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ANL-5305

Radiation Effects on
Reactor Materials

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STABILITY OF DIPHENYL UNDER FAST FLUX IRRADIATION
IN A DYNAMIC SYSTEM

by

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Price \$ 0.30

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

Reactor Engineering Division

October, 1954

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DATE FEB 15 1957 *ml*

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STABILITY OF DIPHENYL UNDER FAST FLUX IRRADIATION IN A DYNAMIC SYSTEM

by

Sherman Greenberg*

ABSTRACT

Two runs, of 25 and 73.5 hours duration, respectively, were made with diphenyl heated to temperatures in the range of 300-450F in a circulating loop in the Experimental Breeder Reactor to determine radiation stability and possibility of carbon deposition on heater surfaces. Estimates of the rate of radiation damage in diphenyl were made. These were based on the amount of diphenyl exposed to epithermal flux, the amount of radiological products produced in the system, and the calculated flux. These specific damage values, expressed as percentage of material in the flux zone damaged per 10^{18} nvt, range from 25 to 34 per cent. Some carbonaceous deposit was observed during the 74 hour run, but it could not definitely be attributed to irradiation.

I. INTRODUCTION

Organic compounds such as diphenyl have been studied as reactor coolants and moderators because of several attractive properties, among them the relatively low vapor pressure at high temperatures and very low corrosion attack on uranium and structural materials. In a series of static, high temperature irradiation tests (300-700F) conducted by California Research Corporation,^{1,2} a number of compounds displayed sufficient stability to warrant further consideration for reactor use; of these diphenyl was selected for this investigation because of ready availability and relatively low cost.

*A. Amorosi, W. K. Anderson, D. F. McGinnis (EBR), M. Novick (EBR), G. L. Reed (on loan from Dow-Detroit Project), and G. L. Wigle assisted in execution of various phases of the test. L. W. Fromm and W. W. Galbreath, Jr. assisted in the preparation of the report.

¹R. O. Bolt, J. G. Carroll, "Research on Irradiation Stability of Organic Fluids," Summary Report, TID-5094.

²R. O. Bolt, J. G. Carroll, "Research on Irradiation Stability of Organic Fluids," Progress Report No. 4, TID-5132, January 9, 1953.

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The principal effect of irradiation of diphenyl is the formation of a large variety of higher molecular weight compounds such as the terphenyls, tetraphenyls, alkyl benzenes, etc.* Thus, irradiation results in a mixture of undamaged diphenyl and these compounds. The composition of the mixture at any time is a function of irradiation exposure, and at early stages of exposure the mixture may retain the initial desirable properties of diphenyl. It is recognized, however, that eventual decomposition of all material to carbon and gaseous products will occur under sufficient irradiation exposure, and that deposition of this carbon on heat generating surfaces could seriously impair heat transfer to the coolant. The problem in utilizing diphenyl as a reactor coolant then becomes one of adjusting the rate of removal of radiological products and addition of diphenyl so that, on the one hand, carbon deposition is avoided, but, on the other hand, the diphenyl requirements do not become prohibitive on an economic or (in the case of mobile power reactors) logistic basis.

In order to evaluate diphenyl as a reactor coolant, it is necessary to determine (1) the rate of radiological attack, (2) the characteristics of the products of irradiation, and (3) the relationship of carbon deposition to coolant composition, as it is probable that the rate of carbon deposition is a function of the over-all carbon content of the coolant mixture. Carbon deposition is also influenced by the temperature of the heat generating surfaces and therefore by the rate of heat generation. The question of thermal stability has been more thoroughly studied by Kermit Anderson.³

The specific objectives of this test were to determine:

- (1) The degree of radiation damage to diphenyl as a function of neutron dosage in a dynamic system, and
- (2) The amount of carbon deposition in a flowing system on heat generating surfaces under irradiation, if any.

*Hereafter in this report, the term "higher polyphenyls" is used to describe the group of varied compounds resulting from diphenyl irradiation.

³Kermit Anderson, "Pyrolytic Reactions of Diphenyl Under High Heat Flux Conditions," August 19, 1954, ANL-5304.

