

# Reflux Modification of Ethylene Tar (ETP) into Mesophase Pitch Precursor With Less Amounts of Aluminum Chloride

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The modification of ETP under reflux conditions was effective to reduce the amount of  $\text{AlCl}_3$ . The volatile fraction which can stay or recycle in the modification system by the reflux can reduce the viscosity of the system and transfer its hydrogens to the condensed heavy molecules, accelerating the catalytic turnover of  $\text{AlCl}_3$  to assure the homogeneous modification of ETP molecules in the preparation of the mesophase pitch precursor.

## INTRODUCTION

Ethylene tar pitch (ETP), which is a major by-product of naphtha cracking process, is highly aromatic to be one of important feedstocks for carbon materials, however, as-received form is difficult to be converted into spinnable mesophase pitch. The present authors have reported in previous papers [1,2] very effective modification of ETP with  $\text{AlCl}_3$  into needle coke, coking additive and mesophase pitch feedstock, where fairly large amount of  $\text{AlCl}_3$  (10 wt%) was required to achieve homogeneous modification of constitute molecules of ETP. Smaller amount of  $\text{AlCl}_3$  (5 wt%) tended to produce so much highly condensed substance insoluble even in quinoline after the mesophase pitch preparation.

In the present study, the modification of ETP under the reflux conditions was investigated to reduce the amount of  $\text{AlCl}_3$  required.

## EXPERIMENTAL

ETP was supplied by Koa Oil Co., LTD.  $\text{AlCl}_3$  was reagent grade (Nakarai Chemicals Co., LTD.) and used without further purification. Some analytical data of ETP were summarized in Table 1.

The modification was carried out in a Pyrex glass tube (50 mm in diameter) which was equipped with a condensor and a stirrer. ETP (50 g) and  $\text{AlCl}_3$  (2.5 g) were put in the reactor and heated to 250 - 280 °C at the heating rate of 5°C/min without reflux to remove the lightest fraction (the first stage). After stirring for 1 h at the prescribed temperature, reflux was allowed to take place while the temperature was raised to the prescribed temperature (the second stage) at the heating rates of 5 - 10 °C/min. These modification conditions are summarized in Table 2 along with the residual pitch yield.

Thus modified pitches were washed first with diluted HCl and then with water to remove  $\text{AlCl}_3$ . After drying under vacuum, the residual pitch yield was measured. The mesophase pitch was prepared at 340 or 380 °C essentially according to

the UCC patent [3].

## RESULTS AND DISCUSSION

Fig. 1 illustrates the yield, solubility and anisotropic content of the mesophase pitches prepared from the modified ETPs. According to the severity of the modification conditions, the anisotropic content in the mesophase pitch prepared at 380 °C increased up to 100 vol%.

MR1-ETP, modified at the lowest temperature, provided a fairly high yield of the mesophase pitch by the preparation at 380 °C for 15 h, however, the anisotropic content was as low as 22 % which corresponded to the content of pyridine-insoluble (PI).

MR2-ETP, modified at higher temperatures, gave much more anisotropic content of 71 vol% under the same conditions. The content of PI was only a half of the anisotropic content. The modification at a higher temperature in the second stage appears very effective to endow potentiality for anisotropic development.

MR3-ETP, the best modified pitch, provided the mesophase pitch of 100 vol% anisotropic content, whose solubilities in THF and quinoline were as high as 50 and 65 wt%, respectively. Such solubilities were much better than those of the mesophase pitch prepared from M3-ETP (modified with 10 wt% of  $\text{AlCl}_3$  without reflux) in a previous paper [2].

The lower temperature (340 °C) for the preparation of mesophase pitch maintained the high solubilities in THF and quinoline as high as 65 and 75 wt%, respectively, although the anisotropic content was slightly less than 100 vol%. Thus, the modification under reflux could provide a better precursor from ETP for the mesophase pitch with less amount of  $\text{AlCl}_3$ .

The yield of modified pitch depended very much on the severity of the modification conditions as shown in Table 2, however, that of the mesophase pitch was around 38 wt% regardless of the modification conditions examined

Table 1 Some properties of ETP and modified ETP

	H/C	fa <sup>1)</sup>	Rnus/Rtus <sup>2)</sup>	BS <sup>3)</sup>	THFS <sup>4)</sup>	PS <sup>5)</sup>	QS <sup>6)</sup>
				(wt%)	(wt%)	(wt%)	(wt%)
ETP	0.94	0.76	0.00	100	-	-	-
MR1-ETP	0.90	0.77	0.03	87	92	100	-
MR2-ETP	0.92	0.75	0.09	85	95	100	-
MR3-ETP	0.86	0.75	0.23	66	69	89	100
M3-ETP <sup>7)</sup>	0.86	0.74	0.24	82	95	100	100

1) aromaticity

2) Rnus: number of naphthenic ring in unit structure  
Rtus: number of ring in unit structure

3) benzene soluble, 4) THF soluble,

5) pyridine soluble, 6) quinoline soluble,

7) prepared in a previous paper [2] without the second modification

Table 2 Modification conditions of ETP

	amount of AlCl <sub>3</sub> (wt%)	1st modification (without reflux) (°C-h)	2nd modification (with reflux) (°C-h)	residual pitch yield (wt%)
MR1-ETP	5	250-1	320-4	90
MR2-ETP	5	260-1	340-4	83
MR3-ETP	5	280-1	340-14	64
M3-ETP <sup>1)</sup>	10	250-7	-	62

1) prepared in a previous paper [2] without the second modification

in the present study.

