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Chemical and Biological Effects of Heavy Distillate Recycle in the SRC-II Process

B. W. Wilson
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December 1983

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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CHEMICAL AND BIOLOGICAL EFFECTS OF HEAVY
DISTILLATE RECYCLE IN THE SRC-II PROCESS

PNL--4815

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EXECUTIVE SUMMARY

Recent work from the Merriam Laboratory continuous coal liquefaction unit shows that heavy distillate from the SRC-II process can be recycled to extinction, and hence a distillate product boiling entirely below 310°C (590°F) (or other selected boiling points) is feasible. In these runs distillate yield was not reduced; gas make was unaffected; and hydrogen consumption was increased only slightly, in keeping with the generally higher hydrogen content of lighter end products. Total distillate yield (C₅-590°F) was 56 wt%, MAF coal in runs with subbituminous coal from the Amax Belle Ayr mine. Product endpoint is well below 371°C (700°F), the temperature above which coal distillates appear to become genotoxic; and the product was shown to be free of mutagenic activity in the Ames test.

Chemical analyses showed both the <270°C (<518°F) and the <310°C (<590°F) distillates to be essentially devoid of several reference polycyclic compounds known to be carcinogenic in laboratory animals. Tests for tumorigenic or carcinogenic activity were not carried out on these materials. However, a comparison of chemical data from the Merriam heavy distillate samples with data on the other SRC-II distillates where carcinogenesis or tumorigenesis data is available leads to the expectation that <371°C (<700°F) materials from the Merriam Laboratory will have greatly reduced tumorigenic and carcinogenic activity in skin painting tests. Other studies suggest the product should be more readily upgraded than full-range (C₅-900°F) distillate.

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1.0 INTRODUCTION

A primary goal of the coal liquefaction health effects studies supported by the Department of Energy has been the use of resultant data in the improvement of the coal liquefaction processes. Work first published for solvent refined coal (SRC) derived materials in 1980 showed that genotoxicity in microbial mutagenicity assays using S. typhimurium was strongly dependent upon the distillation temperature range of the coal liquids. Work by Pacific Northwest Laboratory (PNL) and other laboratories showed that in general genotoxicity, initiation of tumorigenicity, and mouse skin carcinogenicity are increased for the coal liquids which have upper distillation cut point temperatures above about 343°C (650°F) to 371°C (700°F).

Studies on fractionally distilled SRC-II derived material from the Harmarville process development unit (PDU) have confirmed that in laboratory tests for both microbial and mammalian cell mutagenicity, initiation of mouse skin tumorigenicity, mouse skin carcinogenicity, and teratology in mice, cuts boiling below 371°C (700°F) are essentially inactive. Studies of this type show in general that coal liquid distillates with upper temperature cut points of less than about 371°C (700°F) were no more genotoxic than certain domestic crude petroleums. The reduced genotoxicity and carcinogenicity of these lower boiling distillates is due mainly to the separation of higher molecular weight, neutral and nitrogen-containing polycyclic aromatic hydrocarbons into fractions boiling above 371°C (700°F) to 399°C (750°F).

Catalytic hydrogenation has also been shown to be effective in reducing the genotoxicity of both SRC-II and other direct liquefaction materials.⁽¹⁻³⁾ For the SRC-II process, however, it appeared that elimination of the heavy-end components by recycling them to extinction within the process may constitute a direct and relatively inexpensive route to improving distillate quality. This report focuses on experiments carried out on the Merriam Kansas bench scale continuous coal liquefaction unit by Gulf Research and Development Co. Their purpose was to investigate the effects of recycling the heavy oil fraction of the coal liquid products on the chemical and biological characteristics of the

resulting distillates. Results from the engineering and analytical chemistry work as well as data from bioassays conducted on these materials are presented and discussed.

2.0 PROCESS ENGINEERING

2.1 EXPERIMENTAL

2.1.1 Bench Scale Unit

Results presented in this paper were obtained with a small (20 lb of coal/day) continuous coal liquefaction unit (Figure 2.1) at Gulf Research and Development Company's Merriam Laboratory. This unit, which is operated with recycle of solvent or slurry until steady state operation is achieved, has been shown to give results essentially equivalent to large scale coal liquefaction facilities. The continuous unit has been described previously⁽⁴⁾ and will only be described here to the extent necessary to permit understanding of the variations between "conventional" recycle and recycle of heavy distillate to extinction.

All effluent from the dissolver flows into a high temperature, high pressure (HTHP) separator. HTHP separator bottoms contain middle and heavy distillates, SRC, insoluble organic matter (IOM) and ash. A fraction of the HTHP bottoms is used for recycle; the remainder is available for product recovery. In a plant this material would be sent to a vacuum flash while in the Merriam unit the material is subjected to a vacuum distillation in laboratory glassware. The distillation is completed at 270°C (518°F) vapor temperature at 2 mm Hg vacuum. This distillate contains primarily middle and heavy distillate while the bottoms contain SRC, IOM, and ash; in a plant this would be used for gasifier feed. HTHP separator overhead goes into a series of separators; materials removed from the unit are gas, ambient temperature separator bottoms (primarily water and naphtha), and on-line atmospheric distillation column bottoms and overhead.

The variation between conventional recycle and heavy distillate recycle is in how these materials are used in slurry formulation. (Figure 2.2 shows heavy distillate yield as a function of heavy distillate concentration in the feed slurry in the SRC-II process). Slurry formulation for heavy distillate recycle is discussed in the following section.

FIGURE 2.1. Merriam Laboratory Bench Scale Coal Liquefaction Unit

FIGURE 2.2. Yield of Heavy Distillate versus Heavy Distillate Concentration in Feed Slurry

2.1.2 Recycle Techniques

A simplified flow scheme for a "conventional" recycle run is shown in Figure 2.3. Primary components used in feed slurry formulation are coal and recycle HTHP bottoms (containing middle and heavy distillates, SRC, IOM, and ash). Distillate is also used in the feed slurry formulation to control total feed slurry solids level. This distillate is obtained from two sources: atmospheric distillation bottoms and vacuum distillate (each source supplies both middle and heavy distillates). Distillates from these sources not used in slurry formulation become a net product of the process.

