



OXIDATIVE DENITROGENATION OF A SIMULATED FUEL UNDER A BIPHASIC GREEN SYSTEM

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Resumo

Este trabalho trata da desnitrificação catalítica de um combustível simulado (quinolina (QN) em 2,2,4-trimetilpentano) por oxidação com peróxido de hidrogénio em meio bifásico. Como catalisadores, foram utilizados três materiais: (i) ferro suportado em alumina (Fe/Al₂O₃) obtido por sol-gel, (ii) nanotubos de carbono (CNT) produzidos através da deposição química em fase de vapor de propileno (PP) sobre o catalisador anterior (Fe/Al₂O₃), e (iii) os CNT fornecidos pela Sigma Aldrich. A contribuição da adsorção e da extração foi avaliada, sendo ambas consideradas desprezáveis ou pouco efetivas para a remoção da QN. O desempenho de cada material foi analisado em testes de reação de 4 h, a 80 °C, através da monitorização da degradação de H₂O₂ e da concentração de QN em meio oleoso e aquoso. Como resultados, todos os materiais utilizados atenderam ao objetivo proposto, sendo 100% da QN removida da fase oleosa nos ensaios de oxidação bifásica. Em resumo, todos os catalisadores produzidos foram eficientes no processo proposto e são comparáveis ao desempenho obtido pelo CNT comercial.

Palavras-chave: desnitrificação oxidativa, quinolina, oxidação bifásica, nanomateriais de carbono, peróxido de hidrogénio.

Abstract

This work deals with the catalytic denitrogenation of a simulated fuel (quinoline (QN) in 2,2,4-trimethylpentane) by oxidation with hydrogen peroxide in a biphasic medium. As catalysts, three materials were used (i) iron supported on alumina (Fe/Al₂O₃) obtained by sol-gel, carbon nanotubes (CNT) produced by chemical vapor deposition of propylene (PP) growth on the previous catalyst (Fe/Al₂O₃) and (iii) a commercial sample of CNT supplied by Sigma Aldrich. The contribution of adsorption and extraction was also assessed, both being considered negligible or ineffective for the removal of QN. The performance of each catalyst was analysed in 4 h reaction tests, at 80 °C, by monitoring the degradation of H₂O₂ and the concentration of QN in the oily and aqueous media. As a result, all catalysts used met the proposed objective, with 100% of QN being removed from the oily phase in the biphasic oxidation tests. In summary, all the catalysts produced were efficient in the proposed process and are comparable to the performance obtained by the commercial CNT sample.

Keywords: oxidative denitrogenation, quinoline, biphasic oxidation, carbon nanomaterials, hydrogen peroxide.

1. Introduction

The global energy demand has experienced a steady growth due to the global upsurge in population and industrialization. Between 1971 and 2017, world energy consumption has increased by almost three times, reaching a value around 13,972 Mtoe. Among the several types of energy resources, fossil fuels represent the primary source of energy all over the world [1]. COVID-19 crisis caused a historic decline in global oil demand in 2020, but not necessarily a lasting effect, and the global oil demand is expected to increase for years to come [2]. Thus, the present level of living standards requires energy to move on [3]; however, there are economic and environmental implications associated with the use of fossil fuels [1]. In this context, new technologies must be developed to avoid the impacts caused by oil-based energy.

In the area of crude oil treatment, oil-refining industries need to cope with the specifications of commercialized fuels, which are driven by environmental concerns. Sulfur and nitrogen levels are among the main concerns, since sulfur and nitrogen-containing compounds result in harmful gases during combustion (such as SO_x and NO_x). The presence of NO_x gases (NO , NO_2 and N_2O) is ascribed to reduction of visibility, acid rain, and harmful effects to human beings, including chronic bronchitis, dyspnea and pulmonary edema [4]. Those gases are known as acidic gases owing to their contribution towards acid rain, being able to blend with water and other particles before reaching the ground [4]. Thus, an increase in strictness in the emissions of NO_x has been observed worldwide, which includes limiting their content in fuels to control those emissions. As a result, refineries or end users' terminals need to convert fuel oil into higher quality products [5].

The conventional treatment of crude oils consists in three main steps: separation, conversion, and treatment processes. The first processes aim at separating fractions according to their boiling points. Conversion ones are based on the reduction of the length of carbon chains compared to the initial feed [6]. Finally, treatment processes, such as hydrotreating, aims at cleaning fuels by removing contaminants, such as sulfur and nitrogen compounds [7].

