Role of Gallic Acid in the Synthesis of Carbon-Encapsulated Iron Nanoparticles by Hydrothermal Carbonization: Selecting Iron Oxide Composition

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ABSTRACT: In this work, the role of phenolic compounds in the hydrothermal synthesis of carbon-encapsulated iron nanoparticles (CEINs) was studied. To model phenolic compounds, gallic acid (GA) was selected, with glucose as the carbon source. Iron was found as $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, Fe$_3$O$_4$, and zero-valent iron (ZVI) depending on the synthesis pH and GA/Fe molar ratio. For GA/Fe = 1, the CEINs' yield increased significantly. In the samples with phenolics, increasing the initial pH increased the amount of $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ and enhanced the iron oxide encapsulation due to enhanced chelating ability. Reducing the GA/Fe ratio to 0.2 resulted in CEINs with stronger magnetization due to the presence of Fe$_3$O$_4$. Ash weight, HCl digestion, and Raman spectroscopy were used in conjunction to characterize the composition of the CEINs. The magnetization of the samples was compared using a simple magnetic weight setup. A scheme for the reactions occurring during the hydrothermal carbonization of GA–Fe complexes was proposed.

INTRODUCTION

Hydrothermal carbonization (HTC) reactions are being thoroughly investigated due to their ability to transform carbonaceous waste into higher-value products, such as hydrochar (HC) and biodiesel, using cheap catalysts while being environmentally benign. In this process, wet biomass and liquid waste rich in dissolved carbon are subjected to temperatures higher than 100 °C in a sealed reactor that can sustain the autogenous pressure. As a result, the carbon can turn into gaseous, liquid, and solid products. During HTC, hydrocarbons initially undergo many chemical reactions (dehydration, hydrolysis, etc.), turning into simpler molecules and organic acids. In the case of saccharides, the main products are organic acids and furfural compounds (FCs). FCs act as structural units, condensing and polymerizing under hydrothermal conditions, resulting in an amorphous carbon matrix that grows into carbon microspheres. Iron salts are known to catalyze this reaction, enhancing the dehydration of saccharides and the production of FCs even at low temperatures. When iron salts are added, they precipitate into oxides and ZVI, which are incorporated into the carbon matrix. These are known as carbon-encapsulated iron nanoparticles (CEINs).

CEINs are a promising catalyst in fuel technology and environmental remediation. Obtaining cheap catalysts for the Fischer–Tropsch synthesis (FTS) is paramount to escalate synthetic fuel production. Yu et al. were the first to study the viability of CEINs synthesized from HTC for the hydrogenation of CO. These were synthesized from cheap reagents, glucose as the carbonaceous source, and iron nitrate as the catalyst for carbonization. The carbon matrix of the CEINs prevented aggregation of the metal species, and their small size resulted in high CO conversion rates even after a long treatment time. The chemistry of the carbon matrix also has a strong impact on catalytic behavior. Guo et al. synthesized N-doped CEINs with different nitrogenated reagents under mild hydrothermal conditions (150 °C) and found that the catalytic activity toward CO$_2$ hydrogenation depended heavily on the N precursor. Recently, CEINs have also been employed in microbial fuel cells, obtaining a 50% increase in power density compared to expensive Pt/C-based electrocatalysts. In environmental remediation, CEINs combine the reducing capabilities of metallic iron due to its ZVI content and enhanced adsorption due to the carbon surface chemistry.

Calderon et al. studied the hydrothermal synthesis of CEINs using olive mill wastewater (OMW) and iron nitrate. These were compared to CEINs synthesized with glucose and iron nitrate. OMW has a high content of metal-chelating ligands, which could promote the formation of CEINs.

