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Polymerization of Deasphalted Vacuum Residue Mixed with Gum Rosin for Mesophase Pitch Production

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Abstract. Waste from vacuum distillation of crude oil refineries in Indonesia is still not fully utilized. Vacuum residue is potential to be used as a feedstock to produce mesophase pitch by removing its asphaltene content (deasphalting) followed by thermal polymerization of the remaining aromatic compounds performed at low heating rate. Mesophase pitch is regarded as an excellent precursor for making a wide variety of industrial and advanced engineering carbon products such as carbon fibers, needle coke, Li-ion battery anodes. The objective of the present research is to investigate the effect of gum rosin addition to the deasphalted vacuum residue on the extent of the polymerization of aromatic compounds. Gum rosin is a residue of pine trees containing conjugated double bond compounds. It was used to maintain mesophase condition during polymerization to maintain polyaromatic formation. High polyaromatic composition forms anisotropic crystallite and favors high mechanical strength as the mesophase pitch is converted to engineering carbon. The polymerization occurred in a stirred tank reactor at heating rate of 5°C/min, maximum temperature of 350°C, and N₂ flowrate of 100 mL/min. The amount of gum rosin mixed with the deasphalted vacuum residue was varied at 0% wt, 5% wt, 10% wt, and 15% wt of deasphalted vacuum residue. The result of analysis on mesophase pitches shows that increasing gum rosin composition from 0 to 10% reduced aromatic composition in mesophase pitch from 23 to 10%, but increased to 67% as the gum rosin content was increased to 15% wt. The largest crystallite size in the mesophase pitch, i.e. 44.5 Angstrom was achieved as the polymerization used 15% wt of gum rosin. All mesophase pitches have interlayer distance in average 4.12 Angstrom, slightly higher than 3.35 Angstrom (interlayer distance of fully ordered crystalline graphite).

INTRODUCTION

Pitch is a residue of petroleum distillation or coal tar which is a complex mixture containing thousands of aromatic hydrocarbons with 3-8 fused ring systems. Mesophase pitch is a phase of carbon material between solid and liquid (mesophase) resulting from the polymerization of aromatic materials of vacuum residue or coal tar to produce crystalline and planar polyaromatics [1]. This material is regarded as a very useful precursor for the manufacture of carbon products such as carbon fiber, Li-ion battery anode, carbon foam and others [2].

Most organic materials can be carbonized on heat treatment at a high temperature above 700–800°C under inert atmosphere. The resulting carbons are classified mainly into the two categories, graphitizable and non-graphitizable carbons. Carbons of the former class exhibit a characteristic of structural conversion on heat treatment above 2000°C, by which the hexagonal carbon-carbon networks are highly oriented in the three-dimensional order. But the latter carbons, non-graphitizable carbons, do not exhibit such a characteristic [3]. Mesophase pitch is known as one of the most typical graphitizable carbonaceous materials. Otani et al. and Singer have independently investigated carbon fiber precursors and reported that high performance carbon fiber (HPCF) with high orientation and crystallinity of graphite can be readily obtained from mesophase pitch [3].

In Indonesia, coal tar is not available because there is no destructive distillation unit of coal, whereas vacuum residue is widely available in oil refineries. Vacuum residue currently not fully utilized in Indonesia has a potential to become the raw material for mesophase pitch. Both materials contain alkanes, asphaltene, resins and aromatics, but the coal tar has a higher asphaltene content of about 35%, while the vacuum residue is about 15% [4]. The

asphaltene content of the vacuum residue has a negative effect on the mesophase pitch due to its isotropic and amorphous nature, which degrades mechanical strength as the mesophase pitch is converted to engineering carbon [1]. The desired product is mesophase pitch with high crystalline polyaromatic and low amorphous polyaromatics. To increase the crystalline polyaromatic content, the isotropic polyaromatic content naturally present in the coal tar or vacuum residue needs to be removed first through the deasphalting process [1].

