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Asphaltenes – Problems and Solutions in E&P of Brazilian Crude Oils

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1. Introduction

The history of oil in Brazil began in 1858, when the Marquis of Olinda signed Decree No. 2266 granting Barros Pimentel the right to extract mineral asphalt for the manufacture of kerosene, on land situated on the banks of the Rio Marau in the province of Bahia. But who really came to be known as the discoverer of oil in Brazil was Monteiro Lobato that on January 21, 1939, already under the jurisdiction of the newly created Department of National Production, began drilling the well DNPM-163 in Bahia.

Only in 1953 began the research of Brazilian oil by the government of Vargas, which established the state oil monopoly, with the creation of Petrobras.

Petrobras - Petroleo Brasileiro S/A was founded on October 3, 1953 and headquartered in Rio de Janeiro, now operates in 28 countries in the energy sector, primarily in the areas of exploration, production, refining, marketing and transportation of oil and derivatives in Brazil and abroad. Its current motto is "An integrated energy company that works with social and environmental responsibility" (<http://pt.wikipedia.org/wiki/Petrobras>).

Since its creation, Petrobras has discovered oil in several states, and in every decade, new oil fields are discovered. Oil production in Brazil grew from 750 m³/day at the time of the creation of Petrobras to more than 182,000 m³/day in the late '90s thanks to continuous technological advances in drilling and production on the continental shelf.

In 2006, Brazil managed to achieve sustainable self-sufficiency in oil production with the operations of the FPSO (Floating Production Storage Offloading) P-50 in giant Albacora East field, in northern of Bacia de Campos in the state of Rio de Janeiro (www.autosuficiencia.com.br).

In 2007, Brazil announced the discovery of oil in the so-called pre-salt, which later turned out to be a large oil field, extending over 800km off the Brazilian coast, from the state of Espírito Santo to Santa Catarina, below thick layer of salt (rock salt) and covering sedimentary basins of Espírito Santo, Campos and Santos. The first pre-salt oil extracted in 2008 (www.petrobras.com.br).

The year 2009 was marked by the beginning of production in pre-salt layer in the Santos Basin, and in August 2010, Brazil had a record of oil production, with 2, 078 million barrels per day, up 6% over the same period in 2009.

According to the National Petroleum Agency (ANP), the volume exceeds one thousand barrels the previous record from April 2010. Produced in the Tupi, Jubarte and Cachalote fields, the pre-salt oil contributed 43, 087 thousand barrels per day in volume in August (www.monitormercantil.com.br).

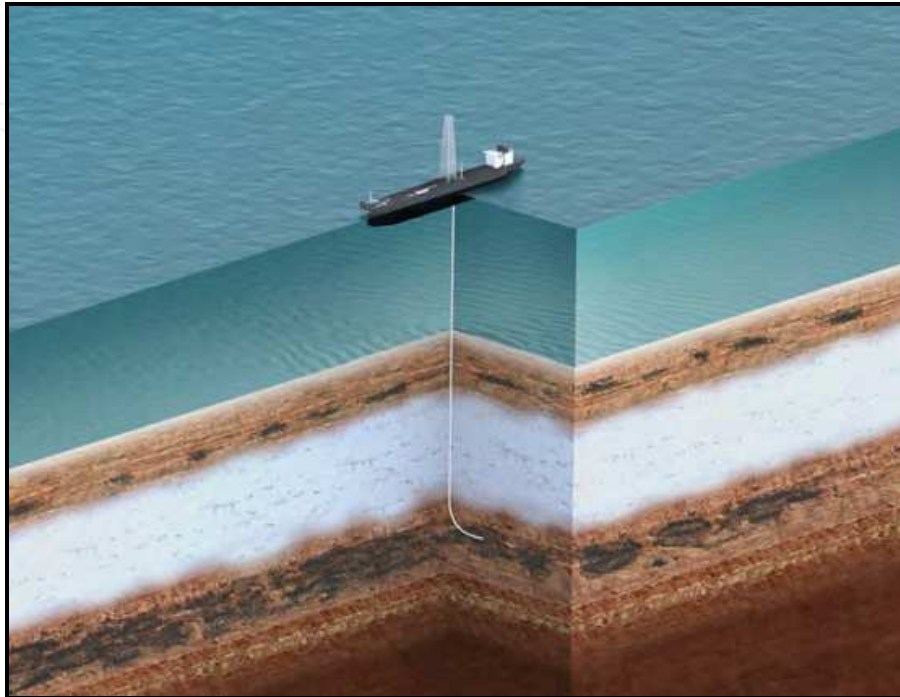


Fig. 1. Pre-salt layer. Source: www.anp.gov.br

The company ranks second among the largest publicly traded oil in the world. In market value, it is the second largest in the Americas and the fourth largest in the world in 2010. In September 2010, it became the second largest energy company in the world, always in terms of market value, according to Bloomberg data and the Agency Brazil.

It became internationally famous for having made in October 2010 the largest capitalization of all publicly traded history of mankind: US\$ 72.8 billion (R\$ 127.4 billion), almost double the record so far, the post office in Japan (Nippon Telegraph and Telephone), with US\$ 36.8 billion capitalized in 1987. In August 2011 the company broke two more records for net income: US\$ 10.94 billion in the second quarter, and also the record of R\$ 21.9 billion in the first half of the year. ([Http://pt.wikipedia.org/wiki/Petrobras](http://pt.wikipedia.org/wiki/Petrobras)).

2. Proved reserves

In 2010, the proved oil reserves in the world reached about 1.38 trillion barrels, after a 0.5% increase over 2009.

In South and Central America, the rise was driven by Colombia, Brazil and Peru, which saw its proved reserves grow 39.7%, 10.7% and 10.6% in that order.

With this increase, partly due to the findings in the pre-salt, the Brazilian proved reserves reached 14.2 billion barrels of oil, and placed the country in 15th position in world ranking of reserves.

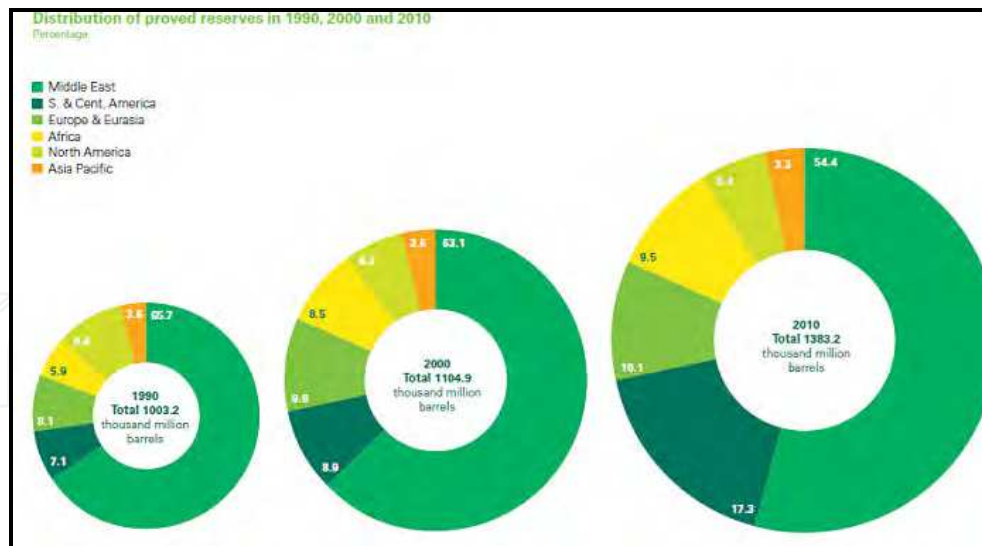


Fig. 2. Statistical Review of World Energy 2011. Source: www.bp.com

3. Consumption

In 2010, world oil consumption was 3.2% over 2009, totaling 87.4 million barrels/day. The oil was more consumed in the region of Asia-Pacific, with a total of 27.2 million barrels/day or 31.2% of the total. Consumption growth was 5.3% over 2009, especially to China which, after the United States was the country with the second largest consumer in the world, 9.1 million barrels/day, 10, 4% more than last year.

The Central and South America also recorded high in its consumption, as a result of increases in almost all countries, except Chile, which had a low of 6.2%. Thus, the increase in consumption in the region was 4.8%, reaching 6.1 million barrels/day or 7% of the world. Brazil was the country with the largest increase in consumption in the region - 8.6% - and reached 2.6 million barrels / day or 3% of world total. Thus, the country jumped to seventh in the ranking of the largest consumers of oil in the world.

