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Qualitative analysis by *online* nuclear magnetic resonance using Carr–Purcell–Meiboom–Gill sequence with low refocusing flip angles

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ABSTRACT

The Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence has been used in many applications of magnetic resonance imaging (MRI) and low-resolution NMR (LRNMR) spectroscopy. Recently, CPMG was used in *online* LRNMR measurements that use long RF pulse trains, causing an increase in probe temperature and, therefore, tuning and matching maladjustments. To minimize this problem, the use of a low-power CPMG sequence based on low refocusing pulse flip angles (LRFA) was studied experimentally and theoretically. This approach has been used in several MRI protocols to reduce incident RF power and meet the specific absorption rate. The results for CPMG with LRFA of $3\pi/4$ ($CPMG_{135}$), $\pi/2$ ($CPMG_{90}$) and $\pi/4$ ($CPMG_{45}$) were compared with conventional CPMG with refocusing π pulses. For a homogeneous field, with linewidth equal to $\Delta\upsilon = 15$ Hz, the refocusing flip angles can be as low as $\pi/4$ to obtain the transverse relaxation time (T_2) value with errors below 5%. For a less homogeneous magnetic field, $\Delta\upsilon = 100$ Hz, the choice of the LRFA has to take into account the reduction in the intensity of the CPMG signal and the increase in the time constant of the CPMG decay that also becomes dependent on longitudinal relaxation time (T_1). We have compared the T_2 values measured by conventional CPMG and $CPMG_{90}$ for 30 oilseed species, and a good correlation coefficient, $r = 0.98$, was obtained. Therefore, for oilseeds, the T_2 measurements performed with $\pi/2$ refocusing pulses ($CPMG_{90}$), with the same pulse width of conventional CPMG, use only 25% of the RF power. This reduces the heating problem in the probe and reduces the power deposition in the samples.

1. Introduction

The Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence is the standard spin–echo method to measure the transverse relaxation time (T_2) [1]. The sequence uses one excitation $\pi/2$ pulse, followed by a train of refocusing π pulses with a 90° phase shift from the excitation pulse. The time interval between refocusing pulses is twice (2τ) that between the excitation pulse and the first refocusing pulse. The phase shift between the excitation and refocusing pulses was introduced in the Carr–Purcell sequence [2] by Meiboom–Gill [1] to avoid cumulative errors caused by deviation from the π pulse. This phase shift made the sequence very robust and quite insensitive to errors in the refocusing pulses [3]. The magnitude of the CPMG signal is close to the maximum even when the refocusing pulses differ as much as 40° from the nominal π [3].

CPMG pulse sequence is used in several fast magnetic resonance imaging (MRI) methods, such as RARE (rapid acquisition with relaxation enhancement) [4] and FSE (fast spin–echo imaging) or TSE (turbo spin–echo) [5–7]. CPMG is also the most important sequence for qualitative measurements in low-resolution NMR (LRNMR). It has been used to measure the quality of food and agricultural products [8–13]. In the petroleum industry, the CPMG sequence is used in well-logging sensors and in the laboratory to measure oil viscosity, rock porosity and many other properties [14–16].

Most of the qualitative applications of CPMG in LRNMR are based on the measurement of T_2, which is related to several physical and chemical properties such as viscosity, diffusivity, porosity, surface area, fatty acid composition and many other properties [12,17]. CPMG data has also been analyzed using chemometric methods such as principal component analysis (PCA), hierarchic cluster analysis (HCA) and partial least square (PLS) [12]. Recently, CPMG was used as a fast and automatic LRNMR method (*online* NMR) to analyze the oil quality in thousands of oilseed samples per hour [12]. This method was used to measure the oil quality in intact seeds, giving information about several properties related to biodiesel quality such as oil viscosity, cetane number and iodine value [12]. However, this *online* CPMG method uses long RF pulse trains that cause an increase in probe temperature and, therefore, cause tuning and matching maladjustments. It may also cause sample heating that leads to erroneous T_2 measurements.

