler and spent coolant. These results make the process more general so that it is not dependent on present solvent compositions or sources. The results also showed that isoöctane (branched chain aliphatic) does not give maximum yields of reclaimed coolant.

Electron irradiation on Santowax-omp solutions of reclaimed high boiler gave residue values (after distillation) which were decreased by 40-50% compared to residue values from the m-terphenyl blank.

Wiped-film distillation of OMRE Core II high boiler using a commercial pilot plant Kontro "Ajust-O-Film" still gave a 27% yield of reclaimed coolant at its maximum temperature (323°C) and minimum pressure (0.5 mm Hg). An economic evaluation of this process gives a profit of

\$322,000 per year when compared to the case where high boiler is discarded and replaced with new terphenyl.

Optimum conditions for hydrocracking 15.8% partially reduced high boiler using copper chromite catalyst have been obtained. The process can operate from 495 to 550°C, at 500 to 1500 psig, and with a liquid hourly space velocity of 1.8 to 4.8 hr⁻¹. The process is characterized by low coke formation under all conditions. A six-hour run gave a coke yield of 0.4 wt %/hour based on feed material. The product shows considerably better coolant properties than high boiler or partially reduced high boiler. Good yields (60-80%) of product having low viscosity (0.8 cp at 265°C), low average molecular weight (254-350), an increased thermal decomposition temperature (390°C), and low fouling tendency (~5 mg) are obtained. Cost evaluations of a 60, 70, and 80% yield process show a profit of -\$142,000, +\$100,000, and +\$259,000 per year when compared to the process where high boiler is burned and replaced with new terphenyl.

The fundamental aspects of the coolant program have begun. Dihydroresorcinol ethylenol ether (680 g), 3-phenylcyclohexen-2-one (200 g), and 3-bromo-ethylbenzene (140 g), intermediates in the synthesis of mono-methyl and -ethyl terphenyls and 1-phenyl-3-xenyl-cyclohexadiene-1,3 (dihydroquaterphenyl) were synthesized. The radiation and thermal stability of the methyl- and ethyl terphenyls as well as the fouling ability will be determined.

III. FRACTIONATION METHODS

A. SOLVENT DISTRIBUTION

1. Introduction Final laboratory-scale development work on the solvent distribution technique of reclaiming terphenyl spent coolant or high boiler has been completed. A few product evaluation tests must be completed; when this is done the program objectives will have been met. These objectives were: (1) to separate high boiler or spent coolant containing 5-50% high boiler into high and low molecular weight fractions with appropriate blends of hydrocarbon solvents, (2) to evaluate the low molecular weight fractions for reuse as reactor coolant moderators, and (3) to develop a technically sound and economical process.

2. Results and Discussion Spent coolant samples of various high boiler concentrations were reclaimed by solvent distribution. Samples of 5, 10, 30, 40 and 50 wt % high boiler in Santowax-omp were reclaimed using Esso VM & P Naphtha. Runs were made using two aromatic: aliphatic solvent ratios, 20:80 and 30:70. The experiments were designed to show that the solvent distribution technique is applicable as a reclamation procedure over a wide range of coolant composition. Table 1 gives product yields as well as concentration of spent coolant and high boiler reclaimed in each run.

2.

Table 1

PRODUCT YIELDS FROM RECLAMATION OF FORMULATED SPENT COOLANTS OF VARYING
HIGH BOILER CONCENTRATION

Aromatic/ Aliphatic Wt. Ratio	HB ^a conc. in Santowax C.I.D	Wt SC ^b reclaimed per liter solvent,g	Wt HB reclaimed per liter solvent,g	Yields, Wt %	
				Reclaimed SC	High Mol. Wt. Fraction
20:80	5	198	9.9	99.5	1.0
20:80	10	210	21	91.0	2.4
20:80	22 ^c	241	53	87.2	9.7
20:80	30	270	81	91.5	6.3
20:80	40	315	126	90.8	5.6
20:80	50	378	189	89.2	10.0
30:70	5	340	17	99.0	1.0
30:70	10	360	36	96.0	1.5
30:70	22 ^c	414	91	84.5	10.1
30:70	30	449	135	94.0	4.8
30:70	40	540	216	90.0	6.9
30:70	50	648	324	88.0	7.9

^a HB is high boiler (Core II)

^b SC is spent coolant (Core II HB in Santowax omp)

^c Core II spent coolant

Table 1 shows that yields obtained at a given high boiler concentration do not change significantly when the aromatic:aliphatic solvent weight ratio is increased from 20:80 to 30:70. Since the weight of spent coolant reclaimed per liter of solvent (VM & P Naphtha) is increased markedly at the 30:70 ratio with no loss in fractionation efficiency, this solvent ratio is more economical. At a ratio of 40:60 or lower, no fractionation is achieved. Table 1 also shows that even when a 30:70 aromatic:aliphatic reclaiming mixture is used, the weight of the high boiler reclaimed per liter of solvent is only 17 grams at 5% HB concentration and 36 grams at 10% HB concentration. At the decomposition rates expected at these high boiler concentrations and to maintain the high boiler concentrations at 5 to 10% the rate of coolant processing would be 40,000-17,000 lb/hr, respectively (ref.6). This processing rate is unsound economically as shown in the cost evaluation section of this report. On the other hand, such a process is economically sound at high boiler concentrations of 20% or higher.

Products were evaluated for degree of separation achieved between high and low molecular weight fraction, thermal stability, and the film forming capacity of the low molecular weight fractions. These data are given in Table 2.

Table 2

EVALUATION OF RECLAIMED SPENT COOLANTS AND HIGH MOLECULAR WEIGHT FRACTIONS

HB Conc. in Santo- wax-omp Wt. %	C/H	Thermal Decomp. Temp, °C ^b	PCFT value mg film	High Mol. Wt. Fraction		
				C/H	No. Ave. Mol. Wt.	Wt % ϕ_3 Unrecovered
5	-	-	5	1.40	1159	0.7
10	1.31	476	-	1.43	584	0.2
22	-	-	8	1.55	525	2.9
30	-	438	4	-	1770	0.1
40	-	445 ^a	4	-	566	1.8
50	1.35	366	9	1.49	748	1.7

^a Run on sample from 20:80 solvent ratio; all other data from 30:70 ratio samples.

^b Defined as the temperature at which 1 mole percent per hour decomposes.

In general, it appears from the C/H ratios and molecular weights cited in Table 2 that the high molecular weight fractions separated are roughly equivalent in each case. The rather high molecular weights for the 10 and 30% runs could result from the presence of undissolved solute in the diphenyl ether used as solvent in the cryoscopic molecular weight determination. The total amount of terphenyl hold-up by the high molecular weight fractions is between 0.1 and 2.9%. This loss is influenced highly by the efficiency of the washing operation of the filter cake. In 12 out of 15 runs it was held below 2% and in 9 out of 15 below 1% using a single-leaf laboratory filter. The PCFT data on these reclaimed coolants show values generally an order of magnitude lower than those obtained with Core II spent coolant (~50 mg) and 30% Core II high boiler in Santowax (42 mg). From a coolant management standpoint, solvent distribution could offer a means of reducing coolant fouling ability. As expected, the thermal decomposition temperatures show a gradual increase with decreasing high boiler concentration. Reclaimed spent coolant containing 10% high boiler having a thermal decomposition temperature of 476°C is nearly as stable as Santowax-OMP (490°C) evaluated under the same experimental conditions.

