Hydrothermal Catalytic Deoxygenation of Palmitic Acid over Nickel Catalyst

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Abstract

Fatty acid has recently received considerable interest as a possible precursor for producing renewable hydrocarbon. In this study, we investigated hydrothermal catalytic deoxygenation of palmitic acid to produce paraffin over a Ni/ZrO₂ catalyst with no or low-pressure (100 psi) external supply of H₂. The results show that the presence of water greatly improved conversion of palmitic acid and paraffin yield. Significant improvement was attributed to the formation of in-situ H₂. Without an external H₂ supply, a 64.2 C% conversion of palmitic acid was achieved in the presence of water, while only a 17.2 C% conversion was achieved without water. The results also show that the presence of water suppressed the side reactions of palmitic acid, specifically ketonization and esterification. We concluded that, compared with decarboxylation and hydrodeoxygenation, decarbonylation was the major route for palmitic acid deoxygenation catalyzed by Ni/ZrO₂. Varieties of shorter-chain paraffin (C₈-C₁₄) were formed through hydrogenolysis, which also produced a considerable amount of CH₄. A viable reaction pathway for hydrothermal catalytic deoxygenation of palmitic acid in the presence of Ni/ZrO₂ was suggested. The results show that hydrogenolysis and decarbonylation were the major reactions that occurred. This study demonstrates that this hydrothermal catalytic process is a promising approach for producing liquid paraffin (C₈-C₁₅) from fatty acids under no or low-pressure H₂.

Key words: Hydrothermal catalytic deoxygenation, Fatty acid, In-situ H₂, Decarbonylation, Hydrogenolysis, Paraffin

1. Introduction

Fatty acid and its derivatives are considered to be a promising precursor for producing diesel and jet fuel range of hydrocarbon. Oleaginous microbes, including algae, yeast, and fungi, are receiving increasing attention for use in fatty acid production [1-7]. Compared to traditional crop oil biomass, oleaginous microbes have short life cycles, rapid growth rates, and high oil yields [8].

However, the use of fatty acids and their derivatives as fuel is limited by their high oxygen content, which leads to a low heating value, as well as a high cloud and pour points [9, 10]. Hydrothermal decarboxylation is one of the technologies extensively investigated to remove oxygen from fatty acids [9, 11-13]. Watanabe, et al. (2006) explored the hydrothermal decarboxylation of stearic acid in supercritical water with an alkali catalyst (KOH and NaOH) at 400 °C for 30 min, which yielded heptadecane as the main product. While this study demonstrated the feasibility of hydrothermal decarboxylation of fatty acid, it showed a low yield of hydrocarbon (<15%) at the high temperature studied. Savage, et al. (2010, 2011) investigated fatty acid hydrothermal decarboxylation over two heterogeneous catalysts, 5% Pd/C and 5% Pt/C [9, 12]. Both catalysts were effective for palmitic acid (PA) decarboxylation, leading to 63 and 76 % (molar yields) of pentadecane, respectively. However, despite the high-performance of Pd/C and Pt/C catalysts, their high cost is the most critical restriction to their viability as industrial scale catalysts [14].

Compared with noble metals such as Pd and Pt, Ni has attracted increasing interest as a catalyst for fatty acid deoxygenation due to its high hydrogenation activity and low cost [10, 15-18]. Snare, et al. (2006) compared different transition metals on equivalent supports for their deoxygenation activity [19]. Ni was ranked third, following Pd and Pt. Peng, et al. (2013)

conducted palmitic acid deoxygenation on Ni based catalyst, achieving 100% conversion of PA with a 90% (carbon molar) yield of pentadecane at 260 °C and 12 bar H₂ for 6h [10]. Their research indicates that decarbonylation is the main route for PA deoxygenation over Ni/ZrO₂.