Compared to 2009, the volume of oil produced worldwide in 2010 increased 2.3%, from 80.3 to 82.1 million barrels/day.

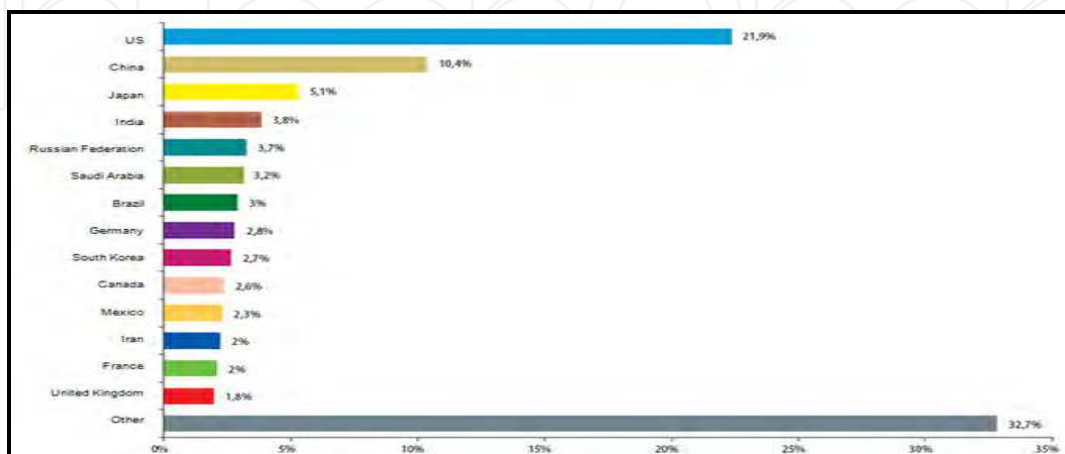


Fig. 3. World consumption of oil. Source: www.anp.gov.br

4. Production

Compared to 2009, the volume of oil produced worldwide in 2010 increased 2.3%, from 80.3 to 82.1 million barrels/day.

Oil production in Central and South America rose by 3.5%, driven mainly by increases in Colombia, Peru and Brazil, respectively, 16.8%, 8.2% and 5.3%. With the increase in the volume of oil produced, Brazil reached the 12th position among the world's largest producers of oil in 2010.

Oil: Production *											Change	2010	
Thousand barrels daily	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2010 over 2009	share of total
US	7733	7669	7626	7400	7228	6895	6841	6847	6734	7271	7513	3.2%	8.7%
Canada	2721	2677	2858	3004	3085	3041	3208	3297	3251	3224	3336	4.3%	4.2%
Mexico	3450	3560	3585	3789	3824	3760	3683	3471	3167	2979	2958	-0.8%	3.7%
Total North America	13904	13906	14069	14193	14137	13696	13732	13616	13152	13474	13808	2.5%	16.6%
Brazil	1268	1337	1499	1555	1542	1716	1809	1833	1899	2029	2137	5.3%	2.7%
Venezuela	3239	3142	2895	2554	2907	2937	2808	2613	2558	2438	2471	1.4%	3.2%
Total S. & Cent. America	6813	6722	6619	6314	6680	6898	6865	6635	6676	6753	6989	3.5%	8.9%
Kazakhstan	744	836	1018	1111	1297	1356	1426	1484	1554	1688	1757	4.4%	2.1%
Norway	3346	3418	3333	3264	3189	2969	2779	2551	2459	2358	2137	-9.4%	2.5%
Russian Federation	6536	7056	7698	8544	9287	9552	9769	9978	9888	10035	10270	2.2%	12.9%
United Kingdom	2667	2476	2463	2257	2028	1809	1636	1638	1526	1452	1339	-7.7%	1.6%
Total Europe & Eurasia	14950	15450	16289	16973	17580	17542	17599	17815	17590	17745	17661	-0.4%	21.8%
Iran	3855	3892	3709	4183	4248	4234	4286	4322	4327	4199	4245	0.9%	5.2%
Iraq	2614	2523	2116	1344	2030	1833	1999	2143	2428	2442	2460	0.6%	3.1%
Kuwait	2206	2148	1995	2329	2475	2618	2690	2636	2782	2489	2508	0.6%	3.1%
Saudi Arabia	9491	9209	8928	10164	10638	11114	10853	10449	10846	9893	10007	0.7%	12.0%
United Arab Emirates	2620	2551	2390	2695	2847	2983	3149	3053	3088	2750	2849	3.5%	3.3%
Total Middle East	23547	23120	21858	23442	24981	25488	25675	25309	26338	24629	25188	1.7%	30.3%
Angola	746	742	905	870	1103	1405	1421	1684	1875	1784	1851	3.8%	2.3%
Nigeria	2155	2274	2103	2238	2431	2499	2420	2305	2113	2061	2402	16.2%	2.9%
Total Africa	7804	7897	8028	8411	9336	9902	9918	10218	10204	9698	10098	4.2%	12.2%
China	3252	3306	3346	3401	3481	3637	3705	3737	3809	3800	4071	7.1%	5.2%
India	726	727	753	756	773	738	762	769	768	754	826	9.8%	1.0%
Indonesia	1456	1387	1289	1176	1130	1090	996	972	1003	990	986	-0.3%	1.2%
Total Asia Pacific	7874	7811	7837	7742	7854	7959	7940	7951	8054	7978	8350	4.9%	10.2%
Total World	74893	74906	74700	77075	80568	81485	81729	81544	82015	80278	82095	2.2%	100.0%
of which: OECD	21531	21314	21440	21174	20775	19870	19463	19114	18414	18471	18490	0.2%	22.1%
Non-OECD	53361	53592	53260	55900	59793	61616	62266	62430	63600	61807	63605	2.7%	77.9%
OPEC	31145	30640	29261	31020	33776	34951	35098	34757	35722	33365	34324	2.5%	41.5%
Non-OPEC £	35734	35606	35907	35556	35385	34695	34315	33991	33466	33699	34287	1.9%	41.7%
European Union #	3493	3285	3339	3128	2902	2659	2422	2388	2222	2088	1951	-6.5%	2.4%
Former Soviet Union	8014	8660	9533	10499	11407	11839	12316	12795	12827	13214	13484	2.0%	16.8%

* Includes crude oil, shale oil, oil sands and NGLs (the liquid content of natural gas where this is recovered separately).
Excludes liquid fuels from other sources such as biomass and coal derivatives.
^ Less than 0.05.
w Less than 0.05%.
£ Excludes Former Soviet Union.
Excludes Estonia, Latvia and Lithuania prior to 1985 and Slovenia prior to 1991.
Notes: Annual changes and shares of total are calculated using million tonnes per annum figures.

Table 1. World production of oil. Source: www.bp.com

5. The origin of oil

The oldest formations of the world's oil has about 500 million years and it is a result of the slow process of nature, which produced deposits of sediment in large depressions in the bottom of seas and lakes, accumulating for thousands of years, successive layers of sedimentary rock containing microorganisms, animals and plants.

The action of heat and weight of these layers on the deeper sedimentary deposits has been transforming the organic matter through thermochemical reactions in kerogen, the initial stage of oil, then by the action of higher temperatures and pressures, they were broken, making it on deposits of oil and gas.

5.1 Constituents of oil

Oil can be defined as to its chemical composition as a naturally occurring complex mixture consisting predominantly of hydrocarbons (up to more than 90% of its composition) and derived organic sulfur, nitrogen, oxygen and organometallic.

The oils from different oil reservoirs have different characteristics. Within this complex mixture, there is a fraction with high molecular weight components called asphaltenes that causes serious precipitation problems, since its production by refining (Carvalho, 2003).

The hydrocarbons present in oil can be classified into four main classes: saturated (alkanes and cycloparaffins), aromatics (hydrocarbons, mono, di and polyaromatic), resins (fractions consist of polar molecules containing heteroatoms such as N, O or S) and asphaltenes (they are molecules similar to the resins, but with a higher molecular weight and polyaromatic core). This classification is known as SARA (Wang et al, 2002; Speight, 2001; Tissot and Welt, 1978).

