



Pyrolysis of polyunsaturated fatty acids

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ABSTRACT

The primary goal of this work was to study the thermal conversion of polyunsaturated fatty acids to hydrocarbon for use as renewable chemicals and fuels. Linoleic acid (*cis,cis*-9,12-octadecadienoic acid) was selected as a model polyunsaturated fatty acid. Batch pyrolysis reactions were conducted at temperatures from 350 to 450 °C for 0.5 to 8 h reaction times. Gas chromatography and mass spectrometry were used to analyze and identify products in the gas and liquid product fractions. Analysis of the gas phase showed concurrent production of CO and CO₂, indicating that deoxygenation reaction proceeded through both decarbonylation and decarboxylation mechanisms. The gas product encompassed alkanes and alkenes with carbon numbers ranging C1–C5 with ethane and propane as the major products. Analysis of the liquid fraction revealed series of *n*-alkanes, alkenes, cyclic alkanes and alkenes, and fatty acids. The presence of the unsaturation resulted in cracking at the allylic C–C and predominance of C6 to C10 hydrocarbons and C9 and C10 fatty acids. This work uncovers the dominant reaction pathways in the pyrolysis of free polyunsaturated fatty acids and demonstrates the viability of this pyrolysis to produce renewable hydrocarbons immediately compatible with the existing petrochemical infrastructure.

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1. Introduction

The development of renewable fuels and chemical has been the focus of many research programs. The motivations driving these efforts are the rising cost of petroleum and its dwindling reserves [1–3] as well as energy policy agenda of both advanced and emerging economies in response to both geopolitical and environmental concerns [4,5]. To this end several techniques have been developed to convert renewable feedstock (biomass) into renewable fuels and platform chemicals. Conversion technologies such as fermentation, transesterification, gasification and pyrolysis are the most used and studied [6–8]. Pyrolysis is a thermal conversion technology in near absence of oxygen (air) [8]. Pyrolysis is especially attractive because it employs well-established methodologies and produces a range of compounds that may be integrated into existing petroleum infrastructure [4,9,10].

Fats and oils are composed primarily of triglycerides which are tri-esters of fatty acids and glycerol [11]. Product composition and distribution of fat and oil pyrolysis depends on the source of the fat or oil [2,4,12–14]. The most common fatty acids in naturally occurring fats and oils are saturated, palmitic (hexadecanoic acid) and stearic (octadecanoic acid), monounsaturated oleic (9-octadecenoic acid) and diunsaturated linoleic (9,12-octadecadienoic acid) [11,14].

While the pyrolysis of whole triglycerides has been extensively studied and information abounds in the literature, little work has been done on the thermal pyrolysis of free fatty acids recovered from

hydrolysis of fats and oils. Our research group studied the pyrolysis of stearic acid and provided detailed fundamental information on the thermal decarboxylation and subsequent pyrolysis of the *n*-alkane resulting from the decarboxylation of stearic acid [15]. Information on the thermal pyrolysis of polyunsaturated free fatty acids, key components of lipids and fats is also very limited. While the presence of unsaturated carbon–carbon bonds is known to play an important role in the formation of cyclic and aromatic compounds through the Diels–Alder reaction in olefins [13,16–18], little is known about these reactions in the presence of unsaturated fatty acids. Similarly, the role played by the unsaturation on the alkane and alkene distribution in the pyrolysates is virtually unknown in the literature.

This work seeks to address these existing knowledge gaps by investigating the dominant chemical pathways occurring during pyrolysis of linoleic acid and to characterize the chemical profile of the resulting pyrolysates.

2. Materials and methods

2.1. Materials

Linoleic acid (≥99%), nonadecanoic acid methyl ester (≥98%), pentane (≥99%), diethyl ether (≥99%), CO (≥99%), gaseous alkanes and alkene standards (C1–C4) were purchased from Sigma-Aldrich (St. Louis, MO). Diazomethane for derivatization of fatty acids was prepared using a Diazald kit (Sigma-Aldrich, St. Louis, MO) following the manufacturer's procedures. N₂, H₂, CO₂ and CH₄ standards were

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purchased from Praxair (Praxair Inc., Danbury, CT). All chemicals were used as received.

2.2. Pyrolysis reactions

Pyrolysis reactions were conducted in 15 mL batch microreactors constructed with stainless steel Swagelok fittings and tubing (0.75 in.) and heated in a fluidized bed sand bath (Techne, Burlington, NJ) as previously described for the pyrolysis of stearic acid [15]. Similar microreactors have also been used in previous studies [15–18].

Approximately 1 g of linoleic acid was weighed into a clean and dry microreactor which was then closed, checked for leaks, purged with nitrogen (PP 4.8, Praxair), and sealed. The microreactor was heated at the desired temperature under constant agitation for the desired length of time and then quenched in a bucket of water at room temperature. The microreactor was then cleaned and dried using compressed air to ensure it was clean of sand.

2.3. Analytical methods

2.3.1. Liquid product analysis

After venting, the microreactors were opened to extract the pyrolysis product. 10 mL of pentane with approximately 1 mg/mL of nonadecanoic acid methyl ester as internal standard was added to the content of the microreactor, a spatula was used to carefully mix, allowed to stand for 15 min and the content was poured into sample vials and capped with Teflon® lined screw cap. The extracted samples were then stored at 4 °C prior to analysis. Any solid material left in the reactor after pentane extraction was considered as pentane insoluble residue. To determine the weight of pentane insoluble residue, the microreactor was allowed to stand in a fume hood until all the solvent has evaporated, and then weighed before and after thoroughly cleaning the inside of the microreactor.