Since nickel favors decarbonylation reaction, a key issue with Ni based catalysts for fatty acid deoxygenation is that they require additional H₂ [18]. This requires one mole of H₂ to decarbonylate one mole of fatty acid. Hence, without an external H₂ supply, nickel-based catalysts showed low activity toward fatty acid deoxygenation (~20% conversion rate) [10, 18, 19]. Santillan-Jimenez, et al. studied stearic acid deoxygenation over Ni/C catalyst using different concentrations of H₂ [18]. Only a 19% stearic acid conversion was achieved under 0% H₂, while 64% and 80% conversion were obtained under 10% H₂ and 100% H₂ at 300 °C, 135 psi for 1.5 h, respectively. Thus, it is very important to develop a process to improve the fatty acid conversion and hydrocarbon yield under no or low external H₂ pressure (<100 psi). Vardon et al. investigated the impact of hydrogen on catalytic deoxygenation of fatty acid in hydrothermal media, using external glycerol to generate H₂ via aqueous reforming reaction. Although this process successfully reduced the consumption of H₂, the cost of glycerol also needs to be considered [20]

In this paper we explore the potential of the hydrothermal process to generate in-situ H₂ from fatty acid itself and subsequently use it to promote decarbonylation. The in-situ H₂ could be formed through the water-gas shift and reforming reactions [21, 22]. In a hydrothermal environment, CO is expected to be released via decarbonylation, and react with H₂O to produce in-situ H₂ [23, 24]. Aqueous phase reforming of organic acids has also been reported over Ni and Ru-based catalysts, generating CO₂ and H₂ as the main products [23, 25, 26]. Under

hydrothermal conditions aqueous phase reforming and water-gas shift could produce the required external H_2 for fatty acid deoxygenation over the Ni catalyst.

This study attempts to fill an important information gap by using in-situ, self-generated H_2 to deoxygenate fatty acid. We investigated the performance of fatty acid hydrothermal catalytic deoxygenation, using palmitic acid (PA) as a model compound and Ni/ZrO₂ as a catalyst. We selected a saturated fatty acid as the model compounds because unsaturated fatty acid is first hydrogenated to saturated fatty acid, which will be subsequently deoxygenated to hydrocarbon [12]. Compared to the unsaturated fatty acid hydrogenation, deoxygenation of saturated fatty acid is the rate limiting step. Zirconia was selected as the support, due to its extremely stable physical structure [27] and its capability to accelerate fatty acid decarbonylation [10, 15]. We tested different Ni metal loadings to illustrate the role of Ni metal and ZrO₂ on PA deoxygenation. By investigating the effect of H_2 pressure and presence of water, we demonstrated the significance of H_2 and H_2O in PA hydrothermal deoxygenation, and described the reaction pathway.

2. Method

In this study, we explored the potential of hydrothermal catalytic deoxygenation of PA over Ni/ZrO₂ catalyst for the production of hydrocarbons without or with very low hydrogen pressure. The effects of Ni metal loading, reaction temperature, initial H_2 pressure, and the presence of H_2O on PA deoxygenation were studied to elucidate the possible reaction pathway.

2.1 Catalyst preparation and analysis

The catalytic material used in this work was nickel supported on zirconia, synthesized via incipient wetness impregnation. In the typical procedure, a calculated amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in water and then slowly dropped into the support ZrO_2 under continuous stirring. After drying at an ambient temperature for 4 h, the solution was dried at 110 °C for 12 h in an oven, and then calcined in dry synthetic air at 400 °C for 4 h. Finally, the catalyst was activated by reduction with 100 mL/min of pure H_2 at 500 °C for 6 h at a heating rate of 5 °C/min. The surface area of the unloaded support was 100 m²/g (data from supplier). Four different metal loadings were used in the experiments (0, 5, 10, and 20 wt. %), with the latter sufficient to produce a monolayer of Ni on the support surface. All chemicals for catalyst synthesis and testing were purchased from Sigma Aldrich. After preparing the catalyst and running the reaction, catalyst was characterized by XRD and EDX. The bulk structure of the spent sample (10% Ni/ ZrO_2) was analyzed by powder X-ray diffraction (XRD) on a Philips diffractometer using $\text{Co K}\alpha$ radiation with an iron filter. The composition of the spent catalyst sample (10% Ni/ ZrO_2) was examined using EDX on a FEI Sirion operated at 15 kV.

