

GEOCHEMISTRY OF PETROLEUM: ASPHALTENES AS A SOURCE OF GEOCHEMISTRY INFORMATION

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ABSTRACT. Because of physical and geochemical similarity of asphaltenes with kerogen, the study of asphaltenes provides information for applications in geochemical petroleum. Either by thermal or by chemical oxidation, the substances obtained from asphaltenes are well correlated with the substances generated by the source rock during natural conditions. In this work, a theoretical study is performed from the information obtained from the research performed with asphaltenes, and their impact and applicability in the petrochemical and environmental industry is investigated.

Keywords: Asphaltenes; pyrolytic process; chemical oxidation; structure, composition and properties of asphaltenes.

RESUMO. Geoquímica do petróleo: asfaltenos como fonte de informação geoquímica. Devido à semelhança física e geoquímica dos asfaltenos com querogénio, o estudo de asfaltenos fornece informações para aplicações em geoquímica do petróleo. Seja por oxidação térmica ou química, as substâncias obtidas a partir de asfaltenos são bem correlacionadas com as substâncias geradas pela rocha fonte em condições naturais. Neste artigo é apresentado um estudo teórico a partir das informações obtidas em uma pesquisa realizada com asfaltenos, e seu impacto e a sua aplicabilidade na indústria petroquímica e ambiental é investigada.

Palavras-chave: asfaltenos; processo pirolítico; oxidação química; estrutura, composição e propriedades dos asfaltenos.

INTRODUCTION

With an increase in industrial and anthropogenic activities, demand for energy sources that enable their development will also increase. Fossil fuels, such as crude oil, coal and natural gas, are the largest source of non-renewable energy and raw material for many industrial processes. With massive consumption, reserves and deposits of fossil fuels will be exhausted. The time for its operation and the technological challenges associated with processing are also important. The difficulty extracting fossil fuels due to poor access to reservoirs and quarries, the compositional complexity of crude oil and the environmental requirements increases demand. With respect to oil, there are large reserves of crude oil that are categorized as being of low quality or having low viability, as a result of high viscosity and

density, thus increasing the complexity and cost of processing crude oil (AKBARZADEH et al., 2007; ALBOUDWAREJ et al., 2006; PINEDA-FLORES; BOLL-ARGÜELLO; MESTA-HOWARD, 2002; SOUSA; GONZALEZ; LUCAS, 2001). The content of NSO compounds (resins and asphaltenes) determines the quality of crude oil and is inversely related to the degree of density or viscosity and API gravity, i.e., greater content of NSO compounds corresponds a lower °API (ALAYÓN, 2004; BECKER, 1997; CHIABERGE et al., 2009; DELGADO, 2006; MÁRQUEZ; ALEJANDRE ; BENCOMO, 2006; SHARMIN; AMIT, 2014). Although a crude oil with a high asphaltene content (API <25, [10]) may cause complications in processing, transport and storage, reservoirs and deposits have large quantities that are yet untapped and can be an energy source and raw material for

innumerable industrial activities (AKBARZADEH et al., 2007; ALBOUDWAREJ et al., 2006; GONÇALVES; SILVA, 2010; LEHNE, 2008; MENDOZA et al., 2009; HALL et al., 2014).

The physicochemical properties and the inherent composition of the asphaltenes result in high resistance to degradative processes and high complexity in industrial processes. Chemically and structurally, asphaltenes are similar to kerogen. Therefore, to study asphaltene, it is important to obtain a particular geochemical oil from a particular origin (BECKER, 1997; CHRISTY; DAHL, Olav, 1989; DIECKMANN; CACCIALANZA; GALIMBERTIA, 2002; LEHNE; DIECKMANN, 2007; NALI ; CACCIALANZA, 2000; BUSHNEV; BURDEL'NAYA, 2009; HALL et al., 2014; SHARMIN; AMIT, 2014).

In considering the exposure, it is important to note the importance of studies and research directed at understanding the physical chemistry of the heavier petroleum fractions, i.e., resins and asphaltenes. This research aims to describe the physical chemistry of asphaltenes and its relation to kerogen as generating hydrocarbons and, therefore, as a source of geochemical information.

ASPHALTENES

Oil can be separated into two main fractions: maltenes, which correspond to saturated hydrocarbons, aromatic hydrocarbons and resins [18], and asphaltenes. Maltenes are also called deasphalted oil (LUO; WANG; GU, 2010).

Asphaltenes correspond to a more complex and heavy fraction of crude oil, and according to the definition given by Boussingault in 1837, asphaltenes correspond to residues of bitumen distillation, which are soluble in alcohol and insoluble in turpentine (AKBARZADEH et al., 2007; LEHNE, 2008; BUSHNEV; BURDEL'NAYA, 2009; OSPINO-CARO, 2009; PINEDA-FLORES; MESTA-HOWARD, 2001; QUINTERO, 2009; SÁNCHEZ, 2011). In general, asphaltenes are insoluble in an excess of normal alkanes (mainly n-pentane, n-hexane or n-heptane) and are soluble in polar or aromatic solvents, such as toluene, benzene or dichloromethane (AKBARZADEH et al., 2007; ALAYÓN, 2004; BECKER, 1997; DELGADO, 2006; MÁRQUEZ; ALEJANDRE; BENCOMO, 2006; OSPINO-CARO, 2009; SÁNCHEZ, 2011; GONZALEZ et al., 2010; JONES; DOUGLAS, 1987; THEUERKORN et al., 2008; SHARMIN; AMIT, 2014).

Chemically, asphaltenes consist of macromolecules that have high aromaticity and include the presence of heteroatoms, such as nitrogen, oxygen and sulfur, and metals, such as nickel and vanadium, which together form metal-organic compounds called porphyrins (SOUSA et al., 2001; BECKER, 1997; MENDOZA et al., 2009;

BUSHNEV; BURDEL'NAYA, 2009; SÁNCHEZ, 2011; MULLINS et al., 2007; PETERS; MOLDOVAN, 1990; PREMOVIC; JOVANOVIC, 1997; TISSOT; WELTE, 1982; SNOWDON et al., 2015; SHARMIN; AMIT, 2014).

Because of their complex physical chemistry, asphaltenes are highly stable and resistant to degradative processes. As a result, studying asphaltenes allows us to determine the geochemical characteristics of degraded or immature oil, and the information obtained can be used to determine the parameters associated with the geochemical type of the organic matter that produced said oil, as well as the maturity level and the depositional paleo-environment among other factors.

