



REMOVAL OF NITROGEN COMPOUNDS FROM BRAZILIAN PETROLEUM SAMPLES BY OXIDATION FOLLOWED BY LIQUID-LIQUID EXTRACTION

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ABSTRACT

This work reports liquid-liquid extraction of nitrogen compounds from oxidized and non-oxidized Brazilian petroleum samples. The experiments were accomplished in a laboratory-scale liquid-liquid apparatus in the temperature range of 303 K-323 K, using methanol, n-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF), and their mixtures as extraction solvents, employing solvent to sample volume ratios of 1:2, 1:1 and 2:1, exploring up to three separation stages. Results show that an increase in temperature, solvent to oil ratio, and number of equilibrium stages greatly improves the nitrogen removal from the oxidized sample (from 2600 to 200 ppm). The employed oxidation scheme is thus demonstrated to be an essential and efficient step of sample preparation for the selective liquid-liquid removal of nitrogen compounds. It is shown that the use of mixtures of DMF and NMP as well their use as co-solvents with methanol did not prove to be useful for selective nitrogen extraction since great oil losses were observed in the final process.

KEYWORDS

liquid-liquid extraction; nitrogen removal; petroleum samples; oxidation; equilibrium stages

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1. INTRODUCTION

Nitrogen compounds present in crude petroleum or in its fractions are considered as undesirable due to problems they may cause in the refining process, such as catalyst poisoning, corrosion and gum or color formation in final products (Albert, 1978; Choi and Gray, 1991; Green *et al.*, 1984). Moreover, it is well known that several basic and even neutral nitrogen compounds are toxic with proved carcinogenic activity (Oliveira *et al.*, 2004).

Air pollution, caused by oil exhaust gas (SO_x and NO_x), is one of the most serious problem in the world, and much attention has been paid to the thorough desulfurization of combustible oils. Nowadays hydrotreatment is the most widely used method for the removal of pollutants from fossil fuels. Many works focus on the removal of sulfur compounds from different gas-oil fractions (Ali *et al.*, 2009; Brunet *et al.*, 2005; Mello *et al.*, 2009; Pedernera *et al.*, 2003; Solís *et al.*, 2004; Trakarnpruk and Rujiraworawut, 2009; Van Looj *et al.*, 1998; Wang *et al.*, 2009; Zannikos *et al.*, 1995). Several parameters were studied such as oxidant nature, reaction temperature, kinetics, adsorption process and extraction with solvents. The most used oxidizing agent was hydrogen peroxide/acetic acid (Collins *et al.*, 1997; Filho *et al.*, 2001; Filho *et al.*, 2003; Filho *et al.*, 2004; Zannikos *et al.*, 1995). In all these works nitrogen compounds are not considered, and it is well known that the presence of nitrogen compounds has a negative effect on hydrodesulfurization treatment (HDS) (Briker *et al.*, 2003; Jaramillo *et al.*, 2004; Yin and Xia, 2004). This process alone is ineffective and expensive (Conceição *et al.*, 2005). In view of this, it is important to study the removal of nitrogen compounds prior to the HDS treatment (Wiwel *et al.*, 2000).

Literature reports that the main nitrogen compounds present in petroleum are aliphatic amines, anilines, heterocyclic compounds (pyrrolic and pyridinic), aromatic heterocycles with multiple rings, acridine, indol, alkyl carbazoles and alkyl benzocarbazoles (Varma and Naicker, 1999).

Oxidation reactions can help removing nitrogen compounds from petroleum fractions (Attar and Corcoran, 1978), but unfortunately, these reactions

may also oxidize other classes of compounds, like olefins, that are important raw materials for the industry.

In this context, the main objective of this work is to investigate the removal of nitrogen compounds from oxidized and non-oxidized Brazilian petroleum samples through liquid-liquid extraction. For this purpose, the selective oxidation of organic nitrogen compounds found in one of the gas-oil samples was first performed according to a procedure reported recently, with minimum effect over other classes of compounds (Conceição *et al.*, 2005).