In earlier runs⁽⁵⁾ the levels of middle and heavy distillate in the feed slurry were controlled by varying the temperature of the HTHP separator and, more importantly, by varying the amounts of vacuum distillate and atmospheric column bottoms used in the slurry formulation. Over the range of compositions studied at that time, increasing the heavy distillate concentration in the feed slurry (while holding the total oil concentration approximately constant) reduced the heavy distillate concentration in the product. Results of this prior study are summarized in Figure 2.2, which shows heavy distillate yield as a function of heavy distillate concentrations in the feed slurry.

To recycle all heavy distillate to extinction, the following variation was adopted. All oils from the unit (including vacuum distillate, naphtha, atmospheric column overhead, and bottoms) were combined and distilled in laboratory glassware to the specified cutpoint [e.g., 270°C (518°F)]. All of the overhead is the net product of the process while all of the bottoms are recycled. Runs in which this technique was practiced are referred to as heavy distillate recycle runs.

2.1.3 Conditions

Two standard sets of conditions were used in these investigations: one for subbituminous coal runs and a second for the bituminous coal runs. Conditions used for the subbituminous coal runs were those established for investigations of the use of the disposable catalysts in the processing of western coals. Conditions used for the bituminous coal runs were those established

FIGURE 2.3. Conventional Recycle

earlier when evaluating feedstock candidates for the SRC-II Demonstration Plant Project. Conditions are summarized in Table 2.1.

2.1.4 Coals

The subbituminous coal used in this work was from the Amax Belle Ayr Mine in Campbell County, Wyoming (Wyodak-Anderson seam). This coal has been used extensively at the Merriam Laboratory in disposable catalyst studies. Analyses are provided in Table 2.2. Since this coal is low in native pyrite and since earlier work had indicated unsatisfactory operability and yields in the absence of added pyrite, mined pyrite was added at a 0.8 wt% level, slurry basis (from C-E Minerals, Washington, Georgia, which had been ground under nitrogen by Jet Pulverizer, Palmyra, New Jersey).

The bituminous coal used in this work was Pittsburgh seam coal from North American Coal Company's Powhatan No. 3 Mine in Belmont County, Ohio. Analyses are provided in Table 2.2. This coal had been run previously during evaluation of feedstock candidates for the SRC-II Demonstration Plant Project.

TABLE 2.1. Conditions Summary^(a)

	<u>DOE</u> <u>453RB</u>	<u>DOE</u> <u>467RA</u>	<u>DOE</u> <u>467RB</u>	<u>DOE</u> <u>467RC</u>	<u>DOE</u> <u>409R</u>	<u>DOE</u> <u>466R</u>
Coal	←-----Belle Ayr-----→				←---Powhatan---→	
Temperature, °C	←-----450-----→				457	458
°F	←-----842-----→				855	856
Pressure, psig	←-----2250-----→				←---1800---→	
Dissolver Nominal Slurry Residence Time, h	←-----1.0-----→					
Added Pyrite, wt% slurry basis	←-----0.8-----→				←---None---→	
Feed Slurry Solids, wt%	47.5	41.8	43.5	45.0	44.4	46.3
Cut Point for Heavy Dis- tillate Recycle, °C	--	270	290	310	--	270
°F	--	518	554	590	--	518

(a) All with a 30% coal concentration in the feed slurry and a hydrogen feed rate of 4.0 wt%, slurry basis.

TABLE 2.2. Coal Analyses^(a)

	<u>Powhatan</u>	<u>Belle Ayr</u>		<u>Powhatan</u>	<u>Belle Ayr</u>
Proximate, wt%			Ultimate, wt%		
Ash	10.8	7.5	Carbon	72.1	68.9
Volatile Matter	42.3	48.0	Hydrogen	5.1	5.0
Fixed Carbon	46.9	44.5	Nitrogen	1.3	0.8
			Chlorine	0.1	0.0
Sulfur Forms, wt%			Sulfur	4.6	0.7
Pyrite	2.0	0.4	Ash	10.8	7.5
Sulfate	0.1	0.0	Oxygen	6.1	17.1
Organic	2.5	0.3	Moisture, as run, wt%	1.3	5.9
			Equilibrium		
			Moisture, wt%	2.7	27.7

(a) All analyses except moisture are by Commercial Testing & Engineering Co. and are on a dry coal basis.

2.2 RESULTS

2.2.1 Run Descriptions and Yields

2.2.1.1 Subbituminous Coal

Run DOE 467R was continued for 28 days without interruption. Heavy distillate was recycled to extinction throughout the run. Four different conditions were investigated: the first three used subbituminous coal from the Amax Bell Ayr Mine; the fourth used another subbituminous coal from Kemmerer's Elkol-Sorensen Mine. Results for the Elkol Sorensen coal will not be presented here but will be available elsewhere.⁽⁶⁾

The first three parts of the run varied only in the cutpoint between net product and recycled oil. A 270°C (518°F) cutpoint was used in part A, a 290°C (554°F) cutpoint was used in part B, and a 310°C (590°F) cutpoint was used in part C. No operability problems were experienced; a satisfactory line-out was achieved in each part of the run; and there was no evidence for buildup of any refractory material in the recycle oil stream.

Run 453RB was made in the conventional recycle mode. The distillate used in slurry formulation came from the on-line atmospheric distillation column bottoms and overhead from vacuum distillation of HTHP separator bottoms.