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II. EQUIPMENT AND METHODS

A relatively simple, closed circulating loop was constructed and installed in the Experimental Breeder Reactor (EBR). Essentially, the loop was a closed, stainless steel circuit consisting of a vertical reactor tube (the bottom 15 in. of which was in the maximum flux zone), a pump, a supply tank, an adsorption removal system, and associated control, make-up, and sampling equipment. A schematic drawing of the loop is shown in Fig. 1. Fig. 2 shows the loop as installed in the EBR. Fig. 3 shows the reactor tube as assembled at Argonne prior to shipment to the EBR site.

The reactor tube consisted of a 16-ft long, 5/8-in. ID outer tube and a concentric 3/8-in. ID, 7/16-in. OD inner tube arranged so that the test liquid passed down into the flux zone through the annular space between inner and outer tubes, and returned through the inner tube. An aluminum-sheathed, calrod type immersion heater was placed in the center of the inner tube. Heat generation from the heater was limited by space and design considerations to 1565 Btu/(hr)(sq ft). The reactor tube was located in inner blanket hole No. 239, 4.36 in. from the core center.

Fluid was circulated by a small-size, Allis Chalmers hermetically sealed centrifugal pump equipped with fluid piston type bearings.

Both adsorption and distillation were considered as methods for removal of radiological products. Adsorption was chosen for these tests because of ease of installation and operation. Two adsorption columns, each containing 315 gm of silica gel, were installed in parallel in a by-pass line around the reactor tube.

The control equipment for the loop included means for gas pressurization and for measuring flow, temperature, and pressure. All piping, tanks, valves, liquid meters, and pumps were electrically heated with wrap-around heaters.

Samples of circulating diphenyl were taken periodically for analysis. Radiological attack on diphenyl results in compounds of both higher and lower molecular weight. The analytical method used consisted of a simple distillation of the sample, which produced a distillate of 99+% diphenyl and a high boiling residue of higher polyphenyls. The residue was weighed and the percent higher polyphenyls in the original sample computed, correcting for the result obtained with unirradiated diphenyl. Duplicate samples were forwarded to California Research Corporation to determine individual radiological products. Preliminary results from the latter analyses confirm the percentage breakdown into diphenyl and higher polyphenyls obtained by the simple distillation method.

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FIG. 1
SCHEMATIC DIAGRAM OF
ORGANIC TEST LOOP

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FIG. 2
ORGANIC LOOP INSTALLATION AT EBR

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FIG. 3
ORGANIC LOOP REACTOR TUBE

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The quantity of higher polyphenyls collected in the adsorption column was determined by Soxhlet extraction of organic materials from the silica gel followed by simple distillation of the extracted material as described above. Adsorption column performance was evaluated only by analysis of the gel at the conclusion of each run.

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III. RESULTS

A. Run I (25 Hours)

This run was made with a 4,750 gm charge of diphenyl that had been previously used in nonirradiated shakedown runs. For this run the lower 15 in. section of the heater was replaced with a nonheated aluminum rod, 3/16 in. in diameter. Argon pressure was maintained on the system, but no attempt was made to remove air before the start of the run. Flow in the main section of the diphenyl loop was maintained at approximately 2 gpm; flow in the by-pass adsorption system was not measured. Only one adsorption column was used during the run. The calculated average epithermal flux (greater than 1 ev) over the bottom 15 in. of the pile tube was 1.0×10^{14} nv, and over the bottom 25 in. was 0.72×10^{14} nv.

Operation of the test was coincidental with operation of the EBR at 1200 kw power over a period of five days. The temperature of the circulating system was maintained between 320F and 400F, except for approximately two hours during reactor start-ups as shown in the temperature-time curve of Fig. 4. The average operating temperature was about 375F. The temperature of the adsorption column was maintained between 220F and 325F as shown in Fig. 4. No make-up material was added during the run.

The system gas pressure varied from 6 to 15 psig. The gas pressure built up slightly during the early part of the test, and gas was bled off about midway through the run. No increase of pressure was noted after the bleed-out. The amount of gas produced was not measured. A gas sample was taken at the end of the run, and the analysis is given in Table I.