Regarding industrial applications, by analyzing a sample of asphaltic or degraded oil, it is possible to determine oil/oil and oil/source rock correlations and generate technology tools that support the processing, treatment and disposal of asphaltenic substances (PINEDA-FLORES; BOLL-ARGÜELLO; MESTA-HOWARD, 2002; GONZALEZ et al., 2010; ORTEGA et al., 2007; QUINTERO et al., 2007; SNOWDON et al., 2015).

Physical Properties of Asphaltenes

One model to describe the physical and chemical behavior of asphaltenes in a certain crude oil is based on thermodynamic models of colloids (AKBARZADEH et al., 2007; ALAYÓN, 2004; DELGADO, 2006; GÜRGEY, 1998; QUINTERO et al., 2007; DUNN; YEN, 2006; JONES; DOUGLAS, 1988). In this model, asphaltenes are immersed in maltenes as rigid micellar aggregates (colloid type), and these aggregates are maintained in suspension through the action of resins, which that generate a surface film of conglomerate asphaltenics through a temporary intermolecular association (AKBARZADEH et al., 2007; SOUSA et al., 2001; DELGADO, 2006; MÁRQUEZ; ALEJANDRE; BENCOMO, 2006; GÜRGEY, 1998; OSPINO-CARO, 2009; SÁNCHEZ, 2011; MULLINS et al., 2007; ALI; GHALOUM; HAUSER, 2006; MURGICH; ABANERO, 1999; SHARMIN ; AMIT, 2014). The forces of attraction, such as repulsion type electrostatic and van der Waals, are generated at the interface of maltenes and asphaltenes and are responsible for maintaining the asphaltenes in suspension in the maltenic phase (DELGADO, 2006; OSPINO-CARO, 2009; SÁNCHEZ, 2011; QUINTERO et al., 2007).

The concentration of asphaltenes directly influences the rheological properties of a specific crude oil. In conditions of normal atmospheric pressure and temperature, aggregate asphaltenics increase the conglomerate size, and the concentration of asphaltenes increases (DELGADO, 2006; MÁRQUEZ; ALEJANDRE; BENCOMO, 2006; MULLINS et al., 2007; MUHAMMAD; ABBOTT, 2013; SHARMIN; AMIT,

2014). as a result of an increase in the weight of the crude oil and an increase in the viscosity and density of the crude oil due to decreasing the maltene-asphaltene interface (DELGADO, 2006).

Studies by Akbarzadeh et al. (2007), Delgado (2006), Gürgey (1998), Luo et al. (2010) and Sánchez (2011), have assessed the solubility and the separation of asphaltenes. These studies have provided information concerning the characteristics of the asphaltenes that depend on the type of n-alkane that was used in the separation of asphaltenes based on their solubility/insolubility and the level of asphaltenic aggregation in the presence of linear alkanes.

The solubility limit and the separation of an asphaltene contained in a certain crude oil are influenced by the n-alkane used in the process, the ratio of oil to asphaltene, the contact time, the temperature and the type of physical process used for the separation (ALAYÓN, 2004; DELGADO, 2006; GÜRGEY, 1998; LUO et al., 2010; SÁNCHEZ, 2011; MULLINS et al., 2007; JONES; DOUGLAS, 1988; MUHAMMAD; ABBOTT, 2013; ANGLE et al., 2006; SHARMIN; AMIT, 2014). The separation produces asphaltenes with various molecular weights and diverse polarities (DELGADO, 2006; GÜRGEY, 1998). For instance, asphaltenes obtained from precipitation with n-heptane have a greater molecular weight and a greater polarity, which reflects the chemical complexity compared to asphaltenes separated with n-octane (DELGADO, 2006). Differences in molecular weights and polarities are possibly associated with the co-precipitation of small amounts of maltenes that are adhered on the surface of the asphaltene (GÜRGEY, 1998).

Chemical Properties

Asphaltenes are mainly composed of the following elements: carbon, hydrogen, nitrogen, sulfur, oxygen, nickel and vanadium (Table 1). Asphaltenes exhibit high aromaticity and include structures such as benzenic, ciclopentadénics, pyridines, pyrolytic, tiophenics, terpenes, phenolic resins, ketones, carboxylic acids, amino, amide, conjugated bonds with heteroatoms, polyaromatic rings and organometallic structures coordinated with nickel and vanadium (PINEDA-FLORES BOLL-ARGÜELLO; MESTA-HOWARD, 2002; ALAYÓN, 2004; BECKER, 1997; CHIABERGE et al., 2009; DELGADO, 2006; LEHNE, 2008; MENDOZA et al.,

2009; CHRISTY; DAHI; Olav, 1989; LUO; WANG; GU, 2010; OSPINO-CARO, 2009; PINEDA-FLORES; MESTA-HOWARD, 2001; QUINTERO, 2009; GONZALEZ et al., 2010; JONES; DOUGLAS, 1987; MULLINS et al., 2007; PREMOVIC; JOVANOVIC, 1997; ORTEGA et al., 2007; JONES; DOUGLAS, 1988; MURGICH; ABANERO, 1999; MUHAMMAD; ABBOTT, 2013; AZEVEDO; FREITAS; BASTOS, 2009; LIAO et al., 2006a; LIAO et al., 2006b; HALL, 2014).

The high level of aromaticity of asphaltenes favors the generation of electron clouds of type π - π on the molecular surface of the asphaltene (OSPINO-CARO, 2009; QUINTERO, 2009; ORTEGA et al., 2007; MUHAMMAD; Abbott, 2013; BUENROSTRO-GONZALEZ, et al., 2001; LIAO et al., 2005). The high polarity of asphaltenes is associated with the presence of multiple bonds and the presence of the heteroatoms nitrogen, sulfur and oxygen (DELGADO, 2006; QUINTERO et al., 2007; SNOWDON et al., 2015).

