

LABORATORY PITCHES PAH AND POM STUDY

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ABSTRACT

The polynuclear aromatic hydrocarbon (PAH) measurements for a series of pitches are reported as a function of feedstocks and product softening points. The relationships of PAHs to polycyclic organic matter (POM) which evolve during pitch carbonization are also studied. By combining selected feedstocks and manufacturing processes, a reduction in PAH and POM content in pitches can be achieved.

INTRODUCTION

Various studies have reported on the need to reduce PAH emission from Soderberg potroom operations.^{1,2,3,4} PAHs are present because of incomplete combustion of the pitch binder during the Soderberg anode cell baking phase. The standard means of reducing PAH emissions are by scrubbing, condensing or combusting the volatile matter.

This report demonstrates another action that can be used in conjunction with these control methods; i.e., the reduction of PAHs using specific pitch manufacturing techniques.

In general, the pitch PAH content is expressed as the measurement of 17 key compounds targeted by the National Institute for Occupational Safety and Health.⁵ These compounds are listed in Table I. Mirtchi and Noel have reported on the development of relative potency factors (RPF) for each of the 14 higher boiling PAHs.⁶ Benzo(a)pyrene [B(a)P] is the reference PAH and assigned an RPF value of one (1.000). The B(a)P equivalent value is calculated by multiplying the individual concentration of each compound by the respective RPF listed in Table I and totaling the results. A relative B(a)P equivalent value can be calculated for each pitch sample studied. It is therefore easier to compare one value characterizing a pitch sample than comparing 14 individual compounds. One technique for removing the more toxic PAHs is distillation. Because of the high boiling points for the more toxic PAH compounds (see Table I), high temperature and/or high vacuum is required in the distillation process. Bench scale distillations were performed in this study on three different feedstocks to determine the effect of pitch softening point

on PAH reduction and on the POM emitted during the carbonization (baking) cycle.

EXPERIMENTAL PROCEDURE

1. A wide variety of crude coal tar sources were characterized by quinoline insoluble (QI) content and High Performance Liquid Chromatography (HPLC) measurement of PAHs.
2. Three coal tar samples were selected for the study.
3. Each tar feedstock was vacuum distilled in the laboratory to a series of pitch softening points ranging from 110°C to 165°C.
4. The pitch products were characterized by PAH analysis and other routine testing.
5. Each pitch sample was baked to 600°C and the evolved POM was collected.
6. The evolved POM was measured and characterized by HPLC analysis.
7. Control and new experimental pitches were similarly processed and characterized.
8. All results were analyzed and summarized.

Feedstock and pitch testing methods used in this study are listed in Table II.

EXPERIMENTAL RESULTS

Pitch Making and Analyses:

Properties for the three feedstocks selected for this trial series are summarized in Table III. Tar feedstocks R and T have similar QI content but contrasting aromaticity levels. The AD tar was added to the study because of its high QI content.

TABLE I. COMPOUNDS USED IN PAH MEASUREMENT

Compound (by M.W.)	Empirical Formula	Molecular Weight	Boiling Point (°C)**	RPF**
1. Naphthalene	C ₁₀ H ₈	128.17	218	-
2. Acenaphthalene	C ₁₂ H ₈	152.20	265-275	-
3. Acenaphthene	C ₁₂ H ₁₀	154.21	279	-
4. Fluorene	C ₁₃ H ₁₀	166.22	293-295	-
5. Anthracene	C ₁₄ H ₁₀	178.23	340	-
6. Phenanthrene	C ₁₄ H ₁₀	178.23	340	-
7. Fluoranthene	C ₁₆ H ₁₀	202.26	375	0.034
8. Pyrene	C ₁₆ H ₁₀	202.26	399	-
9. Benzo(a)Anthracene	C ₁₈ H ₁₂	228.29	435	0.033
10. Chrysene	C ₁₈ H ₁₂	228.29	448	0.260
11. Benzo(b)Fluoranthene	C ₂₀ H ₁₂	252.32	481	0.100
12. Benzo(k)Fluoranthene	C ₂₀ H ₁₂	252.32	480	0.010
13. Benzo(a)Pyrene	C ₂₀ H ₁₂	252.32	496	1.000
14. Benzo(e)Pyrene	C ₂₀ H ₁₂	252.32	493	0.050
15. Benzo(g,h,i)Perylene	C ₂₂ H ₁₂	276.34	-	1.000
16. Indeno(1,2,3-c,d)Pyrene	C ₂₂ H ₁₂	276.34	-	0.100
17. Dibenzo(a,h)Anthracene	C ₂₂ H ₁₄	278.35	518	1.400

*Many of these compounds will sublime.

