

Effects of pressure during the synthesis of petroleum pitch precursors in open and closed systems

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Abstract

We examined the pressure effects on petroleum pitch synthesis by using open and closed reaction systems. The pressure effects that occur during the pitch synthesis were investigated in three pressure systems: a closed system of high pressure and two open systems under either an atmosphere or vacuum. A thermal reaction in the closed system led to the high product yield of a pitch by suppressing the release of light components in pyrolysis fuel oil. Atmospheric treatment mainly enhanced the polymerization degree of the pitch via condensation and a polymerization reaction. Vacuum treatment results in a softening point increase due to the removal of components with low molecular weights. To utilize such characteristic effects of system pressure during pitch preparations, we proposed a method for synthesizing cost-competitive pitch precursors for carbon materials. The first step is to increase product yield by using a closed system; the second step is to increase the degree of polymerization toward the desired molecular distribution, followed by the use of vacuum treatment to adjust softening points. Thus, we obtained an experimental quinoline insolubles-free pitch of product yield over 45% with softening points of approximately 130°C. The proposed method shows the possibility to prepare cost-competitive pitch precursors for carbon materials by enhancing product yield and other properties.

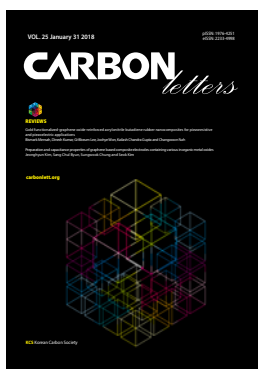
Key words: petroleum pitch, pyrolysis fuel oil, carbon material

1. Introduction

Pitch is a widely used precursor for manufacturing advanced carbon materials, such as carbon fiber, needle coke, carbon foam, and carbon/carbon composites [1,2]. Pitch is generally prepared from petroleum residues or coal-tar. The properties of pitches are largely influenced by the properties of the raw materials due to its inherent complexity [3].

Petroleum residues are typically classified according to the refinery unit process. Fluid catalytic cracking decant oil, pyrolysis fuel oil (PFO), vacuum residue, and so forth, belong to the petroleum residues and have different chemical compositions. Even residues of the same type vary in composition depending on the refining operation condition. Therefore, it is difficult to define the chemical components in petroleum residues, which makes it difficult to determine the optimal conditions for pitch synthesis [4]. PFO is obtained from a naphtha cracking center and mainly consists of hundreds of polycyclic aromatic hydrocarbons (PAHs). PFO is considered as a potential feedstock for pitch production due to its low impurities and higher aromatic contents [5].

Pitches are generally produced through thermal treatment under various conditions. Temperature and pressure are important variables that influence properties, such as coke formation, mesophase content and quinoline insolubles (QI), of the pitch by controlling the molecular structures and distributions. Temperature and pressure also affect the product yield of the pitch. Pressure affects the product yield regardless of the composition of the feedstock.



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The effect of temperature on product yield depends on the composition of the residues [2,6]. Vacuum treatment can be used for pitch synthesis [7,8]. A catalyst or an additive may be used to lower the reaction temperature and improve the polymerization degree, and blends of two or three materials can also be used [9-11].

In the current study, basic pitches with a low softening point and without QI were synthesized from PFO via thermal treatment in the open and closed reaction systems. The basic pitches synthesized in the open system were characterized using an atmospheric treatment and vacuum treatment, while those synthesized in the closed system were examined using a completely sealed autoclave reactor. In addition, pitches were produced through combinations of closed and open systems, and their properties were compared.

2. Experimental

2.1. Material and thermal treatment

PFO (Hanwha Total Petrochemical Co., Ltd., Korea) was used as a feedstock for pitch synthesis. A 1 L autoclave reactor and approximately 500 g of PFO was used to synthesize the basic pitches in open and closed systems. All the basic pitches were prepared under conditions without generating impurities, such as QI. At all the treatments in open and closed systems, the reactor was flushed with nitrogen (N_2) gas several times to remove air.

