

## Influence of oxidative and non-oxidative conditions on petroleum pitch properties

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A series of pitches were prepared by thermal treatment of petroleum feedstock under oxidative and non-oxidative conditions at 350-450°C, to study transformation behavior of feed components. Influence of type of oxidizing gas and oxidizing agent on softening point (SP), coking value (CV), quinoline insolubles (QI) and toluene insolubles (TI) was studied. Rate of increase of SP of pitch has been found more in oxidative conditions than in non-oxidative conditions. Oxidative conditions may also lead to reduction in stabilization period for making carbon fibers and activated carbon spheres. Formation of TI/QI is more under air/oxygen purging as compared to nitrogen purging.

**Keywords:** IR, Non-oxidation, Oxidation, Petroleum pitch

### Introduction

Pitch<sup>1</sup> is one of the cheapest starting materials as compared to its counterpart polymers [polyvinyl chloride (PVC), polyacrylonitrile (PAN) etc.] and has an enormous potential for conversion into advanced carbon materials. Pitch is thermo-plastic<sup>2</sup> and is a complex mixture of polynuclear aromatic hydrocarbons. Isotropic pitch has low softening point (SP), coking value (CV), quinoline insolubles (QI) and toluene insolubles (TI). However, high SP pitches<sup>3</sup> are required in preparation of activated carbon spheres (ACS) and carbon fibers. Generally, SP of pitch is increased by blowing air, NO<sub>2</sub> or halogen gases in isotropic pitches<sup>4-7</sup>. A lot of work has been done on air blowing of coal-based pitches<sup>8-10</sup>, however, a very limited work has been done on petroleum pitches.

In this study, petroleum pitches were prepared by thermal treatment of aromatic rich feedstock under purging of various gases (N<sub>2</sub>, O<sub>2</sub>, air) or by adding liquid oxidizing agent in the feedstock directly, instead of purging gas/adding oxidant in the isotropic pitch, and differences were examined in properties of final pitches prepared in oxidative and non-oxidative conditions. It was also studied as to how the binding of oxygen with aromatic molecules increases SP and improves other properties of pitches.

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### Experimental Details

A petrochemical stream, naphtha cracker bottom was used as a feedstock for pitch making. This feedstock was subjected to atmospheric distillation for removing highly volatile, low molecular weight, light aromatic hydrocarbons that do not contribute much towards pitch yield. The pitches were prepared by thermal treatment of feedstock in a glass reactor at a fixed temperature for a fixed/varied residence period under continuous purging of gases like N<sub>2</sub>, O<sub>2</sub> and air and, in presence of liquid oxidant (a mixture of acetic acid and nitric acid). The resultant pitches were characterized for CV, SP, TI and QI.

#### Softening Point (SP)

SP of pitches was determined using a Mettler Toledo FP 90 as per ASTM D-3104-97 test. Molten pitch sample (0.5 mg) was poured in small cup (with a pierced bottom), placed in Mettler furnace, and programmed for a given temperature range. Furnace temperature was increased at a rate of 2°C/min until a drop of pitch passed out through the hole. Sensor senses pitch drop and gives exact value of pitch SP.

#### Coking Value (CV)

CV of pitch was determined by using Micro Carbon Residue (MCR) tester of Tanaka Scientific Ltd. A sample (150 mg) was placed in a glass vial and then carbonized

Table 1—Physico-chemical properties of petroleum pitches

Code	Oxidant	Time, h	SP <sup>a</sup>	CV <sup>b</sup>	TI <sup>c</sup>	QI <sup>d</sup>	$\beta$ -Resin <sup>e</sup>
PP – 1	N <sub>2</sub> purging	5	78	42.3	18	3.5	14.5
PP – 2	Air purging	5	138	63.9	35.2	9.3	25.9
PP – 3	O <sub>2</sub> purging	5	195	82.5	48	11.1	36.9
PP – 4	CH <sub>3</sub> COOH + HNO <sub>3</sub>	5	200	81.7	49.8	6.4	43.4
PP – 5	N <sub>2</sub> purging	14	123	57.2	11	5.3	5.7
PP – 6	N <sub>2</sub> purging	17	202	80	18	6.9	11.1
PP – 7	O <sub>2</sub> purging	8.5	ND	ND	ND	ND	ND

