# STUDIES ON MAKING PITCHES FROM CLARIFIED OIL

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## 1. INTRODUCTION

Impregnating pitch is a vital constituent for making ultra high power (UHP) graphite electrodes. Originally, coal tar was the only source of impregnating pitch but in recent years coal tar supply became inadequate due to closure of several coke ovens in many parts of the world due to strict environmental regulations imposed by environmental protection agencies. Thus the search of alternate feedstocks for conversion into pitch become mandatory(1). Petroleum derived stream like clarified oils (CLOs) has good potential for making impregnating pitches. Further, petroleum pitches being lower in quinoline insolubles and softening point show excellent impregnating characteristics.

In the present study an energy efficient process for making impregnating pitch has been developed. This process involves solvent extraction of clarified oil(s) followed by thermal soaking in presence of free radical inititator.

## 2. EXPERIMENTAL

Two clarified oils F1 and F2, procured from different refineries have been modified through solvent extraction to meet the BMCI value requirement for making pitch.

Impregnating pitches were prepared by thermal soaking (at 430°C) of aromatic extract in presence of small dose of free radical initiator (1wt%) at atmospheric pressure, under continuous purging of nitrogen gas. Thermal soaking was continued for a required period to get the pitch of desired softening point and other impregnating properties. Pitches P1 and P2 were prepared from modified feed MF1 and MF2, prepared from parent feed F1 and F2 respectively.

Pitches were characterized by a variety of tests specific to impregnating properties like softening point (Ring & Ball ASTM D-3626), coking value (IP-13), quinoline insolubles (ASTM D2318) and toluene insolubles (ASTM D-473).

Structural characterization of feedstocks and pitches was carried out by $^1H$ and $^{13}C$ NMR spectroscopy.

## 3. RESULTS AND DISCUSSION

Physico-chemical properties and structural parameters of clarified oils and their modified forms are summarized in Table-1. A careful examination of data shows that both the clarified oils F1 and F2 has large proportion of paraffinic constituents. Higher values of pour point (+48 for both) also confirm the higher concentration of paraffinic type hydrocarbons which may be present either in the form of saturated hydrocarbons or as long alkyl side chains on aromatic molecules. As the information(2) available in literature, feedstocks having BMCI more than 100 are suitable for direct conversion into pitch. Since both the feeds, F1(36) and F2(56)have BMCI value much lower than 100, their direct use for conversion into pitch is not feasible. Improvement in aromaticity was achieved by removing unwanted saturate constituents by solvent extraction.

$^1H$ NMR data indicate that F1 and F2 are paraffinic in nature as indicated by high value of β-$CH_2$, which was also supported by $C_{sat}$, and $C_{ar\text{-}alk}$ values from $^{13}C$ NMR. These observation are in good agreement with the inference drawn from physico-chemical characteristics on aromaticity.

Aromatic rich portion from NMP extraction of F1 and F2 (MF1 and MF2 respectively) were used for pitch making. Aromatic extracts MF1 and MF2 have remarkable improvement in properties, in general, and BMCI in particular. There were decrease in pour point and increase in density and Kin. Viscosity. On solvent extraction the BMCI of feed F1 and F2 were increased to 116 and 100 from 36 and 56 respectively. In terms of aromaticity feed MF1 appears to be more suitable for pitch making as compared to MF2. This is also supported by $H_{ar(poly)}$

data. [1]H and [13]C NMR data of aromatic extract MF1 and MF2 are in good aggrement with changes occurred in their physico-chemical properties. Increase in concentration of $H_{ar}$ and $C_{ar}$ and decrease in $\beta CH_2$ and $C_{sat}$ in the aromatic extract is the indication of increased concentration of aromatics.

Physico-chemical characteristics of pitches alongwith their $^1$H NMR data are given in Table-2. Physico-chemical properties show that pitch P1 is very well matched with reference A-240 petroleum pitch in all respects, except average molecular weight (565) which is a higher than A-240 (445). Pitch P2 is also matching with A-240 but has little lower coking value (49.00) due to higher amount of $\beta CH_2$ in this pitch. $^1$H NMR data indicates that although pitch P1 is very similar to A-240 in physico-chemical properties but it has minor structural differences with P1. Pitch P1 has lower concentration of polyaromatics and alkyl side chains present on aromatics are branched in nature as evidenced by $H_\gamma / H_\beta$ values. P1 also has higher concentration of naphthenic type structures ($\beta$N) Pitches P1 and P2 contain lower concentration of polyaromatics 6.72% and 4.25% respectively than A-240 (11.0%).

