# One-Step Process for the Production of BTEX and LPG-like fuel from Pentanediol

Sungtak Kim,[†] Michael K. Mayeda,[‡] Erdem Sasmaz,[†] and Jochen Lauterbach*,[†]

[†]Department of Chemical Engineering, University of South Carolina, 541 Main Street, Room 135, Horizon I, Columbia, South Carolina 29201, United States

[‡]Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Colburn Laboratory, Newark, Delaware 19716, United States

Ⓢ *Supporting Information*

ABSTRACT: We report on a one-step process to produce value-added organic chemicals via deoxygenation of pentanediol (PeD) over HZSM-5 at temperatures between 325 and 450 °C and atmospheric pressure. The conversion efficiency of PeD to petroleum gas (C_2–C_5) and aromatics (benzene, toluene, ethylbenzene, and xylenes) reached up to 94% (carbon yield); we observed minimal CO, CO_2, and coke production. Furthermore, the carbon yield to the desired products remained near 91.5% with a steady product distribution for 40 h. No severe degradation of catalytic activity of HZSM-5 due to the presence of water in the product stream was observed after multiple regenerations. The catalytic process represents a valuable step toward displacing petroleum-based chemicals.

KEYWORDS: *Pentanediol, deoxygenation, ZSM-5, LPG, BTEX*
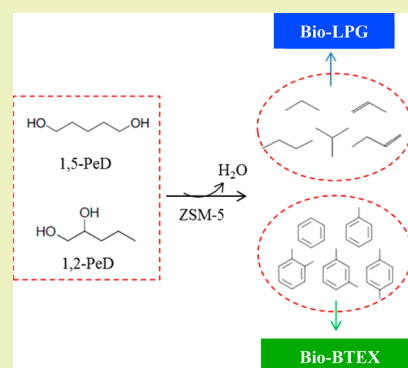
INTRODUCTION

Current global energy policies have encouraged the development of renewable, clean, and sustainable chemical sources in an effort to minimize greenhouse gas emissions and dependence on petroleum.[1,2] In this context, lignocellulosic biomass and its derivatives are a promising feedstock, because it is abundant, inexpensive, and does not compete with food supplies.[1,3−5] In particular, furfural (FFL), levulinic acid (LA), and γ-valerolactone (GVL) have recently drawn great attention for biofuel applications.[6−10] Here, we focus on pentanediol (PeD), a molecule that has previously been regarded as a potential monomer for the production of polyesters and polyurethanes.[11,12] It can also be considered as a promising biomass feedstock for biofuel applications due to facile deoxygenation of PeD and its high production yield from other platform chemicals. For instance, it has been shown that PeD can be produced from FFL, LA, tetrahydrofurfural alcohol, and GVL with high yield (from 60% up to 95%).[4,7,13−16] Furthermore, deoxygenation of PeD inherently requires less hydrogen supply and milder reaction conditions than that of FFL, LA, and GVL, which all possess ring structures and/or covalent bonds (C=C or C=O).[17] To the best of our knowledge, there has been no successful attempt to use PeD for biofuel production and this work suggests a novel route for production of biofuels from lignocellulosic biomass feedstock.

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are important industrial solvents and primary chemicals for the production of polymers and transportation fuels.[18] Although BTEX is traditionally a petroleum distillate, recent studies used fast pyrolysis and thermal deoxygenation methods to produce BTEX from solid biomass feedstock and its derivatives.[19−22] However, low BTEX purity and high carbon yields for coke (≈30%), CO (≈10%), and CO_2 (≈10%) from those methods prevented their widespread adoption and required further improvement.[19−22] Thus, new routes for BTEX production from biomass are required to overcome these technical barriers.

