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SEPARATION OF FRACTIONS FROM VACUUM RESIDUE BY SUPERCRITICAL EXTRACTION

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ABSTRACT

The Instituto Colombiano del Petróleo (ICP), has implemented a methodology for separating vacuum residue fractions using the technique of supercritical fluid extraction at the pilot scale. The present study evaluates the efficiency of extraction of fractions of a typical vacuum residue in the Barrancabermeja refinery. The extraction test was carried out with n-hexane under supercritical conditions of temperature and pressure of the 265°C in the range from 450 to 1250 psi, respectively. Finally, each of the fractions were analyzed for their density, viscosity, sulfur content, Conradson Carbon Residue (CCR) content, SARA compositional analysis, and metals.

Keywords: *supercritical extraction, vacuum residues, physical properties.*

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RESUMEN

El Instituto Colombiano del Petróleo (ICP) ha implementando una metodología de separación de fracciones de fondos de vacío mediante la técnica de extracción con fluidos supercríticos a escala piloto. El presente estudio evalúa el rendimiento de extracción de fracciones de un fondo de vacío típico de la refinería de Barrancabermeja. La prueba de extracción se realizó con n-hexano bajo condiciones supercríticas de temperatura y presión de 265°C y 450 a 1250 psi, respectivamente. Finalmente, cada una de las fracciones se les determinó su densidad, viscosidad, contenido de azufre, residuo Carbón Conradson, análisis composicional SARA y metales.

Palabras clave: *extracción supercrítica, fondos de vacio, propiedades físicoquímicas.*

1. INTRODUCTION

A supercritical fluid is defined as a pure component found in the region with temperature and pressure greater than or equal to the critical conditions, $T_r \geq 1,0$, $P_r \geq 10$, where liquid and vapor states are not differentiable. Supercritical fluids (SF) have properties similar to the liquid form (i.e. density) and properties similar to the gaseous form (i.e. diffusivity, viscosity, and zero surface tension). These properties vary with changes in temperature and pressure, which substantially affect the mass transfer, (Han, Yang, Ke, Mao, & Yan, 1998; Gallego & Cardona, 2004).

The solvent power of supercritical fluids depends on its density. These fluids are able to dissolve weakly volatile substances and easily penetrate solid matrices (respective properties of traditional liquid solvents and gases when they reach values close to those of a liquid under supercritical conditions. Thus, supercritical fluids are considered to be effective solvents.

The advantages of supercritical fluids compared with those of other solvents are: low power consumption, easy separation of the solvent and the extracted fraction, high selectivity, and low resistance to mass transfer. The supercritical extraction technique began in the XIX century with the research done by Hannay and Hogarth (1897) in the study of solubility of inorganic salts (*KI, KBr*, and $CaCl_2$) in supercritical ethanol, methane, ethane and carbon dioxide, Hannay and Hogarth (1897). With the release in 1930 of vapor-liquid diagrams (VLE) of hydrocarbons at high pressures, it was possible to develop the first industrial application of solvent deasphalting of crude in 1943, (Messmore, 1943; Northup & Sloan, 1986).

The supercritical fluid extraction technique has impacted several sectors in industry since the 1970's and 1980's. Many authors have evaluated the effect of variations in temperature, pressure, time, flow and nature of the solvent in the extraction of natural essences, such as pesticides from solid waste and refined oils, (Gallego & Cardona, 2004 and Esquivel & Vargas, 2007).

Subramanian and Hanson (1998) proposed a method for supercritical fluid extraction in oil sands using propane as a solvent. Along the same lines, Masaka, Motonobu, & Tsutomu (1997) and Suoqui, Zhiming, Chunming, Keng, & Chung (2005) applied the extrac technique to waste oils, in order to get free fraction asphaltene fractions using n-pentane as solvent. Sh Li, Sheng-Sheng, Yun-Hua, & Suo-Qi (1984); Tie- Yun-Xiang, Tong, & Ren-An (1997) and Guangua Ren-An (1999) characterized the fractions obtai from heavy crude oil, and vacuum residue with Prop Butane and Pentane in supercritical conditions. Swar Dollimore, & Diehl (1985) evaluated the conversio ficiency and extraction conditions of light fractions ent in coal by supercritical extraction with solvents s as pentane, hexane, heptane, octane and cyclohexa

With the steady depletion of reserves of light cr refineries have been forced to rethink their proce with new feed mixtures, based on heavy crude oil v a projected in high increase atmospheric and vacu residue. However, to adjust the refining process resi vacuum is essential to know their physicochem properties, because this characterization allows t crease the efficiency of conversion processes.

