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An Initial Study of the Catalytic Reforming of Crop Oil-Derived 1-Alkenes with HZSM-5 to
Aromatic Hydrocarbons

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Abstract

This study explored the production of aromatic hydrocarbons from the longer-chain alkenes produced by the pyrolysis/cracking of crop oils. 1-Tetradecene, serving as a model compound for these alkenes, was reformed in a batch reactor with a HZSM-5 catalyst to produce a liquid hydrocarbon mixture with a high-aromatic content. These reactions resulted in a >99% conversion of the 1-tetradecene feedstock with a yield of up to 22 wt% of aromatic hydrocarbons. Surprisingly, isomers of C₃-substituted benzenes along with xylenes and diaromatics (lower homologs of alkyl-substituted indanes and naphthalenes) were the main aromatic products rather than their lower-molecular-weight (MW) homologs, benzene, toluene, ethylbenzene and xylenes, which are commonly formed with high selectivity during zeolite-catalyzed reforming. The recovery of higher-MW aromatics, and particularly bicyclic naphthalenes and indanes, provides mechanistic insights for zeolite-catalyzed alkene reforming reactions suggesting that these higher-MW aromatics are likely formed near the catalyst surface at pore openings. Furthermore, the production of acyclic diene intermediates in the size range of C₇–C₁₀ provides insight into the overall reaction pathway. The results suggest that this reaction pathway may be a commercially viable option for the production of renewable C₃-substituted aromatic chemicals/ chemical intermediates as coproducts to complement the kerosene and diesel fuel blendstocks that are the primary products from crop oil cracking.

Keywords: Renewable aromatics, Catalytic reforming, HZSM-5, Crop oils, Alkylbenzenes

Introduction

Previous work reporting the noncatalytic cracking of crop oils in a continuous pilot scale system has shown that, under low-pressure conditions, a significant fraction of the liquid product is obtained in the form of 1-alkenes (Seames et al., 2017). The 1-tetradecene and other C14–C17 terminal alkenes, which are formed as a result of the deoxygenation or cleavage of C16 and C18 fatty acids, may be valuable feedstocks. These fatty acids are the main structural components of triacylglycerol oils, such as crop oils (soy, corn, canola, etc.), algal oil, and microbial oils, and of fatty acids such as restaurant waste cooking oils and animal fats.

Rather than simply hydrogenating these alkenes to alkanes, it may be possible to convert them into aromatic compounds, which may be more useful for some applications. For example, aromatic hydrocarbons are used in motor gasoline to increase its octane rating and as chemical intermediates for the manufacture of polymers, resins, industrial fibers, and elastomers. Low-molecular-weight (MW) aromatics, particularly BTEX (benzene, toluene, ethylbenzene, and xylenes), are also used as solvents.

Recent research has primarily focused on the production of aromatic compounds from light alkanes and alkenes (Bhan and Delgass, 2008; Smiešková et al., 2004). ZSM-5 catalysts, either in their plain hydrogen form or doped with transition metals (Ga, Zn), have been shown to be efficient catalysts for facilitating the aromatization of light alkenes such as ethene, propene, and butene (Fegade et al., 2013). This particular zeolite proved to be most selective, as both the BTEX products and the anticipated C₂ intermediates are known to fit perfectly into this zeolite's cavity (Olson et al., 1981). Indeed, BTEX has been shown to be the primary class of cyclic products generated, with toluene being the main product within the BTEX group (Bhan and Delgass, 2008; Fegade et al., 2013; Hodala et al., 2016; Smiešková et al., 2004).

Long et al. observed a similar trend to light alkene reforming when *n*-octene was used as a feedstock. Toluene and xylenes were shown to be the major products from the aromatization of *n*-octene over nanoscale HZSM-5 catalysts (Long et al., 2009). Similar to light alkene aromatization, *n*-octene aromatization over nanoscale HZSM-5 catalysts produced greater yields of xylenes at lower temperatures, whereas benzene and toluene dominated the products at higher temperatures (Long et al., 2008). A similar trend was observed by Nash et al. for 1-hexane and 1-octene conversion using Ga-doped HZSM-5 (Nash et al., 1996), although the two studies on 1-octene conversion showed significant differences both in the aromatics yield (30–45% vs. 10–20% and 50–75% (Long et al., 2008; Long et al., 2009 ; Nash et al., 1996)) and selectivity (xylenes vs. toluene being the main aromatic product (Long et al., 2009; Nash et al., 1996)). These and similar observations can be explained by zeolite-catalyzed dealkylation of C8 and higher-MW aromatics at higher temperatures (Asomaning et al., 2014a, 2014b; Bhat and Halgeri, 1993; Mäki-Arvela et al., 2007; Maslyanskii et al., 1965). It is also worth noting that significant concentrations of larger-sized BTEX aromatics, i.e., xylenes, have been produced from 1-hexene and octene when the residence time is increased, suggesting that even higher-MW aromatics may become major products under certain conditions (Long et al., 2009; Nash et al., 1996).

For the present study, we postulated the production of similar aromatics to those found in the previous studies with longer carbon chain-length feedstock alkenes. However, to the best of our knowledge, no work has been conducted to date to study the aromatization of 1-alkenes having a chain length greater than 10 carbon atoms. Thus, this study represents a first exploratory effort in this area of research.

1-Tetradecene was selected as the feedstock as this is a representative compound for the longer carbon chain-length alkenes generated during cracking (Seames et al., 2017). The primary

objective of this work was to determine if these longer-chain 1-alkenes, as represented by the model compound 1-tetradecene, can be efficiently converted into aromatics, and whether the aromatic products' speciation and homology profile would be different compared to those obtained with lighter alkenes.

