



## Elucidation of the catalytic cracking pathway for unsaturated mono-, di-, and triacylglycerides on solid acid catalysts

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### ABSTRACT

Heterogeneous catalytic transformation of lipids to transportation fuels offers a unique opportunity to provide sustainable energy while utilizing the current petroleum refining infrastructure. The reaction chemistry for the heterogeneous catalytic cracking of unsaturated acylglycerides was studied. Mono-, di-, and triolein, which are acylglycerides with oleic acid as the fatty acid constituent, were reacted at 400 °C over H<sup>+</sup>ZSM-5, faujasite, and silica–alumina catalysts. Reactions were carried out using a pulse-type microreactor utilizing online GC analysis. This technique allowed real time evaluation of reaction products using mass spectrometry and quantitation using a thermal conductivity detector. Selected products of these reactions were further reacted in an effort to elucidate the reaction pathway for producing green fuels from unsaturated lipids. The results indicated the removal of the heteroatom from the oxygenated feedstock by formation of CO and CO<sub>2</sub>. The shape-selective zeolite catalysts (i.e. H<sup>+</sup>ZSM-5 and faujasite) promoted the formation of aromatic compounds as tertiary cracking products. Silica–alumina, an amorphous catalyst, promoted the formation of linear dienes. A reaction scheme has been proposed for the deoxygenation of lipid compounds. These results reveal the potential of using lipid feedstocks for transportation fuels.

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### 1. Introduction

Renewable fuels will be essential if we are to displace large quantities of petroleum fuels as the dominant means of transportation energy. This can be readily seen with the exponential growths of both the fuel–ethanol and biodiesel industries [1,2]. Renewable fuels have the potential to reduce CO<sub>2</sub> emissions in the biosphere, eliminate U.S. dependence on foreign oil, and provide sustainable transportation energy.

Biodiesel is a mixture of fatty acid methyl esters currently produced from vegetable oils and animal fats. It could also be produced from other lipid feedstocks, such as algae, oleaginous yeasts, and Chinese tallow. These other lipid feedstocks have the potential of displacing billions of gallons of petroleum without competing with food related applications. As these non-conventional lipid sources become available, challenges associated with the biodiesel production process will have to be overcome for biodiesel to remain cost competitive with other biofuels. For example, lipids used to produce biodiesel using conventional base-catalyzed transesterification require removal of trace metals, free fatty acids, and unsaponifiable materials. It is difficult to conform with the biodiesel

quality standard (ASTM D-6751) without these refining steps, which add to the cost of the oil. Most biodiesel facilities in the U.S. use refined, bleached, and deodorized soy bean oil, which is the most expensive oil available for biofuels production.

Another challenge that biodiesel producers are experiencing is the reduction in market price of glycerine over the last 5 years. Some producers are paying to dispose of the glycerine, selling the glycerine at less than \$0.10/lb, or storing it for future disposal. Finally, there are concerns regarding the compatibility of biodiesel and petroleum diesel. Biodiesel is an excellent solvent and could wash a pipeline of deposits that are not desirable in the final product. Refineries, therefore, will not allow biodiesel to be transported via pipeline because it would adversely impact fuel quality. For these reasons, biodiesel requires a separate distribution system apart from petroleum diesel, which adds to its overall cost.

One option to using less refined oils to produce biofuels is the catalytic cracking of lipids into green gasoline and green diesel. These are motor fuels composed of equivalent types of compounds as traditional petroleum fuels. This process may be capable of processing row-crop oils as raw materials, as well as lipids from animal sources and microbial sources, such as oleaginous yeasts, oil-rich algae, and municipal waste sludges. Moreover, undesired byproducts could be reduced, or eliminated, in the fuel produced from the catalytic cracking process. Another advantage to this approach

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would be employment of current petroleum refining practices for renewable fuel production and distribution.

Bakhshi and co-workers and Bhatia and co-workers have investigated the cracking of canola and palm oils, respectively [3–8]. The results from these works indicated that plant oils, which are mostly triglycerides, could be converted to gasoline range organics (GRO) and diesel range organics (DRO). While these findings are significant in the development of renewable fuels, little is known about the cracking chemistry of oxygenated compounds. Information from the catalytic cracking of lipids will be necessary as ideal catalysts and reaction conditions are sought for industrial production of “green fuels.” The catalytic conversion of canola oil to fuels indicated that 60–95 wt.% conversion was achieved at 340 °C and 400 °C, respectively. The products formed were an organic liquid product (OLP), C<sub>3</sub>–C<sub>4</sub> paraffinic gases, CO, CO<sub>2</sub>, and water. The OLP was mainly gasoline range organics that were 60–70 wt.% aromatics [9].