Another subset of chemicals that are traditionally synthesized from petroleum is liquefied petroleum gas (LPG). LPG (C_2–C_5, primarily propane and butane) is a versatile fuel that can be used for heating, cooking, and power generation. LPG combustion produces lower emissions (i.e., hydrocarbons, CO, CO_2, and NO_x) in comparison to coal, diesel, and gasoline.[23,24] In addition, LPG is easier and cheaper to liquefy, store, and transport than biogas.[25] LPG could be produced from biomass-sourced syngas and CO_2; but undesired by-products, such as polynuclear aromatics and oxygenates, and the energy-intensive biomass gasification processes were unavoidable.[26−28] Furthermore, high operating pressures and multiple reaction steps to obtain intermediate molecules were required.[26−28] Thus, a simple method to produce LPG from biomass has yet to be proven.

Table 1. Carbon Yield to Coke, LPG, Gas Product, BTEX, and OLP

feed composition	T (°C)	carbon yield (%)				
		coke	LPG	gas product	BTEX	OLP
1,5-PeD	325	0.8	28.8 ± 1.0	32.6 ± 1.0	48.3 ± 1.0	63.8 ± 1.0
1,5-PeD	375	0.8	32.4 ± 1.1	36.0 ± 1.3	55.3 ± 1.0	62.6 ± 1.2
1,5-PeD	450	1.1	35.3 ± 0.6	41.1 ± 1.0	53.3 ± 1.2	56.4 ± 1.0
1,5-PeD/H$_2$O (30/70)	375	0.4	35.6 ± 0.5	41.2 ± 0.7	51.7 ± 0.9	56.5 ± 1.0
1,2-PeD	375	0.7	34.4 ± 0.8	37.6 ± 1.4	59.7 ± 1.1	61.7 ± 1.4

ZSM-5 based catalysts have been used for bio-oil upgrading and polyol conversion into value-added chemicals such as light olefins and aromatics. The catalyst is an attractive candidate for PeD conversion due to its high surface area, high crystallinity, shape selectivity, and solid-acid properties.[29−32] The HZSM-5 catalyst provides strong acid sites, which are required to instigate deoxygenation of PeD in the gas phase.[33] After deoxygenation, the resulting carbocations can undergo two pathways: (1) protonation and cracking to produce light hydrocarbons (C_1−C_5) or (2) oligomerization, disproportionation, and subsequent aromatization to produce aromatics.[34−36] Herein, we demonstrate a simple one-step process that uses HZSM-5 to produce BTEX and LPG-like fuel from PeD with up to 94% carbon yield and low coke (<1%) formation.

■ EXPERIMENTAL SECTION

The catalytic conversion of 1,2-PeD, and 1,5-PeD was investigated using a HZSM-5 catalyst (Alfa Aesar, SiO$_2$:Al$_2$O$_3$ = 50:1) under atmospheric pressure and at reaction temperatures between 325 and 450 °C. PeD was fed by a peristaltic pump (Cole-Parmer, Masterflex L/S) into a custom-built stainless steel evaporator, which operated at 280 °C. The vaporized PeD was combined with industrial grade He and then passed through a fixed-bed quartz reactor (2.5 cm OD) with a weight-hourly space velocity of 2 h^{-1}. The effluent gas was cooled in a condenser (5 °C) to separate the liquid product from the gaseous product. The liquid product contained two immiscible phases, which were separated by decanting. Both aqueous and organic liquid phases were analyzed by a ^{1}H nuclear magnetic resonance (NMR) spectrometer (Bruker Avance III HD 300; d-chloroform and d-methanol, Cambridge Isotopes) and gas chromatography−mass spectrometry (GC−MS, Shimadzu GC-MS QP 2010 Plus), equipped with a Rtx-5MS fused-silica capillary column (0.25 mm ID × 30 m, Restek). The gas product was analyzed by GC (Shimadzu GC-MS QP 2010 Plus), using a HayeSep-D fused-silica capillary column (0.53 mm ID × 30 m; VICI) and a flame ionization detector. Carbon yields for each product component were evaluated on a mass basis and defined as (carbon weight of product out)/(carbon weight of PeD in). LPG was defined as the sum of C_2 to C_5 hydrocarbons. The catalyst was regenerated in air after 8 h on stream; regenerations were performed at 475 °C for 3 h to ensure complete coke removal. Fourier transform infrared (FT-IR) spectra were recorded using a FT-IR spectrometer equipped with a mercury−cadmium-telluride B detector (Thermo Electron, Nicolet 4700). The spectra were collected in single beam absorbance mode with a spectral resolution of 8 cm^{-1} at room temperature after pretreating (200 °C in He) the catalyst for 1 h. ^{27}Al MAS NMR was carried out using a Bruker Avance III HD 500 MHz system with a 1.9 mm solid-state MAS probe. Rotors were spun at 10 kHz with 10° flip angles, and an irradiation power of 63 kHz was applied.