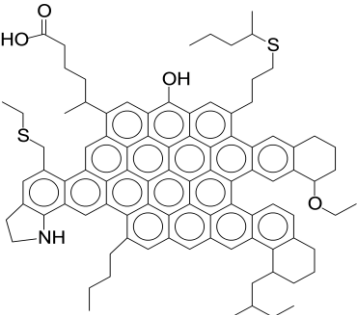
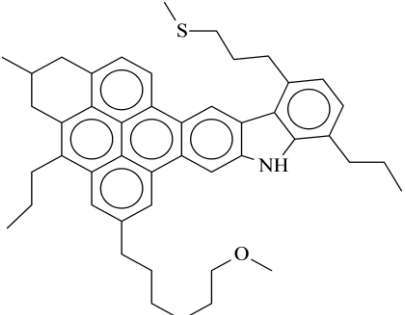
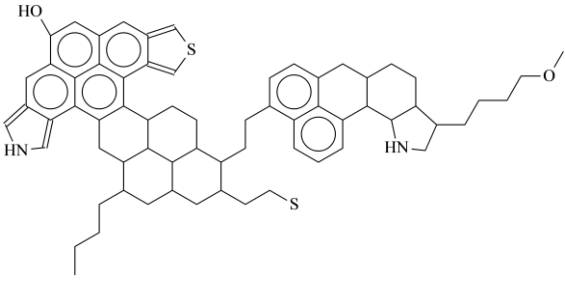
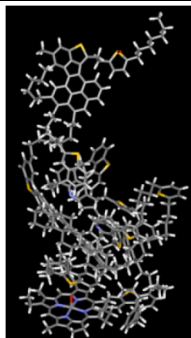
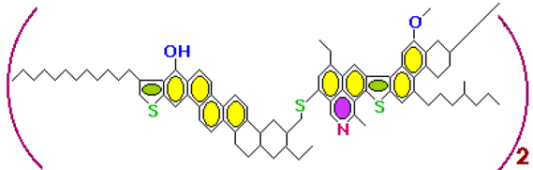
Defining the chemical structure of asphaltene has required several research studies and the application of various analytical tools in addition to extensive knowledge of organic chemistry that allows for the possible elucidation of the asphaltenic structure. Some specific chemical structures of asphaltenes have been described hypothetically, and some have been described with great accuracy. Table 2 shows the molecules found as a result of this research.

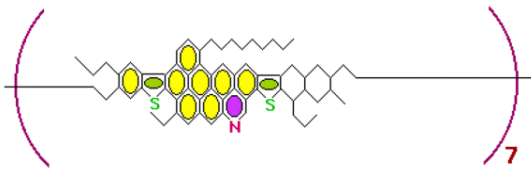
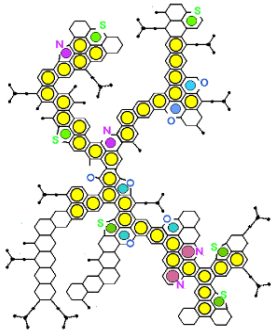
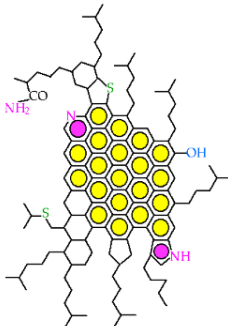
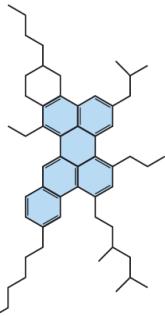
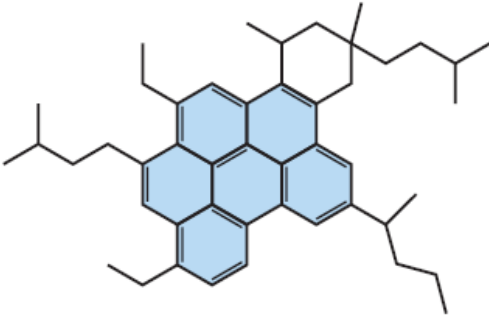
As asphaltenes are composed of macromolecules and are complex, there has been much controversy in determining the exact molecular mass of asphaltene. Similarly, depending on the type of asphaltene, it is possible to know the structure and the composition, and the molecular weight of asphaltene can range from 5 to 2,000,000 Daltons (AKBARZADEH et al., 2007; PINEDA-FLORES; BOLL-ARGÜELLO; MESTA-HOWARD, 2002; DELGADO, 2006; MÁRQUEZ; ALEJANDRE; BENCOMO, 2006; LEHNE, 2008; QUINTERO, 2009; JONES; DOUGLAS, 1987; MULLINS et al., 2007; QUINTERO et al., 2007; ALI; GHALOUM; HAUSER, 2006; AZEVEDO; FREITAS; BASTOS, 2009; LIAO et al., 2006a; GROENZIN; MULLINS, 2000; CARVALHO et al., 2003; BUENROSTRO-GONZALEZ et al., 2001; KEYM, 2008; LIAO et al., 2005; XIANMING et al., 1998; SNOWDON et al., 2015).

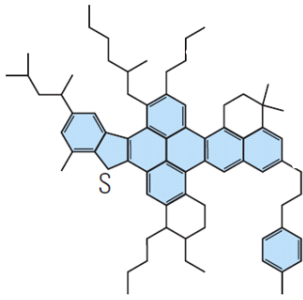
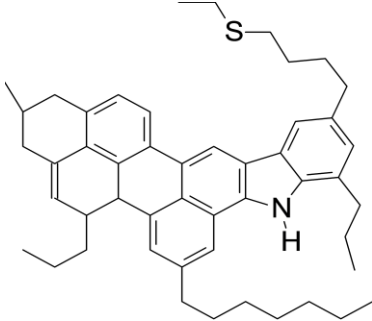
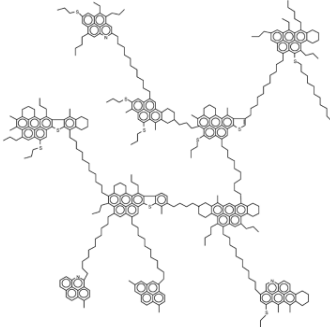
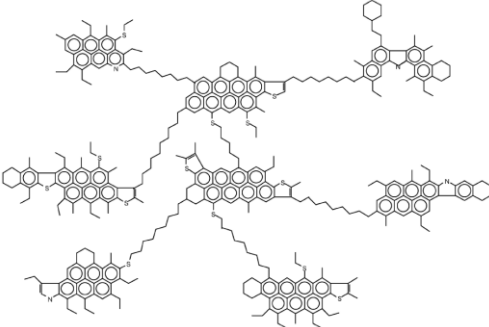
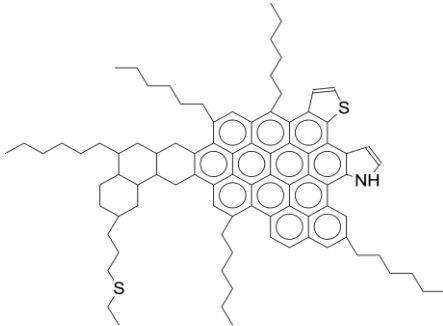
Table 1- General characteristics of asphaltenes determined from the references consulted. Values presented correspond to the extreme values found