The solvent distribution process should be related not only to complex mixtures of currently available commercial solvents such as Esso VM and P Naphtha, but more generally to blends of specific hydrocarbons. These simpler blends can then be related to petroleum compositions commercially available at any future time. Thus, if a particular petroleum brand name becomes unavailable later, a satisfactory substitute can easily be found using the data reported. In the Third Annual Report (ref. 1), several factors involved in the selection of particular petroleum cuts were described. Among them, aromatic-aliphatic-alicyclic hydrocarbon ratio was found to be significant. In addition, trace amounts of high boiling components in certain solvents were nearly impossible to remove and contributed to heavy film formation in the PCFT (pyrolytic capsule fouling test) unit. These factors were taken into consideration in formulating blends of known hydrocarbons for reclamation experiments. The hydrocarbon ratios were chosen on the basis of FIA* and mass spectral data obtained on commercially available solvents which gave the best reclamation process (ref. 2). All reagents showed 98-99+ % purity as measured by vapor phase chromatography (VPC). The boiling points ranged from 99°C (2,2,4-trimethylpentane) to 174°C (n-decane). Solvent blends used and yields obtained with Core II HB and spent coolant are given in Table 3. Carbon-hydrogen analyses, molecular weight determinations, and PCFT runs are currently being carried out.

* Fluorescent Indicator Analysis

Table 3

PRODUCT YIELDS FROM RECLAMATION OF CORE II SPENT COOLANT AND HIGH BOILER USING FORMULATED SOLVENTS

Run No.	Solvent Composition	Aromatic: Aliphatic Ratio	Wt % Reclaimed HB ^c	Wt % HMWF ^d	Wt % Rec. SC	Wt % HMWF ^d
1	n-Decane (100%)	30:70 ^a	----	----	91.8	8.2
2	2,2,4-Trimethyl-pentane (100%)	30:70	----	----	77.2	22.8
3	n-Decane (70%) p-Xylene (30%)	30:70 ^b	72.5	27.5	----	----
4	n-Decane (47.1%) p-Xylene (11.6%) Cycloheptane (41.3%)	30:70	----	----	90.3	9.7
5	n-Decane (28.3%) 2,2,4-Trimethyl-pentane (18.8%) p-Xylene (11.6%) Cycloheptane (41.3%)	30:70	----	----	87.5	12.5

^a For spent coolant runs, aromatic solvent is taken as total weight of terphenyls present and aliphatic as total weight of formulated solvent added.

^b Aromatic:Aliphatic Volume Ratio in added solvent.

^c Initial weight of HB used was 50 grams in 150 ml solvent or 333 grams per liter.

^d HMWF = High Molecular Weight Fraction.

Results obtained from these runs are similar to those obtained with complex petroleum mixtures with the same aromatic-aliphatic-alicyclic composition. The data serve not only as a basis upon which to choose solvents or solvent mixtures if a particular commercial solvent becomes unavailable, but also serve to eliminate certain hydrocarbons that give low yields. For example, 2,2,4-trimethylpentane (isooctane) gives a yield of 77.2% reclaimed spent coolant (run 2).

n-Decane alone (run 1) gives a yield of 91.8%, a 14.6% increase over isoöctane. The addition of isoöctane to solvent mixtures has the effect of decreasing the yield even in the presence of alicyclics that are good solvents for the process (runs 4 and 5). Therefore, in order to obtain maximum yield with a solvent having a 30:70 aromatic:aliphatic solvent ratio, excessive amounts of isoöctane and similar branched-chain compounds should be avoided. If they are present, the aromatic content should be increased to a point where maximum yield and fractionation are obtained.

The yield results obtained on high boiler with a 30:70 p-xylene-n-decane ratio are about equal to those obtained with xylol-kerosene solvent pair (ref. 3) and Esso Varsol-2 (ref. 4), but greater than with benzene-hexane solvent pair all of the same aromatic-aliphatic composition. The yield from benzene-hexane at this ratio is 58% (ref.5).

Some general comments concerning the process can be made.

1. High boiling solvents ($>175^{\circ}\text{C}$) should be avoided because these are difficult to separate from the reclaimed spent coolant and also are potential sources of fouling (ref. 1).
2. Straight-chain aliphatics and alicyclics containing 8 to 10 carbon atoms are good solvents for the process.
3. Isoöctane and similar branched-chain aliphatics decrease the yield and should not be used in excessive amounts.
4. C_8 to C_9 hydrocarbons (straight-chain and alicyclics) also give low yields (ref. 5).

Evaluation of reclaimed high boiler and reclaimed spent coolant for radiolytic stability has been partially completed. Studies have been made using the Van de Graaff electron accelerator at our Dayton Laboratories. Some samples remain to be completed at Dayton. In addition, samples are currently being exposed to gamma and neutron irradiation at the Materials Testing Reactor, Idaho, under the supervision of California Research Corporation. Table 4 summarizes electron radiolysis results on Santowax solutions of reclaimed high boiler obtained from benzene-hexane and xylol-kerosene solvent pairs.

Table 4

RADIOLYTIC DECOMPOSITION OF RECLAIMED HB IN SANTOWAX OMP BY VAN de GRAAFF
2 MEV ELECTRONS AT 400°C AND 20 WATT-HR PER GRAM

Sample No. ^a	Solvent pair used in Reclamation	% Decomposition after Corrections			
		Gas ^b	Volatiles ^c	Residue ^d	Total ^e
17077H	Xylol:Kerosene (90:10)	2.39	0.23	9.73	12.36
17075B	Xylol:Kerosene (50:50)	1.32	0.21	7.38	8.92
17077K	Xylol:Kerosene (30:70)	0.14	0.25	9.76	10.15
17077B	Xylol:Kerosene (10:90)	2.70	0.21	10.33	13.25
15872E	Benzene Hexane (70:30)	1.12	0.51	6.66	8.29
15872F	Benzene Hexane (50:50)	-0.08	0.24	7.65	7.82
15872G	Benzene Hexane (30:70)	0.54	0.22	8.73	9.49
15872H	Benzene Hexane (10:90)	1.83	0.12	7.32	9.28
m-φ ₃		0.21	0.37	14.96	15.54

^a Samples are 30 wt % Core I HB in Santowax OMP.

^b Gas values are determined by weight loss after irradiation.

^c Volatiles represent the weight loss from the irradiated sample for two hours at 200°C and atmospheric pressure.

^d Residue remaining after distilling an aliquot of the irradiated sample for 4 hours at 200°C and 0.05 mm Hg.

^e All samples were run in duplicate and the average is given except for 17077K, a single determination.

Table 4 shows that the per cent decomposition products measured in each sample is generally lower than that obtained for meta-terphenyl above. Some reduction is expected if one considers the inhibiting (ref 6) effect of high boiler on the decomposition of terphenyl and also the effect of diluting terphenyl with high boiler. The dilution effect alone does not explain the 40% decrease in decomposition products relative to m-terphenyl. In addition to improved radiation resistance reclamation by solvent distribution improves substantially the overall coolant properties. These include average molecular weight (lower) thermal decomposition temperature (higher), and fouling potential (greatly reduced). As far as coolant management is concerned, these gains coupled with increased radiation stability over fresh coolant are significant.

B. WIPED FILM DISTILLATION

1. Introduction Research on fractionation of coolant containing high boiler has also been directed at distillation techniques. Distillation using the CMS-5 centrifugal molecular still was unsuccessful because of major mechanical problems associated with distilling high boiler. However, during this quarter a successful distillation of high boiler was carried out at Artisan Metal Products, Inc., Waltham, Mass., using a commercial pilot plant Kontro "Ajust-O-Films" still.