Yields are compared in Table 2.3. As the cutpoint is increased, there is less distillate to be used in the slurry formulation. Yields vary in the expected manner with the cutpoint variation. As distillate used in the formulation is decreased, the feed slurry solids and SRC concentration in the feed slurry both increase. Both can have a beneficial effect on conversion of SRC to distillate, but the increased recycle ash (catalyst) is probably the most important factor.

These results show that heavy distillate [319°C (>590°F)] can be recycled to extinction without any detrimental effect on yields. If a still lighter distillate is desired, this also can be obtained but with a minor decrease in total distillate yield. Although not experimentally verified, it is expected that a lighter product with the same total distillate yield could be obtained by reducing the cutpoint and increasing slurry residence time.

TABLE 2.3. Yields for Runs 467RA, 467RB, 467RC, 453RB Using Subbituminous Coal

	DOE 467RA	DOE 467RB	DOE 467RC	DOE 453RB
Oil Recycle	All (+518°F) 270°C Recycled	All (+554°F) 290°C Recycled	All (+590°F) 310°C Recycled	Conventional
Total Solids in Feed Slurry, wt%	41.8	43.5	45.0	47.5
Yields, wt% MF Coal				
C ₁ -C ₄	10.7	10.5	10.4	11.7
Total Oil	48.1	50.0	52.4	52.8
SRC	21.3	19.7	18.2	15.9
IOM	2.5	2.3	2.3	2.5
H ₂ Consumed ^(a) wt% MF Coal	5.5	5.3	5.6	5.0

(a) Determined via gas balance.

2.2.1.2 Bituminous Coal

Pittsburgh seam coal from the Powhatan No. 3 Mine was used in run DOE 466R. This run, with all heavy distillate [270°C (>518°F)] being recycled to extinction, was continued for 14 days at a single set of conditions without interruption. One of the main considerations for analysis of materials in this experiment was to determine if the heavy distillate recycle technique allowed the accumulation of some unreactive species in the return stream to the reactor. No evidence for such buildup of refractory materials was found. The recycle stream and the net product streams were analyzed throughout the run. Analytical techniques used included high performance liquid chromatography (HPLC), proton nuclear magnetic resonance (NMR) and determination of basic nitrogen and total nitrogen. Total nitrogen content in the recycle stream increased during the first 200 hours of the run and then leveled out. No additional systematic changes in recycle stream composition were apparent via the other analytical techniques.⁽⁶⁾

The 14-day heavy distillate recycle run was terminated by a plugged reactor. The reason for the plugging is unknown but is not believed to be related to any fundamental problem with the concept of heavy distillate recycle.

Yields for the conventional recycle and heavy distillate recycle runs are compared in Table 2.4. In run 466R all heavy distillate 270°C (>518°F) was recycled to extinction and conventional recycle was used in DOE 409R.

In this case, the total oil yield for the heavy distillate recycle run was slightly lower (and SRC yield higher) than that for the conventional recycle run. The difference was unexpected and only slightly greater than the expected experimental uncertainty. Approximately 20 months had elapsed between the two runs during which time the coal was stored in a sealed drum under air. The effect of this storage on coal reactivity is unknown.

Two additional runs, 483RA and RB,⁽⁷⁾ were made to compare conventional recycle with heavy distillate recycle with bituminous coal (Powhatan Mine No. 6). The alternate operating conditions (2250 psig, 450°C) were used and a

TABLE 2.4. Yields for Runs 466R and 409R Using Bituminous Coal

	<u>DOE 466R</u>	<u>DOE 409R</u>
Oil Recycle	All 270°C (+518°F) Recycled	Conventional
Total Solids in Feed Slurry, wt%	46.3	44.4
Yields, wt% MF Coal		
C ₁ -C ₄	13.6	14.2
Total Oil	36.0	39.9
SRC	28.2	25.2
IOM	6.7	5.4
H ₂ Consumed ^(a) wt% MF Coal	4.7	4.2

(a) Determined via gas balance.

cutpoint of 310°C (590°F) in the heavy distillate recycle run was used. There was no detrimental effect of heavy distillate recycle on yields.

2.2.2 Boiling Point Distributions

Differences in the boiling point distributions for the conventional and heavy distillate recycle runs are most apparent in the high boiling end; simulated distillation results are compared in Table 2.5. The net distillation product from the heavy distillate recycle runs are shown by simulated distillation (using gas chromatography) to contain 6-11% of material distilling above the specified cutpoint. Similar results were obtained by actual redistillation of the overhead product. If it were found that the presence of this higher boiling material were detrimental to product quality, it also could be recycled to extinction. This was in fact done in a more recent run⁽⁷⁾ in which the overhead from the initial distillation was redistilled to the same cutpoint and the bottoms from the redistillation was also recycled to extinction.

In comparison, the two conventional control runs have 32 to 36% of material distilling above 270°C (518°F). Further differences in the high boiling end are shown Table 2.5. Mutagenic activity is shown in the Ames test with

TABLE 2.5. Net Distillate Product Simulated Distillation Results

	Subbituminous Coal					Bituminous Coal	
	453RB	454RA	467RA	467RB	467RC	409R	466R
Recycle	Conventional	+518°F	+554°F	+590°F		Conven- tional	+518°F
Distilling Above Cutpoint	32(a)	35(a)	10	9	6	36(a)	11
90 (b)	642	646	516	547	563	651	520
95 (b)	711	703	558	576	606	707	559
FBP(c)	856	833	671	689	718	808	685

(a) Distilling above 270°C (518°F).

(b) Percent distilling below the indicated temperature, °F.

(c) Final Boiling Point, °F.

materials distilling above 371°C (700°F). The 95% point (95% distilled) for the three conventional runs is just into the active area while the 95% point for the 270°C (+518°F) recycle runs is approximately 150°F lower. Only in the 310°C (+590°F) recycle run did the simulated distillation final boiling point reach into the active range (at 718°F). Interestingly, this is the one material from the heavy distillate recycle runs which showed a hint of biological activity. However, this activity was not statistically different from the background (see Section 4).

