

Catalytic Conversion of Biomass-Derived Ethanol to Liquid Hydrocarbon Blendstock: Effect of Light Gas Recirculation

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Supporting Information

ABSTRACT: We describe a light gas recirculation (LGR) method to increase the liquid hydrocarbon yield with a reduced aromatic content from catalytic conversion of ethanol to hydrocarbons. The previous liquid hydrocarbon yield is ~40% from one-pass ethanol conversion over the V-ZSM-5 catalyst at 350 °C and atmospheric pressure, where the remaining ~60% yield is light gas hydrocarbons. In comparison, the liquid hydrocarbon yield increases to 80% when a simulated light gas hydrocarbon stream is co-fed at a rate of 0.053 mol g⁻¹ h⁻¹ with ethanol as a result of the conversion of most of the light olefins. The LGR also significantly improves the quality of the liquid hydrocarbon blendstock by reducing the aromatic content and overall benzene concentration. For 0.027 mol g⁻¹ h⁻¹ light gas mixture co-feeding, the average aromatic content in liquid hydrocarbons is 51.5% compared to 62.5% aromatic content in the ethanol only experiment. The average benzene concentration decreases from 3.75 to 1.5%, which is highly desirable because the United States Environmental Protection Agency (U.S. EPA) limits the benzene concentration in gasoline to 0.62%. As a result of a low benzene concentration, the blend wall for ethanol-derived liquid hydrocarbons changes from ~18 to 43%. The remaining light paraffins and olefins can be further converted to valuable benzene, toluene, and xylenes (BTX) products (94% BTX in the liquid) over Ga-ZSM-5 at 500 °C. Thus, the LGR is an effective approach to convert ethanol to liquid hydrocarbons with a higher liquid yield and low aromatic content, especially a low benzene concentration, which could be blended with gasoline in a much higher ratio than ethanol or ethanol-derived hydrocarbon blendstock.

1. INTRODUCTION

The successful introduction of biomass-derived ethanol as a transportation fuel has created a demand for ~14 billion gallons of ethanol per year. The ethanol market is at a saturation point in the transportation sector because its use is limited by the 10–15% blend wall as a result of technological and infrastructure constraints.¹ There have been efforts^{2–4} to convert ethanol into hydrocarbon blendstock that can be mixed with petroleum-derived fuels with less constraint, thereby increasing the use of biofuels to meet the requirements of the U.S. Energy Security Act of 2007, which mandates the use of 36 billion gallons of biofuel by 2022. This approach is especially desirable in view of anticipated cellulosic ethanol plants becoming operational in the near future, creating an excess supply of ethanol. The conversion of ethanol to ethylene is already commercial,^{5,6} and conversion to hydrocarbon blendstock has been successfully demonstrated at a laboratory scale.^{2–4} Efforts are in progress to scale up zeolitic catalytic conversion of ethanol to C₃₊ hydrocarbons for commercialization.^{7–9}

A typical stream from catalytic conversion of ethanol over M-ZSM-5 (M = H or metals) type catalysts contains C₂–C₁₂ hydrocarbons, and the yield of the light fraction (C₂–C₄) depends upon the catalysts and operating conditions.^{10,11} It is highly desirable to produce primarily C₅₊ hydrocarbons at distilleries from excess ethanol because the liquid hydrocarbons can be sent to a blender using the existing infrastructure for mixing with appropriate petroleum-derived streams to produce

gasoline, diesel, or jet fuels that meet United States Environmental Protection Agency (U.S. EPA) and ASTM requirements, e.g., olefins, total aromatics (28–32%), and benzene (0.62%).¹² Previous efforts to increase the C₅₊ fraction have focused on operating conditions and catalyst optimization, and yields as high as ~72% liquid have been reported. For example, Ramasamy and Wang¹³ have shown that the liquid hydrocarbon yield increases from 50 to 60% when the reactor pressure is increased from ambient pressure to 300 psi. Costa et al.¹⁴ showed that a 65% liquid yield is achieved with H-ZSM-5 at 20 bar and 400 °C with a weight hourly space velocity (WHSV) of 0.5 h⁻¹. Saha and Sivasanker¹⁵ also found that a 68% liquid yield was obtained with H-ZSM-5 at 360 °C and 10 bar with a WHSV of 1 h⁻¹. H-ZSM-5, after modifying with Zn and Ga, increased the liquid yield to 72% at 10 bar.¹⁵ For benzene reduction, alkylation of benzene at a high pressure has been attempted.^{16,17}