Nowadays, hydrodenitrogenation (HDN) is the main process used to achieve low levels of nitrogen in fuels. However, this process requires severe operating conditions of pressure and temperature (5 – 170 bar and 260 – 425 °C, respectively). A complementary or alternative process is oxidative

denitrogenation (ODN) [8]. This technique targets the oxidation of nitrogen-containing compounds to form oxygenated derivatives [9].

ODN is a process conducted in two sequential steps: (1) oxidation and (2) removal of oxidized compounds with an extractant. However, simultaneous presence of the oxidant and the extractant allows conducting the two steps concomitantly. Hydrogen peroxide is considered a green oxidant commonly used for this purpose [10]. Likewise, the use of water as extractant phase results in a greener process. Thus, ODN can be conducted in a biphasic system, formed by an aqueous phase, in which H_2O_2 is solubilized, and the oily phase (fuel) including the N-containing compounds. A catalyst allows overcoming issues such as the high temperature required in ODN or the low mass transfer ascribed to biphasic systems [11]. There are several materials presenting suitable catalytic activity towards ODN [12, 13]. Especially, carbon-based materials and composites have received increased attention due to their known ability towards the decomposition of hydrogen peroxide into hydroxyl radicals, as well as to its suitable lipophilic properties, that allow closer contact with lipophilic pollutants [12]. Additionally, one of the main attractive characteristics of carbon-based catalysts is the possibility to obtain materials from C-rich waste sources, such as plastic solid waste (PSW) [14].

Under the exposed context, this work deals with the ODN of a simulated fuel (quinoline in 2,2,4-trimethylpentane) under a biphasic system, considering hydrogen peroxide as oxidant and water as extractant phase. The catalysts used in the process are $\text{Fe}/\text{Al}_2\text{O}_3$, carbon nanotubes (CNT) synthesized by chemical vapor deposition (CVD) of the gaseous products resulting from the pyrolysis of polypropylene (PP) used as carbon source (simulating PSW) over an iron-based catalyst and a commercial CNT sample.

2. Experimental

The iron-based catalyst ($\text{Fe}/\text{Al}_2\text{O}_3$) was synthesized by a sol-gel methodology. 10 mmol of FeCl_2 was dissolved in 20 mL of ethanol and heated until reaching its boiling point. 20 mmol of FeCl_3 was dissolved in 80 mL of ethylene glycol and heated to 60 °C for 5 min. Both Fe-containing solutions were then loaded into an ice bath until reaching the temperature equilibrium. The solutions were mixed in one beaker with Al_2O_3 (6.6 g), and the mixture was heated to 60 °C for 2 h in a heating plate under stirring. Then, the temperature was increased to 120 °C and the

mixture was left at this temperature until reaching a gel-like texture. The temperature was then increased to 200 °C until reaching a powder texture. The obtained powder was subjected to a thermal treatment under nitrogen flow at 300 °C for 12 h and 600 °C for 24 h, leading to Fe/Al₂O₃.

The CVD process was carried out in a vertical oven (TH/TV, Termolab) considering PP as carbon source. 1 g of the Fe/Al₂O₃ catalyst was loaded in the lower region of the oven and 5 g of the polymer on the upper region. The synthesis was conducted at 800 °C with 1 h hold time upon reaching the desired temperature, under a nitrogen atmosphere (40 mL min⁻¹). After synthesis, the CNT was subjected to acid washing to reduce the quantity of the metal catalyst attached to the structure (50% v/v H₂SO₄, 140 °C, 3 h, under reflux), as described elsewhere [15]. After cooling down, the material was abundantly washed with distilled water to remove excess acid and then dried in oven at 60 °C for 12 h, leading to CNT-PP. For comparison purposes, the catalyst used in the CNT growth (Fe/Al₂O₃) and a commercial sample of CNT (CNT-C), provided by Sigma-Aldrich, were also used. Textural properties for CNT-PP and CNT-C were measured from N₂ adsorption-desorption isotherms at 77 K in a Quantachrome NOVATOUGH XL4. The specific surface area (S_{BET}) was calculated in the range of p/p_0 0.05 - 0.35. The total pore volume (V_{Total}) was determined at $p/p_0 = 0.98$. Thermogravimetric analysis (TGA) was performed in a NETZSCH STA 409 PC/PG in air atmosphere from 50 to 900 °C at a rate of 10 °C min⁻¹ for CNT-PP.