**Relative potency factors used to calculate B(a)P equivalent value.⁶

Note: Naphthalene, acenaphthalene, and acenaphthene are included in this table. Because of the low boiling point of these compounds, their presence in the pitch products is insignificant.

TABLE II. FEEDSTOCK AND PITCH MEASUREMENT METHODS

Characterization	Unit	Method
Softening Point (sp)	°C	ASTM D 3104
Toluene Insoluble (TI)	wt. %	ASTM D 4072
Quinoline Insoluble (QI)	wt. %	ASTM D 4746
B-Resin (B-R)	wt. %	TI less QI
Modified Conradson Coking Value(MCC)	wt. %	ASTM D 2416
Aromatic Hydrogen: Aliphatic Hydrogen Ratio		NMR
Polynuclear Aromatic Hydrocarbons reported as B(a)P or B(a)P equivalent	ppm	HPLC

TABLE III. PROPERTIES OF FEEDSTOCKS SELECTED FOR THE PITCH PROCESSING STUDY

Sample ID	QI, wt. %	B-Resin, wt. %	H _A /H _N , NMR	B(a)P, ppm
AD	17.2	3.4	7.2	9100
R	7.3	2.1	5.7	7800
T	8.1	3.3	8.1	8200

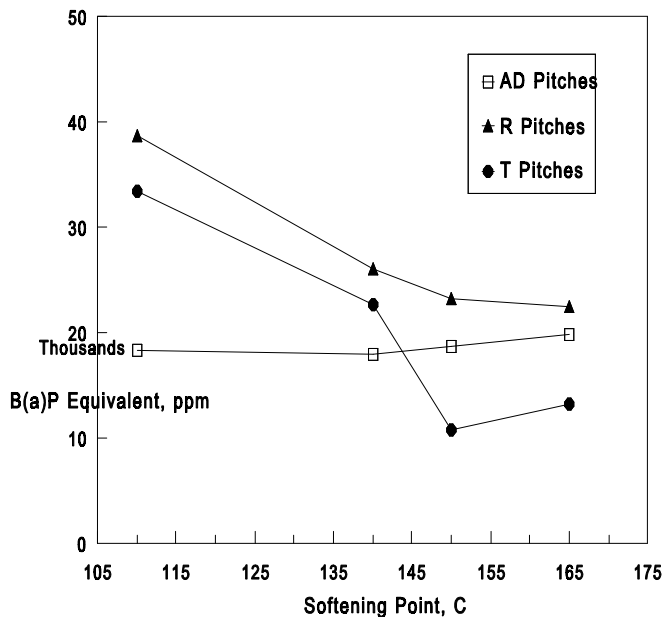
The laboratory distilled pitch data in Table IV show the typical increases in insolubles and coking value with respect to softening point. For feedstock R and T, the whole pitch B(a)P equivalent levels generally decrease with softening point increase (see Figure 1). However, no real change occurs in the B(a)P equivalent in the AD feedstock pitch series. The lack of B(a)P reduction in the AD pitch

series relates to the higher pitch yield for this tar; i.e., less distillate needs to be removed to increase the AD tar pitch softening point. In reality, to maintain a B(a)P equivalent level for a series of increasing softening points, some of the PAH compounds are being removed (see Figure 2). The high QI content of AD pitches makes them undesirable for most domestic applications.