For the thermal reaction in a closed system, the reactor was completely sealed to prevent contact with the external gas. During thermal reaction, the reactor was in a sealed state, and the internal pressure in the reactor increased due to the generated gas. The reaction temperature was 370°C, the reaction pressure started at atmospheric pressure, and the soaking time was 3 h.

Vacuum and atmospheric treatments were used for the thermal reaction in an open system. Vacuum treatment was performed at 260°C for 3 h, and pressure was maintained at 0.1 bar by a vacuum pump during the thermal reaction. Atmospheric treatment was carried out at 370°C for 3 h under atmospheric pressure. During the thermal reaction, nitrogen gas was continuously flowed through the system at a rate of 200 mL min^{-1} .

2.2. Characterizations of PFO and the experimental pitches

Thermogravimetric analysis (TGA) was carried out at a heating rate of 10°C/min and at temperatures of up to 900°C in an N_2 atmosphere. Softening points of the experimental pitches were measured using a DP-70 (Mettler Toledo, USA) instrument according to ASTM D3416. The heating rate was 3°C/min in an N_2 atmosphere.

The coke formation was analyzed using an Alcor MCRT-160 tester according to ASTM D4530. Toluene insolubles and QI were measured according to ASTM D4312 and D2318, respectively. The elemental analysis (EA) was conducted to confirm the C/H atomic ratio of PFO and the experimental pitches using a Thermo Scientific FLASH EA-2000 Organic Elemental Analyzer.

The compositions of liquid and gas products were analyzed using an Agilent 6890N GC/Mass spectrometer equipped with a DB-1HT (30 m×0.25 mm×0.1 μm) and HP-PLOT/Q (30 m×0.53 mm×40 μm) column, respectively. A simulated distillation system (SIMDIS) was used according to ASTM D7169 (AC HT750 system).

The saturated, aromatic, resin, and asphaltene (SARA) fractions were measured via thin-layer chromatography (TLC) using a frame ionization detector (FID) (IATROSCAN MK-6s instrument) according to ASTM D4124. A 0.1 g sample dissolved in 10 mg of DCM was injected into the TLC column with n-hexane, toluene, and a ratio of DCM to methanol (57:3) solution, respectively. These columns were then analyzed using the FID instrument.

The molecular weight distribution was measured by matrix-assisted laser desorption/ionization time of flight mass (MALDI-TOF-MS) spectrometer (JEOL, JMS-S3000), and α -cyano-4-hydroxycinnamic acid was used as a matrix. A sample and the matrix were mixed after dissolved in tetrahydrofuran at a concentration of 10 mg mL^{-1} , respectively. A 1 μL sample mixture was deposited on spot target plate.

3. Results and Discussion

3.1. Closed system

An autoclave system was used to investigate the characteristics of pitches synthesized in a closed system. The reaction temperature was set at 370°C where polymerization reactions can occur without the formation of QI. In the closed system, pressure increased with time and temperature, and it is difficult to predict its variation. During thermal reaction in the closed system, temperature and pressure variation curves inside the reactor are shown in Fig 1. Not only the reaction pressure increased with the reaction temperature increase but also it gradually increased while the reaction temperature was maintained. The reaction pressure started at atmospheric pressure, and the final pressure at the end of the reaction was approximately 15 bar.

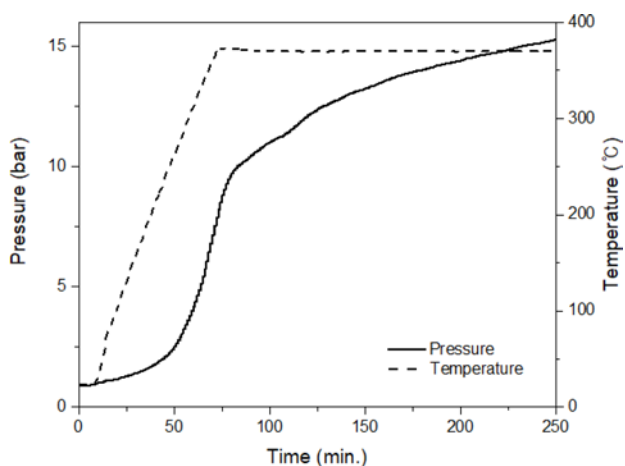


Fig. 1. Variation curves of the temperature and pressure in closed system.