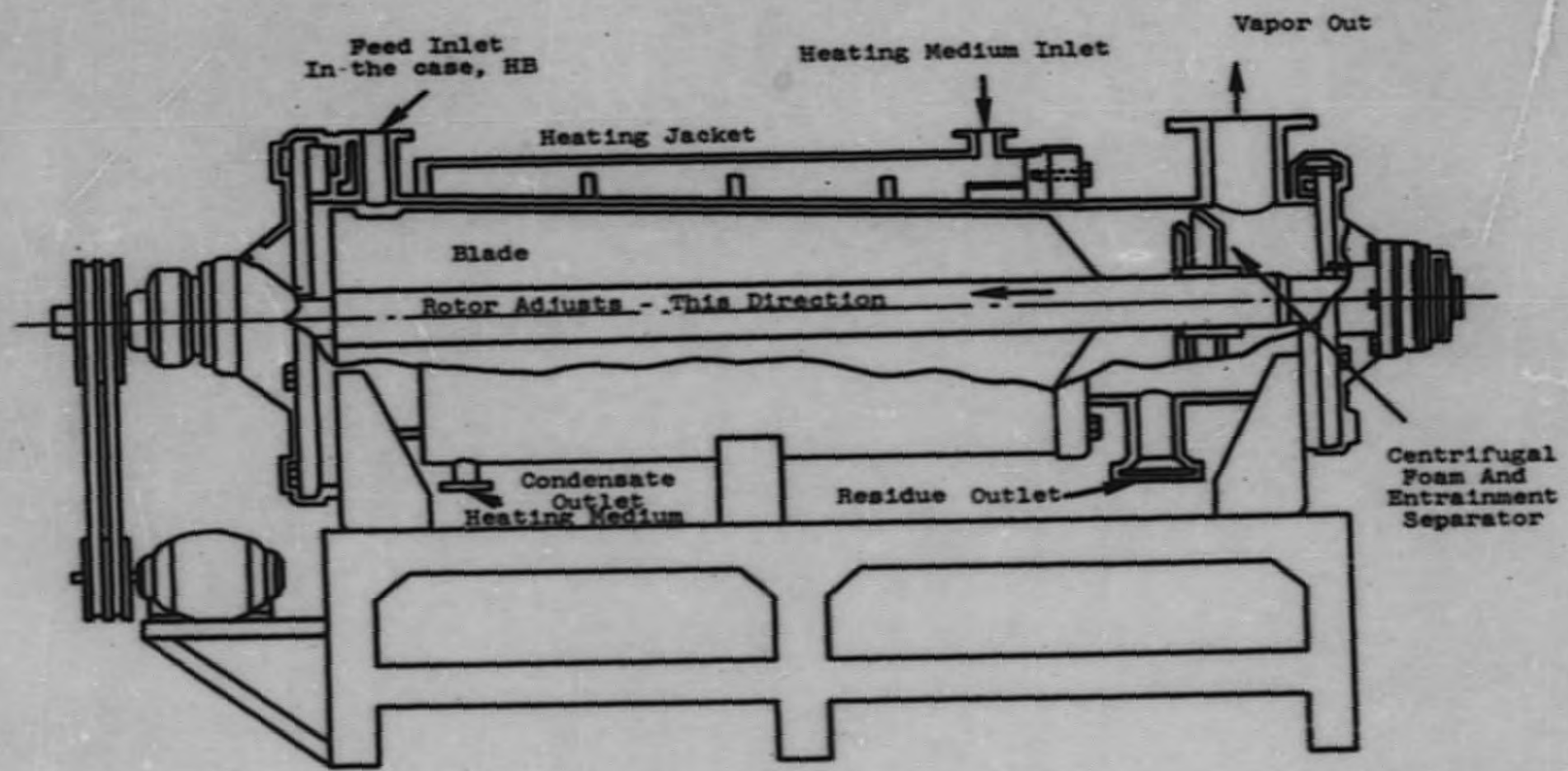
2. Apparatus Figure 1 is a drawing of the still. The still is 1 square foot, horizontal, forward-taper machine (stator) with blade clearance adjusting feature. Inside the stator, a rotor, equipped with blades, is mounted on the center axis. The still operates on a centrifugally wiped, thin-film principle, with minimum clearance between the tips of the rotor blades and the heat transfer wall. The cylindrical body is surrounded by a heating jacket for the heat transfer fluid. As the blades rotate at 1400 RPM, feed material (introduced into the still at the wide end of the stator) is picked up by the blades, and immediately forms a thin film on the inside wall. The volatile materials are quickly vaporized and the less volatile materials flow out at the bottom of the stator. The temperatures, pressure, residue time (feed rate) and film thickness can be controlled to vary the distillation conditions.

3. Results The results of the distillation are shown in table 5. The unit was operated at its maximum temperature (323°C) and minimum pressure (~0.5 mm) with varying feed rates.

Table 5

CONDITIONS USED IN WIPED-FILM DISTILLATION OF OMRE CORE II HIGH BOILER

<u>Cut No.</u>	<u>Feed rate lb/hr</u>	<u>Still Temp °C</u>	<u>Pressure, mm Hg</u>	<u>Yield Wt %</u>
1	40.5	312	0.45	19.2
2	23	311	0.37	23
3	14.6	312	0.34	25.4
4	11.9	317	0.36	26.0
5	12	323	0.39	27.0



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Figure 1. Ajust-O-Film[®] Horizontal Wiped-Film Still

Table 6

PROPERTIES OF DISTILLATE AND RESIDUE FROM
WIPED-FILM DISTILLATION

	HB ^a	Cut No. 2		Cut No. 5	
		Distillate	Residue	Distillate	Residue
Wt% Yield	----	23	64 ^g	27	60 ^g
No. Ave. Mol. Wt.	550	297	690	343	749
C/H Ratio	1.40	1.27	1.52	1.36	1.49
Viscosity, cp	10.7 ^b	2.33 ^c	13.5 ^d	3.60 ^c	22.3 ^d
PCPT, mg film	----	4.0 ^e	38.5 ^e	6.2 ^f	47.5 ^e
Thermal Decom. Temp., °C ^h	360	----	----	402	330
δ ₃ content, wt%	10	----	0.6	----	none

^a High Boiler (Core II) placed here for comparison

^b At 265°C

^c At 200°C

^d At 354°C

^e 37.5% in Santowax OMP

^f 25% in Santowax OMP

^g Some terphenyl and volatiles were lost in the lines leading to the vacuum traps. Hence, the distillate and residue yields are lower.

^h See page 4 for definition.

Table 5 shows that reducing the feed rate from 23 lb/hr, (cut no. 2), to 11 lb/hr (cut no. 5), had only a small effect on the distillate yield. It, therefore, appears that the still was operating near its maximum efficiency at this temperature (311-323°C). The experiment was a success from a mechanical and operational standpoint, but the yield fell short of the goal (50-70%) set for this type of process. It is felt that higher yields can be obtained if the stainless steel pilot plant is modified for operation at higher temperatures (400-450°C).

Product and residue of two cuts (Nos. 2 and 5) were evaluated; these data are shown in Table 6. The results show that a low molecular weight fraction was separated from a high molecular weight fraction. Average molecular weights of the distillates (297; 343) and residue (590; 741) as well as the carbon-to-hydrogen ratio of the distillates (1.27; 1.38) and residues (1.52; 1.49) provide adequate evidence for the fractionation. Viscosity, thermal decomposition temperatures, and PCFT data provide additional evidence. The viscosities of both distillates were measured at 265°C. The residues were not completely melted at this temperature so that the viscosities reported for them are for 354°C. The difference in viscosity, even at these two temperatures is indeed large. The viscosity of the residue at 354°C is 22.3 cp (cut No. 5) while that of the distillate at 200°C is 3.60 cp. The residue value, however, is still far below the 50,000 cp limit that the Kontrol still is reported to be able to handle.

The pyrolytic fouling capsule test (PCFT) values and thermal decomposition temperatures are improved considerably compared with values for the residue and starting high boiler.