We have recently shown that biomass-derived aqueous ethanol can be quantitatively converted to a hydrocarbon blendstock at 350 °C and atmospheric pressure over V-ZSM-5 or InV-ZSM-5.⁴ We proposed that this occurred via a hydrocarbon pool mechanism. The light gas product stream (C₂–C₄) was rich in C₃ and C₄ hydrocarbons. Furthermore, the

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liquid product stream (C_{5+}) was low in paraffins and high in aromatics, leading us to consider mixing the blendstock with petroleum-derived paraffins to make it a fungible fuel. For this technology to be deployed at bioethanol production plants, it is necessary to minimize the light gas fraction to make liquid blendstock suitable for transportation by the existing infrastructure. Gasoline only requires ~2% butane summer blend and ~10% butane winter blend to achieve the required Reid vapor pressure.¹⁸ Here, deployment refers to a bolt-on catalyst unit that can be made operational when demand for ethanol decreases and biomass-derived fuel demand remains high. It is appropriate to mention that, while the technology to convert lights (C_2 – C_4) into alkylates exists,¹⁹ it is practical only at a large petrochemical refinery.

Now, we report that light gases, when co-fed with ethanol, can dramatically increase the liquid hydrocarbon yield and reduce the aromatic content of the product stream from the catalyst unit. In our approach, olefins in the light gas are converted to C_{5+} hydrocarbons on V-ZSM-5 and the unconverted C_3 and C_4 paraffins (propane, butane, and isobutane) are available for adjusting the Reid vapor pressure and vapor/liquid ratio.^{18,20} To simplify the operation and effectively understand the effect of lights co-feeding on the liquid product yield and liquid composition, we use a single pass-through method by co-feeding light hydrocarbons with ethanol on V-ZSM-5. This simulates a process scheme where the ethanol hydrocarbon products are split into lights and liquids and the lights are recycled. However, it should be obvious that multiple recycles of lights can be carried out during industrial-scale operations to further reduce C_2 – C_4 hydrocarbons in the final product stream. The light gas co-feeding does not require changes in operating conditions, and ethanol and lights can be converted to C_{5+} hydrocarbons over V-ZSM-5 at 350 °C and 1 atm.⁴ The decreased aromatics and benzene content in liquid hydrocarbons obtained from the light gas co-feeding makes this blendstock suitable for much higher blending into petroleum stream. The unreacted paraffins can be further converted to value-added benzene, toluene, and xylenes (BTX) over Ga-ZSM-5 at 500 °C and 1 atm.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. Commercial NH_4 -ZSM-5 (CBV2314) was purchased from Zeolyst Corporation and used as received. V-ZSM-5 was prepared by a previously described procedure.⁴ Briefly, a 0.05 M solution of $V(III)Cl_3$ was prepared by dissolving 2.5 g of $V(III)Cl_3$ into 320 mL of distilled water, and 12.17 g of NH_4 -ZSM-5 ($SiO_2/Al_2O_3 = 23$) was added. The reaction mixture was heated to 80 °C with stirring and kept at that temperature for 16 h. The reaction mixture was cooled to 25 °C and vacuum-filtered to collect a light blue powder, which was dried at 105 °C overnight. The powder was then calcined at 500 °C for 4 h, to obtain a light yellow V-ZSM-5 catalyst. Ga-ZSM-5 is synthesized using a similar procedure with $Ga(NO_3)_3$ as the precursor.

2.2. Catalytic Conversion of Ethanol. A quartz reactor (8 mm internal diameter $\times$ 25 cm height) was loaded with 0.2 g of catalyst (125–250 μm) between two layers of quartz wool. Two thermocouples were used to measure the gas inlet and catalyst bed temperatures. All of the reported temperatures in this paper are the catalyst bed temperature, unless stated otherwise. A tube furnace was used to heat the catalyst to the reaction temperature under a flow of a mixture of 45 cm^3/min helium and 5 cm^3/min nitrogen.