2.2 Activity tests

Test runs were conducted in mini-batch reactors assembled from 3/8-inch stainless steel parts. Reactor volume was approximately 10 ml. Reactor parts were washed with dichloromethane and dried in an oven to remove any residual materials from the manufacturing process. In a typical run, 500 mg of fatty acid, 4.5 mL of E-pure water, and 500 mg of catalyst were carefully loaded into the reactor. Subsequently, the reactor was sealed, purged with N_2 to flush the whole reactor, and then H_2 and/or N_2 was introduced into the reactor depending on the studied condition. The reactor was then placed inside a small furnace made with heat tape and insulation. After the

reaction, the reactor was quenched to room temperature by introducing it into a cooling water bath. Gas phase products were analyzed after 30 min of cooling to ensure that the temperature of the reactor was lower than 20 °C. Next, methylene chloride was added to the reactor to extract organic products, which were paper-filtered to remove the catalyst and then evaporated methylene chloride from the organic phase using rotary evaporator.

PA was selected as a model compound for investigating the catalytic performance of Ni/ZrO₂. Yields were calculated as the number of moles of C in each product divided by the total number of moles of C loaded with the fatty acid. The conversion was calculated as the number of moles of C in the reacted fatty acid divided by the number of moles of C loaded with the fatty acid. Selectivity was calculated as the number of moles of C in each product divided by the total number of moles of C in the reacted fatty acid. Experiments were repeated in triplicate.

$$\text{Conversion (C\%)} = \frac{\text{Mole of C in the reacted PA}}{\text{Mole of C in PA}}$$

$$\text{Yield of product (C\%)} = \frac{\text{Mole of C in the product}}{\text{Mole of C in PA}}$$

$$\text{Selectivity of product (C\%)} = \frac{\text{Mole of C in the product}}{\text{Mole of C in the reacted PA}}$$

2.3 GC-MS, GC-FID analysis of organic and gaseous phase products

Liquid phase products were analyzed using an Agilent 7890A gas chromatograph with an Agilent 5975C mass detector (MS) and a HP-5 MS column (30 m × 0.25 mm ID × 0.25 μm thick film). Eicosane was used as internal standard for the quantification of organic products. Helium was employed as a carrier gas at a flow rate of 1 mL/min. The analysis was performed with a split ratio of 20:1 and an injection temperature of 325 °C [9]. The oven temperature begun at

60 °C, ramped at 2 °C/min to 80 °C and then to 300 °C at 10 °C/min, and held at 300 °C for 15 min. Compounds were identified by comparing the mass spectral data with an NIST library. The vapor phase was analyzed with an Agilent CP490 Micro GC equipped with four columns (5Å molecular sieve, PPQ, Al₂O₃, and non-polar SiO₂) and TCD detectors with the method employed by Li et al. (2013) [28]. Standards of n-paraffin (C₈-C₂₂) were purchased from Sigma and calibration solutions were prepared and injected. The calibration curve obtained was used to quantify the content of the targeted compounds.

3. Results and discussion

3.1 Effect of nickel loading on the deoxygenation of PA

Figure 1 shows the effect of metal loading on PA conversion and paraffin yields. An increase in metal loading from 0 wt. % to 20 wt. % led to much higher PA conversion and paraffin yields. The increased metal loading increased the PA conversion from 6.6 to 100 C% and the paraffin yield from 0.07 to 66 C%. This suggests that metallic sites play a key role on the formation of alkanes. Pure ZrO₂ support converted approximately 6.6 C% of the PA; however, most of this went to palmitone via ketonization (see Table 1), leading to a paraffin yield less than 0.1 C%. A high selectivity to palmitone (51 C%) was exhibited with no Ni loading, but was quickly reduced to 0 C% with increased metal loading to 20 wt. % due to the decreased exposure of ZrO₂ sites.

A frequent issue observed with Ni catalysts is deactivation and subsequent loss of activity due to oxidation of nickel in the aqueous phase [29]. This is also caused by a cracking reaction that forms carbon deposits preventing access of the reactant molecules to active sites [14]. Catalyst samples with Ni loadings of 10 and 20 wt. % were analyzed with X-ray diffraction

(XRD) to determine the presence of nickel oxide (Figure S1). Results showed that no nickel oxide was formed during the tests. In addition, energy-dispersive X-ray spectroscopy (EDX) was used to measure carbon concentration (Figure S2). This yielded only minute amounts of carbon on the tested samples.