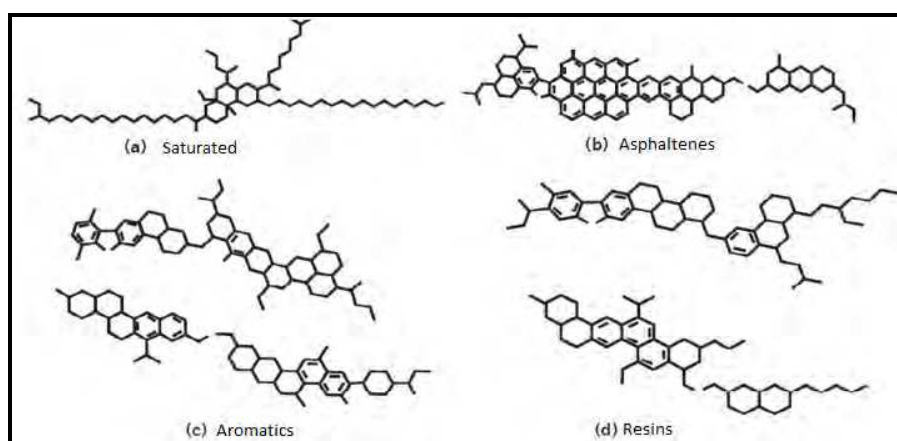


Fig. 4. Structures representing saturated, asphaltenes, aromatics and resins. Source: Bernucci et al., 2006.

Table 04 shows the elemental analysis of five Brazilian oils performed in DOPOLAB - Laboratory of Development and Optimization of Process Organic, showing considerable amounts of asphaltenes present.

Oil	Saturated (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
A	22.4	22.8	36.4	18.4
B	20.7	29.8	30.4	19.1
C	16.0	25.1	25.0	33.9
D	14.2	40.5	24.7	20.5
E	19.4	36.7	12.6	31.2

Table 2. Chemical composition of Brazilian oil. Source: DOPOLAB, 2011.

The relative amounts of individual compounds within each group of hydrocarbons is characteristic of each type of oil.

Metals can be found at levels ranging from 1 to 1200 ppm, the main being iron, zinc, copper, lead, molybdenum, cobalt, arsenic, manganese, chromium, sodium, nickel and vanadium, the latter two with the highest incidence.

5.2 Classification of oil

The classification of oils, according to their constituents, it has an interest from geochemists to the refiners. The first aim is to characterize the oil is to relate it to the rock and measure its degree of degradation and the refiners seek to know the amount of the various fractions that can be obtained, as well as its composition and physical properties.

Such information is important because: paraffinic oils are excellent for the production of aviation kerosene (jet fuel), diesel, lubricants and paraffins; naphthenic oils produce significant fractions of gasoline, naphtha, aviation fuel and lubricants; while the aromatic oils are best suited for the production of gasoline, solvents and asphalt (Thomas, 2001).

5.3 Petroleum refining

The processing of oil, called refining, begins by distillation, a unit operation, consisting of the vaporization and subsequent condensation fractional of its constituents by the action of temperature and pressure due to the difference in their boiling points. Thus, with the variation of the conditions of a heating oil, it is possible vaporization of compounds light, medium and heavy that can be separated when they condense. In parallel, there is the formation of a heavy residue that consists mainly of high molecular weight hydrocarbons, which under the conditions of temperature and pressure at which the distillation is performed, does not vaporize (Mariano, 2005).

Oil refineries are a complex system of multiple operations that depend on the properties of the oil that will be refined as well as the desired products. For these reasons, the refineries may be very different. Depending on the type of oil being processed and the profile of the refinery, i.e., the existing treatment units, you get larger or smaller portions of each type of fraction.

Oil: Refinery capacities											Change	2010	
Thousand barrels daily *	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2010 over 2009	share of total
US	16395	16785	16757	16894	17125	17339	17443	17594	17672	17688	17594	-0.5%	19.2%
Canada	1861	1917	1923	1959	1915	1896	1914	1907	1951	1976	1914	-3.1%	2.1%
Mexico	1481	1481	1463	1463	1463	1463	1463	1463	1463	1463	1463	-	1.6%
Total North America	19937	20183	20143	20316	20503	20698	20821	20964	21086	21127	20971	-0.7%	22.8%
Brazil	1849	1849	1854	1915	1915	1916	1916	1935	2045	2095	2095	-	2.3%
Venezuela	1269	1269	1269	1269	1284	1291	1294	1303	1303	1303	1303	-	1.4%
Total S. & Cent. America	6271	6246	6296	6353	6377	6405	6413	6502	6658	6688	6707	0.3%	7.3%
Germany	2262	2274	2286	2304	2320	2322	2390	2390	2366	2362	2091	-11.5%	2.3%
Italy	2485	2485	2485	2485	2497	2515	2526	2497	2396	2396	2396	-	2.6%
Russian Federation	5655	5628	5590	5454	5457	5522	5599	5596	5549	5527	5555	0.5%	6.1%
United Kingdom	1778	1769	1785	1813	1848	1819	1836	1819	1827	1757	1757	-	1.9%
Total Europe & Eurasia	25399	25276	25159	25005	25066	24999	25042	24966	24840	24761	24516	-1.0%	26.7%
Iran	1597	1597	1597	1607	1642	1642	1727	1772	1805	1860	1860	-	2.0%
Saudi Arabia	1806	1806	1810	1890	2075	2100	2100	2100	2100	2100	2100	-	2.3%
Total Middle East	6491	6746	6915	7039	7256	7284	7409	7522	7598	7818	7911	1.2%	8.6%
Total Africa	2897	3164	3228	3177	3116	3224	3049	3037	3171	3022	3292	8.9%	3.6%
China	5407	5643	5933	6295	6603	7165	7865	8399	8722	9479	10121	6.8%	11.0%
India	2219	2261	2303	2293	2558	2558	2872	2983	2992	3574	3703	3.6%	4.0%
Japan	5010	4705	4721	4683	4567	4529	4542	4598	4650	4621	4463	-3.4%	4.9%
South Korea	2598	2598	2598	2598	2598	2598	2633	2671	2712	2712	2712	-	3.0%
Total Asia Pacific	21478	21853	22444	22579	23037	23537	24693	25561	26094	27653	28394	2.7%	30.9%
Total World	82473	83469	84183	84468	85355	86147	87427	88552	89446	91068	91791	0.8%	100.0%
of which: OECD	44761	44697	44900	45024	45169	45202	45422	45634	45784	45742	45124	-1.3%	49.2%
Non-OECD	37712	38771	39283	39444	40187	40945	42005	42918	43662	45326	46667	3.0%	50.8%
European Union #	15456	15540	15691	15729	15803	15811	15857	15784	15658	15553	15240	-2.0%	16.6%
Former Soviet Union	8574	8404	8133	7937	7940	7945	7961	7958	7961	7965	8033	0.9%	8.8%

Source: Includes data from Parpinelli Tecnon.

* Atmospheric distillation capacity on a calendar-day basis.
Excludes Lithuania prior to 1985 and Slovenia prior to 1991.
Note: Annual changes and shares of total are calculated using thousand barrels daily figures.

Table 3. Oil refining capacity worldwide. Source: www.bp.com

Lighter oils produce greater volume of gasoline, LPG and naphtha, and so exhibit a higher commercial value, while heavy fuel oils produce higher volumes of oil yield and asphalt. The average derivatives, such as diesel and kerosene, are also particularly important for our country where the highway is intense and the demand for diesel is great.

In 2010, the effective refining capacity installed worldwide was 91.8 million barrels/day to a world oil production of 82.1 million barrels/day.

The United States retained its first place in ranking global refining capacity (19.2% of total), followed by China (11%), Russia (6.1%), Japan (4.9%) and India (4%). Together, these five countries accounted for 39.6% of global refining capacity.

Brazil has climbed to ninth place in global refining capacity ranking, with 2.1 million barrels/day or 2.3% of world capacity.

6. Asphaltenes

Over the past year, there was a significant increase in studies of asphaltenes due to increased production of heavy oil and due to the diminishing reserves of oil lighter (Yarranton et al, 2000a, 2002; Calemma et al, 1995).

The asphaltenes are a mixture of high molecular weight aromatic components oil shale. Coal and oil can vary from 1% by weight in light oils, up to 17% in heavy oils. According to Leon et al (2001), the asphaltenes are considered the fraction of oil that has the highest number of aromatic rings and higher molecular weight.