Adsorption was performed considering only the oily phase (C_{QN} = 1000 mg L⁻¹), as well as a biphasic system (C_{QN, oil} = 1000 mg L⁻¹, oil:water ratio 80:20, pH_{water} = 3.0). 2,2,4-trimethylpentane was chosen as oily phase, simulating a gasoline fuel. Both adsorption runs were conducted at 80 °C and at 200 rpm. Upon reaching the desired temperature, the adsorbent (C_{cat} = 2.5 g L⁻¹, considering the total volume of the system) was added. Adsorption runs were conducted for 4 h. QN was analysed by UV/Vis spectrophotometry at 313 nm, both for aqueous and oily phases.

Oxidation runs were carried out in aqueous system (C_{QN, water} = 100 mg L⁻¹) as well as in biphasic system (C_{QN, oil} = 1000 mg L⁻¹, oil:water ratio 80:20, pH_{water} = 3.0). The concentration of H₂O₂ was 10 times the theoretical concentration needed for complete QN mineralization (C_{H₂O₂, water} = 6.2 and 247 mg L⁻¹ for aqueous and biphasic systems, respectively). The experiments were performed in a round-bottom glass flask immersed

in a silicone bath, which was set at 80 °C. Upon reaching 80 °C, H₂O₂ was added to the system, followed by adding the catalyst (C_{cat} = 2.5 g L⁻¹, considering the total volume of the system). The reactions were carried out during 4 h. QN concentration in the aqueous phase was monitored via HPLC (column "NUCLEOSIL 100-5C18, 15 cm × 2.1 mm), with a flow of 0.5 mL min⁻¹, and a mobile phase consisting of 20% of acetonitrile and 80% of a 20 mM phosphate buffer solution at a pH of 6.5. QN concentration in the oily phase was measured by UV/Vis spectrophotometry at 313 nm. H₂O₂ concentration was determined via TiOSO₄ method by UV/Vis spectrophotometry at 405 nm, as described elsewhere [16]. By the end of both reactions, the catalyst and the reaction medium were separated by filtration.

3. Results and discussion

3.1 Characterization of catalysts

The textural properties for CNT-PP and CNT-C are described in Table 1. As it can be seen, the CNT obtained from PP has a surface area and a total pore volume that are similar to the ones obtained for the commercial sample. These values are similar to other reports in the literature for CNTs prepared from pure gases [17-19] and for CNTs derived from other polyolefins [20].

Table 1. Textural properties of the catalysts.

Material	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)
CNT-PP	242	0.595
CNT-C	254	0.691

The TGA and DTG profiles for the CNT-PP sample is seen in Figure 1.

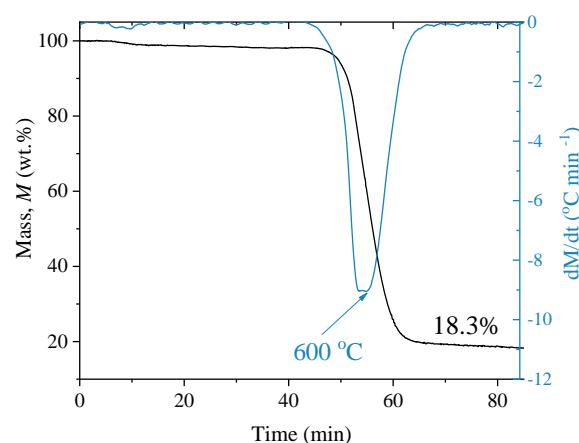


Figure 1. TGA (left Y axis, black) and DTG (right Y axis, blue) profiles for CNT-PP.

The remaining weight after burning in air atmosphere, ascribed to the ashes content of the CNT sample, is 18%, which is in accordance with the other reports in the literature [17]. This ash content refers to the catalyst that is mostly

contained within the structure of the CNT and cannot be removed during acid washing. Similarly, the value obtained for the oxidation peak (600 °C), as determined by the DTG profile, is ascribed to the formation of multi-walled CNTs [17]. The oxidation range for multi-walled CNTs usually varies between 400-650 °C, whereas other contaminants, such as amorphous carbon, lies in the range between 200-300 °C [17]. Similar values were observed in the literature for CNTs derived from pure gases [15, 21] and also from PP [22].