■ RESULTS AND DISCUSSION

Direct conversion of LA, FFL, GVL, and 1,5-PeD was investigated over HZSM-5 at various temperatures (Figure S1 and Table S1, Supporting Information), and consequently, 1,5-PeD can be regarded as a promising biomass feedstock for production of LPG-like fuel. Table 1 summarizes the effect of temperature and feed composition on carbon yield to coke, gas product, and organic liquid product (OLP). Within the gas product, LPG was identified as lightweight hydrocarbons, C_2−C_5. BTEX and other C_{9+} hydrocarbons were identified in the OLP. For all reaction conditions investigated here, mass balance was calculated by taking the mass ratio of reactants (PeD in) to products (gas product + liquid product + water + coke) and found to be 100% ± 3.6%. The carbon yield of the total gas product, increased with temperature; on the other hand, the OLP yield showed the opposite trend. In all cases, coke production (up to 1.1% carbon yield) was significantly less than that produced during catalytic fast pyrolysis (up to 30% carbon yield).[20] The catalytic conversion of 1,2-PeD resulted in a similar distribution in comparison to that of 1,5-PeD under the same reaction conditions, i.e., 32.4% and 34.4% of LPG yield, and 55.3% and 59.7% of BTEX yield from 1,5-PeD and 1,2-PeD, respectively. Therefore, it can be concluded that the removal of the oxygen atoms from PeD was successfully performed on both isomers.

In a separate experiment, 1,5-PeD was cofed with water at 375 °C to achieve a higher carbon yield toward BTEX and LPG.[9] The addition of water resulted in less coke formation and a selectivity shift that favored gas products over OLP. Adding water reduced coke formation by two mechanisms at the reaction temperature of 375 °C: (1) as a diluent, water reduced the interaction between PeD and catalyst acid sites; (2) as a reactant, water contributed to the partial gasification of carbon deposits.[37] The selectivity shift was possibly caused by a rate reduction for the hydrogen transfer reaction between intermediate molecules.[38] These results are in agreement with a previous study that cofed water with plant oil,[37−39] thus cofeeding water could be used as a mechanism to control the coke formation and the product composition.