Pure ethanol (unless stated otherwise) was fed to the reactor at a rate of 0.4 mL/h (corresponding WHSV of 1.6 h^{-1} and feed rate of 0.034 $mol\ g^{-1}\ h^{-1}$) employing a syringe pump. After stabilization for 1.0 h, product analysis was performed by an online gas chromatograph

(GC, Agilent 7820A) employing a HP-Plot Q capillary column (dimension of 30.0 m $\times$ 320 μm $\times$ 20.0 μm) and a flame ionization detector (FID). The transfer line between the reactor and the GC/FID was heated to ~250 °C to prevent condensation of heavy products. For analysis, the GC was held at 50 °C for 3 min, ramped to 250 °C at 15 °C/min, and then held at that temperature for 35 min. A constant pressure mode of 9.51 psi was used, and the inlet temperature was 250 °C. A gas calibration mixture (6% ethylene, 3% propene, 3% propane, 2% *cis*-2-butene, 1.04% isobutene, 1000 ppm of isobutane, and balance nitrogen) was used to calibrate C_2 – C_4 hydrocarbons. Standards of benzene, toluene, *p*-xylene, ethylbenzene, and cumene were used to quantify aromatic compounds.

For light gas recirculation (LGR) experiments, a gaseous mixture of 6% ethylene, 3% propene, 3% propane, 1000 ppm of isobutane, 2% *cis*-2-butene, 1.04% isobutylene, and balance nitrogen was co-fed with 0.4 mL/h ethanol flow on V-ZSM-5. The total flow of He and light gas mixture remained at 50 cm^3/min for all of the experiments. Two different light gas mixture flow rates were used, 10 cm^3/min [ethanol equivalent (EE) feed rate of 0.027 $mol\ g^{-1}\ h^{-1}$] and 20 cm^3/min (EE feed rate of 0.053 $mol\ g^{-1}\ h^{-1}$). The EE feed rate was calculated by normalizing the lights to C_2 and employing the following equation:

$$EE\text{ feed rate} = \sum(\text{feed rate} \times \text{carbon number})/2 \quad (1)$$

All liquid hydrocarbon yields are based on ethanol for both pure ethanol and ethanol–lights co-feeding experiments.

The conversion of individual light gas is calculated based on

$$\text{conversion} = (v_{i,\text{feed}} - (v_{i,t,\text{co-feed}} - v_{i,t,\text{ethanol}}))/v_{i,\text{feed}} \quad (2)$$

where $v_{i,\text{feed}}$ is the individual gas i molar flow rate (mol/h) in the feed light gas, $v_{i,t,\text{co-feed}}$ is the individual gas i molar flow rate (mol/h) at time t in the product stream during the co-feeding experiment, and $v_{i,t,\text{ethanol}}$ is the individual gas i molar flow rate (mol/h) at time t in the product stream during the ethanol only experiment.

The ethanol-derived hydrocarbon blendstock blend wall or blending ratio is defined in eq 3, to achieve the gasoline requirement (aromatic content, benzene concentration, and olefin content)

$$\text{blend wall} = m_E/(m_E + m_G) \times 100\% = C_G/C_E \times 100\% \quad (3)$$

where m_E is the mass of ethanol-derived hydrocarbon blendstock, m_G is the mass of the gasoline fraction, C_G is the required component concentration in gasoline, and C_E is the component content in ethanol-derived hydrocarbon blendstock, e.g., aromatic content.

3. RESULTS AND DISCUSSION

For laboratory LGR experiments, we employed a simulated C_2 – C_4 light hydrocarbon mixture comprising 6% ethylene, 3% propene, 3% propane, 1000 ppm of isobutane, 2% *cis*-2-butene, 1.04% isobutylene, and balance nitrogen. This co-feeding of the light hydrocarbon mixture with ethanol models the LGR part of the system (schematics shown in Figure 1). In the LGR system, ethanol is fed into the first catalytic reactor over V-ZSM-5. We have previously published our work on ethanol conversion over V-ZSM-5. This catalyst was chosen as a result of its high oxydehydrogenation activity and its ability to produce lower ethylene.^{4,21,22} The addition of V onto H-ZSM-5 could also modify the acidity and inhibit the ethanol dehydration reaction. The products are separated with column 1 to condense C_{5+} hydrocarbons and water, and the light gas is recycled back to the first reactor via a gas compressor.