<sup>a</sup>Softening point °C (Mettler Toledo, ASTM D- 3104), <sup>b</sup>Coking value wt% (Micro Carbon Residue ASTM 4530-85) <sup>c</sup>Toluene insolubles wt % (ASTM – D4312), <sup>d</sup>Quinoline insolubles wt % (ASTM – D-2318), <sup>e</sup> $\beta$ -Resin=TI – QI, ND-Not determined

in MCR tester, under pre-programmed conditions according to ASTM D-4530-85 test.

#### Toluene and quinoline Insolubles (TI & QI)

TI and QI in pitches were determined by modified ASTM D-4312-95 and ASTM D-2318-98 method respectively. For this, 1 part of pitch was mixed with 25 parts of solvent (toluene or quinoline) and heated to boiling point of solvent and maintained this temperature for 1 h. The resulting solution was filtered in G-4 crucible under reduced pressure. The insoluble material, deposited as black layer in G-4 crucible, was washed several times with same solvent as used in extraction. Finally, insoluble materials were washed with acetone and dried at 110°C in vacuum oven and finally weighed for determining TI and QI.

#### NMR and IR Spectroscopy

Spectrum has been recorded on a Bruker DRX 300 NMR spectrometers operating at 300.13 MHz. Chemical shifts have been measured using tetramethylsilane (TMS) as an internal reference. <sup>1</sup>H NMR spectrum has been recorded at 300°K using 10% (w/w) sample solution in CDCl<sub>3</sub> (99.8 atom % from Sigma Aldrich). A total of 16 scans have been acquired for each sample using 6.8  $\mu$ s pulse with a 12s delay time between scan and a sweep width of 15 kHz.

FTIR spectra were recorded on a Perkin–Elmer Spectrometer using dried KBr pellets. Spectra were recorded between 4000-600 cm<sup>-1</sup>.

#### Results and Discussion

Physico-chemical properties of feedstock are as follows: Density ( $d_4^{15}$ ), 1.0612 g/ml; API, 1.82; kinematic viscosity, 2.05 cSt (at 100°C), 3.40 cSt (at 70°C), 7.33 cSt (at 40°C); flash point, <100°C; pour point, (-27°C); average molecular weight, 215 dalton; micro carbon residue, 12.68 wt%; ash content, 0.002 wt%; carbon, 89.0% and hydrogen, 6.0%. High density and high MCR show that feed is rich in aromatics, which is also supported by its high Bureau of Mines Correlation Index (BMCI) value (133). However, feed has low molecular weight (215) and boiling point.

<sup>1</sup>H NMR data of pitch feedstock are as follows: H<sub>ar</sub>, 65.1%; H<sub>ar (mono)}</sub>, 12.0; H<sub>ar (di)}</sub>, 49.6; H<sub>ar (poly)}</sub>, 3.5; H <sub>$\alpha'$</sub> , 24.2; H <sub>$\beta$</sub> , 7.7; H <sub>$\gamma$</sub> , 0.5; H <sub>$\delta$</sub> , 2.5; Ar-CH<sub>2</sub>-Ar, 2.0;  $\alpha$ -Ph, 22.1;  $\beta$ -N, 3.5;  $\beta$ -CH<sub>2</sub>, 4.2; and  $\gamma$ -CH<sub>3</sub>, 0.5%. The data supports physico-chemical analysis of the feed. Value of H<sub>ar</sub> (65.1%) for feedstock shows that it is rich in aromatics. Further distribution of aromatic protons indicates that feed is rich in di-aromatics type compounds (naphthalene and its derivatives). Feedstock has sufficient amount of H <sub>$\alpha$</sub> , (24.2%) and H <sub>$\beta$</sub> , (7.7%), which are desirable for