Corma et al. [10] reported on the reaction pathways for the conversion of glycerol to olefins and aromatics. They described a scenario in which the catalytic cracking of glycerol could undergo hydrogen producing reactions and hydrogen consuming reactions for deoxygenation of biomass derived feedstocks [10]. Deoxygenation pathways for free fatty acids have been studied through a combination of homogeneous and heterogeneous reaction techniques [11,12]. This combination has shown to be an ideal confluence demonstrating what specific reaction steps occur as oleic acid, reacted in a highly acidic environment, proceeds via protonation of the double bond and eventual cracking of the fatty acid to low molecular weight hydrocarbons.

The present work seeks to establish the reaction pathway for the heterogeneous catalytic cracking of acylglycerides. The acylglycerides studied were 1-monoolein, 1,3-diolein, and triolein. These lipids have a glycerol backbone with oleic acid as the fatty acid constituent. Acylglycerides are found in many plant, animal, and microbial sources and have a potential use in the renewable fuels market. Because of their abundance in potential feedstocks, these acylglycerides were chosen as model reactants for the identification of reaction pathways for catalytically cracked lipids. Oleic acid is a common unsaturated fatty acid constituent found in many plant and animal lipid sources.

The catalysts used in this study were H<sup>+</sup>ZSM-5 and faujasite, which are highly crystalline, highly acidic, and well-characterized zeolites [13–16] and silica–alumina, which is an amorphous catalyst. Physical characteristics of the catalysts used can be found in Table 1. Due to the shape-selectivity characteristics of the zeolite catalysts, expected hydrocarbon reaction products would be aliphatic and aromatic hydrocarbons. Although H<sup>+</sup>ZSM-5 is not

**Table 1**  
Physical characteristics for cracking catalysts.

Catalyst	Crystallinity	Pore size	Surface area
ZSM-5	Crystalline	5.4	425
Faujasite	Crystalline	7.4	780
Silica–alumina	Amorphous	65–130	300–600

a commercially used catalyst due to its instability at high temperatures, its intrinsically high acidity works well for reaction mechanistic studies [17].

The objective of this work was to develop the specific reaction steps as glycerides were cracked into green fuel related compounds in the absence of hydrogen. To our knowledge, the use of model acylglyceride compounds has not been studied to determine specific reaction steps during catalytic cracking of these compounds.

## 2. Experimental

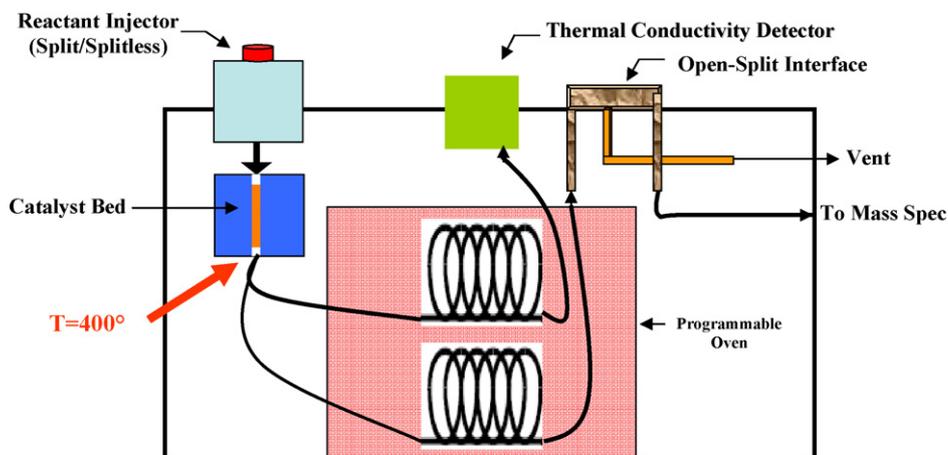
### 2.1. Chemicals

All lipid reactants (1-monoolein, 1,3-diolein, and triolein) were obtained from Larodan, Inc. (Malmo, Sweden). These were received at their highest available purity and were used without further purification. Helium carrier gas was of ultra-high purity grade.

The H<sup>+</sup>ZSM-5, faujasite, and silica–alumina were obtained from Zeolyst International (Valley Forge, PA, USA) in the sodium form. The catalyst was converted to the ammonium form by ion exchange and then calcined to develop the proton form (i.e. H<sup>+</sup>ZSM-5). The framework SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of the H<sup>+</sup>ZSM-5 was determined to be 35/1 using the Hoffman elimination technique for the titration with *n*-propylamine [18].

