THE EFFECT OF THERMAL TREATMENT ON INDUSTRIAL PITCH AND CARBON ANODE PROPERTIES - PART 1

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ABSTRACT

A number of industrial-type pitches were produced from feedstocks categorized by quinoline insoluble content and aromaticity. A pilot unit was used to simulate production processing. Controlled process thermal treatment was used to increase β-resin and avoid the formation of mesophase. The effect of thermal treatment on pitch properties is explained. The β-resin effect on carbon properties is being determined and will be reported next year.

INTRODUCTION

In the vacuum distillation of tars to pitches, low boiling constituents are removed to form various softening point residues (see Figure 1). As a result, the quinoline insoluble (QI) and β-resin [the difference between toluene insoluble (TI) and QI] increase in concentration.

Low thermal treatment (usually in the 300-390°C range) increases β-resin content by dehydrogenation and dealkylation, leaving free radicals which can then combine to form larger polynuclear molecules. It is generally accepted that more extensive thermal treatment will produce mesophase which is commonly referred to as secondary QI. As shown in Figure 2, β-resin can continue to increase during early mesophase formation; however, during extended thermal treatment β-resin formation will subside as mesophase content increases.[1]

The three most recent volumes of *Light Metals* (1990-1992) have ten papers discussing primary and secondary quinoline insolubles in binder pitches. During this time there were only a few brief comments about aromaticity and β-resin. Saint Romain and LaGassie associated heat treatment to aromaticity and wetting properties of pitch.[2] Boenigk et al related β-resin content to bench scale anode compressive strength.[3]

To determine the importance of aromaticity and β-resin characteristics on industrial pitch properties, we have designed a series of experiments to illustrate the effect of these variables in pitch and carbon anode manufacture.

This is an active, on-going project and a series of reports will result. Phase 1 outlines the work to date and possibly, experimental design changes may occur as the project proceeds. For example, the original list of feedstocks may be modified to include tars with higher reactivity rates.

EXPERIMENTAL PROCEDURE

Phase 1

A. Examine a wide variety of feedstocks and segregate by levels of aromaticity as a function of QI.

B. Select representative feedstocks of both low and high QI and aromaticity levels for initial pitch preparation.

C. Distill each selected feedstock to a 40°C softening point pitch, atmospherically thermal treat at 390°C for various time periods up to 12 hours, and vacuum distill to a 110°C softening point.

D. Characterize pitch products and determine the optimum feedstocks and processing conditions to use for larger production batches.

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FIGURE 1. SOLVENT FRACTIONS OF CRUDE TAR AND STRAIGHT DISTILLED PITCHES (HYPOTHETICAL MATERIALS)

