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Extraction of Hydrocarbons from Crude Oil Tank Bottom Sludges using Supercritical Ethane

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Abstract: A custom-built, solvent recirculating, supercritical fluid extraction (SFE) apparatus was used to study the extraction of hydrocarbons from a crude oil tank bottom sludge (COTBS) with supercritical ethane. The SFE experiments were carried out varying the pressure (10 MPa and 17.20 MPa) and temperature (35°C and 65°C). The yield of the extracted hydrocarbon fraction increased with increase in extraction pressure at constant temperature, and decreased with increase in extraction temperature at constant pressure. The maximum extraction yield was obtained at the pressure and temperature conditions that lead to the highest solvent density. The extracted hydrocarbon fraction was a significantly upgraded liquid relative to the original untreated COTBS.

Keywords: Supercritical fluid extraction, ethane, crude oil tank bottom sludges, hydrocarbons recovery

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INTRODUCTION

As a result of the production and storage processes of crude oil, the world petroleum industry annually produces large quantities of crude oil tank bottom sludges (COTBS). It appears that the formation of sludge during the bulk storage of crude oil is an unavoidable phenomenon resulting from the settling out of suspended and agglomerated constituents of crude oil (1). Unfortunately, COTBS generation causes several problems in most of the refineries worldwide. For example, COTBS accumulation may result in a loss of the storage capacity in refinery crude storage tanks, and can ultimately provoke refinery problems when fractions of the sludges are introduced into process plants (2). In addition, the storage of COTBS represents an environmental threat, as many of their components may ultimately find their way into the air, water, and the soil.

COTBS mainly consist of sediments, water, oil emulsions, and heavy hydrocarbons such as asphaltenes. However, its global composition is highly variable and could widely vary from facility to facility and from tank to tank within the same facility, and it is dependent upon the composition of the stored product, the storage conditions, the length of the storage time, and the condition of the sludge tank (3).

In the past many refineries used to manage the problem of COTBS generation just by accumulating the sludges in some of their crude tanks, and then disposing them simply by landfilling the solid wastes into a refinery's own landfarm or into commercial landfills (2). However, since the arrival of more stringent environmental regulations the options available for the disposal of this kind of sludges have been limited and both environmentally and economically prohibitive (2).

During the past few years supercritical fluid extraction (SFE) has attracted much attention in several fields that involve separation operations. Because of its advantages in sample preparation, extraction efficiency, ease of phase separation, fast mass transfer rate, low-energy consumption of solvent recovery, and elimination of toxic solvents, SFE has been used in several processes focused on the fractionation and upgrading of petroleum and petroleum related feedstocks (4–14). Several supercritical solvents such as carbon dioxide, ethane, and propane have been used in these processes. However, supercritical ethane is a much better solvent than carbon dioxide for the treating of complex hydrocarbons mixtures (6).

In this work we present the results obtained after extracting, with supercritical ethane, a crude oil tank bottom sludge generated from the storage of an Isthmus Mexican crude oil. Experimental conditions of pressure and temperature were varied to determine their impact on the extraction capacity of the solvent. The main purposes of the work were to evaluate the capacity of SFE for treating the COTBS, and to determine the potential of supercritical ethane to

1. treat and reduce the volume of sludges that are formed as a result of the crude oil storage, in order to reduce the amount of the generated solid waste and consequently the disposal cost, and

2. to extract and recover a potentially valuable hydrocarbon fraction from the waste, which could be reused as a process feedstock.

EXPERIMENTAL

Reagents and Materials

A sample of a crude oil tank bottom sludge generated from the storage of an Isthmus Mexican crude oil provided by Petróleos Mexicanos (PEMEX; the Mexican State Oil Company) was used to evaluate the extraction capacity of supercritical ethane. Ethane used in the extraction experiments was purchased from Praxair (Tultitlán, México), with a purity greater than 99%. Chemicals used in other experimental determinations were 1,1,2-trichloro-1,2,2-trifluoroethane 99% (E. I. Dupont de Nemours, Wilmington, DW), hydrochloric acid 36.5–38% (J.T. Baker, Xalostoc, México), silica gel (60–200 mesh) for chromatography (J.T. Baker, Xalostoc, México), and carbon tetrachloride, 99.8% (Merck, Darmstadt, Germany). Other reagents were supplied by Aldrich (Milwaukee, WI) with the following stated purities chlorobenzene (spectrophotometric grade), $\geq$99%; pentane (anhydrous), $\geq$99%; cyclohexane (anhydrous), 99.5%; hexane (for GC), $\geq$99.0%; heptane, 99%; hexadecane, 99%; octane (anhydrous), $\geq$99 + %; pentadecane, $\geq$99%; toluene, 99%; 2,2,4-trimetylpentane, $\geq$99%; acetone, $\geq$99%; dichlor-omethane (HPLC grade), 99.9%; calcium chloride (anhydrous beads, -10 mesh), 99.9 + %, dibutyl sulfide, 96%; nitric acid (reagent grade, fuming), $>$90%; and sulfuric acid (reagent grade), 95–98%. All the reagents were used without further purification. Water used in the experiments was type 1 reagent from an Ultrapure water system, model Easypure RF (Barnstead Thermoline, Dubuque, IA).