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This problem is similar to the one observed in fast MRI sequences based on CPMG [4,6,18,19]. The long pulse trains used in MRI sequences when using π pulses may exceed the specific absorption rate (SAR) due to high RF power deposition. To meet the safety guidelines in these fast MRI experiments, low refocusing flip angles were used to reduce the RF power deposition [4,6,18,19].

In this paper, we have studied the same approach to reduce the heating problem using CPMG sequence in *online* qualitative measurements. The experimental and theoretical simulations, using Bloch equation [20,21] of CPMG sequence with low refocusing pulse flip angles (LRFA) was studied in two magnetic field homogeneities, three T_1/T_2 ratios and several echo times, τ. The results show that CPMG with refocusing pulses as low as $\pi/4$ can be used in qualitative analysis in low-resolution experiments. Depending on the magnetic field homogeneity, the RF power used in refocusing pulses can be reduced more than 4-fold.

2. Experimental

The samples studied with different relaxation times were deionized water and soybean and castor bean seed oil. For the validation of the CPMG sequence with LRFA, we used commercial seeds and nuts such as pumpkin, cotton, almond, peanut, Brazil nut, coffee, walnut, cashew nut, coconut, sesame, sunflower, linseed, macadamia nut, castor bean, watermelon, moringa, pistachio, radish and soybean and seeds from wild-type species, such as *Fevillea trilobata*, *Dipteryx alata*, *Luffa cylindrica*, *Acrocomia aculeata*, *Thevetia peruviana*, *Syagrus botryophora*, *Caryocar brasiliense*, *Attalea funifera*, *Jatropha curcas*, *Guizotia abyssinica* and *Astrocaryum aculeatum*.

2.1. Experimental data

The CPMG experiments were performed at $22 \pm 1\,^{\circ}$C using a CAT-100 transceiver (Tecmag, Houston) and a 2.1 T Oxford superconducting magnet (Oxford, UK). The experiments were performed using two magnetic field homogeneities (ΔB_0), equivalent to full width at half maximum (FWHM) of $\Delta \upsilon$ ($\Delta \upsilon = \gamma \Delta B_0/2\pi$), equal to 15 Hz (in the center of magnet) and 100 Hz (10 cm off the center).

The T_2 values were acquired according to the CPMG sequence $\pi/2_{x'} - \tau - (\theta_{y'} - \tau - (echo) - \tau)_n$ using refocusing flip angles θ equal to π (CPMG), $3\pi/4$ ($CPMG_{135}$), $\pi/2$ ($CPMG_{90}$) and $\pi/4$ ($CPMG_{45}$) and echo time τ of 0.1, 0.4 and 2 ms. The refocusing pulse widths were 16, 12, 8 and 4 μs, respectively. The T_1 values were measured using the Inversion-Recovery (IR) sequence [22].

2.2. Theoretical analysis

The algorithm for the simulation of the theoretical T_2 signals with the Bloch equations and a matrix approach [20,21] was written in the C language.

For the calculation of the NMR signals in CPMG sequences, we considered the normalized total magnetization M_0 after the first RF pulse in the transversal plane given by the column vector (Eq. (1)):

$$M_1 = \begin{bmatrix} 0 \\ M_0 \\ 0 \end{bmatrix} \tag{1}$$

Since the total magnetization is in the y'-axis, the system suffers the effect of relaxation during echo time τ in the reference frame rotating with an offset frequency or offset angle $\Delta\omega$. This is represented by the multiplication of the offset dephasing matrix and the relaxation matrix for the magnetization state (Eq. (2)):

$$M_2 = \begin{bmatrix} \cos(\Delta\omega\tau) & -\sin(\Delta\omega\tau) & 0 \\ \sin(\Delta\omega\tau) & \cos(\Delta\omega\tau) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} e^{-\frac{\tau}{T_2}} & 0_\tau & 0 \\ 0 & e^{-\frac{\tau}{T_2}} & 0_\tau \\ 0 & 0 & e^{-\frac{\tau}{T_1}} \end{bmatrix} \times \begin{bmatrix} M_1x \\ M_1y \\ M_1z \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ M_0 \end{bmatrix} M_0\,(1 - e^{-\frac{\tau}{T_2}}) \tag{2}$$

The term added in Eq. (2) is the longitudinal relaxation time component that makes the system to return to thermal equilibrium.