To make a broad characterization and estimatio physicochemical properties such as density, visco and molecular weight among others, is not an easy because to get significant amounts of these fract involves a complicated task with traditional meth such as the SARA separation method.

Ecopetrol S.A. in the Instituto Colombiano Petróleo (ICP), has built a pilot unit of supercrit fluid extraction and fractionation with two purpo first, to extract significant quantities of a large num of fractions of a different nature from vacuum resi for further characterization. Second, deepening on behavior of heavier petroleum fractions to improve integrate new and future refining schemes.

Although there are a variety of works in the of supercritical extraction solvent paraffinic from pane to pentane, this research was selected over o n-hexane solvent, due to the fact that the solubilit supercritical conditions on high molecular weigh drocarbons tends to be higher, as indicated by Swar *et al*. (1985).

The purpose of this study is to evaluate the metho ogy of supercritical extraction implemented by Ecope S. A., in a vacuum residue typical refinery in Barranca

meja using as solvent n-hexane under operating conditions of 265ºC at pressure range between 550 and 1250 psi.

2. EXPERIMENTAL METHODOLOGY

Materials

Vacuum residue typical Barrancabermeja refinery, and n-hexane (density at 25ºC = 0,655 g/ml, Pc = 436,9 psi, Tc = 234,7°C).

Description of the extraction process

The extraction unit consists of two high-pressure pumps for solvent and vacuum residue (2, 6), an extraction column (3), a pressure regulator (4), a container to decompress the solvent and collect the samples at each pressure condition (5), and a solvent drum to recover the solvent (1), as shown in Figure 1.

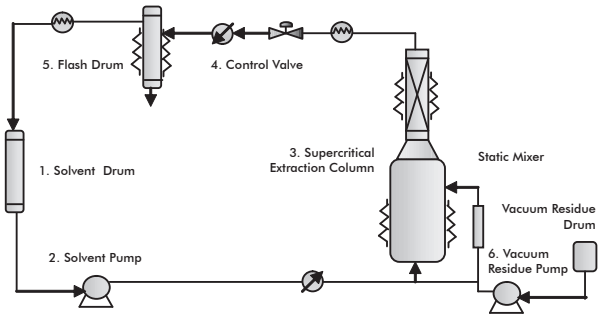


Figure 1 Schematic of supercritical extraction process

The process begins by heating and transporting a quantity of vacuum residue (900 grams) to the supercritical extraction column (3) with the appropriate pump (6). After reaching the operating conditions of temperature and pressure defined through electrical resistance and pressure regulator for regulating the pressure drop (4), begins the extraction of fractions of vacuum residue are carried by the solvent and led to flash drum (5).

The fraction accumulates in the flash drum for subsequent removal. The solvent is released by decompression and is recovered by condensation using a heat exchanger. The recovered solvent is stored again in the solvent drum (1) and restart the process of recirculation. Throughout the process there is a continuous solvent renewal and recovery.

After extracting for approximately 90 minutes, other operating conditions are adjusted and the extraction procedure is repeated. The extraction process ends when the last set pressure value is reached or until securing significant traces of fractions in the flash drum is no longer possible. Finally, the supercritical extraction column is depressurized and cooled gently to drain the residue contents and conduct the respective mass balance.

The above work was conducted in two stages. Initially, the methodology of supercritical extraction fractionation with n-hexane (operating conditions: 265ºC and 450 to 1250 psi) was evaluated. Secondly, a characterization of the fractions was made.

The fractions obtained in the flash drum were collected in a glass Erlenmeyer flask with 24/40 ground-glass head, and purified in a rotary vacuum distilled. A nitrogen flow is then used eliminate traces of the solvent. Mass balances end efficiency were calculated using the above quantities.