Experimental Procedures

Experimental Approach and Test Matrix

A total of 16 experiments were conducted to meet the objective of this work. First, a set of exploratory experiments was performed at varied temperatures (300–375 °C), 1-tetradecene-to-catalyst ratios (TCR, 10–20), and reaction times (30–60 min) following a two level, three factor, and full-factorial experimental design methodology. The main goal of these eight experiments was to narrow the operating range of the key reaction parameters. The reaction conditions of each experiment can be found in Table 1.

Following the exploratory experiments, eight defining experiments were then performed. These defining experiments were used to identify the reaction conditions that produce the largest yield of aromatics. Homology profiles were then developed to determine the quantity of the various aromatic isomers produced. In addition to their use for assessing commercial viability, the results obtained from these experiments were also used to draw conclusions regarding the reforming mechanisms that occurred during the reaction of crop oil-derived C14–C17 terminal alkenes. The reaction conditions of the defining experiments can be found in Table 2. One set of the defining experimental conditions was run in duplicate to determine the consistency of the experimental results (Experiments 9 and 10). The experimental conditions for these two runs replicated the conditions of Run 3 from the exploratory experiments to verify consistency between the two experimental sets.

Exp. no.	Reaction temp (°C)	Time (min)	1-Tetradecene -to-catalyst ratio	BTEX (wt%)
1	300	30	10	0.1
2	300	60	10	0.2
3	375	30	10	3.5
4	375	60	10	2.2
5	375	60	20	1.1
6	300	60	20	0.3
7	375	30	20	0.7
8	300	30	20	0

Table 1 Operating conditions applied and BTEX product concentrations (wt% of inlet 1-tetradecene) obtained in the exploratory experiments

Exp. no.	Reaction temp (°C)	Time (min)	TCR ^a	Gas yield	Liquid yield	Coke yield	Total recovery	BTEX
9	375	30	10	14	68	1.3	83	3.1
10	375	30	10	9.2	66	1.4	77	3.4
11	375	30	10	22	61	1.6	90	5.5
12	320	30	5	11	56	4	80	1.7
13	320	30	10	2.7	82	0.7	88	0.4
14	350	30	5	43	38	3.1	96	8.8
15	350	30	10	6.2	75	0.8	83	1.6
16	350	30	20	6.6	73	0.8	80	0.7
17	375	30	20	14	72	0.2	87	1.4

Table 2 Operating conditions applied as well as gas, liquid, and coke yields, and BTEX product concentrations obtained in the defining experiments (mass fraction of 1-tetradecene feedstock converted into the indicated category, expressed as a %)

^a TCR means 1-Tetradecene-to-catalyst ratio.

Experimental Setup and the Reforming Reactor

A Parr (Moline, IL, USA) series 4575 fixed head, bench top, high-temperature, and high-pressure autoclave-type reactor was used as the reforming reactor, as shown in Fig. 1. This reactor (500 mL) was equipped with a cooling channel to control the reaction temperature and a stirrer that agitated the catalyst and reaction mixture. The reaction temperature was controlled and monitored using a K-type thermocouple connected to a Parr 4843 controller, which also

monitored and controlled the impeller speed. The reactor was equipped with a gas inlet connected to a nitrogen cylinder to maintain the initial reaction pressures.

Experimental Procedure

The ZSM-5 catalyst (CBV 2314–SiO₂/Al₂O₃ ratio = 23) was purchased from Zeolyst International, Conshohocken, PA, USA in the ammonium form. As this is a well documented commercially available catalyst (Lechert et al., 1989), characterization was not performed. The ammonium form was converted into the hydrogen form by calcination at 550 °C for 5 h in an air-circulated oven, generating an activated HZSM-5 catalyst. 1-Tetradecene (97% purity) and GC grade standards were purchased from Sigma-Aldrich (Saint Louis, MO, USA). The standards used in the analytical work can be found in Tables S1 and S2, Supporting information.

To start the reaction, the required quantities of the catalyst (5–20 g) and 1-tetradecene (100 g) were introduced to the reactor based on the TCR, shown in Tables 1 and 2. The reactor was then purged with nitrogen prior to heating. Once purged, the reactor was heated to the desired temperature. The contents were then allowed to react for the allotted time while being stirred at 300 rpm after reaching the desired temperature, which took 1–4 h depending on the reaction conditions. Upon completion, the reactor contents were cooled down to room temperature. Gases were not collected during the exploratory experiments. However, in the defining experiments, the gaseous products (at pressures ranging from 100 to 800 kPa) were collected in Tedlar gas bags by slowly opening the reactor vent.

For the exploratory experiments, the reactor contents were then filtered and the liquid reformat was collected after the contents of the reactor were cooled. For the defining experiments, the entire reactor contents were weighed and filtered to separate the coke/solid particles from the liquid reformates. The collected weights were then used to perform mass-

balance closure. The quantity of coke formed was determined by subtracting the weight of the catalyst fed to the reactor from the solid particles collected after the reaction. The gas bags collected at the completion of the reaction were weighed to estimate the gaseous product mass. The amounts of liquid, solid, and gas collected in the defining experiments are shown in Table 2.