Table 1. Characterization results of the experimental pitches prepared in the open and closed systems

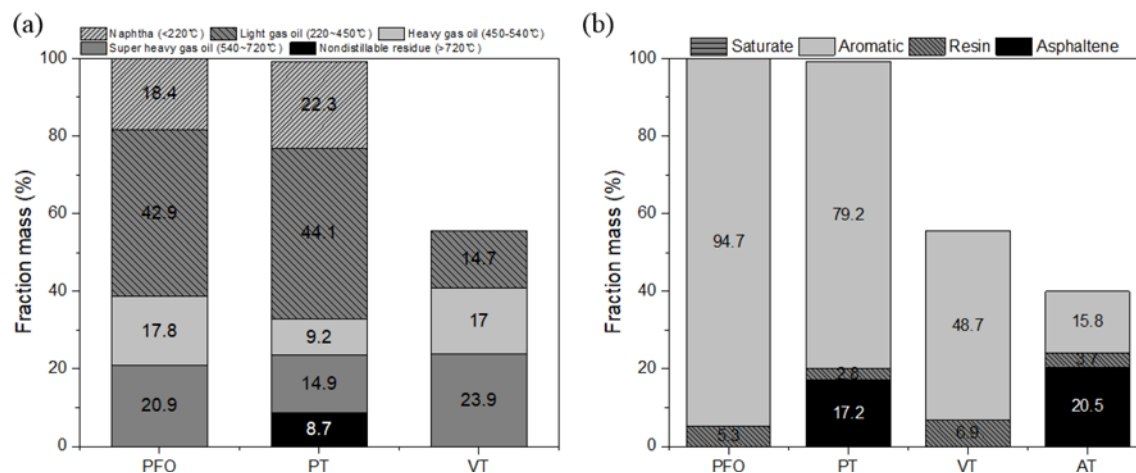
	Feedstock	Closed system	Open system	
	PFO	PT	VT	AT
Softening point (°C)	-	-	130.4	100.7
Product yield (wt%)	-	99.2	55.6	40.0
MCR (wt%)	14.0	20.4	26.1	45.3
Quinoline insolubles (wt%)	0.03	0.05	0.04	0.10
Toluene insolubles (wt%)	0.05	3.29	0.04	12.98
C/H atomic ratio	1.06	1.09	1.07	1.22
α -Resin (wt%)	0.03	0.05	0.04	0.10
β -Resin (wt%)	0.02	3.24	0.0	12.88
γ -Resin (wt%)	99.95	96.71	99.96	87.12

Pressure treated pitch (PT), prepared in a closed system, was characterized and the results are listed in Table 1. After the reaction, PT was a liquid phase without having solid components and showed a 99.2% product yield. Microcarbon residue (MCR), which can be interpreted as coke amounts, increased to approximately 20.4% compared to PFO (14.0%). In addition, PFO is only composed of γ -resins without α - and β -resins, but 3.29% of β -resins were formed in PT. MCR is an important factor in determining coke formation, and it is known that the relationship between coke formation and carbon residue is linear [12-14]. The resin types in PFO and the experimental pitches were calculated based on TI and QI contents. These factors are related to the polymerization degree. γ -Resins are mainly composed of volatiles and monomers. β -Resins are composed of mesogens, and the α -resins contain mesophase and coke. It is known that the formation and consumption of β -resins result

from the disappearance of γ -resins and formation of α -resins, respectively [15,16].

As shown in Fig. 2a, PFO and PT were divided into five fractions based on the SIMDIS analysis [17], and it was confirmed that the naphtha fractions increased to approximately 22.3% but the heavy and super heavy gas oil fractions decreased to approximately 9.2% and 14.9%, respectively, compared to PFO. In addition, 8.8% of the nondistillable residue fraction was formed, which does not exist in PFO. As results of the SARA analysis, a TLC based analysis separating saturate, aromatics, resin, and asphaltene, the PT showed aromatic and resin decreased to approximately 79.2% and 2.8%, respectively, and about 17.2% asphaltene was newly produced (Fig. 2b). Coke formation is related to the amount of asphaltenes. Asphaltenes are similar to a stack or cluster of naphthenic and aromatic molecules and are formed from aromatics and resins. Cokes formed from asphaltens are important in the carbonization step for carbon material production [18,19]. The formation of nondistillable residue, asphaltene and β -resins represents the polymerization of components in PFO.