3.2 Effects of temperature on hydrothermal deoxygenation of PA

Figure 2 shows the PA conversion and paraffin yield obtained at different temperatures using 800 psi of H₂ and a Ni loading of 10 wt. %. Increasing temperature from 250°C to 290°C increased conversion of PA from 5.2 to 97.2 C%, also raised paraffin yield (C₈-C₁₆) from 2.8 to 60.5 C%. At or below 270°C, the reaction was very slow, resulting in low conversion rates (only 5.2 C% at 250°C and 22.1 C% at 270°C). At or above 290°C, the conversions achieved were greater than 95 C%, with approximately 60 C% of paraffin yields. Yield to gas products also increased as temperatures increased from 250 to 290°C. At 300°C, CH₄ and CO₂ were the main gas products, yielding 18.6 and 5.1 C%, respectively (see Table 2).

Deoxygenation of fatty acids can proceed through hydrodeoxygenation (HDO), decarbonylation, and decarboxylation pathways [14, 30]. Table 2 shows the yield of different products at different reaction temperatures. This table indicates that 30.2 C% pentadecane was produced, while only 2.8 C% hexadecane was formed. This demonstrates that Ni/ZrO₂ catalyst prefers decarbonylation/decarboxylation (forming pentadecane) to HDO (forming hexadecane) under this condition (Table 2). As reaction temperature increases, short-chain paraffins (C₈-C₁₄) gradually increased from 0% at 270°C to 26 C% at 300°C due to the C-C cleavage [10]. Comparing products obtained at 290°C and 300°C, the paraffin yield appeared to be similar, with values of 60.5 and 59.5 C%, respectively. However, the greater yield of short-chain paraffins

(C₈-C₁₄) was obtained at 300 °C (26.0 C%) compared to 21.4 C% at 290 °C. This difference could be due to cracking of hydrocarbons over Ni catalysts, which becomes more active at higher temperatures [16]. This effect can be advantageously exploited to produce hydrocarbons within the boiling point range of aviation grade fuels.

3.3 Effect of H₂ pressure on hydrothermal deoxygenation of PA

Figure 3a shows PA conversion and paraffin yield over 10% Ni/ZrO₂ under various H₂ pressure at 300°C. The results show that PA conversion gradually improved with increasing H₂ pressure, from 66.4 C% at 0 psi H₂ to 99.8 C% at 800 psi H₂. The yield of paraffins also increased from 38 C% to 60 C% as H₂ pressure increased from 0 to 100 psi. Above 100 psi H₂, the yield of paraffins did not change significantly.

These results clearly demonstrated that a minimal amount of initial hydrogen pressure was necessary to increase the conversion of PA and the yield of paraffin. At a H₂ pressure of 800 psi, PA conversion was around 100 C%; however, paraffin yield remained at 60 C%. This may be because, at higher hydrogen pressures, the formations of hexadecanol and palmityl palmitate were promoted (see Table 3). This, then improved PA conversion, but reduced selectivity to paraffin. Thus, a H₂ pressure of 100 psi was sufficient for achieving the highest paraffin yield.

Within the H₂ pressure range tested in this study, Ni/ZrO₂ appeared to favor decarboxylation/decarbonylation (deCOx) over the hydrodeoxygenation (HDO) reaction. This was due to the higher yield of pentadecane than hexadecane (Table 3), which follows the trend found in the study of different reaction temperatures. The HDO reaction under high initial hydrogen pressure (800 psi) displayed slightly higher activity than under low hydrogen pressure (100 and 250 psi). This was inferred from the increased yield of hexadecane. However, the

activity of HDO was still lower than the activity of the decarboxylation/decarbonylation reactions.

In terms of the tendency for decarbonylation or decarboxylation, previous studies showed that nickel favors decarbonylation over decarboxylation, since CH_3CO^* was adsorbed more than CH_3COO^* after adsorption of acetic acid under Ni [10]. However, our results were inconclusive regarding whether decarbonylation was favored by nickel, since the released carbon monoxide from decarbonylation was not detected perhaps due to the consumption of CO through fast water-gas shift or methanation reactions [26]. The main gaseous products in this study were methane and carbon dioxide. As shown in Figure 3b, selectivity of methane increased in the presence of hydrogen, whereas carbon dioxide generally decreased with increasing H_2 pressure. These results suggest that in the presence of H_2 , methane can form through the methanation reaction of CO_2 [3].