The compositions of the gas product and the OLP are shown in Table S2 (Supporting Information). In both phases, higher reaction temperatures shifted the selectivity toward smaller hydrocarbon products. The fraction of C_1 and C_2 hydrocarbon species, albeit small, increased with an increase in temperature from 325−450 °C. On the other hand, C_4 and C_5 production steadily decreased with increasing temperature. Propane production and the paraffin:olefin ratio exhibited a maximum at 375 °C. Thus, the sum of propane and butane fractions also showed the highest yield (85.2%) at 375 °C. This fraction is very similar to commercial LPG, as defined by the American Society of Testing and Materials.[40] Furthermore, cofeeding water increased the production of C_2−C_4 olefins because of the aforementioned reduction in the hydrogen transfer reaction rate. Therefore, cofeeding water may not be beneficial with regard to production of propane, butane, and BTEX; but, it could be used as a mechanism to control the product composition.
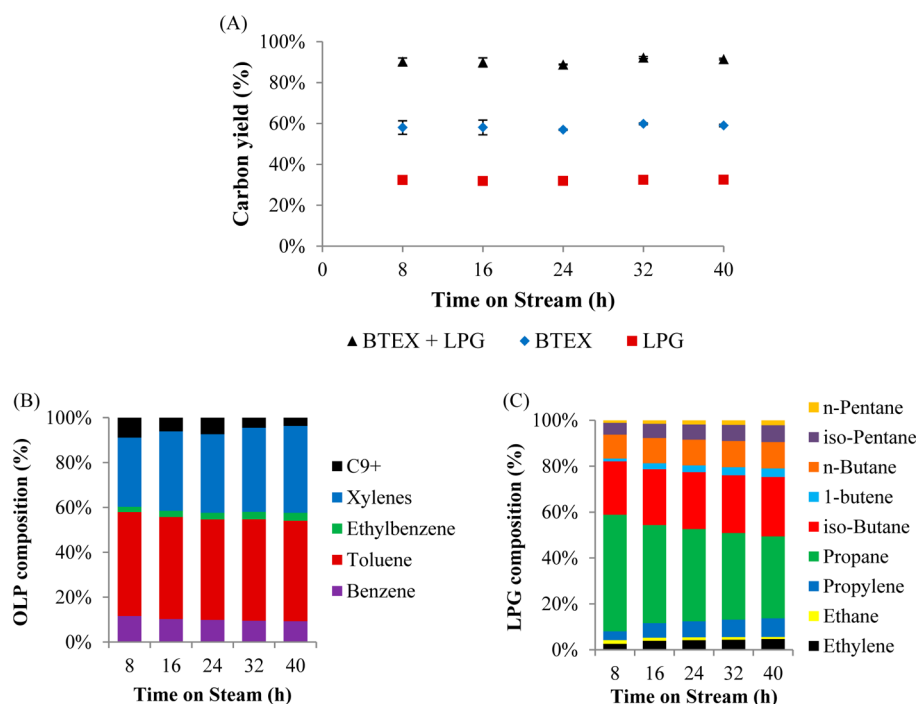
Figure 1. Carbon yield to BTEX + LPG, BTEX, and LPG (A), OLP composition (B) and LPG composition (C) from catalytic conversion of 1,5-PeD over HZSM-5 at 375 °C versus time on stream. Error range of the OLP and LPG compositions in panels B and C was ±5% of each value.

For the biphasic liquid product, ^{1}H NMR analysis (Figure S2, Supporting Information) indicated that the aqueous phase did not contain any unreacted PeD, but only water (>99 wt %). This also implied that PeD conversion was 100% in all cases. A majority of the organic phase (Table S2, Supporting Information) was composed of toluene and xylenes; the remainder of the OLP contained benzene, ethylbenzene, and C_{9+} aromatics. No oxygenated compounds were found in the OLP, which indicated that the PeD hydroxyl groups were converted into water, CO, and CO_2. Similar to the gas product composition, as temperature increased, the product composition in OLP shifted toward smaller aromatics, such as benzene and toluene. Higher temperatures possibly caused further cracking after the oligomerization step and before the aromatization step. In this case, more benzene and toluene and less xylenes and C_{9+} aromatics were produced.

In summary, a reaction temperature of 375 °C was determined to be the optimum temperature for converting PeD into value-added chemicals. The carbon yield to LPG-like fuel and BTEX reached 91% for 1,5-PeD and 94% for 1,2-PeD. The reaction temperature was relatively low in comparison to that of fast pyrolysis and thermal deoxygenation methods. Therefore, the catalytic deoxygenation process could be beneficial in terms of energy efficiency.[19−22]

Time on stream (TOS) experiments were performed at 375 °C for up to 40 h. As shown in Figure 1A, the carbon yield of BTEX and LPG remained unchanged near 90% after 8 h of reaction. However, both LPG and OLP composition, analyzed via GC and GC−MS, exhibited slight changes in their distributions (Figure 1B,C). Over 40 h, the fraction of xylenes in OLP increased by 7.9%, whereas that of C_{9+} aromatics decreased by 5.2% (Figure 1B). Furthermore, the fraction of propane in LPG decreased by 14.5%, whereas the fraction of the olefins increased by 8.1% (Figure 1C). As a result, C_2−C_5 paraffin production before regeneration and after 1st−4th regeneration steps were 84.4%, 78.1%, 76.2%, 74.4%, and

73.1%, respectively. The gradual change in the fraction of xylenes and paraffins over the multiple regeneration steps suggests that hydrogen transfer between the intermediate carbenium ions formed after deoxygenation of PeD gradually decreased.