Gum rosin can be added to deasphalted vacuum residue to improve polymerization. Gum rosin can be found in some pine forests in Indonesia. The rosin contains functional groups of cycloparaffin, conjugated double bonds, and carboxyl group [5]. Cycloparaffin and conjugated double bonds make the mesophase pitch relatively stable at high temperatures by decreasing the melting point of the pitch [5] so that the polymerization proceeds more evenly. The polymerization step can be accelerated by the presence of free radicals from carboxyl groups of gum rosin. The authors are unaware that synthesis of mesophase pitch using gum rosin has been investigated before. The objective of the present research is to investigate the effect of gum rosin addition to the deasphalted vacuum residue on the extent of the polymerization of aromatic compounds.

EXPERIMENTAL

The study was conducted in three stages, the first was the process of asphaltene removal from vacuum residue. In the deasphalting process, hexane was used as solvent with a weight ratio of vacuum residue to hexane 1:10 at a temperature of 65°C and then the mixture was settled overnight to separate the asphaltene which eventually precipitated. The second stage was the mixing of deasphalted vacuum residue with rosin gum in a stirred tank reactor with amount of gum rosin varied 0% wt, 5% wt, 10% wt, and 15% wt of vacuum residue. Maximum temperature of mixing was 150°C maintained for 30 minutes with a heating rate of 5 °C/min from ambient temperature. The last stage was the polymerization of mixture of deasphalted vacuum residue and gum rosin in the stirred tank reactor. The polymerization stage has a maximum temperature of 350°C maintained for 30 minutes with a heating rate of 5°C/min from ambient temperature. The flowrate of N₂ was kept at 100 mL/min

The synthesized mesophase pitch samples were analyzed by H-NMR method before and after polymerization to analyze composition distribution of monoaromatics, diaromatics and polyaromatics as result of polymerization. The samples from post-polymerization were also analyzed by C-NMR method to analyze effect of gum rosin addition on the extent of polymerization by comparing compositions of saturated carbon and aromatic carbon. XRD analysis was conducted to analyze the morphology of mesophase pitch, crystalline size and interlayer distance. Before the polymerization, deasphalted vacuum residue was analyzed by the TGA method to analyze pyrolysis and polymerization temperature limits required for the polymerization process.

RESULTS AND DISCUSSION

TGA Analysis of Deasphalted Vacuum Residue

The TGA (thermal gravimetry analysis) and DTG (differential temperature gravimetry) analysis, derived from TGA, were conducted before polymerization on deasphalted vacuum residue samples prepared with its mixture with gum rosin. The addition of gum rosin was varied 0%, 5%, 10%, and 15% weight of deasphalted vacuum residue. The corresponding samples were named DVR0%, DVR5%, DVR, DVR10%, and DVR15%, respectively. This analysis was used to determine temperatures of polymerization of the mixture of deasphalted vacuum residue and gum rosin.

Figures 1 and 2 show that there are two phases of the mass reduction. The first stage is the removal of light molecules and gases generated during pyrolysis of the samples and removal of residual hexane up to a maximum temperature of about 300 to 318°C depending on gum rosin added, the higher the gum rosin added, the less was the maximum temperature [5]. The second stage was the mass reduction of the vacuum residue samples up to a temperature of about 470 °C for all samples due to pyrolysis coinciding with polymerization [5]. Starting from 470°C as identified by dos Santos Lima et al [6], polymerization rates were lower and lower as the temperature was higher as shown by Figure 2. In the current work, polymerization was maintained to occur at 350°C where there was transition between removal of light molecules and gases and pyrolysis of the mixture of deasphalted vacuum residue and gum rosin. Therefore, the pyrolysis was minimized while polymerization was occurring.