Table 3 shows that some short-chain fatty acids and paraffins formed in the hydrothermal catalytic deoxygenation of PA. The aqueous phase PA reforming may contribute to short-chain paraffin through the C-C scission of PA accompanied by the formation of in-situ H_2 , and CO_2 [26]. Another possible pathway for producing short-chain paraffin ($\text{C}_8\text{-C}_{14}$) is hydrogenolysis, promoted by Ni catalysts in H_2 atmospheres [31, 32]. A series of light-chain paraffins from tetradecane to octane were quantified indicating that light paraffins formed progressively through hydrogenolysis, starting with pentadecane [33]. Methane forms as the major gaseous product of the C-C bond scission as a result of the hydrogenolysis of n-paraffins.

As shown in Table 3 palmityl palmitate formed at different initial H_2 pressures, suggesting that side reactions took place. This occurred via the hydrogenation of PA to 1-hexadecanol, followed by the esterification reaction of PA with 1-hexadecanol, to produce palmityl palmitate

[34]. Our results show that at low H₂ pressures, palmityl palmitate is produced at a very low yield (<0.4 C%), which may be due to low levels of 1-hexadecanol formation (<0.2 C%). However, at high H₂ pressures, hydrogenation of PA to hexadecanol proceeds at higher levels, increasing rates of palmityl palmitate formation.

3.4 Effect of water on catalytic deoxygenation of PA

Figure 4b shows that without H₂, PA conversion increases from 17.2 C% in the absence of H₂O to 64.2 C% in the presence of H₂O. Paraffin yield also increased from 1.8 to 35.5 C%. Figure 4a summarizes the performance obtained at 100 psi of H₂. PA conversion and paraffin yield in the absence of water were 60.7 and 35.5 C%, respectively. With water, PA conversion and paraffin yields were increased to 88.2 and 66.8 C%, respectively. Figure 4a-b demonstrated that the presence of water promoted both PA conversion and paraffin yields.

According to the reaction equations of PA decarboxylation (Eq. 1) and decarbonylation (Eq. 2), decarboxylation does not require the presence of H₂, while decarbonylation requires one mole of H₂ per mole of PA. Based on Figure 4b, the low yield of paraffin formed without H₂ and H₂O suggests that Ni/ZrO₂ favors the decarbonylation pathway over the decarboxylation route. This also explains our results in the absence of H₂O, where PA conversion and paraffin yield significantly increased from 17.2 to 66.8 C% and 1.8 to 35.5 C%, respectively, after the introduction of 100 psi H₂.

Without an initial H₂ input condition but in the presence of water, PA conversion and paraffin yield increased significantly, suggesting that H₂ is formed during this process. Under this

condition, 0.1 mole of H_2 was produced per mole of PA (data was obtained by GC gas phase analysis). The aqueous-phase reforming of PA may facilitate the in-situ formation of H_2 [25, 26]. Moreover, the decarbonylation reaction described by Eq.(2) indicates formation of CO, which then produce H_2 through the water-gas shift reaction. This suggests the possibility of a self-sustaining process, where CO is not only a reaction product, but also a key intermediate for the formation of H_2 required by the decarbonylation process [14, 16, 18]

In addition to paraffin, two major side products were detected in this study: palmitone and palmityl palmitate. In the absence of H_2 , selectivity to palmitone decreased from 70.2 % without H_2O to 0.3 C% with H_2O . Similarly, in the presence of H_2 , selectivity decreased from 11.6 C% without H_2O to 0.2 C% with H_2O . The formation of palmityl palmitate displays a similar behavior. In the absence of water, selectivity to palmityl palmitate was 11.0 and 18 C% at H_2 pressures of 0 and 100 psi, respectively. The presence of water also decreased the selectivity to 0.5 C% in the absence of H_2 and 0.9 C% at an H_2 pressure of 100 psi.

The formation of palmitone via ketonization is described below. This reaction is typically catalyzed by bifunctional acid-base oxides such as ZrO_2 , CeO_2 , and TiO_2 [35, 36]. The mechanism involves adsorption of PA at oxygen defect sites to form palmitate. Meanwhile, a ketene is also formed by α -H abstraction. In the absence of H_2 , palmitone is formed through the reaction between ketene and palmitate, while hexadecanal is formed under high concentrations of H_2 [10, 35]. As noted previously, in the absence of water, selectivity to palmitone appears to sharply decrease with increasing H_2 pressure. This is because H_2 suppresses the formation of palmitone from ketene. In addition, a significant reduction in the selectivity to palmitone was observed in the presence of water. Water operates as a blockade by impeding the formation of

the surface palmitate from PA and the palmitic anhydride, an intermediate of PA ketonization [37].