2.2.3 Elemental Analysis

Elemental analyses for the net distillate products are compared in Table 2.6. Differences between the conventional and heavy distillate recycle runs are minor. In the subbituminous series, nitrogen content increased very slightly as the cutpoint in the heavy distillate recycle runs was raised. Hydrogen content of the net distillate product from the heavy distillate recycle runs was slightly higher than that from the conventional runs and nitrogen content was slightly lower.

TABLE 2.6. Distillate Analyses

	Subbituminous Coal					Bituminous Coal	
	453RB	454RA	467RA	467RB	467RC	409R	466R
Recycle	Conventional		+518°F	+554°F	+590°F	Conven- tional	+518°F
Net Oil Product Analyses							
Carbon	82.25	85.68	84.43	84.55	89.75	86.43	85.49
Hydrogen	10.35	10.34	10.75	10.53	10.63	9.76	9.92
Nitrogen	0.71	0.65	0.56	0.60	0.63	0.83	0.73
Sulfur	0.06	0.11	0.05	0.08	0.09	0.38	0.32
Oxygen	3.63	3.22	4.21	4.24	3.90	2.60	3.54
Basic Nitrogen, wt%			0.39	0.42	0.40	0.64	0.57
Satuates, ASTM D1019, vol%			29.0	28.0	32.0		
Phehols, Aqueous NaOH, vol%			27.0	28.0	25.0		

2.3 DISCUSSION

Recent studies at the Merriam Laboratory have extended the performance envelope of coal liquefaction using disposable catalysts in a variety of ways. Western subbituminous and lignite coals have been liquefied with good operability by addition of mined pyrite and other disposable catalysts.^(6,8) These less costly coals have also been found to give higher liquid yields than in the case of bituminous coals, (52-57 wt%, MAF coal as C₅-900°F liquid versus about 45 wt%); and C₁ - C₄ gas make was reduced by more than 20% compared to the bituminous coals. Thus, hydrogen is used more selectively to manufacture liquids.

The method of operation described here extends this performance envelope further. It allows production of liquid products free from material boiling above 371°C (700°F), or some other selected endpoint near that temperature. There should be no loss in liquid yield and gas make will remain essentially unchanged. Hydrogen consumption increases only slightly, which is typical of the generally higher hydrogen content of lower boiling range products. Evidently the additional hydrocracking required to extinguish heavy distillate is not accompanied by significant gas production.

3.0 CHEMICAL ANALYSIS

3.1 METHODS

3.1.1 Sample Origin

Chemical analyses were carried out on the <270°C (<518°F) and the <310°C (<590°F) distillates from bottoms recycle operation at the Merriam bench scale unit as described in the engineering section. In addition, samples of a 2.9:1 blend of SRC-II middle and heavy distillate, designated as SRC-II fuel oil blend (FOB), as well as severely hydrotreated FOB were analyzed by the same methods for comparison. The FOB samples were from the Fort Lewis, Wa. SRC-II pilot plant and are described in detail in PNL 3464.⁽⁹⁾

3.1.2 Separations

Samples were fractionated into chemical classes by alumina column chromatography according to the method of Later et al.⁽¹⁰⁾ The method is used in this laboratory to prepare coal liquid samples for biological testing and affords a good initial preseparation prior to further chemical analysis. The initial level of separation yields aliphatic hydrocarbon (AH), neutral polycyclic aromatic hydrocarbon (PAH), nitrogen-containing polycyclic aromatic compound (N-PAC), and hydroxylated polycyclic aromatic hydrocarbon (HPAH) fractions. The N-PAC may be further separated to yield primary, secondary and tertiary amine subfractions designated as amino-PAH (APAH), carbazoles and azaarenes, respectively.

3.1.3 Gas Chromatography

Gas chromatographic (GC), mass spectral (MS), and GCMS analyses were performed on several samples from the bottoms recycle operation mode. Results obtained were compared to those from analysis of SRC-II materials obtained by distillation which had comparable boiling point ranges.

High resolution gas chromatography was used to quantitatively determine levels of approximately 70 compounds in the various fractions of the coal liquids in order to relate, where possible, differences in biological activity to chemical composition. An HP 5880A gas chromatograph equipped with a 25 M x 0.25 mm i.d. fused-silica capillary column coated with DB-5 and flame

ionization detection was used. The oven was temperature programmed from 50°C to 300°C at 3°C/min. Helium carrier gas was used with splitless injection. Quantitative results for the fractions were determined by average response factors of individual standards calculated from seven concentration levels ranging over two orders of magnitude. When standards were not available, the response factor for a compound of the same chemical class with a similar retention time was used. An internal standard, 2-chloroanthracene, was added and fractions were quantitated at three different concentration levels (2 mg/ml, 4 mg/ml, and 8 mg/ml). Identification of components quantified was determined by retention time and retention index measurements. Hydroaromatic species in the coal liquids were identified by GCMS, which also served to confirm the identification of other major compounds in the gas chromatograms of these materials. Relative molecular weight distributions were compared by probe inlet mass spectrometry.

3.2 RESULTS

Data comparing the chemical class distribution of the <270°C (518°F) and <310°C (590°F) distillates into chemical classes after alumina column fractionation are shown in Table 3.1. These fractions are compared to the analogous fractions from nonhydrotreated and hydrotreated FOB. Differences in chemical distribution of the products from the heavy distillate recycle runs were not significant, as determined by this separation. There are, however, significant differences between FOB and hydrotreated FOB. Due to the lower boiling points of the distillates from the heavy distillate recycle runs, chemical class fractionation recoveries were low and therefore not as reliable as for FOB for heavy distillate materials.

