

Characterization of Products Formed During
Coliquefaction of Lignin and Bituminous Coal at 400°C

by

Paul Altieri

and

Robert W. Coughlin

Department of Chemical Engineering
University of Connecticut
Storrs, Connecticut 06268

Abstract

The filterable solids from coliquefaction were about 30% benzene soluble compared to about 10% soluble when the same amounts of coal and lignin were reacted individually. In the case of coliquefaction, far more of the benzene-soluble material was also pentane-soluble oil. As a result of coreaction, significant amounts of nitrogen from the coal appeared in the liquid product in contrast to no observable nitrogen in the liquefaction product of coal alone under comparable conditions. Gaseous products were significant and contained CO₂ as a major component. More carbon-14 from the lignin got incorporated into the liquid product during coliquefaction of coal and lignin than in the case of liquefaction of lignin alone under comparable conditions.

Introduction

Recent reports (1, 8) have shown that liquefaction of bituminous coal can occur at temperatures as low as 300°C when the potentially abundant, renewable raw material, lignin, is present in the reaction mixture. Previous processes²⁻⁵ have generally required temperatures above about 400°C in order to rupture carbon-carbon bonds, a necessary step for depolymerization of coal. Lignin degrades thermally at temperatures as low as 300° with the production of substituted phenoxyl radicals. Heredy and Neuworth⁶ and Larsen et al⁷ reported that the presence of phenolic components in the reaction mixture aids the depolymerization of coal resulting in substantial coal liquefaction.

Thus it was hypothesized,⁽⁸⁾ that phenoxy radicals produced by lignin at temperatures ordinarily too low for depolymerization of coal abstract hydrogen from carbon-carbon bonds of coal molecules thereby making them more susceptible to thermal scission.

This paper reports the characterization of the liquid and solid products recovered after co-liquefying coal and lignin in the presence of the hydrogen donor solvent, tetralin. Products were investigated from three separate reactions:

1. Lignin and coal reacted together in tetralin
2. Lignin reacted in tetralin
3. Coal reacted in tetralin

Experimental

Materials And Reagents

Lignin

The lignin used was a "caustic" type obtained from autohydrolysis of aspen. It was purchased from Stake Technology LTD, Ontario, Canada. The lignin was dried in a vacuum oven at 85°C under low pressure (10 torr) for 24 hours and then stored in a dessicator for later use without any further purification.

Coal

Illinois No. 6 bituminous coal (particle size 74-105 micrometers) was obtained from the Pittsburgh Energy Technology Center. This coal has been found to have a 13.6% ash content which was accounted for when computing results on a moisture and ash free basis (maf basis). Crushed coal was sieved to the 74-105 micrometer particle size range, then dried and stored in the same manner as the lignin.

Reagents

All solvents were "Baker analyzed grade" from J. T. Baker Co. except guaiacol which was obtained from Pfaltz and Bauer Co. and tetralin which was obtained from Eastman Kodak Co. Hydrogen and nitrogen gases (98%) were supplied by AERO-All Gas Co.

High Pressure Liquefaction

Tetralin (200 ml), lignin (25 g), coal (25 g), and catalyst were mixed in an inner cylindrical vessel of sheet stainless steel. This was inserted in a one-liter 316 s.s. Magna-drive autoclave manufactured by Autoclave Engineers Inc. The bomb was sealed, pressure tested, flushed with hydrogen, and then pressurized with 1000 psig hydrogen. The system was then heated with agitation at 1500 rpm to 400°C for 1 hour. Approximately 45-60 minutes were required during which time the pressure rose from 1000 psi to 1900-2400 psi. After one hour at the desired reaction temperature, the system was cooled to around 40°C by flowing water through the internal coil for about two hours. Pressure in the cooled reaction vessel ranged

between 700-1000 psig. After venting gases the product material in the liner was removed and transferred to a tared container. Any liquid that remained in the bottom of the autoclave was removed with a pipette and added to the products together with liquid from rinsing the autoclave and liner with known amounts of fresh tetralin.

The product mixture consisting of both insoluble residue and liquid was weighed and then filtered through a tared glass fritted filter (ASTM 10-15). This insoluble, filtered residue was dried at 85°C under vacuum to constant weight.

Determination of Benzene and Pyridine-Soluble Fractions

The filtered residue material was extracted in a tared Soxhlet extraction thimble using benzene until the extract became clear (about 24-48 hours). The thimble was then dried at 85 C under vacuum to constant weight. The weight loss is reported as material which is benzene soluble.