2. MATERIALS AND METHODS

2.1 Reagents

Analytical grade (methanol 99.9%, NMP, 99.5% and DMF 99.8%, from Merck, Brazil) were employed. Prior to use, solvents were twice distilled. Acetic acid (Quimex, 99.7 %), hydrogen peroxide (Synth, 30%), alcoholic solution of NaOH (Aldrich, 97%), NaCl (Vetec, 99%), Na_2SO_3 (Quimex, 99%) and MgSO_4 (Synth, 98%) were used as received.

2.2 Petroleum Samples

In this work three samples were kindly provided by CENPES-PETROBRAS-Brazil. One of the samples was composed of heavy diesel, light gas oil and clarified oil mixed at a ratio of 60, 30 and 10% by volume, respectively, labeled as C3. The other fraction is a heavier fraction coming from the vacuum distillation of atmospheric residue and is usually referred to in the petroleum industry as HVGO (heavy vacuum gasoil). In order to propose a more comprehensive investigation, crude petroleum samples were also employed in the liquid-liquid extractions for broader comparison. The first sample, C3, was submitted to oxidation and the other two ones were used without any further treatment. Determination of total nitrogen content (ppm) was carried out with the Kjeldhal method (Harris, 2005). Analysis of the investigated samples resulted in 4696, 4177 and 2600 for crude petroleum Marlim, GOP and oxidized C3 (OC3),

respectively. Duplicate Kjeldhal analyses were carried out for some samples resulting in overall standard deviation of 5%. A detailed chemical characterization of the petroleum samples utilized in this work can be found in the references (Campos *et al.*, 2006; Conceição *et al.*, 2005; Oliveira *et al.*, 2004; Oliveira *et al.* 2006). It may be convenient to mention that the three samples employed in this work are presumably the most important input and output streams in the machinery of petroleum industry, since many (lighter) compounds (light gases, gasoline, diesel, kerosene, etc.) are derived from these samples, thus conferring relevance to the execution of this work.

2.3 Oxidation Reaction

The procedure adopted for sample oxidation reaction was that reported by Conceição *et al.* (2005), and considering that it is not the focus of this work, only a brief description is provided. Basically, a sample volume of 150 mL was transferred to a two-neck glass flask provided with a thermometer and was heated to 343 K (oil bath) under magnetic stirring. When the reaction temperature was reached, a mixture of 17 mL of acetic acid and 10.6 mL of hydrogen peroxide (30% wt) was added and the mixture was kept under stirring for 1h. Then the mixture was transferred to a separation funnel where separation of the phases took place, and two aliquots of 1 mL of the oil phase were submitted to analysis of peroxide by iodometry and acidity by titration with 0.3 mL of an alcoholic solution of NaOH 0.1 N.

The aqueous phase was washed twice to eliminate traces of oxidant. The first wash was carried out with 50 mL of NaCl (20% wt) and after separation of oil and aqueous phases, the oil phase samples were submitted to acidity and peroxide measurements. The second wash was performed with 50 mL of a mixture of NaCl (15% wt) and Na₂SO₃ (5% wt) mixture. After separation of oil and aqueous phases, 3 g of anhydrous MgSO₄ were added to the separation funnel and the mixture was shaken vigorously. Then, the oil phase was filtered under vacuum and stored. The oil weight was monitored during all the process. In a previous work (Conceição *et al.*, 2005) it was shown by liquid ion exchange chromatography (LIEC) that the reaction scheme used in this work is preferential for nitrogen compounds oxidation and keeps unchanged the distribution of the other classes of compounds in gas oil samples. Figure 1 shows the mechanism of peracid formation and nitrogen compounds oxidation, which leads to an increase of nitrogen compounds polarity.