3.2 Adsorption and extraction runs

Adsorption of QN in the oily medium resulted in a removal of only 5, 11 and 5% in the presence of Fe/Al₂O₃, CNT-PP and CNT-C, respectively, as shown in Figure 2 (black bars). Those values can be considered negligible for the goal of attaining complete removal of nitrogenated compounds from liquid fuels. Extraction using acidified water is also not suitable to remove QN, as seen in Figure 2 (blue bar), resulting in 7% of QN removal in 4 h of extraction. Likewise, combining adsorption with extraction (both catalyst and extraction phase are present in the system) also accounts for less than 10 % of QN removal in 4 h of experiment, regardless of the catalyst chosen (yellow bars in Fig. 2). After 4 h of contact, the oily phase still contained 94, 85 and 88% of the initial amount of QN (considering both effects of adsorption and extraction) in the presence of Fe/Al₂O₃, CNT-PP and CNT-C, respectively. Thus, adsorption, extraction or a system that combines extraction and adsorption is not sufficient to remove QN from 2,2,4-trimethylpentane.

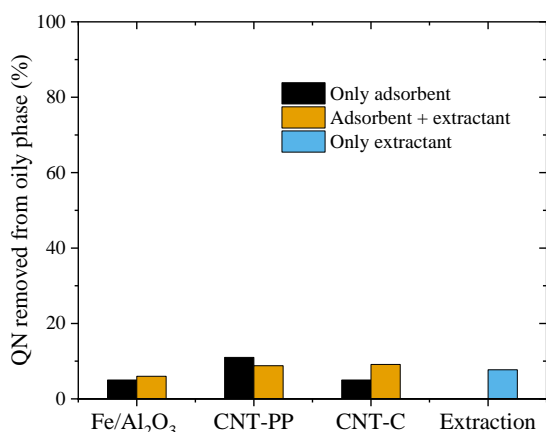


Figure 2. QN removed from the oily phase by adsorption, extraction or a combination of both strategies with each catalyst (80 °C, O:W = 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$, $C_{QN,0} = 1000 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $pH_w = 3.0$, 4 h).

3.3 Oxidation runs in aqueous phase

Oxidation reactions were then carried out in aqueous systems to investigate the ability of the catalysts to decompose H₂O₂ and degrade QN. The results can be observed in Figure 3. QN was completely degraded in the presence of any of the catalysts proposed in 4 h of reaction (Fig. 3, a). In fact, in the presence of CNT-PP, 2 h is enough to completely degrade QN (data not shown). Likewise, all catalysts were able to decompose the oxidant. In the presence of Fe/Al₂O₃, CNT-PP and CNT-C, H₂O₂ decomposition achieved values of 80, 82 and 40%, respectively (Fig. 3, b). For comparison purposes, a non-catalytic run was also carried out (data not represented), resulting in 2% of decomposition of H₂O₂ and a degradation of 83% of QN under the same conditions. Therefore, all the materials tested so far have proved to act as catalysts in the oxidation of QN with H₂O₂ and led to higher QN removals if compared to the non-catalytic experiment.

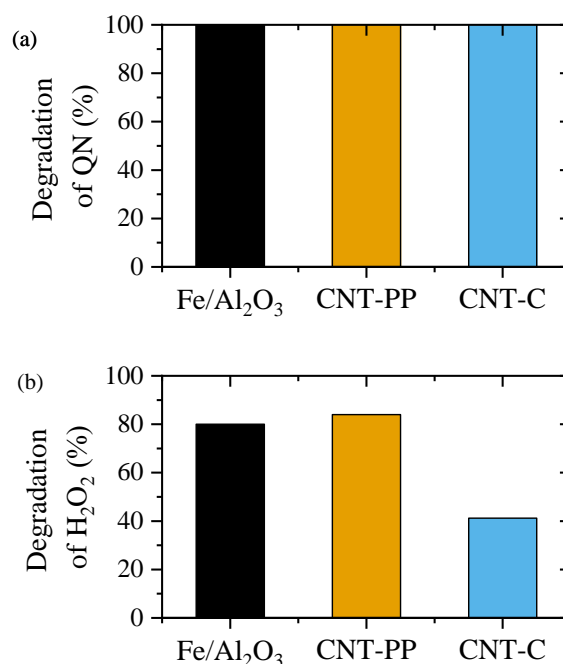


Figure 3. Oxidation of QN in an aqueous medium. (a) Degradation of QN and (b) degradation of H₂O₂ (80 °C, $pH_0 = 3$, $C_{QN} = 100 \text{ mg L}^{-1}$ in water, $C_{cat} = 2.5 \text{ g L}^{-1}$, $C_{H_2O_2} = 6.2 \text{ g L}^{-1}$, 4 h).

