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Review

Chromatographic and spectroscopic analysis of heavy crude oil mixtures with emphasis in nuclear magnetic resonance spectroscopy: A review

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ABSTRACT

The state of the art in the characterization of heavy crude oil mixtures is presented. This characterization can be done by different techniques, such as gas chromatography (GC), high performance liquid chromatography (HPLC), thin layer chromatography (TLC), infrared spectroscopy (IR), Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS). Nuclear magnetic resonance spectroscopy is the technique of choice due to its capability to provide information on the chemical nature of individual types of hydrogen and carbon atoms in different and complex mixtures of crude oils. The progress made in the interpretation of the NMR spectra with the development of new NMR techniques and different multivariate data analyses could give relevant information about the identification and characterization of hydrocarbons and their physical and chemical properties. These progresses can improve the refining industries operation as a result of the better knowledge on the crude composition that is fed in the refining process, as well as in the prediction of better operating conditions to obtain refined products with desired specifications and in quantities desirable to meet the market demands. The improvement in the refining operation conditions is reflected in economical benefits.

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1. Introduction

1.1. Petroleum industry

Nowadays, the great challenge for the crude oil refining industry is to refine large quantities of heavy crude oils and to transform them into specific sets of refined products to meet the market's demands [1]. This means that all the crude mixtures should be converted from heavy fractions to light distillate products in multiple complex refining steps, including distillation, catalytic cracking, hydrocracking, and coking [2]. The complex mixtures are composed by many compounds (Table 1), ranging in size from the smallest to large compounds where the quantity of carbon atoms varies, which has different quantities of various compounds and special properties depending on the geographical source. It is necessary to make periodic reviews and to characterize these substances in terms of chemical structure and their physical and chemical properties. The need of a specialised and exhaustive characterization is related to different compositions, namely different concentration of asphaltenes, sulfur, nitrogen and metal ions (normally heavy crude oils have high concentrations), and hence different chemical and physical properties that characterized heavy crude oils. Even heavy crude oils being such a complex mixture it is notable that due to the increase in the competitiveness of the markets, the demand and the high cost associated to the conventional oils, it is more notorious the need to process crude oil with a great variety of heavy components, sulfur and nitrogen. For these and to adjust the production to meet market demands, to obtain products with high quality and respect the environmental specifications most of the refineries around the world have the necessity to change and improve their refinery units and process aiming to make an accurate control and know very well the composition of the heavy crude oils.

Some examples showing the importance of knowing the composition of raw materials and currents in a refining unit are presented:

1.1.1. Composition of crude oil fractions

There are some compounds like polyaromatics, that are toxic or carcinogenic [3], sulfur and heavy metals in high concentrations, which have environmental implications and cause huge problems in the refining process due to the corrosion and poisoning of the catalysts [4], and asphaltenes which cause environmental problems as well as problems in the refining process, due to their tendency to flocculate and precipitate. The higher concentration of these compounds that can lead to a greater formation of coke and the possibility to increase the deactivation of catalysts [5], have a negative effect on the smoke point of a jet fuel [6] and also the risk of affecting the combustion process in various motors [7]. In addition, the presence of conjugated dienes can bring serious problems in the industry because their presence can decrease the quality of the final products, due to their tendency to polymerize, being important to remove them from the oil fractions [8].

1.1.2. Yield of heavy aromatic compounds

The presence of heavy aromatic compounds can have a negative effect on the smoke point of a jet fuel and on the cetane number of a diesel.

1.1.3. Paraffins in heavy crude oil

It is important to control the presence of paraffins due to the tendency of some of these structures to the crackability [5], and in the crude blending. The control of the paraffins is related to the prevention of some problems that may occur during the transport in the pipeline and the storage due to its high pour point. The crude blending can bring some advantages to the transportation, due to the flow properties that became better, to the value of the product that increase and also to the efficiency of the refining [9]. On the other hand it is possible, due to the blending, that instability (in the pre-heated train heat exchangers during processing) increases as well as some inconveniences in the refinery, *e.g.*, precipitation of the asphaltenes and fouling problems [9,10].

1.1.4. Feedstock properties [4,5]

It is important to know the feedstock properties since these properties depend on the source of crude oil. The knowledge of the properties of crude oil is very important in the industry for the right choice of the crude processing units [11]. The chemical and physical properties, such as the viscosity and the density, of the crude oil are important factors to control. For example, it is important to control the viscosity index since it is widely used to define the oil quality and due to the facility of knowing the effect of the