After that, a θ RF refocusing pulse is applied in the y'-axis (Eq. (3)) to rotate the magnetization in the transversal plane. After this refocusing pulse, an echo is obtained at a time τ. The θ RF refocusing pulse is repeated n times until the decay of the CPMG signal.

$$M_3 = \begin{bmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0) & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \begin{bmatrix} M_2x \\ M_2y \\ M_2z \end{bmatrix} \tag{3}$$

For this study, we used refocusing pulses θ of π, $3\pi/4$, $\pi/2$ and $\pi/4$ to call CPMG, $CPMG_{135}$, $CPMG_{90}$ and $CPMG_{45}$, respectively.

The echo amplitude ($\left|M_{xy}\right| = \sqrt{M_x^2 + M_y^2}$) given for each cycle pulse sequence depends on the initial state $M_{(t)} = [M_x(t)\,M_y(t)\,M_z(t)]$ in the following way (Eq. (4)):

$$\begin{aligned} &\left|M_{xy}(t+2\tau)\right| \\ &= \Bigg(\Bigg(\cos(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}\left(\cos(\theta)(\cos(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}M_x(t) + \sin(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}M_z(t))\right) + \sin(\theta)\left(-e^{-\frac{\tau}{T_2}}M_y(t) + \sqrt{M_x^2(t)+M_y^2(t)}(1-e^{-\frac{\tau}{T_1}})\right)\Bigg) + \sin(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}(-\sin(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}M_x(t) + \cos(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}M_z(t))\Bigg)^2 \\ &\quad + \left(-\sin(\Delta\omega\tau)^{-e}\frac{\tau}{T_2}\left(\cos(\theta)(\cos(\Delta\omega\tau)e\frac{\tau}{T_2}M_x(t) + \sin(\Delta\omega\tau)^{-e}\frac{\tau}{T_2}M_z(t) + \sin(\theta)\left(-e^{-\frac{\tau}{T_2}}M_y(t) + \sqrt{M_x^2(t)+M_y^2(t)+M_z^2(t)}(1-e^{-\frac{\tau}{T_2}})\right)\right) + \cos(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}(-\sin(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}M_x(t) + \cos(\Delta\omega\tau)e^{-\frac{\tau}{T_2}}M_z(t))^2\right)^{(1/2)} \end{aligned} \tag{4}$$

When θ is equal to π, as in conventional CPMG, the echo intensity is dependent only on τ, M_0 and T_2 (Eq. (5)).

$$echo = e^{-\frac{2\tau}{T_2}} M_0 \tag{5}$$

For the simulations, we used T_2 and T_1 values obtained experimentally and inhomogeneous B_0 equivalent to $\Delta\omega = 2\pi\nu$, assuming a Lorentzian lineshape equivalent to a FWHM value of $\Delta\upsilon = 15$ Hz and 100 Hz. The B_1 inhomogeneity was simulated using the refocusing flip angle with ±30% variation. The B_1 inhomogeneity reduces or eliminated a high frequency oscillation observed in simulated signals when using single flip angle value.