According to several researchers (Ortiz et al 2010; Nordgard et al, 2009, Yasar et al, 2007; Ancheyta and Trejo, 2007; Deo et al, 2004; Mullins et al, 2003; Kilpatrick et al, 2003a and 2003b; Speight, 2001; Leon et al, 2001 and 2000; Bauget et al, 2001; Gafanova and Yarranton, 2001; Yarranton et al, 2000a and b; Rogel, 2000, Andersen and Speight, 1999; Murgich et al, 1999; Speight et al, 1994; Speight and Long, 1995), the most accepted definition for asphaltenes is related to their solubility and says that asphaltenes are insoluble in aliphatic hydrocarbons such as n-heptane or n-pentane and soluble in aromatic hydrocarbons such as toluene. According Shkalikov et al (2010) asphaltenes represent insoluble precipitates obtained from solutions of oil in alkanes of lower molecular weight such as pentane, hexane and heptane.

According Oseghale and Ebhodaghe, 2011; Mustafa et al, 2011; Ortiz et al, 2010; Nordgard et al, 2009; Gauthier et al, 2008; Yasar, 2007; Ancheyta et al, 2004; Kilpatrick et al, 2003; Mullins, 2003; Siddiqui, 2003; Murgich, 2002; Priyanto et al, 2001; Sheu, 2002; Speight, 2001; Leon et al, 2000; Rogel, 2000; Yarranton et al, 2000b; Murgich et al, 1999; Calemma et al, 1995, the asphaltenes consist of a heterogeneous complex mixture of molecules highly polydisperse in size and with a chemical composition poly condensed aromatic rings, aliphatic chains, naphthenic rings, and containing heteroatoms such as nitrogen, oxygen, sulfur, presenting itself in the form of carboxylic acids, amides, amines and alcohols, and metals such as iron, nickel and vanadium. Different types of metals (Ni, V, Fe, Al, Na, Ca, Mg) are present in crude oils and tend to accumulate in the asphaltenic fraction in trace amounts. Vanadium and nickel are the most commonly found and in most cases present as porphyrin complexes, being responsible for the poisoning of catalysts in the improvement of oil (Mustafa et al, 2011; Nordgard et al, 2009; Ancheyta and Trejo, 2007).

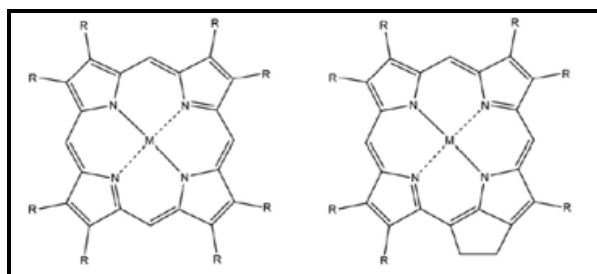


Fig. 5. Structures of metal porphyrins. Source: Mustafa et al, 2011.

The asphaltenes are arguably the most complex fraction of oil. In variations of pressure, temperature or composition of oil, asphaltenes tend to associate and precipitate causing several costly operational problems from transport to refining (Trejo et al, 2007; Lira-Galeana and Duda, 2006).

Among all the oil fractions, the molecular structure of asphaltenes is the least understood (Trejo et al, 2007). Several researchers (Carvalho, 2003; Speight, 1999 a; Speight, 1999 b; Andersen and Speight, 1999; Speight et al, 1984) have concentrated their efforts on improving the information about this mixture, deepening their knowledge of the chemical structures involved, characterizing the functions and establishing their behavior against solvents. They also seek to explain the way their molecules are stabilized and dispersed in the oil.

Overall, the researchers concluded that the level and nature of asphaltenes in a sample is due to a series of parameters such as the origin of oil, the flocculating agent, the time used for precipitation, temperature, procedure used and ratio oil / flocculant agent. All these combined parameters not only influence the amount of asphaltene precipitated, but also in its composition, which can be obtained from an asphaltene solid dark brown to a black (Silva, 2003).

The elemental composition of asphaltenes varies in a ratio of C/H of $1.15 \pm 0.05\%$, however, values outside this range are sometimes found, according to Speight (1999 a).



Fig. 6. Illustration of Asphaltenes. Source: Lima, 2008.

Notable variations may occur, particularly in the proportions of heteroatoms such as oxygen and sulfur, but they are always exposed in a very characteristic manner. For example, nitrogen occurs in the asphaltenes in various heterocyclic chains, the oxygen can be identified as carboxylic, phenolic and ketone (Speight et al, 1994); while sulfur is in the form of thiols, thiophenes, benzothiophenes, dibenzothiophenes and naphtebenzothiophenes as well as in systems such as sulphide, alkyl-aryl, aryl-aryl and alky- laryl (Speight et al, 1984).

Examples of structures present in the asphaltenic fraction based on data from infrared, ^1H NMR and ^{13}C with Venezuelan oils (A, B, C, D) are shown in Figure 07.

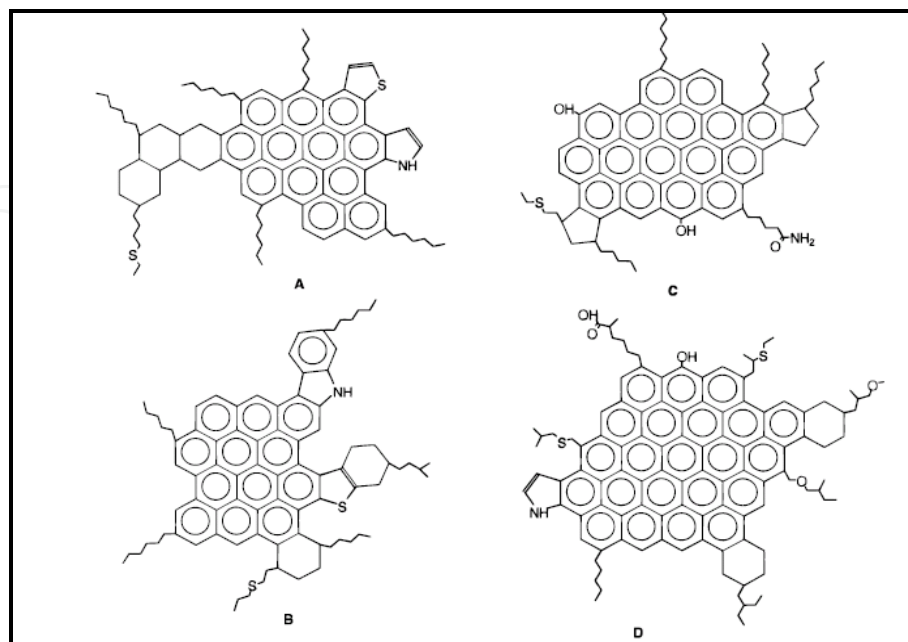


Fig. 7. Hypothetical structures of asphaltenes. Source: Leon et al, 2000.

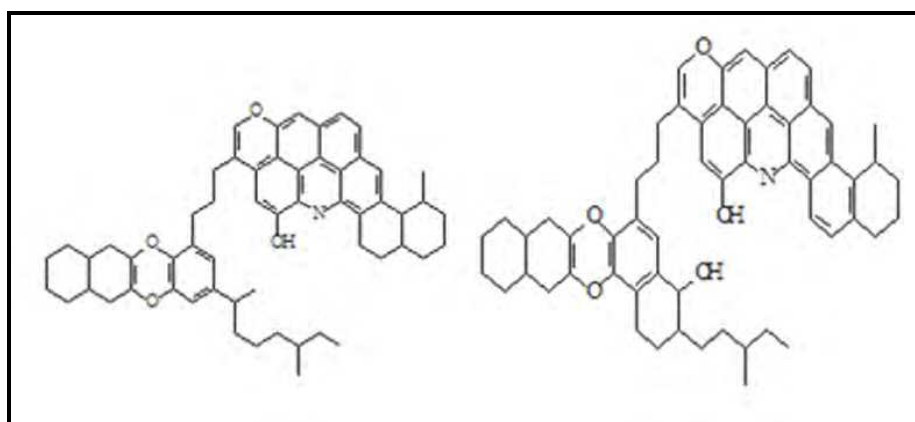


Fig. 8. Structures representing asphaltenes. Source: Lima, 2008.

The basic structure of asphaltenes consists of a number of rings polycondensates, replaced by aliphatic or naphthenic groups, and there may be between 6 and 20 rings. These structures gather in piles at the level of the aromatic rings forming, then, particles, each particle made up 4 to 6 structures. These particles can come together to form a structure called the aggregate. The size of an aggregate is clearly dependent on the structures involved in the same (Caldas, 1997).