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polyphenols. After the introduction of iron nitrate, the polyphenols formed iron chelates. Their carbonization resulted in CEINs with higher ZVI and oxide content. The morphology was also different from the typical microspheres obtained from glucose. Instead, CEINs from OMW formed agglomerated nanospheres. This different morphology granted a higher surface area. The CEINs were used for the sequestration of heavy metal cations, where the carbon shell prevented the release of contaminants. To further increase the surface area and ZVI content, CEINs are activated via pyrolysis under an inert atmosphere, reducing the oxides encapsulated to metallic iron due to carbothermal reduction. CEINs and activated CEINs (a-CEINs) have been used to remediate heavy metals and organic contaminants. While a-CEINs have greater sorption capabilities, the synthesis requires high temperatures (550–900 °C) and they have lower regeneration capabilities. Activation can be detrimental for the sequestration of heavy metals since the presence of amorphous carbon and iron oxides in the CEINs’ surface facilitates the adsorption of metal cations. CEINs can have appreciable magnetization due to their metal content, which allows for facile extraction after remediation. The composition of CEINs is of great importance for their area of application: small iron oxides are required for high activity in FTS synthesis while a high content of ZVI is necessary for the effective reduction of organic pollutants.

CEINs can be synthesized from diverse carbonaceous precursors and iron salts with different results depending on the conditions and post-treatment. Both phenolic compounds and iron salts are catalysts that modify the products of HTC. Phenolic compounds with specific ligand configurations can bind to transition metal ions, creating a ligand to metal charge transfer (LMCT) complex. These complexes are characterized by their strong molar absorptivity, which gives them an intense coloration depending on the number of molecules forming the complex. The more common ligands involved in the metal-binding process are adjacent ortho-hydroxyl (–OH) groups although other ligands might also be involved when various phenolic compounds are present. For binding to take place, the chelating ligand must be deprotonated, meaning that the process heavily depends on the pH. The GA molecule can chelate Fe through –COOH (pK_a = 4.5) and –OH (pK_a = 10) groups.

Other chelating agents such as EDTA, citric acid, and tannic acid have been used in the past to synthesize CEINs and other nanomaterials, but GA has not been used yet in the HTC synthesis of CEINs. This work aims to study the role of phenolics in the HTC synthesis of CEINs using a ferric salt and a solution of glucose with GA. GA was chosen as a model phenolic compound due to its wide presence in plant-based biomass and its ability to form iron complexes. Through adjustment of the initial pH, the –COOH and –OH groups of GA were deprotonated, altering polymerization and ultimately the CEIN yield, morphology, and composition.

## ANALYSIS AND METHODS

The mass of iron species encapsulated in the CEINs was measured by the ash weight. To obtain the ashes, a quantity of at least 150 mg of CEINs was heated in air at 950 °C for 3 h to volatilize their HC content. The resulting ashes were Fe_2O_3 from the encapsulated iron species. A blank sample of HC from glucose and GA was treated in the same manner to find if other inorganics were present in the ash. No ashes were found for these samples, indicating that Fe_2O_3 was the only ash material. To assess the ZVI content, the CEINs were digested in HCl in a sealed vessel. The increase in pressure due to the generation of hydrogen gas (as follows in eq 1) was used to estimate the ZVI through the ideal gas law. In the procedure, 0.2 g of CEINs was introduced in 120 mL glass bottles. Then, 5 mL of 37% HCl was rapidly introduced, and the bottles were sealed immediately with a septum. The mixtures were left to react for 2 h for a complete reaction. Then, the pressure generated was measured with a digital pressure meter with a needle by perforating the septum. The pressures generated ranged from 40 to 100 mbar. The measurements were performed in duplicate, and the mean was used.

\[
2\text{Fe(s)} + 6\text{HCl(l)} \rightarrow 2\text{FeCl}_3(aq) + 3\text{H}_2(g)
\]  

The ZVI content was subtracted from the ashes, leading to the iron oxide content. From this data, the mass percentage of HC (%HC), iron species (%Fe), iron oxides (%Ox), and ZVI (%ZVI) of the CEINs were calculated. The quantities follow eqs 2 and 3.

\[
100\% = \%\text{HC} + \%\text{Fe}
\]

\[
\%\text{Fe} = \%\text{Ox} + \%\text{ZVI}
\]

The yield of CEINs (Y_{CEIN}) was calculated using eq 4, where m_{Glucose} and m_{GA} are the mass of D-Glucose and GA, respectively, m_{Fe} is the mass of iron in the iron nitrate, and m_{CEIN} is the dry mass of CEINs.

\[
Y_{CEIN} = \frac{m_{CEIN}}{m_{Glucose} + m_{GA} + m_{Fe}}
\]

The phases of the iron oxides were identified via dispersive Raman spectroscopy using a LabRam (Jobin-Ivon) spectrometer with a 632 nm laser. Iron oxides present active vibrational modes between 200 and 1000 cm\(^{-1}\) (Table S1). These can be used to distinguish the iron oxide phases despite their low crystallinity in the CEINs. The oxide peaks were fitted to those found in the work of Testa-Anta et al. The carbon peaks from these samples were compared for insight into the HC structure of the CEINs (Table S2).