3. RESULTS

The characterization vacuum residue and the fractions obtained was performed according to ASTM methods described in Table 1.

Efficiency of the extraction process

Table 1 reports an extraction yield of 82,6% compared to the total of vacuum residue used in the test. However, if we consider the extraction yield in relation to the vacuum residue without the fraction of asphaltenes, is possible to extract high yields of species maltenes fraction distributed in a large number of fractions.

Table 2 shows the amounts of the fractions obtained by supercritical fluid extraction and fraction SFEF.

In view of the results, close to 92,6 % of the free fractions of asphaltenes from the selected vacuum residue were separated with n-hexane when maintaining the temperature of the supercritical extraction process at 265ºC (far from the decomposition temperature of the vacuum residue).

Comparing the results obtained by Simulated distillation of high temperature according to ASTM D6352-04 (Figure 2) with the results of the technique of supercritical extraction can be said that the technique of simulated distillation requires temperatures near 720°C to recover for 67% of vacuum residue, while the supercritical extraction technique is possible to extract about 92,6%.

The results show that the technique of supercritical extraction is a very interesting tool for obtaining high yields of deep fractions from vacuum residue of varying nature. In Figure 3, illustrates the appearance of the fractions obtained by supercritical extraction technique.

Table 1 Characterization of the vacuum residue

Property	Value
Sulfur, %wt. (ASTM D 4294-10)	1,85
Density to 15°C, g/ml. (ASTM D 4052-09)	1,0115
CCR, %wt. (ASTM D 4530-07)	8,3
Saturates, %wt. (ASTM D2007-03)	
Aromatics, %wt. (ASTM D2007-03)	19,8
Resins, %wt. (ASTM D2007-03)	13,46
Asphaltenes, %wt. (ASTM D2007-03))	49,98
Níckel, mg/kg. (ICP/MS1)	25,76
Vanadium, mg/kg. (ICP/MS1)	10,8
Níckel, mg/kg	102,1
Vanadium, mg/kg	196,4

Table 2 Efficiency of extraction of fractions to 265°C

Time Accumulated, hr	Pressure, psi	% Wt
1,5	550	4,1
3	650	10,0
4,5	750	31,9
6	850	55,8
7,5	950	66,6
9	1050	75,6
10,5	1150	79,9
12	1250	82,6
	Residue	100,0

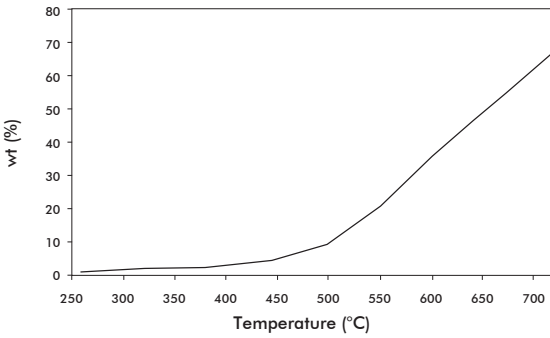


Figure 2 Curve simulated distillation for high temperature vacu residue with the method ASTM D-6352-04 (2009)

The supercritical extraction method with v tion of pressure at constant temperature, presents advantage to obtain a wide separation of fract with sufficient amounts that may be used for a br characterization.

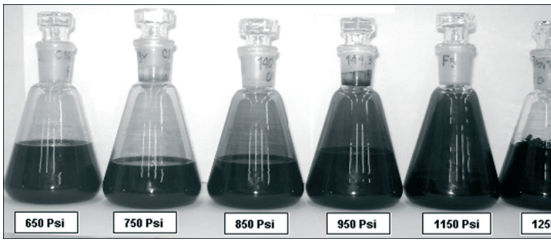
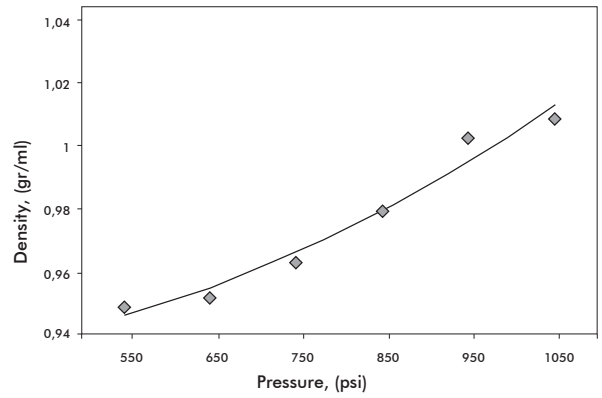