Experimental Apparatus and Procedure

The supercritical fluid extraction (SFE) apparatus used in this work was custom-built in our laboratory, and was a modification of a device previously used to study the solubility of saturated lineal hydrocarbons in supercritical carbon dioxide (15). A schematic representation of the experimental apparatus developed in this work is presented in Fig. 1.

The SFE apparatus consisted of three main sections: the feeding section, the extraction section, and the separation and solvent recycling section.

The feeding section was constituted by a commercial ethane gas cylinder [1], two storage cells [2 and 3] and a LabAlliance positive displacement pump [4], model SFC-24 (State College, PA). The storage cells (constructed in 316 stainless steel, with an individual volume of 220 cm^3) were used for storing ethane previous to load it into the extraction section. In addition, storage cell [2] was also used as a mean to increase the pressure into the system (by increasing the temperature of the stored gas) when the pressure

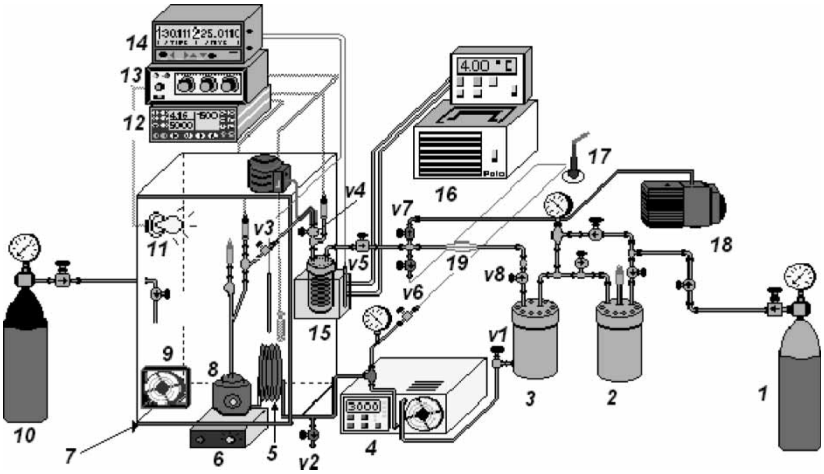

Figure 1. Schematic diagram of the supercritical fluid extraction apparatus used in this work.

provided by the commercial gas cylinder was not enough to reach the desired working pressure of the pump. The positive displacement pump allowed to provide a reliable, accurate, and reproducible pumping of liquid ethane during the extraction process.

The extraction section was enclosed into an air bath [7]. In this section the extraction of the sample of COTBS was carried out, at the pressure and temperature of interest. The main component of this section was the extraction cell [8]. This cell, constructed in 316 stainless steel, had an internal volume of 14 cm^3. The cell was adapted with two optical quality sapphire windows (25 mm o.d. × 5 mm thick) provided by Thoughtventions Unlimited LLC (Glastonbury, CT). The temperature in the extraction section was kept at the desired value by a heat source [11], and regulated through a YSI proportional temperature controller [13], model 72 (Yellow Springs, OH). Homogeneity of the temperature in the extraction section was reached by a temperature homogenizer fan [9]. The thermometer [14] used to register the temperature in the extraction section was a Systemteknik AB digital thermometer, model S1220 (Lindigo, Sweden), adapted with a platinum resistance sensor, calibrated by comparison with a standard platinum resistance thermometer whose calibration was traceable to NIST. The platinum resistance sensor was directly adapted to the external surface of the extraction cell. The average uncertainty of the temperature measurements was of $\pm 0.15°C$. The equilibrium pressure during the extraction process was registered through a Druck multifunction pressure indicator [12], model DPI 145 (Leicester, UK). The pressure indicator was calibrated against a dead weight pressure gauge. Considering all possible uncertainty sources the average uncertainty for equilibrium pressure measurements was estimated to be ±0.21 MPa.

The separation and the solvent recycling section was constituted by a recovery stainless steel cell [15]. This cell (internal volume of 60 cm^3) was used to reduce the pressure and temperature of the fluid leaving the extraction section in order to separate the extracted phase from the solvent. The solvent was then sent to the storage cell [3] to reuse it in a new extraction step. With the aim of avoiding the dragging of solid particles from the extraction cell to the storage cell a Hoke micron filter [19], model 6313G4B, was adapted into the stainless steel line after the recovery cell.

To carry out a supercritical extraction experiment, a given mass of sample (between 1.5 and 2.6 g) was weighted and loaded into the extraction cell. With the aim of ensuring the homogeneity of the studied sample, all samples loaded into the extraction cell were subsampled from the laboratory sample (i.e. the sample received in the laboratory) (16), according to a method developed in our laboratory for properly subsampling highly heterogeneous solid matrixes.