A JEOL JEM-1400 Plus was used to acquire TEM images of the CEINs and the encapsulated iron species. A comparative measure of magnetization was obtained using a magnetic weight setup. In short, a sample holder above and separated from the balance was filled with a mass of CEINs. In contact with the balance, a holder with a magnet could be lifted or lowered with a lever. The magnet was situated between the CEINs and the encapsulated iron species. A comparative measure of magnetization was obtained using a magnetic weight setup. The mass of iron species encapsulated in the CEINs is the dry mass of CEINs.

\[
\Delta \sigma = \frac{F_z}{m_{FB_z}} - F_z = \Delta m \cdot g
\]

where \(\sigma\) (emu/kg) is the mass magnetization of the sample, \(F_z\) (N) is the magnet weight, \(\Delta m\) (kg) is the mass change due to the pull exerted by the CEINs to the magnet, \(VB_z (T/m)\) is the magnetic field gradient of the magnet in the z-direction, and \(m_s\) (kg) is the CEINs’ sample mass. Comparisons were drawn using the mass normalized force exerted at a certain distance, \((\Delta m/m_s)\). The measurements were carried out with the least amount of CEINs possible to avoid artifacts arising from the geometry and always using the same \(VB_z\). The maximum standard error was 6% at the minimum distance. This error can be reduced with better control of the distance between the
magnet and the sample. In any case, the purpose was to provide a quick visual representation of the magnetization of the CEINs.

**RESULTS AND DISCUSSION**

**CEINs’ Yield and Ultimate Analysis.** For samples C0−1 and C0−4, iron was initially present as aqueous Fe³⁺. Due to the pH₀ adjustment, Fe³⁺ precipitated into Fe(OH)₃ for samples C₀−7, C₀−10, and C₀−12. During HTC, glucose decomposed into FCs and organic acids, reducing the pH below 7. This results in the redissolution of Fe(OH)₃ into Fe³⁺ for samples C₀−7, C₀−10, and C₀−12. The FCs polymerized incorporating a fraction of the total Fe³⁺ introduced. Figure 1a shows that Y_CEIN was higher between pH₀ 4 and 10. Also, Figure 1b shows that %HC and %Fe were minimum and maximum between pH₀ 7 and 10. The production of FCs from saccharides depends strongly on the pH₀ and the presence of heterogeneous catalysts.²⁷,²⁸ The decrease of Y_CEIN beyond pH₀ 10 is due to a reduction in the production of FCs that would produce the CEINs.

Introducing Fe³⁺ into a GA solution leads to the formation of GA−Fe complexes. These complexes retain Fe³⁺ in the whole pH₀ range, inhibiting the precipitation of Fe(OH)₃. As seen in Figure 1a, the Y_CEIN values for batch C₀.2 were similar to those of batch C₀ at each pH₀. Due to the low GA/Glucose ratio (0.06), the production of CEINs was still highly dependent on the pH₀. Despite this, the addition of GA resulted in different %HC and %Fe trends with pH₀. For batch C₀, %HC diminished and %Fe increased toward pH₀ 7, while for batch C₀.2 %HC diminished and %Fe increased with higher pH₀ (Figure 1b,c). The decrease of %HC and increase of %Fe in batch C₀.2 were more significant between pH₀ 4 and 7 and pH₀ 10 and 12. These ranges of pH₀ correspond to the deprotonation of −COOH (pKₐ = 4.5) and −OH (pKₐ = 10) from GA. After deprotonation, these groups can chelate and incorporate more Fe³⁺, resulting in lower %HC and higher %Fe.

