Asphaltenes and preasphaltenes from coal liquid extracts: feedstocks to obtain carbon mesophase

Asfáltenos y preasfáltenos de extractos líquidos de carbones: materia prima para obtener mesofase de carbono

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Abstract

The aim of this work was to produce mesophase by using preasphaltenes and asphaltenes from coal liquid extracts obtained in a Direct Coal Liquefaction (DCL) process. Preasphaltenes and asphaltenes were carbonized at inert atmosphere at temperatures of 350, 400 and 450 °C during 180 min. The mesophase identification and quantification was performed by polarized light microscopy. The results showed that the highest concentration of mesophase (79% v/v), with mass yield of 12,4% w/w, was obtained from the asphaltenes treated at 400 °C. The highest mesophase global yield (with respect to coal fed) was 4,4% w/w.

---------- *Keywords:* Mesophase, asphaltenes, preasphaltenes, coal liquid extract

Resumen

El objetivo de este trabajo fue producir mesofase usando como materia prima asfáltenos y preasfáltenos de extractos líquidos de carbones obtenido en un proceso de Licuefacción de Carbón Directa (LCD). Los asfáltenos y preasfáltenos se carbonizaron en atmosfera inerte a las temperaturas de 350, 400 and 450 °C durante 180 min. La identificación y cuantificación de la mesofase se realizó por microscopía de luz polarizada. Los resultados mostraron que la mayor concentración de mesofase (79% v/v) con rendimientos másicos de 12,4% p/p se obtuvo de los asfáltenos carbonizados a 400 °C. El mayor rendimiento global de mesofase obtenida respecto al carbón alimentado fue de 4,4 % p/p.

---------- *Palabras clave:* Mesofase, asfáltenos, preasfáltenos, extracto liquido de carbón

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Introduction

The carbonaceous mesophase plays an important role as a precursor in the manufacture of carbon fibers and other valuable materials. The mesophase consists of high molecular weight planar aromatic compounds with considerable molecular order that separate into isotropic liquids and look like spherical drops. Various materials have been used to produce carbonaceous mesophase to obtain carbon fibers: polyvinylchloride [1], polyacrylonitriles [2], naphthenes [3], and coal and petroleum liquid extracts [4, 5].

The coal extract is classified into four groups: saturated, aromatic naphthenes, polar aromatics, and asphaltenes. The saturated group includes low molecular weight aliphatic compounds, while asphaltenes represent the fraction presenting the highest molecular weights [6]. Mesophase production from coal liquid extracts involves two stages: 1) removal of low molecular weight species usually through extraction with solvent (extraction) and 2) heat treatment of high molecular weight fractions (carbonization). During the first stage, the coal liquid extract is extracted with solvents – like toluene and hexane – to remove soluble and insoluble fractions denominated asphaltenes and preasphaltenes, which are used to produce the mesophase. During the second stage, the insoluble fraction is heated to temperatures between 300 and 500 °C, to volatilize low molecular weight hydrocarbons, leading to polymerization and condensation reactions of the hydrocarbons.

Research has been conducted related to thermogravimetric analysis of extracts and mixtures from coal and petroleum to obtain the mesophase [7]. Also, the behavior of those coal liquid extracts has been evaluated during recent carbonization stages [8]. Likewise, it has been reported that the mesophase from petroleum and coal liquid extracts has been obtained by using carbonization temperatures between 400 and 500 °C with residence times between 180 and 300 min under nitrogen inert atmosphere [9].

The mesophase can be separated from the isotropic phase during heat treatment, using centrifuge at high temperatures [6, 7]. Additionally, through analysis of the mesophase, the naphthenes and short-chain alkyls are essential to make the mesophase have a low softening point and, consequently, reactivity of reasonable stabilization [10]. In order to improve the mesophase, the heavy fraction of the coal liquid extract was also hydrogenated by introducing naphthenic groups into the precursor with the aid of a hydrogen donor solvent (tetrahydroquinoline) or a catalyst [11]. A recent work [12] evaluated the effect of using oxidation in two petroleum liquid extracts on the properties and production of carbonaceous mesophase produced.