Figure 3 Fractions obtained by the method of supercritical flu extraction and fraction SFEF at 265°C

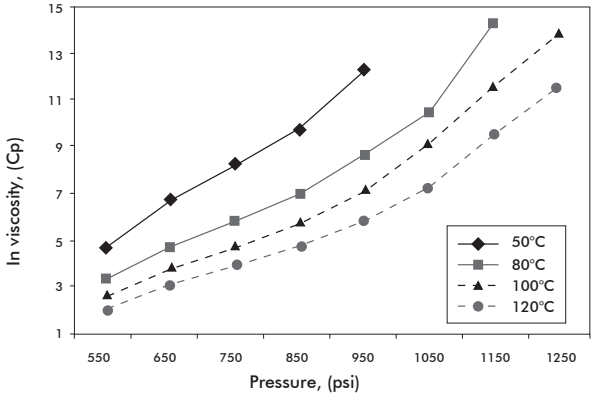
The supercritical extraction can be extende future work, in order to evaluate the performanc extraction and characterization of the fractions obta from crudes of the different nature, based on the st variables and operating conditions such as natur solvent, temperature and pressure.

Figure 4, illustrates the physicochemical proper of the fractions obtained by supercritical extrac from vacuum residue typical of the Barrancaber Refinery. The results indicate that as the condi is increased pressure to extract fractions at cons temperature increases the density and viscosity, wh indicates that the fractions become heavier.

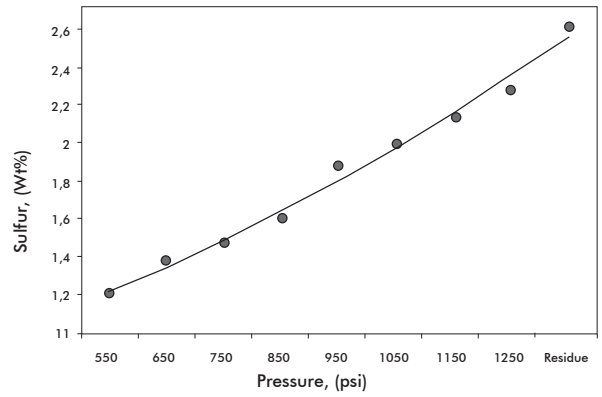
The distributions of sulfur, CCR, nickel, and v dium indicate that the concentration of these spe increases as the fractions become heavier. Researc



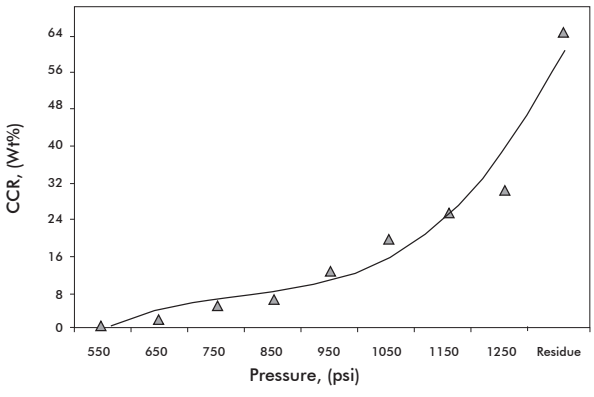
(a)



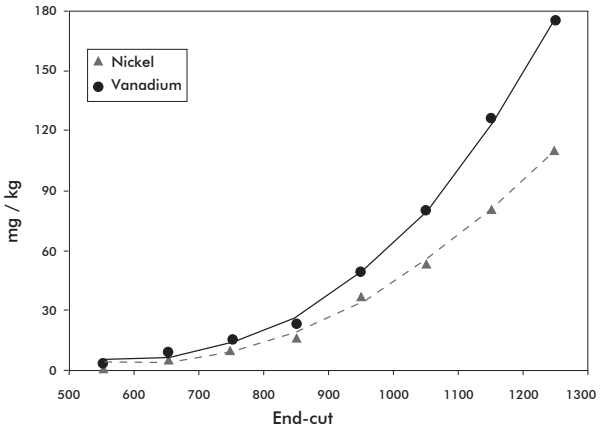
(b)