After loading the sample, the extraction cell was connected to the extraction section as shown in Fig. 1. Then, the air in the extraction and recovery cells, as well as the air in the stainless steel line between valves *v2* and *v8*, was eliminated through a vacuum pump [18]. After this process, liquid ethane was pumped to the extraction section by the positive displacement pump [4]. The pressure in the extraction section was increased as a result of the pumping process and controlled at the desired value (10.00 or 17.20 MPa). The temperature of the ethane entering the extraction cell was fixed above its critical temperature. To ensure the proper homogeneity in its temperature, the ethane was preheated in a stainless steel coil (3 m × 0.30 cm O.D) [5]. With the aim of reducing the possibility of generating a dangerous concentration of ethane in the extraction section (for example, as a result of an undetectable leak of solvent) a continuous flow of nitrogen (from cylinder *10*) was kept into the constant temperature bath.

The solvent, at supercritical conditions, entered the bottom of the extraction cell and flowed upwards, removing the soluble portion of the crude oil tank bottom sludge. To improve the extraction process, the content of the extraction cell (sludge + solvent) was stirred by a teflon coated stirring magnet activated by a PMC stirring hot plate [6], model 502A (Dubuque, IO).

The resulting phase left the extraction cell and passed through the *v3* valve towards the recovery cell. In this cell, and by means of a micrometric valve (*v4*), the pressure of the fluid was reduced to about 4.14 MPa. The temperature was also reduced to about 4°C, by means of a Julabo refrigerated/heating circulator [16], model F32 (Seelbach, Germany). As a result of the reduction in the pressure and temperature conditions the extracted hydrocarbons were precipitated into the recovery stainless steel cell, and the released ethane was sent back to the storage cell [3]. The recovered ethane was subsequently used to continue the extraction process until the desired total extraction volume was reached.

At the end of the experiment, the positive displacement pump was turned off, the system was depressurized, and any excess of ethane was burned out by means of burner [17]. Once the pressure in the experimental system reached the atmospheric pressure, the extraction and the recovery cells were disconnected and weighted to carry out the mass balance that allowed to determine the yield of the recovered hydrocarbon fraction.

Analytical Methods

The total petroleum hydrocarbons (TPH) content in the studied COTBS samples was determined by a method similar to EPA method 418.1 (17). Determinations of asphaltenes, metals (nickel, vanadium, iron), sulfur, and characteristic groups (saturates, aromatics, and polar compounds) were carried out according to methods described in ASTM D 6560 (18), D 5863 (19), D 2622 (20), and D 2007 (21), respectively.

Chromatographic characterization of the extracted hydrocarbon fraction was carried out using an HP 6890 Series gas chromatography system coupled to a 5973 mass selective detector, MSD (Agilent Technologies, Palo Alto, CA). The column used was a capillary column (30 m × 0.25 mm × 0.25 μm film thickness) coated with a non-polar stationary phase (HP-5 ms; 5%-phenyl-methylpolysiloxane). The operation conditions were the following: the oven temperature was set initially at 50°C (5 min hold), increased to 120°C at 5°C/min (5 min hold), and finally increased to 210°C at 10°C/min (5 min hold). Helium was used as the carrier gas at a flow rate of 1.0 cm^3/min. Injector and transference line temperature was held at 280°C and 290°C, respectively. The splitless mode was used for injecting 0.5 μl of the extracted hydrocarbon fraction (diluted in hexane, in a volume fraction of 50%) into the gas chromatograph. The MSD was operated in the electron impact ionization mode (EI, 70 eV) and full scan mode (m/z 40–500), with the source heated to 230°C and the quadrupole heated to 150°C. The chromatographic analyses were run by triplicate.

RESULTS AND DISCUSSION

Yield of the Supercritical Extraction Process

A series of experiments were conducted to determine the effect of pressure and temperature on the supercritical extraction process.

Two different temperatures (35°C and 65°C) and two different pressures (10.00 MPa and 17.20 MPa) were chosen as the experimental conditions to evaluate the extraction capacity of supercritical ethane. The effect of these parameters on the cumulative quantity of the hydrocarbon fraction recovered from the treated sample of the Isthmus COTBS (as a function of the solvent volume used in the extraction) is shown in Table 1, as well as in Figs. 2 and 3.

The density of the supercritical ethane at the studied pressures and temperatures was also calculated and included in Table 1. Density calculations were carried out by making use of the NIST tool for estimating thermophysical properties of fluid systems (22). Reduced densities were calculated considering the critical density value for ethane reported by Ambrose and Tsonopoulos (23).

As observed in Fig. 2, at a given temperature, as the pressure increased, the amount of the extracted hydrocarbon fraction increased too. This effect was more evident at the temperature of 65°C. For example, at 10.00 MPa, approximately a mass fraction of 40% of the original COTBS was extracted after the sludge was in contact with about 1450 cm^3 of ethane. When the pressure was increased to 17.20 MPa, the amount of the hydrocarbon extract recovered, with approximately the same amount of solvent, increased to a mass fraction of about 50%.

On the other hand, at a given constant pressure (Fig. 3), as the operating temperature decreased, the amount of the recovered extract increased. This effect was more evident at a pressure of 10.00 MPa. For example, a comparison of the cumulative mass fraction of the extract recovered after the contact of the sludge with about 1230 cm^3 of ethane showed that the mass fraction increased from about 40% at 65°C to approximately 49% at 35°C.