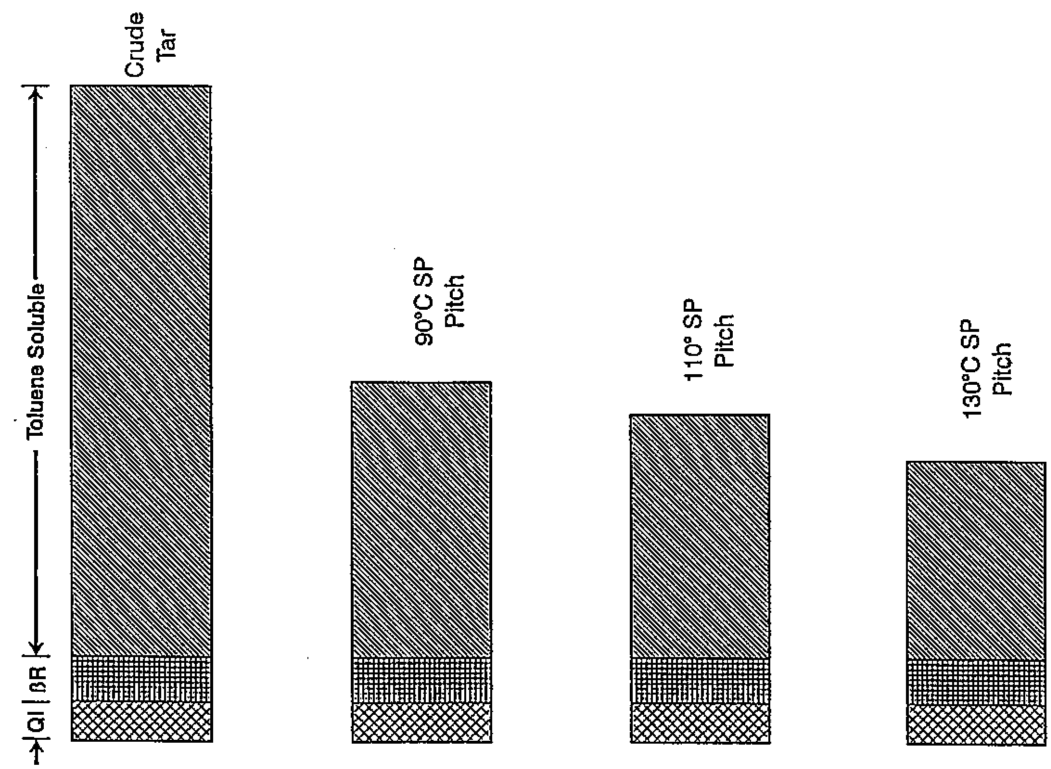
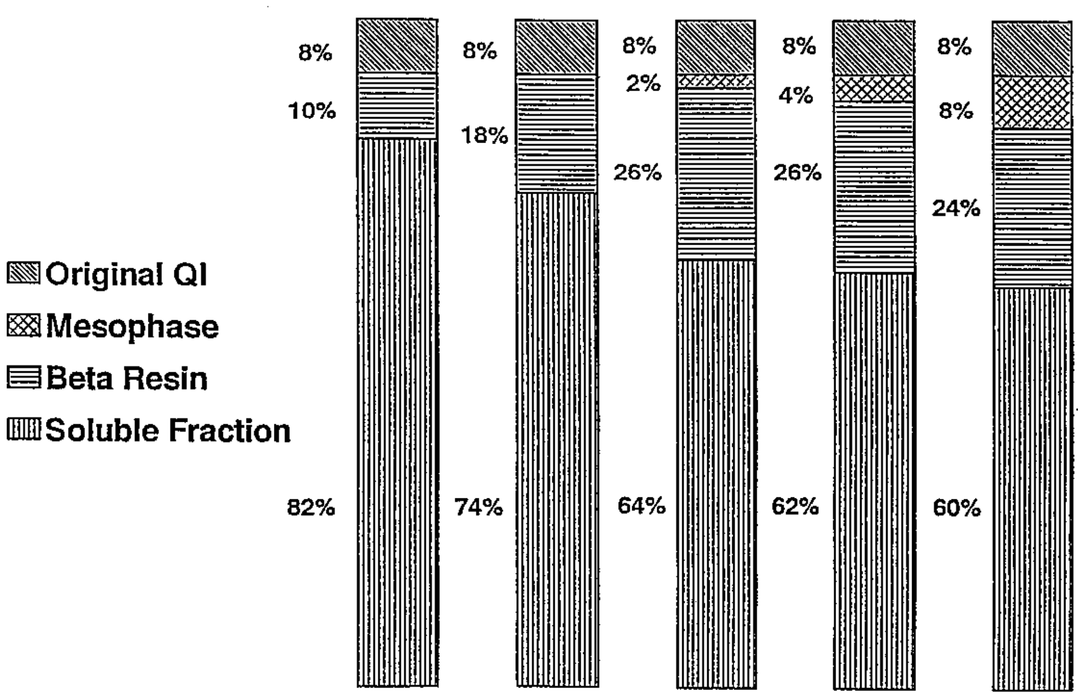


FIGURE 2. CHANGE OF FRACTION CONCENTRATION DURING THE HEAT TREATMENT OF PITCH



Phase 2

A. Employing optimum conditions established in Phase 1, prepare larger quantities of both thermal treated and untreated pitches.

