Low-field nuclear magnetic resonance for petroleum distillate characterization

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ABSTRACT

Low field nuclear magnetic resonance (LF-NMR) has several applications in the oilfield industry such as in predicting the viscosity and evaluating porosity, permeability, fluid saturation of reservoir rocks, and the water content in fluids. However, the studies to determine the physical and chemical properties of petroleum distillates are uncommon. So, the aim of this study was to determine the physical and chemical properties of distillates using the transverse relaxation time (T_2) in the range from 73.43 to 1810.74 ms. LF-NMR was employed in this research, due to its rapid and non-destructive analytical method. From LF-NMR data, it was possible to estimate the molar mass, correlation index, characterization factor, API gravity, relative hydrogen index, and number of hydrogen in distillates obtained up to 350 °C. T_2 and the properties determined by standard methodologies (ASTM D-1218, D-445-06, D-664-06, D-2892, and D-4052) were strongly correlated. So, low field NMR constitutes an interesting alternative to ASTM methods. The results also show that changes in the chemical and physical properties depend on boiling point and molecular mobility. Besides, LF-NMR enabled the classification of the fractions into gasoline, kerosene, and light and heavy gas oil.

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1. Introduction

Knowledge of the physical and chemical properties of petroleum fractions is indispensable for the adequate industrial production of petroleum derivatives. The standard methods frequently used to determine these properties are very laborious; involving the use of solvents and presenting high costs as well as destroying samples during the trials. A possible alternative to traditional methods is the low-field nuclear magnetic resonance (LF-NMR). This technique has numerous applications in the oilfield industry because of its potential uses both in situ and ex situ to estimate fluid and rock properties. Also is used to identify and classify crude oil that is extracted from different reservoirs and fields, as well as crude oil fractions [1]; to estimate viscosity [2–4]; to evaluate the petrophysical characteristics (porosity, permeability, fluid saturation) of reservoir rocks [5–9]; to determine the droplet size distribution of emulsions [9–12]; and to quantify the water content in biphasic mixtures [13]. A recently developed application of LF-NMR involves the use of two-dimensional pulse sequences to measure longitudinal relaxation time (T_1) and transverse relaxation time (T_2), T_1–T_2, and the diffusion coefficient and T_2 (D-T_2), in a unique measurement [14]. The above-mentioned sequences are applied in researches about the dynamics of reservoirs, the properties of fluids, and the size distribution chain of molecular groups [15,16]. NMR logs constitute an

important technique, where hydrogen frequency lower than 2 MHz is applied to evaluate the reservoir profile [17]. Xiao et al. [18] from the analysis of 54 core samples, developed a new calibration technique for the construction of capillary pressure curves with the aim to predict the pore throat radius and reservoir permeability, based on T_2 distribution measure.

NMR phenomena are observed when the nucleus that contains the nuclear spin magnetic moment ($\mathbf{\mu}$) is subjected to a magnetic field ($\mathbf{B_0}$), promoting an interaction and aligning the spins in parallel or opposite to $\mathbf{B_0}$. The result of net alignment with direction and energetic preference is called resultant magnetization ($\mathbf{M_0}$) — a vector quantity characterized by magnitude and direction [19]. Such vector is expressed as the sum of all the magnetic moments of a sample ($\mathbf{M}_0 = \sum_i \mathbf{\mu}_i$).

To a nuclei with spherical charge distributions (e.g., ^{1}H, ^{13}C, and ^{31}P; spin number equal to $-1/2$), relaxation is caused by the fluctuating magnetic field at spin sites; the fluctuation is caused by the thermal motion of molecules [20,21]. Relaxation is defined as the process by which spins return to thermal equilibrium after radiofrequency irradiation. It occurs primarily through two ways: (1) spin–lattice relaxation, which involves energetic exchange between excited nuclear spins and the lattice, to reduce the total energy of the spin population and recover the equilibrium state and (2) spin–spin relaxation, in which spins precess in distinct orientations, i.e., the spins are oriented toward or deviate from the magnetic field, thereby exhibiting "flip-flop" motions. The first process has an enthalpic character, whereas the second has an entropic nature [22].

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After the nuclear spins align parallel to the external magnetic field ($\mathbf{B_o}$), the magnetization vector in the equilibrium state lies along the $\mathbf{B_0}$ direction and the z-direction in the coordinate system. Petroleum or fractions are irradiated at the Larmor frequency (v_0) to enable the petroleum/fractions to reach the resonance condition ($v_0 = \gamma B_0$, where γ is the gyromagnetic ratio).

The relaxation of nuclear spins is described in terms of the magnetization vector rotating at v_0 in the coordinate system. Such consideration is represented by

$$M_z(t) = M_0\left(1 - e^{-(t-t_i)/T_1}\right), \tag{1}$$

where M_z is the magnetization along the z-axis at time t, M_0 is the magnetization in the equilibrium state, t_i denotes the initial time at which a sample is subjected to $\mathbf{B_0}$, and T_1 represents longitudinal relaxation (recovery of the Z-component of vector magnetization with constant time T_1 of a new equilibrium state after system disturbance).

Similar to the previously discussed, another relaxation process consists in the exponential magnetization decay in function of time, governed by constant T_2. This variable corresponds to the disappearance of signals in the transverse plane, i.e., $M_{xy} = 0$:

$$M_{xy}(t) = M_0 e^{\frac{-t}{T_2}}, \tag{2}$$

where T_2 is the transverse relaxation time, and $M_{xy}(t)$ is the transverse magnetization at time t. The phase coherence produced by polarization and transfer to the xy plane via the application of radiofrequency pulses is lost, because the nucleus precesses under the influence of the local magnetic field.