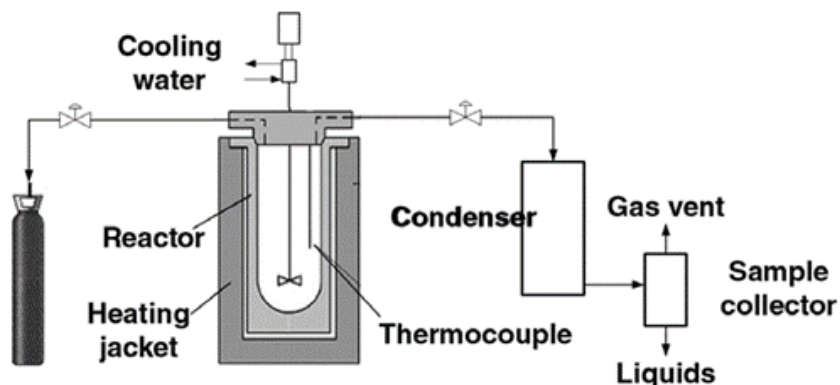


Fig. 1 Batch reactor setup for the aromatization of 1-tetradecene

Liquid Reformate Characterization

For the exploratory experiments, gas chromatography with mass spectrometric detection (GC–MS, Agilent 5890 Series II with 5973 MS [Agilent Technologies, Santa Clara, CA, USA]) was employed for the determination of benzene, toluene, ethylbenzene, and xylenes (BTEX) only as these were the aromatics anticipated based on previous work with shorter chain 1-alkene reforming. The temperatures of the GC injector and a transfer line to the MS detector were set at 300 °C and 280 °C, respectively. The oven temperature program was started at 40 °C for 5 min, then ramped at 15 °C min⁻¹ to 310 °C and held at this temperature for 5 min. The sample injections of 1.0 µL were performed in the split mode (1:20) at a constant helium flow rate of 1.5 mL min⁻¹. A 42-m DB–5MS column (J&W Scientific, Inc., Folsom, CA, USA) with a 0.25-mm I.D. and a 0.25-µm film thickness was used for all separations. The GC–MS analysis was performed with electron ionization and a solvent delay of 4 min in a mass range of 50–500

amu. The BTEX quantification was performed using a calibration between 0.01 and 5.0 wt%, with 2-chlorotoluene as an internal standard to control for volume changes (Table S1).

A more detailed reformat characterization was performed on the collected liquid product of the defining experiments using the GC–MS system described above. The detailed characterization was based on a previously developed method (Štávková et al., 2012) by quantification of specific aromatic compounds. The temperature program started at 35 °C for 5.0 min followed by a 35 °C min⁻¹ gradient to 100 °C, then 10 °C min⁻¹ to 320 °C, and held for 5 min.

The individual aromatics were then identified based on their GC retention time and pattern of homolog and isomer elution as detailed elsewhere (Kubátová et al., 2012; Štávková et al., 2012). The quantification was based on BTEX and monoalkylbenzene (*n*-propyl-, butyl-, and hexyl-), and naphthalene standards using an internal standard calibration based on 1,4-dichlorobenzene. The isomers (e.g., C₃-substituted benzenes) of these compounds were identified based on extracted ion chromatograms (Fig. 2) and mass spectra confirmation. This quantification allowed an estimate of the total aromatic hydrocarbons and their main types to be obtained. The results were reported as the mass fraction of the 1-tetradecene feedstock that was converted into the corresponding compound or compounds, expressed as wt%. It should be noted that this is a more rigorous concentration measure than is often reported in many studies and care should be taken not to compare these concentrations to concentrations reported as a fraction of the normalized total of mass that eluted and was quantified in the MS.

An even more detailed identification and semiquantification, at the level of other individual chemical species (beyond those specified above), was performed for selected samples from Experiments 9, 10, and 13. Due to the limited availability of all isomeric aromatic

hydrocarbons with long side chains, the use of chromatographic standards for all products was not feasible. Thus, only a ‘tentative’ yet likely identification was conducted, being based on either: (1) direct confirmation from a NIST MS 2005 library match of at least 70% or (2) a match of at least 40% when verified by visual mass spectra confirmation combined with a match of the observed elution profile of C_n -substituted isomers with the retention time pattern of the

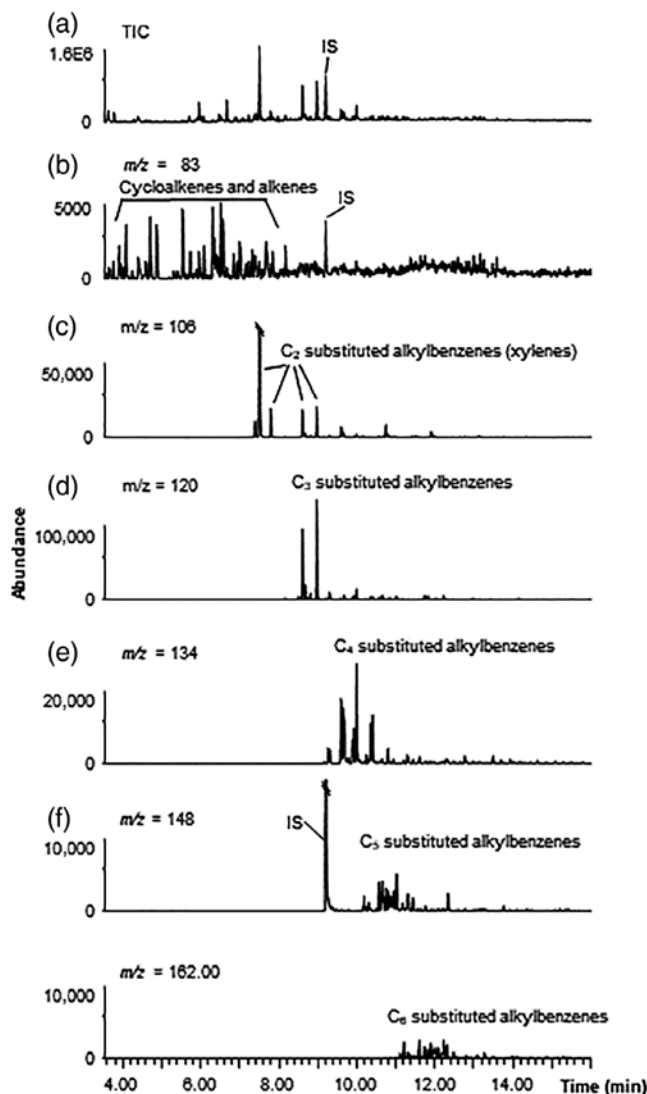


Fig. 2 Representative GC–MS chromatograms obtained using HZSM-5 at 375 °C with a 1-tetradecene–to–catalyst ratio of 10 and reaction time of 30 min. The separate panels show the total ion current (TIC) and extracted ion chromatograms of characteristic ions of alkenes (b) and molecular ions of alkylbenzenes of increasing size (c– g). IS denotes the internal standard, which shows in chromatograms as either one isotopic line at m/z of 148 or a fragmentation product at m/z of 83

corresponding identified C_{n-1} homologs (see references Stanciulescu et al. (2014) and Štávoř et al. (2012) for additional details). This identification provided molecular formulae and assignment to a specific class of compounds.