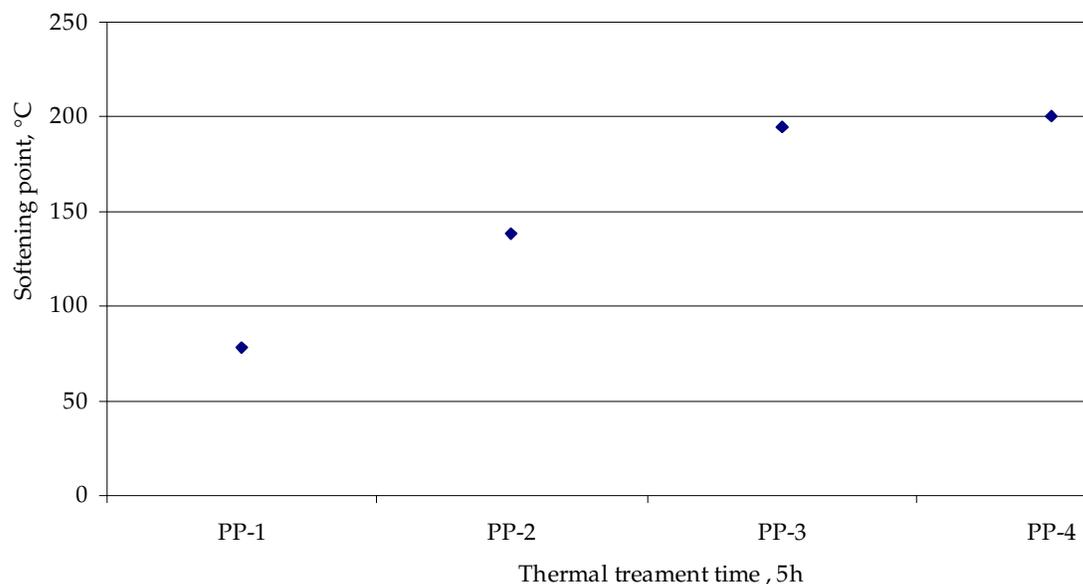


Fig. 1—Variation of softening point at different conditions

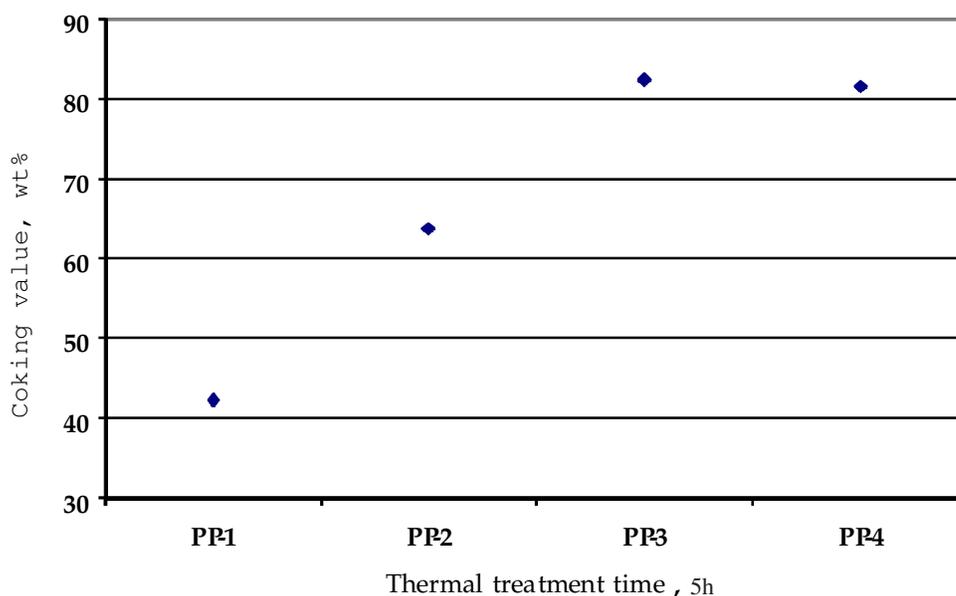


Fig. 2—Variation of coking value at different conditions

thermal cracking and facilitate reaction with oxygen to form cross linkages required to raise SP of pitch.