The still performance and viscosity of the residue indicate that yields greater than 27% can be achieved with the wiped-film still if it could operate at higher temperatures (400-450°C). An advantage of this type of distillation is that the residue time required for distillation of any substance is extremely short. For distillation at higher temperatures (400-450°C), the short residence time would reduce coolant decomposition during the distillation.

An economic evaluation of this deep cut distillation using results from cut No. 5 gives an incremental profit of \$332,000 per year compared to the process where high boiler is discarded and replaced with new terphenyl. The return on investment is 24% (Table 11).

IV. CATALYTIC HYDROCRACKING OF PARTIALLY REDUCED HIGH BOILER

A. INTRODUCTION

During this quarter, research in this area has been devoted to optimizing the hydrocracking process to make this process more economical.

This method of reclaiming high boiler is a two-stage process: (1) partial reduction of high boiler followed by (2) hydrocracking of the partially reduced high boiler.

Process variables of temperature, pressure and space velocity were studied in an effort to optimize the hydrocracking process using 15% partially reduced high boiler as feed and Girdler G-13 copper chromite as the catalyst. In addition to these process studies, three catalysts /results for which were incomplete for the 3rd Annual Report (ref. 7) were also tested. These results are discussed first.

B. EXPERIMENTAL DATA

Results with the three catalysts tested are shown in Tables 7 and 8. Nickel-chroma-alumina and molybdenum sulfide-alumina catalysts gave good results with reclaimed high boiler feed (ref. 7) and equally good results with partially reduced high boiler feed. Product yield was 70%, coke yield 3.9%, and gas yield only 1.9 to 3.7%. Biphenyl and terphenyl concentration was not increased, but alkylterphenyl type compounds were produced in 11-18% yield. Table 8 shows that these catalysts gave product with a much higher carbon-to-hydrogen ratio than the starting material. From the carbon-to-hydrogen ratio, molecular weight, and viscosity data, it is quite apparent that at least two reactions are occurring: (1) hydrocracking of the partially reduced polyphenyls to lower molecular weight polyphenyls and alkyl polyphenyls and (2) aromatization of the polyphenyl species before or after hydrocracking. This explains both the carbon-to-hydrogen increase from 1.14 to 1.30, the molecular weight decrease (550 to 300-350) and viscosity decrease (10.7 cp to 1-3 cp). These catalysts can be considered active hydrocracking catalysts for this feed system and under these conditions.

Table 7

HYDROCRACKING OF PARTIALLY REDUCED HIGH BOILER^a

Pressure: 1500 psig
 Temp: 495 + 10°C
 LHSV: 3.8-4.6 hr⁻¹

Feed: 50 wt% PRHB in p-xylene
 H₂/HC (mole): 9-11
 liters H₂/g total feed: 1.3-1.7

Run No.	164	165	166
Duration of run, min.	120	120	120
Catalyst	N ₁ -Cr-Al ₂ O ₃	MoO ₃ -Al ₂ O ₃	MoS ₂ -Al ₂ O ₃
Yields, wt % Feed charged			
% total recovery	91	77	90
% coke on catalyst	3.9	4.9	--
% gas, C ₁ -C ₃	2.7	5.6	1.9
Yields, wt % PRHB charged			
% PRHB recovery (product)	70	49	72
% Ø ₃ , Ø ₂	0.5	no incr.	0.7
% hydrocarbon boiling above Ø ₂ and below triphenylene, RØ ₂ , RØ ₃	18	15	11
% ØH, RØ	7.4	1.0	8.3
% Conversion	34	55	32
% Selectivity	1.4	--	2

^a Core II
 High boiler reduced with copper chromite catalyst at 230°C, 4000 psig in an autoclave to the extent of 15.8%.

Table 8

YIELDS AND PROPERTIES OF HYDROCRACKED PARTIALLY REDUCED HIGH BOILER

Run No.	HB ^a	PRHB	164	165	166
Catalyst	----	----	N ₁ -Cr-Al ₂ O ₃	MoO ₃ -Al ₂ O ₃	MoS ₂ -Al ₂ O ₃
% Product Yield	---	----	70	49	72
Carbon-to-hydrogen ratio	1.40	1.14	1.35	1.30	1.30
No. Ave. Mol. Wt.	550	518	349	298	344
Viscosity at 265°C, cp	10.7	8.0	3.1	1.3	2.0
Decomposition Temp. °C ^b	360	370	395	396	371
Color and state	blk solid	blk solid	blk tacky tar	blk vis oil	blk vis tar

^a High boiler and 15.8% partially reduced high boiler are placed here for comparison.

^b See page 4 for definition.

The data for the hydrocracking runs using copper chromite catalyst are listed in Tables 9 and 10. They represent the relationship of temperature, pressure, and space velocity to product yield, coke, conversion, and product properties.

The product yields, in general, vary from 60 to 80%. These are lower than those reported for hydrocracking of 7.8% partially reduced high boiler with the same catalyst and reaction conditions, but molecular weight decreases are greater with the present feed (15.8% partially reduced high boiler). Biphenyl and terphenyls are not produced in any appreciable quantity. Alkyl biphenyl and alkyl-terphenyls are produced in 13 to 37% yields. Conversions range from 20 to 50%, but fall mostly in the 40% region.

Low coke yields (3.9 to 8.3%) were obtained over the range of conditions studied. This is significant since the process can be operated over a broad range without excessive coke build-up. At low space velocity, the highest coke yield obtained was 8.3% (run 171). Figure 2 shows the coke yield as a function of pressure. High pressure has the effect of preventing excessive coke deposition on the catalyst. Table 9 and Figure 3 show that increasing the reaction temperature did not cause an increase in coke formation as might be expected. In fact, coke yield appears to decrease with increasing temperature. Under these conditions, more points in the 500°C area are needed.

High temperatures (525 and 550°C) increase conversion, but as shown in Figure 4, the effect of temperature on the product yield is not particularly obvious. More runs were made at the higher temperatures at this space velocity and pressure so that it is difficult to predict whether the yield obtained from the 500°C run represents a trend. It was expected that the yield would decrease as the temperature increased because coke, and gas, and light end yields are expected to increase. This was not the case, however, although high temperatures do have a marked effect on product properties. This is illustrated in Figure 5, which shows that product from the high temperature runs has a considerably lower viscosity than product from the low reaction temperature runs.

Increased pressure reduces the coke yield of the hydrocracking reaction. This is important since the cost of the process is dependent, among other things, on the catalyst cycle time before regeneration and on the catalyst life. Table 9 and Figure 6 show that increasing pressure also appears to decrease the product yield. However, no effect on product properties is noted (Tables 9 and 10).

The liquid hourly space velocity at constant temperature and pressure affects the product yield and product properties. The effect of product yield is shown in Figure 7. Low space velocity (2.2 hr⁻¹) runs gave lower product yield, but products from these runs usually have lower viscosity than product from high space velocity runs. The high space velocity (4.8 hr⁻¹) runs require a temperature of 550°C to yield product exhibiting good coolant properties.