An illustration of the use of a repeating pattern of isomers for a reliable identification of each of the homologs within the chromatographic elution profile is provided in Figs. 2 and 3 for monoaromatic hydrocarbons and naphthalenes, respectively. The MS data were further refined using characteristic ions that differ from each other by 14 amu (the MW of the CH_2 group distinguishing the adjacent homologs) to obtain semiquantitative homology profiles (Figs. 2 and 3). For monoaromatic hydrocarbons (Fig. 2) and highly substituted naphthalenes (Fig. 3), this method resulted in unambiguous peak assignment to certain homologs, e.g., C_4 -substituted benzenes or naphthalenes. However, the common ions used for the identification of naphthalene (top of Fig. 3) and indane homologs turned out to be less specific. For these homologs, the identification was conducted either using standards, as for nonsubstituted naphthalene (or indane, not shown), or by using the library match as described above within a certain window of retention times for specific homologs, as for C_1 – C_2 -substituted naphthalenes (Fig. 3) and all remaining indanes (not shown).

The retention times, standards, quantification, and confirmation ions used for the analysis of the most abundant aromatic hydrocarbons in the defining experiments are listed in Table S2.

Results and Discussion

Exploratory Experiments

Table 1 presents the total BTEX product concentration obtained in the exploratory experiments. The results show that the highest amount of BTEX aromatics produced was 3.5 wt% of the 1-tetradecene feedstock loading (Experiment 3). The remaining experiments only

produced a maximum of 2.2 wt% BTEX. These low BTEX yields were surprising, as we were expecting much higher conversions based on previous work with lower-chain alkenes (Long et al., 2009; Nash et al., 1996). Based on these results, we decided to perform a more comprehensive analysis during the subsequent defining experiments, described below.

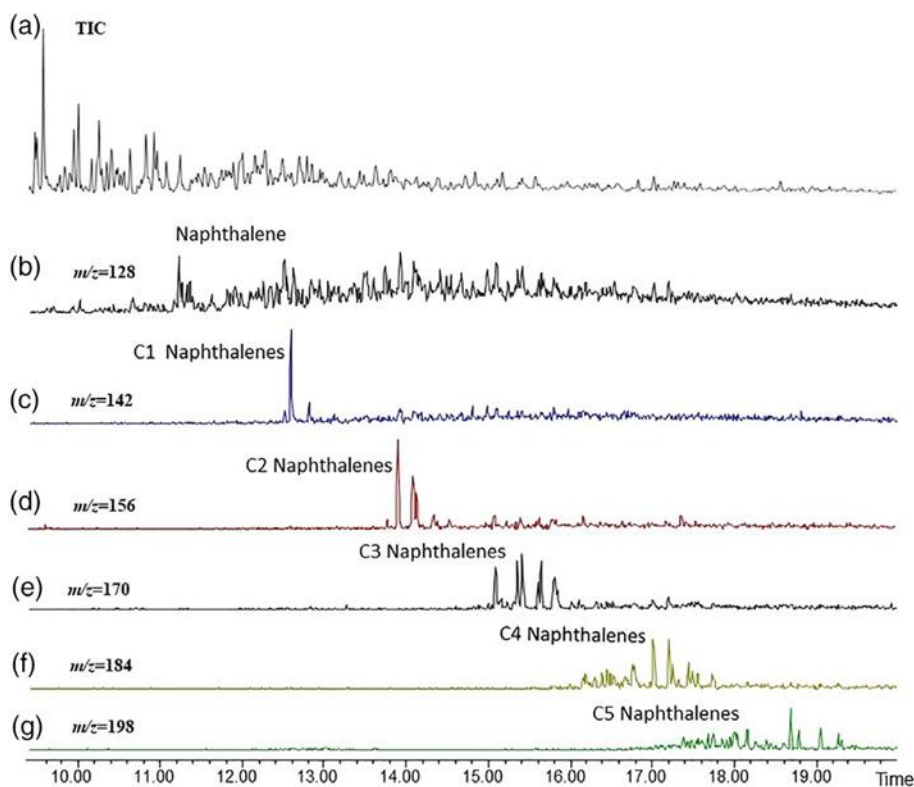


Fig. 3 Representative GC–MS chromatograms obtained using HZSM-5 at 375 °C with a 1-tetradecene–catalyst ratio of 10 and a reaction time of 30 min. The separate panels show the total ion current (TIC) and extracted ion chromatograms of characteristic ions of (b) naphthalene (confirmed by a matching retention time of the corresponding pure standard) and (c–g) alkyl naphthalenes. Multiple peaks for $m/z = 128$ are due to alkyl naphthalene fragmentation

The Table 1 data suggest that a reaction temperature of 300 °C is too low for the conversion of 1-tetradecene into aromatic compounds while reaction temperatures above 375 °C led to very high gaseous product yields (from preliminary experimental observations, data not shown). For these reasons, the subsequent defining experiments (Runs 9–16) were conducted over a temperature range of 320–375 °C to identify the conditions that produce the greatest amount of aromatics while minimizing the formation of coke and gaseous products.

The exploratory experimental data also showed that the reaction time was an insignificant parameter to the total amount of BTEX produced within the bounds of these experiments.