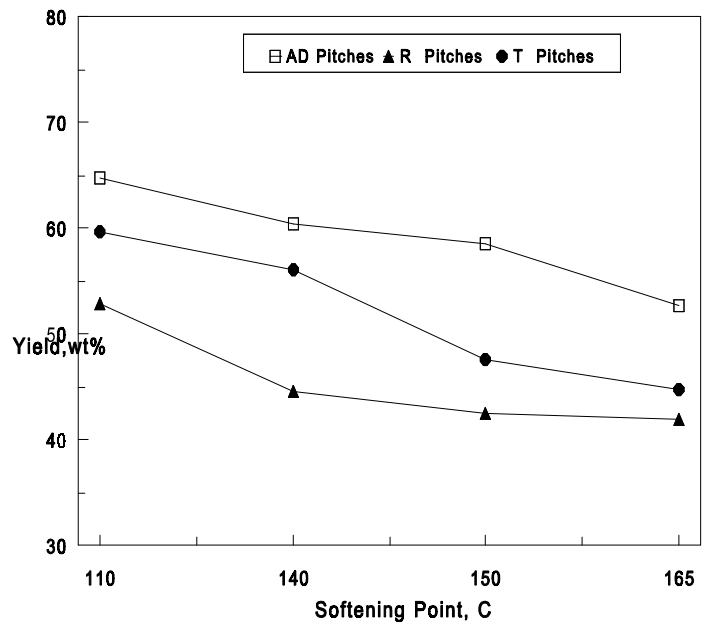
TABLE IV. PITCH PROPERTIES FOR DISTILLATION SERIES OF THREE SEPARATE FEEDSTOCKS

Feedstock	SP, °C	TI, %	QI, %	B-R, %	MCC, %	B(a)P Equiv., ppm
R	110	26.8	12.7	14.1	56.3	38700
R	140	32.0	15.8	16.2	66.7	26100
R	150	34.7	16.6	18.1	69.0	23300
R	165	41.2	17.2	24.0	69.9	22500
T	110	25.3	14.0	11.3	57.4	20900
T	140	30.8	15.3	15.5	64.3	22700
T	150	34.5	16.3	18.2	67.4	10800
T	165	37.8	17.6	20.2	71.6	13300
AD	110	35.4	26.6	8.8	61.0	18400
AD	140	38.0	28.5	9.5	64.6	18000
AD	150	40.8	29.7	11.1	67.5	18700
AD	165	46.7	32.9	13.8	72.9	19800

**Figure 1 - Lab Pitches, Whole Analysis
B(a)P Equivalent vs. Softening Point**



**Figure 2 - Pitch Yield as a Function of
Softening Point For the Distillation Series**



Analysis of Volatiles from Baking

Each pitch sample was baked to 600°C in a tube furnace through which an inert gas was introduced to carry the volatiles from the sample into a series of collection traps.

At the end of each evaluation, the entire system was rinsed with methylene chloride and combined into one solution. This sample solution was then concentrated and analyzed by HPLC for PAH content. For this report, POM content is calculated as the original sample weight minus the pitch residue after baking. (Previous evaluations using this collection system indicate an accountability of 95%-98% is attainable).

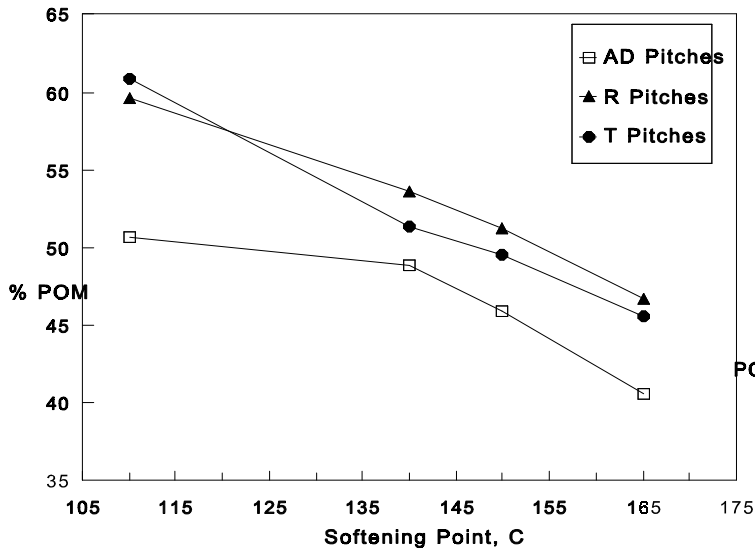
The reduction of volatiles or POM with respect to softening point for the various pitches is illustrated in Figure 3. The higher pitch and coke yielding AD series results in lower volatile evolution during the baking operation.

The B(a)P equivalent for each of the POM samples is plotted in Figure 4. Although the R and T pitch series appear to have greater reduction in pitch and POM B(a)P equivalent with respect to increasing softening point, the AD pitches have less POM and total B(a)P equivalent during the baking operation.