Although much research and development exists, producing mesophase in Colombia from coal liquid extracts has not been well developed. The aim of this work was to obtain mesophase from asphaltene and preasphaltene fractions from the liquid extracts of a Colombian coal obtained in a direct liquefaction process.

Experimental

Materials

This study used coal from Cerrejón mine (Guajira, Colombia), with particle size 100% passing 200 meshing, which was used as raw material in the direct liquefaction process. Anthracene oil was employed in direct liquefaction as coal transporting solvent, while gaseous hydrogen was utilized as free radicals from the thermal decomposition of coal. Tetrahydrofuran (THF) was used as solvent to separate the unconverted mineral material and organic material from the liquid extract obtained, while toluene and hexane were employed to separate the asphaltene and preasphaltene fractions from the liquid extract, respectively. All the solvents were of analytic grade. To prepare the specimens of samples obtained from the carbonization process, it was used a liquid epoxy resin based on bisphenol-α with hardener, while alumina suspensions of 0,5;

0,3, and 0,05 microns were utilized to polish the test tubes.

Equipment

Coal liquefaction was carried out in a 316 stainless steel 500-ml reactor. A reflux system was used to carry out extractions of the product from the direct liquefaction, while a rotaevaporator was employed to recover solvents (THF, toluene, and hexane). Also, a muffle furnace was utilized for carbonization of the asphaltene and preasphaltene samples, while a metallographic microscope was used for analysis and count of mesophase produced in the carbonized samples.

Experimental procedure

The operating conditions of the direct liquefaction were taken from Coley [13], which were 380 °C, anthracene oil/coal ratio: 4:1, and 30-min reaction time. All runs used 60 g of feed (anthracene solvent and coal). Once the reactor was loaded, it was purged and hydrogen was supplied until reaching an internal pressure of 800 psig (~5.5 MPa) in cold. Thereafter, the reactor was mounted on the heating mantle and the reaction temperature was adjusted at 380 °C and the agitation rate at 225 rpm. When the desired temperature was reached, the system reacted during 30 min. Then, sudden cooling (quenching) took place to stop the reaction. Finally, the reactor was depressurized when it reached 30 °C; reaction products were removed, which were subjected to an extraction process through a reflux system.

For the process to obtain asphaltenes and preasphaltenes, a series of extractions were carried out of the coal liquid extract, employing three solvents: THF, toluene, and hexane; using a reflux system as extraction method, with 1-h extraction time for all samples [14]. When the extraction was over, hot vacuum filtering took place to separate insoluble material from each solvent; thereafter, the filtered solvent was recovered through rotoevaporation. The extraction stage with THF was conducted at 85 °C for 1 h, with a solvent/liquid product ratio of

1:1 [11], while the extraction stage with toluene was conducted at 125 °C for 1 h, with a solvent/liquid product ratio of 1:1 [14]. Extraction with hexane was carried out at 85 °C for 1 h, with a solvent/liquid product ratio of 20:1. The insoluble fractions of the liquid coal in the toluene and hexane solvents were analyzed through ultimate analysis according to ASTM D 5373 standard and proximate analysis according to ASTM D 5142, D3172, D5865, and D4239 standards.

The preasphaltenes and asphaltenes obtained from the DCL process were subjected to a carbonization process at 350, 400, and 450 °C in nitrogen atmosphere using a muffle with a heating rate of 2,5 °C/min and nitrogen flow of 0,67 l/min. Upon reaching carbonization temperature, the residence time of the sample was 180 min. The sample amount of asphaltenes and preasphaltenes used in the carbonization was 1,5 g.

In preparing the specimen to be analyzed under the microscope, the epoxy resin was mixed with the hardener at a volumetric proportion of 1:1. The molds were left to dry at room temperature during 6 h. Then the polishing process was carried out with alumina in suspension of 0,5; 0,3, and 0,05 microns.

