Kinetic Studies on the Carbonization Reactivities of Coal Tar Pitches

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Carbonization reactivities of coal tar highly cromatic and its hydrogenated pitches were studied in terms of the rates of anisotropic appearance, QI formation and TS desappearance. Their reactivities were discussed in relation to their staring chemical structure.

Introduction

Hydrotreatment of coal tar pitch has been proved to improve significantly its carbonization properties as feedstocks for the needle cokes and carbon fibers. The hydrotreatment should significantly modyfy chemically its constituents, to results in the modified carbonization properties.

In the present study some kineti aspects in the carbonization of coal tar pitch and its hydrotread derivatives were studied by comparing the weight loss, QI and TI-QS contents during the carbonization to discuss the influences of hydrotreatment on thier carbonization reactivities.

Experimental

Pitches used in the present study are listed in Table 1. Coal tar pitch was treated by an antisolvent method to obtain QI free pitch (CTPAS). CTPAS was hydrogenated with a Ni-Mo catalyst, and then distillated to raise its softening point (HCTP1, HCTP2). HCTP2 was hydrogenated under more severe conditions than HCTP-1.

Table 1. Properties of Samples

	CTPAS	HCTP 1	SCTP 2
Hydrogenation conditions	—	mild	severe
Carbon, wt%	92.3	92.1	92.4
Hydrogen, wt%	5.1	6.1	7.1
Nitrogen, wt%	1.11	0.70	0.43
Sulfur, wt%	0.42	0.11	0.03
H/C, mol ratio	0.66	0.79	0.92
Toluene insoluble, wt%	9.1	3.7	1.5
Carbon residue, wt%	37.	26.	22.
Softening point, °C	37.	53.	52.

Carbonization of pitch (20g) was performed in a 100 ml Pyrex tube under nitrogen flow (5°C/min) at the heating rate of 150°C/hr. The carbonized pitch was rapidly cooled for the solubility measurement in toluene and quinoline, respectively.

Results

Figures. 1 and 2 show weight loss and QI contents during the carbonization of HCTP1 (mildly hydrogenated sample) and original CTP, respectively at some temperatures. Such kinetic parameters smoothly increased with the residense time. The rates of increase are very much dependent upon the pitches and temperature. HCTP1 showed a larger weight loss and slower QI formation than CTPAS, notwithstanding the higher softening point and larger average molecular meight. Much more $C_3 \sim C_4$ gaseous products were found from HCTP1 than CTPAS. The contents of QI are plotted against weight losses in Fig. 3. Regardless of the carbonization conditions a single monotonous curve is obtained with the respective pitch. The curves of two pitches are quite similar, although the levels of weight loss was significantly different.

Fig. 4 shows the contents of TI-QS fraction (based on feed) during the carbonization. Although HCTP1 and HCTP2 exhibited very similer profiles in spite of different severity in their hydrogenation, showing the maximum content at 170 min. CTPAS did a maximum at 0 min, indicating that the fraction was produced during the temperature rising.

Discussion

Kinetic influences of hydrotreatment on the carbonization reactivities of the coal tar are summarized as following

1) The rates of TI-QS and QI formations are suppressed
2) Weight loss during the carbonization is much enhanced