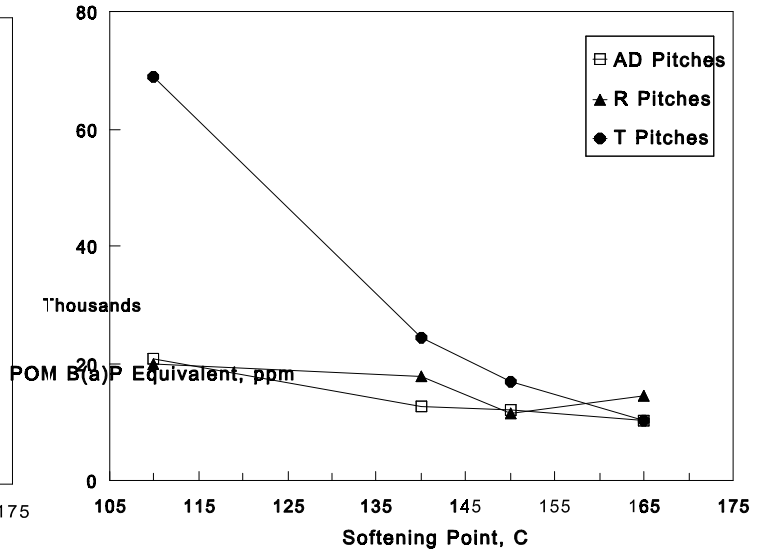
We have previously described how Type B coal-tar/petro pitches (≤ 40 percent petroleum material) can be designed to reduce B(a)P equivalent level.⁷ The practical application of this technology is demonstrated in Table V. Comparisons are shown between the specially engineered low PAH Type B pitch, standard 110°C softening point pitch and the three 110°C softening point pitches from this report.

The coal-tar/petro Type B pitch has significant lower levels of both whole pitch and POM B(a)P equivalents than the other 110°C softening point pitches. The AD pitch has a lower B(a)P equivalent level than the other coal-tar pitches; however, it has 25.6 percent QI and would require high binder levels for acceptable mix rheology.

**Figure 3 - Lab Prepared Pitches
% POM vs. Softening Point**



**Figure 4 - Lab Pitch POM
B(a)P Equivalent vs Softening Point**



**TABLE V. PROPERTIES OF VARIOUS 110°C
SOFTENING POINT PITCHES**

Pitch	T.I., wt. %	Q.I., wt. %	Beta-Resin wt. %	MCC wt. %	Whole Pitch B(a)P Equiv.,ppm	POM wt. %	POM B(a)P Equiv., ppm
AD	35.4	26.6	8.8	61.0	18400	50.7	20700
R	26.8	12.7	14.1	56.3	38700	60.0	20000
T	25.3	14.0	11.3	57.4	20900	59.6	68800
Std.	30.3	14.7	15.6	57.8	24900	56.0	30300
Type B	22.5	10.1	12.4	57.0	15000	58.8	8600

CONCLUSIONS

1. The initial PAH content and potential to reduce PAH compounds in pitch distillation depend on the molecular distribution in the starting tar feedstocks.
2. The required vacuum and temperature conditions must be reached to significantly remove the high boiling genotoxic PAH compounds in pitch distillation.
3. The pitch coking value can contribute to reducing total pitch POM and B(a)P equivalent evolved during the baking operation.
4. The B(a)P equivalent in pitch and POM cannot be predicted by standard analyses of coal tar feedstocks.
5. By combining feedstock characteristics as outlined in this study with coal-tar/petro pitch technology, significant reductions in pitch PAH and POM values can be obtained.

FUTURE STUDY RECOMMENDATIONS

1. Continue to develop PAH and POM measuring and correlation techniques.
2. Study thermal effects on PAH distribution during distillation process.
3. Study solvent solubility of PAH compounds using HPLC techniques.
4. Study PAH and POM characteristics of a wider variety of feedstocks.

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REFERENCES

1. Proulx, A. L., "Performance of a Dry Paste for Horizontal Stud Soderberg Anode," Light Metals 1987, pp. 561-562.
2. Proulx, A. L., Barber, M. A., "Performance of a Paste with a High Softening Point Pitch for Soderberg Anodes," CIM Proceedings, 1988, pp. 67-72.
3. Mirtchi, A. A., Proulx, A. L., Castonguay, L., "Reduction of the PAH Emissions for Horizontal Stud Soderberg Potrooms," Light metals 1995, pp. 601-607.
4. Leber, B. P., Smeil, P. F., "Characterizing Emissions from a Soderberg Aluminum Smelter," Journal of Metals, May 1995, pp. 20-21.
5. NIOSH, U. S. Department of Health and Human Services, Physical and Chemical Analytical Method No. 5506, Polynuclear Aromatic Hydrocarbons, 3rd Edition, 1985.
6. Mirtchi, A. A., Noel, L., "Polycyclic Aromatic Hydrocarbons (PAHs) in Pitches Used in the Aluminum Industry," Carbon '94, pp. 794-795.
7. McHenry, E. R., "Coal-Tar/Petro Binder Studies," Proceedings of the Fifth Australasian Aluminium Smelter Technology Workshop, Sydney, October 22-27, 1995.