All pitches have been prepared by a two-stage process, which includes pre-fractionation of feedstock followed by thermal treatment. Pre-fractionation is carried out to remove low boiling aromatic compounds, which have

boiling points much below the thermal treatment temperature and do not participate in pitch formation. Thermal treatment was given to pre-fractionated feedstock under continuous purging of non-oxidizing ( $N_2$ ) and oxidizing (air,  $O_2$ ) gases to make pitches PP-1, PP-2 and PP-3. Pitch PP-4 was prepared by adding liquid oxidizing agent ( $CH_3COOH + HNO_3$ ).

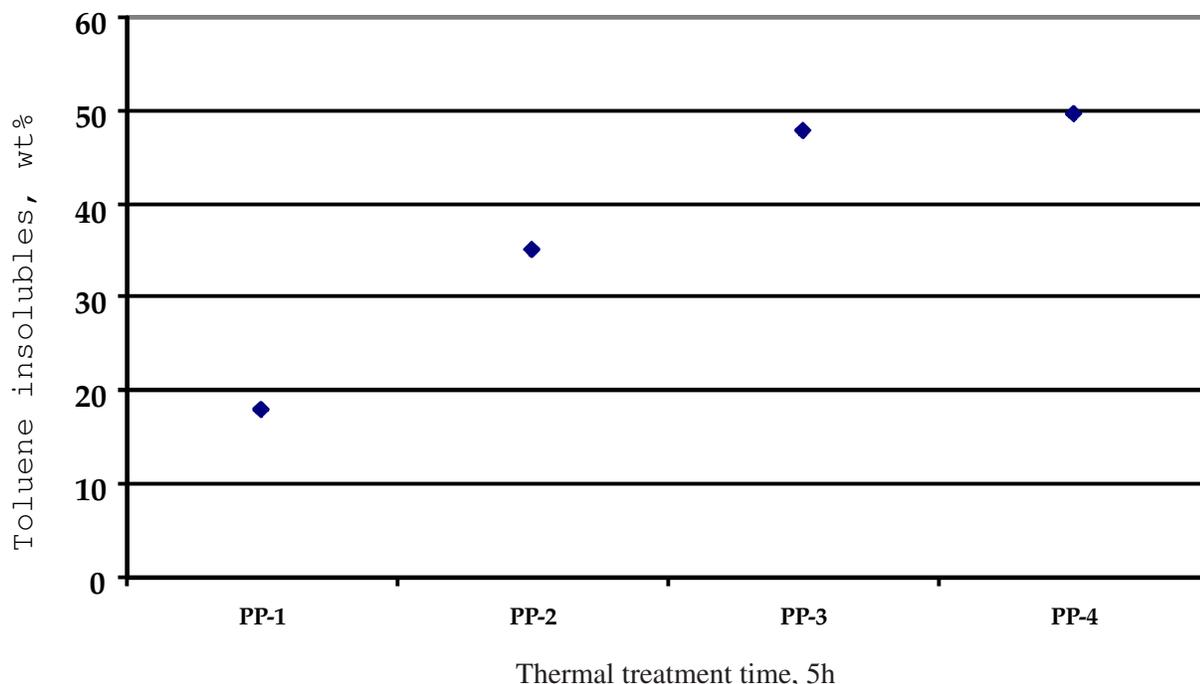


Fig. 3—Variation of toluene insolubles at different conditions

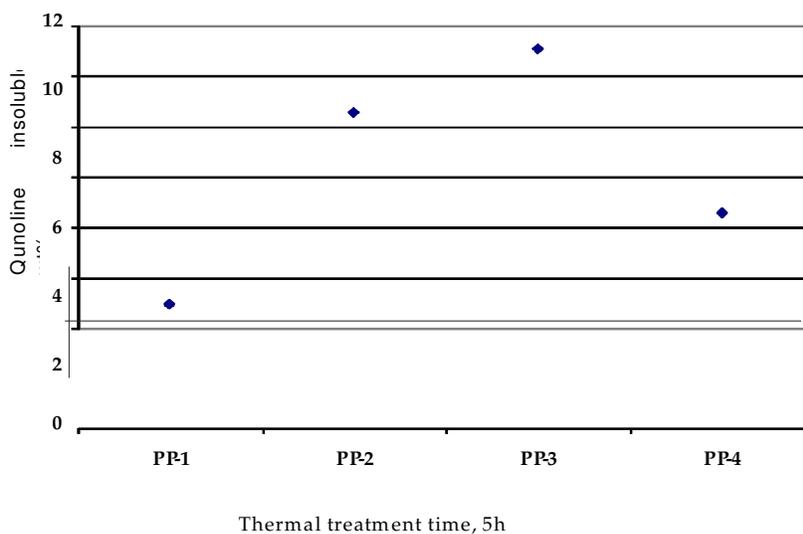


Fig. 4—Variation of quinoline insolubles at different conditions

All pitches (PP-1, PP-2, PP-3 and PP-4) were prepared (Table 1) for same thermal treatment time (5 h). PP-1 prepared under  $N_2$  purging (Fig. 1) has lowest SP (70°C), while PP-2 prepared by air purging at same thermal treatment temperature and time has higher SP (138°C), indicating that air purging promotes dehydrogenative-polymerization reactions, which causes increase in SP<sup>10</sup>. Purging of dried  $O_2$  during thermal treatment produces pitch PP-3, which has high SP (195°C). This is because

$O_2$  purging promotes dehydrogenative-polymerization, and also develops cross linkages and produces complex aromatic molecules, which are usually insoluble in common organic solvents like toluene and quinoline. The result is progressive increase in CV (Fig. 2), TI (Fig. 3) and QI (Fig. 4) from PP-1 to PP-2 to PP-3.

Low QI in PP-4 (Fig. 4) as compared to air-purged pitch PP-3, may be good for specific applications such as for making carbon fibers etc. Main drawback of liquid