B. Prepare 6 X 9 X 12 inch vibroformed anodes using these pitches as binders. Bake the anodes to 1125°C.

C. Compare pitch and anode physical properties for each binder type.

Testing Methods

The aromaticity is ranked using both infrared index (I_A) and nuclear magnetic resonance (NMR). I_A is the ratio of the absorbencies of the aryl and alkyl CH groups. In NMR, the aromatic hydrogen to aliphatic hydrogen in the spectra are compared to yield the listed ratio.

Other standard testing methods used in this study are listed in Table I.

TABLE I
TAR AND PITCH MEASUREMENT METHODS

Characterization	Unit	Method
Softening Pt. (sp)	°C	ASTM D 3104
Viscosity	cP	ASTM D 5018
Density at 25°C	g/cm^3	ASTM D 71
Coking Value	wt.%	ASTM D 2416
Toluene Insoluble	wt.%	ASTM D 4072
Quinoline Insoluble	wt.%	ASTM D 4746
ß-Resin	wt.%	TI less QI
Primary, Secondary and Coarse QI	vol. %	ASTM D 4616

Phase 1 Experimental Results

A total of 21 samples were characterized as potential feedstocks for inclusion in this study. As Table II shows, the aromaticity level generally increases with QI content.

TABLE II
PROPERTIES OF FEEDSTOCKS CONSIDERED FOR THE PITCH PROCESSING STUDY

Sample I.D.	TI, wt.%	QI, wt.%	ß-resin wt.%	I_A IR	Ha/Hn NMR
A*	4.3	2.2	2.1	2.2	3.5
B	4.9	2.5	2.4	3.4	N.A.
C*	5.4	2.7	2.8	2.8	5.1
D*	4.6	2.8	1.8	N.A.	5.7
E	3.9	2.8	1.1	2.8	N.A.
F	5.6	2.9	2.7	N.A.	6.1
G	4.4	2.9	1.5	3.5	N.A.
H	5.0	3.2	1.8	4.0	7.3
I*	5.3	3.6	1.7	2.6	4.1
J*	5.7	3.7	2.0	N.A.	5.1
K	6.0	4.1	1.9	3.6	6.2
L*	7.6	4.6	3.0	N.A.	5.7
M	7.7	5.3	2.4	4.2	N.A.
N	7.5	5.7	1.8	2.7	6.0
O	9.0	6.0	3.0	4.0	7.7
P*	9.5	6.9	2.6	3.4	5.7
Q*	10.5	7.2	3.2	3.9	8.0
R	9.4	7.4	1.9	N.A.	6.3
S*	12.1	8.7	3.4	N.A.	8.7
T*	16.7	12.0	4.7	4.9	N.A.
U	18.7	14.5	4.2	4.9	N.A.

* Larger quantity drum samples received for more extensive testing.

N.A. - Not analyzed.

From the ten tars chosen for more extensive evaluation, samples A, C, P, and Q were selected for pitch preparation in our initial study. The first two samples represent two different aromaticity levels of QI in the 2.5 wt.% range. The latter two samples have variable aromaticity for QI in the 7 wt.% range.

The effect of thermal treatment on QI and β-resin for the four tars is illustrated in Figures 3 and 4. Projected insoluble levels are calculated for a 110°C softening point pitch from the feedstock yield characteristics (CALC). A high level of β-resin was produced during the straight vacuum distillation without added thermal treatment (C.P.).