3. Results and discussion

The CPMG pulse sequence with π refocusing pulses (θ) phase-shifted by $\pi/2$ from the excitation phase is a very robust sequence, and the signal intensity, as shown by Eq. (5), is dependent only on T_2, τ and M_0. In the absence of bulk flow and neglecting diffusion, the CPMG sequence refocus all magnetization on the transversal plane, and the signal decay is dependent on T_2, even in the inhomogeneous magnetic field used in LRNMR [1,15]. However, when the refocusing pulses (θ) are lower than π, the CPMG decay

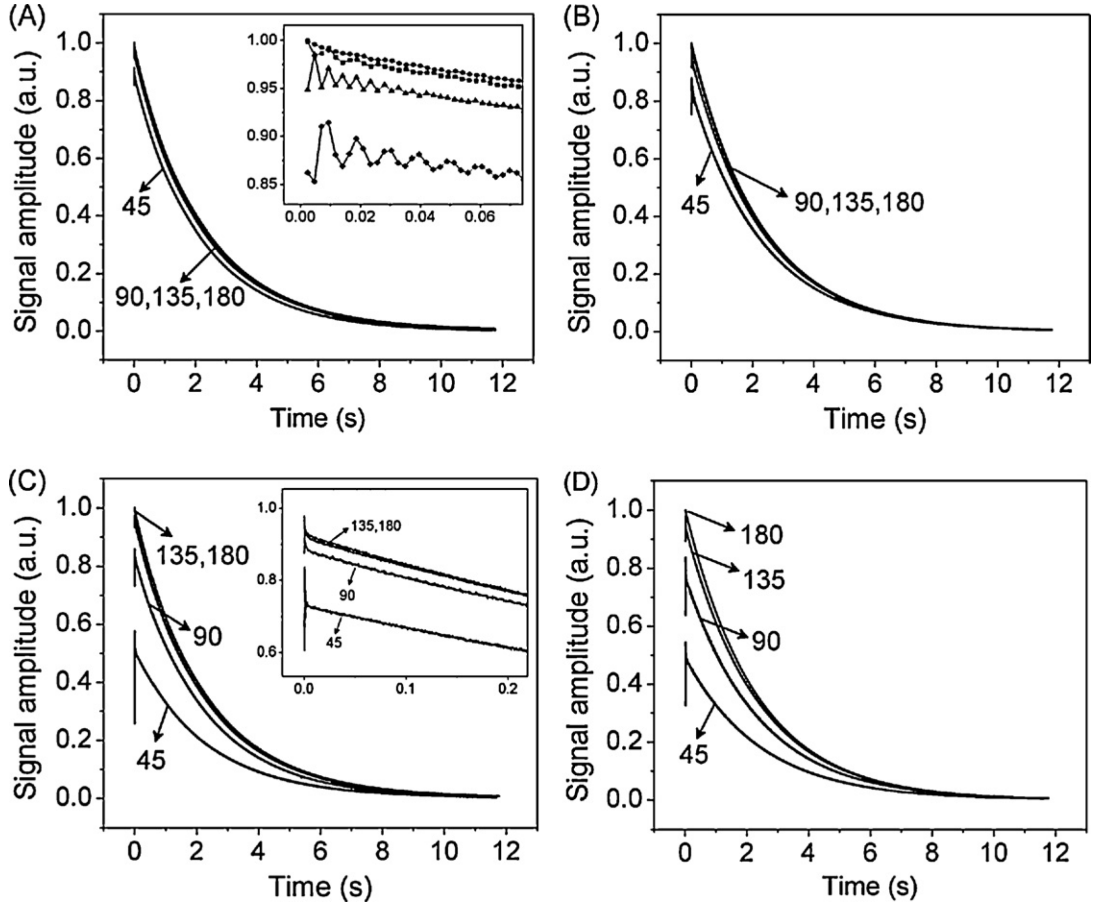

Fig. 1. Experimental (left) and simulated (right) signals of deionized water obtained *on-resonance* with CPMG (●), $CPMG_{135}$ (■), $CPMG_{90}$ (▲) and $CPMG_{45}$ (♦) with magnetic field homogeneity equivalent to $\Delta\upsilon = 15$ Hz (A and B) and 100 Hz (C and D), $\tau = 2$ ms. The inset in A, shows the oscillation for the first refocusing pulses. The inset in C shows the CPMG decays with $\tau = 0.1$ ms.

also depends on the magnetic field inhomogeneity (ΔB_0) and T_1. The ΔB_0 is equivalent to a resonance linewidth $\Delta\upsilon$, where $\Delta\upsilon = \Delta\omega/2\pi = \gamma\Delta B_0/2\pi$.