The pentane extracts were derivatized with diazomethane to convert any fatty acid present into their methyl ester equivalent allowing greater GC resolution and analyzed on an Agilent 6890N GC–FID with Agilent 7683 series autosampler and injector with an Agilent HP-5 ms column (30 m × 0.32 mm, film thickness 0.25 µm) (Agilent Technologies, Santa Clara, CA). The injector and detector temperature were kept constant at 300 °C and 350 °C respectively and the GC oven temperature program was initially set at 35 °C for 0.1 min and then increased at 10 °C/min to 280 °C and held for another 5.4 min for a total run time of 30 min. The carrier gas was helium at a constant flow of 1 mL/min and injection volume was 1 µL.

Mass spectrometry (MS) analysis was conducted on an Agilent GC 6890N coupled to an Agilent 5975B EI/CI MS instrument operated in electron ionization (EI) mode. The column and conditions used in the GC–MS were similar to those used in the GC–FID as described above. The temperature of the GC–MS interface was kept constant at 320 °C.

2.3.2. Gas product analysis

The weight of the gas produced after each reaction was determined by difference in weight before and after venting of the microreactor. To sample gas product for gas chromatograph (GC) analysis, a 0.25 in. stainless steel Swagelok tube fitting with a septum was screws onto the microreactor. Using either a 50 µL or a 250 µL Hamilton gas tight microsyringe and syringe guide (Hamilton Co., Reno, NV), gas product was directly sampled from the microreactor by inserting the syringe's needle through the septum and opening the reactor valve. The gas product sample was then directly injected manually onto the GC.

CO₂ analysis was carried out on a Hewlett Packard (HP) Series II 5890 GC coupled to a thermal conductivity detector (TCD) with an Agilent HP-PLOT Q column (30 m × 0.56 mm, film thickness of 40 µm). The injector and detector temperature was kept constant at 170 °C and GC oven temperature program was 60 °C for 2 min and then increased at 10 °C/min to 200 °C and held for an additional 4 min to achieve a

total run time of 20 min. Helium was used as carrier gas with a constant pressure of 12 psi (82.7 kPa) and injection volume was 50 µL.

Analysis of N₂ and CO was carried out on a HP Series II 5890 GC–TCD with an Agilent HP-Molsieve column (30 m × 0.32 mm, film thickness of 12 µm). The injector and detector temperature was kept constant at 170 °C and GC oven temperature program was 40 °C for 3 min and then increased at 10 °C/min to 200 °C and held for an additional 1 min to achieve a total run time of 20 min. Helium was used as carrier gas with a constant pressure of 12 psi (82.7 kPa) and injection volume was 150 µL. Analysis of H₂ was done using the same equipment and parameters but the carrier gas was changed from helium to argon.

Alkanes and alkenes in the gas product were analyzed on a Varian 3400 GC coupled with a flame ionization detector (FID) (Varian Inc., Palo Alto, CA) and an Agilent CP-Al₂O₃/Na₂SO₄ column (50 m × 0.32 mm, film thickness 5 µL). The injector and detector temperature was kept constant at 170 °C and 230 °C respectively and GC oven temperature program was 70 °C for 0.1 min and then increased at 3 °C/min to 170 °C and held for an additional 26 min to achieve a total run time of 60 min. Helium was used as carrier gas with a constant pressure of 20 psi (137.9 kPa) and injection volume was 250 µL.

2.4. Product identification and quantification

Compounds in the gas product were identified by comparing their retention times with pure standards. All the hydrocarbons in the gas products were quantified using methane as external standard. Liquid products were identified based on retention times and by comparison of the mass spectra to the National Institute of Standards and Testing (NIST) 2011 mass spectral library and recognition of the fragmentation pattern of the mass spectra. Only quality matches 90 and greater were regarded as identified products. Quantification of the compounds in the pentane extract was done semi-quantitatively by comparing the peak areas of the compounds with the peak area of the known concentration of the nonadecanoic acid methyl ester internal standard.

3. Results and discussion

3.1. Identification of products in the liquid fraction

Pyrolysis of linoleic acid resulted in products structured as a periodic set of peaks on GC. Six distinct peaks were identified: an *n*-alkane peak, 1-alkene peak, two cyclic alkanes and alkenes peak (series 1 before and series 2 after the *n*-alkane peak) and internal alkene peaks (Fig. 1). It is important to note that while Fig. 1 shows a general trend observed for most of the conditions tested, some deviations were observed especially as the carbon number increased. For example, the cyclic alkanes and alkenes were not observed after C13 at high reaction temperature conditions for a longer period of time. A similar observation was made in the pyrolysis of stearic acid [15]. However, the cyclic alkanes and alkenes series were not observed in the pyrolysis product of stearic acid.

The products formed in linoleic acid pyrolysis were clearly dependent on the reaction conditions, with higher reaction temperatures and longer reaction times resulting in the formation of a greater proportion of lower molecular weight compounds. Fig. 2 shows the chromatograms of linoleic acid pyrolysis at 390 °C and 450 °C for various reaction times. Due to the method used in the extraction of the liquid product, only compounds which elute after pentane in the GC analysis were identified and quantified, enabling a direct comparison with results from pyrolysis of stearic acid. The major products in the liquid fraction at low temperature and reaction time were hexane (C6) to decane (C10) alkanes, heptanoic acid (C7:0), octanoic acid (C8:0) and nonanoic acid (C9:0), 8-heptadecene and *n*-heptadecane as well as 8-octadecenoic acid and octadecanoic acid. Minor products included 1-alkenes (C6 to C10), cycloalkanes and alkenes (C6 to C13), and aromatic compounds (C6 to C10). As temperature and time increased, a reduction in fatty acids, 1-alkenes and internal alkenes was observed concurrently with

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