FIGURE 3. QI AND ß-RESIN AS A FUNCTION OF THERMAL TREATMENT FOR LOW QI FEEDSTOCKS

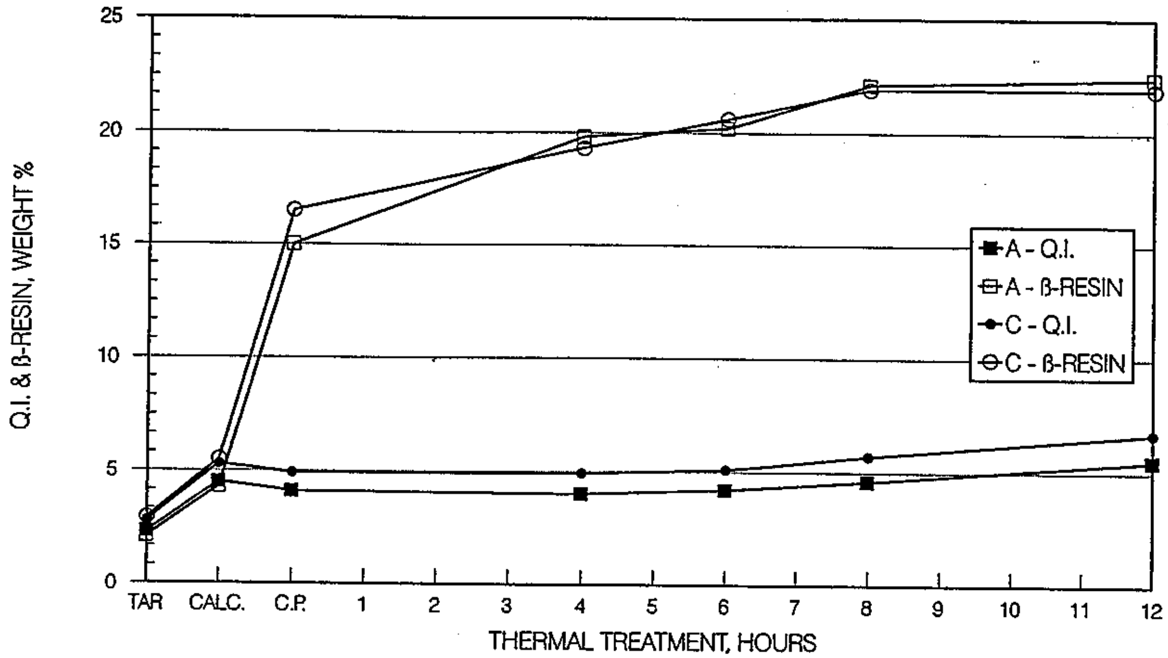
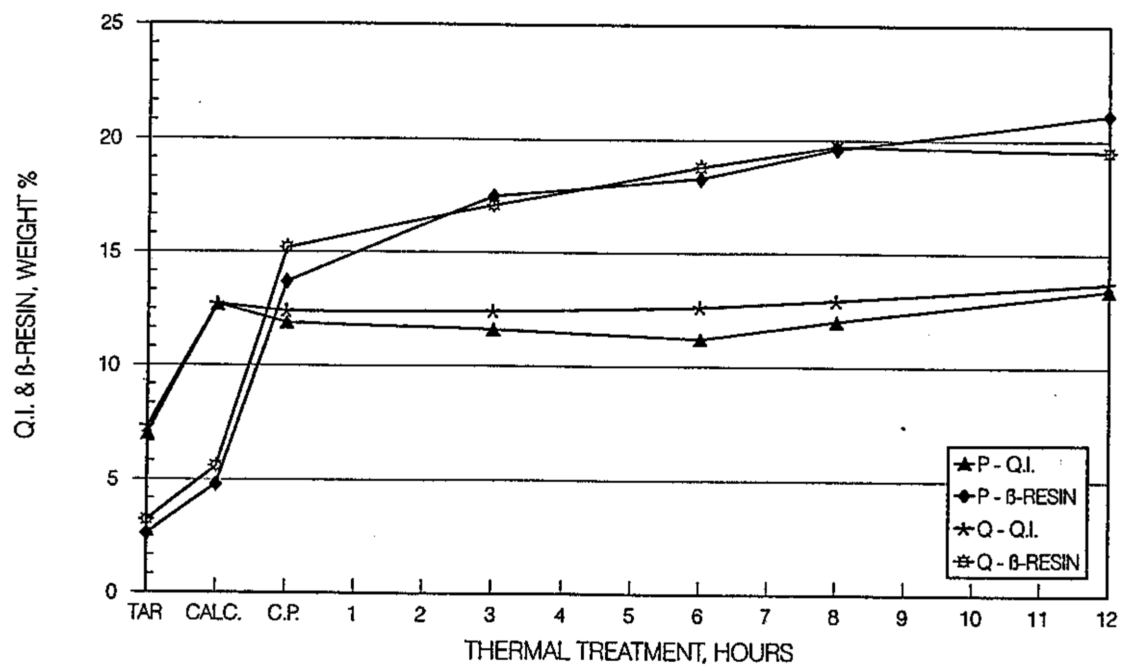