The properties of hydrocracked products differ markedly from the starting partially reduced high boiler. This is shown in Table 10. Molecular weights were decreased from 518 to about 300. The viscosity is changed by a factor of 8 to 10 (8.0 cp compared to 0.64-1.3 cp). The thermal decomposition temperature is increased by about 25°C from 370°C to 395°C. This shows that hydrocracked products, although containing alkyl polyphenyls, are equal to or better than high boiler or partially reduced high boiler in thermal stability. Hydrocracked products are currently being irradiated in the

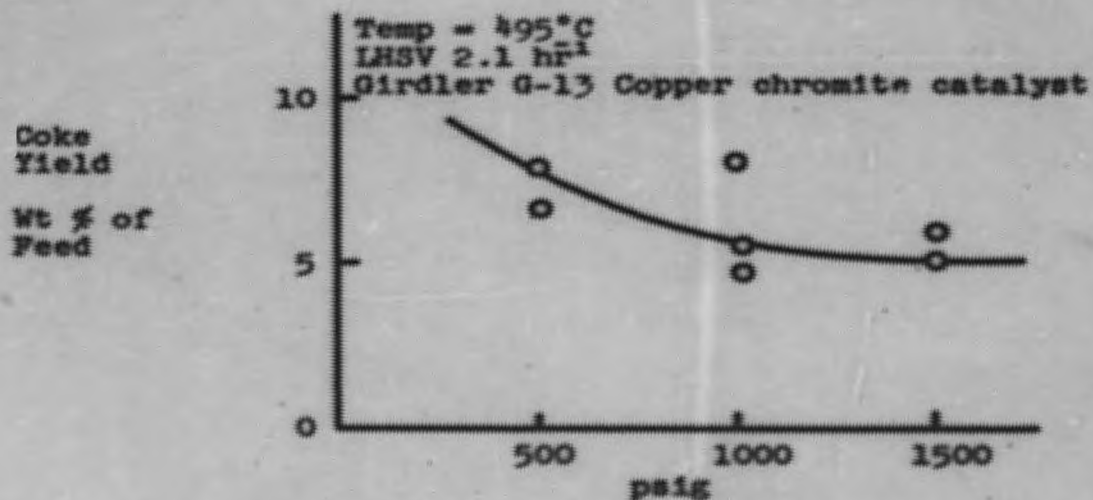


Figure 2. Hydrocracking of Partially Reduced High Boiler

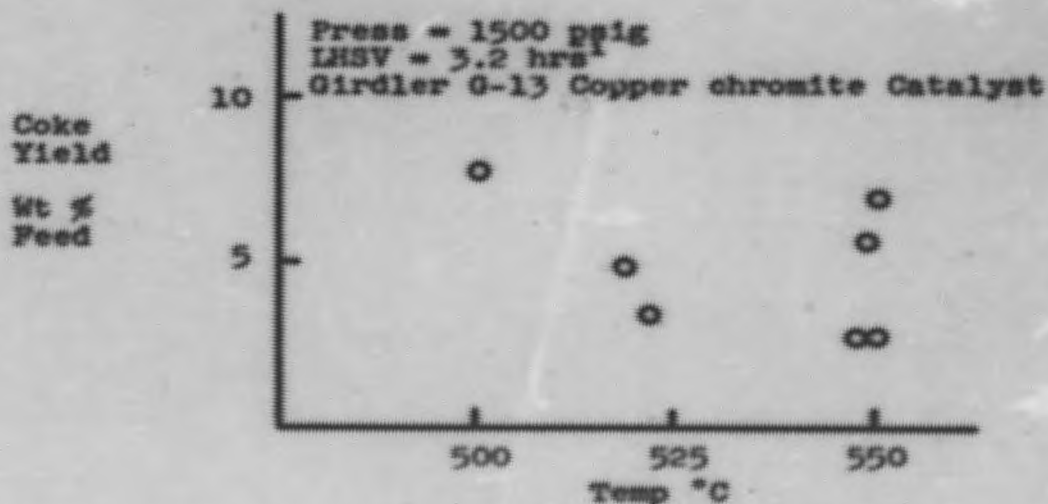


Figure 3. Hydrocracking of Partially Reduced High Boiler

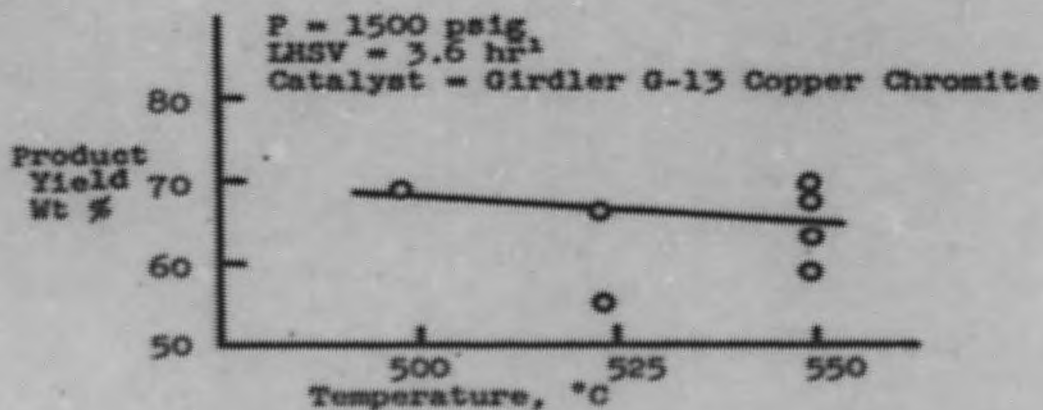


Figure 4. Hydrocracking of Partially Reduced High Boiler Yield vs Temperature

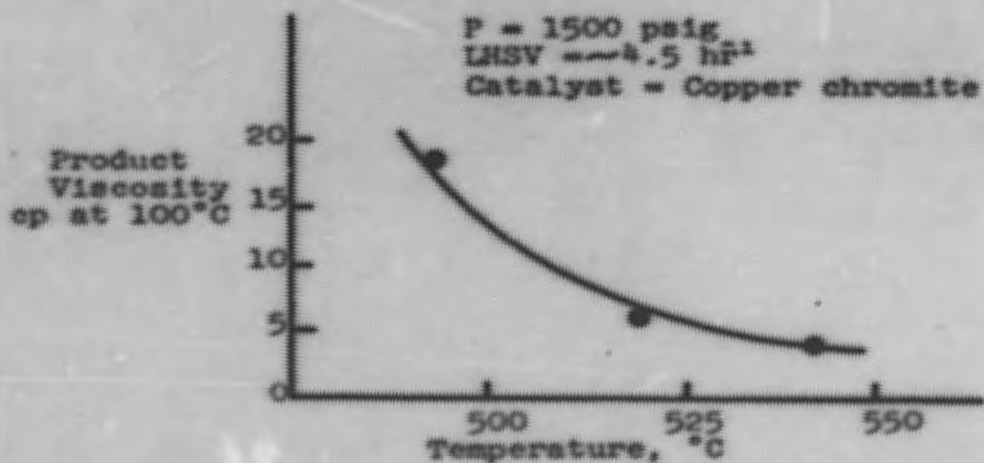


Figure 5. Hydrocracking of Partially Reduced High Boiler Viscosity vs Temperature