### 2.2. Reactions

For this study, the Quatra C (Fig. 1) was used for rapid, online analysis of reaction products. A complete description of the Quatra C can be found elsewhere [19]. This reaction/analysis device uses small amounts of catalyst, usually 5–25 mg, and approximately 1 mg reactant for each experimental run. A typical reaction sequence began with the loading of catalyst into a glass tube using silanized glass wool to hold catalyst in place. The catalyst tube was then loaded into the reaction zone of the Quatra C and the temperature was raised to the desired reaction temperature. Air and water were monitored using the mass spectrometer (MS), and reactions were not initialized until the air was within 5 a.m.u. and water less than 5% of H<sub>2</sub>O<sup>+</sup>/H<sub>2</sub>O. After sufficiently low levels of air and



**Fig. 1.** Diagram of the Quatra C illustrating the use of dual chromatographic columns along with TCD and MS detectors.

water were obtained, reactions were performed by injection of the reactant into the injection port.

Products were identified using GC/MS and quantitated using a GC thermal conductivity detector (TCD). Both electron impact (EI) ionization and chemical ionization (CI) techniques were employed for product characterization. Acetonitrile was used as the CI reagent gas. The chromatographic column used for the MS was an Rxi-1ms (30 m × 0.52 mm, 1.50 μm film thickness) and the column used for the TCD was an RT-QPlot (30 m × 0.53 mm). The thick film, megabore column to the MS was selected to enhance retention of low molecular weight hydrocarbons, as well as, lower molecular weight aromatics. The plot column to the TCD was selected for its ability to separate fixed gases, as well as gasoline range organics that were expected products from the H<sup>+</sup>ZSM-5 catalyst. The temperature profile for the GC oven started at -40 °C, held for 5 min, ramped at 5 °C/min to 60 °C, then ramped at 8 °C/min to 300 °C, and finally held for 12 min. The segmentation parameters on the MS were set to scan 10–80 *m/z* for the first 10 min and then scan 50–200 *m/z* for the remainder of the GC run. Scanning of lower mass ranges during the initial phase of the chromatographic run enabled maximum sensitivity for early eluting lower molecular weight compounds.

All reactions were performed in duplicate, and error bars have been provided. Calculation of error bars was from ±one standard deviation. Data were normalized to reflect the product yield per unit mass of reactant (mg/g).

### 3. Results and discussion

#### 3.1. Identification and quantitation of reaction products

Fig. 2 shows a typical total ion chromatogram from the mass spectrometer of reaction products for the cracking of acylglycerides. Once a peak had been tentatively identified using MS methods, matching of retention times using compound standards was used as further verification of a peak's identity. With respect to chromatography, some differences existed between the reaction products seen in this work and those found in our earlier work [12], in which oleic acid was the reactant. The largest difference occurred with the GC column to the MS at the front-end of the chromatograms where C<sub>1</sub>–C<sub>6</sub> hydrocarbon gases elute. It appeared from these results, that during acylglyceride reactions, production of CO and CO<sub>2</sub> from the cracking reactions disrupted proper elution of small molecular weight hydrocarbon compounds. While oleic acid cracking did also produce CO and CO<sub>2</sub>, it was significantly less compared to the acylglyceride cracking. This poor chromatography was a key reason for adding the RT-QPlot column with TCD analysis, which could offer better separations of low molecular weight compounds. Also, reaction conversions for this study are not available due to inherent

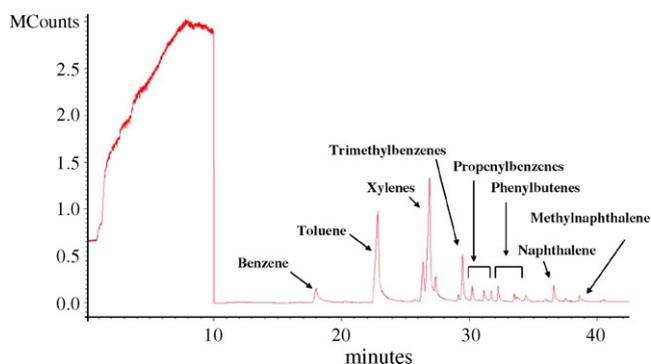


Fig. 2. Typical total ion chromatogram from GC/MS for acylglyceride cracking on H<sup>+</sup>ZSM-5.

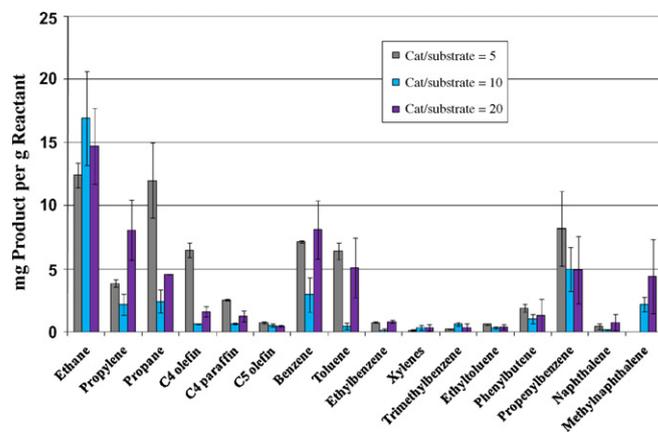


Fig. 3. Product yield of hydrocarbon products from Monoolein cracking on H<sup>+</sup>ZSM-5 (reaction T = 400 °C).