For batch C₁, the GA/Glucose ratio was higher (0.33) and GA had a stronger influence in polymerization, resulting in increased Y_CEIN at higher pH₀. %HC decreased and %Fe increased from pH₀ 4 to 7, but no significant changes were observed at higher pH₀ (Figure 1d).

The %Ox content followed a behavior similar to %Fe in all batches. In contrast, a trend for %ZVI was hard to discern, with the only similarity being that %ZVI was always the maximum at pH₀ 1. ZVI appears due to the reduction of Fe³⁺ to Fe⁰. This has been seen in the synthesis of ZVI nanoparticles using plant extracts with a high content of phenolics, which also act as stabilizers.²⁹,³⁰ Since GA is unable to completely reduce Fe³⁺, the hydrothermal degradation of d-glucose must produce chemicals that are able to perform this reduction. The production of these chemicals would be higher at lower pH₀, explaining the %ZVI maximums at pH₀ 1. However, to confirm the production of stronger reducing organic compounds, further analysis of the HTC liquor would be required.

**Characterization of CEINs.** Apart from the mass composition, it was observed that the samples C₀.2−7, C₀.2−10, and especially C₀.2−12 were magnetic. Raman spectroscopy was used to study the metal oxide content in the batch with a GA/Fe ratio of 0.2. From these results, the iron oxides produced during HTC of Fe−GA complexes were obtained. The spectra obtained also allowed the study of the carbonaceous matrix of the CEINs. The iron oxide phases found were α-Fe₂O₃, γ-Fe₂O₃, and Fe₃O₄. Samples C₀−12 and C₁−10 were also studied for comparison (Figure S1). The composition of the iron oxides is presented in Table 1.

The samples with a GA/Fe ratio of 0.2 all presented similar quantities of α-Fe₂O₃ except for C₀.2−12 which had none. For these samples, the GA reduced part of the Fe³⁺ to Fe²⁺ resulting in the precipitation of Fe₂O₃ nanoparticles. These would gradually oxidate into γ-Fe₂O₃ due to the presence of O₂.
and hydrothermal conditions. At pH < 7, part of the Fe³⁺ of the γ-Fe₂O₃ would dissolve back into solution, later precipitating as α-Fe₂O₃ due to the hydrothermal conditions. This is also the case for sample C₀⁻¹₂, where Fe³⁺ from solution, or from dissolution of Fe(OH)₃ precipitates as α-Fe₂O₃. This mechanism has already been studied with Fe₃O₄ micro-particles. In sample C₀.2⁻¹₂, the pH > 7 during the reaction disabled the oxidative pathway into α-Fe₂O₃. This also occurs for sample C₁⁻¹₀, where all of the iron oxide is γ-Fe₂O₃ due to complete oxidation of Fe₃O₄.

The carbonaceous matrix was studied deconvoluting the Raman spectra between 1000 and 1800 cm⁻¹ (Figure S2). Three bands were identified: D (≈1350 cm⁻¹), A (≈1500 cm⁻¹), and G (≈1580 cm⁻¹). The D band corresponds to disordered graphitic lattices, the A band to amorphous carbon, and the G band to the ideal graphitic lattice. The shape of the spectra varied notably with the pH₀ used. The intensity ratio of the A band and G band (I_A/I_G) is deemed as a good indicator of the amount of amorphous carbon in soot and carbon black. Figure S3 shows that I_A/I_G followed a linear increase in this ratio beyond pH₀ 7, indicating that the amorphous carbon content increased with pH₀.

TEM images were used for further insight into the structural changes. The blank sample consisted of interconnected carbon nanochains and carbon microspheres (Figure 2a,b) corresponding to HTC of GA and FCs, respectively. Using only

| sample   | α-Fe₂O₃ | γ-Fe₂O₃ | Fe₃O₄ |
|----------|---------|---------|-------|
| C₀⁻¹₂    | 100     | 0       | 0     |
| C₀.2⁻⁴   | 45.1    | 43      | 11.9  |
| C₀.2⁻⁷   | 42.1    | 30.9    | 27    |
| C₀.2⁻¹₀  | 42.2    | 34.3    | 23.5  |
| C₀.2⁻¹₂  | 0       | 43.9    | 56.1  |
| C₁⁻¹₀    | 0       | 100     | 0     |