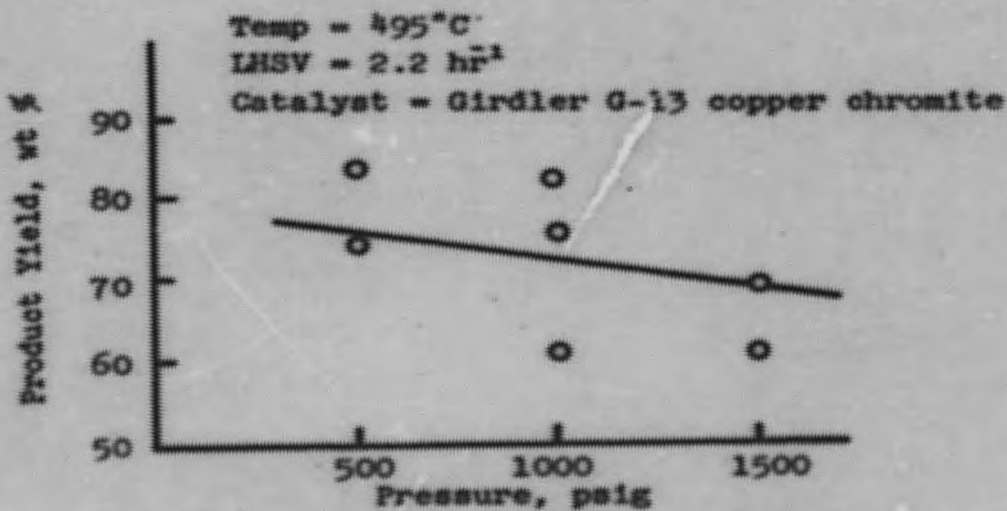


Figure 6. Hydrocracking of Partially Reduced High Boilers; Yield vs Pressure

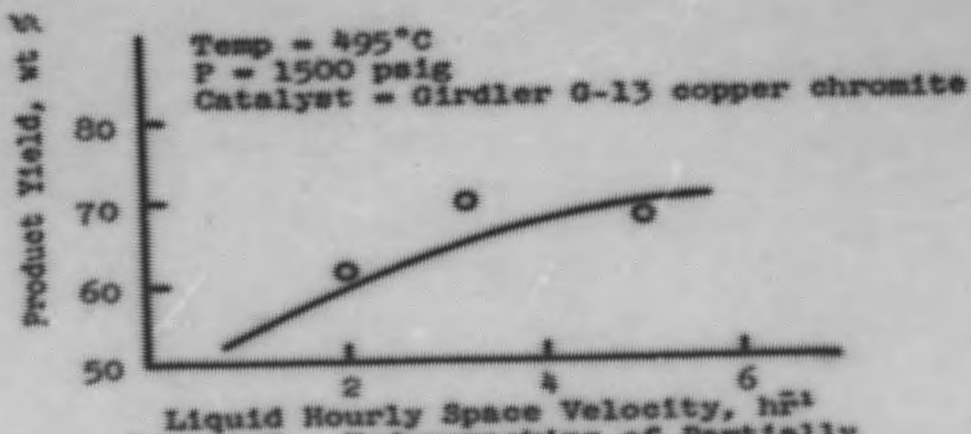


Figure 7. Hydrocracking of Partially Reduced High Boilers; Yield vs LHSV

Table 10
YIELDS AND PROPERTIES OF HYDROCRACKED PARTIALLY REDUCED HIGH BOILER
CATALYST: GIRDLER G-13 COPPER CHROMITE

Run No.	HD ^a	FRHD ^a	178	189	171	180	179	168	170	172	169	182	184	173	183	185	186	187	174
% Product Yield	-	-	92	75	61	83	75	43	61	69	67	55	66	61	69	59	63	68	68
Carbon-to-hydrogen ratio	1.40	1.14	1.20	-	1.12	1.11	-	1.16	1.12	1.12	1.24	1.14	-	1.09	1.18	-	1.18	1.20	1.24
No. Ave. Molec. Wt	550	518	399	-	271	312	-	326	337	263	285	324	-	254	270	-	295	320	253
Viscosity at 265°C, cp	10.7	8.0	-	-	1.35 ^{b,c}	0.64 ^c	-	-	-	-	-	-	-	-	1.12 ^c	-	0.89 ^c	1.23 ^c	1.18 ^{b,c}
Decomposition ^d Temp. °C	360	370	-	-	-	-	-	382	443	393	394	-	-	393	363	-	393	-	397
Color and state	blk solid	blk solid	dk.br. visc. oil	blk. tacky solid	br. oil cryst.	dk.br. tacky solid	blk. tacky tar	dk.br. visc. oil	gr. br. oil-visc. oil	br. oil-visc. oil	blk. visc. oil	dk.br. visc. oil	blk. visc. oil	gr. oil cryst.	y-br. visc. oil	gr.br. oil-cryst.	dk. br. visc. oil	dk. br. visc. oil	gr.-br. oil-cryst.

^a High boiler and 15.8% partially reduced high boiler both placed here for comparison

^b Viscosity at 200°C.

^c In centipoise; multiplication of this value by the density at the test temperature gives the value in centistokes.

^d See page 4 for definition.

Materials Testing Reactor, Idaho. Combined results of heat and irradiation will more clearly determine the usefulness of re-constituted coolant for reactor use.

A six-hour run was made to compare product and coke yields with those of shorter runs. The data for this run (no. 186) are shown in Tables 9 and 10. The product yield, conversion, coke yield, and product properties are similar to those from shorter run times (run 183). This illustrates that catalyst activity was maintained during this period. To verify that no loss of catalytic activity occurred, run 187 was made using the same catalyst as was used in run 186. The results are essentially the same as those obtained with run 186. This further showed that the catalyst system was not appreciably deactivated by coke deposition or catalyst deterioration. The coke yield over the seven-hour period was only 2.7%. This is 0.4 wt % per hour, which is well within limits for a low-coke hydrocracking process.

The results of the hydrocracking process studies show that the process can operate over a broad range of temperatures, pressures, and space velocities. The temperature, pressure, and space velocity are critical variables as far as product yields, coke, and product properties are concerned. Pressure is less important in regulating the product properties. With Girdler G-13 copper chromite catalyst and 15% partially reduced high boiler as feed, the hydrocracking as a once-through operation can be defined within the limits shown below.

<u>Temperature, °C</u>	<u>Pressure psig</u>	<u>Liquid Hourly Space Velocity hr⁻¹</u>	<u>Product Yields Wt %</u>
495-550°C	500-1500	2.1 - 4.8	60-80

The economics of this process are extremely dependent on yield. Cost evaluation of 60, 70, and 80% yield processes show the corresponding yearly profits to be -\$142,000, +\$110,000 and +\$259,000 compared to the case where high boiler is burned and replaced with terphenyl coolant. The corresponding returns on investment for the 70 and 80% yield processes are 3.8 and 9.3%. These calculations are based on a 300 Mw (e) reactor operating at a steady state 30% high boiler concentration and producing high boiler at the rate of 1000 lb/hr.

V. FUNDAMENTAL COOLANT STUDIES

This phase of the program is in the initial stages of planning and preparation. Pure compounds needed for study are being prepared, and a literature search on other aspects of the work is underway. The results of the synthetic work are described below.

A. SYNTHESIS OF REFERENCE COMPOUNDS

1. Introduction A number of alkyl biphenyls and terphenyls are being synthesized in 50-100 gram amounts in order to obtain these pure derivatives for thermal and radiolytic evaluation. It has been shown (8) that high boiler and hydrocracked reclaimed high boiler contain a large proportion of alkyl polyphenyls. Very few data exist on the thermal and radiolytic stability of pure alkyl polyphenyls so that a program undertaken to obtain these data is of fundamental importance in understanding the behavior of reactor coolant. Second, the fouling potential of these pure compounds is of great importance and will also be studied. Third, these materials can be made available to other contractors for use as reference compounds.

2. Results and Discussion Approximately 680 grams of dihydro-resorcinol ethyl enol ether has been synthesized as an intermediate for this program. From some of this material, 200 grams of 3-phenyl-cyclohexen-2-one has been made as a key intermediate. About 5 grams of 3-methyl-m-terphenyl has been synthesized by reaction of 3-phenyl-cyclohexen-2-one with the Grignard reagent of 3-bromotoluene. A large-scale run is planned to make a total of 100 grams. 3-Ethyl-m-terphenyl will be made via a similar reaction using the analogous Grignard made from 3-ethylbromobenzene, which is not available commercially and has been prepared by a Wolff-Kishner reduction of 3-bromoacetophenone. Experimental procedures are described in Appendix A.