Pitches prepared by conventional thermal soaking process (based on only thermally induced polymerization) have all desired properties but conversion of feed into pitch requires large thermal soaking period (more than 60 hrs) which hampers the commercial feasibility of process. To overcome this problem an energy efficient process process(3) has been developed. In this process a free radical initiator was added during thermal soaking which helps in reducing thermal soaking period at a great extent. Free radical initiator helps in increasing the reactive free radicals concentration and fastens the polymerisation and condensation reactions. The improved process gives same pitch quality in half of the thermal soaking period (about 24 hrs).

## 4. CONCLUSIONS

From the above discussions it may be concluded that direct use of waxy clarified oil for making pitch is not feasible, but after modification of feedstock by solvent extraction it is possible to make impregnating pitch equivalant to A-240. Further use of free radical initiator shortens thermal soaking period nearly half, without affecting pitch properties.

## REFERENCES


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Table 1 : Properties and NMR Data of Feedstock

| Properties/Parameters | F1 | MF1 | F2 | MF2 |
|---|---|---|---|---|
| Density d4 (gm/ml) | 0.90 | 1.07 | 0.94 | 1.03 |
| Kin. Visc. (cSt) | 4.84 | 14.41 | 5.71 | 9.35 |
| Av. Mol. wt. (Dalton) | 324 | 293 | 345 | - |
| Pour point,(°C) | + 48 | + 36 | + 48 | + 42 |
| CCR (% wt) | 0.87 | 6.96 | 2.90 | 5.58 |
| **BMCI** | **36** | **116** | **56** | **100** |
| H/C Atomic Ratio | 1.67 | 1.21 | 1.32 | 0.93 |
| $H_{ar}$ | 10.15 | 25.91 | 7.44 | 20.43 |
| $H_{ar(Mono)}$ | 2.77 | 2.02 | 0.32 | 4.84 |
| $H_{ar(Di)}$ | 6.15 | 20.65 | 6.43 | 15.59 |
| $H_{ar(Poly)}$ | 1.23 | 3.24 | 0.64 | 0 |
| Ar-$CH_2$-Ar | 0.62 | 1.62 | 1.62 | 0.54 |
| $\alpha$-Ph | 3.07 | 25.91 | 14.89 | 24.73 |
| $\beta$-N | 0.92 | 4.05 | 6.80 | 3.76 |
| $\beta$-$CH_2$ | 61.85 | 28.34 | 50.81 | 35.49 |
| $\gamma$-$CH_3$ | 23.38 | 14.17 | 19.09 | 15.05 |
| $C_{sat}$ | 78.32 | 36.46 | 66.95 | 33.85 |
| $C_{ar-}$ | 21.68 | 63.54 | 33.05 | 66.15 |
| $C_{ar-alk}$ | 4.19 | 15.47 | 4.52 | 6.22 |

Table 2 : Properties and $^1$H NMR Data of Pitches

| Properties/Parameters | A-240 | P-1 | P-2 |
|---|---|---|---|
| Softening Point (°C) | 115 | 112 | 125 |
| Coking Value (% wt) | 51.38 | 51.30 | 49.00 |
| Quinoline Insolubles (% wt) | 0.07 | 0.02 | - |
| Toluene Insoluble (% wt) | 0.42 | 6.20 | - |
| Av. Mol. wt(Dalton) | 445 | 565 | - |
| H/C Atomic Ratio | 0.77 | 0.74 | 1.63 |
| $H_{ar}$ | 50.20 | 50.70 | 50.21 |
| $H_{ar(Mono)}$ | 2.80 | 7.28 | 5.96 |
| $H_{ar(Di)}$ | 36.40 | 36.70 | 40.00 |
| $H_{ar(Poly)}$ | 11.00 | 6.72 | 4.25 |
| Ar-$CH_2$-Ar | 4.10 | 3.36 | 0.85 |
| $\alpha$-Ph | 30.20 | 29.70 | 32.34 |
| $\beta$-N | 2.80 | 6.16 | 5.11 |
| $\beta$-$CH_2$ | 7.90 | 7.84 | 9.36 |
| $\gamma$-$CH_3$ | 1.80 | 3.64 | 2.98 |