PFO and PT were analyzed using the GC-MS (Fig. 3a and Table 2). The contents of benzene derivatives with alkyl chains, such as ethyl, dimethyl and propyl, in PT doubled in comparison with those in PFO. PFO is mainly composed of many PAHs and their derivatives. These derivatives have aryl-aryl bridges, including methylene bridges. Thermal treatment leads to the thermal cracking reaction of aryl-aryl bridges from large molecules and produces smaller PAH derivatives [20]. Biphenyl and fluorene derivatives slightly increased, but PAHs with more than three rings, such as phenanthrene, and their derivatives slightly decreased. These results indicate that large PAH molecules were converted into smaller PAHs due to the thermal cracking reaction in the closed reaction systems. PAH molecules with a cyclopentene ring, such as indene, their derivatives and acenaphthylene decreased, but indane, its derivatives and acenaphthene increased. This result indicates that hydrogenation of the cyclopentene ring occurred. It was reported that a volatile gas, including 5.4–8.3% hydrogen, can be generated by heat treatment of petroleum residues when system pressure increased over 10 bar


Fig. 2. SIMDIS and SARA analysis of PFO: the experimental pitches were considered based on the product yields of the experimental pitch prepared in the open and closed systems.

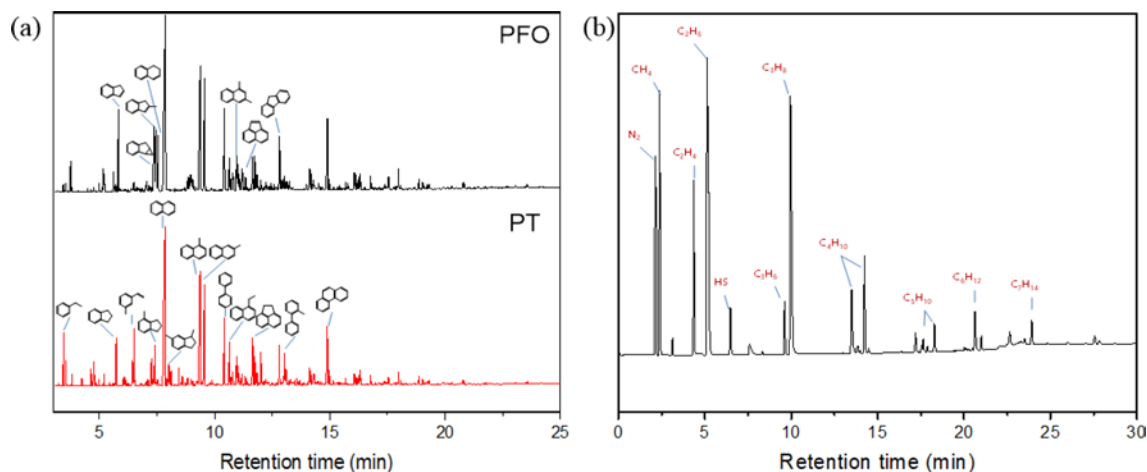


Fig. 3. GC-MS chromatogram of (a) PFO and a liquid pitch, and (b) gases emitted during the thermal reaction in the closed system.

Table 2. Components of PFO and the experimental liquid pitch determined by using GC-MS

Component (%)	PFO	PT
Benzene derivatives	5.45	12.04
Indene	3.62	-
Indane	-	2.30
Indene derivatives	12.22	-
Indane derivatives	-	7.14
Naphthalene	20.19	19.55
Naphthalene derivatives	26.30	25.56
Biphenyl	4.39	3.87
Biphenyl derivatives	3.07	5.74
Acenaphthylene	1.52	-
Acenaphthene	1.74	2.81
Fluorene	2.99	2.31
Fluorene derivatives	2.50	3.69
Phenanthrene	4.73	4.49
Phenanthrene derivatives	2.42	2.37
4 Ring-PAHs	2.68	1.69
Others	6.17	6.46

[6]. The gases generated in a closed system can participate in the reaction again. It is presumed that hydrogen gas is generated by pressurization in a closed system, and the hydrogenation reaction is induced by this hydrogen.