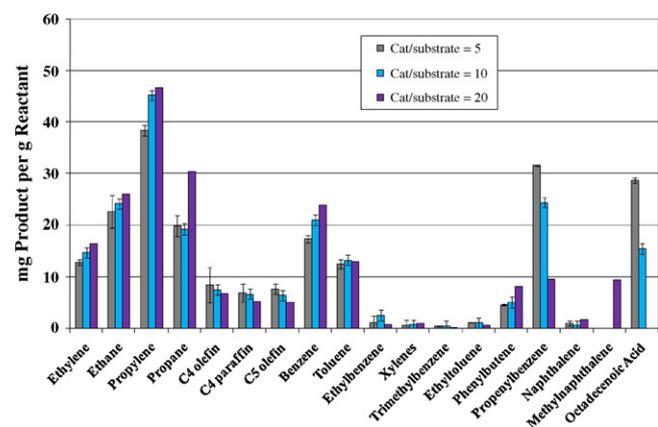


Fig. 4. Product yield of hydrocarbon products from Diolein cracking on H<sup>+</sup>ZSM-5 (reaction T = 400 °C).

limitations in determining reactant concentrations for which the molecular weights of the reactants exceed 300.

#### 3.1.1. Product distribution on H<sup>+</sup>ZSM-5

Figs. 3–5 show the product yields for all three lipid reactants on the H<sup>+</sup>ZSM-5. Each of the reactants was reacted at three levels of catalyst to glyceride ratios (5, 10, and 20 mass of catalyst/mass of substrate). This demonstrated the change in product yields with increasing residence times. For diolein and triolein, as reactor

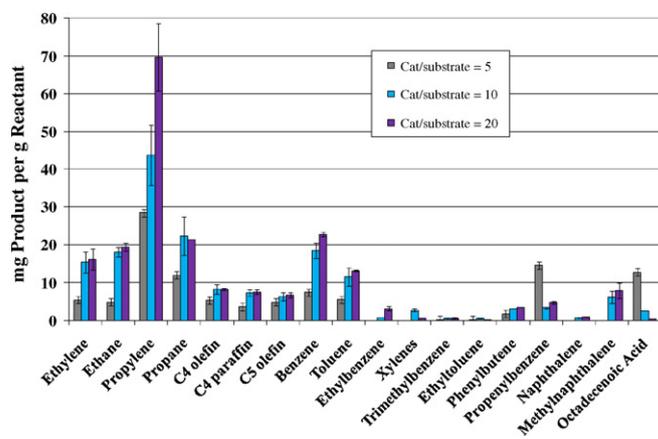


Fig. 5. Product yield of hydrocarbon products from Triolein cracking on H<sup>+</sup>ZSM-5 (reaction T = 400 °C).

**Table 2**  
Yield of octadecanoic acid intermediate on H<sup>+</sup>ZSM-5 at 400 °C.

	Catalyst to substrate ratio		
	5	10	20
Dirolein	13.3	7.4	0
Trirolein	13.4	1.5	0.2

residence times increased, so did the production of propylene and propane in the light hydrocarbon region and benzene, toluene, naphthalene, and methylnaphthalene, in the aromatics region. Also, the yield of propenylbenzene decreased with increased residence times, suggesting that propenylbenzene was a reaction intermediate. The reaction yield for the remaining aromatics was low (<10 mg/g reactant) and gave no specific trend in regards to increasing catalyst to substrate ratios. However, these same trends were not true for monoolein. This is perhaps due to initial cracking occurring along the olein chain and not the glycerol backbone. This could also explain the relative increase in product yields of propylene as additional fatty acid chains are attached to the glycerol backbone. If initial cracking was occurring along the glycerol backbone, then there would be little change in propylene yields as the number of glycerol carbons is always equal to three.

Also appearing in the product distributions for the dirolein and trirolein reactants was octadecanoic acid (either oleic acid or an isomer thereof) (Figs. 4 and 5). Production of the free fatty acid was not seen with the monoolein reactant. This was perhaps due to the possibility that the monoolein co-eluted with any free fatty acid formed from the reaction. Dirolein and trirolein compounds are too large to chromatograph on the thick film, boiling point column during the online analysis of reactions, and therefore, do not interfere with the elution of the free fatty acid. As can be seen from Table 2, the product yield of octadecanoic acid was greatest at low catalyst to substrate ratios, and because empty bed reactions indicated no presence of octadecanoic acid (i.e. at zero conversion), this species was believed to be an intermediate.