Part of the light gas flow (after the compressor) is fed to the second reactor with Ga-ZSM-5, which can convert the light paraffins (e.g., ethane, propane, and butanes) and remaining light olefins. The first reactor with V-ZSM-5 cannot convert light paraffins, resulting in gradual accumulation of the light paraffins in the post-reactor 1 stream. When the light paraffins in the recycle loop reach a certain concentration, the flow after

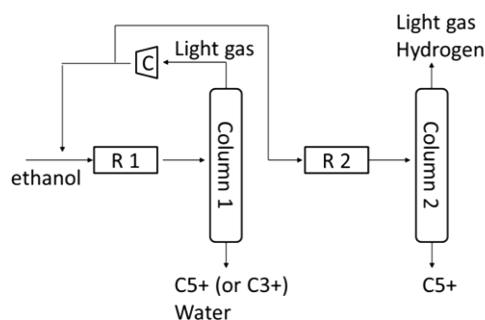


Figure 1. Schematic diagram of the LGR system: R1, first reactor with V-ZSM-5; column 1, first condensation column to separate C_{5+} (or C_{3+}) and water from light gas (C_2 – C_4); C, gas compressor; R2, second reactor with Ga-ZSM-5; and column 2, second condensation column to separate C_{5+} from light gas (C_2 – C_4) and hydrogen.

the compressor can be directed to reactor 2 to produce C_{5+} hydrocarbons or released from the system. Column 1 can also be operated to condense butanes or propane because they are important components in raising the Reid vapor pressure of gasoline, as mentioned in the [Introduction](#). For the whole system, only the external feed is ethanol, so that all of the liquid hydrocarbon yields are calculated on the basis of the ethanol feed for our light gas co-feeding experiment.

3.1. Light Gas Conversion over V-ZSM-5. We initiated this work by first carrying out the conversion of lights alone (EE feed rate of $0.027 \text{ mol g}^{-1} \text{ h}^{-1}$) over V-ZSM-5 at 350°C and atmospheric pressure to determine the extent of conversion under our previously optimized ethanol upgrading conditions.⁴

Our results show that high conversions of isobutylene (86%), 2-butene (93%), ethylene (86%), and propene (73%) are achieved on the fresh catalyst ([Figure 2a](#)). The liquid product yield is 30%, of which $\sim 70\%$ is aromatics, with toluene and xylenes being the major fractions ([Table S1](#) of the Supporting Information). There is minimal conversion of propane and isobutane; instead, more propane and isobutane are produced from olefin conversion ([Figure 2](#)). Olefin isomerization, oligomerization, aromatization, cracking, and hydrogen transfer reactions are some of the possible pathways for liquid hydrocarbon formation and light paraffin production that have been reported for light gas conversion over ZSM-5 catalysts.^{23–25}