The above results are, in general, similar to those obtained in other studies reported in the literature which indicate that during the fractionation of solid matrixes, such as bitumen, with supercritical fluids the yield of the extracted fractions increased with increase in the extraction pressure at constant temperature (6, 10, 11, 14), and decreased with increase in the extraction temperature at constant pressure (6, 10, 11).

During the study on the fractionation of bitumen with supercritical ethane, Rose et al. (6) explained the above behavior stating that at low temperatures and high pressures the density of ethane reaches values similar to the liquid density of ethane (24), and under those conditions, the system behaves similar to a liquid-liquid extraction process. Since these kinds of systems have higher solubilities as a result of the increase in the attractive forces compared to vapor solvents (25), then the solubility of the fractions recovered from the bitumen was much higher and therefore a much higher amount of such fractions could be recovered. On the other hand, at high temperature and low pressure the solvent density could decrease to values much lower than the liquid density (24). Under such conditions the system now acted similar to a vapor-liquid extraction process and consequently, the extraction capacity of the solvent was decreased. This resulted in a smaller amount of the fraction recovered from the solid matrix. In addition, during the treatment of bitumen samples the extraction yields increased with increases in the density of the solvent, in such a way that the maximum extraction yield was obtained at the highest solvent density (6, 10); thus concluding

Table 1. Yield of the hydrocarbon fraction extracted from the Isthmus crude oil tank-bottom sludge as a function of pressure, temperature and cumulative volume of ethane

Sample No.	P/MPa	t/°C	ρ^a/mol · dm^{-3}	$\rho_r{}^b$	Flow rate^c/ cm^3 · min^{-1}	Mass fraction extracted/%	Extraction time/min	V^d/cm^3
10.00 MPa, 35.00°C								
1	9.96	34.99	12.027	1.751	1.00	28.5 ± 2.8	150	150
2	10.03	34.98	12.048	1.754	1.00	36.4 ± 4.4	292	292
3	10.03	34.98	12.047	1.754	5.00	44.0 ± 4.2	155	775
4	9.87	34.99	12.004	1.747	3.22	48.6 ± 4.3	383	1235
10.00 MPa, 65.00°C								
5	10.01	65.01	8.769	1.276	0.92	16.2 ± 2.2	163	150
6	9.96	64.96	8.736	1.272	1.00	23.0 ± 1.6	300	300
7	9.96	64.92	8.782	1.278	4.84	36.1 ± 4.0	155	750
8	9.99	65.37	8.704	1.267	4.84	40.8 ± 4.1	300	1452

17.20 MPa, 35.00°C								
9	16.95	35.00	13.259	1.930	1.00	27.1 ± 2.7	150	150
10	17.19	35.00	13.289	1.934	1.00	36.7 ± 3.9	300	300
11	17.24	35.42	13.274	1.932	5.59	49.4 ± 4.3	150	838
12	17.30	35.05	13.300	1.936	5.00	58.5 ± 4.4	307	1535
17.20 MPa, 65.00°C								
13	17.22	64.79	11.573	1.685	0.96	42.9 ± 4.0	162	155
14	17.25	64.92	11.573	1.685	1.00	47.0 ± 4.2	275	275
15	17.15	65.32	11.523	1.677	5.00	49.6 ± 4.4	157	785
16	17.29	64.98	11.577	1.685	5.00	54.9 ± 4.6	305	1525

[a] Density of the solvent at the *P* and *t* conditions. Density was calculated making use of the NIST tool for estimating thermophysical properties of fluid systems (22).

[b] Reduced density of the solvent at the *P* and *t* conditions. Reduced density values were calculated considering the critical density of ethane reported by Ambrose and Tsonopoulos (23).

[c] Measured as liquid ethane at the pump.

[d] Cumulative volume of ethane (measured as liquid ethane at the pump).