Formation of palmityl palmitate via hydrogenation (Eq.4) and esterification (Eq.5) are described below. Selectivity to palmityl palmitate was also found to be higher in the absence of water. However, unlike palmitone, formation of palmityl palmitate was slightly enhanced by the presence of H₂. This is associated with the formation of 1-hexadecanol through the hydrodeoxygenation of PA, which then reacts with PA to form palmityl palmitate. Palmityl palmitate was obtained at a very low yield in the presence of water (0.3 C% in the absence of H₂, 0.7 C% at 100psi H₂). This was due to the presence of water, which blocks esterification by advancing the reverse hydrolysis reaction of ester in high temperatures [38]. Therefore, in the hydrothermal environment, formation of palmityl palmitate is significantly suppressed.

3.5 Mechanism of PA under 10% Ni/ZrO₂ in the hydrothermal environment

Figure 5 shows the proposed overall reaction pathway for the hydrothermal catalytic deoxygenation of PA over Ni/ZrO₂. As reported in Table 2, pentadecane and other short paraffins (C₉-C₁₄) were the major products, with decarbonylation (Eq.2) as the main route for the formation of pentadecane. Compared to decarbonylation, decarboxylation and HDO occurred to a less degree.

We propose two possible pathways to the formation of short-chain paraffins (C₉-C₁₄). One is through aqueous-phase reforming of the carboxylic group in the PA, with the subsequent release

of H₂ and CO₂ [25, 26]. The other is via hydrogenolysis, in which the pentadecane resulting from PA decarbonylation reacts with H₂ to produce CH₄ and paraffins with one less carbon number in the structure [31, 33]. Shorter paraffins (C₈-C₁₄) may form following a similar mechanism.

In the vapor phase, we detected CO₂ and CH₄ as the main gas products. Despite the fact that decarbonylation is the predominant reaction pathway for the PA deoxygenation over nickel catalysts [10, 16, 18], we did not detect CO with the GC analysis due to the expected occurrence of water-gas shift reaction and/or methanation [3, 26]. CO₂ was mainly produced through water-gas shift reaction, and partially consumed by methanation. CH₄ was mainly produced through hydrogenation of CO and CO₂, and hydrogenolysis of paraffins.

Compared with the major route for producing paraffins, there are several minor routes for producing paraffins and other side products. Decarboxylation (Eq.1) and HDO (Eq.6) are the minor routes to produce pentadecane and hexadecane, accompanied with hexadecanol as the intermediate product of HDO. Palmityl palmitate and palmitone were produced through esterification and ketonization reactions.

During fatty acid deoxygenation, typically decarboxylation, decarbonylation, and HDO occur simultaneously. However, depending on conditions and catalysts, different pathways may dominate. Decarboxylation dominates under inert conditions, especially when Pd/C and Pt/C are employed as catalysts [39]. HDO of fatty acid occurs in high-pressure, hydrogen-rich conditions, typically over metal supported on zeolite (Ni/HZSM-5 and Ni/HBeta) [34] or sulfide metal supported on alumina [40]. Decarbonylation dominates in the presence of H₂ over metal based

catalysts, such as Ni/C [18] and Ni/ZrO₂ [10]. Our study found that, compared to existing pathways for fatty-acid deoxygenation, this catalytic hydrothermal process enhances fatty acid decarbonylation under no or low-pressure H₂. Reduced H₂ pressure and consumption may also reduce process operating costs. By employing in-situ, self-sustaining H₂ during fatty acid deoxygenation, this process shows promise for economically and effectively producing jet fuel and diesel fuel range hydrocarbons from fatty acids.