Table I

RUN I GAS ANALYSIS

<u>Gas</u>	<u>Per cent by Volume</u>
CO ₂	0.7
Unsaturationes	7.8
O ₂	1.0
CO	6.3
H ₂	34.1
Argon	Balance

During this test the color of the diphenyl changed from water white to dark amber. No change in the pressure drop was observed at any time. Periodically, samples of diphenyl were taken for distillation analysis; data are shown in Table II.

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FIG. 4
VARIATION OF TEMPERATURE WITH TIME, RUN I

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Table II

RUN I DIPHENYL ANALYSES

<u>Time, hr</u>	<u>% Higher Polyphenyls in Circulating System</u>
1.50	0.3
4.25	0.3
11.50	1.3
18.25	1.2
25.00	2.0

At the conclusion of the run the heater was removed from the reactor, and a visual observation showed no deposition on any part of the heater or dummy rod.

Operation of the adsorption column was satisfactory. The determination of higher polyphenyls on the silica gel in the column showed 0.206 gm per gm of gel.

The total amount of irradiation product produced during the run was obtained by adding the amount calculated to be in the circulating system at the end of the run to that calculated to be in the adsorption column.

B. Run II (73.5 Hours)

This run was made with a 3364 gm charge of fresh, commercially pure diphenyl. This quantity was less than for Run I since the system included a supply tank in which the level could be varied over a considerable range without affecting operation. It was desirable to keep the total material to a minimum in order to have the percentage in the flux zone at a maximum. For this run the heater (1/4 in. OD) was active for its entire length, including the portion in the maximum flux zone. The system was evacuated on start-up and argon pressure was maintained throughout the run. Flow in the main section of the diphenyl loop was maintained at 1.5 gpm; flow in the by-pass adsorption system was not measured. Only one of the two adsorption columns was used. Calculated fast fluxes for this run were the same as for Run I.

Operation of the test was coincidental with operation of the EBR at 1200 kw power over a period of 11 days. The temperature of the circulating system was maintained between 300F and 450F for the major part of the run, as shown in the temperature-time curve of Fig. 5. The average operating temperature was about 385F. The temperature of the adsorption column was maintained between 160F and 320F, being, for the majority of time, at about 200F, as shown in Fig. 5.

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FIG. 5
VARIATION OF TEMPERATURE WITH TIME, RUN II

Table III

Gas	Per cent by Volume at	
	23 hr	65.2 hr
CO ₂	0.8	1.2
Unsaturates	3.7	6.8
O ₂	0.0	0.0
CO	0.0	0.0
H ₂	23.4	41.4
Argon	Balance	Balance

During this run the color of the diphenyl changed from water white to dark amber. No change in the pressure drop was observed prior to failure of the pump. Periodically, samples of diphenyl were taken and distillation analyses run. The data are shown in Table IV.

RUN II DIPHENYL ANALYSES

<u>Time, hr</u>	<u>% Higher Polyphenyls in Circulating System</u>
23	1.8
46	4.4
66	4.1
73.5	7.8

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At the conclusion of the run there were adherent black deposits scattered over the entire length of the heater, but the deposits were more concentrated on the portion located in the maximum flux zone. Figure 6 is an over-all view of the heater; Figs. 7 and 8 are close-ups of deposit areas. At the end of the test activity measurements showed 10 mr/hr at 1 in. on the bottom of the heater.

Operation of the adsorption column was satisfactory. Determination of higher polyphenyls on the silica gel in the column showed 0.356 gm per gm of gel.

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FIG. 6
APPEARANCE OF HEATER AFTER RUN II

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FIG. 7
DEPOSIT OBSERVED AFTER RUN II ON
PORTION OF HEATER IN HIGH FLUX ZONE

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FIG. 8
DEPOSIT OBSERVED AFTER RUN II ON PORTION
OF HEATER EXTERNAL TO FLUX ZONE

IV. DISCUSSION

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This relatively short-time irradiation in EBR has provided some information on the two primary objectives. Radiological attack on diphenyl was observed, indicated by the amounts of higher polyphenyls reported in the analyses of diphenyl. However, due to operational difficulties, the question of whether carbonaceous material will deposit on heater surfaces under irradiation in dynamic systems has not been definitely answered.