To show the effect of LRFA in CPMG decays in low-resolution equipment, we analyzed samples with different values of T_1, T_2 and T_1/T_2 in a 2.1 T magnet with different magnetic field inhomogeneities. The samples analyzed were deionized water with $T_1 = 2.86$ s, $T_2 = 2.28$ s and $T_1/T_2 \sim 1$, oil from soybean seed with $T_1 = 0.14$ s, $T_2 = 0.07$ s and $T_1/T_2 = 2$ and oil from castor bean seed with $T_1 = 0.128$ s, $T_2 = 0.014$ s and $T_1/T_2 = 9$.

Fig. 1 shows the experimental and simulated CPMG signals of deionized water obtained *on-resonance* with refocusing flip angles of π (CPMG), $3\pi/4$ ($CPMG_{135}$), $\pi/2$ ($CPMG_{90}$) and $\pi/4$ ($CPMG_{45}$) in magnetic field inhomogeneities $\Delta\upsilon = 15$ Hz and 100 Hz, $\tau = 2$ ms. We performed the experiments reducing the pulse width because it is easy to perform instead of reducing B_1 amplitude. However, the same results were obtained using pulses with reduced power amplitude (data not shown).

Fig. 1A and B shows the experimental and simulated CPMG decays for the deionized water sample obtained with different refocusing flip angles in a more homogeneous magnetic field with $\Delta\upsilon = 15$ Hz. As observed in these figures, the experimental and simulated signals are similar for all flip angles studied, showing the robustness of the CPMG sequence. The difference in the intensity between π and $\pi/4$ flip angles is less than 10%, and the difference in T_2 value (2.28 s and 2.29 s) varies less than 0.5%. The inset in Fig. 1A shows the oscillation for the first refocusing pulses, which increases in time and amplitude with the reduction in the refocusing pulses [4,18].

When a less homogeneous magnetic field ($\Delta\upsilon = 100$ Hz) is used (Fig. 1C and D), this effect is more severe for LRFA. The amplitude of the signals for $\pi/4$, $\pi/2$ and $3\pi/4$ is about 0.50, 0.85 and 0.98 of the amplitude of conventional CPMG, respectively. The T_2 value obtained by $CPMG_{45}$ increases less than 2% than the one obtained using CPMG. The oscillation in the signal after the first pulses increases in time and amplitude with LRFA in a less homogeneous magnetic field when compared to the oscillation in the more homogeneous one (Fig. 1A and B). In a less homogeneous magnetic field (Fig. 1C and D), the spin loses coherence faster than in a more homogeneous one [23] (Fig. 1A and B), resulting in a more pronounced effect. This also occurs because CPMG sequences with LRFA produce echoes out of the transversal plane. This causes the formation of stimulated echoes, which have a dependence on T_1 [4]. Stimulated echoes are formed by the component of the magnetization that is precessing out of the transverse plane, longitudinally, and returns to the transverse plane after the refocusing pulse [4]. As a result, the signal decay does not depend only on T_2 but also on T_1. For samples with $T_1 \sim T_2$, as in deionized water, T_1 does not have a significant effect on decay because only a few stimulated echoes are present [4,5,18].