4. Conclusions

This study demonstrates that hydrothermal catalytic deoxygenation was an effective approach for removing oxygen from PA over Ni/ZrO₂. At 300 °C hydrothermal conditions with 100 psi H₂ pressure, 88.2 C% PA was converted and yielded 60.7% paraffins over a 10 wt. % NiZrO₂ catalyst. The presence of water promoted PA conversion and paraffin yields. In the absence of H₂, PA conversion reached 64.2 C% and paraffin yield reached 38.6 C% with water, which was much higher than results achieved in the absence of water. Decarbonylation was found to be the major route for producing paraffins in hydrothermal catalytic deoxygenation over a Ni/ZrO₂ catalyst. The presence of water enhanced formation of in-situ H₂ that promoted PA decarbonylation and increased paraffin yields. In addition, water significantly suppressed the side reactions of ketonization and esterification, which occurred as a major route in the absence of water. Finally, a significant amount of short-chain paraffin (C₈-C₁₄) and CH₄ were formed, mainly through hydrogenolysis.

Acknowledgements

This work was supported in part by the Department of Energy (DOE) and the Washington State University Agricultural Research Center. The authors would like to thank Jonathan Lomber and Moumita Chakraborty for their assistance in developing GC-MS method to analyze fatty acids, hydrocarbons, and other organic and gaseous products.

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Figure 1. Effect of nickel loading (wt. %) on PA hydrothermal deoxygenation conversion (C%) and paraffin yield (C%).

Experimental conditions: PA (0.5 g), water (4.5 ml), catalyst (0.5 g), 300 °C, 6h, 100 psi H₂, total pressure 800 psi.

Figure 2. Effect of reaction temperature on the hydrothermal deoxygenation of PA.

Experimental conditions: PA (0.5 g), water (4.5 ml), 10% Ni/ZrO₂ (0.5 g), 800 psi H₂, 6h.

Figure 3. Effect of hydrogen pressure on the (a) conversion of PA (C%) and yield of paraffin (C%); (b) selectivity to gas products (C%).

Experimental conditions: PA (0.5 g), water (4.5 ml), 10% Ni/ZrO₂ (0.5 g), 300 °C, 6h, total pressure 800 psi.

Figure 4. Effect of water on the conversion of PA (C%), yield of paraffins (C%), selectivity to palmitone (C%), and selectivity to palmityl palmitate (C%), at 0 and 100 psi H_2 pressure.

Experimental conditions: PA (0.5 g), H_2O (if present, 4.5 ml), 10%Ni/ ZrO_2 (0.5 g), 300 °C, 6h, total pressure 800 psi with N_2 .

Figure 5. Reaction pathway in liquid phase (a) and gas phase (b)

Table 1. Conversion, paraffin yield, and selectivity to palmitone (on C molar basis) for different Ni loadings

Catalyst	Conversion (C%)	Paraffin yield (C%)	Selectivity to palmitone (C%)
ZrO ₂	6.6	0.07	51
5%Ni/ZrO ₂	78	44	7.4
10% Ni/ZrO ₂	88	61	0.17
20% Ni/ZrO ₂	100	66	0

Experimental conditions: PA (0.5 g), water (4.5 ml), catalyst (0.5 g), 300 °C, 6h, 100 psi H₂,
total pressure 800 psi.

Table 2. Yield of different products at different reaction temperatures

T (°C)	Liquid Products (%)			Gas Products (%)		
	C ₁₅	C ₁₆	C ₈ -C ₁₄	CH ₄	CO ₂	C ₂ H ₄
250	2.8	0.0	0.0	0.1	0.0	0.0
270	18.9	0.8	0.0	0.2	0.0	0.0
290	34.6	4.0	21.4	27.6	0.5	0.1
300	30.2	2.8	26.0	18.6	5.1	0.3

Experimental conditions: PA (0.5 g), water (4.5 ml), 10% Ni/ZrO₂ (0.5 g), 800 psi H₂, 6h.

Table 3. Yield of organic products at different initial hydrogen pressures

H ₂ pressure (psi)	Yield C%				
	C ₈ -C ₁₄	C ₁₅	C ₁₆	1-Hexadecanol	Palmityl palmitate
0	22.15	16.12	0.35	0.15	0.31
100	35.01	24.89	0.76	0.00	0.07
250	36.20	23.79	0.77	0.16	0.03
800	26.02	30.19	2.76	0.48	1.67

Experimental conditions: PA (0.5 g), water (4.5 ml), 10% Ni/ZrO₂ (0.5 g), 300 °C, 6h, total
pressure 800 psi.