



# Aromatics from saturated and unsaturated fatty acids via zeolite catalysis in supercritical water



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## ABSTRACT

We investigated the reactions of saturated (palmitic and stearic acids) and unsaturated fatty acids (oleic and linoleic acids) in supercritical water at 400 °C, 240 bar, over zeolites Y, beta, and ZSM-5. The highest total yield of liquid and gaseous products, 97 ± 2 wt%, was obtained from palmitic acid by applying ZSM-5 with a silica/alumina ratio of 23. The liquid products had a high concentration of single-ring aromatics, and the total molar yield of aromatics was 102% (42 wt% yield). This catalyst could be regenerated and reused. ZSM-5 with silica/alumina ratio of 23 gave a total product yield of 76 ± 3 wt% (which includes 40 ± 5 molar yield of xylenes) at its third use, after undergoing regeneration twice previously. We also report herein the effects of different zeolites, catalyst loadings, degrees of unsaturation in the fatty acids, and silica/alumina ratios of zeolite ZSM-5 on the product yields.

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## 1. Introduction

Interest in conversion of biomass to chemicals has increased sharply. The number of journal articles on this topic doubled from 2008 to 2010 [1]. Chemical manufacturers are interested in producing bulk and specialty chemicals from renewable feedstocks because of the increasing global demand for certain chemicals and the sustainability advantage offered by renewables. In the U.S., the net import of benzene/toluene/xylene (BTX) has increased by 300 million liters from 2003 to 2013 [2], indicating that demand is exceeding supply domestically. At the same time, benzene spot prices rose to record highs in 2013 [3]. The shale gas revolution in North America has led to an ongoing shift to lighter feedstocks, which is having a negative impact on heavier refinery co-products such as propylene, butadiene, and aromatics. Yields of those co-products dropped by as much as an estimated 55% [4]. All of these factors point to the need to discover new methods to produce chemicals, and especially aromatics, from renewable resources.

Renewable plant oils, such as those from palm, jatropha, and microalgae, contain significant amounts of triglycerides and fatty acids. Previous research on valorization of vegetable oils and lipid-rich algal biomass has already demonstrated processes that

generate aqueous streams rich in fatty acids [5–8]. Thus, fatty acids in aqueous streams represent a renewable feedstock available for the production of chemicals. The presence of water in these streams suggests its use as the reaction medium for converting the fatty acids to chemicals. The approach we explore herein is zeolite-catalyzed hydrothermal cracking.

Zeolite catalysts are widely used in both petroleum and bio-oil refining [9–11]. They are active for catalytic cracking and aromatization, and previous work has shown that zeolites can convert fatty acids to aromatic compounds, along with paraffins and olefins, in a non-aqueous environment [12–14] and in supercritical water [15].

Our previous work [15] showed that zeolite ZSM-5 can produce BTX and fuel gas (such as methane and propane) from a saturated fatty acid in supercritical water. That discovery motivated the present expansion of scope to determine how broadly this hydrothermal approach of making renewable BTX and fuel gas from fatty acids can be applied. Herein, we elucidate the effects of different types of zeolites, different catalyst loadings, different degrees of unsaturation in the fatty acids, and different silica/alumina molar ratios in the zeolite. We also demonstrate that the catalyst that generates the highest product yield can be regenerated and reused.

## 2. Materials and methods

Palmitic acid (PA, C16:0), stearic acid (SA, C18:0), oleic acid (OA, C18:1), and linoleic acid (LA, C18:2) were acquired from ACROS Organics in high purity (≥98%). The Cx:y notation gives the

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number of carbon atoms ( $x$ ) and the number of double bonds ( $y$ ) in the carbon chain in the fatty acid. The zeolites ZSM-5 (with silica/alumina = 23, 30, 50, and 80), beta (silica/alumina = 38, 300), and Y (silica/alumina = 60) were obtained from Zeolyst International. All of the ZSM-5 materials and the zeolite beta with silica/alumina = 38 came in ammonium nominal cation form. The other materials were obtained in hydrogen form. We converted all of the catalysts that were in ammonium form to the hydrogen form by calcining them in air at 550 °C for 240 min.

Batch reactions were conducted in 4 mL stainless steel Swagelok reactors fitted with High Pressure Equipment Company valves that were connected by a length of 1/8 in. o.d. stainless steel tubing. A total of 150 mg of fatty acid, the desired amount of catalyst (typically 150 mg), and 0.6 mL water, were loaded into each reactor. The 0.6 mL water loading leads to a 0.15 g/mL water density at the supercritical ( $T_c = 374$  °C) reaction conditions (240 bar at 400 °C). Helium was added to each reactor at a pressure of 4 bar to serve as internal standard for gas products analysis. The sealed reactors were then placed into an isothermal fluidized sand bath at 400 °C for 180 min. This reaction temperature and time were chosen because this condition gives high product yields relative to those from reactions at lower temperatures and shorter times [15]. Upon removal from the sand bath, the reactors were submerged in a water bath at ambient temperature to quench the reaction. Gaseous products were analyzed, and then acetone was added to the reactor to dissolve and recover the products remaining therein. We refer to these acetone-soluble products as the liquid products from the reaction.

We identified and quantified liquid products using Agilent 6890 gas chromatographs with a mass spectrometric (GC/MS) and a flame ionization (GC/FID) detector. The gas-phase products were analyzed with a gas chromatograph with a thermal conductivity detector (GC/TCD), with argon as the carrier gas. We report product yields and reactant conversion for each reaction, and the standard deviation of replicate experiments was used as an estimate of the uncertainty. Mo and Savage [15] give more details about the experimental methods and product analysis.