(c)



(d)



(e)

Figure 4 Characterization of the fractions obtained by supercritical extraction: (a) Density, (b) Viscosity, sulfur content (c), (d) CCR content and (e) Content of nickel and vanadium. The residue (end-fractions) contains 377 and 792 mg/kg of nickel and vanadium

like Tie-Pan *et al*. (1997), and Suoqui *et al*. (2005) found a very similar behavior of the species tested in the fractions obtained from heavy oil of at different nature by supercritical extraction process with fractionation.

This may indicate that as larger fractions become heavier, their complexity increases and they present a greater tendency to form structures of high molecular weight with heteroatoms. For example, one of the most common ways to find sulfur in complex petroleum structures is in functional groups such as thiols, sulfides, disulfides, thiophenes, and their derivatives. Moreover there is a high probability of finding metals such as nickel and vanadium in shaped porfirines. (Wauquier, 2004 and Helle, 2005).

The results illustrated in Figure 5 indicate that the saturated fraction is concentrated in the first fractions and then begins to decrease its concentration with increasing pressure at constant temperature. The resin content in the fractions shows an inverse trend compared with the saturated concentration. A possible reason for this is due to increased solvency power of the solvent. Aromatic content distribution has a tendency with little variation in the range of 50 to 55%. This observation is related to the high aromatic content of about 50% in the vacuum residue (Table 1). The cut of residue is mainly composed of asphaltenes and resins.

The high content of aromatics and resins in the fractions obtained show that as the fractions are made heavier its complexity also increases particularly for the contribution of aromatics polycondensates.

The technique of supercritical extraction is a high-impact tool to generate information useful in the characterization of fractions obtained from the heavier

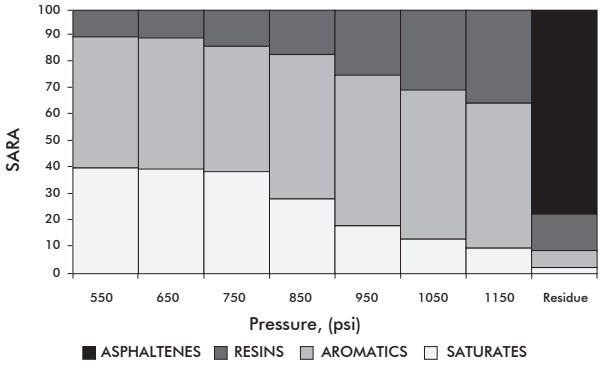


Figure 5 SARA distribution vacuum residue

crude of the nature variable that was not previo had easy access. The new information helps to broa understanding of the behavior of the heavier fract of crude oil refining schemes.

With the basic characterization of the deep fract obtained from the vacuum residue and to the acc paniment of NMR spectroscopic techniques, UV- NIR and molecular reconstruction, is possible adjus base Assays of crude Colombia, and strengthen mo of interest included in the simulators and optimi Ecopetrol´s S. A. Refining.

4. CONCLUSIONS

- The technique of supercritical extraction is a h impact tool to generate information useful in characterization of fractions obtained from heavier crude of the nature variable that was previously had easy access. The new informa helps to broaden understanding of the behavio the heavier fractions of crude oil refining sche

- Under the operating conditions of temperature pressure established in this research, it is poss to recover high percentages of light fraction maltenes that are part of the vacuum residue (rated, aromatics and resins).

- The density, viscosity, distribution of sulfur, CCR, indicate the possibility to obtain fraction different nature from heavy oil and vacuum resi under the specified operating conditions.

- The fractionation of the vacuum residue with sure increases at constant temperature, allows fractions become heavier with increasing den viscosity, sulfur content and CCR. Therefore, distribution profile of heteroatoms, saturated, matics and resins indicates that the complexit the fractions obtained increases.

- Methodology developed by the Instituto Co biano del Petróleo (ICP), will expand in the future knowledge of the characterization of crude base in Colombia.

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