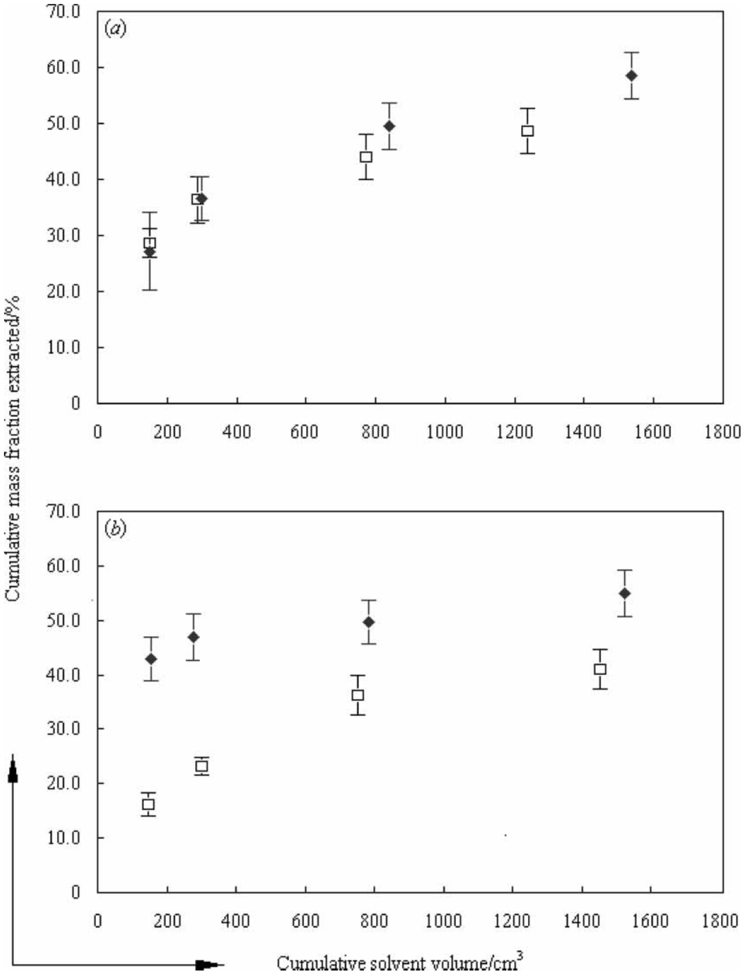

Figure 2. Cumulative amount of the hydrocarbon fraction recovered from the Isthmus crude oil tank bottom sludge, as a function of cumulative volume of ethane for extractions performed at a constant temperature of (*a*) 35°C and (*b*) 65°C at the pressure of (☐) 10.00 MPa and (◆) 17.20 MPa.

that the extraction of bitumen was controlled predominantly by the density of the pure supercritical solvent (6).

As observed in Table 1 (and within the experimental uncertainty of the experimental data), the highest extraction yield (mass fraction, $w_B = 58.5\%$; sample 12) was obtained at the pressure and temperature conditions that conducted to the highest solvent density.

In some cases it has been reported that, in addition to the density of the extraction solvent, other factors such as the proximity of the extraction

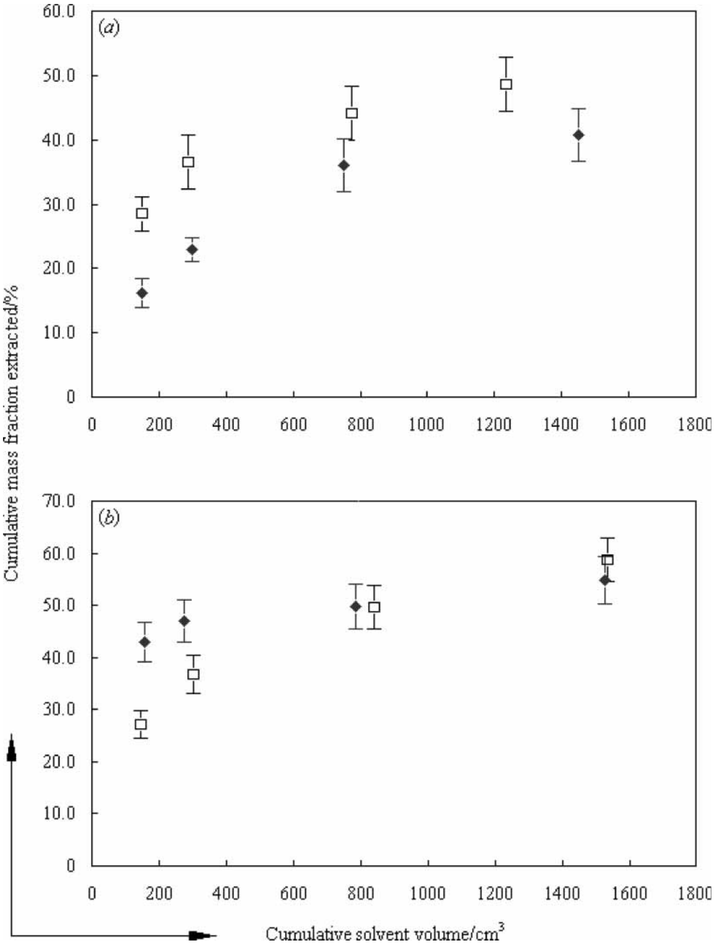

Figure 3. Cumulative amount of the hydrocarbon fraction recovered from the Isthmus crude oil tank bottom sludge, as a function of cumulative volume of ethane for extractions performed at a constant pressure of (*a*) 10.00 MPa, and (*b*) 17.20 MPa at the temperature of (□) 35°C and (◆) 65°C.

conditions to the pure solvent critical temperature, could also control the efficiency of the extraction process (14). For example, during the study on the extraction of bitumen and a bitumen derived liquid by propane, Hwang (13) found that the increase in the density of the extraction solvent does not always contribute to greater extractions yields. In addition, it was also found that despite a reduction of about 20% in the density of propane, during the increase in the extraction temperature from 66°C to 107°C (at a constant pressure of 10.3 MPa), the yield of the extraction remained identical in this temperature range (cumulative volume of the extraction solvent ≈170 L, at standard temperature and pressure, STP). However, there was a significant difference between the two temperatures with respect to the rate of extraction (the amount extracted per unit volume of propane flowed through the system); for example, at 107°C, more oil was extracted at lower-extraction volumes (~between 0 and 100 L, STP). However, it is important to mention that at 66°C and 10.3 MPa the propane is not at supercritical conditions ($P_c = 4.248$ MPa, $t_c = 96.68$°C) (23). Therefore, in this case the diffusional properties of the supercritical media seem to have an important role in the extraction yield. Because of its viscosity and diffusivity close to those of gases, the supercritical propane allows much easier mass transfer than liquid propane, thus facilitating the extraction of compounds from bitumen.