To Merdrignac and Espinat (2007), asphaltenes contain aromatic molecules variables and with different amounts of heteroatoms, metals and functional groups. Such structures can not be represented by a single model of the molecule. Several models are proposed in the literature to describe them, among the main continental and archipelago. Figure 09 presents some of these models.

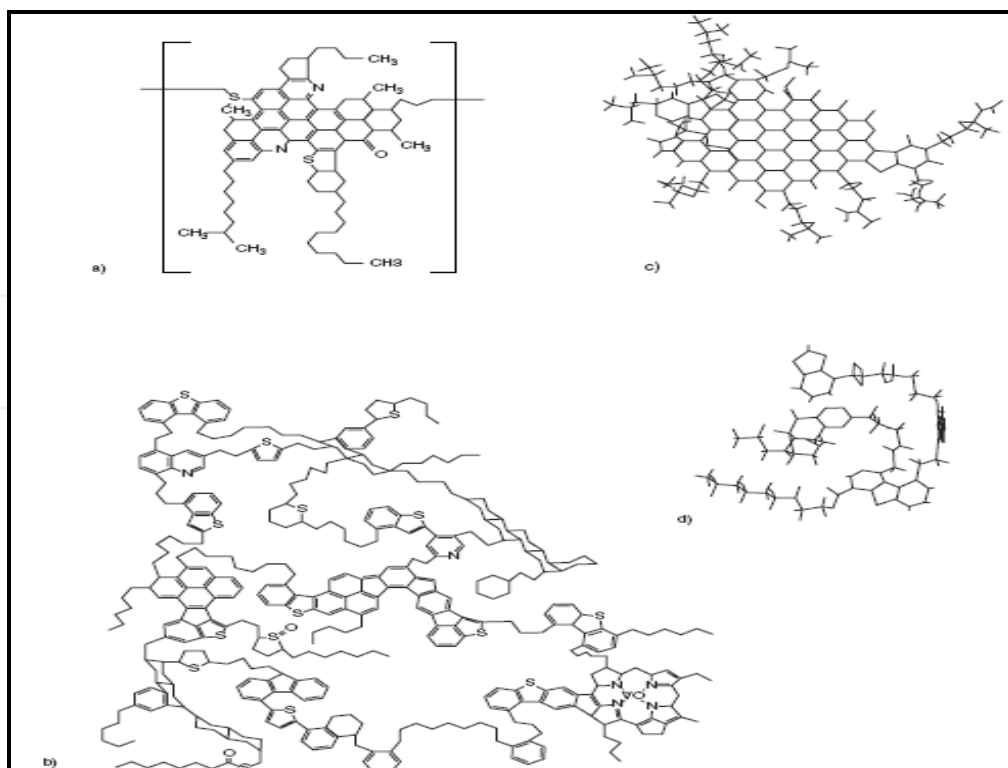


Fig. 9. Examples of structures of asphaltenes: a) crude Venezuelan oil b Athabasca c) continental type structure d) archipelago type structure. Source: Merdrignac and Espinat (2007).

According to Merdrignac and Espinat (2007), the continental structure is defined by asphaltenes with a large central region of aromatic rings while the archipelago structure describes asphaltene molecules with various aromatic regions linked by smaller alkanes.

6.1 Deposition of asphaltenes

Variations in temperature, pressure and chemical composition can cause precipitation of asphaltenes from crude oil. Rainfall and subsequent deposition of asphaltenes can cause problems in all stages of production, for example, transportation and processing, causing the loss of efficiency equipment in steps of production of crude oil. In the reservoir rock, seal can cause partial or complete its pores, resulting in the loss of oil recovery.

The formation of the asphaltenes deposit is one of the most studied phenomena in the production and processing of crude oil. Researches are looking increasingly for the improvement about the chemical structure of molecules present in the asphaltene fraction and, consequently understand its behavior in oil.

According to Leon et al (2000), the main features observed in asphaltene of petroleum that present deposition problems are: high atomic ratio carbon/hydrogen, high aromaticity and high condensation of aromatic rings.

Asphaltenes are found in heavy oil and, therefore, distillation residues, affect refining operations. The asphaltenes act as coke precursors and lead to deactivation of catalysts. They are the main contributors to the formation of deposits in refinery equipment, and

because of this, refinery units must be taken out of service for removal of deposits, thus increasing the costs (Gonçalves et al, 2007).

The cost associated with the asphaltene deposition during production and refining operations is in the order of billions of dollars a year. For this reason, the prevention or minimization of precipitation of asphaltenes is an important goal for many oil companies (Rogel et al, 2010).

6.2 Extraction of asphaltenes

Boussingault (1837) and Marcusson (1931) did a remarkable job on asphaltenes of oil that was used to establish a procedure for the separation of these, developed by Nellensteyn (1933), based on the solubility of asphaltenes in carbon tetrachloride. This procedure converged to the method known today for the separation of asphaltenes using n-heptane or n-pentane as a flocculating agent.

Nellensteyn (1933) proposed not only a method of separation, but also suggested a conceptual outline of the structure of asphaltenes in oil. He proposed that asphaltenes are formed by high molecular weight hydrocarbons that form a colloidal system that can be adsorbed on a surface. This revolutionary idea at the time, is so incredibly precise that although questionable, persists today (Sheu, 2002).

Due to the proposed Nellensteyn (1933), there was an enormous effort in studying the fundamental properties of asphaltene molecules, such as molecular weight, structure and characteristics related to these properties, as well as the influence of extraction method on the type of asphaltene fraction obtained (Silva, 2003).

The Institute of Petroleum of London (Standard Methods for Analysis and Testing of Petroleum and Related Products - vol.1, IP-143) developed a methodology which is a standardized test which consists in the precipitation of part of the oil with n-heptane and then dissolving the precipitate with toluene. The precipitate is soluble in toluene and is then called asphaltenes. This methodology, as well as its American version (ASTM 6560-00), are commonly used by the oil industry for the quantification of asphaltenes.

There are several methods of extraction of asphaltenes, and although these are well accepted, there are questions, due to be a fraction of asphaltene a solubility class. There is debate about the different extraction methods and changes that these procedures can generate on the properties of this asphaltenic fraction.

According Shkalikov et al (2010) the yield of asphaltenes depends on certain factors such as temperature, pressure, ratio sample/solvent, performance of preparation steps such as filtration, repeated washing of the precipitated asphaltenes with solvents and drying. All these variations certainly complicate the comparison of results by generating different asphaltenes. Currently, the most active researchers in this area are already talking about the search for a unique and standards methodology to ensure uniformity of concepts.

To better understand the aggregates generated by asphaltenes during the separation processes, it is also important to characterize the resins, as these are also part of the composition and can also act as surfactants to stabilize emulsions.

6.3 Resinas

The dispersion of asphaltenes is mainly attributed to the resins (polar aromatic). The resin molecules play a role of surfactants in stabilizing colloidal particles of asphaltenes in oil. There are concepts about precipitation of asphaltenes and the most widely accepted says that the dissolution of resins is followed by precipitation of asphaltenes (Shkalikov et al, 2010). On this basis, the stability of oil can be represented by three phase systems: asphaltenes, aromatics (including resins) and saturated, which are delicately balanced (Speight, 1992).

The presence of resins in oil prevents the precipitation of asphaltenes by keeping the same particles in colloidal suspension. When a solvent is added to oil, resins are dissolved in the liquid, leaving active areas of asphaltene particles, which allow the aggregation of the same and, consequently, precipitation (Andersen and Speight, 1999).

According to Oseghale and Ebhodaghe (2011) the stability of asphaltenes in oil depends on the ratio resin/asphaltene in the oil. In contrast to the asphaltenes, resins are soluble in n-alkanes as n-heptane and n-pentane (Shkalikov et al, 2010). According to Speight (1992) is the criterion of solubility which allows setting them and consider that they have a similar structure of asphaltenes, however, with a molecular weight less than these (Andersen and Speight, 1999) (Figure 10).