From the data gained in these tests, it was possible to estimate the rate of radiological attack for diphenyl in the EBR fast flux. Such an estimation was based on the total amount of higher polyphenyls produced during the run, the amount of diphenyl exposed to the fast flux at any one time, and lastly, the flux value over the section of the reactor tube located in the high flux zone. The term specific damage, as used in this report, is defined as

$$\frac{(\text{total weight of higher polyphenyls formed})}{(\text{weight of diphenyl in flux zone at one time})} \times \frac{10^{18}}{\text{exposure in nvt}} \times 100$$

and expresses the per cent of the diphenyl under irradiation (in the flux zone) at any one time which is converted to radiological products during an exposure of 10^{18} nvt epithermal.

The amount of higher polyphenyls produced was obtained from two measurements: first, the percentage in the main circulating system at the end of the run as given in Tables II and IV, and, second, the amount collected in the adsorption column as measured by analysis of a sample of the gel. The sum of these values gave the quantity of higher polyphenyls produced. For each run a rather sharp increase in the per cent higher polyphenyls was obtained on the last sample. The discontinuous variation of per cent higher polyphenyls in the circulating system with time is not surprising in view of the erratic temperature behavior of the adsorption column.

The amount of diphenyl in the high flux zone was calculated from the geometry of the test section. For this test two volumes were considered: the bottom 15 in. of the reactor tube and the bottom 25 in. of the tube; in each case the remainder of the system was considered external to the flux. The epithermal flux level beyond 25 in. was negligible. Increasing the "flux zone" from 15 in. to 25 in. resulted in a small change in specific damage, as indicated in Table V. The average flux over the length of the tube under consideration was computed by graphical integration of the axial flux plot for the reactor tube (Fig. 9). This curve is based on the flux plot (adjusted for reactor operation at 1200 kw)⁵ for hole 235,⁶ which with hole 239 is located symmetrically with respect to the reactor core.

⁵A. J. Ulrich, personal communication.

⁶C. D. Curtis, et al, "A Physical Determination of the Conversion Ratio of the Experimental Breeder Reactor," ANL-5222, August, 1954, Fig. 36, p. 85.

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AVERAGE FOR 15 inches - 1.0×10^{14}
 AVERAGE FOR 25 inches - $.72 \times 10^{14}$

FIG. 9
 EPITHERMAL FLUX PLOT FOR DIPHENYL REACTOR
 TUBE IN EBR OPERATING AT 1200 kw

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Table V

SUMMARY OF EXPERIMENTAL RESULTS

	<u>Run I</u>	<u>Run II</u>
Diphenyl charged, gm	4750	3364
Higher polyphenyls formed, gm		
In circulating system	95	262
In gel	65	113
Total	160	375
Diphenyl under irradiation, gm		
15 in. section	52.2 (375F)	47.3 (385F)
25 in. section	87.2 (375F)	79.0 (385F)
Dosage, nvt epithermal		
15 in. section	9.0×10^{18}	2.6×10^{19}
25 in. section	6.5×10^{18}	1.9×10^{19}
Specific Damage, % per 10^{18} nvt epithermal		
15 in. section	34.1	30.0
25 in. section	28.4	24.9

The values obtained for the average flux over the 15 in. and 25 in. lengths were, respectively, 1.0×10^{14} nv and 0.72×10^{14} nv epithermal (greater than 1 ev). Since reactor powers were the same for both runs, the fluxes for the two runs were assumed to be the same. With the average flux and time of operation known, the neutron dosage was calculated. This dosage included all neutrons about 1 ev. The fraction of neutrons below 4-6 ev (the binding energy of the carbon-hydrogen bond) was negligible (much less than 1 per cent).⁷

Values contributing to the estimation of specific damage to diphenyl in these two runs, together with the calculated results, are given in Table V. The higher values in Run I may have resulted from the presence of oxygen in the system. No oxygen was present to a detectable degree in Run II.