Figures 3.1 and 3.2 show fused-silica capillary gas chromatograms for neutral PAH fractions from the <270°C (518°F) and <310°C (590°F) distillates from the current heavy distillate recycle runs. Chromatograms of the neutral PAH fractions of FOB from the SRC-II process as operated at the Fort Lewis pilot plant are shown in Figure 3.3. Gas chromatograms for the N-PAC fractions of these same materials are shown in Figures 3.4, 3.5 and 3.6 respectively. Identifications for some of the major peaks in the chromatograms are given in Tables 3.2 and 3.3 with quantitative results in Tables 3.4 and 3.5.

TABLE 3.1. Weight Percentage Distribution of Distillates into Chemical Class Fractions

	Heavy Distillate Recycle Runs		FOB	
	270°C (518°F)	<310°C (590°F)	Crude	Hydrotreated
	5226-047 (DOE 467RD)	5226-046 (DOE 467RC)		
Aliphatic Hydrocarbons	23	32	25	69
Neutral PAC	21	24	33	21
Nitrogen Containing PAC	9	9	14	1
Hydroxylated PAC	<u>39</u>	<u>34</u>	<u>29</u>	<u>13</u>
Total Recovery	92%	99%	91%	104%

Data on the chemical composition of both FOB and hydrotreated FOB has been reported previously.^(2,9) FOB data reported here, however, were obtained by the same methods as those used for materials from the heavy distillate recycle runs so that valid comparisons as to the relative composition of the two types of materials could be made.

The most obvious difference between FOB and the materials from the heavy distillate recycle runs is that the molecular weight range and the upper end distillation temperature cut point for the later materials were much lower than that for FOB. [SRC-II HD which was blended into FOB has an upper temperature cut point about 454°C (850°F)]. There do, however, appear to be other differences between the materials that are not related to distillation temperature. For example, in the distillates from the heavy distillate recycle runs there appears to be a greater degree of alkylation association with both the N-PAC and PAH fractions than in the FOB (see Figures 3.4, 3.5, and 3.6). This observation is based on the ratios of C₁, C₂ and C₃ alkyl homologs to the non-alkylated parent compound for several PAH and N-PAC structures. Alkylated to nonalkylated ratios were higher for the heavy distillate recycle product.

Between the <270 (<518°F) and <310°C (<590°F) distillates, there appeared little difference other than that which could be attributed to their respective boiling point ranges.

FIGURE 3.1. Heavy Distillate [$>270^{\circ}\text{C}$, (518°F)] Recycle Runs, $<270^{\circ}\text{C}$ Neutral Fraction Recycle Fraction (numbers refer to peak identifications listed in Table 3.2)

FIGURE 3.2. Heavy Distillate [$>310^{\circ}\text{C}$, (590°F)] Recycle Runs, $<310^{\circ}\text{C}$ Neutral PAH Fraction (numbers refer to peak identifications listed in Table 3.2)

FIGURE 3.3. Fuel Oil Blend: Neutral PAH Fraction (numbers refer to peak identifications listed in Table 3.2)

FIGURE 3.4. Heavy Distillate [$<270^{\circ}\text{C}$, (518°F)] Recycle Run, $<270^{\circ}\text{C}$: Nitrogen-Containing PAC Fraction (numbers refer to peak identification listed in Table 3.3)

FIGURE 3.5. Heavy Distillate [$>310^{\circ}\text{C}$, (590°F)] Recycle Run, $<310^{\circ}\text{C}$ Nitrogen-Containing PAC Fractions (numbers refer to peak identification listed in Table 3.3)

FIGURE 3.6. Fuel Oil Blend Nitrogen-Containing PAC Fraction (numbers refer to peak identification listed in Table 3.3)

TABLE 3.2. Identification of Components in Neutral PAH Fractions

Peak No. (a)	Molecular Weight	Compound (b)
1	128	Naphthalene
2	142	2-Methylnaphthalene
3	143	1-Methylnaphthalene
4	154	Biphenyl
5	156	2-Ethylnaphthalene
6	156	2,6- or 2,7-Dimethylnaphthalene
7	156	1,7,-Dimethylnaphthalene
8	156	1,6- or 1,3-Dimethylnaphthalene
9	156	C ₂ -Naphthalene
10	170	C ₃ -Naphthalene
11	154	Acenaphthene
12	168,170	C ₁ -Biphenyl, C ₃ -Naphthalene
13	170	C ₃ -Naphthalenes
14	168	Dibenzofuran
15	166	Fluorene
16	182	C ₂ -Biphenyl
17	168	C ₁ -Acenaphthene
18	184	C ₄ -Naphthalenes
19	180	9-Methylfluorene
20	182	C ₂ -Acenaphthenes/C ₁ -Dibenzofurans
21	180	C ₁ -Fluorenes
22	184	Dibenzothiophene
23	178	Phenanthrene
24	194,196	C ₂ -Fluorenes, C ₃ -Acenaphthenes, C ₁ -Dibenzothiophenes
25	192	3-Methylphenanthrene
26	192	2-Methylphenanthrene
27	192	1-Methylphenanthrene
28	206	C ₂ -Phenanthrenes
29	212	2-Chloroanthracene, ISTD
30	204	Dihydrofluoranthene

TABLE 3.2. (Contd)

Peak No. ^(a)	Molecular Weight	Compound ^(b)
31	202	Fluoranthene
32	202	Pyrene
33	216	Benzo[a]fluorene
34	216	Benzo[b]fluorene, 2- or 4-methylpyrene
35	216	1-methylpyrene
36	228	Benz[a]anthracene
37	228	Chrysene
38	242	C ₁ -Chrysenes
39	252	Benzo[j or b]fluoranthene
40	252	Benzo[k]fluoranthene
41	252	Benzo[e]pyrene
42	252	Benzo[a]pyrene

(a) Peak number refer to Figures 3.1, 3.2, and 3.3.