Due to the gradual change of the OLP and LPG composition during the TOS experiment (Figure 1B,C), it was important to determine the stability of the catalytic acid sites, in particular Brönsted acid sites, on which deoxygenation and hydrocarbon cracking reactions initiate.[17,34,41,42] FT-IR analysis (Figure S3, Supporting Information) carried out over the fresh and regenerated HZSM-5 after 40 h TOS demonstrated no change of Si−(OH)−Al (3612 cm^{-1}) and Al−OH (3650 cm^{-1}) stretching bands, indicating that strong Brönsted acid sites were preserved and growth of extra framework Al was not observed.[43,44] Similarly, ^{27}Al MAS NMR (Figure S4, Supporting Information) spectra of the fresh and regenerated HZSM-5 implied that the tetrahedrally coordinated Al in the ZSM-5 framework was stable after 40 h TOS. No additional chemical shifts corresponding to extra-framework Al were detected.[45−49]

It was reported that dealumination of ZSM-5 typically occurred above 500 °C in the presence of steam.[50] Our reaction conditions studies never reached such high temperatures. Thus, HZSM-5 dealumination, which would be the main cause for any loss of strong Brönsted acid sites, was not observed during the TOS experiment. On the other hand, a large decrease in silanol groups (3710−3740 cm^{-1}) was observed (Figure S3, Supporting Information). Although fewer silanol groups may have caused the gradual decrease in paraffin production, no oxygenated compounds or significant change in the product distribution were observed over time. It was reported that silanol groups can be assigned as weak Brönsted acid sites[51,52] and minimally impact Brönsted acidic properties of zeolites.[44] Therefore, it can be concluded that a decrease in silanol groups did not affect the catalytic activity of 1,5-PeD but resulted in the

gradual shift of the product distribution toward olefins and xylenes.

CONCLUSIONS

We demonstrated the production of BTEX and LPG-like fuel via catalytic conversion of 1,2-PeD and 1,5-PeD over HZSM-5 in a low-temperature and atmospheric-pressure process. The gas product and OLP were separated by a simple condensation process. The produced LPG could be a direct replacement for commercial LPG. Our results indicated that the product distribution could be controlled by modifying reaction temperature and cofeeding water. An increase in the reaction temperature led to an increase in the olefin fraction in LPG, and benzene and toluene fraction in OLP. Furthermore, the high proportion of BTEX in OLP and LPG-like fuel in gas product enables significantly high carbon efficiency (near 90 wt %) with low CO and CO_2 production. Minimal coke formation simplified the recovery of Brönsted acid sites, which were stable at the given reaction conditions. Therefore, the catalytic conversion of PeD over HZSM-5 opened a novel pathway for production of biofuels based on lignocellulosic biomass feedstock and could be a promising method to displace petroleum-based LPG and BTEX.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional characterization of reaction products using GC, GC−MS, and H NMR of the liquid phase products; FT-IR and Al-NMR characterization of the local environment of Al in the zeolite catalyst. This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*J. Lauterbach. E-mail: lauteraj@cec.sc.edu. Tel: 1-803-777-7904. Fax: 1-803-777-8292.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106* (9), 4044−4098.

(2) Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411−2502.

(3) Huber, G. W.; Dale, B. E. Grassoline at the pump. *Sci. Am.* **2009**, *301* (1), 52−56.

(4) Nakagawa, Y.; Tomishige, K. Production of 1,5-pentanediol from biomass via furfural and tetrahydrofurfuryl alcohol. *Catal. Today* **2012**, *195* (1), 136−143.

(5) Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. Catalytic conversion of biomass to biofuels. *Green Chem.* **2010**, *12* (9), 1493−1513.