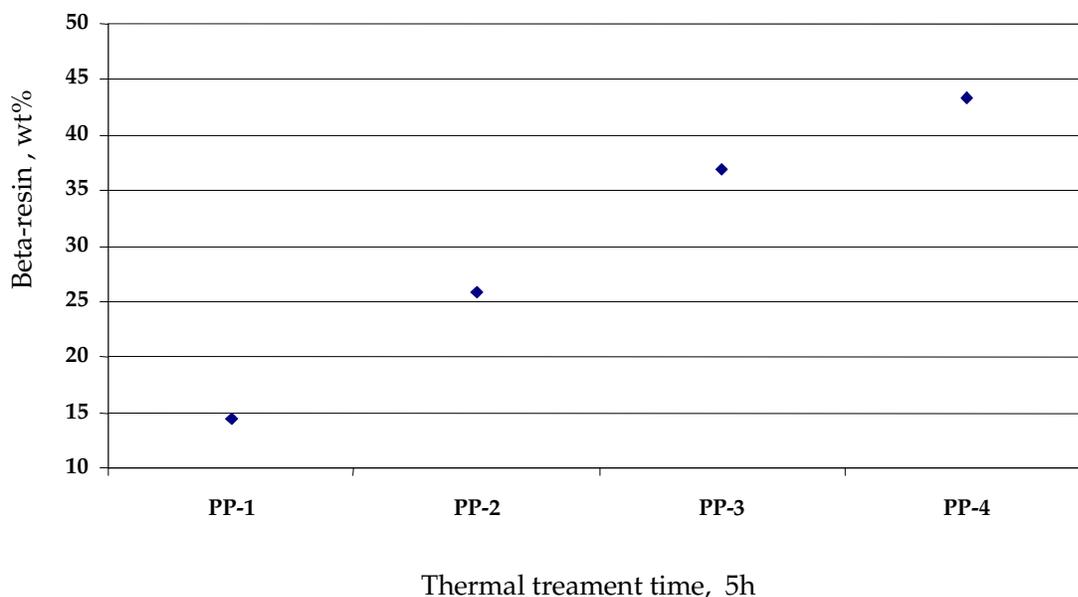


Fig. 5—Variation of beta-resin at different conditions

oxidant treated pitch is that some traces of acid may remain in the pitch and unless these traces are removed prior to processing into carbon products, it will affect/deteriorate final product quality. PP-5 and PP-6 were prepared by extending heat treatment time for 14 h and 17 h respectively, which provides opportunity for polymerization and condensation of aromatics to a greater extent leading to increase in SP, CV, TI and QI, compared to PP-1 prepared in a shorter thermal treatment time of 5 h. In terms of properties, PP-6 is close to PP-3 and PP-4, except that it has low TI (18 wt%), while in PP-3 and PP-4 this value is high (48-49.8wt%). Pitches prepared by  $N_2$  purging take too much time for stabilizing during preparation of ACSs.

PP-7 was prepared by purging of  $O_2$  (98% purity) and giving heat treat to feedstock for 8.5 h to give an infusible, high molecular weight, thermosetting polymeric mass. Due to thermosetting nature of this pitch, no physico-chemical characterization could be done on this infusible sample. Air purging in feed has better control on final pitch properties because air promotes dehydrogenative-polymerization only. On the other hand,  $O_2$  purging not only promotes rapid dehydrogenative-polymerization but also leads to development of cross linkages between aromatics, resulting in rapid formation of infusible coke.

Examination of IR spectra of PP-1, PP-2, PP-3 and PP-4 pitches reveals that spectra for all 4 samples has a band at  $\sim 1599\text{ cm}^{-1}$ , which may be assigned to aromatic

rings. Further PP-1 shows three additional bands at 840, 813 and  $699\text{ cm}^{-1}$ , which can be attributed to C-H out-of-plane vibrations of p-, m- and o- substituted benzene rings. PP-2, PP-3, and PP-4 have two of these bands at  $\sim 813\text{ cm}^{-1}$  and  $\sim 699\text{ cm}^{-1}$ , but these pitches do not exhibit band at  $840\text{ cm}^{-1}$ . These findings indicate that p-substituted aromatics have undergone polymerization in case of PP-2, PP-3, and PP-4. The o- and m-substituted aromatics are less likely to condense due to steric hindrance. Band at  $\sim 1700\text{ cm}^{-1}$ , which appears in spectra for PP-2 and PP-3, may be due to the formation of carbonyl group<sup>11</sup> during air and  $O_2$  purging.

### Conclusions

Thermal soaking increases, physico-chemical properties like softening point, quinoline insoluble and coking value of pitches. For same residence period (5 h), increase in softening point and soaking value is more in case of  $O_2$  purging as compared to  $N_2$  purging. Preparation of pitch under air purging is most effective way to increase softening point and coking value. This type of pitch is suitable for making carbon fibers and activated carbon spheres. Since,  $O_2$  contents in air are less as compared to pure  $O_2$ , it promotes dehydrogenation and polymerization only without developing cross linkages between aromatics. As a result, final properties are easily controllable in case of pitches prepared under air purging. If  $O_2$  is purged for a long period, feedstock is rapidly converted into solid infusible mass due to fast

polymerization and development of cross linkages between aromatic structures. Preparation of pitches in presence of liquid oxidizing agent is most effective way to increase softening point and coking value. The main drawback of this method is likelihood of some residual traces of catalyst remaining with the pitch itself, which may affect quality of the end product.

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