For the microscopy analysis, the samples were observed under an optical microscope with crossed polarizers. The mesophase count was carried out with a 10x eyepiece adjustment and a 50x objective. This count was determined via an analysis of 150 effective points (resin points do not count) selected in orderly fashion 2,6 mm between one point and another. Finally, the volumetric percentage of the mesophase was determined by applying the following expression:

Mesophase (% v/v) = (Number of anisotropic points)*(2/3)

To ensure the presence of the mesophase in the carbonized samples, it was analyzed asphaltene and preasphaltene specimens obtained at the three carbonization temperatures under a microscope (Leitz, Orthoplan) with polarized light equipped with a retarder plate or wedge plate 1/4 λ wave

and a 3-MPixel camera (Motic, Moticam 2300), from the Energy and Fuel Research Laboratory at Universidad Nacional de Colombia, Bogotá.

To capture the images, a Motic Live Imaging Module program was used and the following parameters were established to take the images: 50x objective, 180° polarization angle, 899-ms exposure time, 0 global gain, 0,96 red gain, 1,32 green gain, 0,98 blue gain, 2048 x 1536 resolution, -10 dark current, and 1 gamma. Additionally, immersion oil was used (Leitz Wetzlar) with refraction index (n_e^{23}) of 1,518 to improve image resolution.

Results and discussion

Characterization of the coal

The proximate, ultimate, and petrographic analyses of the coal used are shown in Table 1. Note that the coal presents great proportion in the vitrinite maceral and in the ash content, which may influence on the coal reactivity to obtain high yields of coal liquid extracts.

Table 1 Analysis of coal

Analysis	Value
Proximate, (% w/w, dry basis, db)	
Volatile matter	32.3
Ash	25.4
Fixed Coal	42.3
HHV, Btu/lb	10.160
Ultimate (% w/w, dry ash free, daf)	
C	76.6
H	5.4
N	1.6
S	1.9
O (difference)	14.5
H/C	0.845
O/C	0.142
Maceral, (% v/v, mineral matter free, mmf)	
Vitrinite	92.9
Liptinite	1.7
Inertinite	5.4

Coal liquid extracts

In the direct liquefaction process, two reactions took place, under the same operating conditions, to obtain the necessary amount of asphaltenes and preasphaltenes to subject them to treatments of carbonization, ultimate and proximate analysis, and softening point. The average yield obtained (dry ash-free, daf) from the coal liquid extract was 82% p/p. Those yields agree with yields obtained in another work using the same operating conditions [15].

Asphaltenes and preasphaltenes separated from coal liquid extract

Table 2 shows the compositions of the four fractions separated from the coal liquid extract: 1) residues (unconverted organic and mineral material), 2) preasphaltenes, 3) asphaltenes, and 4) oils. Note that the liquid extract presents a high proportion of oils, followed by the residues, preasphaltenes, and asphaltenes. The asphaltene and preasphaltene mixed fractions represent approximately 25% of the liquid extract, which is a considerable percentage for their conversion into mesophase.

Table 2 Composition of the coal liquid extract obtained during the DCL process

Products	Percentage, % w/w
Residues	17.8
Preasphaltenes	13.2
Asphaltenes	12.0
Oils	57.0

Table 3 presents the ultimate and proximate analyses of the asphaltenes and preasphaltenes obtained. Blanco [16] reported that the percentage of carbon and hydrogen present in asphaltenes and preasphaltenes is related both to their degree of aromaticity and the softening point of the solid organic material. It was also noted [16] that materials presenting the highest C/H ratio have a higher softening point. As it can be observed in Table 3, preasphaltenes presented a higher C/H

ratio than asphaltenes, agreeing with each of their softening points.

Table 3 Ultimate and proximate analyses of asphaltenes and preasphaltenes

	Asphaltenes	*Preasphaltenes*
Ultimate (% w/w, dry basis, db)		
C	87.0	87.9
H	5.0	4.4
N	2.4	1.5
O	4.8	4.5
S_{total}	0.7	0.7
C/H	1.5	1.7
Proximate (% w/w, dry basis, db)		
Volatile matter	59.2	73.8
Ash	0.2	0.9
Fixed Coal	40.6	25.3
HHV (Btu/lb)	15.056	15.872
Softening point, °C	140	150

Sulfur is an undesired element within the molecular structure of mesophase precursor materials because it acts as retarder that inhibits their development [17]. The results from Table 3 also show that preasphaltenes presented higher total sulfur ash percentage than asphaltenes, which affects production of the mesophase obtained from preasphaltenes compared to asphaltenes.