(6) Fitzpatrick, S. W. *Commercialization of the Biofine Technology for Levulinic Acid Production from Paper Sludge*; Report No. DOE/CE/41178; U.S. Department of Energy: Washington, DC, 2002; pp 1−271.

(7) Ding, D. Q.; Wang, J. J.; Xi, J. X.; Liu, X. H.; Lu, G. Z.; Wang, Y. Q. High-yield production of levulinic acid from cellulose and its upgrading to gamma-valerolactone. *Green Chem.* **2014**, *16* (8), 3846−3853.

(8) Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. *Green Chem.* **2013**, *15* (3), 584−595.

(9) Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. Integrated catalytic conversion of gamma-valerolactone to liquid alkenes for transportation fuels. *Science* **2010**, *327* (5969), 1110−4.

(10) Bozell, J. J.; Moens, L.; Elliott, D. C.; Wang, Y.; Neuenscwander, G. G.; Fitzpatrick, S. W.; Bilski, R. J.; Jarnefeld, J. L. Production of levulinic acid and use as a platform chemical for derived products. *Resour., Conserv. Recycl.* **2000**, *28* (3−4), 227−239.

(11) Gallezot, P. Conversion of biomass to selected chemical products. *Chem. Soc. Rev.* **2012**, *41* (4), 1538−1558.

(12) Chen, K. Y.; Koso, S.; Kubota, T.; Nakagawa, Y.; Tomishige, K. Chemoselective hydrogenolysis of tetrahydropyran-2-methanol to 1,6-hexanediol over rhenium-modified carbon-supported rhodium catalysts. *ChemCatChem* **2010**, *2* (5), 547−555.

(13) Li, M. X.; Li, G. Y.; Li, N.; Wang, A. Q.; Dong, W. J.; Wang, X. D.; Cong, Y. Aqueous phase hydrogenation of levulinic acid to 1,4-pentanediol. *Chem. Commun.* **2014**, *50* (12), 1414−1416.

(14) Liu, S.; Amada, Y.; Tamura, M.; Nakagawa, Y.; Tomishige, K. One-pot selective conversion of furfural into 1,5-pentanediol over a Pd-added Ir−ReO$_x$/SiO$_2$ bifunctional catalyst. *Green Chem.* **2014**, *16* (2), 617−626.

(15) Xu, W. J.; Wang, H. F.; Liu, X. H.; Ren, J. W.; Wang, Y. Q.; Lu, G. Z. Direct catalytic conversion of furfural to 1,5-pentanediol by hydrogenolysis of the furan ring under mild conditions over Pt/Co$_2$AlO$_4$ catalyst. *Chem. Commun.* **2011**, *47* (13), 3924−3926.

(16) Mizugaki, T.; Yamakawa, T.; Nagatsu, Y.; Maeno, Z.; Mitsudome, T.; Jitsukawa, K.; Kaneda, K. Direct transformation of furfural to 1,2-pentanediol using a hydrotalcite-supported platinum nanoparticle catalyst. *ACS Sustainable Chem. Eng.* **2014**, *2* (10), 2243−2247.

(17) Solomons, T. W. G. *Organic Chemistry*; Wiley: New York, 1996.

(18) Pellegrino, J. L. *Energy and Envionmental Profile of the U.S. Chemical Industry*; U.S. DOE: Washington, DC, 2000.

(19) French, R.; Czernik, S. Catalytic pyrolysis of biomass for biofuels production. *Fuel Process. Technol.* **2010**, *91* (1), 25−32.

(20) Carlson, T. R.; Vispute, T. P.; Huber, G. W. Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds. *ChemSusChem* **2008**, *1* (5), 397−400.

(21) Schwartz, T. J.; van Heiningen, A. R. P.; Wheeler, M. C. Energy densification of levulinic acid by thermal deoxygenation. *Green Chem.* **2010**, *12* (8), 1353−1356.

(22) Case, P. A.; van Heiningen, A. R. P.; Wheeler, M. C. Liquid hydrocarbon fuels from cellulosic feedstocks via thermal deoxygenation of levulinic acid and formic acid salt mixtures. *Green Chem.* **2012**, *14* (1), 85−89.