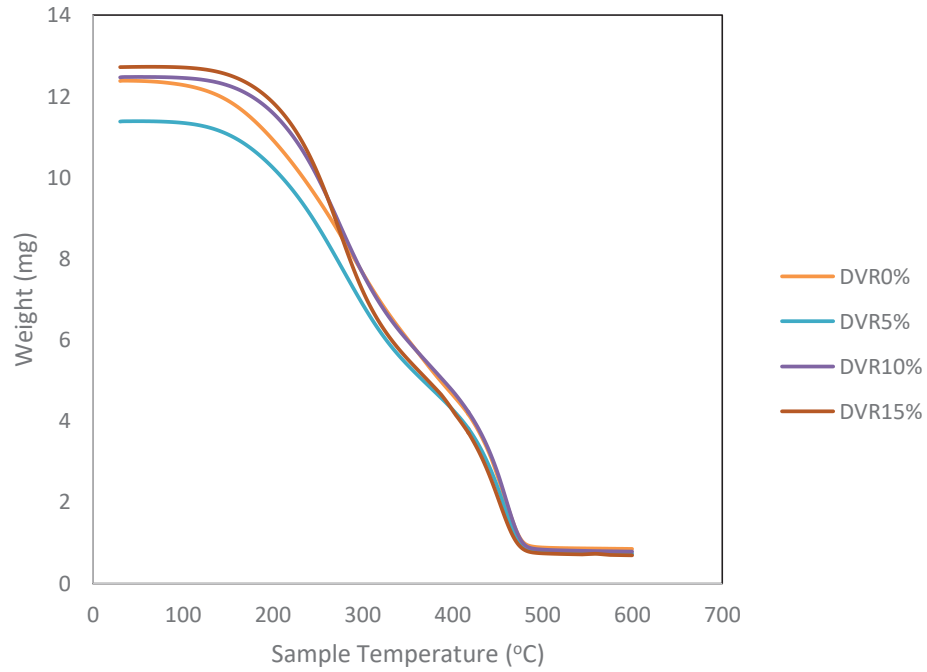


FIGURE 1. TGA Graph of Deasphalted Samples

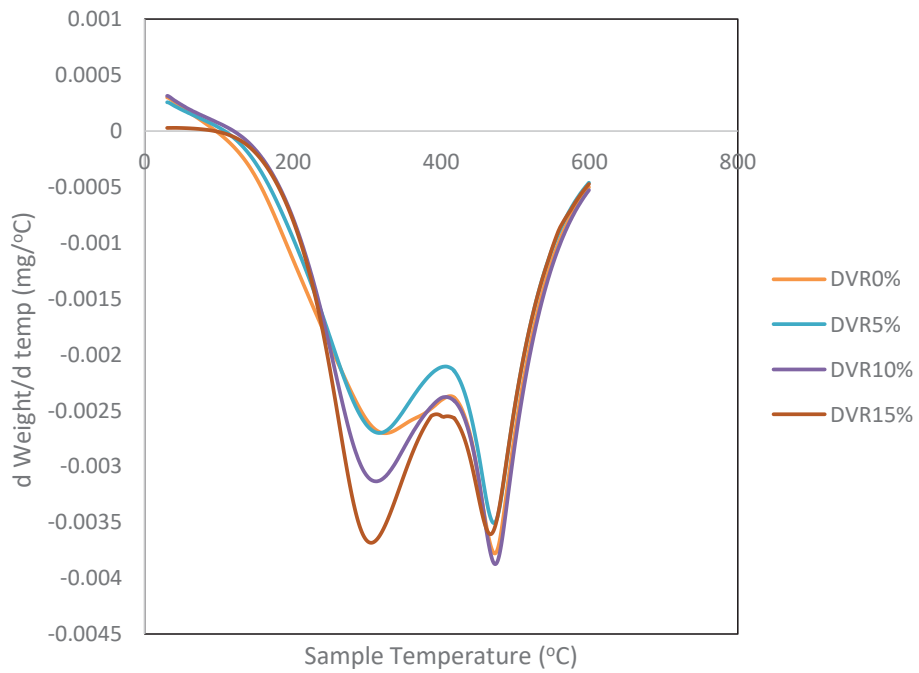


FIGURE 2. DTG Graph of Deasphalted Samples

H-NMR and C-NMR Analysis of Deasphalted Vacuum Residue

H-NMR analysis was performed on samples of deasphalted vacuum residue samples prepared from the mixture of deasphalted vacuum residue and gum rosin before and after polymerization. Gum rosin added was varied 0%, 5%, 10%, and 15% weight of deasphalted vacuum residue. Samples collected before the polymerization process were named DVR0%, DVR5%, DVR10%, and DVR15%. Samples collected after polymerization were named DVR-350-0%; DVR-350-5%; DVR-350-10%; and DVR-350-15%. C-NMR analysis was performed on samples obtained after polymerization. H-NMR and C-NMR integration data based on calculation using MestReNova program.