Also, organic materials with high C/H ratio usually have higher contents of volatile matter. This agrees with the obtained results. Table 3 shows the agreement between values of volatile matter and C/H ratio in preasphaltenes and asphaltenes.

Another aspect related to the C/H ratio of organic materials is represented by the heat of combustion [17]. Higher heat of combustion is usually present with materials presenting high C/H ratio. Results in Table 3 reveal that preasphaltenes presented higher heat of combustion than asphaltenes, which follows the obtained C/H ratio.

Carbonized from asphaltenes and preasphaltenes

The yields of carbonized obtained at 350, 400, and 450 °C during 3 hours, using asphaltenes and preasphaltenes are shown in figure 1.
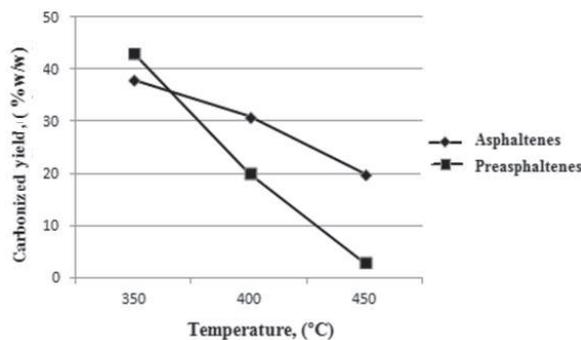

Figure 1 Yield of carbonized from asphaltenes and preasphaltenes as a function of temperature

Figure 1 shows that the yields obtained vary with the type of raw material used (asphaltenes and preasphaltenes), as well as with the temperature conditions. Those results agree with those obtained in other works [16, 17], which found that with higher temperature and reaction time, lower carbonization yields were obtained. It may be due to the release of a higher amount of volatile matter. It was noted that with lower carbonization temperature (350 °C) the yield of carbonized was higher in preasphaltenes than in asphaltenes, while at higher temperatures the behavior was the opposite. This may be due to the preasphaltenes release low amounts of volatile matter at 350 °C, compared to asphaltenes. However, at 400 and 450 °C, preasphaltenes release higher amounts of volatile matter than asphaltenes because of the higher content of volatile matter.

It was also found that preasphaltenes presented the lowest carbonization yield (3,3%) at 450 °C. This result may be due to the high operating temperature and to the high content of volatile matter of preasphaltenes, which was removed.

The ultimate analysis of carbonized asphaltene and preasphaltene samples is presented in Figure

2, showing that as temperature was increased the C/H ratio presented variations, which is evidence of the devolatilization that took place during the carbonization and, hence, the obtained low yields. It is, likewise, observed that the C/H ratio increased between 350 and 400 °C for both asphaltenes and preasphaltenes, indicating that volatile matter was hydrogen rich. While at temperatures above 400 °C this ratio decreased, given the loss of a higher proportion of carbon than hydrogen during carbonization, showing that more carbon-rich volatile matter was dragged.
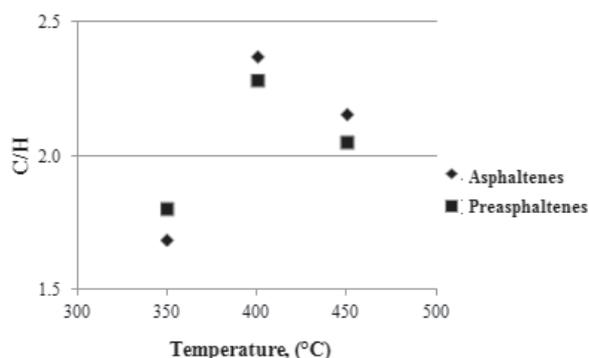
Figure 2 Effect of temperature on the C/H ratio of asphaltenes and preasphaltenes

Identification and quantification of the mesophase

The mesophase produced in the carbonized material from asphaltene and preasphaltene samples was identified via a microscope containing crossed polarizers. In this observation, the mesophase comprised of anisotropic particles presents a change of properties upon reflecting the light from different polarization angles, while the isotropic particles do not present that effect. Figure 3 shows mesophase particles, isotropic particles, and resin for a sample of carbonized material.