(23) Snelgrove, D.; Dupont, P.; Bonetto, R. D. *An investigation into the influence of LPG (autogas) composition on the exhaust emissions and fuel consumption of 3 bi-fuelled renault vehicles*; SAE Paper No. 961170; SAE International: Washington, DC, 1996.

(24) Qi, D. H.; Bian, Y. Z.; Ma, Z. Y.; Zhang, C. H.; Liu, S. Q. Combustion and exhaust emission characteristics of a compression ignition engine using liquefied petroleum gas-diesel blended fuel. *Energy Convers. Manage.* **2007**, *48* (2), 500−509.

(25) Bauer, F.; Persson, T.; Hulteberg, C.; Tamm, D. Biogas upgrading - Technology overview, comparison and perspectives for the future. *Biofuels, Bioprod. Biorefin.* **2013**, *7* (5), 499−511.

(26) Evans, R. J.; Milne, T. A. Molecular characterization of the pyrolysis of biomass, 1. Fundamentals. *Energy Fuels* **1987**, *1* (2), 123−137.

(27) Zhang, Q. W.; Li, X. H.; Asami, K.; Asaoka, S.; Fujimoto, K. Synthesis of LPG from synthesis gas. *Fuel Process. Technol.* **2004**, *85* (8−10), 1139−1150.

(28) Ge, Q. J.; Lian, Y.; Yuan, X. D.; Li, X. H.; Fujimoto, K. High performance Cu-ZnO/Pd-beta catalysts for syngas to LPG. *Catal. Commun.* **2008**, *9* (2), 256−261.

(29) Katikaneni, S. P. R.; Adjaye, J. D.; Bakhshi, N. N. Performance of aluminophosphate molecular-sieve for the production of hydrocarbons from wood-derived and vegetable-oils. *Energy Fuels* **1995**, *9* (6), 1065−1078.

(30) Idem, R. O.; Katikaneni, S. P. R.; Bakhshi, N. N. Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution. *Fuel Process. Technol.* **1997**, *51* (1−2), 101−125.

(31) Gayubo, A. G.; Aguayo, A. T.; Atutxa, A.; Valle, B.; Bilbao, J. Undesired components in the transformation of biomass pyrolysis oil into hydrocarbons on an HZSM-5 zeolite catalyst. *J. Chem. Technol. Biotechnol.* **2005**, *80* (11), 1244−1251.

(32) Benson, T. J.; Hernandez, R.; White, M. G.; French, W. T.; Alley, E. E.; Holmes, W. E.; Thompson, B. Heterogeneous cracking of an unsaturated fatty acid and reaction intermediates on H+ZSM-5 catalyst. *Clean* **2008**, *36* (8), 652−656.

(33) Sato, S.; Takahashi, R.; Yamamoto, N.; Kaneko, E.; Inoue, H. Vapor-phase dehydration of 1,5-pentanediol into 4-penten-1-ol. *Appl. Catal., A* **2008**, *334* (1−2), 84−91.

(34) Wojciechowski, B. W. The reaction mechanism of catalytic cracking: Quantifying activity, selectivity, and catalyst decay. *Catal. Rev.: Sci. Eng.* **1998**, *40* (3), 209−328.

(35) Tanabe, K.; Holderich, W. F. Industrial application of solid acid-base catalysts. *Appl. Catal., A* **1999**, *181* (2), 399−434.

(36) Ong, Y. K.; Bhatia, S. The current status and perspectives of biofuel production via catalytic cracking of edible and non-edible oils. *Energy* **2010**, *35* (1), 111−119.

(37) Katikaneni, S. P. R.; Adjaye, J. D.; Bakhshi, N. N. Studies on the catalytic conversion of canola oil to hydrocarbons - Influenece of hybrid catalysts and steam. *Energy Fuels* **1995**, *9* (4), 599−609.