2.4 Liquid-liquid Extraction

A liquid-liquid equilibrium apparatus was set up in order to acquire the experimental data in the temperature range of 303 K-323 K, using methanol as primary solvent, and N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF) as co-solvents, and their mixtures, in solvent extraction assays, employing solvent-to-sample volume ratios of 1:2, 1:1 and 2:1 and adopting up to three equilibrium separation stages. The equipment used to obtain liquid-liquid equilibrium data consists of three jacketed equilibrium cells having an approximate volume of 80 mL, a thermostatic bath

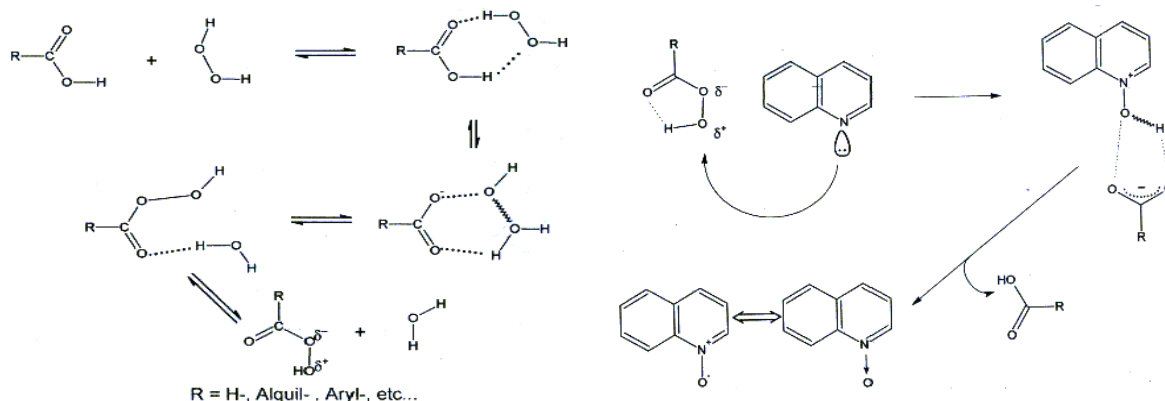


Figure 1. Mechanism of peracid generation and oxidation of nitrogen compounds.

for temperature control, sample withdrawn points, and well-depth where PT-100 thermo-resistances were placed. Initially, a precise amount of oil sample was added to the equilibrium cell followed by the addition of a pre-established solvent volume in order to fill almost the entire equilibrium cell capacity and to give solvent to oil volume ratios of 1:2, 1:1 and 2:1. After the desired temperature was reached, the mixture was kept under vigorous agitation for 60 minutes when then magnetic stirrers were turned off. The whole system was maintained static for 12 - 16h, depending on the system, to allow phase separation. After complete separation, a sample of around 0.5 mL of the heavy phase was withdrawn and submitted to Kjeldhal analysis for total nitrogen determination. Afterwards, the heavy phase was carefully separated and its volume recorded for the purpose of computing process yield. A second and third extraction stages were then accomplished using the same procedure. Triplicate runs were accomplished for all experimental conditions affording an average reproducibility of around $\pm 5\%$.

303 K. The results concentrate on the removal of nitrogen compounds from the heavy phase and yield of the liquid-liquid separation of this phase. Table 1 shows that, in general, an increase in the number of separation stages and solvent-to-oil volume ratio improves the removal of nitrogen compounds but, conversely, also leads to progressive losses in process yields, thereby impairing the recovery of the heavy phase. Yields of heavy oil phase (v/v %) reported throughout the work were determined based on the oil amount remaining from previous extraction step.

This is especially true for the OC3 charge, whose original nitrogen content of 2600 ppm is reduced to around 200-300 ppm, a very appreciable result, but with pronounced oil loss, in the order of 30%. It can be also observed from this table that for crude Marlim and GOP no significant nitrogen removal was reached even at higher solvent-to-oil ratios and higher number of separation stages. In fact, for the latter two samples, nitrogen extraction was negligible with a 1:1 solvent to oil ratio at any stage.

An attempt was made for crude Marlim and GOP, with methanol as solvent, increasing the temperature to 323 K, but as shown in Table 2, a poor selective extraction and important process yield losses were verified, with the content of nitrogen remaining almost unchanged regardless of

3. RESULTS AND DISCUSSION

Data of nitrogen removal and heavy phase yield are shown in Table 1, using methanol as solvent at

Table 1. Results of liquid-liquid extraction of petroleum samples using methanol as solvent at 303 K.