After the reaction, gas components of <1 wt% were emitted. They were analyzed via GC-MS analysis (Fig. 3b). In the analysis, nitrogen was detected because all gases in the reactor were initially replaced with it by purging before the reaction. After

the reaction, most gas components consisted of alkanes (C_1 – C_4 , >78%) and alkenes (C_2 , >7%). The PAH derivatives in PFO have a side chain, such as the alkyl group. During the reaction, gases were emitted due to the dealkylation reaction of the side chains [6,12]. The GC-MS could not detect all the components of PFO and PT. PAHs with over four rings were barely detected. The GC-MS analysis showed the variation of volatiles with a low molecular weight.

After the reaction started in the closed system, the internal pressure exponentially increased with the reaction temperature. It is due to the vapor pressure of initial nitrogen gas and volatile components. The internal pressure also continued to increase after reaching the reaction temperature at 370°C. It seems to be due to the effects of gases and PAHs generating by the cracking reaction.

The thermal properties of the experimental pitches and PFO were analyzed via TGA (Fig. 4). The initial weight loss of PT occurs earlier and increases rapidly compared to that of PFO. A weight loss of up to 50% for PT and PFO appeared at approximately 209 and 261°C, respectively. However, PFO and PT had the same weight loss (approximately 70%) at approximately 356°C, and then the weight loss rate of PT declined. The final residue content of PT increased to approximately 16.6% compared to PFO (7.5%). The derivative thermogravimetric (DTG) curves indirectly exhibited the molecular weight distribution patterns of the experimental pitches. The DTG curves of PT have two major peaks at 130 and 439°C. The DTG curves of PFO have three peaks at 150, 260 and 370°C. The peak at 130°C, which represents volatile molecules with a low molecular weight in PT, is shifted to a lighter molecular fraction, while the peak at 439°C, which represents components with a high molecular weight, is transferred to a heavier molecular fraction compared to that of PFO. These shifts in molecular fractions led to the polarization of molecular fractions in PFO, which resulted from the thermal cracking and polymerization reactions.

The reaction in a closed system promotes the polymerization of molecules with a low molecular weight by suppressing the release of volatile compounds and recycling them. This helps to increase the product yield and degree of polymerization of the pitch.