3.4 Oxidative denitrogenation under a biphasic system

Since all materials have proved to be effective catalysts in the degradation of QN in aqueous phase, their ability in the ODN of QN under a biphasic system with concomitant oxidation and extraction was further assessed. Previous experiments indicate that 2,2,4-trimethylpentane oxidation can be considered negligible under the

studied operating conditions. The results can be observed in Figure 4. QN removal from the oily phase, the main goal of the process, is similar regardless of the catalyst used, when conducted during 4 h (Fig. 4, a). However, in the presence of CNT-PP, over 90% of QN had already been removed from 2,2,4-trimethylpentane in just 60 min of reaction vs 50-60% in the presence of the other 2 catalysts (data not shown). The overall degradation of QN (accounting for both QN present in water and oily phases) followed the trend CNT-PP > CNT-C > Fe/Al₂O₃ (Fig. 4, b), whereas the decomposition of H₂O₂ followed the opposite trend (Fig. 4, c). This may be ascribed to a more efficient consumption of the oxidant. For comparison purposes, a non-catalytic run was also conducted, resulting in no decomposition of H₂O₂ and only 8% removal of QN in 4 h of reaction. Similar results regarding the removal of QN from oily phases using carbon-based materials have been reported in the literature [23-28], although considering much higher concentrations of H₂O₂ and fuels with lower concentration of QN.

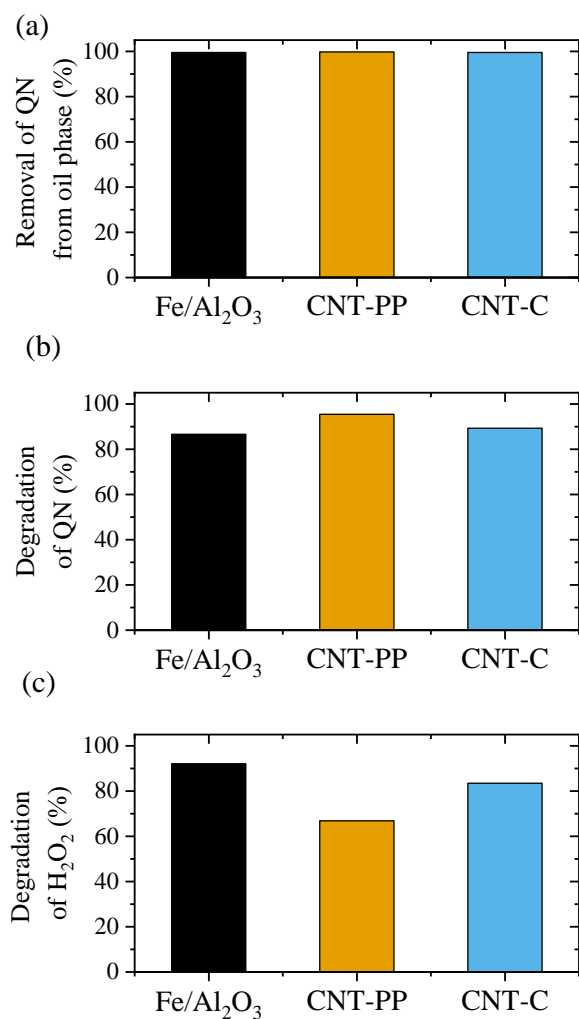


Figure 4. Oxidative denitrogenation of QN from a simulated fuel with H₂O₂. (a) Removal of QN from

oily phase, (b) degradation of QN (accounting for oily and aqueous phase), and (c) decomposition of H₂O₂ (80 °C, pH₀ 3 in aqueous phase, C_{QN} = 1000 mg L⁻¹ in 2,2,4-trimethylpentane, O:W ratio = 80:20, C_{cat} = 2.5 g L⁻¹ considering the total volume of the system, C_{H₂O₂} = 247 g L⁻¹, 4 h).

4. Conclusion

As a general conclusion, all catalysts accomplished the main goal of removing QN from a model fuel by ODN in a biphasic system using water as extractant. It is also possible to conclude that the materials act mostly as catalysts in the oxidation runs, due to the low contribution of adsorption, promoting a faster degradation of H₂O₂ and QN compared to the non-catalytic run. The catalysts studied were also able to increase the interaction of oily and aqueous phases in reactions carried out under biphasic systems, easing the mass transference between the phases, and increasing the contact between the contaminant and the oxidant in the biphasic system. This resulted in a fast removal of quinoline from the oily phase. Furthermore, the synthesized CNT-PP and Fe/Al₂O₃ are comparable with the commercial sample of CNT (CNT-C), as comparable results were obtained.

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