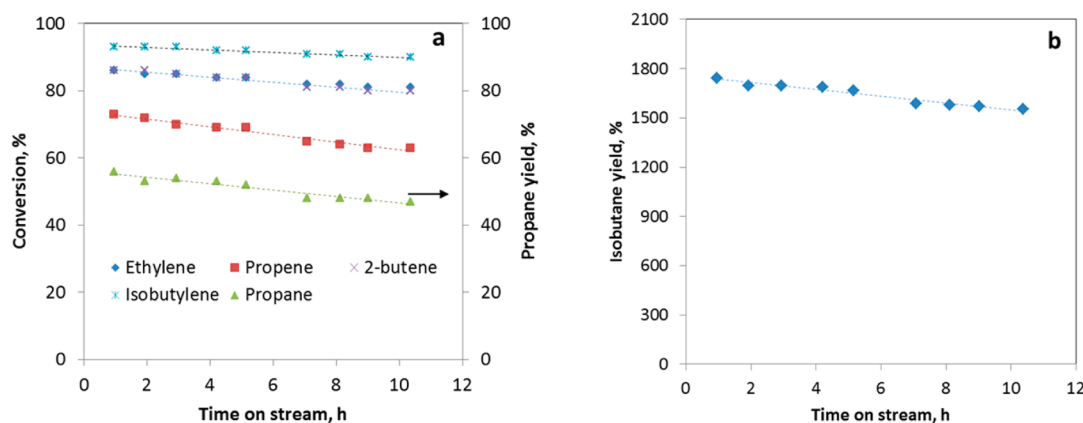


Figure 2. (a) Conversion of ethylene, propene, 2-butene, and isobutylene and yield of propane and (b) isobutane yield versus TOS with the EE feed rate of $0.027 \text{ mol g}^{-1} \text{ h}^{-1}$ on V-ZSM-5 at 350°C .

The conversion of olefins slightly decreases with time on stream (TOS) and drops to 80, 90, 81, and 63% for isobutylene, 2-butene, ethylene, and propene, respectively, over 10 h as a result of coking. As reported by us previously, decoking revives the original performance of the catalyst.⁴ Thus, olefins in the lights can be converted to C_{5+} hydrocarbons under the ethanol conversion conditions, while paraffins remain unconverted. The increased concentration of C_3 and C_4 paraffins in the product stream suggests that olefins also produce C_3 and C_4 paraffins along with C_{5+} hydrocarbon stream.

3.2. LGR with Ethanol over V-ZSM-5. The conversion of ethanol over V-ZSM-5 with an ethanol feed rate of $0.034 \text{ mol g}^{-1} \text{ h}^{-1}$ at 350°C and ambient pressure is quantitative ([Figure S1](#) of the Supporting Information), and the product stream contains $\sim 40 \text{ wt } \%$ liquid hydrocarbons (C_{5+} hydrocarbons) ([Figure 3](#)). The ethanol conversion and liquid product yield do

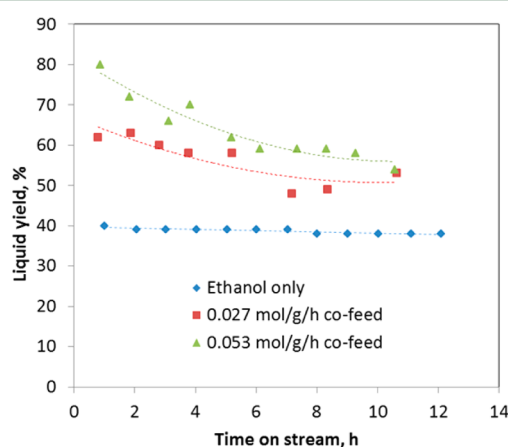


Figure 3. C_{5+} liquid hydrocarbon yield for ethanol only feed ($0.034 \text{ mol g}^{-1} \text{ h}^{-1}$) and lights co-feed at 0.027 and $0.053 \text{ mol g}^{-1} \text{ h}^{-1}$ with $0.034 \text{ mol g}^{-1} \text{ h}^{-1}$ ethanol over V-ZSM-5 at 350°C .

not change much over 12 h ([Figure S1](#) of the Supporting Information and [Figure 3](#)). Co-feeding the light gas mixture at a rate of $0.027 \text{ mol g}^{-1} \text{ h}^{-1}$ with $0.034 \text{ mol g}^{-1} \text{ h}^{-1}$ ethanol leads to an increase in the C_{5+} hydrocarbon yield (on the basis of ethanol) to $\sim 63\%$, which gradually decreases to 53% over 10 h. If the lights are fed at a rate of $0.053 \text{ mol g}^{-1} \text{ h}^{-1}$, the C_{5+} hydrocarbon yield of 80% is obtained after 1 h on stream,