To confirm the presence of the mesophase in the carbonized samples from asphaltenes and preasphaltenes obtained at the three carbonization temperatures, the specimens were analyzed under a microscope with polarized light equipped with a ¼ λ retarder wave plate and the polarization

angle was fixed at 180°. The photography shown in figure 4a was obtained with the retarder plate, while that shown in figure 4b was obtained without retarder plate. In both figures, although slight color differences exist, the presence of the mesophase is observed.
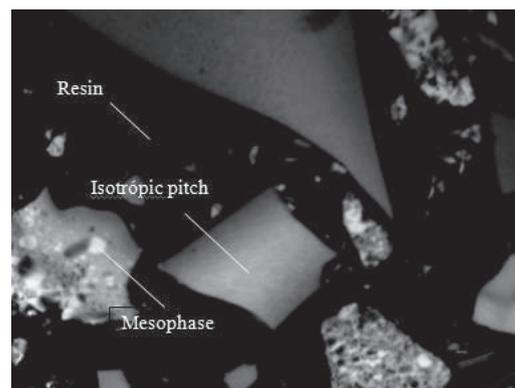

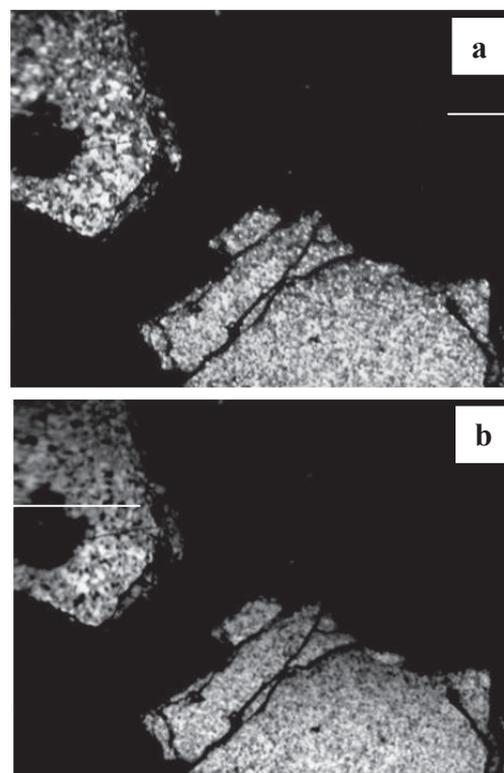**Figure 3** Identification of the mesophase

Figure 4 Photography of the mesophase for a sample of asphaltenes at 400 °C: (a) with a ¼ λ retarder wave plate; (b) without retarder plate