The thimble containing the benzene-extracted solid residue was then extracted with 150 ml pyridine for 24-48 hours. Material soluble in pyridine was computed as weight loss.

Determination of Asphaltenes and Oil

The benzene extract was evaporated and the residue dried to constant weight, then redissolved in a minimum amount of fresh benzene with gentle warming. Then n-pentane (100 ml) was added to precipitate asphaltenes which were filtered and dried to constant weight. The filtrate remaining after asphaltene precipitation was evaporated to recover the "oil" (benzene and pentane soluble).

Carbon-14 Analysis

Various liquid product fractions were analyzed for carbon-14 by New England Nuclear Laboratories using a liquid scintillation spectrometer.

Analysis of Nitrogen Carbon and Hydrogen

Various liquid product fractions were analyzed for nitrogen, carbon and hydrogen content by the American Cyanamid Company. Oxygen content was obtained by difference. Two trials were performed for each sample.

GC/MS Characterization of Evolved Gases

Lignin (25 g), coal (25 g), and tetralin (300 ml) were reacted at 400 degrees centigrade for one hour at 2200 psi in a rocking autoclave (Parr #4021). The procedure was otherwise as discussed above.

After reaction the autoclave was cooled and then connected to the sampling valve of a Hewlet Packard #5985 GC/MS equipped with a stainless-steel column packed with Carbowax. The autoclave vessel was held at $\sim 200^{\circ}\text{C}$ while a small flow of gas was released and periodically sampled for GC/MS analysis. Temperature programming of the GC column from 20°C to 225°C over a time span of 60 minutes permitted adequate separation of components.

Results And Discussion

Table 1 summarizes mass balances for four experiments. The amount of gas formed was computed by difference.

Characterization of Solid Products of Reaction:

Figure 1 summarizes the work up and fractionation of the solid and liquid products of reaction. The individual fractions, P1 through P7 are further identified in Table 2.

Characterization of coal liquids as benzene-soluble and pentane-soluble goes back to Pelipetz et al (9) who viewed solubility in benzene as a measure of the extent to which coal has been hydrogenated; unreacted or partially reacted coal remains insoluble in benzene. Solubility in benzene and pentane is a measure of the "oil" produced. The portion that is soluble in benzene but insoluble in pentane (i.e. precipitated by pentane) is called asphaltenes. Asphaltenes are high-molecular weight intermediate products in coal liquefaction. The presence of asphaltenes in coal-derived liquids has been reported by both Pelipetz (9) and Weller (10). Stern (11) showed that both the quantity and the molecular weight of the asphaltenes present in the coal-derived liquid product affect its viscosity. These methods are also described by Mimal (12). As evident from Figure 1, we also employed pyridine solubility which was used by Whitehurst (13) to represent the extent to which coal is converted to liquid products (13).

The mass of solids filtered from the products of the reactions are plotted in Figure 2 (see Table 3 for experimental conditions). Figure 2 compares the solids from experiment 4-A (in which lignin and coal are co-liquefied) to the sum of the solids filtered in experiment 4-B (in which only lignin is used) plus experiment 4-C (in which only coal is used). The cross-hatched area of each bar graph represents benzene-soluble material (P4) which is greatly increased (by about a factor of four) when lignin is present in the reaction mixture.

Further characterization of the benzene-soluble solids (P4) is shown in Figure 3. Figure 3 shows that when lignin and coal are co-liquefied the production of asphaltenes

(benzene-soluble but pentane insoluble, (P5)) is increased more than the corresponding production of "oil" (soluble in benzene and pentane, (P6)).

The benzene-insoluble residue was partially soluble in pyridine in every case. Co-reacting lignin with the coal does not cause any substantial change in pyridine solubility of the benzene insoluble residue.

Three control experiments (5A, 5B and 5C) were conducted at room temperature but with all other aspects identical to experiments 4A, 4B and 4C. The results shown plotted in Figure 4 indicate essentially no liquefaction took place since the mass of filtered solid product was equal to the mass of coal and/or of lignin charged to the reactor. Benzene soluble solids are only about 2.5g in the case of the control experiments vs about three g for coal and lignin reacted separately at 400°C and about 11 g for the coreaction of coal and lignin at 400°C.

