EFFECTS OF WATERFLOODING AND MEOR RECOVERY TECHNIQUES ON THE POLAR COMPOSITION OF PETROLEUM ASSESSED BY ESI (+) FT-ICR MS

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Introduction

In order to extend the petroleum field life, Enhanced Oil Recovery (EOR) techniques, including Microbial Enhanced Oil Recovery – MEOR, are commonly used. The oil that remains in reservoir has high viscosity and acidity, is rich in polar compounds and difficult to be chemically characterized by conventional analytical techniques (GC-FID and GC-MS). However, this analytical limitation was overcome with the emergence of mass spectrometry techniques with high resolution power, such as Fourier Transform Ion Cyclotron Resonance - FT-ICR MS, which allows the molecular oil analysis when coupled to several ionization sources (Rodgers et al., 2005).

Nonetheless, reports discussing the effects of recovery techniques on the produced oil composition, mainly polar fraction, are not common. In this work, electrospay ionization [ESI(+ FT-ICR MS)] technique was used in order to evaluate the effects of salty water injection (waterflooding) and biosurfactant (MEOR by Bacillus safensis) on basic polar compounds of a Brazilian oil. Oil samples were previously submitted to a displacement test carried out in a porous medium and named as Control Oil (mixture 1:1 of original oil: cyclohexane), and after core flooding experiments as Oil I (brine, 3% NaCl) and Oil II (biosurfactant solution, 96,17 mg/L).

Results

In a previous work (Gicovate et al., 2018), an analysis of geochemical parameters by GC showed that effects of water washing and geochromatography (rock adsorption) could change the neutral composition of recovered oils by waterflooding and MEOR techniques. Herein, it can be observed in Figure 1 that the polar composition can also be altered by these recovery techniques. Analysis of oil samples indicates different class compositions, although Oil I and Control Oil show more similarity in its heteroatomic classes, mainly for the classes N, N₂ and NS (Figure 1). Results demonstrate that the N class is the most abundant in all oil samples, whose compounds can be attributed to pyridine, quinoline and acridine derivatives (Terra et al., 2015). However, Oil II presents more distinct heteroatom class distribution compared to the remain samples, showing a significant decrease in the relative abundance of N class, and relative increase of the N₂ class added to the detection of the classes N₄O₄, NO and NOS above 1%. Possibly, nitrogenous compounds and their analogues may be preferentially adsorbed by rock or carried out by the injected water (Larter et al., 1997).
**Figure 1:** Distribution of the relative abundance of the heteroatomic classes and triangular plot illustrating the effect of waterflooding and MEOR on the oils.

Besides, in order to assess the differences in the compounds distribution of the N class, the most abundant and affected one according to the heteroatomic class distribution, a ternary diagram was plotted with the abundance of the compounds with DBE 7, 10 and 12, being likely quinolines, benzoquinolines, and the most robust aromatic core structure indenoquinolines or azopyrenes, respectively (Figure 1). This plot is normally used to evaluate the maturity level of oils and bitumens, since the general trends in alkylation level, aromatic core ring size and other features are seen in the N heteroatom compound class, measured in ESI (+) mode, with varying oil maturity (Oldenburg et al., 2014). It can be observed in the ternary diagram that there is an apparent alteration in the distribution of compounds in class N, more significant in Oil II, which affects the assessment of maturity. The Oil II presents higher abundance of compounds with DBE 10 and 12 and lower DBE 7 than the other oil samples, indicating that the less aromatic and complex compounds, such as quinolines, were more affected by the adsorption or water washing effects.

**Conclusions**

Analyses of polar compounds class through petroleomics by ESI(+) FT-ICR MS showed that due to aqueous solutions injected into the reservoir, there is a reduction of N class relative abundance, as can be observed by the relative abundance intensity of the analysed classes, especially after MEOR, suggesting that adsorption by rock minerals may have had influence on the compositional changes. In addition, the triangular plot indicates a pronounced decrease of the relative abundance of the inferior benzanulated homologues, when compared to the other oils, indicating that these less robust aromatic core compounds were more affected by the MEOR recovery technique.

**References**