(b) Tentative identifications from retention time and GC/MS data.

Gas chromatograms show that placing the cut points at 270°C (518°F) or 310°C (590°F) essentially eliminates from the distillates those compounds having more than 4 aromatic rings as well as the alkylated catacondensed 4-ring compounds. As expected, the <270°C (<518°F) material has higher concentrations of most one and two ring aromatic species than does the 310°C (590°F) material.

Concentrations for important PAH and NPAC compounds as measured in the distillates and FOB by GC are given in Tables 3.4 and 3.5. Materials from the heavy distillate recycle runs have a slightly higher hydroaromatic content than does the nonhydrotreated FOB. Dihydrofluoranthene is at about twice the concentration of fluoranthene in materials from the heavy distillate recycle runs. Dihydrofluoranthene concentrations in FOB are only about 17% of those measured in the heavy distillate recycle runs.

TABLE 3.3. Identification of Components in Nitrogen-Containing PAC Fractions

Peak No. (a)	Molecular Weight	Compound (b)
1	93	Aniline
2	107	C ₁ -Anilines
3	122	C ₂ -Phenol
4	121	C ₂ -Anilines, C ₃ -Pyridines
5	136	C ₃ -Phenols
6	133	Tetrahydroquinoline
7	129	Quinoline
8	147	C ₁ -Tetrahydroquinoline
9	117	Indole
10	143	C ₁ -Quinolines
11	131	C ₁ -Indoles
12	157	C ₂ -Quinolines
13	145	C ₂ -Indoles
14	171	C ₃ -Quinoline
15	159	C ₃ -Indoles
16	179	Benzo(h)quinoline
17	179	Acridine
18	179	Benzo(f)quinoline, Phenanthridine
19	167	Carbazole
20	181	C ₁ -Carbazoles
21	212	2-Chloroanthracene, ISTD
22	195	C ₂ -Carbazoles
23	203	Azapyrenes/fluoranthenes
24	217	C ₁ -Azapyrenes/fluoranthenes
25	217	Benzo[a]carbazole
26	217	Benzo[b]carbazole
27	217	Benzo[c]carbazole

(a) Numbers refer to peaks in Figures 3.4, 3.5, and 3.6.

(b) Tentative identifications based on retention times and GC/MS data.

TABLE 3.4. Concentrations (parts per million) of Major Components in the Polycyclic Aromatic Hydrocarbon (PAH) Fractions of:

Compound	Heavy Distillate Recycle Runs		Fuel Oil Blend
	<270°C (518°F)	<310°C (590°F)	2.9:1 (MD/HD)
Naphthalene	111 ± 11	101	33700 ± 780
2-Methylnaphthalene	15600 ± 2290	8230 ± 1210	79500 ± 1260
1-Methylnaphthalene	3610 ± 502	2030 ± 308	17100 ± 250
Biphenyl	-	26000 ± 560	
2-Ethylnaphthalene	21720 ± 3070	12250 ± 1860	27800 ± 733
2,6- or 2,7-Dimethylnaphthalene	28600 ± 4090	14300 ± 2210	44500 ± 4080
1,7-Dimethylnaphthalene	8210 ± 977	4750 ± 624	9740 ± 790
1,6- or 1,3-Dimethylnaphthalene	7830 ± 1170	5220 ± 990	6410 ± 267
Acenaphthene	12300 ± 1330	9210 ± 1870	13700 ± 170
C ₃ -Naphthalene	27900 ± 4080	19300 ± 3380	19900 ± 1950
C ₃ -Naphthalene	24700 ± 2770	18600 ± 3420	8280 ± 3510
Dibenzofuran	10000 ± 954	6890 ± 658	15900 ± 220
Fluorene	15100 ± 1400	16100 ± 2050	14400 ± 400
9-Methylfluorene	9830 ± 2730	10600 ± 1960	7940 ± 580
2-Methylfluorene	7500 ± 69	13500 ± 1510	9000 ± 309
1-Methylfluorene	7790 ± 164	11100 ± 1410	679 ± 76
Dibenzothiophene	7210 ± 875	12300 ± 1680	6930 ± 360
Phenanthrene	24900 ± 1720	32900 ± 3810	39600 ± 1870
3-Methylphenanthrene	5210 ± 161	7170 ± 525	6360 ± 110
2-Methylphenanthrene	6040 ± 234	8220 ± 214	8040 ± 220
1-Methylphenanthrene	1930 ± 95	2960 ± 349	2400 ± 60
Dihydrofluoranthene	1730 ± 53	3400 ± 37	1500 ± 30
Fluoranthene	920 ± 66	1130 ± 83	9030 ± 260
Pyrene	4410 ± 145	6820 ± 136	16500 ± 10
Benzo[a]fluorene	350 ± 72	376 ± 111	770 ± 20
Benzo[b]fluorene, 2 or 4-methyl pyrene	1450 ± 51	1220 ± 935	7860 ± 160
1-Methylpyrene*	388 ± 45	402 ± 90	1870 ± 250
Benz[a]anthracene*	-	1330 ± 80	
Chrysene	140	156	1900 ± 120
Benzo[j or b]fluoranthene*	-	500 ± 30	
Benzo[k]fluoranthene*	-	130 ± 20	
Benzo[e]pyrene	-	590 ± 14	
Benzo[a]pyrene*	-	560 ± 20	

PAH with known mutagenic, tumorigenic or carcinogenic activity.