Table 1 indicates that the deasphalted vacuum residue prior to the polymerization step comprised mainly the aliphatic chain. As the heat treatment was conducted, the aliphatic chains broke off and produced active free radicals [3]. The aromatic free radicals obtained were polymerized to give large aromatic molecular sizes useful in the formation of mesophase pitch with large optical textures and high crystalline structures [1]. Therefore, the mesophase pitches of the polymerization stage contains more aromatic protons (H_{ar}) as indicated by the ratio of H_{ar}/H_{al} compared to the mixture prepared for polymerization.

TABLE 1. H-NMR and C-NMR Integration Data

H NMR	DVR-0%	DVR-350-0%	DVR-5%	DVR-350-5%	DVR-10%	DVR-350-10%	DVR-15%	DVR-350-15%
$H_{ar(poly)}$ (%)	0.13	0.18	0.14	0.20	0.19	0.26	0.11	0.22
$H_{ar(di)}$ (%)	3.13	3.04	2.2	3.44	2.35	3.36	2.36	4.77
$H_{ar(mono)}$ (%)	0.22	0.53	0.58	0.57	0.71	0.66	0.51	0.23
% $H_{ar(poly)}$ increase		38.46		42.85		36.84		100
H_{ar} (%)	3.48	3.75	2.92	4.21	3.25	4.28	2.98	5.22
H_{α} (%)	3.37	4.2	3.66	3.82	3.6	4.36	4.93	7.02
H_n (%)	0.71	5.10	0.70	6.84	0.71	6.98	0.72	10.80
H_{β} (%)	70.71	73.18	69.49	73.9	72.44	72.6	71.39	69.73
H_{γ} (%)	22.44	18.87	23.94	18.07	20.71	18.76	20.7	18.03
H_{al} (%)	96.52	96.25	97.09	95.79	96.75	95.72	97.02	94.78
H_{ar}/H_{al}	0.0360	0.0389	0.0301	0.0440	0.0336	0.0447	0.0307	0.0551
C NMR								
C_{ar} (%)		22.96		17.64		9.83		67.55
C_{sat} (%)		77.04		82.36		90.17		32.45
C_{ar}/C_{sat} (%)		0.2980		0.2142		0.1090		2.0817

Notes: $H_{ar(mono)}$ is the abundance of H in monoaromatic rings, $H_{ar(di)}$ is the abundance of H in diaromatic rings, $H_{ar(poly)}$ is the abundance of H in polyaromatic rings, H_{al} is the abundance of H in aliphatic chains, C_{ar} is the abundance of C in all types of aromatic rings, C_{sat} is the abundance of C in saturated aliphatic chains, H_{α} is the abundance of H in C_{α} to aromatic rings, H_{β} is the abundance of H in C_{β} to aromatic rings, H_{γ} is the abundance of H in C_{γ} to aromatic rings, H_n is the abundance of H in naphthenic rings.

According to Li et al [7], raw material with higher aromaticity and more naphthenic (cycloparaffin) structure is easy to form mesophase pitch with lower softening point and more crystalline structure. Table 1 shows that naphthenic protons (H_n) before polymerization were so minute, but they evolved after polymerization which induced the formation of polyaromatics. Data of H_n after polymerization shows that the higher the amount of gum rosin added, the higher was the composition of naphthenic structure in mesophase pitch. This indicates that the evolution of naphthenic structure during polymerization stage can be induced as more gum rosin was added. This evolution in turn was favorable for polyaromatic formation. Data of % H_{ar} increase indicated that polymerization stage increased

the polyaromatic composition. Therefore, gum rosin containing conjugated double bonds had an effect of improving composition of polyaromatics.