As observed in Table 1 and Fig. 2, a behavior similar to that described above was observed for samples 13 and 14. As appreciated, even though the density of these samples was lower than the density of samples 9 and 10, a larger recovery was obtained during the supercritical extraction with ethane. However, in contrast with the study of Hwang (13) all the extraction results presented in this work were obtained employing the solvent under supercritical conditions. Thus, at this time we can not give an explanation for this behavior.

As indicated in Table 1, the highest mass fraction of the extractable hydrocarbon fraction that was recovered was of 58.5%, with respect to the mass of the original treated COTBS sample. In general, the recoveries obtained in this work are of the same order of magnitude that those obtained during the supercritical extraction of other complex hydrocarbon mixtures (6, 9, 10, 12, 14).

To have an additional reference to compare with the extraction capacity of the supercritical ethane we also conducted an additional experiment in which a series of COTBS samples were extracted with dichloromethane in a Soxhlet extractor. After extracting seven independent samples, during an extraction time of six hours, the mass fraction of the recovered phase was (48.7 ± 3.5)%. This value was slightly lower than the value of (58.5 ± 4.4)% obtained during the supercritical extraction at 17.20 MPa, 35°C, and a solvent volume of 1535 cm^3 of ethane. However, the advantages of the supercritical extraction method (a substantial reduction in the use of huge volumes of organic solvents, ease to recover the extracted phase, low-energy consumption for the recovery and reuse of the extraction solvent, etc.) allow to conclude that the supercritical method is a better option for the treatment of the COTBS under study.

During the experimental extraction studies other additional parameters were also varied to determine their effect on the recovery of the hydrocarbon fraction. The parameters considered were the solvent flow rate (1 to 5.59 $cm^3 \cdot min^{-1}$) and the extraction time (150 to 383 min). As observed in Table 1, when the extraction time was kept constant, an increase in the solvent flow rate produced an increase in the total amount of the extracted hydrocarbon phase (compare, for example, the mass fraction extracted in sample number 6 with that extracted in sample number 8, or the fraction extracted in sample number 9 with that extracted in sample number 11). In the same way, when the solvent flow rate was kept constant, an increase in the extraction time it usually produced an increase in the mass fraction of the hydrocarbon phase that was extracted (results in sample number 1 vs results in sample number 2 and results in sample number 9 vs results in sample number 10). In some cases, within the uncertainty of the experimental results, this behavior was not completely defined (e.g. sample number 7 vs sample number 8 and sample number 15 vs sample number 16). We consider that this is due, in part, to the fact that the sample exhaustion was almost achieved.

Quality of the Recovered Hydrocarbon Fraction

Once the capacity of the supercritical ethane to recover the extractable hydrocarbons from the Isthmus COTBS was determined, the samples from the untreated and the treated tank bottom sludge were analyzed in order to determine some of their compositional characteristics and to evaluate the selectivity of the extraction process.

Table 2 presents the asphaltenes and the total petroleum hydrocarbons (TPH) content of the treated (extracted) and untreated (non extracted) Isthmus COTBS. Since the highest recovery in the supercritical extraction process was attained at 17.20 MPa, 35.00°C, and a solvent extraction volume of 1535 cm^3, the sludge sample considered as the treated sample was that obtained after extracting the original COTBS under the experimental conditions

Table 2. Content of total petroleum hydrocarbons (TPH), asphaltenes, and metals in the untreated and treated (extracted with supercritical ethane) Isthmus COTBS

Property	Untreated COTBS	Treated COTBS
TPH[a]/$mg \cdot kg^{-1}$	351543 ± 6673	19663 ± 1293
Asphaltenes[b]/mass%	4.0 ± 0.3	35.0 ± 3.3
Metals		
Iron/$mg \cdot kg^{-1}$	2465 ± 43	—
Nickel/$mg \cdot kg^{-1}$	320 ± 21	—
Vanadium/$mg \cdot kg^{-1}$	359 ± 32	—

[a] TPH content in both untreated and treated samples, as well as the associated uncertainties, were determined from the results obtained in the analysis of seven independent samples.

[b] Asphaltenes in both untreated and treated samples, as well as the associated uncertainties, were determined from the results obtained in the analysis of five independent samples.

above mentioned. Data for asphaltene and TPH content reported in Table 2, correspond to the average of seven and five independent analyses, respectively.

We made use of the TPH determination method (EPA 418.1) as a tool to evaluate the capacity of the supercritical process to recover the extractable hydrocarbon fraction from the studied COTBS, because it is a laboratory test relatively inexpensive and fast, and it has been found to be effective in similar comparative studies (2), even though it is well-known that this type of methods possesses some inherent limitations (26).