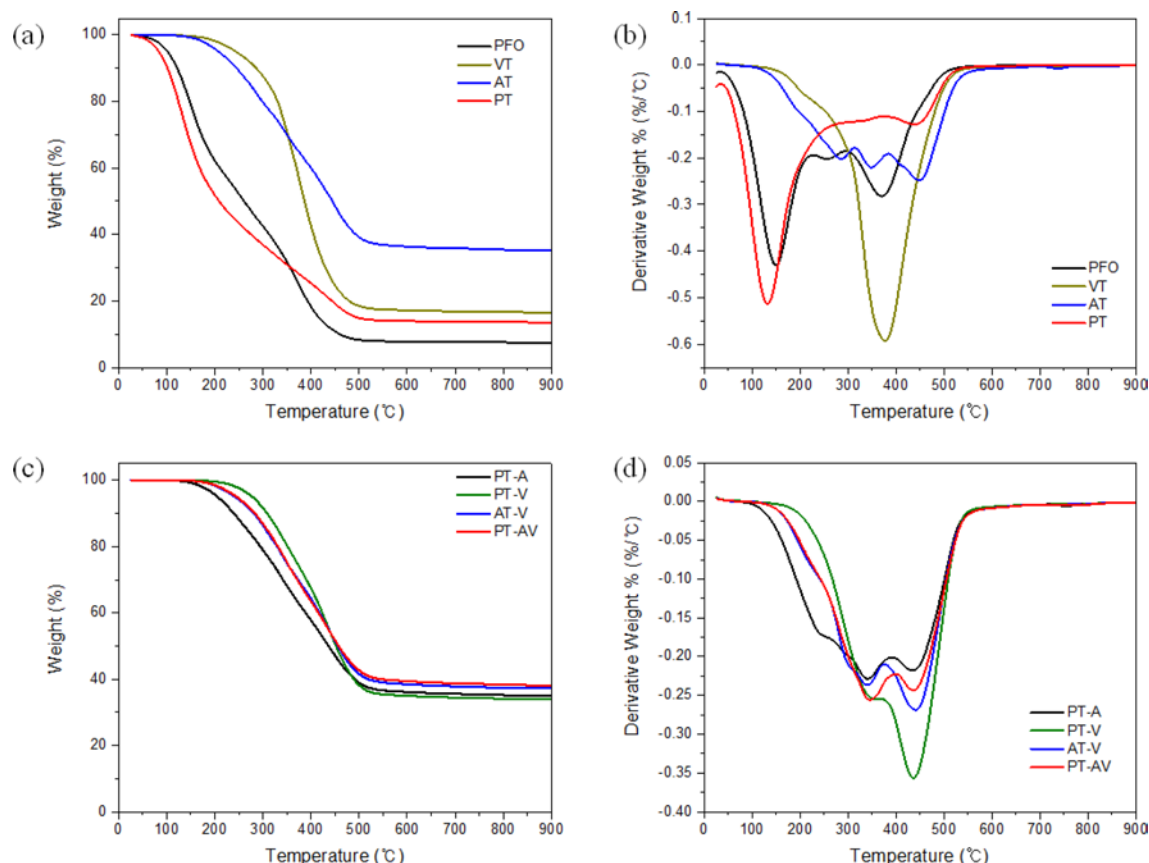


Fig. 4. TG analysis. (a) TG and (b) DTG curve of PFO and the experimental pitches prepared in the open and closed systems. (c) TG and (d) DTG curve of the pitches prepared in the combined system.

3.2. Open system

Two methods were used to compare the characterizations of pitches synthesized in an open system. Atmospheric treatment was performed at the same temperature (370°C) as in the closed system. On the other hand, vacuum treatment was conducted at low temperature (260°C) and pressure (0.1 bar). The reason behind to set system temperature and pressure is to see clear effect of system pressure on the pitch synthesis without low molecular weight components up to anthracene and its derivatives, which do not actively participate the reactions and are removed from the atmosphere treated systems. Changes in the polymerization degree of pitches synthesized through atmospheric treatment and vacuum treatment were investigated and are listed in Table 1.

3.2.1. Vacuum treatment

To see the clear effect of vacuum treatment, vacuum treated pitch (VT) was synthesized in an open system reactor showing 55.6% product yield. As results of TGA, SIMDIS and SARA analysis of vacuum treated PFO, the treatment successfully removed low molecular weight components leaving heavier portion of PFO.

The SIMDIS analysis explains that the naphtha fraction was entirely eliminated by the treatment, but other fractions re-

mained almost unchanged (Fig. 2a). In addition, the aromatic fraction was reduced in the SARA analysis but the resin fraction was almost unchanged (Fig. 2b).

The DTG curve of PFO comprises three peaks at 150, 255, and 370°C, but that of VT has one peak, which is similar to the third peak at 370°C of PFO (Fig. 4b). The results indicate that the polymerization of components is almost negligible, and only the small molecular weight components are removed by the treatment. Most large molecules with a high boiling point remain largely intact without any change in chemical structure. The increase of the MCR and the change of the TG curve occur primarily due by the removal of low molecular weight components, not by the polymerization.

VT had a higher softening point of approximately 130°C than those of PT and AT. The softening point is an important property of pitch because it relates to the rheological properties affecting processing, such as spinning or impregnating of the pitches on each purpose.