Figures 5a and 5b show mesophase particles from carbonized elements of asphaltenes obtained at 350 and 400 °C, respectively. The mesophase shown in figures 5a and 5b presents microspheres, which are distributed throughout the particle, while for a carbonization temperature of 450 °C the mesophase spheres coalesce (figure 5c). Also, the mesophase obtained from the carbonized of preasphaltenes at 350 °C presented isotropic behavior, as shown in figure 5d. For a temperature of 400 °C, figure 5e shows mesophase microspheres distributed throughout the particle and small regions where the mesophase coalesced. Likewise, figure 5f reveals that the mesophase spheres from preasphaltenes coalesced forming big anisotropic regions in the particle.
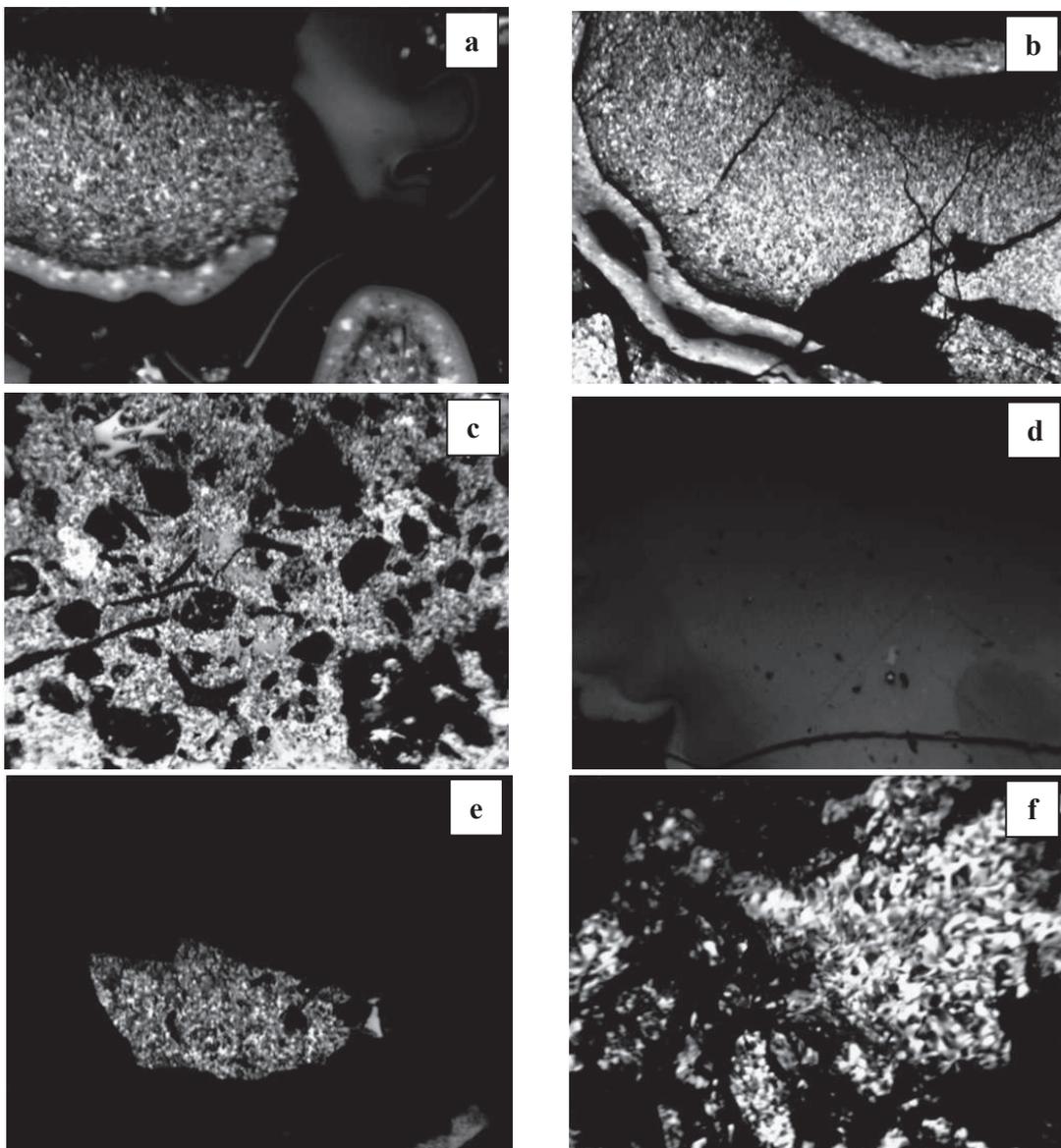

Figure 5 Mesophase obtained from: (a) asphaltenes at 350 °C; (b) asphaltenes at 400 °C; (c) asphaltenes at 450 °C; (d) preasphaltenes at 350 °C; (e) preasphaltenes at 400 °C; and (f) preasphaltenes at 450 °C