To reduce the effect of magnetic field inhomogeneity in the CPMG signal with LRFA (Fig. 1C and D) it is necessary to use small τ values. The inset in Fig. 1C shows the CPMG decay with $\tau = 0.1$ ms. The amplitude of the signals for $\pi/4$ increase from 50% ($\tau = 2$ ms) to 75% ($\tau = 0.1$ ms) when compared to conventional CPMG. However, the reduction of τ to increase the intensity is not always desired due to the large number of pulses necessary to obtain the CPMG decay. For $\tau = 0.1$ ms, it is necessary to use about 55,000 pulses to

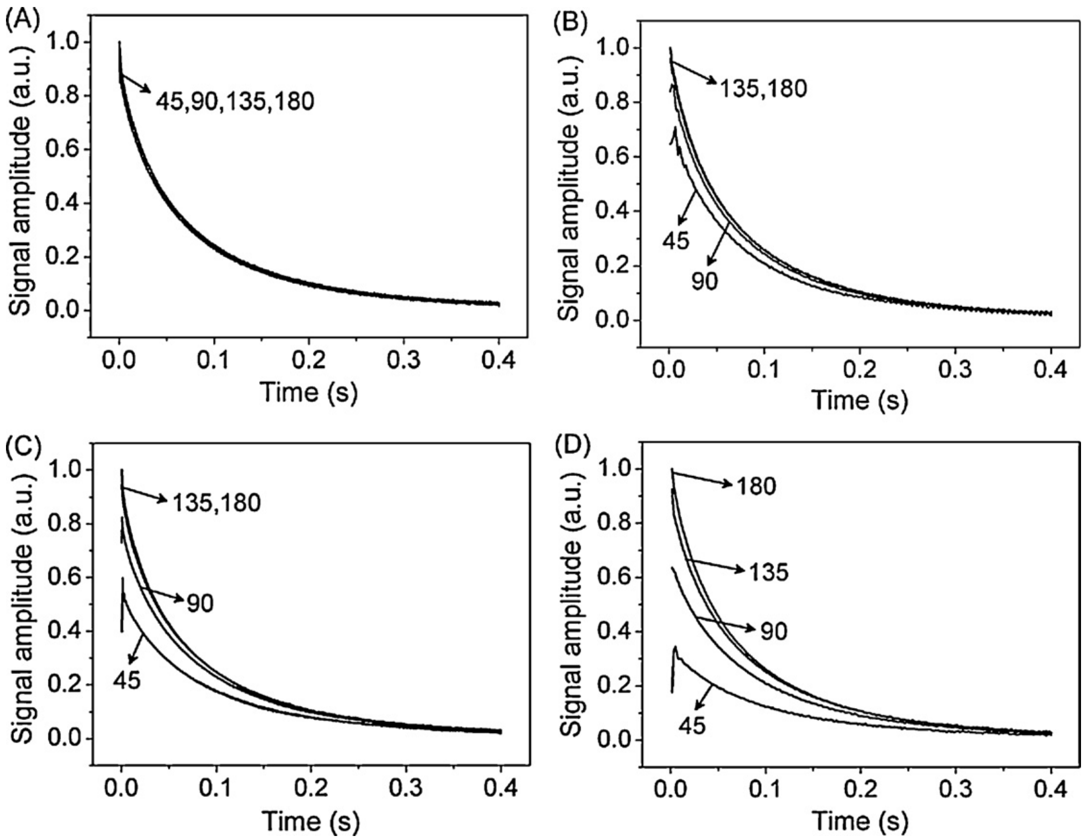

Fig. 2. Experimental signals of soybean oil obtained *on-resonance* with CPMG, $CPMG_{135}$, $CPMG_{90}$ and $CPMG_{45}$ for $\Delta\upsilon = 15$ Hz (A and B) and 100 Hz (C and D), $\tau = 0.1$ ms (left) and 0.4 ms (right).

have a decay equal to $5T_2$ and less than 2750 pulses when $\tau = 2$ ms for the water sample. Because of the fast repetition rates, the power deposition for $\tau = 0.1$ ms is 20-fold higher than that for 2 ms for the same oscillating magnetic field B_1 pulses. Because the reduction in B_1 is proportional to the square root of the applied power ($B_1 \sim P^{1/2}$) [24,25], the reduction in power per pulse is 1.77, 4 and 16 for $3\pi/4$, $\pi/2$ and $\pi/4$ pulses, respectively, when compared with the same pulse width (PW) of π pulses. Therefore, the reduction of the total RF power deposition of the CPMG sequence has to take into account the use of the smallest refocusing flip angle and the longest τ.

