



Thermal cracking of free fatty acids in inert and light hydrocarbon gas atmospheres



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HIGHLIGHTS

- Oleic acid was pyrolyzed under hydrocarbon gases to produce liquid hydrocarbons.
- Saturated hydrocarbon gases did not influence liquid product yield and composition.
- Unsaturated hydrocarbon gases significantly increased conversion and liquid yield.
- Branched compounds significantly increased under unsaturated hydrocarbon gases.
- Deoxygenation was promoted when unsaturated hydrocarbon gases were used.

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ABSTRACT

The aim of this work was to study the pyrolytic conversion of free fatty acids to renewable hydrocarbons in the presence of short-chain alkane and alkene hydrocarbon gases. Oleic acid (cis-9-octadecanoic acid) was used as model for fatty acids produced from hydrolysis of lipids from animal and plant feedstock. Batch pyrolysis reactions were conducted at 410 °C for 2 h at an initial pressure between 130 psi (896.3 kPa) and 500 psi (3447.4 kPa) under constant agitation. Identification and quantification of the pyrolysates in the gas and liquid phase were carried out using gas chromatography and mass spectrometry. Under inert N₂ atmosphere liquid product yields were between 74 and 81 wt% of feed with lower pressure giving the highest product yields. Liquid product was composed mainly of alkanes and alkenes ranging in carbon number from 6 to 19 and fatty acids from carbon numbers 4 to 18. Pyrolysis reactions conducted in the presence of short-chain alkane gases did not appreciably influence the liquid product yield and the composition compared to the inert atmosphere. On the other hand, pyrolysis reaction in presence of short-chain alkene gases resulted in a marked increase in the liquid product yield, the production of branched alkanes and alkenes and increased fatty acid decarboxylation. This work demonstrates a novel approach to concurrently increase the liquid product yield in pyrolysis of free fatty acids and produce highly valuable branched hydrocarbons for fuel and solvent applications.

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1. Introduction

The development of renewable alternatives to petroleum derived fuels and chemicals has become imperative due to socio-economic, geopolitical and environmental concerns. This has led to the development of several technologies to convert lipids and lignocellulosic biomass into renewable chemicals and fuels. One of the most promising technologies being developed for converting biomass is pyrolysis [1–4]. Lipids in the form of triglycerides are a particularly important feedstock because of their high energy density

and widespread availability compared to other biomass sources [5].

Pyrolysis of whole triglycerides has been the focus of intense research and development as well as commercialization efforts. Typical feedstocks include canola oil, soybean oil, sunflower oil, jatropha oil, lard and tallow as well as vegetable oil soaps and waste cooking oils. Pyrolysis products at room temperature and atmospheric pressure may be liquid, gas and/or solids depending on the feedstock used and on process reaction conditions such as temperature, time, pressure, atmosphere, catalyst, etc. [6–9]. An analysis of the main products reported from the pyrolysis of these fats and oils revealed the presence of compounds such linear, branched and cyclic hydrocarbons, aromatics, carbonyls, alcohols,

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carboxylic acids, carbonic gases and hydrogen. The distribution of the classes of compounds is also dependent on the feedstock and reaction conditions employed [10–12]. The thermal and thermo-catalytic deoxygenation and pyrolysis of free fatty acids have also been reported in the literature with product composition and distribution being influenced by the aforementioned feedstock and reaction conditions employed [13–17].

Pyrolysis of biomass has generally been conducted under inert atmosphere with gases such as nitrogen, helium or argon although some studies involving the use of reactive atmosphere have been reported in the literature. Both thermal and thermo-catalytic biomass pyrolysis under steam atmosphere at various temperatures have been studied and compared to inert atmospheres [10,18–20]. In these cases, an increase in organic liquid product yields was measured compared to inert atmospheres. The thermo-catalytic deoxygenation and pyrolysis of fatty acids under hydrogen atmosphere has been reported to increase both reactions rate and product yields over inert atmosphere [15,21–23]. However, Kubatova et al. [12] and Luo et al. [24] found that at reaction temperatures above 400 °C the thermal cracking of canola oil, soybean oil and their methyl esters under hydrogen did not positively impact the liquid product yields.