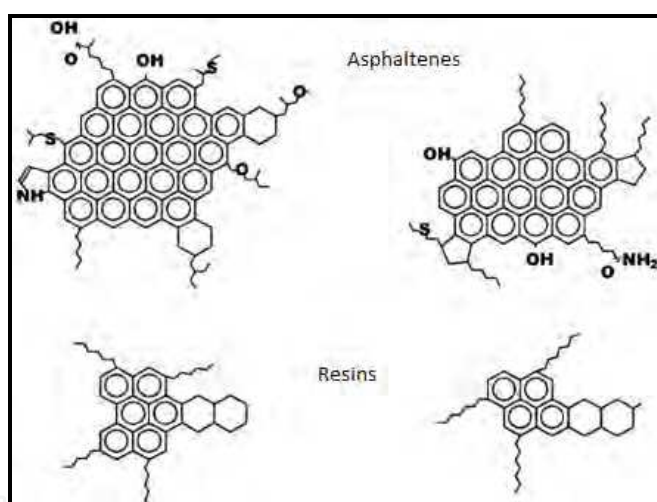


Fig. 10. Structures of hypothetical resins. Source: Rogel (2000).

Resins compared to asphaltenes have a lower content of aromatics, but are rich in heteroatoms, mainly oxygenates (Faria, 2003).

It should be noted that during the process of purification and precipitation of asphaltenes due to the existence of clusters, always exists the possibility of a certain amount of resin precipitate with the asphaltenes.

6.4 Characterization of asphaltenes

The need for knowledge of molecular structure of asphaltenes is the key to developing treatments to prevent their precipitation and may help in understanding its function as a stabilizer of emulsions.

According Merdrignac and Espinat (2007), the detailed structural characterization of heavy fractions is generally difficult to achieve, mainly due to the large complexity of fraction and limitations of analytical techniques. Structural information has been obtained, but can not represent all the chemical and structural variety that these complex mixtures of asphaltenes may contain. Another problem that hinders the characterization of aggregation is the phenomenon presented by the asphaltenes. That is, the asphaltenes have a tendency to form aggregates of high molecular weight, whose distribution depends on the solvent employed, pressure and temperature, making it difficult to know their true distribution in the original oil (Carvalho, 2003).

In recent decades, NMR has been used as a tool for the characterization of mixtures, especially the ^{13}C NMR, providing relevant information about the structure of complex systems such as asphaltenes. Simultaneous use of ^1H and ^{13}C NMR allows the determination of a series of structural parameters such as fraction of aromatic carbon, the average number of carbons in an alkyl attached to aromatic systems and the percentage replacement of this system (Skoog et al, 2002).

The NMR technique, in particular, provides reliable molecular parameters about characteristics of aromatic rings and aliphatic chains of asphaltene structures (Speight, 1999).

6.5 The impact of asphaltenes in petroleum refining

In the activities of the oil industry, the deposition of organic compounds is frequent. Among the deposits that cause operational problems, we can identify two predominant groups: paraffins and asphaltenes. Therefore, it is necessary to determine the conditions under which these deposits occur and the way in which they can be avoided in order to generate the least possible damage to the process (Smith, 2003).

Deposits may occur in reservoir rock and source rock for oil. This impairs the production of the well by causing the blocking of pores of the rock and by changing a very important property of the reservoir rock, its wettability, which is the tendency of a fluid to spread or adhere to a solid surface in the presence of non-miscible fluids, and can be modified by adsorption of polar compounds and/or deposition of organic material and thus affect the migration of oil. This is an extremely serious problem, since it can lead to the loss of the well (Faria, 2003; Menechini, 2006).

The phenomenon of deposition can also occur on the production lines. It is known that the use of any method, chemical (injection of solvents, for example) or mechanical (using scrapers), to remove this type of deposit is an expensive operation and requires a lot of security because any accident can lead to line loss (Carnahan, 1989).

The deposition of asphaltenes can also happen in separators during the final stage depressurization of oil (Almehaideb and Zekri, 2001), as well as in almost all stages of production, processing and transportation of oil and is an extremely serious problem that affects significantly the costs of oil industry.

In refining, these constituents may lead to catalyst deactivation and the formation of waste during the thermal and thermo-chemical processing of heavy residues of oil (Speight, 2001).

Due to the economic impact of this problem, the existing literature about asphaltenes is vast, complex and inconclusive (Chinligarian and Yen, 2000).

The biggest challenge associated with this kind of deposit is: what is chemically known as asphaltenes. For this reason, the asphaltenes have been studied mainly with regard to the identification of chemical structures present in this complex mixture. The molecular knowledge of heavier fractions of oil is not conclusive because of complexity of the molecules involved and the families of molecules that are part of these fractions. Thus, it is recommended that all development work to assist in identifying and characterizing properties of complex molecules present in this fraction, as well as studying the stability of the same over the physical and chemical processes by which oil is to generate products commercial interest that undoubtedly sustain the world economy.

7. Case study

As oil undergoes a series of processes involving heating and atmospheric distillation in order to raise its energy potential Chrisman and Lima, 2009 studied the influence of cutting temperature in the asphaltenic fractions.

In this work, the goal was to identify the differences in the average molecular parameters of asphaltenes obtained during the simulation of atmospheric distillation in the laboratory on five different temperatures. Significant changes were observed in the structures of each of the fractions obtained from two Brazilian oils called A and B, especially in the higher cut temperatures.

The extraction and quantification of content of asphaltenes were performed using the ASTM 6560-00 and characterization of asphaltenes was performed using the analytical techniques: elemental analysis, infrared and nuclear magnetic resonance of ^1H and ^{13}C . Significant changes were observed in almost all molecular parameters during the distillation at different temperatures, using as standard asphaltene of crude oil. The results obtained confirm the occurrence of oxidation with the increase of cut temperature, probably because of aromatization of naphthenic rings and closing of lateral chains. Examples of events are presented in proposals for representative structures of these fractions.

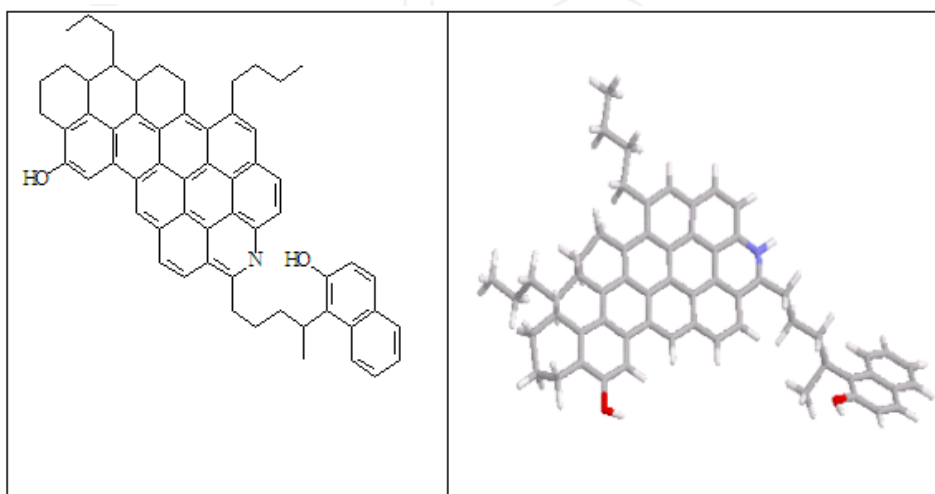


Fig. 11. Structure of asphaltene (crude oil A). Source: Chrisman and Lima, 2009.

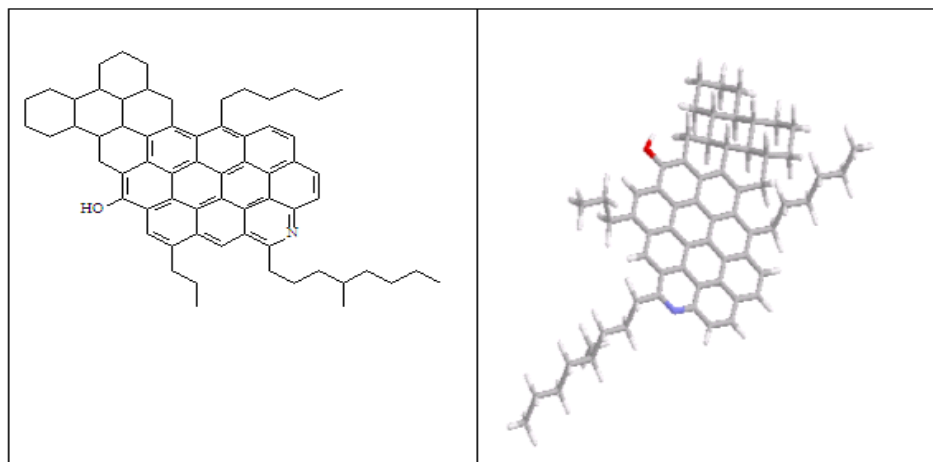


Fig. 12. Structure of asphaltene (residues of cutting to 420°C oil A). Source: Chrisman and Lima, 2009.