Fig. 2 shows the experimental CPMG signals with refocusing pulses of π, $3\pi/4$, $\pi/2$ and $\pi/4$ for soybean oil in different homogeneities ($\Delta\upsilon = 15$ Hz and 100 Hz), $\tau = 0.1$ ms and 0.4 ms.

These values are normally in the range used for T_2 measurements of this type of oilseed as T_2 is about 0.15 s. For $\tau = 0.1$ ms and 0.4 ms, it is necessary to use about 4000 and 1000 refocusing pulses to obtain a decay with $5T_2$. For $\Delta\upsilon = 15$ Hz, the CPMG decays using $\tau = 0.1$ ms (Fig. 2A); the amplitude and T_2 value for all LRFA as low as $\pi/4$ are similar to values for conventional CPMG. For $\Delta\upsilon = 15$ Hz and $\tau = 0.4$ ms (Fig. 2B), the amplitudes of CPMG signals for $\pi/4$, $\pi/2$ and $3\pi/4$ are about 0.70, 0.9 and 0.99, respectively, compared with the conventional CPMG, and for the T_2 value (0.076 s and 0.081 s), there is about 5% variation.

For $\Delta\upsilon = 100$ Hz and $\tau = 0.1$ ms and 0.4 ms (Fig. 2C and D), the amplitudes of CPMG signals for $\pi/4$ are about 0.50 and 0.3 of the conventional CPMG, respectively. The T_2 values for $\pi/4$ increase about 7% and 20% for $\tau = 0.1$ ms and 0.4 ms, respectively.

Fig. 3 shows the experimental CPMG signals with refocusing pulses π, $3\pi/4$, $\pi/2$ and $\pi/4$ for the oil in castor seed ($T_1/T_2 \sim 9$) for $\Delta\upsilon = 100$ Hz, using $\tau = 0.1$ ms (Fig. 3A) and 0.4 ms (Fig. 3B).

Castor bean oil is less susceptible than the soybean oil to CPMG with LRFA, and the signal for $\pi/4$ refocusing angle is identical to π angle for $\Delta\upsilon = 15$ Hz and $\tau = 0.1$ ms (data not shown). For $\Delta\upsilon = 100$ Hz and $\tau = 0.1$ ms (Fig. 3A), the intensity of $\pi/4$ is about 0.8, and T_2 is similar to CPMG with π refocusing pulses. For castor bean oil, the effect of LRFA is strong (Fig. 3B) only in a less homogeneous magnetic field ($\Delta\upsilon = 100$ Hz) and longer echo time ($\tau = 0.4$ ms). For $\pi/4$ refocusing pulses, T_2 is about 50% longer (0.021 s), reflecting the large T_1/T_2 ratio; the intensity is about 0.5 of the ones measured by conventional CPMG. This large variation in the T_2 value measured with CPMG with $\pi/4$ refocusing pulses is not significant for qualitative measurements in oilseeds due to a wide variation in T_2 values observed in oilseeds that can be longer than 0.2 s [12].

With these results, we have shown that for homogeneous fields ($\Delta\upsilon = 15$ Hz), almost any refocusing flip angles down to $\pi/4$ can be used to obtain the T_2 value. However, for less homogeneous fields, the intensity is reduced, and the T_2 values become more dependent on the T_1/T_2 ratio for lower flip angles. Therefore, to use the minimum RF power, it is necessary to take into account the homogeneity of the magnetic field used and the T_1/T_2 ratio of the samples analyzed.