The results obtained from the mesophase count, for carbonized material from asphaltenes and preasphaltenes, are shown in figure 6.
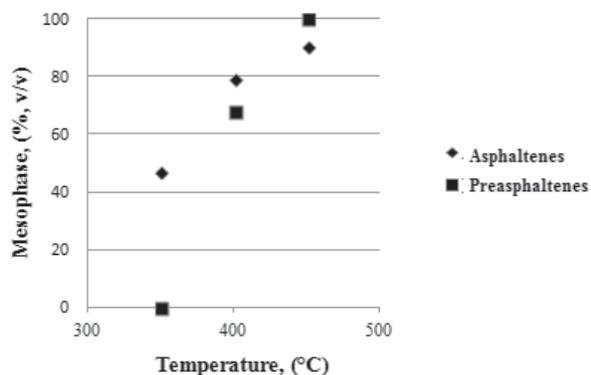

Figure 6 Mesophase obtained as a function of temperature

Upon analyzing the effect of temperature on obtaining the mesophase for either of the two carbonized material, it was noted that when increasing carbonization temperature the percentage of mesophase obtained increased. When comparing the results of the volumetric percentage of the mesophase obtained from carbonization of asphaltenes against preasphaltenes, it was noted that asphaltenes presented a higher percentage of mesophase within the temperature range of 350 to 400 °C; for 450 °C the opposite behavior was obtained. The aforementioned permits appreciating the dependence of the mesophase on temperature and the precursor material.

To determine the precursor and the best carbonization temperature condition producing the highest amount of mesophase, the yield was calculated during the carbonization stage (based on asphaltenes and preasphaltenes feeding the carbonization process) and the global mesophase production yield (based on the coal fed). Results are presented in figure 7 for carbonized material from asphaltenes and preasphaltenes, respectively.
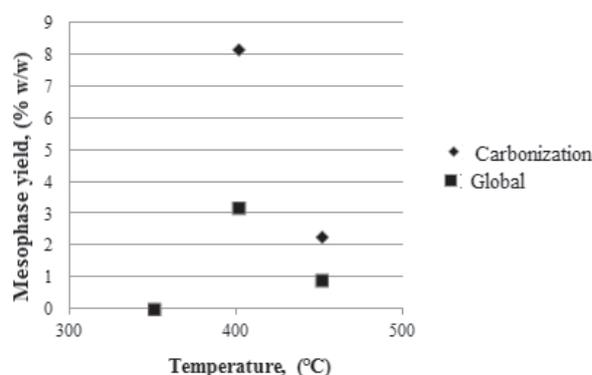

Figure 7 Yield of mesophase relative to carbonization stage and global process from asphaltenes and preasphaltenes

Both figures show that the highest yield of mesophase obtained during the carbonization process was 12,4% w/w, which is derived from asphaltenes carbonized at 400 °C. This due to the lower content of volatile matter of the asphaltenes compared to preasphaltenes. It is also noted that the highest global yield of the mesophase obtained from asphaltenes carbonized at 400 °C was 4,4% w/w. Those above results are relatively low. It can be due to the high release of volatile matter from asphaltenes. Values of mesophase yield from other works were not found.

In general, for all temperatures used, the asphaltenes produced higher mesophase yield during carbonization than the preasphaltenes. Both figures show that for the two yields a tendency exists to increase in the temperature range from 350 to 400 °C. Nevertheless, at 450 °C the mesophase yields decrease, due to the coalescence presented.

Conclusions

The asphaltene and preasphaltene fractions obtained from the coal liquid extract during the DCL process correspond to 25% w/w, representing a notable percentage for their conversion into mesophase. It was found that for asphaltene and preasphaltene fractions, the yields of their carbonized material decrease with increased temperature. The C/H ratio

in the carbonized obtained had a tendency to increase in the temperature range 350 to 400 °C for asphaltenes and preasphaltenes. However, at 450 °C, the C/H ratio diminished. The best precursor to produce mesophase was the fraction of asphaltenes carbonized at 400 °C, given that it produced the highest mesophase yield during the carbonization process (12,4% w/w) and the highest global yield of the process (4,4% w/w).

Acknowledgments

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