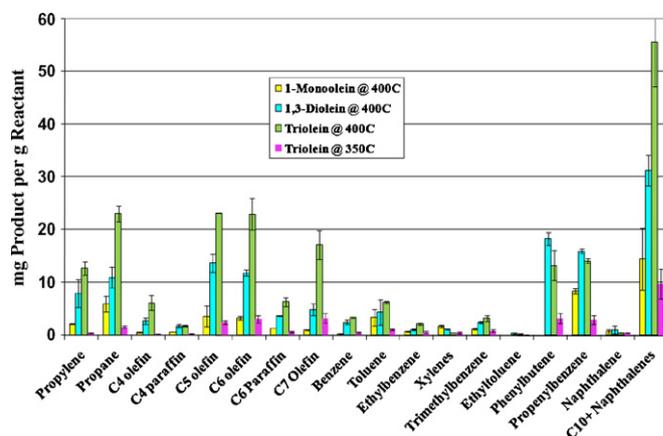
Another comparison can be seen in Table 3, which shows the weight percent composition for each product as fatty acid side chains are added to the glycerol backbone. These results were derived from experiments using the catalyst/substrate = 20. As can be seen from these results, the addition of oleic acid side chains resulted in decreased production of CO, CO<sub>2</sub>, ethane, and propenyl-

**Table 3**  
Product distribution of gas and organic liquid products.

Product	Canola oil <sup>a</sup>	Triolein <sup>b</sup>	Dirolein <sup>b</sup>	Monoolein <sup>b</sup>
MW	n/a	884	621	356
Carbon:oxygen	n/a	9.5	7.8	5.3
Composition (wt.%) in gas phase				
CO + CO <sub>2</sub>	3.7	5.5	9.6	25.3
Methane	5.3	–	–	–
Ethylene	8.7	10.3	10.9	0.0
Ethane	6.9	12.3	17.2	35.8
Propylene	16.1	44.1	30.9	19.6
Propane	18.9	13.6	20.1	11.2
C <sub>4</sub> olefin	11	5.2	4.4	3.9
C <sub>4</sub> paraffin	17.1	4.8	3.5	3.0
C <sub>5</sub> olefin	–	4.3	3.4	1.1
C <sub>5</sub> <sup>+</sup>	11	–	–	–
Composition (wt.%) in liquid phase				
Benzene	8.1	39.3	35.0	30.6
Toluene	18.7	22.8	19.0	19.2
Ethyl benzene	4.4	5.5	1.0	3.1
Xylenes	15	1.1	1.5	1.3
C <sub>9</sub> <sup>+</sup> aromatics	8.8	31.3	43.5	45.9

<sup>a</sup> Canola oil reacted on H<sup>+</sup>ZSM-5 at 400 °C and 83.6% conversion [6].

<sup>b</sup> Model compounds reacted on H<sup>+</sup>ZSM-5 at 400 °C.



**Fig. 6.** Product yield of hydrocarbon products from acylglyceride reactions on Faujasite (Cat/substrate = 20).

benzene and an increased production of propylene, C<sub>4</sub> olefins, C<sub>4</sub> alkanes, and C<sub>5</sub> olefins. All other cracking products remained relatively unchanged. The trends in CO and CO<sub>2</sub> were attributed to the fact that there was an increase in the carbon/oxygen ratio with each additional fatty acid attached to the glycerol backbone. Also, the differences in the trends between aliphatics and aromatics yields can be explained from slower diffusion rates of aromatics from the catalyst surface [20]. For this reason, at a given residence time, aromatic compounds are in contact with the catalyst for longer periods of time. This allows for less time in which aliphatic compounds can oligomerize, cyclize, and aromatize.

### 3.1.2. Effect of different zeolite catalysts on lipid cracking

Fig. 6 shows the product distribution for mono, di, and triolein cracking on faujasite at 400 °C, with triolein being reacted at 350 and 400 °C. A comparison of the results between H<sup>+</sup>ZSM-5 and faujasite catalysts demonstrates the effects that pore size and catalyst acidity have on the product distribution from acylglyceride cracking. H<sup>+</sup>ZSM-5 produced more propylene (factor of 5.4) than faujasite. Also, H<sup>+</sup>ZSM-5 produced more benzene (factor of 6.6) and toluene (factor of 2.1). On the other hand, cracking on faujasite produced more phenylbutene (factor of 3.7), propenylbenzene (factor of 2.9), methylnaphthalene (factor of 5.9), higher molecular weight aliphatics, and other alkyl-substituted naphthalenes.