Using test results reported by California Research Corporation in TID-5094 and TID-5134, obtained in their static irradiation of diphenyl in ampoules placed in thermal reactors, a value of specific damage was calculated. The data used in the calculation included the purity of diphenyl after

⁷Reactor Engineering Division Quarterly Report, ANL-5208, December 15, 1953, Fig. 15, p. 84.

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test, a modified flux value,⁸ and the time of irradiation. Using the procedure indicated above, the calculated specific damage averaged 27% per 10^{18} nvt epithermal. The epithermal spectrum reported for this irradiation included all neutron energies above the cadmium cut-off.*

The agreement between the California Research and the Argonne data is perhaps fortuitous. The major portion of the radiation damage is caused both by neutron collision with the molecule and by resultant free protons. The average energy in the EBR is higher than in a thermal reactor, and therefore higher specific damage values might be expected. However, specific damage figures as calculated in this report depend on the value of the assumed flux. Flux estimates of this type may be subject to errors as great as $\pm 30\%$, and thus the apparent agreement of results is not surprising.

In connection with the question of carbonization on heat generating surfaces, the shorter Run I showed no deposition on the heater, but it should be noted that there was no electric heat generation in the 15 in. section located in the maximum flux region. In the longer Run II, deposition was noted on the heater, with a heavier deposit observed on the portion of the heater located in the 15 in. maximum flux region and a lesser concentration on the heater surface external to the maximum flux region. During the longer run, however, two periods of essentially static operation occurred: first for about four hours during the second day's operation and second for a period of one hour following the pump failure at the end of the run. During the first flow stoppage, observed bulk temperatures increased appreciably. During the second flow stoppage it is probable that again the temperature increased appreciably. In both cases, an increase in the surface temperature of the heater surface must be assumed. With the possibility of high surface temperatures during the periods of no flow, it is rather difficult to attribute the carbonization to irradiation alone, especially since in Run I carbonization was not observed. In summary, it can only be stated that this experiment has indicated that carbonization of diphenyl on heat generation surfaces during irradiation may occur, but additional work is required for any further evaluation.

The adsorption column separation factor, taken as a measure of performance and defined as

$$\alpha = \frac{\left(\frac{\text{weight of higher polyphenyls}}{\text{weight of diphenyl}} \right) \text{ adsorbed on silica gel}}{\left(\frac{\text{weight of higher polyphenyls}}{\text{weight of diphenyl}} \right) \text{ remaining in circulating system}}$$

⁸R. O. Bolt, personal communication.

*The range of neutron energy between 0.2 and 1.5 ev wherein the total microscopic neutron cross section for cadmium drops from 8000 to 10 barns.

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was calculated to be 21 for Run I and 30 for Run II. These high values indicate that the silica gel adsorber provided adequate purification during the runs. The runs were not long enough, however, to determine the ultimate capacity of the gel for higher polyphenyls. The analytical method used on circulating diphenyl samples and on extracted material from the gels pointed out the effectiveness of simple distillation as a method of purification. This demonstrated efficiency and the absence of regeneration problems are factors favoring distillation as the preferred method of purification.

The limited objectives of the two runs reported here precluded investigation of several factors affecting radiation damage and carbon deposition. Any further detailed studies of the behavior of diphenyl should consider the following factors:

1. Gas analyses showed an increase in hydrogen as a function of exposure. Since in ordinary chemical kinetics the rate of a reaction is usually diminished by an increased concentration of reaction products, the effect of initial hydrogen pressurization and, conversely, of continuous hydrogen removal should be observed. The solubility of hydrogen in diphenyl would also have to be determined in order to estimate the degree of pressurization required to obtain the desired concentrations in the diphenyl.

2. If any of the products of diphenyl are more stable to radiological attack than diphenyl itself, then operation with a coolant mixture having a lower concentration of diphenyl and a higher concentration of the stable product would reduce both the diphenyl make-up and the purification system requirements. The radiological damage rate, the tendency toward deposition on heat generating surfaces under irradiation, and the fluid properties such as viscosity and heat transfer characteristics should therefore be investigated for various mixtures of diphenyl with its radiological products.

The very high specific radiological damage values obtained in this dynamic test confirm the earlier static test data. The question of carbon deposition on heat generating surfaces in an irradiation field was not adequately resolved in this test.

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