Table 1 results show that, as the TCR decreased, there was an increase in the BTEX concentration in the resulting product. However, lowering this ratio may further result in a significant increase of the gas-phase product yield, as will be discussed in the next section. To explore the range of this parameter further, the TCR was varied from 5 to 20 in experiments 9–16 (Table 2) to determine the range that produces the highest yield and concentration of aromatics in the reformat.

Defining Experiments

Table 2 provides a comparable summary of the results obtained from the defining experiments as that provided in Table 1 for the exploratory experiments. In these experiments, the gas phase generated during the experiments was captured and the coke generated was quantified to allow complete mass-balance closure. Experiments 9 and 10 duplicated the best conditions from the exploratory runs and they are consistent with those obtained in exploratory Run 3.

The liquid product obtained from the defining experiments was analyzed using a more comprehensive analytical method than the liquid product obtained from the exploratory tests. A significant consequence of using the more comprehensive analytical method was the discovery of substantial quantities of higher-order aromatics in the liquid product. For example, as shown in Table 3, the total concentration of aromatics produced in Experiment 9 was 11%, with only 3.1% of these aromatics identified as BTEX compounds (which matches/verifies the results from exploratory experiment Run 3). This is a surprising result as, to the best of our knowledge, no previous studies have reported a significant generation of higher-order aromatics when the

reforming of 1-alkenes is facilitated by an HZSM-5 type catalyst. Possible explanations are discussed under the heading “mechanistic insights,” below.

The results presented in Table 3 also show that the highest concentration of aromatics produced was 22% (Experiment 13). This result was obtained at an intermediate reaction temperature of 350 °C and a TCR of 5. It should be noted that the gas yield was very high from Experiment 13, namely 48%. When the TCR was increased from 5 (Run 13) to 10 (Run 14), the gas production decreased from 48% to 6%, but the total aromatics yield decreased from 22% to 7%. When the reaction temperature was then increased from 350 °C (Run 14) to 375 °C (Runs 3, 9, and 10), the total aromatics yield increased to ca. 10% while the gas yield increased to ca. 12%. Coke yields were similar and low (less than 2%) for all of these conditions.

Exp. no.	Benzene	Toluene	C ₂ Benzenes	C ₃ Benzenes	C ₄ Benzenes	C ₅ Benzenes	C ₆ Benzenes	Alkyl-naphthalenes	Total aromatics	1-Tetradecene conversion
9	0.17	0.75	2.2	2.6	3.2	0.84	0.43	1.1	11	>99.9
10	0.20	0.89	2.3	2.5	2.7	0.68	0.14	0.71	10	> 99.9
11 ^a	0.12	1.2	4.3	4.4	5.2	0.86	0.37	0.40	17	99.7
12	0.13	0.30	1.2	1.2	2.2	0.68	0.39	0.54	6.7	99.8
13	ND ^b	0.20	0.23	0.46	0.55	ND ^b	0.10	ND ^b	1.5	ND ^b
14	0.34	2.3	6.2	4.4	4.9	1.3	0.47	2.2	22	ND ^b
15	0.13	0.30	1.2	1.4	2.2	0.79	0.39	0.52	7.0	>99.9
16	0.06	0.15	0.46	0.37	0.44	0.05	0.02	0.12	2.5	99.2
17	0.05	0.22	1.1	1.0	1.2	0.23	0.15	0.13	5.0	99.2

Table 3 Occurrence of the main classes of compounds recovered in defining experiments, identified and quantified using GC–MS analysis (the mass fraction of 1-tetradecene feedstock converted into the indicated compound class, expressed as a %)

^a Experiment 11 has been rejected as an outlier.

^b ND denotes below the limits of detection.

These results suggest that the optimum reaction conditions will depend upon the ultimate objective of the process. If the objective is to maximize aromatics production, then the near optimum conditions are those of Run 13 and the total aromatics yield will be on the order of 22 wt% of the 1-alkene feedstock loading. However, if the objective is to coproduce aromatics as a by-product while maximizing liquid-phase hydrocarbons that can be utilized in transportation

fuels or to produce other chemical products, then the near optimum conditions are those of Run 9/10, which generates a total aromatics content of 11/10 wt% with only 14/9% gaseous product production.