These results can be related to the physical and chemical properties of the catalysts. Larger pore sizes within the catalysts generate molecules with larger mean diameters. It is for this reason that C<sub>6</sub> and C<sub>7</sub> aliphatic molecules, more phenylbutene, more propenylbenzene, and higher alkyl-substituted naphthalenes were formed using faujasite catalyst, and H<sup>+</sup>ZSM-5 produced more propylene, benzene, and toluene.

### 3.1.3. Effect of crystallinity on lipid cracking

Fig. 7 shows the product distribution for mono, di, and triolein cracking on silica–alumina at 400 °C, with triolein being reacted at 350 °C and 400 °C. The amorphous character of the silica–alumina permitted the formation of dienes within the sequence of cracking events, but not the formation of aromatic compounds that are within the gasoline range organics. Previous research has shown that amorphous catalysts do not offer the shape-selective characteristics of crystalline catalysts [13]. Crystalline catalysts present the intermediate compounds with more acid sites and uniform pores on which additional reactions can occur. Also, silica–alumina has a lower acidity than the crystalline catalysts. Hence, there is a lower driving force for cracking with the silica–alumina than with the H<sup>+</sup>ZSM-5 or faujasite.

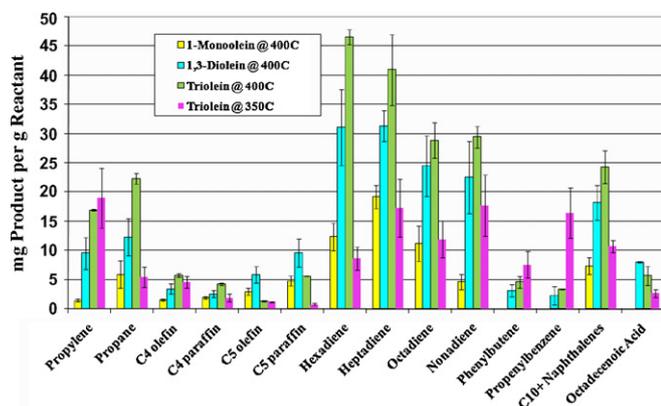
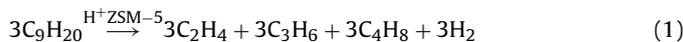


Fig. 7. Product yield of hydrocarbon products from acylglyceride reactions on silica–alumina (Cat/substrate = 20).

#### 4. Proposed reaction pathway

These results suggested that cracking of unsaturated lipids could follow two distinct paths by which olefins and paraffins could oligomerize followed by cyclization and aromatization. Initial products formed from the fatty acid chains appear to be propenylbenzene and phenylbutene. From these experiments, the proposed hypothesis was that propenylbenzene and phenylbutene were the primary products, which then underwent additional methyl shifts and cleavages to form various aromatic compounds. An alternative path suggests that initial cracking occurs along the glycerol backbone, cleaving the C–O bonds. In either case, the development of naphthalene, methyl naphthalene, and dimethyl naphthalene, which are precursors to coke, implied that multiple aromatics fused together to form coke products.

For development of the reaction mechanism, one must first consider a hypothetical reaction sequence that might occur. For this sequence, it was supposed that triolein ( $C_{57}H_{104}O_6$ ) would undergo a series of reactions to produce benzene and toluene, as seen from the cracking results on  $H^+ZSM-5$ . Beginning with the initial protonation and cleavage of the unsaturated bond of the fatty acid, the reactions could go as follows:



These would be hydrogen producing reactions. For this idealized case, there are a total of 15 moles of hydrogen that can be utilized within the generalized reaction for possible hydrogenolysis, decarbonylation, or decarboxylation reactions. Considering that alcohols were not observed within the product distribution, hydrogenolysis is not a probable reaction step. Therefore, decarboxylation and decarbonylation are proposed for the deoxygenation steps responsible for removal of the heteroatoms from the acylglyceride.

The reaction scheme occurring on  $H^+ZSM-5$  may proceed via Route 1 (Fig. 8), which begins with the protonation of the double bond of the fatty acid constituent. The protonated charge may then migrate along the fatty acid carbon chain.  $\beta$ -Scission, occurring after hydride shifts, results in cracking of the fatty acid moiety. Previous work in which a homogeneous super acid was reacted with an unsaturated free fatty acid has shown this reaction chemistry [11]. If the resulting charged species are small enough to readily enter the catalyst pores, additional reactions may occur. These secondary reaction steps were assumed to follow previously described carbenium ion chemistry pathways [21–25]. Cyclization steps result in the formation of aromatic compounds (chiefly propenylbenzene and phenylbutene, which are reaction intermediates). Previous