Catalyst regeneration began with drying the catalyst recovered from several experiments overnight in a 70 °C oven, following by a controlled combustion (heating in air at 2 °C/min to 550 °C, and maintaining that temperature for 240 min) to burn off any coke and calcine the catalyst.

### 3. Results and discussion

This section first presents results from control experiments that were performed to validate the experimental methods and determine the extent of chemical transformation from thermal energy alone. We then discuss the effects of different types of zeolites, catalyst loadings, and the number of double bonds in the reactant. The penultimate portion reports the results from the hydrothermal reactions catalyzed by ZSM-5 with different silica/alumina ratios, and the final topic is catalyst reuse and regeneration.

#### 3.1. Control experiments

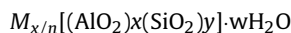
A previous control experiment involved loading palmitic acid, water, and ZSM-5 into reactors but not heating them [15]. The experiment showed a recovery of palmitic acid of  $97 \pm 3$  wt%. We expect SA, OA, and LA to give similar results as the amount of acetone (solvent) needed to dissolve the 150 mg of SA, OA, and LA loaded into the reactors is about two orders of magnitude lower than the 20 mL used experimentally. These calculations are based on the reported solubilities of SA, OA, and LA in acetone [16,17].

Control experiments with no water were also discussed in our previous work [15].

A new set of control experiments involved loading each fatty acid (PA, SA, OA, LA) into reactors with water but no catalyst, and placing them in the sandbath at 400 °C for 180 min. These experiments tested for the influence of thermal, hydrothermal, wall-catalyzed, and corrosion-product-catalyzed reactions. Gas yields were less than 4 wt%. The total yield of liquid products (acetone solubles) from PA, SA, OA, and LA were  $12 \pm 5$ ,  $7 \pm 2$ ,  $19 \pm 12$ , and  $41 \pm 5$  wt% respectively. Xylenes, toluene, and 2-methyl-pentane were the major products. The conversions were  $34 \pm 5\%$ ,  $54 \pm 8\%$ ,  $22 \pm 11\%$ , and  $80 \pm 18\%$ , respectively. Thus, non-zeolitic cracking could be responsible for up to 12 wt% liquid product yield from the saturated fatty acids (PA and SA) at 400 °C, 240 bar, and 180 min. However, non-zeolitic cracking could be responsible for about 19 wt% and 41 wt% liquid products for the two unsaturated fatty acids. The higher conversion and product yields from the unsaturated fatty acids are reasonable since the presence of unsaturation would be expected to increase the thermal reactivity. It was also observed by Shin et al. [18], that unsaturated fatty acids have lower thermal stability in water near critical point.

#### 3.2. Effect of different zeolites

Zeolites are attractive catalysts because they have a well-defined pore structure, high activity per acid site, and can be produced at a reasonable price [19]. Zeolites are crystalline, hydrated aluminosilicates. The conventional textbook chemical formula for zeolites is:



where  $M$  is a positive counter ion of valence  $+n$  that balances the charge due to the  $x(\text{AlO}_2^-)$  groups. The ratio  $y/x$  represents the atomic Si/Al ratio. We will make frequent reference to the silica/alumina ratio, which is  $y/(x/2)$ . This quantity is an important characteristic of zeolites that we will discuss further in Section 3.5.

Zeolites ZSM-5, Beta, and Y are traditional cracking zeolites [20]. Therefore, we selected these three materials for the present study. ZSM-5 has a tube type micropore system with free diameters in the tubes of about 5 Å and a surface area of about 400 m<sup>2</sup>/g. Zeolite beta has pore diameters of 5–7 Å and a surface area of 600–700 m<sup>2</sup>/g. Zeolite Y has a three-dimensional pore network consisting of large spherical cavities with free diameters of about 12 Å and a surface area of  $\sim 700$  m<sup>2</sup>/g [21]. Thus, zeolites Y and beta generally have large pores and higher surface areas than zeolite ZSM-5. Zeolites Y and beta, however, were less stable than zeolite ZSM-5 in hot liquid water at 150 and 200 °C [19]. We desired to examine these different types of zeolites to determine their effectiveness for hydrothermal catalytic conversion of fatty acids to aromatics.

We performed reactions of palmitic acid with zeolites beta (silica/alumina = 38, 300), ZSM-5 (silica/alumina = 30), and Y (silica/alumina = 60) in supercritical water at 400 °C, 240 bar, for 180 min. Table 1 gives the results (runs 1–4). As will be discussed later, the mass balances being less than 100% can be attributed to the formation of products not detectable by our analytical methods.

From runs 1 to 4 in Table 1, ZSM-5 gave the highest conversion of  $95 \pm 4\%$ . The conversion with zeolite Y was about 50%, and zeolite beta gave the lowest PA conversion ( $\sim 30\%$ ). Zeolites beta and Y gave 2-methyl-pentane as the most abundant liquid product, while ZSM-5 gave toluene and xylenes as the major products. The molar yield of toluene was  $22 \pm 3\%$  and that of xylenes was  $49 \pm 8\%$  with ZSM-5. The highest yields of aromatics being obtained from ZSM-5 is consistent with previous work with these three materials in the gas phase cracking of n-octane at 500 °C [20].

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