The ultimate analyses and structural analyses based on the Brown and Ladner method of modified pitches are summarized in Table 1. MR1- and MR2-ETP lost a little hydrogens during the modification, being slightly modified as shown by Rnus/Rtus ratio, although 10 and 17 wt% of the lighter fraction was evaporated during the modification.

In contrast, MR3-ETP appeared to be rather extensively modified as suggested by the significant formation of solvent insoluble substance, although the whole pitch stayed soluble in quinoline. In spite of considerable decrease of H/C ratio, the amount of THF soluble and the value of Rnus/Rtus increased as shown in Table 1. It is noted that the fa (aromaticity) of modified pitch stayed around 0.76 regardless of the modification conditions.

AlCl<sub>3</sub> is an excellent catalyst to prepare the precursor for the mesophase pitch. However, AlCl<sub>3</sub>, a strong Lewis acid is strongly bonded to the condensed aromatic ring, being difficult to shuttle from one aromatic molecule to other (turn over is about 2), so that its fairly large amount is required to condense the whole aromatic molecules in the pitch evenly to the suitable size of polymerization as shown in Fig. 2. A less amount of the catalyst tends to produce so much the pyridine insoluble fraction without reflux under the severe conditions required for the sufficient modification as shown in Fig. 2c, since the catalyst tends to stay at a molecule to continue the condensation leading to the excess size. Rapid volatilization of lighter fraction at the initial stage of modification, tends to increase the viscosity of the system. In contrast, the reflux conditions keep in the modification system the lighter substances which can maintain the viscosity of the system low and transfer their hydrogens to the reacting site of condensed molecule to decrease its basicity. Such effects assist the shuttling of the catalyst, ensuring the smaller amount of the catalyst to

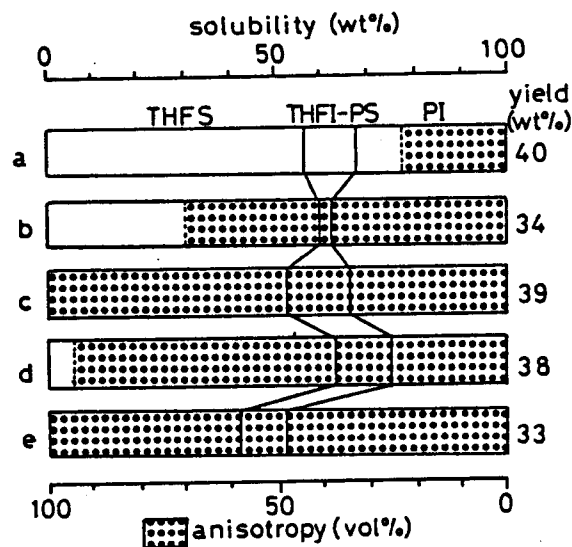


Fig. 1 Anisotropic content and solubilities of mesophase pitch. (modified pitch/mesophase preparation conditions (°C-h))

- (a) MR1-ETP/380-15, (b) MR2-ETP/380-15,  
(c) MR3-ETP/380-15, (d) MR3-ETP/340-15,  
(e) M3-ETP/380-15

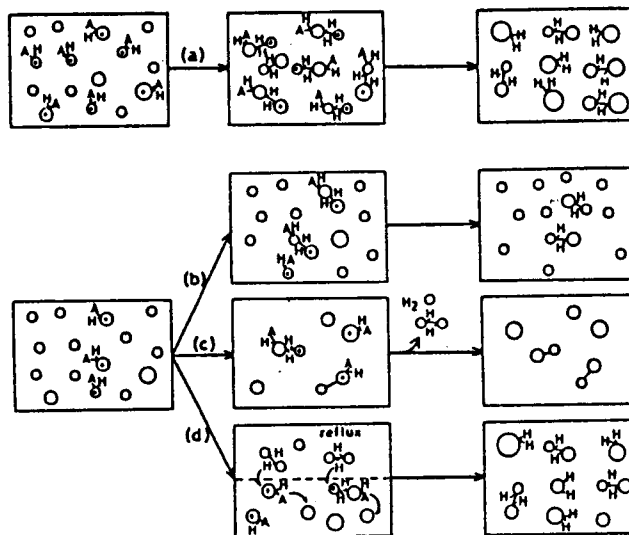


Fig. 2 The modification schemes of ETP

A: AlCl<sub>3</sub>, H: naphthenic hydrogen

- (a) The large amount of AlCl<sub>3</sub>,  
(b) The small amount of AlCl<sub>3</sub> without reflux,  
(the same conditions to (a))  
(c) The small amount of AlCl<sub>3</sub> without reflux,  
(higher temperature to promote modification)  
(d) The small amount of AlCl<sub>3</sub> under reflux

activate more molecules evenly as shown Fig. 2d. Thus, the reflux modification is favourable to prepare the precursor pitch suitable for the mesophase pitch.

## REFERENCES

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