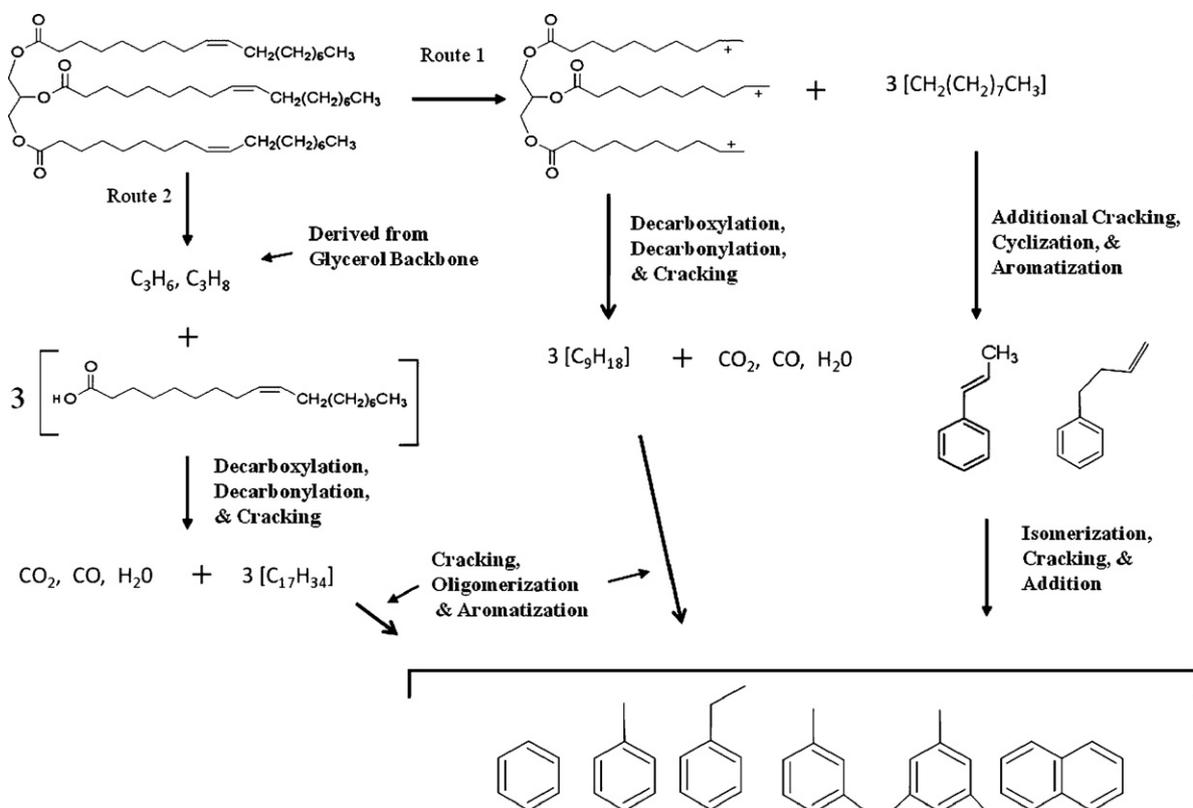


Fig. 8. Reaction scheme for the transformation of acylglycerides to green gasoline.

work by the authors, whereby heterogeneous cracking of oleic acid occurred on H<sup>+</sup>ZSM-5, demonstrated this reaction chemistry [12]. The cyclization and aromatization steps are believed to occur in like fashion as reported by Vedrine et al. [21] in which olefins were reacted with carbenium ion intermediates to form benzene, toluene, and xylenes [21].

The authors would like to comment on two possible routes for phenylbutene transformations. First is the possibility that additional cracking of the allyl chain produces small olefins and a single ring aromatic (with and without alkyl substitutions), as seen from previously reported work [25]. The second is that naphthalene may be produced from subsequent reactions of phenylbutene. This agrees with the findings reported by Mathauser and Teplyakov [26] where 4-phenyl-1-butene was shown to form naphthalene through a two-step dehydrocyclization process [26]. Both, we believe, are reasonable pathways for additional reactions occurring *via* this intermediate.

Decarboxylation and decarbonylation steps are believed to be responsible for the formation of CO<sub>2</sub> and CO, respectively. Once decarboxylation and decarbonylation occur, the resulting reaction intermediates are believed to follow similar reactions as seen from reactions of linear alkanes and alkenes on H<sup>+</sup>ZSM-5 [22,23]. As can be seen from Eqs. (1)–(3), there would be an ample supply of hydrogen atoms for the decarboxylation and decarbonylation steps that are hydrogen consuming reactions.

Also, *via* Route 2 (Fig. 8), cleavage of the C–O bonds along the glycerol backbone may result in the formation of fatty acids and propane or propylene. Subsequent reactions of the C<sub>18</sub> fatty acids through decarboxylation and decarbonylation are responsible for the formation of CO<sub>2</sub> and CO, respectively. These reactions are hydrogen consuming and are in agreement with the findings of Maki-Arvela et al. [27] whereby ethyl stearate, a saturated fatty acid ethyl ester, was shown to produce ethylene and *n*-heptadecane through decarbonylation and decarboxylation pathways [27].