It can be observed in the structures shown in Figures 11 and 12 that with increasing temperature, naphthenic rings were formed from lateral chains and even being in some cases, the oxidized aromatic rings. At the temperature of 420°C it was observed aromatization of naphthenic rings.

8. Emulsions

Emulsions are defined as a heterogeneous liquid system consisting of immiscible liquids with one another where one liquid is dispersed in another in the form of drops. The emulsions are distinguished by the amount of liquid dispersed in another one.

An emulsion consists basically of two phases: a continuous phase (external), where the droplets are dispersed, and a dispersed phase (internal or discontinuous), which are themselves dispersed droplets.

Three conditions are necessary for the formation of an emulsion:

- immiscibility between liquid of emulsion
- Shaking to disperse one liquid in another
- Presence of emulsifying agents (surfactants)

The characteristics of an emulsion are constantly changing since the beginning of formation until their complete resolution and vary with temperature, pressure, degree of agitation and time of formation. From a purely thermodynamic point of view, an emulsion is considered an unstable system due to a natural tendency of the system liquid/liquid separation and to reduce their interfacial area and thus their interfacial energy. However, most of the emulsion is stable for a period of time, have kinetic stability that is due to smaller drop sizes and the presence of an interfacial film around the drop.

8.1 Stability of an emulsion

The stability of emulsion can be determined by the type and amount of surface active agents or surfactants that can occur naturally in crude oil, for example, the asphaltenes. These

surfactants tend to concentrate in the water/oil interface where form interfacial films stabilizing the emulsion by reducing the interfacial tension (IFT) and promotion of emulsification and dispersion of droplets (Lee, 1999). When energy is added to the system, the particles are broken down into smaller parts and with higher energy, become smaller and, consequently, greater its stability, it is more difficult to treat (Silva, 2008).

Some fine solid particles present in crude oil are able to stabilize emulsions by diffusion into the oil/water interface to form rigid structures that can sterically prevent the coalescence of droplets. To act as stabilizers, the particles must be much smaller than the size of emulsion droplets. They must present themselves at the interface and be sprayed with two phases (aqueous and oily) to stabilize the emulsion. Examples of wet solids in oil are wax and asphaltenes and examples of wet solids in water are inorganic compounds such as, for example, CaCO_3 and CaSO_4 , clay and sand.

The temperature can modify the physical properties of oil, water, interfacial films and the solubility of surfactants in oily and aqueous phases affecting the stability of an emulsion. When increasing the temperature, it is observed a decrease in viscosity of emulsion caused primarily by a decrease in oil viscosity. The temperature increases the thermal energy of drops and, consequently, increases the frequency of drop collisions. This also reduces the interfacial viscosity and results in a rate of faster drainage of the film, thus increasing the coalescence of droplets. The temperature increase leads to a gradual destabilization of interfacial films.

The drop size distribution affects the viscosity of emulsion, which is larger when the droplets are smaller. Usually the emulsion with smaller droplet size is more stable and the time for separation of water must be larger. The viscosity of emulsion will also be higher when the droplet size distribution is narrow (ie, the droplet size is fairly constant).

The pH of aqueous phase has a strong influence on the stability and the type of emulsion formed, it affects the rigidity of the interfacial film. The low pH (acid) generally produces emulsions W/ O (corresponding to wettability in oil, solid films) and high pH (basic) produces emulsion O/W (corresponding to the water wettability, mobile movies).

The emulsions are stabilized by films that are formed around the drops of water in water/oil interface. These films are the result of adsorption of polar molecules of high molecular weight that are interfacial active, i.e. show behavior similar to surfactants. These films increase emulsion stability by reducing the IFT and increased interfacial viscosity. Highly viscous interfacial films act as a mechanical barrier to coalescence. The characteristics of interfacial films vary depending on the type, composition and concentration of polar molecules present in crude oil, temperature and pH of the water. (Kokal, 2005 and Ortiz et al, 2010).

8.2 Viscosity of emulsions

The viscosity of an emulsion is directly proportional to the viscosity of continuous phase and is defined as the relationship between stress and shear rate. Highly viscous oils usually form more stable emulsions These oils cause emulsions difficult to treat, because they decrease the movement of droplets, retarding the coalescence.

The volume fraction of the dispersed phase is the most important factor that affects the viscosity of emulsions. With increasing volume fraction of dispersed phase, the internal circulation is reduced, and the viscosity of emulsion increases.

The effect of particle size distribution on the viscosity of emulsions is very important for high values of concentration of the dispersed phase. For lower concentrations, however, the effect is much smaller. When the average size of water droplets dispersed is lower, higher is the residence time of emulsion.

The shear rate influences the viscosity of emulsions only when it has characteristics of a non-Newtonian fluid. For low values of concentration of dispersed phase, the emulsion exhibits characteristics of Newtonian fluid and, consequently, the shear rate does not affect the viscosity of emulsion. For high values of concentration of dispersed phase, the emulsions exhibit features non-Newtonian (pseudoplastic fluids) and the apparent viscosity decreases significantly with an increasing shear rate (Kokal, 2005 and Silva, 2008).

8.3 The impact of asphaltenes in oil emulsions

The formation of an emulsion W/O can be a serious obstacle for the production of oil, and some oils are particularly prone to form more emulsions than others (Muller et al, 2009). According to Ortiz et al (2010), treatment of these emulsions W/O is still a challenge in the oil industry due to the high stability versus coalescence.

Phenomenological investigations of physical and chemical properties related to the strength of emulsion are described in the literature in terms of mechanisms, properties and classes of potential compounds that stabilize emulsions.

Characteristics commonly linked to w/o emulsions are the API gravity, total acidity index (TAI) and asphaltene content (Muller et al, 2009). In the petroleum industry, most of emulsions produced is of type A/O. Figure 13 illustrates an emulsion W/O, where water droplets are dispersed in oil. It is observed from this figure that stable emulsions are characterized by properties that prevent the coalescence of small drops of water, while in unstable emulsions the water droplets coalesce rapidly.

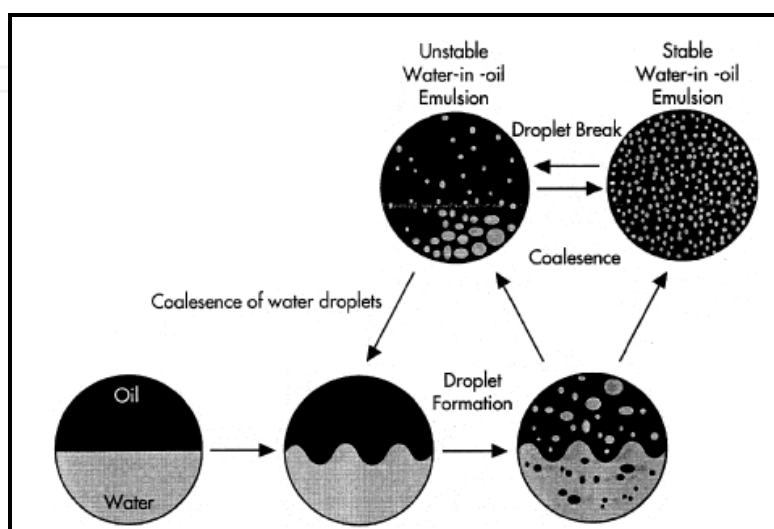


Fig. 13. Formation of emulsions A / O. Source: Lee, 1999.

A stable emulsion W/O consists of an aqueous phase, an oil phase and an emulsifying agent. Certain compounds and particles found in crude oil can act as emulsifying agents (surfactants) and thus promote and stabilize these emulsions. Surfactants have hydrophilic and hydrophobic regions so as to fall within the oil-water interface and stabilize emulsions. If the concentration of particles and surfactants are sufficiently high, then the coalescence of water droplets is prevented, leading to stable emulsions. Figure 14 shows the stabilization of a drop of water in an oily continuous phase by the presence of surfactant.