Characterization of Liquid Products:

Liquid products from reactions 4A and 4B were further characterized by analysis for carbon-14 and nitrogen. Because coal contains significant nitrogen but lignin contains very little, nitrogen analysis of liquid products indicates the relative contribution of coal. Because lignin contains significant carbon-14 but coal does not, the carbon-14 content of the liquid indicates the relative contribution of lignin. The half life of carbon-14 is 5730 years and coal was formed from biomass millions of years ago; therefore the carbon-14 remaining in coal is unmeasurable. Any detectable carbon-14 in the liquid must be contributed by the lignin which contains carbon-14 comparable in isotopic abundance to that in carbon dioxide in the atmosphere because the lignin was prepared from wood cut within recent years. Tetralin used as the solvent in the experiments contributed negligible carbon-14 because it was produced from petroleum formed millions of years ago.

Table 4 reports carbon-14 contents of the liquid products for the case when lignin and coal are present in the reaction mixture as well as when only lignin was present in the reaction mixture. The greater concentration of carbon-14 observed when lignin and coal are co-liquefied suggests ruptured coal molecules may incorporate lignin fragments. Coal may also catalyze the liquefaction of lignin or more lignin may get incorporated into the liquid because it reacts with coal fragments rather than self-polymerizing into a solid.

Table 5 shows the elemental analysis of the coal and Stake lignin used in the experiments. Table 6 shows that the liquid filtrate obtained from experiment 4-A when coal and lignin are coreacted contains 0.1% nitrogen compared to no detectable nitrogen in the liquid formed by reaction of coal alone.

The absence of nitrogen in liquid products from coal reacted alone at 400°C (experiment 4B) indicates that the nitrogen-containing portions of the coal molecules were not depolymerized. During co-reaction with lignin under the same conditions (experiment 4A), however, nitrogen does appear in the liquid products indicating more extensive depolymerization of coal molecules. The content of nitrogen (0.1%) indicates a rather uniform disintegration of the coal to form liquid because this value is close to what one would compute using the original nitrogen content of the coal and the apparent fraction of coal that was liquefied. Table 6 also shows the nitrogen content of three distilled fractions of the liquid obtained from experiment 4A. The lowest-boiling fraction is tetralin and contains no nitrogen. It appears the nitrogen is concentrated in the non-distillable residue as might be expected if the nitrogen occurs in the larger molecular fragments contributed by the coal.

Characterization of Gaseous Products

Mass balances (see Table 1) suggest the formation of significant amounts of gases during the reaction. An experiment was performed in which coal and lignin were reacted as in experiment 4-A and the reactor then cooled under pressure. Later, the reactor was heated to about 200°C and the product gas was sampled from the reactor at this temperature and analyzed by GC-MS. Table 7 shows the mass balance for this experiment and the components detected in the vented gas.

Based on the respective peak heights of the GC chromatogram, carbon dioxide was the most abundant gaseous product with water vapor being next. The gases estimated in Table 1 by difference from mass balances contain only a small contribution from water vapor, however, because liquid and solid products were collected and weighed after the reactor was opened at room temperature. The reactor was sampled for gas analysis by GCMS at 200°C, however, at which temperature the gas phase would contain considerably more water vapor than at room temperature.

Acknowledgement

The authors are grateful for support from the National Science Foundation under Grant No. CPE 8303505 and for nitrogen assays performed by the American Cyanamide Company.

References

1. Couglin, R. W., F. Davoudzadeh, *Nature*, 303, 5920, pg. 789-91, (1983)
2. Thorogood, R. M., C. L. Yeh and S. M. Morris, "Scaleup of the SRC-I Coal Liquefaction Process", paper presented at 3rd Annual Conference Coal Gasification and Liquefaction, University of Pittsburgh, August 3-5, 1976.
3. Schmid, B. K. and D. M. Jackson, "The SRC-II Process", paper presented at 3rd Annual Conference Coal Gasification and Liquefaction, University of Pittsburgh, August 3-5, 1976.
4. EDS Coal Liquefaction Process Development, U. S. DOE Report No. EE-2353-2, October 1977, Contract No. Ex-76-C-01-2353.
5. H-Coal Integrated Pilot Plant Phase I-Final Report, U. S. ERDA, No. HCP/T-1554/ (Vol. II) UC-90d, November 1977, Contract No. EX-76-C-01-1544.
6. Heredy, L. A. and M. B. Neuworth, *Fuel*, 41, 221 (1962).
7. Larsen, J. W., T. L. Sanis, B. R. Rodges, *Fuel*, 60, 335 (1981).
8. Coughlin, R. W., and F. Davoudzadeh, *Fuel*, Vol. 65, pg. 95-106 (1986).
9. Pelipetz, J., *Ind. Eng. Chem.* 40, 1259-64 (1948).
10. Weller, S. and J. Pelipetz, *Fuel* 29, 208-11 (1951).
11. Sternberg, W., *ACS Symposium Series*, Vol. 20, 111-122 (1975).
12. Mima, M. J., Analytical Methods for Coal Products, Vol 1, Ch. 19, (1979).
13. Whitehurst, D., Coal Liquefaction Fundamentals, ACS, Washington, D.C., (1980).