VI. ECONOMIC EVALUATION OF VARIOUS RECLAMATION PROCESSES

An economic evaluation of various reclamation processes was reported in the 3rd annual report (ref. 1, p. 83). Since then, the various reclamation processes have been re-evaluated by our process engineering group to check out the previous estimates. In addition, the following cost estimates were made: (1) economic evaluations of the solvent distribution method for reclaiming spent coolant containing 5, 10, 15 and 22 wt % high boiler; and (2) economic evaluation of the partial reduction-hydrocracking reclamation process using product yields of 60, 70, and 80%. These results are shown in Tables 11, 12, and 13.

The calculations are based on a 300 MW(e) reactor operating at a steady state high boiler concentration of 30% and producing high boiler at the rate of 1000 lb/hr. Steady state HB concentrations of 5, 10, 15, and 22% with the corresponding high boiler production rates of 2000, 1700, 1400, and 1100 lb/hr were also used.

The economic trend in this and the previous evaluation is the same, but the fixed capital and operating costs are greater in the present evaluation. The profits are lower because operating costs have been increased. Physical methods are more economical than chemical methods, except for partial reduction of high boiler (process 16) where a profit of \$725,000/year is shown over the base case (process 1).

To illustrate cost patterns in the event a reactor were to operate at high boiler concentration, other than 30 wt%, cost evaluations of reclamation using the solvent distribution process were made. In the base case spent coolant is distilled to remove reusable terphenyl coolant, and the high boiler residue is burned and replaced with fresh terphenyl coolant. Table 12 shows that base cases with spent coolant containing 5, and 10% high boiler have high fixed capital and operating costs, and it is questionable whether or not a reactor can operate economically at these HB concentrations (no reclamation). Reclamation at these concentrations is not economically sound and even at the 15% HB level, it is questionable. Reclamation using the solvent distribution process becomes profitable at the 20% HB level and above. The capital and operating cost became increasingly higher at low level HB concentrations because at these levels the terphenyl decomposition rate is high. Therefore, large amounts of coolant must be processed to maintain steady state HB concentrations of 5-15%.

The same trends would most likely apply to any process that operates at reduced HB concentrations (15% or less).

Except for processes 3, 4, 11, and 12, the reclamation processes shown are supported by experimental evidence and are technically feasible.

The solvent distribution process on spent coolant containing 20% or greater high boiler is the most profitable of those shown (processes 8, 9). Processes 6 and 7 show equally good profits, but the operating and fixed capital costs are high. The per cent return on investment (18-22%) in these two cases can be considered marginal because of the high investment and operating costs. The next best process is wiped-film distillation of high boiler using the Kontro "Ajust-O-film" still (case 2). Processes 3 and 4 are good processes but are not supported by experimental data. Process 3, however, has a high probability of being successful based on case 2 results. The

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Table 11
 ECONOMIC EVALUATION OF PHYSICAL RECLAMATION PROCESSES
 (300 MW(e) Reactor, Steady State 30% HB Concentration)

Physical Methods	Fixed Capital \$	Operating Cost and make-up \$ at 17¢/lb. \$	Incremental Profit over Base Case \$	% Return on Investment	Operating Cost/lb. Reclaimed Coolant ¢/lb.	Operating and Make-up Cost/lb. Reclaimed Coolant ¢/lb	Payout Time, yr
<u>Distillation Process</u>							
1. Primary distillation (1000 lb/hr disposal) Base Case ^a	950,000	2,055,000	--	--	2.77	10.1	--
2. Primary distillation and wiped-film distilla- tion (750 lb/hr disposal rate)	1,350,000	1,733,000	322,000	23.8	3.48	7.64	4.20
3. Primary distillation and wiped-film distillation (500 lb/hr disposal rate)	1,354,000	1,529,000	526,000	38.8	3.16	6.15	2.60
4. Primary distillation and forced circulation dis- tillation (500 lb/hr disposal rate)	854,000	1,365,000	690,000	81	2.10	5.5	1.24

^a Applies to processes 2, 3, and 4

25.

Table 12
ECONOMIC EVALUATION OF PHYSICAL RECLAMATION PROCESSES
 (300 MW(e) Reactor, Steady State HB Concentration Specified in Process Description)

Physical Methods	Base Case		Fixed Capital \$	Operating Cost and Make-up \$ _a at 17¢/lb.	Incremental Profit over Base Case \$	% Return on Investment	Operating Cost/lb. Reclaimed Coolant \$/lb.	Operating and Make-up Cost/lb. Reclaimed Coolant \$/lb.	Payout Time, yr
	Fixed Capital \$	Operating Cost and Make-up \$ _a at 17¢/lb.							
5. Solvent distribution on spent coolant (5% HB content, 606 lb/hr disposal rate) Base Case	--	--	8,600,000	3,508,000	36,500	0.42	0.75	1.01	2.98
	5,450,000	3,545,000	--	--	--	--	0.17	1.03	--
6. Solvent distribution on spent coolant (10% HB content, 511 lb/hr disposal rate) Base Case	--	--	4,700,000	2,257,000	838,000	17.8	1.04	1.56	5.6
	3,000,000	3,095,000	--	--	--	--	0.39	2.1	--
7. Solvent distribution on spent coolant (15% HB content, 422 lb/hr disposal rate) Base Case	--	--	3,100,000	1,947,500	703,000	22.5	1.69	2.50	4.5
	1,970,000	2,651,000	--	--	--	--	0.72	3.4	--
8. Solvent distribution on spent coolant (20% HB content, 353 lb/hr disposal rate) Base Case	--	--	2,010,000	1,423,700	780,300	37.7	2.26	3.48	2.7
	1,280,000	2,204,000	--	--	--	--	1.4	5.4	--
9. Solvent distribution on spent coolant (30% HB content, 303 lb/hr disposal rate) Base Case	--	--	1,500,000	1,302,000	753,000	50	3.20	4.92	2.0
	950,000	2,055,000	--	--	--	--	2.8	10.1	--
10. Primary distillation and solvent distribution on HB (from 30 wt % spent coolant) 250 lb/hr disposal rate Base Case ^b	--	--	1,350,000	1,314,000	741,000	55	3.49	4.95	1.8
	950,000	2,055,000	--	--	--	--	2.8	10.1	--

^a The base case is processes 5, 6, 7, 8, and 9 plus primary distillation, burning of the HB residue and additional make-up of fresh feed terphenyl.
^b Same as process 1.

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Table 13
ECONOMIC EVALUATION OF CHEMICAL RECLAMATION PROCESSES
 (300 MW(e) Reactor, Steady State 30% HS Concentration)

Chemical Methods	Fixed Capital \$	Operating Cost and Make-up \$ ₂ at 17¢/lb.	Incremental Profit over Base Case \$	% Return on Investment	Operating Cost/lb. Reclaimed Coolant \$/lb.	Operating and Make-up Cost/lb. Reclaimed Coolant \$/lb	Payout Time, Yr
1. Primary distillation (1000 lb/hr disposal rate) Base Case ^a	950,000	2,055,000	--	--	2.8	10.1	--
11. Primary distillation and HS hydrocracking (200 lb/hr disposal rate)	2,522,000	1,684,000	371,000	15	5.1	6.1	6.7
12. Primary distillation and HS hydrocracking (300 lb/hr disposal rate)	2,522,000	1,833,000	222,000	8.8	5.1	6.9	11.4
13. Primary distillation and partial reduction and hydrocracking (200 lb/hr disposal rate)	2,775,000	1,796,000	259,000	9.3	5.5	6.5	10.7
14. Primary distillation and partial reduction and hydrocracking (300 lb/hr disposal rate)	2,800,000	1,945,000	110,000	3.8	5.5	7.2	26
15. Primary distillation and partial reduction and hydrocracking (400 lb/hr disposal rate)	2,929,000	2,197,000	-142,000	neg.	6.2	8.5	--
16. Primary distillation and partial reduction of HS (150 lb/hr disposal rate)	2,045,000	1,322,000	723,000	35.8	3.9	4.8	2.8

^a Applies to processes 11, 12, 13, 14, 15 and 16.

partial reduction-hydrocracking process (process 13) follows those mentioned but again the process is characterized with operating and fixed capital costs, moderate profits (259,000) and a low per cent return on investment (9.3%).