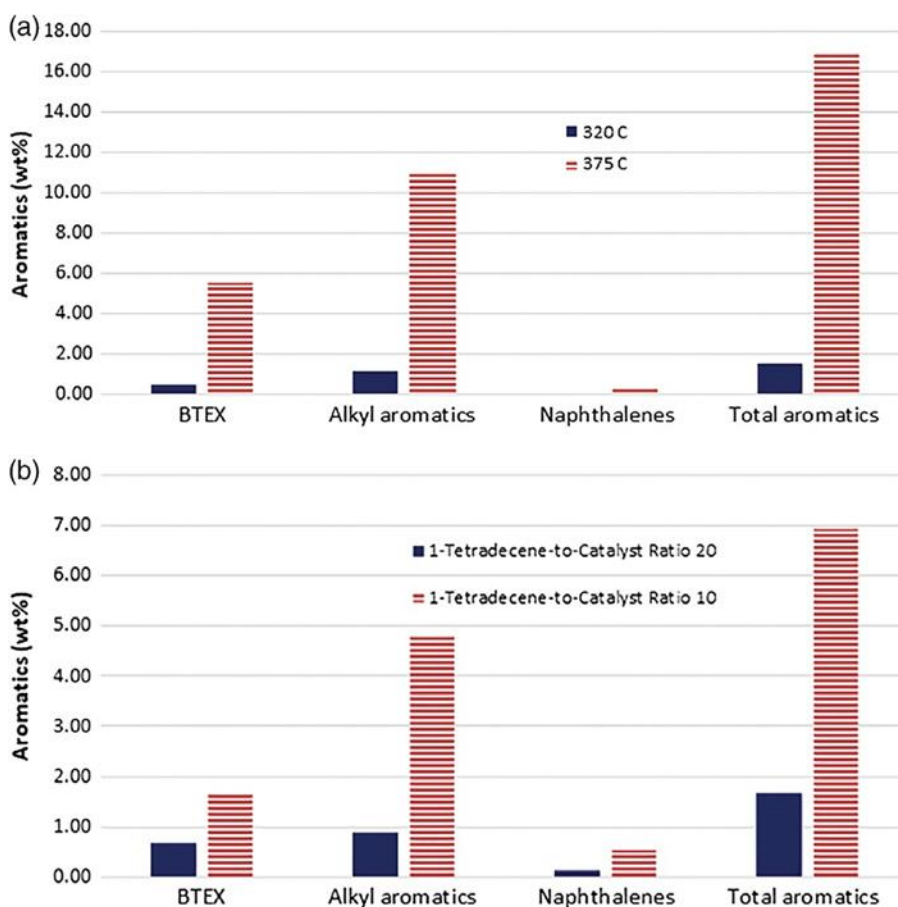


Fig. 4 Comparison of aromatic hydrocarbon yields obtained by 1-tetradecene aromatization in the exploratory experiments when varying: (a) reaction temperature (where the 1-tetradecene-to-catalyst ratio was 10 and time was 30 min) and (b) the 1-tetradecene-to-catalyst ratio (where temperature was 350 °C and time was 30 min). The Y axis represents the concentration (wt%) of aromatic hydrocarbons in the product

Trend Analysis from the Detailed Analytical Results

The trends in alkyl-aromatic hydrocarbon yields, as shown in Fig. 4, are similar for BTEX and their higher-MW homologs. A lower TCR and higher temperature promoted the formation of all aromatics. The TCR trend confirms that the catalyst does play a role in facilitating the aromatization reactions. The trend, along with the gas yield data from Table 2,

also shows that as greater amounts of catalyst are added (thus lowering the TCR), the formation of small C₂– C₃-size intermediates of aromatization increases, leading both to more gas-phase products and higher yields of aromatics.

The reaction temperature trend suggests that, due to the length of the 1-tetradecene molecule, it needs to cleave into small-chain alkenes prior to the aromatization process. Previous work has shown that such cleavage or cracking reactions become significant as temperatures near or exceed 400 °C (Seames et al., 2010), with or without a catalyst. Thus, it is not surprising that higher yields were observed at reaction temperatures exceeding 350 °C.

Therefore, the general main reactions for high-MW alkenes, such as 1-tetradecene, appear to be similar to those postulated in the literature for zeolite catalytic conversion of low-MW alkenes into aromatic hydrocarbons. However, the data presented in Fig. 4 and Table 3 show one significant and surprising difference in the product composition compared to zeolite-catalyzed reforming of lower-MW alkenes, the predominance of alkylbenzenes of a size larger than BTEX as the main aromatic products. To gain a better understanding of these results, an examination of the homology profiles was performed.

The Homology Profiles of the Defining Experiments

A detailed distribution of compounds in the reformat for the experimental conditions that yielded the greatest concentration of aromatic products in the resulting reactor liquid product (Run 13, Table 2) and also for the replicated experiments that resulted in the greatest yield of BTEX during the exploratory experiments (Run 3, Table 1 and Runs 9 and 10, Table 2) was developed. The data were obtained from the defining experiments while using the most detailed analytical procedure, which allowed all of the major groups of products to be quantitated. The homology profiles of the major groups of compounds identified are depicted in Fig. 5.