TABLE 3.5. Concentrations (parts per million) of Major Components in the Nitrogen Containing Polycyclic Aromatic Compounds (NPAC) Fractions of:

Compound	Heavy Distillate Recycle Runs		FOB
	<270°C (518°F)	<310°C (590°F)	
	$\bar{x} \pm s$	$\bar{x} \pm s$	$\bar{x} \pm s$
Tetrahydroquinoline	12000 $\pm$ 1230	4870 $\pm$ 416	6480 $\pm$ 2120
Quinoline	10100 $\pm$ 1200	3990 $\pm$ 861	10600 $\pm$ 2340
Indole	30300 $\pm$ 2610	19700 $\pm$ 1190	16700 $\pm$ 3170
2-Methylquinoline	18600 $\pm$ 2060	7300 $\pm$ 1080	14800 $\pm$ 2950
8-Methylquinoline	3570 $\pm$ 815	2200 $\pm$ 455	1990 $\pm$ 247
Methylindole	18600 $\pm$ 2070	17700 $\pm$ 540	9470 $\pm$ 2400
2,5-Dimethylindole	5490 $\pm$ 1310	10900 $\pm$ 1120	4200 $\pm$ 894
2,3-Dimethylindole	5720 $\pm$ 955	10200 $\pm$ 960	3560 $\pm$ 618
Benzo[h]quinoline	767 $\pm$ 74.1	2420 $\pm$ 317	2200 $\pm$ 29.4
Benzo[f]quinoline	728 $\pm$ 55.5	2500 $\pm$ 273	3280 $\pm$ 126
Carbazole	3080 $\pm$ 48.5	8830 $\pm$ 441	16000 $\pm$ 616
1-Methylcarbazole	937 $\pm$ 23.2	2340 $\pm$ 41.7	5150 $\pm$ 216
Methylcarbazole	622 $\pm$ 19.3	1490 $\pm$ 38.6	3600 $\pm$ 142
Benzo[a]carbazole*	-	-	2790 $\pm$ 1070
Benzo[b]carbazole*	-	-	1570 $\pm$ 590
Benzo[c]carbazole*	-	-	2650 $\pm$ 1250

* NPAC with known mutagenic, carcinogenic or tumorigenic activity.

Table 3.4 shows that the five ring PAH, many of which have mutagenic or carcinogenic activity, such as the benzofluoranthenes and benzopyrenes are absent from the current runs. Table 3.5 shows that materials from the heavy distillate recycle runs are also essentially devoid of the benzocarbazoles and higher carbazole benzologs, some of which exhibit carcinogenic activity and are present in FOB.

4.0 BIOLOGICAL ASSAY

4.1 METHODS

Crude distillate materials and their chemical fractions were assayed for mutagenic activity using Salmonella typhimurium TA98 in the standard plate incorporation assay essentially as described by Ames et al.⁽¹¹⁾ Dimethylsulfoxide was used as a solvent. Rat liver (S-9) homogenate was used for metabolic activation of the test materials. Optimum concentrations of activating enzyme levels were determined prior to running the experiments. Mutagen activating enzymes were induced with Aroclor 1254, 250 mg/kg body weight, injected intraperitoneally into male Sprague-Dawley rats. Rats were sacrificed on the fourth day after injection. After sacrifice, livers were perfused with ice-cold 0.154 M KCl and removed for preparation of S9 homogenates, following standard procedures. Revertant colonies were counted electronically with data acquisition and statistics performed by computer. Positive controls included benzo[a]pyrene and 2-aminoanthracene as well as a complex basic fraction from SRC-II heavy distillate. Negative controls included the test strain TA98 with and without metabolic activation as well as appropriate solvent controls.

Crude distillates were assayed for mutagenicity at concentrations of 2, 4, 8, 10, 20 and 50 μg or 0.2, 0.4, 0.8, 1.0, and 2.0 μg per petri plate. Each concentration was assayed in duplicate. Stock solutions of SRC-II distillate were prepared at concentration of 10,000 $\mu\text{g}/\text{ml}$ in DMSO and stored at -80°C when not in use. Fractions prepared from distillates were usually assayed in the same concentration ranges described for crudes; i.e., 2 to 50 μg or 0.2 to 5.0 μg . Fractions were stored at -80°C in DMSO under a nitrogen atmosphere.

Specific mutagenic activity of boiling point cuts or chemical fractions was expressed as revertant colonies of S. typhimurium TA98/ μg of test material, estimated by linear regression analysis of dose-response data. A positive test was one having a maximum mutagenic response in revertant colonies twofold or greater above background, and a correlation coefficient 0.8 or above.

4.2 RESULTS

4.2.1 Mutagenicity Testing

Crude materials were assayed for mutagenic activity in the standard Ames test with S. typhimurium TA98. Results are summarized below. Included are a set of fractionally distilled samples which first indicated⁽⁵⁾ the relationship between boiling point and mutagenic activity.

All of the net products from heavy distillate recycle runs were free of activity in the Ames test. It is interesting to note that the sample with the highest cutpoint between recycled oil and net product [467RC, 310°C (590°F) cutpoint] showed a hint of activity (although not statistically different from the background). The final boiling point of this material is the point at which mutagenic activity begins.

The conventional recycle run with subbituminous coal (454RA) showed a significant level of mutagenic activity although far lower than for the high boiling fractions from the earlier work.⁽¹²⁾ This lower activity may be attributable to the relatively low amount of high boiling material present.

TABLE 4.1. Mutagenic Activity as Determined Against S. typhimurium TA98. Previous Work for Distillate Fractions of SRC-II from Harmonville PDU

<u>Temperature Range of SRC-II Fractional Distillate^(a)</u>	<u>Mutagenicity^(b)</u>
b.p. 300-700°F	Not Active
700-750°F	28.9
750-800°F	35.8
800-850°F	123.8
850°F+ 88.8	

(a) Specific Mutagenic Activity in revertants/μg.
TA98 with metabolic activation.

(b) Replicate of 453RA.