(38) Prasad, Y. S.; Bakhshi, N. N.; Mathews, J. F.; Eager, R. L. Catalytic conversion of canola oil to fuels and chemical feedstocks, 1. Effect of process conditions on the performance of HZSM-5 catalyst. *Can. J. Chem. Eng.* **1986**, *64* (2), 278−284.

(39) Katikaneni, S. P. R.; Adjaye, J. D.; Bakhshi, N. N. Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts. *Can. J. Chem. Eng.* **1995**, *73* (4), 484−497.

(40) ASTM. *Standard Specification for Liquefied Petroleum (LP) Gases*; ASTM Standard D1835; ASTM International: West Conshohocken, PA, 2013.

(41) Sato, S.; Takahashi, R.; Kobune, M.; Inoue, H.; Izawa, Y.; Ohno, H.; Takahashi, K. Dehydration of 1,4-butanediol over rare earth oxides. *Appl. Catal., A* **2009**, *356* (1), 64−71.

(42) Sato, F.; Okazaki, H.; Sato, S. Dehydration of 1,5-pentanediol over rare earth oxides. *Appl. Catal., A* **2012**, *419*, 41−48.

(43) Borade, R.; Sayari, A.; Adnot, A.; Kaliaguine, S. Characterization of acidity in ZSM-5 zeolites - An X-ray photoelectron and IR spectroscopy study. *J. Phys. Chem.* **1990**, *94* (15), 5989−5994.

(44) Groen, J. C.; Moulijn, J. A.; Perez-Ramirez, J. Decoupling mesoporosity formation and acidity modification in ZSM-5 zeolites by sequential desilication-dealumination. *Microporous Mesoporous Mater.* **2005**, *87* (2), 153−161.

(45) Derouane, E. G.; Nagy, J. B.; Gabelica, Z.; Blom, N. An Al 27NMR investigation of ZSM-5 type zeolite aluminosilicate precursor species. *Zeolites* **1982**, *2* (4), 299−302.

(46) Fyfe, C. A.; Gobbi, G. C.; Hartman, J. S.; Klinowski, J.; Thomas, J. M. Solid state magic angle spinning Al 27 nuclear magnetic-resonance studies of zeolites using A 400-MHz high-resolution spectrometer. *J. Phys. Chem.* **1982**, *86* (8), 1247−1250.

(47) Gilson, J. P.; Edwards, G. C.; Peters, A. W.; Rajagopalan, K.; Wormsbecher, R. F.; Roberie, T. G.; Shatlock, M. P. Pentacoordinated aluminum in zeolites and aluminosilicates. *J. Chem. Soc., Chem. Commun.* **1987**, No. 2, 91−92.

(48) Samoson, A.; Lippmaa, E.; Engelhardt, G.; Lohse, U.; Jerschkewitz, H. G. Quantitative high-resolution Al 27 NMR -

Tetrahedral nonframework aluminum in hydrothermally treated zeolites. *Chem. Phys. Lett.* **1987**, *134* (6), 589−592.

(49) Sanz, J.; Fornes, V.; Corma, A. Extraframework aluminum in steam-dealuminated and SiCl$_4$-dealuminated Y-zeolite - A Al 27 and Si 29 nuclear magnetic resonance study. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 3113−3119.

(50) Rozwadowski, M.; Kornatowski, J.; Wloch, J.; Erdmann, K.; Golembiewski, R. Attempt to apply the fractal geometry for characterisation of dealuminated ZSM-5 zeolite. *Appl. Surf. Sci.* **2002**, *191* (1−4), 352−361.

(51) Zecchina, A.; Bordiga, S.; Spoto, G.; Marchese, L.; Petrini, G.; Leofanti, G.; Padovan, M. Silicalite characterization, 2. IR spectroscopy of the interaction of CO with internal and external hydroxyl groups. *J. Phys. Chem.* **1992**, *96* (12), 4991−4997.

(52) Woolery, G. L.; Kuehl, G. H.; Timken, H. C.; Chester, A. W.; Vartuli, J. C. On the nature of framework Bronsted and Lewis acid sites in ZSM-5. *Zeolites* **1997**, *19* (4), 288−296.