Several physical and chemical properties are estimated on the basis of T_2, which is an important NMR parameter typically obtained by Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence. Because of molecular diffusion (one of the most important relaxation mechanisms in liquids), the transverse relaxation rate (T_2^{-1}) is affected by the molecular weight (MW), molecular mobility, and size of molecules, as described by Coates et al. [17]. An intuitive phenomenon is that no molecular diffusion occurs in solid samples when these are analyzed in a solid-state NMR experiment; thus, dipolar decay and intermolecular motion contribute to T_1 to be higher than T_2 [23].

For small molecules in liquids, T_1 and T_2 values have the same order of magnitude (i.e., several seconds), but in solids or large molecules, T_2 may be shorter than T_1 because of the loss in synchrony due to nuclear precession [23]. Such relaxation times are intrinsic to the molecular mobility of a material. Depending on the material, only one relaxometric component (e.g., water bulk) or multiple relaxometric components (e.g., crude oil in saturated reservoir rocks) are produced [4].

Bryan et al. [3] correlated the relative hydrogen index (RHI) with dynamic viscosity (η) and geometric mean transverse relaxation time (T_{2gm}). Such viscosity model was applied to estimate a viscosity in the range of 1,000,000–3,000,000 mPa·s^{-1}. Studies have demonstrated the relationship between RHI and the viscosity of crude oil [4]. This parameter is determined by Eq. (3) [3]:

$$RHI = AI_{(oil)}/AI_{(water)}, \tag{3}$$

where $AI_{(Oil)}$ is the amplitude index of the signal of oil, and $AI_{(water)}$ denotes the amplitude index of the signal of water. The amplitude index is the ratio between amplitude and mass.

Kantzas [2] determined a correlation between the logarithmic mean of transverse relaxation time (T_{2LM}) and the hydrogen index (HI). At low viscosity, T_{2LM} strongly depends on viscosity, but the HI is insensitive to changes. The HI quantifies hydrogen in a given mass of crude oil vis-à-vis hydrogen content in the same mass of water.

After production and primary treatment, crude oil is transported to a refinery, where it is converted into a consumable product. Crude oil refining involves three main steps: separation, conversion, and

accomplishment. The most common separation step is distillation, which is initiated in a column where compounds are separated on the basis of differences in boiling point [24–26].

Crude oil and distillates contain a substantial amount of chemical compounds; thus, the best approach to analyzing them is through their physical properties [25]. MW is an indication of molecular size. This important property is normally determined by chromatographic techniques (ASTM-D 5296) and cryoscopic methods (ASTM-D 2503) [24].

In this work, the MW of petroleum fractions was obtained by the Pedersen equation (Eq. (4)). This mathematical expression relates MW to density and mean boiling point [24,26]:

$$MW = 42.965\ exp\left(2.097 \times 10^{-4} - 7.78712 \cdot \rho + 2.08476 \times 10^{-3} T_b \rho\right) T_b^{1.26007} \rho^{4.9803}, \tag{4}$$

where T_b is the mean boiling temperature in Kelvin, and ρ represents the specific gravity.

The correlation index (CI) is another relevant parameter that can provide information about the chemical nature of fractions [25]. CI values are estimated thus:

$$CI = 473.3 \cdot \rho - 456.8 + 48,640/T_b, \tag{5}$$

where ρ denotes the specific gravity (g cm^{-3}), and T_b (°C) is the mean boiling point of the petroleum fraction determined by a standard distillation method (ASTM D-86 or ASTM D-1160). According to Speight [25], a CI between 0 and 15 reflects the predominance of paraffinic hydrocarbons, values of 15 to 50 indicate the predominance of either naphthenes or a mixture of compounds (paraffins + naphthenes), and a CI higher than 50 indicates the predominance of aromatic species in a fraction.

An equally relevant parameter for characterization is the universal oil product called the characterization factor (K), which is widely used in characterizing petroleum. It is expressed as

$$K = \sqrt[3]{T_b}/\rho, \tag{6}$$

where T_b is the mean boiling point in Rankin degrees (°F + 460), and ρ is the specific gravity at 60 °F.

Numeric values of K can be used to determine the chemical nature of petroleum and distillates. For example, highly paraffinic oils have a K between 12.5 and 13.0, naphthenic oils present $K \approx 10.5$–12.5, and aromatics exhibit a K value lower than 10.5 [25].

CI and K are critical to the oilfield industry because they can be used to acquire relevant qualitative information about the chemical properties of petroleum or fractions. Scientists and engineers can use the values as reference for deciding on the best production and refining strategies. On the basis of such knowledge, as well, a refinery can evaluate which refining processes (alkylation, isomerization, catalytic reforming, catalytic cracking, thermal cracking, hydrocracking, coking) excellently convert distillates into desired consumable products, such as kerosene, gasoline, diesel, and lubricants.

As previously stated, several studies have used LF-NMR to analyze crude oil, but the use of such technique to investigate distillates is rare. Barbosa et al. [27] conducted a pioneering study that involved the determination of the physical properties of petroleum distillates by LF-NMR. The authors used a transverse relaxation time in the range of 25–675 ms to predict the viscosity, total acid number, refractive index, and API gravity of heavy oil distillates. The main advantages highlighted in the study are that the technique enables rapid analysis and presents the possibility of simultaneously determining the aforementioned properties.

The aim of the present study was to estimate the physical and chemical properties of petroleum fractions, as well as the parameters that are important to the petroleum industry, on the basis of transverse relaxation time (T_2). The parameters estimated included API gravity, correlation index, characterization factor, RHI, molar weight, molecular