Table 1. Iron Oxide Composition of CEINs

Figure 2. TEM images of the (a, b) blank, (c, d) C₀⁻¹₂, and (e, f) C₀.2⁻⁴.
glucose and iron nitrate at pH0 12 led to smaller chains filled with α-Fe₂O₃ and ZVI instead of the usual carbon microspheres (Figure 2c,d). Combining GA, glucose, and iron nitrate resulted in a mixture of these two structures: carbon nanochains with agglomerated metal oxides and ZVI (Figure 2e,f). Increasing pH0 led to a progressive shrinkage and aggregation of the carbon nanochains, finally creating highly packed CEINs at pH0 12 (Figure 3a−c). The difference in packing behavior resulted from having a higher quantity of deprotonated ligands at higher pH. In conjunction with Raman analysis, we confirm that the GA/Fe ratio and pH0 have a substantial effect on the formation of the CEINs.

Finally, a homemade magnetic weight system was used to study the magnetization of the samples with a GA/Fe ratio of

Scheme 1. Reactions during HTC of a Carbonaceous Precursor with and without GA. Iron Will Be Initially Present in Different Forms Depending on the Presence of Phenolics and the Initial pH

Figure 3. TEM images of samples (a) C₀.₂−₇, (b) C₀.₂−₁₀, and (c) C₀.₂−₁₂. The features between change significantly with pH₀.
An exponential increase in magnetization occurs for the experiment at pH\textsubscript{0} 12 (Figure S4). A possible explanation for this increase is the formation of tightly packed Fe\textsubscript{3}O\textsubscript{4} in the amorphous carbon matrix (Figure 3c). The packing results in an increased density of magnetically coupled Fe\textsubscript{3}O\textsubscript{4} nanoparticles, which would behave as single magnetic domains under a magnetic field\textsuperscript{34,35} The lack of $\alpha$-Fe\textsubscript{2}O\textsubscript{3} would also facilitate the formation of such domains.

Based on these results, two different pathways for the formation of CEINs are proposed (Scheme 1). When saccharides are present, the iron is present as either Fe\textsuperscript{3+} or precipitated Fe(OH)\textsubscript{3} depending on the pH\textsubscript{0}. During the first stage of HTC, the saccharides degrade producing FCs and organic acids that acidify the solution (if pH\textsubscript{0} is above 3). Following, the FCs start polymerizing, while the Fe\textsuperscript{3+} precipitates or Fe(OH)\textsubscript{3} dehydrates into $\alpha$-Fe\textsubscript{2}O\textsubscript{3}. The $\alpha$-Fe\textsubscript{2}O\textsubscript{3} is integrated into the carbon microspheres forming CEINs. A fraction of Fe\textsuperscript{3+} is reduced to Fe\textsuperscript{0}, resulting in ZVI in the CEINs. For GA and other simple polyphenols, Fe\textsuperscript{3+} is chelated, forming Ga–Fe complexes. Depending on the pH\textsubscript{0}, carboxylic and hydroxyl groups deprotonate, opening different paths to chelate Fe\textsuperscript{3+} and polymerization. During HTC, the chelated iron precipitates as Fe\textsubscript{2}O\textsubscript{3} due to reduction to Fe\textsuperscript{2+} in the Ga–Fe complex. These precipitates are encapsulated by GA molecules that polymerize, finally forming the CEINs. During HTC, the high temperature and aerobic environment result in the partial or complete oxidation of Fe\textsubscript{2}O\textsubscript{3} into $\gamma$-Fe\textsubscript{2}O\textsubscript{3}. If the pH during HTC was below 7, $\gamma$-Fe\textsubscript{2}O\textsubscript{3} could dissolve as Fe\textsuperscript{3+} and later precipitate as $\alpha$-Fe\textsubscript{2}O\textsubscript{3} in the CEINs. Similarly, ZVI was also found in these CEINs.