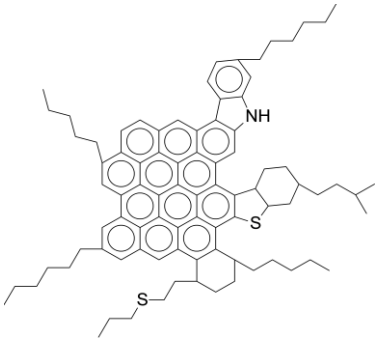
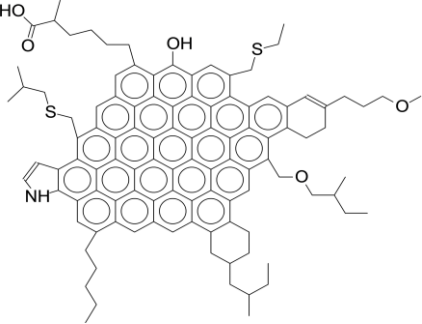
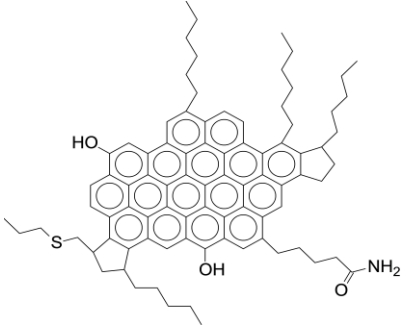
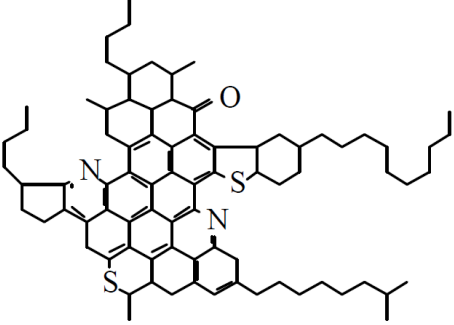
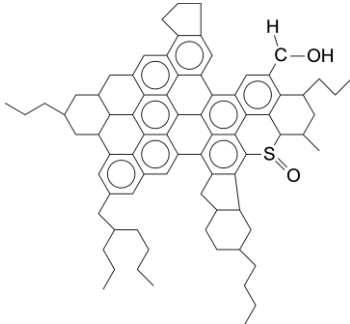
PROPERTY	QUANTITY	OBSERVATION	REFERENCES
<i>Primary composition:</i>			
Carbon, C (%)	80,0 – 84,0	Extreme values from references consulted for primary components of asphaltenes.	Sousa et al., 2011; Alayón, 2004; Becker, 1997; Chiaberge et al., 2009; Delgado, 2006; Márquez; Alejandre; Bencomo, 2006; Pineda-Flores; Mesta-Howard, 2001; Groenzin; Mullins, 2000; Koopmans et al., 1999; Silva et al., 2008; Sonibare et al., 2009.
Hydrogen, H ₂ (%)	8,0 – 10,0		
Nitrogen, N ₂ (%)	0,2 – 1,2		
Sulfur, S (%)	1,2 – 3,0		
Oxygen, O ₂ (%)	0,2 – 0,7		
Nickel, Ni (%)	0,8 – 6,0		
Vanadium, V (%)	0,3 – 4,4		
<i>Mean of atomic ratio:</i>			
C/H	0,9	Increased ratio of carbon/heteroatom indicates increased polarity and aromaticity of asphaltene and direct indication of decreased C/H.	Buenrostro-Gonzalez et al., 2007; Alayón, 2004; Delgado, 2006; Quintero, 2009; Carvalho et al., 2003
C/O	47,7		
C/S	29,0		
C/N	84,2		
<i>Type compounds:</i>		<i>Grupos funcionais:</i>	
Saturated acyclic and cyclic hydrocarbons; Aromatic hydrocarbons; Heterocyclic compounds, with nitrogen, sulfur and/or oxygen; Organometallic compounds, mainly with nickel, vanadium and iron.	Not reported	Naphthalene; Terpenes; Carboxylic acids: alkyl, aryl and mixed; Ketone and Aldehyde; Benzothiophene and dibenzothiophene; Naftenobenzothiophene; Alkyl and aryl sulfide and mixed; Alkyl benzene and Aryl benzene; Pyrrole; Pyridine; Thiophenes; Porphyrins - among the most frequent.	Sousa et al., 2001; Becker, 1997; Chiaberge et al., 2009; Delgado, 2006; Lehne, 2008; Christy; Dahi; Kvalheim, 1989; Luo; Wang; Gu, 2010; Ospino-Caro, 2009; Pineda-Flores; Mesta-Howard, 2001; Quintero, 2009; Gonzalez et al., 2010; Jones; Douglas, 1987; Mullins et al., 2007; Premovic; Jovanovic, 1997; Jones; Douglas; Connan, 1988; Murgich; Abanero, 1999; Liao et al., 1996, 2006a,b; Sonibare et al., 2009.
<i>Molecular mass:</i>			
a.m.u.	5 to 2000000	a.m.u.: atomic mass units. 1 a.m.u. ≈ 1 Dalton	Akbarzadeh et al., 2007; Alboudwarej et al., 2006; Becker, 1997; Gúrgey, 1998; Jones; Douglas, 1987; Murgich; Abanero, 1999; Liao et al., 2006a; Liao et al., 2006b; Liao et al., 1996; Buenrostro-Gonzalez et al., 2001; Liao et al., 2005; Barth et al., 1995; Fowler; Brooks, 1987; Lewan, 2011; Michels et al., 1996; Mukhopadhyay; Wade; Kruge, 1995.
<i>Mean Density:</i>			
g/mL	1,2	Equivalent mean reported by researchers.	Delgado, 2006; Quintero, 2009
<i>Smallest unit:</i>			
Colloid	Thousands of angstroms	Equivalent to three-dimensional networks for forming temporary micellar colloids.	Delgado, 2006; Murgich, Abanero, 1999
<i>Precipitating agent:</i>			
n-alkane	1:20 to 1:40	<i>Primarily:</i> n-pentane, n-hexane, n-heptane e n-octane. Proportion by weight of oil: precipitant.	Akbarzadeh et al., 2007; Alayón, 2004; Becker, 1997; Delgado, 2006; Márquez; Alejandre; Bencomo, 2006; Luo; Wang; Gu, 2010; Ospino-Caro, 2009; Sánchez, 2011; Gonzalez et al., 2010; Jones; Douglas, 1987; Theuerkorn et al., 2008.