Data of %C_{ar} and the ratio of C_{ar}/Cal in Table 1 shows that the improvement of polyaromatics can be significant when the gum rosin added was 15%. The resulting mesophase pitch shows that increasing gum rosin composition from 0 to 10% reduced aromatic composition in mesophase pitch from 23 to 10%, but increased to 67% as the gum rosin content was increased to 15% wt. It seems that there was few aromatization during the polymerization stage when the composition of gum rosin was added from 0 to 10% causing less and less values of %C_{ar} and the ratio of C_{ar}/Cal. Therefore, it is worth considering using gum rosin more than 15% to acquire more polyaromatic composition. According to Greinke [8] the extent of polymerization towards higher molecular weight in petroleum pitch can be attained at longer polymerization stages. He suggested to keep the polymerization stage minimum 2 hours to obtain significant change of molecular weight distribution containing high molecular weight. However, in the current work, the polymerization stage was set for 30 minutes, which may have been insufficient to obtain high degree of polymerization.

XRD Analysis of Mesophase Pitch

The XRD analysis was performed on mesophase pitch samples which had been undergoing polymerization up to 350°C. Four samples were analyzed DVR-350-0%; DVR-350-5%; DVR-350-10%; and DVR-350-15% corresponding to 0%, 5%, 10%, and 15% weight of gum rosin added, respectively. Analysis of mesophase pitch samples was performed using a Cu K α radiation source. Measurements were made with angle 2 θ range of 2-80° and step size of 0.2° and rate of measurement of 1°/min. XRD analysis aims to find out the crystallite size and interlayer spacing of mesophase pitch, respectively using the Scherrer and Bragg equations as follows [9].

$$Dp = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

$$2d \sin \theta = n\lambda \quad (2)$$

where

Dp = the mean size of the crystallite domains, which may be smaller or equal to grain size

K = a dimensionless shape factor, with a value close to unity, but it varies with the actual shape of crystallite.

λ = X-ray wavelength

β = the line broadening at half the maximum intensity after subtracting the instrumental line broadening, in radian

θ = the diffraction (Bragg) angle

d = the interlayer distance

n = positive integer

Table 2 shows calculation results of interlayer distances using Bragg method indicating that mesophase pitches had interlayer distances slightly above the interlayer distance of 3.35 Angstrom, which is the distance of fully ordered graphite structure [1]. This means that mesophase pitches still contained some amorphous carbon and requires longer polymerization time to approach fully ordered crystalline structure. Table 2 indicates that with increasing gum rosin mixed with deasphalted vacuum residue increased the crystallite size. More cycloparaffin and conjugated double bonds in gum rosin made the pitch became stable at high temperature [10] thus accommodating the evolution of crystalline polyaromatics during heat treatment [11].

TABLE 2. XRD Results of Mesophase Pitch

Sample	Crystallite Size (Å)	Interlayer Distance (Å)
DVR-350-0%	31.32	4.13
DVR-350-5%	39.27	4.11
DVR-350-10%	42.35	4.13
DVR-350-15%	44.46	4.12

CONCLUSIONS

The present work gives some conclusions as follows:

1. Comparison of polymerization at different additions of gum rosin to the deasphalted vacuum residue from 0 to 15% results suggests that addition of 15% gum rosin produced mesophase pitch with highest increase of polyaromatic content with aromatic carbon comprising 67.55% of the mesophase pitch, whereas additions of 5 and 10% adversely resulted in lower aromatic carbon compositions compared to that of pure vacuum residue.
2. Increasing addition of gum rosin to the deasphalted vacuum residue resulted in more crystallite size in mesophase pitch. The largest crystallite size in the mesophase pitch, i.e. 44.5 Angstrom. Interlayer distance in mesophase pitch acquired was about 15% higher than the interlayer distance of fully ordered graphite structure of 3.35 Angstrom.

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