TABLE 1
Mass Balances For Liquefaction Experiments

Expt # (1)	Initial Mass Charged (g)			Total Mass Charged (g)	Liquid and Solid Pdts (g)	Gaseous(3) Pdts, % of Total
	Lignin	Coal	Solv.			
2-B(2)	25	25	223.0	277.0	241.6	12.8
4-A	25	25	190.8	240.8	215.3	10.6
4-B	25	0	190.8	215.8	186.2	13.7
4-C	0	25	191.0	216	203.0	6.0

- (1) Reactions run at 400°C for one hour in tetralin and 1000 psi hydrogen initial pressure.
 (2) Reaction run at 300°C for 3 hours in guaiacol.
 (3) Gaseous products are computed by difference.

TABLE 2
Definition of Quantities Used for Characterization of Reaction Products

- P1 = Mass of Liquid Filtrate (g)
 P2 = Mass of Solid Filtered (g)
 P3 = Mass of Benzene-Insoluble Solids (g)
 P4 = Mass of Benzene-Soluble Solids (g)
 P5 = Mass of Benzene-Soluble Solids Precipitated by Pentane (g)
 P6 = Mass of Benzene-Soluble Solids that are Pentane Soluble (g)
 P7 = Mass of Benzene-Insoluble Solids that are Pyridine Soluble (g)

TABLE 3
Experimental Conditions

Expt #	Mass of Lignin (g)	Mass of Coal (g)	Volume of Tetralin (ml)	Reaction Temp. (C)	Reaction Time (hr)
4-A	25.0	25.0	200	400	1
4-B	25.0	-	200	400	1
4-C	-	25.0	200	400	1
5-A*	25.0	25.0	200	25	100
5-B*	25.0	-	200	25	100
5-C*	-	25.0	200	25	100

* - Control experiments

TABLE 4

Carbon 14 Analysis of Liquefaction Product

<u>Expt #</u>	<u>Reported Activity</u> <u>(1)</u>	<u>Experiment Description</u> <u>(2)</u>	<u>Lignin Molecules/ml</u>	<u>Carbon-14 Atoms/ml</u>
4-A	4.56*	Coal/lignin	4.58×10^{20}	1.98×10^{10}
4-B	3.30*	Lignin	3.82×10^{20}	1.65×10^{10}

- (1) Carbon-14 activity determined by liquid scintillation spectrometry, performed by New England Nuclear Company.
 (2) Reactions performed at 400 C for 1 hour with tetralin used as the solvent.

* Represents value obtained after background count of 2.5 dpm/ml has been subtracted.

TABLE 5

Elemental Analysis of Unreacted Lignin And Coal
(maf basis)

	<u>Stake Lignin</u>	<u>Illinois No. 6 Coal</u>
% C	60.58	82.20
% H	5.30	5.20
% O	34.11	6.81
% N	-	1.38
% S	-	4.15

TABLE 6

Results of Nitrogen Analysis of Liquid Filtrate Products⁽¹⁾

<u>Experiment</u>	<u>% Carbon</u>	<u>% Hydrogen</u>	<u>% Nitrogen</u>
4-A*	76.6	5.9	0.1
4-B**	76.3	6.1	-

Atmospheric Distillation of Liquid Product From Experiment 4A

<u>Fraction #</u>	<u>Boiling Range (°C)</u>	<u>Volume of Fraction (ml)</u>	<u>% Nitrogen</u>
1	188 - 190	130	-
2	192 - 195	5	.04
3	> 195	-	.34

* Coal and lignin co-liquefied at 400 C.

** Coal alone reacted at 400 C.

(1) Nitrogen analysis was performed by American Cyanamid Co.