3.2.2. Atmospheric treatment

To capture clear temperature effect, we prepared an atmosphere treated pitch (AT) of 40.0% product yield by thermal treatment of PFO at the open system. In addition, the C/H atomic ratio in AT was higher than that of PFO and PT. A lower C/H ratio indirectly implies a lower aromaticity and the existence of

Table 3. Characterization results of the experimental pitches prepared in the combined systems

	2-Combined system		3-Combined system	
	PT-A	PT-V	AT-V	PT-AV
Softening point (°C)	94.4	130.7	131.2	131.8
Production yield (wt%)	49.7	42.8	37.9	45.7
MCR (wt%)	46.3	47.7	48.7	52.0
Quinoline insolubles (wt%)	0.09	0.15	0.15	0.15
Toluene insolubles (wt%)	13.67	7.22	15.08	17.66
C/H atomic ratio	1.23	1.20	1.24	1.29
α -Resin (wt%)	0.09	0.15	0.15	0.15
β -Resin (wt%)	13.58	7.07	14.93	17.51
γ -Resin (wt%)	86.33	92.78	84.92	82.34

a naphthenic structure and alkyl substitute in the aromatic ring due to higher aliphatic hydrogen contents [10,14,21]. A higher C/H ratio indicates a more condensed aromatic structure and higher polymerization degree [9]. It was confirmed that 12.88% of β -resins were formed in AT, which is higher than that for PFO and other pitches. The formation of β -resins in AT represents the polymerization of components in PFO and leads to the increase in MCR. In other words, the higher C/H ratio, β -resins and MCR of AT indicate a higher polymerization degree compared to that of others.

In the SARA analysis, a considerably high asphaltene fraction of 20.5% was formed (Fig. 2b). This indicates that some aromatic components in PFO were removed from the system and that some were polymerized. The SIMDIS analysis of solid pitches was not conducted due to its detection limit.

In the TG curve, the weight loss of both AT and VT began at approximately 109°C, but the initial weight loss of AT was higher than that of VT (Fig. 4a). However, after approximately 353°C, the weight loss of VT exceeded that of AT, and VT had a lower residue content. The DTG curve of AT has three peaks at 283, 347, and 450°C. The peak at 283°C represents volatile molecules with a low molecular weight, and the peak at 450°C represents components with a high molecular weight. These peaks indicate that the thermal cracking reaction and polymerization occur together during atmospheric treatment (Fig. 4b). AT showed a lower softening point than the vacuum treated pitch of VT, because of its high amount of low molecular weight components.

Overall, vacuum treatment is a method used to control the softening points of pitches by removing only those volatile molecules of low molecular weight, without significant polymerization reactions. In contrast, atmospheric treatment is a method to increase the degree of polymerization.

3.3. Combined system

We have confirmed the characteristics of the pitches synthesized in both open and closed systems. To improve the product yield and polymerization degree of the pitches, we combined

all the three different reaction systems for pitch synthesis: the closed system to increase the product yield; the atmospheric treatment to facilitate polymerization reaction; the vacuum treatment to adjust the softening point to 130°C. Characteristics of pitches prepared following the combined systems are listed in Table 3.

We have synthesized several experimental pitches according to the combination; PT-A was prepared the closed system followed by atmospheric treatment of PFO, PT-V was synthesized by the closed system followed by vacuum treatment, AT-V was formulated by the atmospheric treatment followed by vacuum treatment, and PT-AV was finally produced by the series of treatment from a closed system, atmospheric treatment, and vacuum treatment. All the pitches prepared using the combination systems were QI-free pitches without QI that can be considered as such impurities (<0.2%).

The softening point of PT-A is approximately 94.4°C and lower than that of AT. However, the MCR, β -resin and C/H atomic ratio of PT-A are slightly higher than those of AT; in particular, the product yield increased to approximately 49.7% compared to that of AT (40.0%). The molecular fractions of PT are polarized compared to those of PFO. This characteristic affects polymerization during the atmospheric treatment and produces a pitch with a higher polymerization degree while lowering the softening point. PT-A has a higher β -resin and C/H ratio but showed an approximately 36°C lower softening point compared to that of PT-V. In the TG and DTG curves, PT-A has more fraction with a low molecular weight due to the cracking reaction occurred during atmospheric treatment, which lowers the softening points (Fig. 4).