Recycling of the product gas stream has been suggested as an economical way of operating large scale pyrolysis plants [9,25]. The gas product stream is typically composed of CO, CO₂, light hydrocarbons and H₂ depending on the feedstock composition and reactions conditions [26–28]. Literature on biomass pyrolysis under CO, CO₂ and hydrocarbon atmosphere to study the effect of recycling the gas product is scarce. Mante and co-workers [29] and Zhang et al. [26] studied the effect of lignocellulosic biomass pyrolysis under the non-condensable gases CO, CO₂, CH₄ and compared it with reactions done under inert atmospheres. Both studies reported an increase in liquid product yield. In the case of Mante's work, a decrease in char/coke yield was also observed. To the best of our knowledge, there are no studies reported in the literature on the pyrolysis of lipids, particularly fatty acids from under reactive non-condensable hydrocarbon gases. The purpose of this work is to address these knowledge gaps by studying the effect of short-chain non-condensable alkane and alkene gases on the pyrolysis of free fatty acids by uncovering the dominant chemical pathways. In particular this work seeks to study the effect of such gases on the product portfolio and the overall product yield.

2. Materials and methods

2.1. Materials

Oleic acid ($\geq 99\%$), internal standard for GC analysis of liquid product, nonadecanoic acid methyl ester ($\geq 99\%$), pentane ($\geq 99\%$), diethyl ether ($\geq 99\%$), CO standard ($\geq 99\%$), gaseous alkanes and alkene standards (C1–C4) were purchased from Sigma–Aldrich (St. Louis, MO). N₂ (99.998%), CO₂ standard (99.9%), methane (99%), ethane (99%), ethylene (99%), propane (99%) and propylene (99%) were obtained from Praxair (Mississauga, ON). Diazomethane for derivatization of fatty acids was prepared using a Diazald kit (Sigma–Aldrich, St. Louis, MO) following the manufacturer's procedures. 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 [13]. Approximately 1 g of oleic acid was weighed into a clean and dry microreactor which was then closed, checked for leaks, purged with the desired gas (N₂,

methane, ethane, ethylene, propane or propylene). The reactor was then pressurized to between 130 and 500 psi (896.3 and 3447.4 kPa) with the desired gas and the microreactor was sealed. The microreactor was heated at 410 °C under constant agitation for 2 h and then immediately quenched in a bucket of water at room temperature. The reaction temperature and time used were selected based on work conducted by our group on the thermal cracking of oleic acids [28]. The reaction conditions selected for this study maximizes fatty acid feed conversion and liquid product yield while minimizing gas, aromatic compounds and solids formation. The outside surface of the microreactor was then cleaned and dried using compressed air to ensure the microreactor was clean of sand from the sand bath.

2.3. Analytical methods – Gas product analysis

The weight of the gas fraction produced was determined by weighing the microreactors before and after venting the gas product in the microreactor. A 0.25 in. stainless steel Swagelok tube fitting with a septum was screwed onto the microreactor in order to sample gas product for gas chromatograph (GC) analysis according to the method described by Maher et al. [13]. Gas samples were then analyzed on a GC–FID and GC–TCD using instruments, supplies and methods described elsewhere [28].

2.4. Analytical methods – Liquid product analysis

After venting, the microreactors were opened and the weight of liquid product was determined. The liquid product was then analyzed on GC–FID and GC–MS using instruments, supplies and methods described elsewhere [28].

2.5. Elemental composition of liquid product

The elemental composition (C, H, N, S and by difference O) of the liquid was performed using a Carlo Erba EA1108 Elemental Analyzer at the Analytical and Instrumentation Laboratory at the Chemistry Department, University of Alberta.

2.6. Products identification and quantification

Compounds in the gas product were identified by comparing their retention times with the retention times of known standards and quantified using external standards of the pure compounds. Hydrocarbons in the gas phase 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 tentatively 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. Liquid product yield

Pyrolysis of oleic acid under nitrogen and light hydrocarbons resulted in the formation of liquid and gas products under all the conditions tested. Solid products were not observed in any experiments. A water/aqueous fraction was not observed in the liquid product obtained under all conditions. It is important to note that this does not imply water was not produced during the reaction. The reason why

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