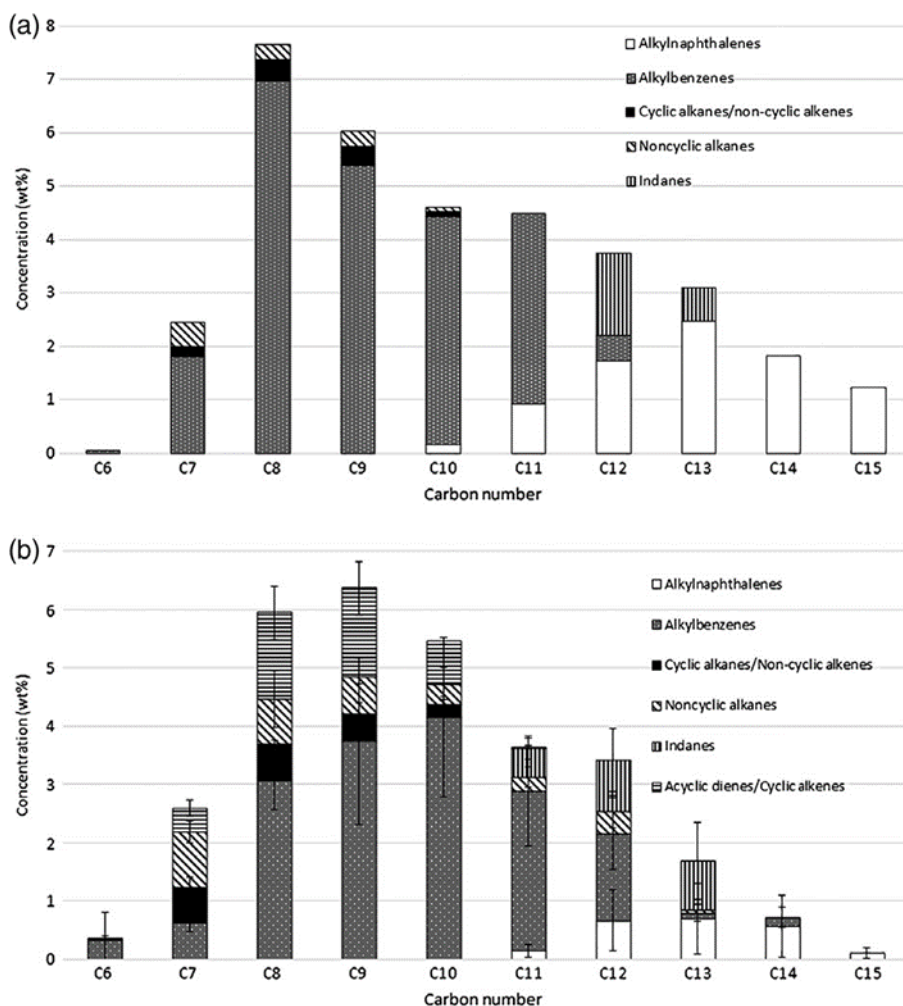


Fig. 5 Homology profiles of all the major compounds identified during the reforming reaction experiments: (a) the results of Experiment 13 under the reforming reaction conditions of 350 oC, a 1-tetradecene-to-catalyst ratio of 5, and a reaction time of 30 min, and (b) the average results from experiments 9 and 10 under the reforming reaction conditions of 375 oC, a 1-tetradecene-to-catalyst ratio of 10, and a reaction time of 30 min

A broad range of possible isomers were formed, although their relative amounts varied.

For C₃-substituted and C₄-substituted benzenes, isomers were observed in a reasonable abundance cf. Fig. 2. By contrast, fewer C₅-substituted and C₆-substituted aromatic products were observed, despite an increase in the theoretical number of isomers in this homological series. Apparently, some isomers of higher MW were formed in lower amounts, below their limit of quantification or even identification. These compounds remain unresolved in the obtained chromatograms, i.e., they form no distinct peaks but instead contribute to a slight increase in the

background baseline.

The observed homology profile (Fig. 5) corroborated the hypothesis stated above that higher than C₄-substituted aromatic products (C₉–C₁₀ isomers shown in Fig. 5) were formed in a lower abundance. Furthermore, the C₈–C₁₀ aromatics range turned out to be the most abundant range in contrast to that reported in previous studies where C₆–C₈ BTEX were the most abundant products resulting from the zeolite-facilitated reforming reactions (Bhan and Delgass, 2008; Fegade et al., 2013; Hodala et al., 2016; Long et al., 2008, 2009; Nash et al., 1996; Olson et al., 1981; Smiešková et al., 2004), although a relatively large C₉ aromatic fraction was observed in the case of *n*-octene conversion (Long et al., 2009), corroborating the results obtained in our study.

A notable shift of the homology profile toward slightly lower size was observed in Experiments 9 and 10, which had a higher TCR (Fig. 5b) compared to Experiment 13, which had a lower TCR (Fig. 5a). Consistent with the available literature on zeolites, this observation may be ascribed to the cracking of long-chain isomers on the catalyst surface. This phenomenon is more prevalent when the catalyst surface is more accessible as it would be when the TCR decreases. A similar shift may explain the differences in toluene/xylene observed in two studies on 1-octene conversion with HZSM-5 (Long et al., 2009; Nash et al., 1996).

It was also noted that large amounts of higher-MW alkylnaphthalene and indane diaromatics were produced, with C₁₅ naphthalene (i.e., C₅ substituted) being the most abundant. These products were not observed previously in smaller-size alkene reforming (Bhat and Halgeri, 1993; Hodala et al., 2016; Long et al., 2008, 2009; Maslyanskii et al., 1965; Nash et al., 1996; Olson et al., 1981). Also, acyclic dienes were identified only in Experiments 9 and 10 by their library match, based on the fragmentation pattern, which was different from those of the

corresponding isomers, cycloalkenes and acyclic alkynes (the computergenerated library match was confirmed by the manual case-to-case matching of the available MS spectra). Even though the concentration of these diene products was so low that they could not be shown in Fig. 5a, recovery of these two groups of products leads to the important mechanistic implications discussed below.

Mechanistic Implications of Defining Experiments

Detailed product analysis (Table 3) showed the nearly complete disappearance of the original feedstock, 1-tetradecene, which was recovered only in trace amounts under near optimum reaction conditions. Furthermore, scanning the product chromatogram for hydrogen-unsaturated non-aromatic hydrocarbons revealed that there was less than 3% of alkenes plus cycloalkanes species, Fig. 5. Thus, the alkene conversion was nearly complete.

As for the aromatic products, their average size was larger than that of BTEX, which are formed when C₂ (adsorbed ethene) intermediates are postulated to dominate the reaction mechanism (Asomaning et al., 2014a, 2014b; Bhat and Halgeri, 1993; Fegade et al., 2013; Hodala et al., 2016; Kubátová et al., 2012; Long et al., 2008, 2009; Mäki-Arvela et al., 2007; Maslyanskii et al., 1965; Nash et al., 1996; Olson et al., 1981; Stanciulescu et al., 2014; Štávková et al., 2012). Small-sized *primary* intermediates definitely form, as the gas-phase product yield increases with a decrease of the TCR. However, the results suggest that some of the *subsequent*, *secondary* intermediates formed as a result of 1-tetradecene cracking are of larger size. This conclusion may at first glance contradict the well-known match between the sizes of BTEX molecules and the size of zeolite pore openings (Olson et al., 1981). However, larger alkylbenzene molecules may be formed from larger intermediates within the near-surface pores where the average pore diameter is larger.

This suggestion is corroborated by the formation of significant concentrations of bicyclic indanes and naphthalenes in addition to aromatics (see Fig. 5). While the monoaromatics peak at C₈–C₁₀, the formation of even larger indanes and naphthalenes, indicates that bicyclic aromatic hydrocarbons are formed at sites that are large enough to accommodate these larger intermediates. Furthermore, more diaromatics are formed when the TCR is lower, i.e., the catalytic sites are less saturated (Fig. 5a compared to 5b). The aromatic product homology profile in Fig. 5a then even becomes bimodal, with one maximum at the C₈ size for monoaromatics and the other one at C₁₂–C₁₃ for diaromatics. Thus, two types of sites appear to be involved.