## CONCLUSIONS

The HTC of a solution comprising glucose and iron nitrate and different ratios of GA/Fe and pH\textsubscript{0} were used to explore the changes brought by the presence of phenolic compounds in the synthesis of CEINs. The procedure allowed the synthesis of CEINs containing different iron oxides by tuning the GA/Fe molar ratio and pH\textsubscript{0} while maintaining an equal treatment time and temperature. The morphology, structure, and magnetic properties of the CEINs were also severely affected by these parameters. These changes were attributed to the quantity of available ligands for chelation and polymerization. A scheme for the different reactions occurring during HTC of Ga–Fe complexes was drawn. The differences in iron loading are significant in the activation process of the CEINs for the synthesis of FTS catalysts. Also, the different morphologies and magnetic behavior might be of interest for contaminant remediation.

## EXPERIMENTAL SECTION

**Reagents.** Chemical reagents used were D-glucose (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}, Merck, 99.5%), gallic acid (C\textsubscript{7}H\textsubscript{6}O\textsubscript{5}, Sigma-Aldrich, 97.5%), iron nitrate nonahydrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Fischer Chemical, 99.1%), sodium hydroxide (NaOH, Fischer Chemical, 97%), and 37% hydrochloric acid (HCl, Labkem). The solutions were prepared using deionized water.

**CEIN Synthesis.** In a beaker with 30 mL of deionized water, glucose (16.6 or 8.3 mmol) and GA (2.8 or 1 mmol) were stirred until complete dissolution. The samples without GA used 16.6 mmol glucose. Afterward, iron (III) nitrate nonahydrate (4.3, 4, or 2.8 mmol) was introduced, which turned the transparent solution into a dark purple color. Then, the solution pH was adjusted using a 20% (w/v) NaOH solution, if required. The volumes were increased to 50 mL, and the solutions were introduced into 80 mL Teflon-lined autoclave reactors and sealed. The autoclaves were then heated to 180 °C for 5 h maintaining the autogenous pressure in a furnace to perform the HTC. After treatment, the autoclaves were left to cool overnight. The contents were vacuum filtered with 5–13 μm qualitative filter paper (VWR) and thoroughly washed with deionized water and methanol. The supernatant was stored to measure the final pH of the solution. The solid product was dried under aerobic conditions in a furnace for 12 h at 60 °C. Afterward, the remaining solids were crushed in a mortar, obtaining a fine black powder. Table 2 presents the GA concentrations ($C_{GA}$) and molar ratios used. The iron-to-carbon molar ratio (Fe/C) was constant to ensure that possible changes in the yield and morphology were due to the GA and iron content. The molar carbon included both carbons from glucose and GA. The samples were named after their GA/Fe molar ratio ($X$) and initial pH ($Y$) ($C_{0.2}^{-1}$). A blank was prepared using a glucose and GA solution. For batch $C_{0.2}$, the higher pH was limited to 10 to avoid fouling of the CEINs. Another point (pH 9) was taken instead. Sample $C_{1.0}$ had very fine CEINs in solution. To recuperate them, the contents of the autoclave were first completely dried at 90 °C. Then, the remaining solid was washed with methanol and vacuum filtered in the same conditions. The powders were stored for further analysis.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03692.

**Table 2. GA Concentration and Iron-to-Carbon (Fe/C), GA-to-Iron (GA/Fe), and GA-to-Glucose (GA/Glu) Molar Ratios**

| sample | $C_{GA}$ (mM) | Fe/C | GA/Fe | GA/Glu |
|--------|---------------|------|-------|--------|
| blank  | 20            | 0.04 | 0     | 0.06   |
| $C_{0.2}$ | 0.04 | 0.2  | 0.06  |
| $C_{1.0}$ | 20        | 0.04 | 0.2   | 0.06   |
| $C_{1.4}$ | 56        | 0.04 | 1     | 0.33   |
| $C_{1.7}$ | 0.04 | 1     | 0.33  |
| $C_{1.9}$ | 0.04 | 1     | 0.33  |
| $C_{1.10}$ | 0.04 | 1     | 0.33  |
weight for samples C_{0.12}, C_{1.10}, and C_{2.4} to C_{2.12} (Figure S4). Peak data extracted from the Raman spectra between 200 and 800 cm\(^{-1}\) for C_{0.12}, C_{2.4} to C_{2.12} and C_{1.10} (Table S1) and peak data extracted from the Raman spectra between 1000 and 1800 cm\(^{-1}\) for C_{2.4} to C_{2.12} (Table S2) (PDF)

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Notes
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