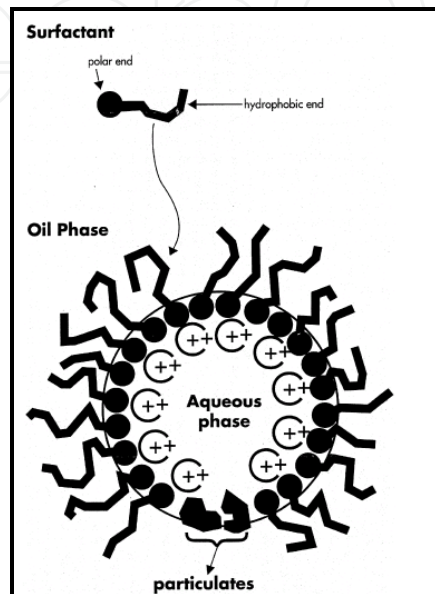


Fig. 14. Emulsion A/O stabilized by surfactants. Source: Lee, 1999.

Certain fractions of polar and high molecular weight exist in crude oil, natural surfactants considered, contribute to the formation of emulsions A / O. These fractions include waxes, asphaltenes and resins and can be dissolved or particulate form (Wei et al, 2011; Ortiz et al, 2010; Kokal, 2005; Lee, 1999). These compounds are seen as the main constituents of interfacial films, where they accumulate and thus stabilize the droplets and, consequently, the emulsion formed around the droplets.

The accumulation of asphaltenes at the interface results in the formation of a hard film. According to Ortiz (2010) when asphaltenes adsorb on the water/oil interface, they form an interfacial film with high elasticity.

The state of asphaltenes in crude oil also has an effect on its stabilizing properties of emulsions. The asphaltenes will stabilize emulsions when they are present in colloidal form. There is strong evidence that its properties are significantly increased when stabilizers are precipitated in the oil.

If emulsifying agents do not exist in crude oil, the instability of the system contributes to the coalescence, facilitating phase separation. If there is the presence of an emulsifying agent, there will be a greater stability of droplets hindering the natural separation of the phases.

The schematic diagram shown in Figure 15 represents a drop of water stabilized by asphaltenes and paraffin crystals. A region not stabilized is shown with the formation of an incomplete barrier.

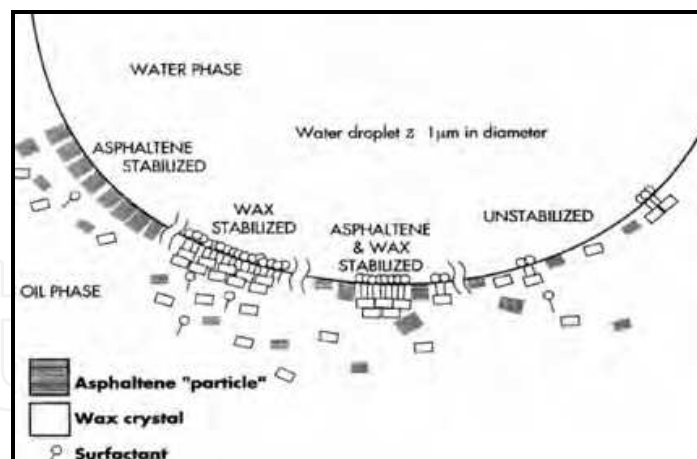


Fig. 15. Stabilization of a drop of water. Source: Lee, 1999.

Several studies demonstrate the importance of asphaltenes, resins and paraffins existing in crude oil in the promotion and stabilization of emulsions of water-in-oil.

9. Case study

Petrobras has about 65% of the area of its offshore exploration blocks in water depths greater than 400m, consequently it is increasing its activities in exploratory drilling in ever deeper waters, resulting in emulsions in almost all phases of production and processing of oil.

Therefore, there is a great need to understand the mechanism of stabilization of emulsions of oil in order to increase production rates and the efficiency of separation that can be accomplished by applying methods such as thermal, mechanical, electrical and/or chemical (Kokal, 2005; Nordgard et al, 2009).

Studies on the form of interaction between natural surfactants species present in oil and interfacial film can assist in developing more efficient methods of separation. From this point of view, asphaltenes can be studied by seeking a greater understanding of this complex fraction in terms of structure and composition, as a species that can contribute to the stabilization of these emulsions.

The laboratory DOPOLAB is currently studying the influence of asphaltenes and resins in the stability of Brazilian oil emulsions. For this, certain physico-chemical characteristics of oil are determined such as viscosity, density, °API, water content, chloride content, total acidity index; extraction of asphaltenes following the standard ASTM6560/00 and characterization of asphaltenes and resins through techniques of elemental analysis, IR and ^1H and ^{13}C NMR.

Interfacial tension tests, electrocoalescence and interfacial rheology studies using resins and asphaltenic fractions are in progress.

As preliminary tests to show surfactant properties of asphaltenes were performed interfacial tension measures in a Krüss Tensiometer DSA100 using the pendant drop method. The analysis time was 90min and a needle with a diameter of 1.463 mm and a 500 μL syringe used.

The toluene + asphaltenes solutions were made solubilizing 0.5 g of asphaltene in 100 ml of toluene. First the interfacial tension was measured between toluene and water to have a default value and can then compare the results. The interfacial tension measurements of toluene+ asphaltenes solutions were determined in duplicate, so the values of the interfacial tension shown in Table 04 are the averages of duplicates determined.

Sample	Interfacial
Toluene	33,69 ± 0,09
Toluene + AA	23,35 ± 1,14
Toluene + AB	30,73 ± 0,04
Toluene + AC	30,19 ± 0,38
Toluene + AD	21,43 ± 0,06
Toluene + AE	28,67 ± 0,14
Toluene + AF	30,93 ± 0,65

Table 4. Values of interfacial tension for asphaltenes. Source: DOPOLAB, 2011.

Analyzing the results, it is observed that the value of interfacial tension between water/toluene was 33.69 mN/m and that for all solutions containing asphaltenes the value was less than this. With these preliminary data we can see that asphaltenes have surfactant properties as the interfacial tension decreased.

Figure 16 shows graphically the behavior of the interfacial tension of each asphaltene studied.

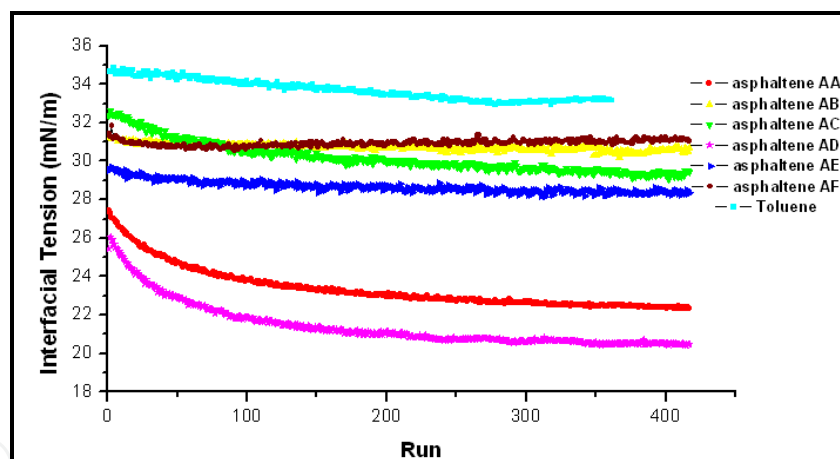


Fig. 16. Graph Interfacial Tension versus race of asphaltenes. Source: DOPOLAB, 2011.

Interfacial rheology tests are being carried out by varying the concentration of asphaltenes, resins and asphaltenes/resins to better understand the surfactant properties of these species in the oil.

10. Conclusion

In conclusion we mention that although the literature on asphaltenes is being quite extensive and current, much remains to understanding this complex fraction. The understanding of chemical structures present in this asphaltenic fraction seems to be really important and helpful in understanding their properties, and assist in proposing mechanisms to explain: their interactions with other species (resins), its precipitation;

participation in the stabilization of emulsions, and many other problems can be avoided and/or minimized since then.

11. Acknowledgment

The authors would like to thank Petrobras for providing the oil samples and give financial support.

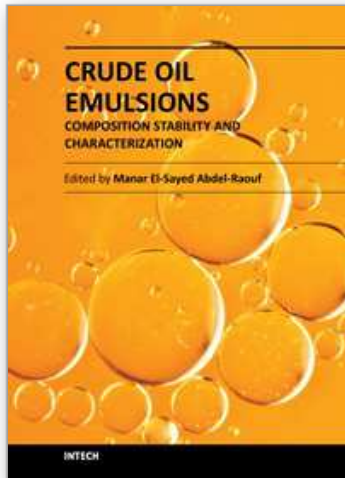
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Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

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