The carbonization reaction can be described by the

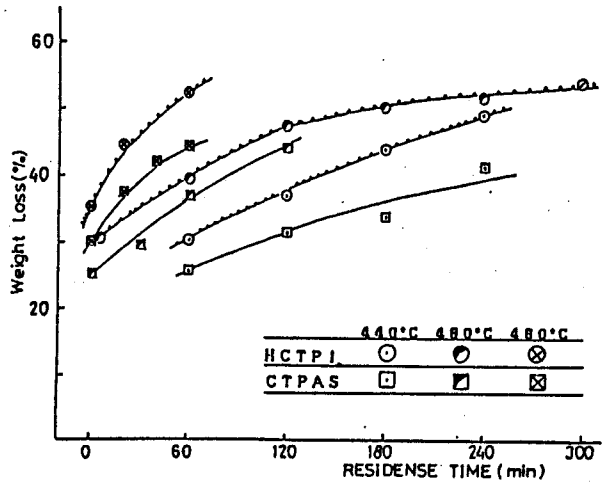

Fig. 1. Residense time versus weight loss

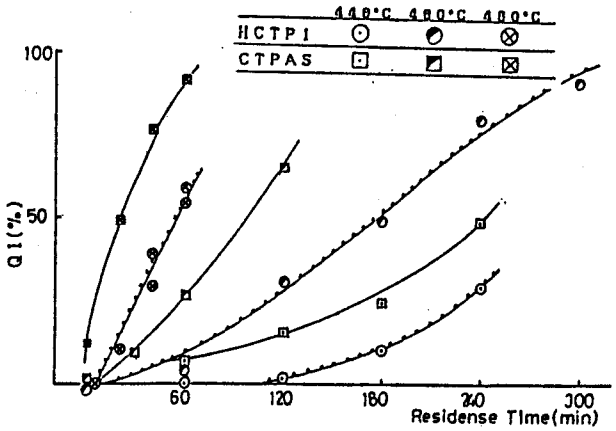

Fig. 2. Residense time versus QI (%)

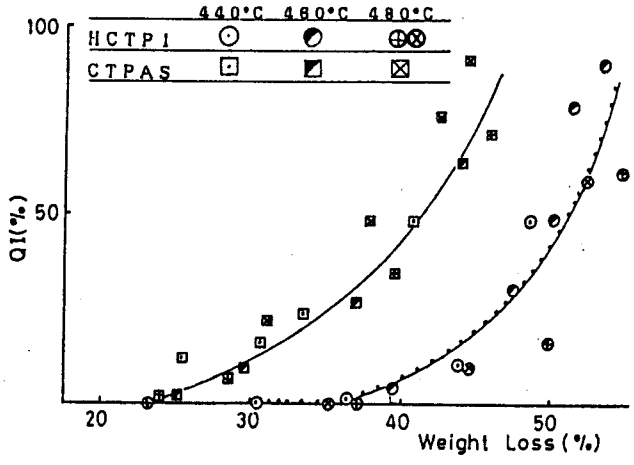

Fig. 3. Weight loss versus QI (%)

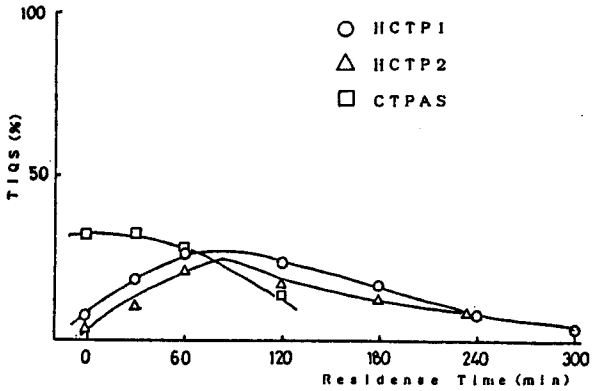

Fig. 4. Residense versus TIQS (%)

follwing scheme of two consecutive reactions.

$$TS \longrightarrow TIQS \longrightarrow QI$$

The hydrogenation produces the hydroaromatics, of which hydrogens are transferreed during the carbonization to suppress the chain reactions of condensation, the retarting the formation of TI-QS and QI.

The major difference in weight loss from CTPAS and HCTPI is observed before the formation of QI as shown in Fig. 3, indicating that the conversion of TS into TI-QS in the latter pitch causes more weitht loss. Hydroaromatics of TS decompose more extensively to be converted into TI-QS. Similar reactivities of HCTP 1 and 2 suggest that hydrogenation extent over a level causes small differences in the reactivity although the structure was considerably changed.