When asphaltenes are precipitated from a crude oil, some other materials, such as ash, fine clays, and some adsorbed hydrocarbons also precipitate, thus affecting the asphaltenes quantification (27). Since these materials are not soluble in toluene, they must be removed, previous to the analysis, in order to measure and quantify the true content of asphaltenes (27). Since the ASTM D 6560 method involves a removal of the above-mentioned materials, previous to the asphaltene determination, that method was followed for such determination.

It is observed in Table 2 that supercritical ethane extracted about the 95% (mass fraction) of the original TPH content (as determined by EPA method 418.1) of the untreated Isthmus COTBS. In addition, as a consequence of the drastic reduction in the TPH content of the treated sludge, its asphaltenes content increases dramatically, with respect to the asphaltenes content in the untreated sludge. Table 2 shows that the concentration of asphaltenes in the treated sample of the COTBS increased by a factor of nine. A similar increase of the asphaltene content in the residual fractions was observed by Hwang (13), during the supercritical fluid extraction of bitumen with propane.

It has been found that, despite the polar nature of asphaltenes carbon dioxide is able to extract them from crude oil (28). However, in this work we did not determine if some asphaltenes present in the original Isthmus COTBS were extracted by supercritical ethane.

With respect to the content of metals in the untreated COTBS (Table 2) it was found that its nickel and vanadium content was appreciably higher than that found in a typical Isthmus crude oil (29, 30). This could indicate a selective concentration of the metals in the Isthmus COTBS as a result of the storage process.

Additional compositional results of the recovered hydrocarbon fraction, extracted from the Isthmus COTBS (17.20 MPa, 35°C, solvent extraction volume of 1535 cm^3) are presented in Table 3 and Fig. 4.

As indicated in Table 3, the recovered hydrocarbon fraction extracted from the studied COTBS with supercritical ethane was mainly composed of saturates (∼58 mass%) and aromatics (∼38 mass%). Figure 4 shows that the extract contained a substantial portion of saturated lineal and branched (such as pristane and phytane) hydrocarbons. The number of carbon atoms of lineal and branched hydrocarbons ranged from 9 to 22. Moreover, an additional portion of the GC/MS chromatogram consists of a complex mixture of cyclic hydrocarbons (not indicated in the chromatogram, for

Table 3. Compositional results of the recovered hydrocarbon fraction extracted from the Isthmus COTBS

Extraction Conditions	
P/MPa	17.20
t/°C	35.00
V^a/cm^3	1535
ρ^b/mol · dm^{-3}	13.3
Product yield	
Extract phase/mass%	58.5
Residual phase/mass%	41.5
Compositional results	
Saturates/mass%	57.7 ± 0.9
Aromatics/mass%	37.7 ± 0.7
Polar compounds/mass%	4.62 ± 0.03
Sulfur/mass%	0.898 ± 0.019
Iron/mg · kg^{-1}	25.1 ± 0.8
Nickel/mg · kg^{-1}	15.4 ± 0.2
Vanadium/mg · kg^{-1}	45.4 ± 0.8

[a] Cumulative ethane volume (measured as liquid ethane at the pump).

[b] Ethane density at the indicated P and t conditions.

clarity reasons) and aromatic hydrocarbons (essentially alkyl benzenes and alkyl naphthalenes). Some sulfur compounds such as methyldibenzothiophene were also detected.

Liquid and supercritical hydrocarbons such as propane, are able to extract metallic compounds from complex systems such as used lubricant oils (31). The results in Table 3 indicate that supercritical ethane was also able to extract part of the iron, nickel, and vanadium content present in the original Isthmus COTBS (Table 2). However, as appreciated the concentration of Fe, Ni, and V in the extracted hydrocarbon fraction was significantly lower than the corresponding concentrations in the original untreated sludge (for example, two orders of magnitude lower in the case of iron). It is important to mention that the nickel and vanadium content in the extracted oil fraction was similar to that found in a typical Isthmus crude oil (29, 30). On the other hand, the sulfur content in the extracted hydrocarbon fraction was lower than the sulfur content found in a typical Isthmus crude oil, and even lower than that found in the lighter Olmeca crude oil (29).

From the results presented in Tables 2 and 3, as well as in Fig. 4, it is evident that the quality of the recovered hydrocarbon fraction extracted from the Isthmus crude oil tank bottom sludge could be good enough to be used as a feedstock to obtain valuable refinery products.