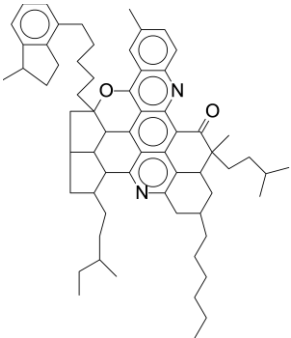
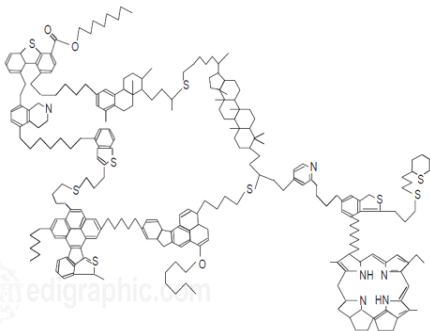
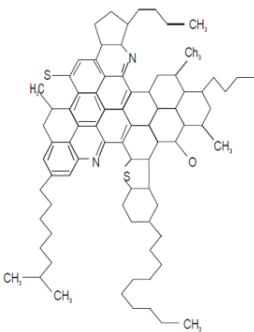
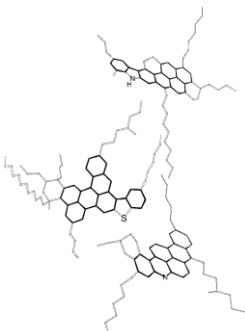
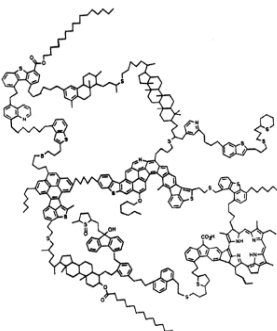
Table 2 - Possible structures for the asphaltene molecule that have been proposed by several researchers

STRUCTURE	OBSERVATIONS	REFERENCE
	<p>Continental-type structure proposed for high molecular weight asphaltenes.</p>	<p>Sánchez, 2011</p>
	<p>Archipelago-type structure proposed for lower molecular weight asphaltenes.</p>	<p>Sánchez, 2011</p>
	<p>Possible chemical structure of an asphaltene molecule.</p>	<p>Sánchez, 2011</p>
	<p>3D model for an asphaltene molecule.</p>	<p>Buenrostro-Gonzalez,201</p>
	<p>Average molecular structural models of Athabasca fractions of bitumen and bituminous sandstone; asphaltene fraction of bituminous sandstone.</p>	<p>Lehne,2008</p>

	<p>Average molecular structural models of Athabasca fractions of bitumen and bituminous sandstone; asphaltene fraction proposed by Suzuki et al. (1982).</p>	<p>Lehne,2008</p>
	<p>Asphaltenic molecular structure proposed for crude oil from the Maya of Mexico.</p>	<p>Lehne,2008</p>
	<p>Asphaltenic molecular structure proposed for a 510°C residue of a crude oil from Venezuela.</p>	<p>Lehne,2008</p>
	<p>Asphaltenic molecular structure, blue aromatic rings. Includes a cyclohexane ring and aliphatic chains around the aromatic nucleus.</p>	<p>Akbarzadeh et al.,2007</p>
	<p>Asphaltenic molecular structure, blue aromatic rings. Includes a cyclohexane ring and aliphatic chains around the aromatic nucleus.</p>	<p>Akbarzadeh et al.,2007</p>

	<p>Asphaltenic molecular structure, blue aromatic rings. Rings include cyclohexane in aliphatic chains around the aromatic nucleus and sulfur within a heteroatomic pentacyclo.</p>	<p>Akbarzadeh et al.,2007</p>
	<p>Proposed molecular structure for asphaltenes from oil illustrating the different sizes of rings and the content of aliphatic and heteroatoms.</p>	<p>Mullins et al.,2007</p>
	<p>Asphaltenic structure presented for number 4 GPC obtained from asphaltenes VR - Kuway. GPC: <i>Gel-Permeation Chromatography</i>.</p>	<p>Ali; Ghaloum; Hauser,2006</p>
	<p>Asphaltenic structure presented for number 4 GPC obtained from asphaltenes AR – Kuway. GPC: <i>Gel-Permeation Chromatography</i>.</p>	<p>Ali;Ghaloum;Hauser,2006</p>
	<p>Asphaltenic structure: condensed aromatic core with aliphatic side chains and the presence of heteroatoms inserted into linear and cyclic structures.</p>	<p>Delgado,2006</p>

	<p>Asphaltenic structure: condensed aromatic core with aliphatic side chains and the presence of heteroatoms inserted into linear and cyclic structures.</p>	<p>Delgado,2006</p>
	<p>Asphaltenic structure: aromatic nucleus condensed with aliphatic side chains and presence of heteroatoms inserted into a linear structures.</p>	<p>Delgado,2006</p>
	<p>Asphaltenic structure: aromatic nucleus condensed with aliphatic side chains and presence of heteroatoms inserted into a linear structures.</p>	<p>Delgado,2006</p>
	<p>Hypothetical structure for samples of asphaltenes, oils sedimentary basins of Brazil.</p>	<p>Silva;Azevedo, 2010</p>
	<p>Chemical structure for a sample of asphaltene.</p>	<p>Alayón,2004</p>

 <p>A complex chemical structure of asphaltene, featuring a central polycyclic aromatic hydrocarbon core with multiple fused rings. It is heavily substituted with various side chains, including long alkyl chains, branched alkyl groups, and heteroatoms like oxygen and nitrogen. The structure is highly branched and irregular.</p>	<p>Chemical structure for a sample of asphaltene.</p>	<p>Alayón,2004</p>
 <p>A highly branched and complex molecular structure of asphaltene, showing a large, interconnected network of fused aromatic rings. The structure includes numerous sulfur and nitrogen atoms, along with long alkyl chains and other functional groups. A watermark 'medigraphic.com' is visible in the lower-left area.</p>	<p>Asphaltene molecular structure proposed by Strausz and Murginch (1999).</p>	<p>Pineda-Flores,2001</p>
 <p>A complex asphaltene molecular structure with a central polycyclic aromatic core. It features several methyl groups (CH₃) and long alkyl chains attached to the core. The structure is highly branched and includes sulfur and nitrogen atoms.</p>	<p>Asphaltene molecular structure proposed by Speight and Moschopedis (1981).</p>	<p>Pineda-Flores,2001</p>
 <p>A hypothetical asphaltene molecular structure showing a large, interconnected network of fused aromatic rings. The aromatic rings are highlighted with darker lines, and the structure is highly branched and irregular.</p>	<p>Hypothetical molecular structure, which is consistent with the molecular size and chemical speciation of asphaltenes. The aromatic rings are shown with darker lines.</p>	<p>Groenzin; Mullins,2000</p>
 <p>A complex asphaltene molecular structure showing a large, interconnected network of fused aromatic rings. The structure is highly branched and irregular, with many long alkyl chains and other functional groups attached to the core.</p>	<p>Proposal for the dimensional molecular structure of asphaltenes from a sample of Athabasca bituminous sandstone.</p>	<p>Murgich; Abanero,1999</p>