This information warrants the question, why these products were not discovered earlier? As bicyclic products are not characteristic of the cyclization of smaller-size alkenes, it appears that their formation results from a larger-sized starting material, which at least partially cleaves into larger than ethene intermediates. While smaller-size intermediates from the initial 1-tetradecene zeolite-catalyzed cleavage are forced into the depth of the catalyst pores, which stabilizes BTEX as products, larger-size primary intermediates may form larger-size secondary cyclic intermediates upon cyclization, which are forced toward the catalyst surface where they are either released as larger-size monoaromatic products, cracked to smaller-size aromatics, or undergo a second cyclization to form bicyclic aromatics. This may explain the shift of the aromatic homology profile from C₇–C for smaller-size alkene feedstocks to C₈–C₁₀ for 1-tetradecene. Corroborating this hypothesis, C₉–C₁₁ aromatics were found to be predominant when the carboxylic acids of triacylglycerols, which are also large molecules, were treated with zeolites under similar conditions (Benson et al., 2008; Fegade et al., 2015).

Detailed chemical analysis may also indicate the maximum size of intermediates based on the recovery of dienes in Experiments 9 and 10, which had a higher TCR, but not in

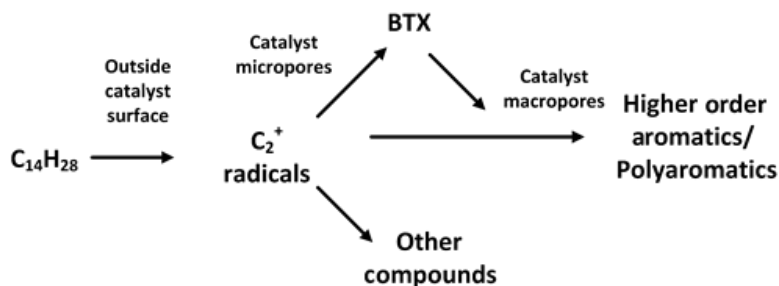


Fig. 6 A general overview of the postulated reaction scheme for 1-tetradecene reforming facilitated by a HZSM-5 catalyst

Experiment 14, which had a lower TCR. Only dienes within the narrow size range, C_7 – C_{10} , were observed, matching the size of both alkenes recovered in smaller amounts and the ultimate products, monoaromatic hydrocarbons (Fig. 5). Such a significant size specificity, combined with the observation of diene formation only when there is apparently insufficient catalyst to effect complete conversion (high TCR, Fig. 5b), indicates that both dienes and alkenes of this size may be direct precursors of the corresponding monoaromatic products. This conclusion stands even if some of these tentatively MS-identified acyclic dienes and alkenes are actually their isomers, cyclic alkenes and alkanes, respectively.

Fig. 6 summarizes the overall reaction scheme described above. Under the appropriate reaction conditions, 1-tetradecene will decompose into smaller fragments, with the most prevalent postulated to be C_2^+ radicals on the external surface of the catalyst. Some of these fragments migrate to the interior micropores of the zeolite, where they recombine to form primarily BTX. Some of these C_2^+ radicals combine with larger fragments or with previously formed BTX to form higher-order aromatics and polyaromatics in the macropores (entry points of the micropores) of the catalyst. The remaining C_2^+ radicals and other larger fragments terminate as other compounds.

Conclusions

A preliminary study was conducted to explore the reforming of crop oil-derived C_{14} – C_{17}

terminal alkenes, which are formed as a result of the deoxygenation or cleavage of C₁₆ and C₁₈ fatty acids into aromatics that could be recovered as valuable coproducts from a crop oil biorefinery utilizing noncatalytic cracking or similar technologies. 1-Tetradecene was used as a model compound to define the near optimum reaction conditions and to evaluate the feasibility of aromatics generation from these compounds.

In the presence of HZSM-5, a fraction of the original 1-tetradecene feedstock can be converted to aromatic hydrocarbons, but these will be predominantly larger in size than benzene and toluene (>C₇). A reaction temperature in the range of 350–375 °C and a TCR in the range of 5–10 increases the aromatics yield, although gas-phase products may also be formed in abundance when the reaction temperature is at the high end of this range and the TCR is at the low end of this range.

With 10–22 wt% of the 1-tetradecene loading converted into aromatic hydrocarbons, it may be concluded that these initial results suggest that this reaction pathway may, with further development, be a commercially viable option for the production of renewable C₃-substituted aromatic chemicals/chemical intermediaries from 1-alkenes that originate as crop oils. The remainder of the organic liquid product generated during the reforming reactions needs to be explored to identify and quantify the other compounds in this mixture, so that these can also be exploited. One suggested area of improvement would be to develop catalyst formulations that are optimized for alkylbenzene formation from large MW alkenes such as 1-tetradecene.

Besides aromatics, significant amounts of naphthalenes are recovered, with smaller amounts of indanes, alkanes, alkenes, and dienes. Given that the size of the zeolite pores matches those of BTEX molecules, larger-size monocyclic and, particularly, bicyclic aromatic hydrocarbons are most likely formed at the pore opening, near the zeolite surface rather than

within the pores themselves as previously postulated. This factor may be characteristic and specific for substrates of a large molecular size, such as 1-tetradecene. Therefore, in future studies using HZSM-5 to reform other large-sized substrates, particularly those associated with crop oil such as waxes, triacylglycerols, etc., it is recommended that the analytical methods employed look for and account for aromatics compounds larger than BTEX.

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Conflict of Interest The authors declare that they have no conflict of interest.

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