THERMAL STUDIES OF PETROLEUM PITCHES

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Introduction

Thermoanalytical methods are one of the most promising tool for the characterization of pitches due to their close relationship with the common uses of the pitches. These methods are particularly useful for the characterization of pitches as they not only allow to differentiate between the pitches prepared from different feedstocks but also between the pitches from same feedstocks but with different processes [1,2]. Aromaticity value had been used for the structural information from these pitches for the prediction of ability of mesophase formation. In the present work, we studied the thermal behavior of pitches having comparable aromaticity value as obtained from solid state NMR parameters.

Experimental

Four pitches were prepared from petroleum feedstocks namely, clarified oil and pyrolysis tar. Two of the pitches were prepared from clarified oils obtained from different sources. These oils were pretreated differently prior to the heat treatment. Two of the pitches were prepared from pyrolysis tar; one being prepared from original tar after distillation while for other initiator was used. Petroleum pitch P-2 is used as a reference pitch for our studies. Solid state NMR was used for determining aromaticity value of these pitches by ^{13}C-SPE technique recorded on Bruker's 75.4 MHz DRX 300 instrument. The thermal behavior of pitches (TG and DTG) were done on Mettler Tolledo TA 8000. The pitches were studied in the temperature range of 50-850°C under a nitrogen atmosphere with a nitrogen flowrate of 100 ml/min.

Results and Discussions

The physical characteristics of petroleum pitches prepared alongwith their feedstocks and aromaticity value are given in the Table 1. The %wt loss of materials as a function of the temperature obtained from TG are plotted as a bar diagram in the Fig. 1 while the % wt loss of the sample in different temperature ranges were given in the Fig. 2.

As is evident from the aromaticity value (Table 1), pitches could not be differentiated, although they are prepared from different feedstocks and processes. These data suggests that pitches will show almost similar behavior during the mesophase formation. But, the thermal behavior of these pitches are different which may be utilized to differentiate between them.

The pitches prepared from clarified oils P-58 & P-23 differs in the amount of low boiling materials. P-58 being prepared from 350+ cut of clarified oil contains relativity lesser amount of low boiling materials as compared to P-23 pitch which is prepared from aromatic extract of clarified oil. The maximum wt loss for P-23 in temperature range 300-400°C while for P-58 it is in 350-400°C range. Similarly, the pitches prepared from modified pyrolysis tar as such and with free radical initiator i.e. P-37 and P-43 respectively also differs from each other in the amount of these low boiling materials.

Pitches prepared from clarified oil and pyrolysis tar could also be compared. P-37 is comparable to P-23 as far as the wt loss is concerned and is different from P-58. But these pitches (P-37 & P-23) could be differentiated by the wt loss in different temperature ranges, which clearly shows that the maximum wt loss for P-37 occurs at 350°C and for the P-23 it occurs at 320°C and 390°C.

The TG thermograms further gives the amount of low boiling materials which distills (< 400°C). This material may not play any part in the mesophase formation in these pitches. Hence, the pitch which contains less amount of these material could give the maximum quantity of mesophase. This inference is being verified by High temperature ^{1}H NMR study of these pitches.

Conclusion

The thermal behavior of pitch could be used alongwith aromaticity of pitches to predict the suitability of pitches for the production of high performance carbon materials.

References

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2. Weber JV, Swistek M, Darif M, Schneider M, Fixari B, Wolszczak J and Lauer JC. CR Acad. Sci. Paris Ser. II;1990;311;1001.

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Table I. Feedstock, physical characteristics and aromaticity of pitches.