Asphaltenes with respect to Kerogen

Because of their compositional and structural similarities with kerogen, asphaltenes are considered to be part of the kerogen group. There is a hypothesis that defines the origin of asphaltenes as the intermediate state between normal kerogen and the hydrocarbons generated by organic matter in the oil generation window (DELGADO, 2006; LEHNE, 2008; SILVA et al., 2008; GENG; LIAO, 2002; LEHNE et al., 2009; PRIMIO di; HORSFIELD; GUZMAN-VEGA, 2000; VANDENBROUCK; LARGEAU, 2007). In the reservoir, asphaltenes are a more unstable fraction of kerogen (SILVA et al., 2008; GENG; LIAO, 2002) or a soluble fraction of kerogen (LIAO et al., 2005).

Another hypothesis that relates asphaltenes to kerogen is based on the physicochemical characteristics of asphaltenes, which, owing to their high aromatic composition, are sometimes interconnected by aliphatic chains and cause asphaltenes to have certain dimensional structures in the form of "cages" or boxes (AZEVEDO; FREITAS; BASTOS, 2009; LIAO et al., 2006a). These structures favor the storage or "occlusion" of certain hydrocarbon-type substances. These well-preserved hydrocarbons are "extracted" or recovered by oxidative, non-aggressive processes to study and evaluate the similarity of the geochemical information obtained from the compounds (AZEVEDO; FREITAS; BASTOS, 2009; SILVA et al., 2008; PRIMIO di; HORSFIELD; GUZMAN-VEGA, 2000).

Thermal oxidation

Pyrolytic techniques are used to produce hydrocarbons based on the hypothesis that asphaltenes are part of the kerogen group (SANTAMARÍA OROZCO; AMEZCUA ALLIERI; CARRILLO HERNÁNDEZ, 2009). Geng e Liao (2002) and Primio et al. (2000) presented papers in which the pyrolysis of asphaltenes is used as a tool to determine the kinetic characteristics and thermal maturity level of some of asphaltenes and degraded oils (bituminous sandstones) to correlate with the data from the R_o (Vitrinite reflectance) of the kerogen precursor. These authors evaluated T_{max} , S_1 and S_2 (T_{max} is the maximum temperature generation of hydrocarbons during pyrolysis, S_1 is the amount of hydrocarbons freely adsorbed on the surface of shale, and S_2 is the potential generator of the shale oil. S_1 and S_2 are expressed as hydrocarbons in milligrams per gram of rock) and the profile of the hydrocarbons generated by using a pyrochromatograph. The results showed that the asphaltenes that were evaluated were from various types of kerogen, and these asphaltenes have great potential to produce hydrocarbons. In the same context, Barth and colleagues (BARTH; SEIM; CHRISTY, 1995) used multivariate modeling based

on a Fourier transform. The geochemical behavior of kerogen and asphaltene samples analyzed followed models to determine the maturity of the natural kerogen parameters and the pyrolyzed asphaltenes.

In 1979, D.M. Lewan and colleagues implemented a technique based on pyrolysis, but they used water as reaction medium. This technique is called hydrolysis (LEWAN, 2011; LEWAN; WINTERS; MCDONALD, 1979) and resulted in a series of studies that had great accuracy in elucidating the mechanisms and routes of hydrocarbon generation from kerogen. The presence of water during artificial thermal oxidation is a result of the fact that water becomes a source of hydrogen and oxygen and is similar to geochemical reactions that occur in nature (LEWAN; WINTERS; MCDONALD, 1979; BARKER; LEWAN, 2010; LEWAN; ROY, 2011; LEWAN, 2010; PAN et al., 2008).

Although pyrolysis allows the generation of light hydrocarbons (KÖK; PAMIR, 1995), more complex molecules, such as biological markers, are not obtained in sufficiently abundant molecular quantities to be evaluated by analytical techniques such as mass chromatography. This is where the presence of water, hydrogen and oxygen will react with the active sites of free radicals present in the molecular asphaltene or kerogen during cracking or hydrothermal oxidation (Figure 1).

To guarantee that the compounds generated during thermal oxidation are products of complex cracking fractions of asphaltene or kerogen, it is necessary to ensure that the sample is free of the lighter fractions, such as saturated hydrocarbons, aromatics or resins, which may be easily oxidized for the substances of interest.

Chemical oxidation (soft oxidation)

The oxidation chemistry is based on the hypothesis that the three-dimensional structure of asphaltene compounds is preserved. In soft oxidation, (Figure 2), an oxidizing agent, which is in a basic or acid medium, reacts on pi (π)-type links of the aromatic nuclei or unsaturated chains, which breaks the multiple bonds and introduces a functional group (hydroxy or acid, for example), which allows the product to be differentiated and occluded within the "oxidized" structure (SÁNCHEZ, 2011; AZEVEDO; FREITAS; BASTOS, 2009; LIAO et al., 2006a; LIAO et al., 2006b; SILVA; SILVA; AZEVEDO, 2010).

Based on the model described by Sanchez (2011), Ali et al. (2006) achieved soft oxidation and a model asphaltene molecule (Table 2). Figure 3 describes "hypothetical" soft oxidation. Initially, an asphaltene grouping is linked by chains or aliphatic "bridges". The oxidation occurs in fraction "A" where the aliphatic bridge is attached to an aromatic carbon in an upright (sp type) manner, and in fraction "B",

the aliphatic chain is linked to a carbon sp^2 . At the end of the oxidative process, the fractions that are liberated contain "hydroxy" functional groups, which will differentiate the fractions entrapped within the open structure as a result of the soft oxidation.

As the soft oxidation process requires thermal oxidation in advance, the sample must be free of asphaltenes, maltenes and resins adsorbed on their surface.

INFORMATION OBTAINED FROM THE STUDY OF ASPHALTENES

According to the type and the focus of the research, studying asphaltene can provide significant information about the physical and geochemical properties of oil and have a wide range of applications. Table 3 (page 96) summarizes some work based on the study of asphaltenes and the type of information provided by such investigations.