ZSM-5 and faujasite catalysts are shape-selective catalysts, and their elliptically shaped pores and intersecting channels are ideal for producing aromatic compounds [13]. Light olefins, C<sub>2</sub>–C<sub>4</sub>, readily react with one another inside the catalyst pores and form the aromatic compounds. The newly formed aromatic compounds will then either diffuse from the catalyst or will remain inside the pores forming coke.

Due to molecular size inhibitions, protonation is believed to occur on the outside surface of the catalyst and not within the pores. AM-1 calculations using Spartan software (Wavefunction, Inc., Irvine, CA, USA) were used to determine the molecular size of triolein. As can be seen from Fig. 9, the molecular dimensions of triolein were estimated to be from 6.252 Å to 43.706 Å. As the H<sup>+</sup>ZSM-5 catalyst has a pore diameter of 5.4 Å, these calculations suggest that the size and shape of the substrate does not allow it to enter the pores of the zeolite and offer evidence that cracking of

the acylglycerides begins at the acidic sites found along the outside surface of the catalyst.

Additions of mono-aromatic compounds result in the formation of naphthalene and methylnaphthalene. Both of these compounds are precursors to coke, which is a rather ill-defined, inherent byproduct of high-temperature, heterogeneous catalytic cracking reactions [17,28,29]. Coke is a mixture of polynuclear aromatics that form inside the catalyst pores. When a coke molecule becomes too large to exit the catalyst pore, it poisons the catalyst by blocking catalytic sites for future carbenium ion formations. In industrial applications, catalysts are regenerated by burning off of the coke in an air stream using higher temperatures than that required for carbenium ion cracking reactions [29].

The reaction scheme shown in Fig. 8 demonstrates the deoxygenation of lipid molecules. The products observed in this work (i.e. mostly aromatics) are a consequence of the H<sup>+</sup>ZSM-5 catalyst, which is a shape selective, highly acidic catalyst. The composition of green diesel, however, is comprised mostly long chain aliphatic compounds, which is also a function of the catalyst used. Green diesel is generally produced by reacting vegetable oils and animal fats on standard hydroprocessing catalysts [30]. The catalysts used in this work served as benchmark catalysts that would promote the deoxygenation of lipid molecules with the intent of identifying specific deoxygenation steps, and is therefore, not intended to be used as a commercial catalyst to produce renewable fuels.

## 5. Conclusions

Mono-, di-, and triolein were used as model compounds to study the catalytic transformation of lipids to green fuels in a gas-phase heterogeneous reaction system. The catalytic cracking of these compounds leads to a wide range of products: C<sub>2</sub>–C<sub>5</sub> paraffins and olefins, aromatics, CO, and CO<sub>2</sub>. From these products and from previously reported work using model reaction intermediates, a reaction scheme has been proposed. While the pathway shown here may not be the only pathway that occurs, it provides a plausible explanation for the initial reaction products seen in this work. Additional conclusions can be summed up as follows:

- The unsaturated acylglycerides had similar cracking patterns with regards to the amounts of products formed. Product yields were high with light hydrocarbon gases (especially propylene) and included the formation of aromatic compounds.
- All model lipids studied showed the formation of propenylbenzene and phenylbutene from cracking on three separate and unique catalysts. Propenylbenzene yield decreased from monoolein to diolein to triolein. The weight percent of propenylbenzene decreased with increased catalyst to substrate ratios of 5, 10, and 20. No specific trends in yield were observed for phenylbutene.
- The proposed cracking mechanism includes the cracking of the unsaturated fatty acid side chains outside the catalyst pores. Additional steps include cyclization and aromatization within the catalyst pores to form mono- and di-aromatic compounds.
- The proposed cracking mechanism also includes the cleavage of the glycerol carbons forming propane, propylene, and fatty acids. Additional reactions are necessary for heteroatom removal from the fatty acid.

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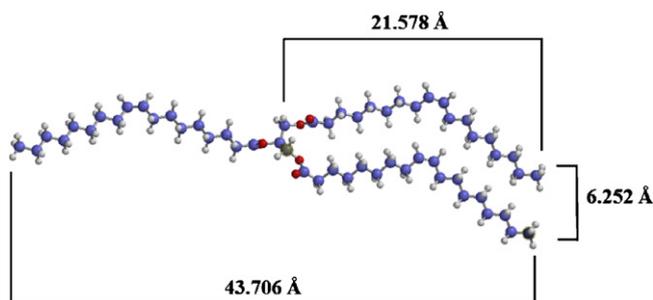


Fig. 9. Molecular geometry of triolein (equilibrium geometry from semi-empirical AM-1 calculations).

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