Pitch	Feedstock	Softening point (°C)	C.C.R %wt	Aromaticity, %
P-2	GIL, Bangalore	112	54.71	86.6
P-23	Aromatic extract of Clarified oil (IOC)	108	53.3	88.99
P-37	250°+ cut Pyrolysis Tar	127	48.14	76.89
P-43	Pyrolysis tar + Initiator	120	45.3	79.71
P-58	350° + cut of clarified oil	140	66.6	87.47

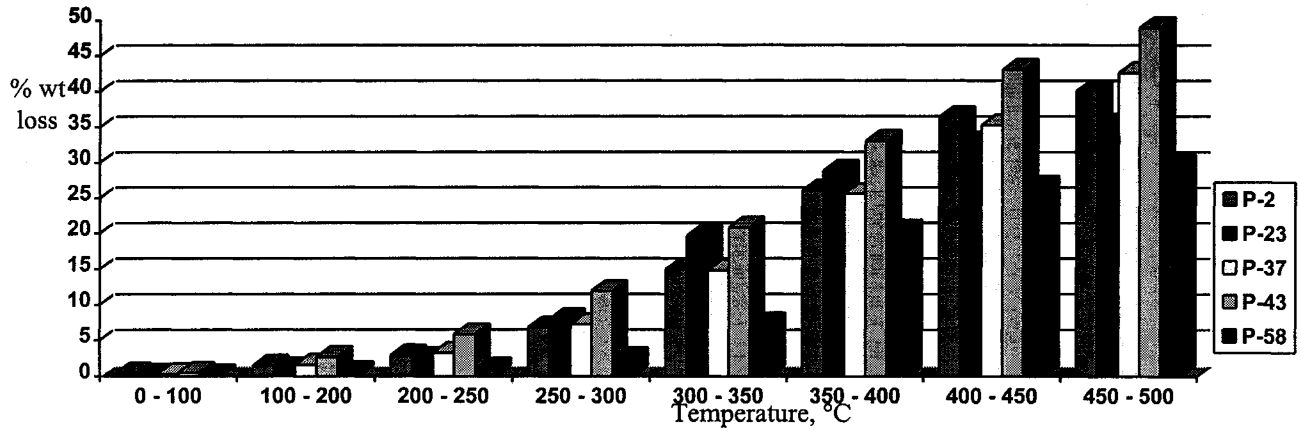

Figure 1. % wt loss of material as a function of temperature as obtained from TG thermograms.

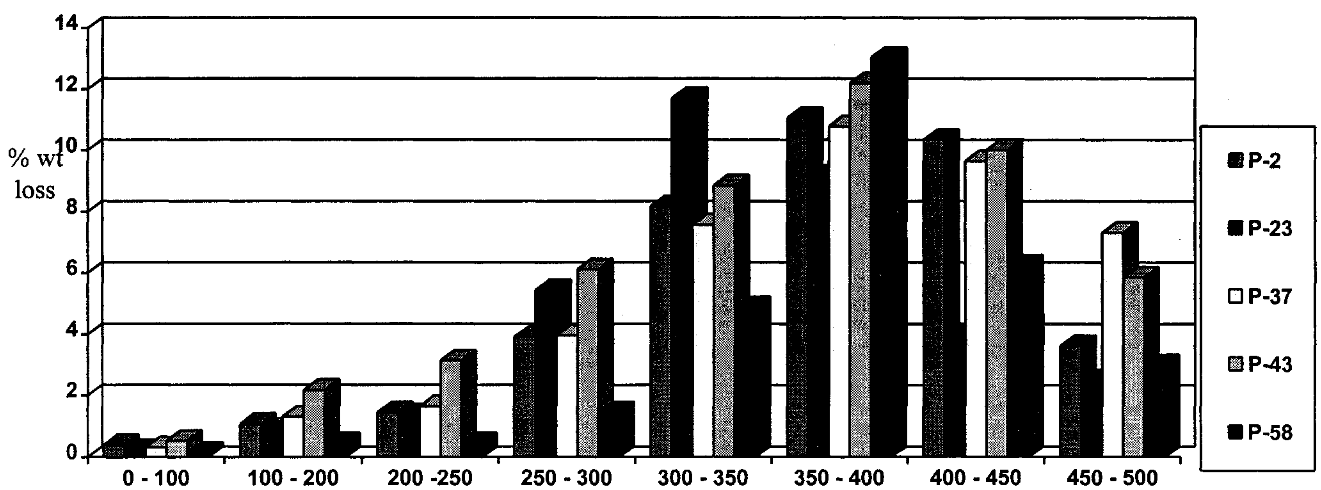

Figure 2. % wt loss of the material in the different temperature ranges.