Figure 1 - Suggested reaction paths for the thermal cracking of organic matter, kerogen type or asphaltene in a closed system and in the presence or absence of water (hydropyrolysis and pyrolysis). Adapted from Lewan (2010)

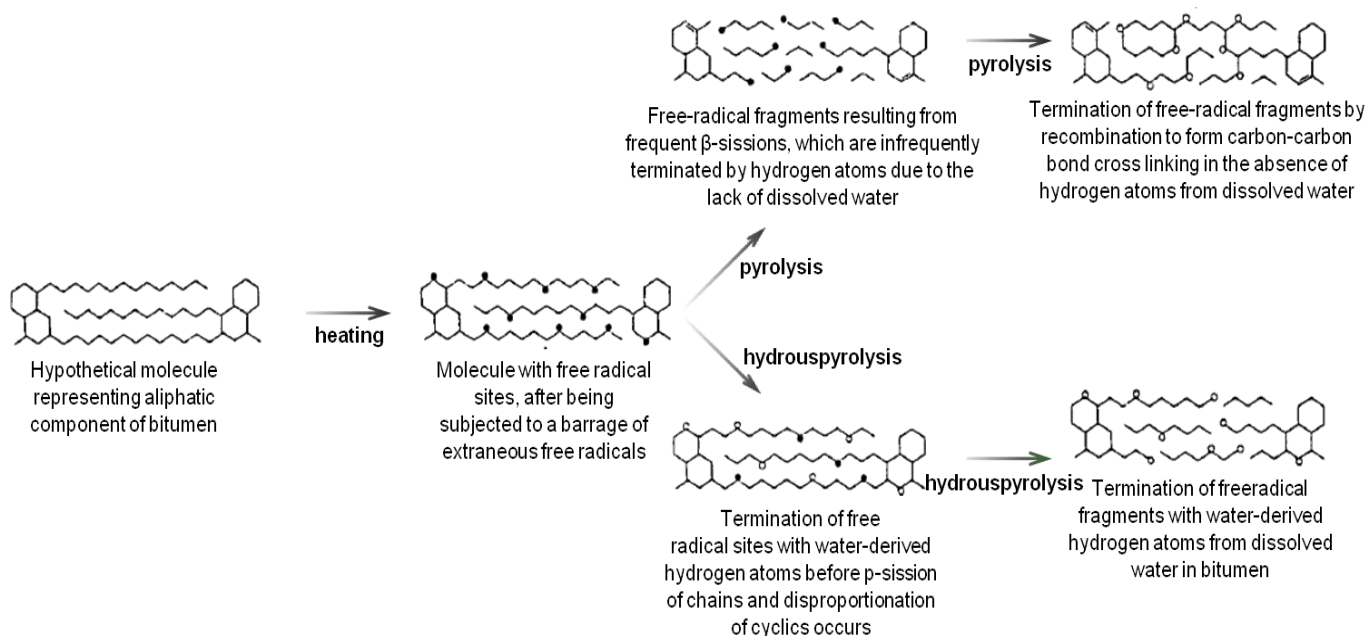


Figure 2 - Soft oxidation of asphaltenes groups. Adapted from Sánchez (2011)

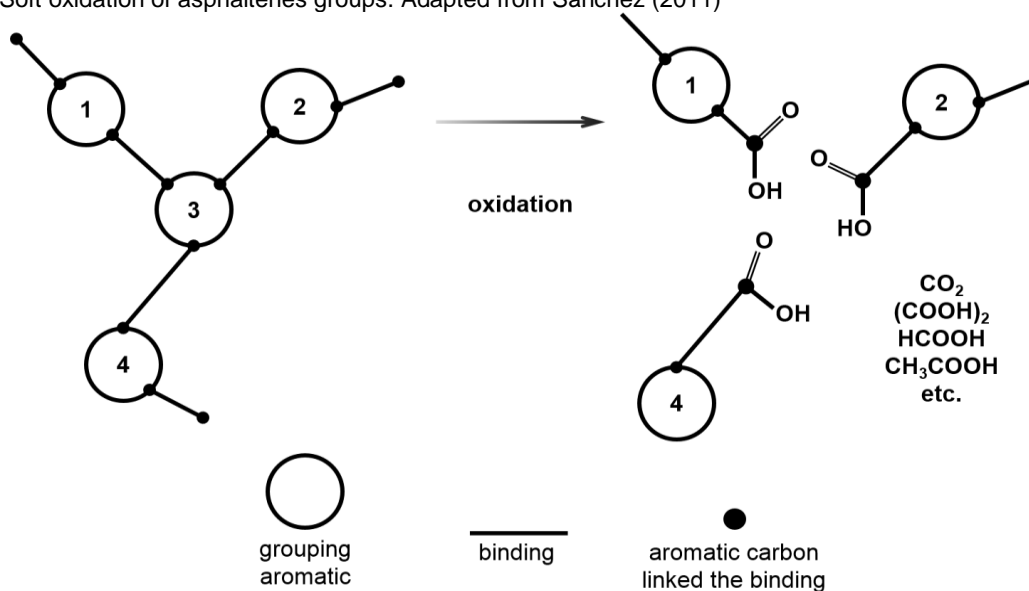
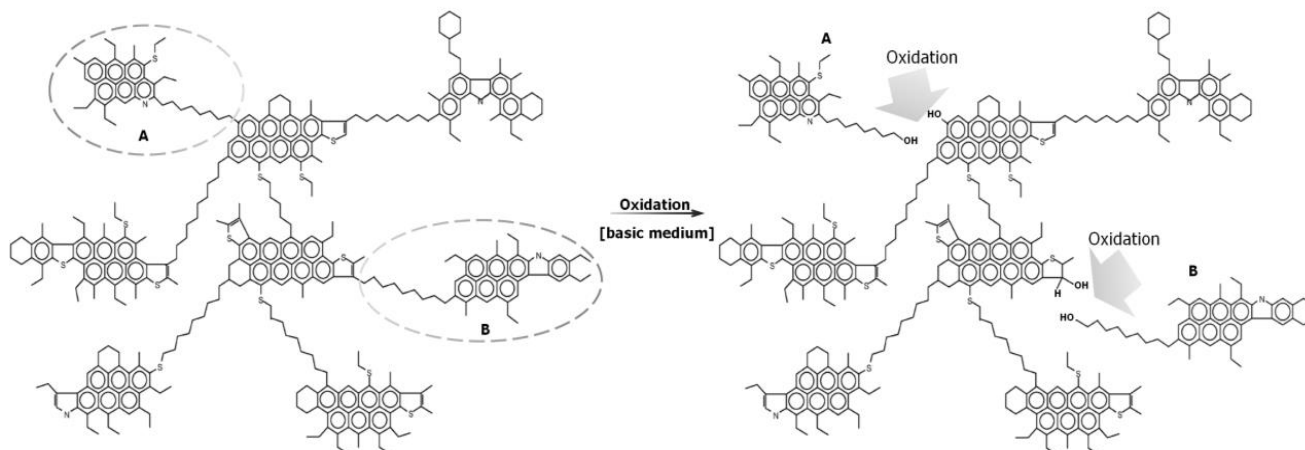