Partial reduction of high boiler (process 16) is equally as good as solvent distribution (processes 8 and 9) but evaluation of the product to determine the technical worth of this process has not been completed as yet.

The economically attractive processes (processes 2, 3, 8, 9 and possibly 16) should be further developed on a pilot plant scale. Block diagrams of all the processes will be shown in a future report.

VII. REFERENCES

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APPENDIX A

EXPERIMENTAL SYNTHESIS WORK

A. DIHYDRORESORCINOL ETHYL ENOL ETHER

To a five-liter, three-necked flask equipped with stirring motor and a Dean-Stark trap surmounted by a Friedrichs condenser was added 350 grams of moist dihydroresorcinol (containing 4% sodium chloride as an impurity) and 2315 ml of benzene. The third neck of the flask was equipped with a nitrogen inlet to maintain a nitrogen atmosphere during the drying operation and during the course of the reaction. The dihydroresorcinol-benzene solution was refluxed while stirring to remove water. After 50 ml water was removed, (leaving about 286 grams, 2.55 moles of dihydroresorcinol), 535 ml (9.17 moles) of absolute ethanol and 11.7 grams of practical grade p-toluenesulfonic acid were added. Stirring at reflux was continued until 42.5 ml water was collected (10 hours). The reaction mixture was cooled to room temperature and washed with 1080 ml of a cold, saturated solution of sodium bicarbonate. The organic layer was then washed with four 250-ml portions of ice cold 1M potassium carbonate solution followed by washes with ice water until neutral. All aqueous washes were saved and subsequently extracted with ether. Both the benzene and ether solutions were dried over anhydrous magnesium sulfate. These solutions were then concentrated in a rotary evaporator and subsequently distilled through a Vigreux column. The major fraction boiled between 65-67°C at 0.35-0.45 mm yielding 220.2 grams of a nearly colorless liquid, $n_D^{20} = 1.5052$ (ref. 9, $n_D^{20} = 1.5040$). The ether extract yielded an additional 11.1 g boiling at the same temperature and pressure. The yield based on pure dihydroresorcinol was 64.7%. The purity of the product was 98.5 area-% as determined by gas chromatography.

B. 3-PHENYLCYCLOHEXEN-2-ONE

To a three-liter, four-necked flask equipped with stirring motor, reflux condenser (protected with a calcium sulfate drying tube), a 500-ml pressure-equalizing dropping funnel with nitrogen inlet adapter and a thermometer was added 54.5 g (2.22 moles) magnesium turnings. The system was heated with a low Bunsen flame to drive off adsorbed moisture. Anhydrous ether (750 ml) was added followed by a dropwise addition of 40 ml of bromobenzene (reagent grade). Refluxing for fifteen minutes initiated formation of the Grignard reagent, after which the remaining bromobenzene (2.42 moles total) was added dropwise over a two-hour period. Dihydroresorcinol ethyl enol ether (171.3 g, 1.22 moles) dissolved in 630 ml of anhydrous ether was added dropwise to the reaction flask over a three-hour period, while maintaining temperature of the reaction mixture between 5 and 10°C. At the end of this time the reaction was allowed to reflux with stirring for one-half hour. The reaction mixture was then

cooled and one liter of 1.7 M sulfuric acid was added slowly with stirring and cooling with an ice bath. After hydrolysis the mixture was steam distilled until 3.6 liters of distillate containing the excess bromobenzene and some biphenyl was collected. The distilland, which consisted of a heavy red oil and an aqueous phase, was separated. The water layer was extracted with ether and the ether extract combined with the oily material. This solution was washed three times with 5% sodium bicarbonate solution and then with water and dried over anhydrous magnesium sulfate. The ether solution was concentrated and the residue distilled through a Vigreux column. The major fraction (133.4 g, 71.7% yield) boiling between 121-124°C at 0.6 mm Hg was collected. The distillate was a viscous, pale-yellow oil that crystallized on standing, mp 63-65°C (literature ref. 10 63-65°C). Vapor phase chromatography showed 97 area-% purity. Infrared spectrum was consistent with the 3-phenylcyclohexen-2-one structure.

C. 3-METHYL-DIHYDRO-M-TERPHENYL/1-(3-TOLYL)-3-PHENYLCYCLOHEXADIENE-1,3/

A four-necked flask equipped with reflux condenser, dropping funnel, stirring motor, and thermometer was charged with 15.8 g (0.56 mole) of magnesium turnings. The system was flamed out, and 450 ml of anhydrous ether was added through the dropping funnel. 3-Bromotoluene (120 g, 0.70 mole) was charged to the dropping funnel and about one-fourth was added to the flask to initiate the Grignard preparation. The reaction was begun only after addition of a small amount of ethyl bromide. After preparation of the Grignard reagent was complete (2 hr) 59.5 g (0.346 mole) 3-phenylcyclohexen-2-one dissolved in 500 ml of anhydrous ether was added dropwise with stirring (one hour) while maintaining the temperature at 20°C. When the addition was complete, the reaction mixture was stirred at reflux for 30 minutes. Upon cooling, 380 ml of 9.5 % sulfuric acid solution was slowly added while maintaining the flask contents at 5-10°C with cooling and stirring. The ether layer was separated and washed three times with 250-ml portions of 5% potassium carbonate solution followed by water washes until neutral. After the ether solution was dried over anhydrous magnesium sulfate, it was concentrated in a rotary evaporator, and the residue was then distilled. A forerun containing bromotoluene, biphenyl and 3,3'-dimethylbiphenyl was collected. The major fraction boiled between 160-163°C at 0.3 mm.

A total of 64.5 grams representing a crude yield of 75.8% of 3-methyl-dihydro-m-terphenyl, was collected. (Vapor phase chromatography indicated that part of the dihydroterphenyl derivative had dehydrogenated thermally to 3-methyl-m-terphenyl during distillation).

D. 3-BROMOETHYLBENZENE

A 300-ml, 3-necked flask was equipped with a reflux condenser and thermometer. To the flask was added 25.2 g (0.127 mole) of 3'-bromoacetophenone (reagent grade), 140 ml of diethylene glycol (practical) 12 ml of 85% hydrazine hydrate solution (0.21 mole hydrazine), and 17.5 g (0.3 mole) potassium hydroxide. The reaction mixture was refluxed at a pot temperature of 136°C for 1.5 hours. A Dean-Stark trap was placed between the reaction vessel and condenser, and refluxing was continued with subsequent removal of water and product until the reaction temperature reached 105°C. The reaction mixture was allowed to reflux for an additional three hours. The reaction mixture was then cooled, neutralized with 200 ml of dilute hydrochloric acid and the heavy oil product separated. The water diethylene glycol layer was then extracted with benzene and these extracts combined with the oil and distillate (collected in the Dean Stark trap). The benzene solution was dried over anhydrous magnesium sulfate, concentrated, and the residue distilled. The major fraction boiled between 78-80°C at 11 mm and amounted to 18 grams (76.5% yield). Vapor phase chromatography showed it to be 99.6 area-% pure with no starting 3'-bromoacetophenone present. The infrared spectrum was consistent with 3-bromoethylbenzene structure.

END