For the property comparison, we carefully adjusted the softening points of all experimental pitches approximately 130°C. However, the three pitches of PT-V, AT-V, and PT-AV showed different polymerization degrees and product yield. Molecular weight distributions of the pitches were identified by MALDI-TOF analysis and they were grouped according to their molecular weight (Fig. 5). Molecular weight distribution variations increase and are shifted to higher fractions as follows: PT-V < AT-V < PT-AV. While the molecular distri-

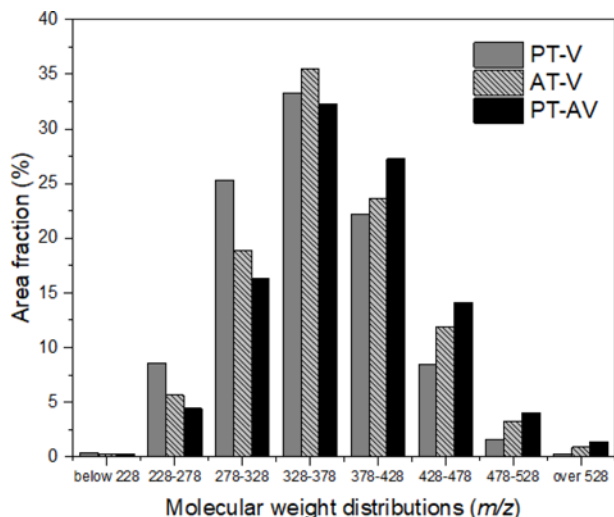


Fig. 5. Diagram of the molecular weight fraction of PT-V, AT-V, and PT-AV prepared in the combined system.

bution of PT-V was higher in the fractions below 328 m/z , that of PT-AV was higher than 378 m/z . These differences of molecular distribution affect MCR, β -resins and C/H ratio. The higher the molecular fraction of a pitch, the higher its MCR, β -resins and C/H ratio. These indicate increase of a polymerization degree.

Compared to AT-V, PT-V has a higher product yield because low molecular weighted volatile molecules are forced to participate in the polymerization reaction in the closed system. Since the polymerization of large molecules is inhibited under pressure, its MCR, β -resins and C/H ratio are lower than those of AT-V [2].

In the TG curve, the initial weight loss of PT-V occurs later compared to that of AT-V and PT-AV. The weight loss of PT-V starts at approximately 168°C, while those of AT-V and PT-AV start at approximately 144°C. However, the weight loss rate of PT-V increases rapidly, and PT-V has a lower residue content than that of others. The TG curves of AT-V and PT-AV exhibit similar patterns, but PT-AV has slightly higher residue content (Fig. 4c).

PT-AV has the highest β -resins, C/H ratio, and MCR among the experimental pitches. In a closed system, the thermal reaction involves thermal cracking and dealkylation. Some PAH molecules formed by these reactions contain more numbers of radicals and remain without distillation. The resultant radicals lead to a polymerization reaction, such as the polycondensation in atmospheric treatment [12]. In other words, more γ -resins that can be converted to β -resins are formed, and more molecules participate in the polymerization reaction. Accordingly, the product yield, MCR, β -resins, and C/H ratio increase by the atmospheric treatment. Finally, volatile molecules with a low molecular weight are eliminated in vacuum treatment. This series of processes enhances the polymerization degree and the product yield of the pitch without the generation of impurities.

4. Conclusions

To understand the basic characteristics of the petroleum pitch synthesis, basic pitches were synthesized under different pressure conditions using open and closed systems. In the closed system reaction, low-molecular-weight components in PFO, which usually do not attend the synthesis, were forced to join the reaction, resulting in an increase in the product yield. The primary role of atmospheric treatment was to enhance the degree of polymerization during pitch synthesis. Vacuum treatment was shown as an efficient way of controlling softening points by removing the low molecular weight and low boiling point components. Considering the advantages of all three systems, the combination of open and closed systems can provide a versatile method to improve MCR, β -resin, C/H ratio and product yield.

Therefore, we proposed a three-step method for the preparation of cost-competitive petroleum pitch precursors; the first step to enhance the product yield by using a closed system, the second step to increase the degree of polymerization via atmospheric treatment, and the last step to control the softening points via vacuum treatment. In conclusions, we have successfully revealed the effects of system pressure during petroleum pitch synthesis and proposed a cost-effective method based on the results.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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