TABLE 7

Characterization of Vented Gas for Experiment # 6-A

Expt# (1)	Initial Mass			Total Mass Charged (g)	Liquid and Solid Prod. (g)	Gaseous (2) Products,% of Total
	<u>Lignin</u>	<u>Coal</u>	<u>Solv.</u>			
6-A	24.8	25.0	220.8	270.6	244.0	9.98

- (1) Reaction run at 400C for 1 hour in tetralin and 1000 psi hydrogen initial pressure.
 (2) Gaseous products computed by difference.

Components detected in gas:

Major: CO₂, H₂O, CH₃OH

Minor: bicyclo(7,1,0)decane
 naphthalene
 1-nonyne
 tetralin
 methyl thiofurate

Figure Captions

- Flow diagram of treatment and characterization of solid and liquid products.
- Benzene solubility of solids filtered from products of experiments 4A, 4B and 4C. P3-benzene-insoluble portion. P4-benzene-soluble portion.
- Pentane solubility of benzene-soluble material extracted from solid products of reaction. P5-pentane-insoluble portion. P6-pentane-soluble portion.
- Benzene solubility of products from control experiments conducted at room temperature. Compare to Figure 2.

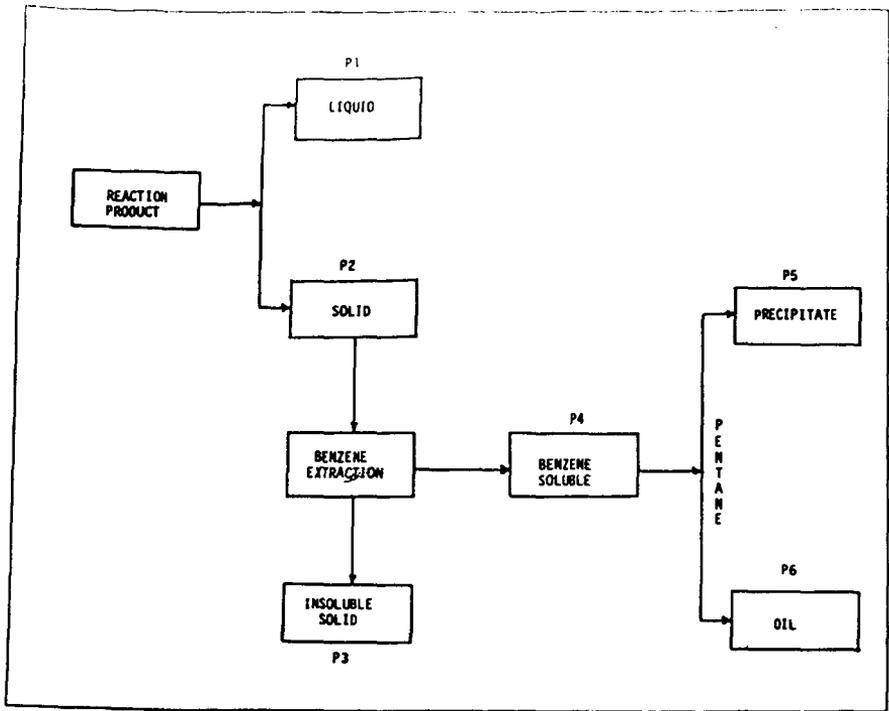


FIGURE 1

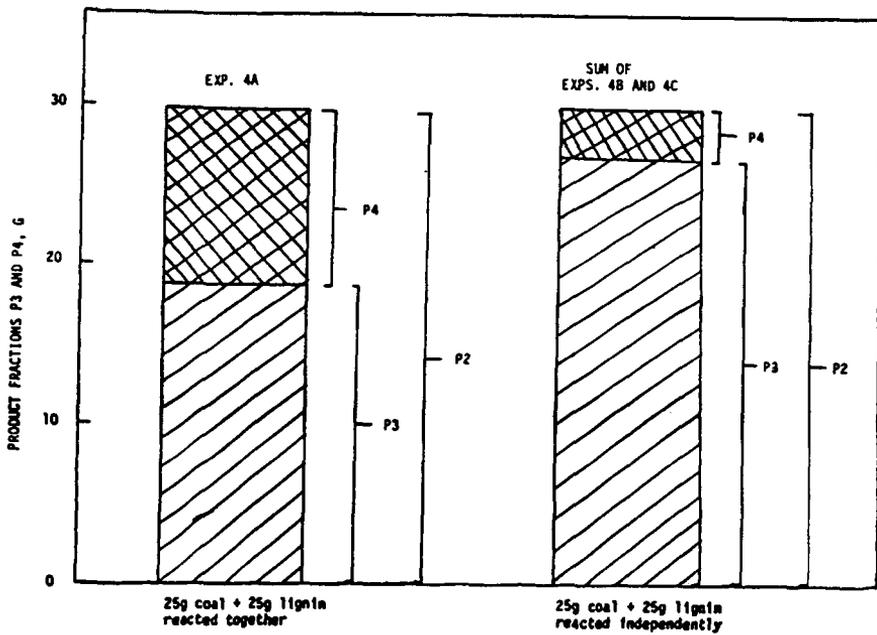


FIGURE 2

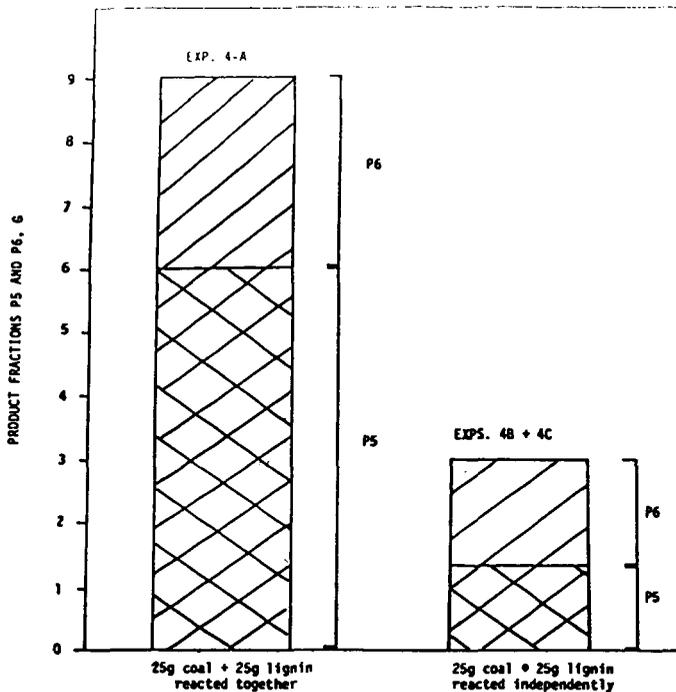


FIGURE 3

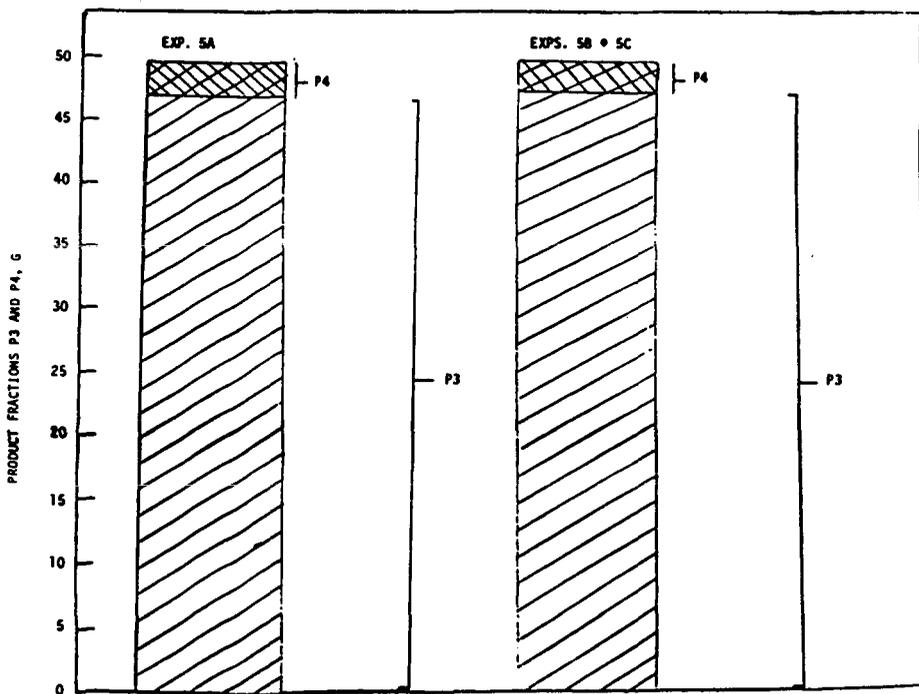


FIGURE 4