The nominal storage capacity of crude oil of the Mexican State Oil Company (Petróleos Mexicanos) is of 23.9 million barrels (32). Thus, the results presented in this work will be relevant to reduce the large quantities

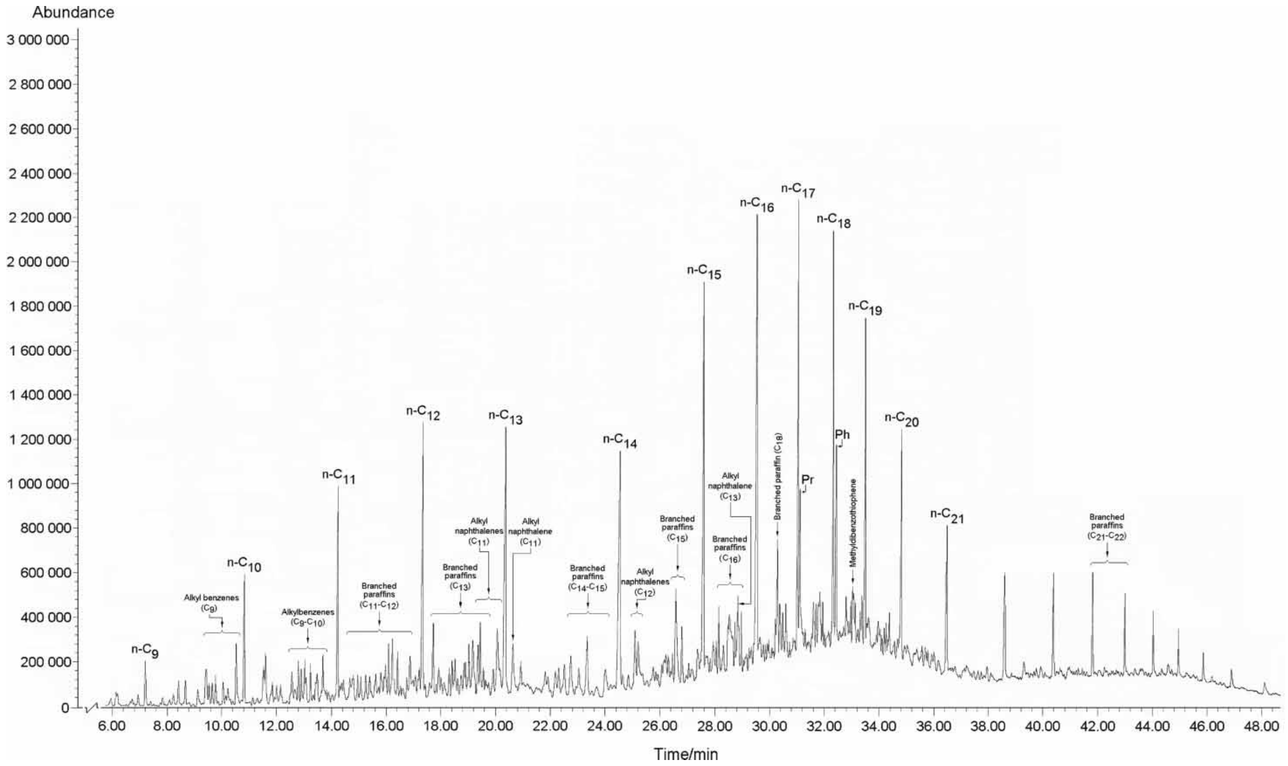

Figure 4. GC/MS chromatograms of the hydrocarbon fraction extracted by SFE from the Isthmus COTBS at 17.20 MPa and 35°C. n-C_a: linear alkanes (a = carbon atom number), Pr: branched alkane pristane, Ph: branched alkane phytane.

of crude oil tank bottom sludges produced by the oil industry, as well as to reduce the unavoidable economic and environmental problems linked to the COTBS generation and accumulation. In addition, the valuable recovered hydrocarbons can be incorporated into a refinery as a valuable feedstock, ensuring thus that they are not sent off site and possibly increasing revenues and offsetting operating costs.

We are currently studying the capacity of supercritical ethane to extract and recover valuable hydrocarbon fractions from the tank bottom sludge generated from the storage of Maya crude oil (a Mexican crude oil heavier than the Isthmus crude oil), and will be the subject of a future report.

CONCLUSIONS

In this work an experimental apparatus suitable to extract and recover valuable hydrocarbon fractions from a crude oil tank bottom sludge, using a supercritical solvent, was constructed and applied. Because of its design, the experimental apparatus allows to recirculate the supercritical solvent during the extraction process, thus significantly reducing the amount of fresh solvent used in each study.

Experimental results indicate that the extraction process was dependent on the operating conditions (pressure, temperature, solvent volume). In general, the extraction yields increased with increase in extraction pressure at constant temperature and decreased with increase in extraction temperature at constant pressure. Within the studied pressure and temperature ranges, the maximum extraction yield was obtained at the pressure and temperature conditions that conducted to the highest solvent density (17.20 MPa, 35.00°C).

From an analysis of parameters such as the TPH, asphaltenes, metals (nickel, vanadium, iron), and sulfur content, as well as from the characterization of the type of its constituents, it was evident that the extracted hydrocarbon fraction was significantly upgraded with respect to the original matrix treated.

Extraction yields of up to 58.5 mass%, as well as the quality of the extracts obtained allow us to state that supercritical fluid extraction with ethane is a promising technique for treating the large amount of COTBS annually produced by the oil industry; in order to reduce the amount of solid wastes generated by this industry (and the associated disposal cost), as well as to recover hydrocarbon fractions, which could be incorporated into the refinery process as a valuable feedstock.

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