Stage	Total nitrogen (ppm)			Yield of heavy oil phase (v/v %)			Nitrogen removal (%)	
1 st 2 nd 3 rd	Oil to solvent ratio: 2:1							
	Marlim crude	HVGO	OC3	Marlim crude	HVGO	OC3	Marlim crude	HVGO
	-	-	1300	-	-	97.9	-	-
	-	-	848	-	-	96.4	-	-
	-	-	422	-	-	90.7	-	-
	Oil to solvent ratio: 1:1							
1 st 2 nd 3 rd	Marlim crude	HVGO	OC3	Marlim crude	HVGO	OC3	Marlim crude	HVGO
	4027	3264	814	95.7	94.4	94.7	14	22
	3930	3190	292	94.8	93.3	92.0	16	24
	3930	3145	231	87.1	79.2	83.7	16	25
	oil to solvent ratio: 1:2							
	Marlim crude	HVGO	OC3	Marlim crude	HVGO	OC3	Marlim crude	HVGO
1 st 2 nd 3 rd	3919	3431	547	87.0	90.0	94.3	16	18
	3816	2859	398	86.7	88.0	91.0	19	31
	3601	2842	316	86.0	88.0	83.3	23	32

Table 2. Results of liquid-liquid extraction of petroleum samples using methanol as solvent at 323 K.

Stage	Total nitrogen (ppm)		Yield of heavy oil phase (v/v %)		Nitrogen removal (%)	
			oil to solvent ratio: 1:1			
	Marlim crude	HVGO	Marlim crude	HVGO	Marlim crude	HVGO
1 st	3929	3421	90.5	94.0	16	19
2 nd	3899	3362	89.7	91.7	17	19
3 rd	3738	3362	85.7	83.3	20	18
			oil to solvent ratio: 1:2			
	Marlim crude	HVGO	Marlim crude	HVGO	Marlim crude	HVGO
1 st	4426	3255	92.3	93.1	6	22
2 nd	4183	3126	86.2	91.0	11	25
3 rd	4035	2747	85.1	82.0	14	34

the number of separation stages and the solvent-to-oil volume ratio. These results just emphasize the need of sample preparation, like the oxidation performed in this work for C3 charge, to increase the polarity of nitrogen compounds, before submitting it to liquid-liquid extraction.

The next step towards improving process efficiency was to apply mixtures of potential extraction solvents such as NMP and DMF to the OC3 charge. However, the use of nitrogen solvents presented difficulties for solvent removal from the heavy phase, especially at higher numbers of stages. This fact induced to an incorrect interpretation of the results of total nitrogen analysis. To overcome this drawback, after preliminary tests, we have chosen to carry out the extraction assays in only one stage, and wash the heavy phase with a solution of potassium phosphate several times. Nevertheless, results presented in Table 3 show that the use of DMF and NMP provided low yields and poor removal of nitrogen compounds. This may be due to the existing chemical affinity between solvent and heavy phase. It should also be noted from this table that solvent mixtures did not show a

synergistic effect and the best results were achieved with pure methanol.

4. CONCLUSIONS

The oxidation process via peracid demonstrated the potential of using solvent and liquid-liquid extraction techniques as essential steps to achieve acceptable levels of removal of nitrogen compounds from petroleum samples. The use of separation stages and variable solvent-to-oil ratios proved to be efficient for nitrogen removal from OC3 charge, affording a total nitrogen contents as low as 200 ppm. However, the process yield must be improved. It was also shown that the use of DMF and NMP as well as mixtures of these solvents with methanol did not prove to be useful for selective nitrogen extraction since great oil losses are observed in the final process. Results obtained in this work may be relevant to researchers and personnel involved in plant design, operation and processing of petroleum charges. Naturally, since relatively large amounts of high-cost and toxic solvents are used in the work, it is crucial to

Table 3. Data for initializing the fractured model.

Solvent or solvent mixture (equal-volume ratio)	Total nitrogen (ppm)	Yield of heavy oil phase (% v/v) *	Nitrogen removal (%)
Methanol	231	83.7	91
Methanol/NMP	1562	67	40
Methanol/DMF	1910	62	26
DMF/NMP	1909	57	26
Methanol/DMF/NMP	2331	52	10

*Yields after washing three times with potassium phosphate solution.

perform an economical and careful environmental analysis before proceeding with industrial plant considerations.

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