FIGURE 4. QI AND ß-RESIN AS A FUNCTION OF THERMAL TREATMENT FOR HIGH QI FEEDSTOCKS



Progressive thermal treatment as monitored by the gas flow from the reaction, resulted in consistent production of β-resin. The lower aromatic feedstocks resulted in higher β-resin pitches than the higher aromatic tars. Although the extended thermal treatment resulted in minor QI increases, the apparent mesophase formation was not readily visible by microscopy.

The coking values plotted in Figure 5 tend to increase marginally with thermal treatment. The more aromatic low QI feedstocks produce products with coking values similar to the high QI feedstocks.

As shown in Figure 6, viscosity tends to increase with prolonged thermal treatment. The increase is more pronounced for the high QI feedstocks.

FIGURE 5. COKING VALUE AS A FUNCTION OF THERMAL TREATMENT

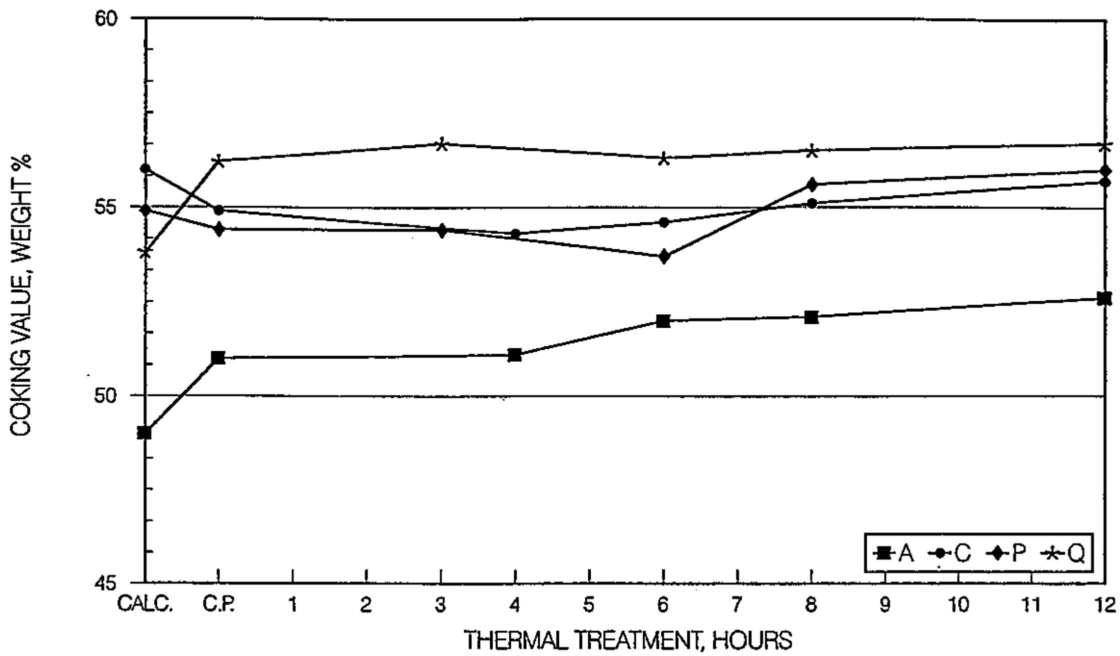
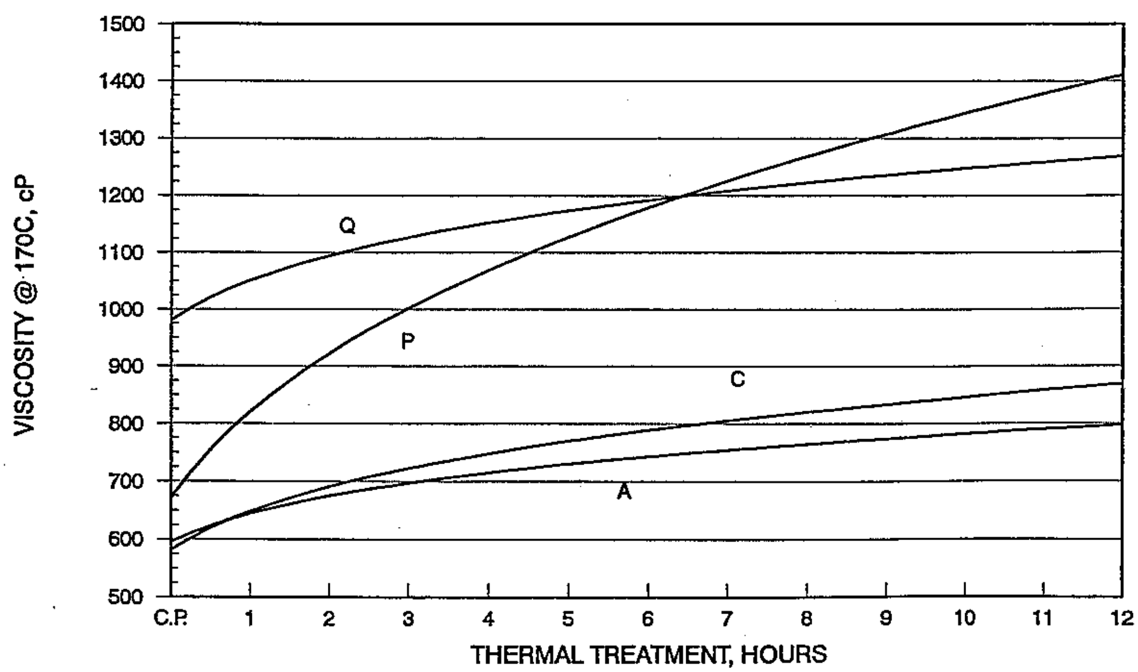


FIGURE 6. VISCOSITY AS A FUNCTION OF THERMAL TREATMENT



CONCLUSIONS FROM PHASE 1

1. Generally, the feedstock aromaticity is directly related to QI content.

2. The low aromatic feedstocks demonstrated a marked increase of pitch β-resin content with thermal treatment when compared to those produced from high aromatic feedstocks.

3. Laboratory determined coking value is not significantly affected by β-resin formed during thermal treatment.

4. Viscosity increases during thermal treatment are more pronounced for high QI than low QI feedstocks.

5. Experimental data to date indicate that thermal treatment longer than eight hours results in a decreased rate of β-resin formation with a corresponding increase in QI content.

FUTURE WORK

1. Conduct confirmation studies relating the effects of aromaticity, β-resin, and QI on coking value and viscosity.

2. Perform carbon anode evaluations as outlined in Phase 2 of Experimental Procedure (see above section).

Invitation

In order to consider all perspectives in this ongoing study, we welcome comments and suggestions.

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