Fig. 4 shows the high correlation ($r = 0.98$) between the T_2 measured by conventional CPMG and $CPMG_{90}$ for the oilseeds of 30 plant species using the same τ value and the same pulse refocusing pulse width (reduced B_1 amplitude). Therefore, for oilseeds, the T_2 measurements can be performed with $\pi/2$ refocusing pulses ($CPMG_{90}$), which use only 25% of the RF power used in conventional CPMG. This reduces the probe heating problem and reduces the RF power deposition in the sample.

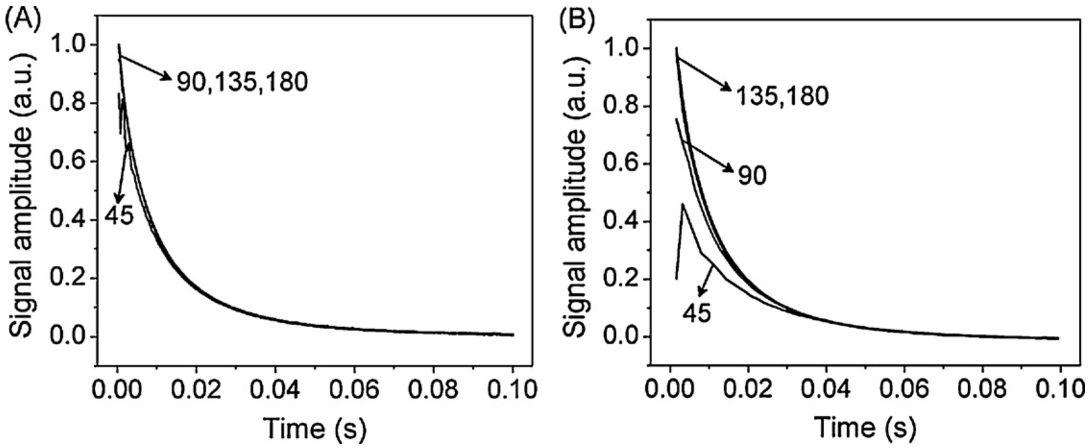

Fig. 3. Experimental signals of castor bean seed obtained *on-resonance* with CPMG, $CPMG_{135}$, $CPMG_{90}$ and $CPMG_{45}$ for $\Delta\upsilon = 100$ Hz, $\tau = 0.1$ ms (A) and 0.4 ms (B).

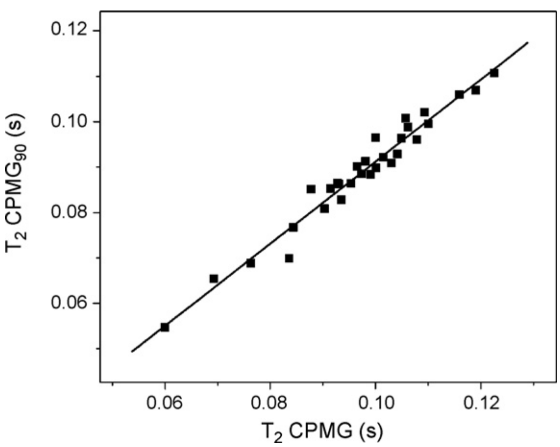

Fig. 4. Correlation between T_2 values obtained with CPMG and $CPMG_{90}$, using 30 oilseed species; $r = 0.98$.

4. Conclusion

For homogeneous fields ($\Delta\upsilon = 15$ Hz), almost any refocusing flip angles can be used to obtain the T_2 value, and LRFA can be used to reduce the incident power. However, for an inhomogeneous magnetic field, $\Delta\upsilon = 100$ Hz, the choice of the lowest refocusing flip angle has to take into account the reduction in the intensity of the CPMG signal and the increase in the time constant that becomes more dependent on the T_1/T_2 ratio for lower flip angles.

Therefore, the use of LRFA can be used as an alternative to reduce RF power in *online* CPMG experiments. Indeed, we were able to use $CPMG_{90}$ in the qualitative analysis of oilseeds using only 25% of the RF power used in conventional CPMG.

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