TABLE 4.2. Mutagenic Activity as Determined Against S. typhimurium TA98. Current Work for Distillate Fractions of SRC-II from Merriam Kansas Unit

<u>Material</u>	<u>Recycle Mode</u>	<u>Mutagenicity^(a)</u>
Subbituminous Coal		
454RA ^(b)	Conventional	5.5
467RA	270°C (<518°F)	Not Active
467RB	290°C (<554°F)	Not Active
467RC	310°C (<590°F)	Not Active
Bituminous Coal		
466R	270°C (<518°F)	Not Active

(a) Specific Mutagenic Activity in revertants/μg. TA98 with metabolic activation.

(b) Replicate of 453RA.

5.0 DISCUSSION

Previous work has shown that <371°C (<700°F) SRC-II materials obtained by fractional distillation are in general not significantly different from certain crude petroleums in their dermal carcinogenic activity as determined by chronic skin painting assays in mice.⁽¹³⁾ In the present studies, in vivo tests to determine the tumorigenicity and/or carcinogenicity of the Merriam samples were not carried out. However, chemical properties and mutagenicity of the distillates from the heavy distillate recycle runs are essentially what would be expected based on work with SRC liquids. Microbial mutagenicity, using S. typhimurium TA58, has been a reasonably good predictor of in vivo tumorigenicity for SRC materials, providing they have not been catalytically hydrogenated. The increase in mutagenic activity for materials with boiling points above about 371°C (700°F) is quantitatively similar to those increases observed in carcinogenicity as determined by chronic skin painting and for tumorigenicity as determined by the initiation/promotion assay.

In addition, preliminary results from teratogenicity assays in mice show essentially no teratisms for those endpoints determined in the assays from administration of <371°C (<700°F) distillates. In contrast, mixtures of distillate materials containing components boiling above 427°C (800°F) showed significant teratological effects including diaphragmatic hernia, cleft palate and reduced lung weight.

Figure 5.1 is a composite of PNL data from several investigators, who have studied the chemical composition and biological activity of fractionally distilled SRC-II materials. The figure compares results from chronic skin painting as reported by Renne, from initiation promotion skin tumorigenicity assay as reported by Mahlum, and from microbial mutagenicity as reported by Pelroy. Information on typical chemical compositions of these fractions as shown in the lower portion of the figure are from Wright and Later, and are compiled from data in this report.

The figure shows the concordance among these bioassays for the 10°C (50°F) fractionally distilled cuts as well as illustrating the important features of relative chemical composition for fractions above and below 371°C (700°F).

FIGURE 5.1. Comparison of Composition and Biological Activity of Boiling Point Cuts of SRC-II Product Produced With Heavy Distillate Recycled to Extinction

Consistent with the lowered genetic activity of the Merriam samples was the observation that the <310°C (<590°F) or <270°C (<518°F) distillate recycle materials were almost devoid of PAH with more than 4 aromatic rings. The 310°C (590°F) and 270°C (518°F) cut points also essentially eliminate from the distillate, alkylated catacondensed 4 ring PAH, including those which have been shown to be carcinogenic such as the methylchrysenes and dimethylbenzanthracenes.

One additional observation in comparing the heavy distillate recycle results to those from other SRC materials in the PNL data base is of interest. In mouse skin initiation assays for tumorigenic activity, a 149°C (300°F) to 371°C (700°F) distillate cut from the Harmarville SRC-II material, was shown to be inactive both by tumor yield and tumor incidence criteria. This same material was also inactive in the microbial mutagenicity tests using standard plate incorporation. However, SRC-II FOB (studied previously, PNL-3464), which had been hydrotreated and then topped to yield a hydrotreated distillate of approximately the same boiling range as the Merriam feed, showed very slight activity in the initiation assay. Thus by the criteria of skin tumor initiation, the nonhydrotreated 371°C (<700°F) distillate appeared less active than the hydrotreated FOB. These same assays also indicated that the 371°C (<700°F) distillate was less active than the Wilmington Crude petroleum control.

In earlier work on materials from the SRC-II process, the mutagenicity of FOB was essentially eliminated by hydrogenation.⁽²⁾ In the hydrotreated product there were no amino PAH present at concentrations above the limit of detection (ca 10 ppm) for the GCMS method used. GCMS analysis for amino PAH in materials from the current Merriam runs are not completed; however, considering the longer effective residence time of the Merriam heavy distillate recycle materials in the liquefaction reactor, and the increased aromatic carbon-carbon bond cleavage evident for both the PAH and N-PAC fractions, amino-PAH levels in the Merriam heavy distillate recycle runs should be lower than for SRC materials of comparable boiling point range. Figure 5.1 shows that the highest molecular weight amines likely to be present in a (<590°F) material such as the bottoms recycle distillates would be alkyl anilines or possibly aminoindans, neither of which are active in the microbial mutagenicity test used.

Aside from effects on biological activity, the quality of the Merriam liquid product is improved from a process engineering standpoint. Chevron Research Company, for example, found that the cost of upgrading H-coal distillate products to petroleum fuel specifications increased significantly as a significant proportion of the coal liquid boiled above 343°C (650°F). Even relatively small amounts of >343°C (>650°F) material was enough to increase the cost of production. It seems likely that absence of >343°C (>650°F) liquid from the Merriam product may lead to lower upgrading costs than those calculated by Chevron Research for C₅-900°F product.

Hydrocarbon Research Incorporated has recently reported results of a very similar operating strategy employed in the H-Coal process: liquid boiling above 650°F was recycled to extinction to provide better feedstock for upgrading to gasoline and diesel fuel. An increase in reactor volume of 25% over base conditions, together with some other process changes, increased liquefaction costs somewhat. Nevertheless, HRI calculated that there is an economic incentive for operating in this way, if fully refined products are the goal, due to the reduced costs of final upgrading.

The 343°C (650°F) to 482°C (900°F) yield obtained in normal operation at Merriam is low enough that its complete recycle does not change the total amount of recycle solvent, only its boiling range. No increase in reactor volume should be necessary to operate in the heavy distillate recycle mode described in this paper.

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