Figure 3 – Hypothetical soft oxidation of asphaltene groups. Adapted from Sánchez (2011) e Ali et al. (2006)

CONCLUDING REMARKS

Because of physicochemical similarities of asphaltenes with kerogen, it is possible to study the generation of the information obtained from the compounds originating from the oxidation of asphaltenes. This information has wide application both within science and in technological industries, such as in the petroleum and environmental industries.

The geochemistry of asphaltenes is a line of scientific and technological research that presents great advantages to study the application due to the plurality of heavy oils in the asphaltene.

Discerning the physical geochemistry of asphaltenes will provide fundamental knowledge concerning the target geochemistry of petroleum, environmental geochemistry and technologies and methodologies related to the processing of heavy oils, degraded oils and waste accumulations or backgrounds rich in asphaltenes.

In the near future, we can anticipate a growth of publications devoted to new approaches of studies to the asphaltenes because today there is a great interest in the recovery of heavy oil in petroleum reservoirs. Also is priority of studies of recalcitrant fractions of oil in case of spills.

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Table 3 - Information provided from the study of asphaltenes based on the publications reviewed in this paper

THE INFORMATION PROVIDED ASPHALTENES	IMPLICATIONS GEOCHEMICAL OR PHYSICOCHEMICAL	REFERENCE
Description of the chemical and physical properties.	Knowledge of the rheological characteristics: density, viscosity and solubility. Elucidation of possible chemical structures.	Akbarzadeh et al., 2007; Becker, 1997; Quintero, 2009; Mullins et al., 2007; Ortega et al., 2007; Quintero et al., 2007
Description of physical properties.	Knowledge of the rheological characteristics: density, viscosity, solubility and flocculation.	Sousa; Gonzalez; Lucas, 2001; Alayón, 2004; Delgado, 2006; Márquez; Alejandre; Bencomo, 2006; Mendola et al., 2009; Theuerkorn et al., 2008; Angle et al., 2006
Structure and composition.	Description of the chemical structure.	Ali; Ghaloum; Hauser, 2006; Murgich; Abanero, 1999
Biomarkers occluded.	Description geochemistry, defining the parameters and geochemical profile.	Sánchez, 2011; Azevedo; Freitas; Bastos, 2009; Liao et al., 2006a,b; Silva et al., 2008; Liao et al., 2005; Silva; Azevedo, 2010; Silva; Silva; Azevedo, 2010
Parameters of maturity.	Correlation of the maturity parameter obtained from the asphaltenes with those obtained from the pyrolysis of source rock.	Lewan, 2011
Composition molecular weight.	Physicochemical description of heavy oils.	Borges; Acevedo, 2007
Chemical properties.	Definition of chemistry composition.	Buenrostro-Gonzalez et al., 2001
Solubility.	Influences the structure and composition depending on the solubility.	Luo; Wang; Gu, 2010; Carvalho et al., 2003
Chemical structure.	Evaluation of the elemental composition and the degree of aromaticity of the presence of the heteroatoms nitrogen, sulfur and oxygen.	Chiaberge et al., 2009
Chemical structure.	Similarity between resins, asphaltenes and kerogen.	Christy; Dahi; Olav, 1989; Philp; Bakel; Galvez-Sinibaldi, 1988.
Generation of hydrocarbons and biomarkers.	Correlation kinetics of oil generation, study of the geochemistry of the oils generated and correlation with the source rock. Evaluation geochemistry and oil/rock and oil/oil correlation.	Lehne, 2008; Dieckmann; Caccialanza; Galimbertia, 2002; Yasar; Trauth; Klein, 2001; Dominguez; Poley; Azevedo, 2008; Silva; Silva; Azevedo, 2010.
Route reaction.	Geochemical behavior and type of chemical reactions: radicals, isomerization, oxidation, dehidrociclação, hydrogenation-dehydrogenation.	Dunn; Yen, 2006.
Geochemical parameters	Composition geochemistry, reservoir geochemistry and geochemical degraded oils.	Ospino-Caro, 2009; Jones; Douglas, 1987; 1988; Koopmans et al., 1999; Sonibare et al., 2009; Keym, 2008; Fowler; Brooks, 1987; Mukhopadhyay; Wade; Kruge, 1995; Silva; Silva; Azevedo, 2010; Philp et al., 1988; Ehrenberg; Skjevra; Gilje, 1995; Huseby et al., 1996; Magnier; Huc, 1995; Pierp et al., 1996; Sardiñas, 2008; Schlepp et al., 2001; Sofer, 1988.
Kinetics parameters	Behavior kinetic parameters of maturity and source rock geochemistry.	Pineda-Flores; Boll-Argüello; Mesta-Howard, 2002; Delgado, 2006; Mendoza et al., 2009; Ospino-Caro, 2009; Vandenbrouck; Largeau, 2007; Borges; Acevedo, 2007.
Molecular mass	Parameters of maturity.	Nali et al., 2000; Gonzalez et al., 2010; Silva; Silva; Azevedo, 2010.
Size and molecular structure.	Geochemistry of asphaltenes.	Groenzin; Mullins, 2000; Nguyen; Hsieh; Philp, 1999; Peters; Walters; Moldowan, 2005; Tenses et al., 1985.
Composition of biological markers	Stability of oil geochemistry, geochemical parameters and geochemical asphaltenes and maltenes.	Gúrgey, 1998.
Study porphyrins.	Genesis of asphaltenes, similarity between asphaltenes and kerogen.	Premovic; Jovanovic, 1997; Huseby et al., 1996.
Geochemical composition	Application of environmental geochemistry. Generation of tools degradation.	Pineda-Flores; Boll-Argüello; Mesta-Howard, 2002; Pineda-Flores; Mesta-Howard, 2001; Martin-Gil et al., 2008.
Properties optics.	Geochemistry of asphaltenes.	Xianming et al., 1998.

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