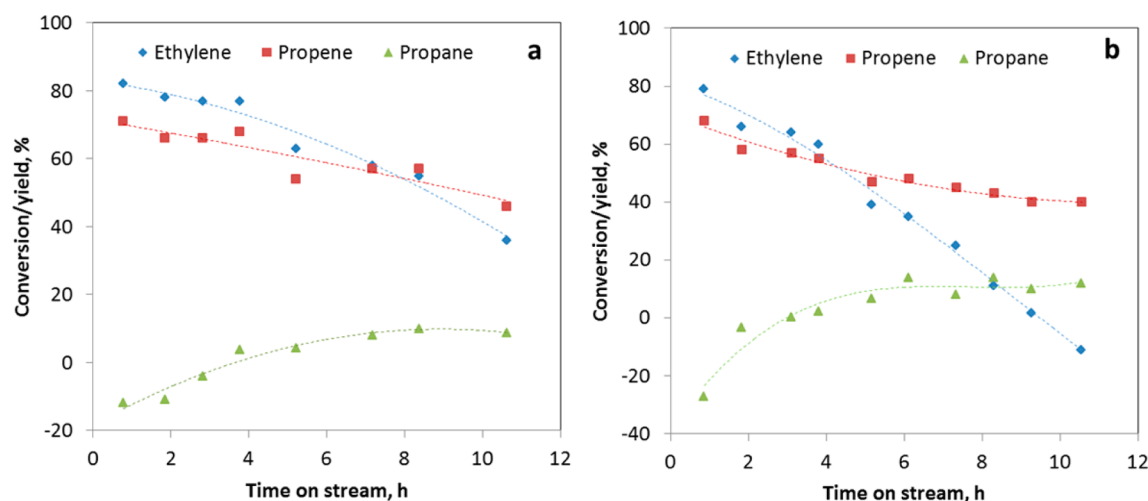


Figure 4. Conversion of ethylene and propene and the yield of propane for (a) 0.027 mol g⁻¹ h⁻¹ and (b) 0.053 mol g⁻¹ h⁻¹ co-feeding gas with 0.034 mol g⁻¹ h⁻¹ ethanol over V-ZSM-5 at 350 °C.

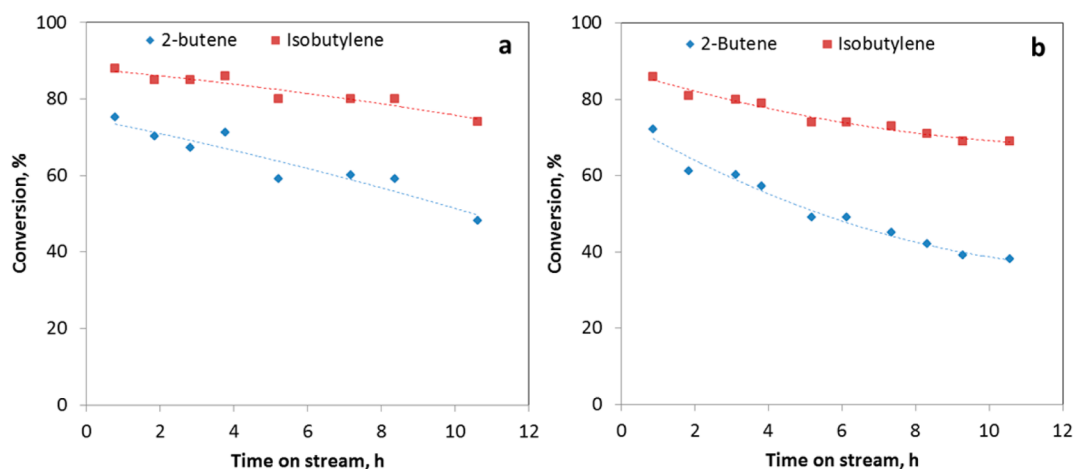


Figure 5. Isobutylene and 2-butene conversion for (a) 0.027 mol g⁻¹ h⁻¹ and (b) 0.053 mol g⁻¹ h⁻¹ co-feeding gas with 0.034 mol g⁻¹ h⁻¹ ethanol over V-ZSM-5 at 350 °C.

which slowly decreases to ~54% C₅₊ over 10 h on stream. Among individual components of light gases, ethylene conversion on fresh catalyst is 82% but decreases to 36% only over 10 h at 0.027 mol g⁻¹ h⁻¹ co-fed light gas (Figure 4a). Similarly, propylene conversion changes from 71 to 46%. The product stream shows 12% more propane after 10 h TOS than that from input stream; it must have been formed from olefin conversion because alkanes do not convert under these conditions.

At a higher co-feeding rate of 0.053 mol g⁻¹ h⁻¹, the trend is very similar, except ethylene conversion drops more dramatically and there is no ethylene conversion at 9 h TOS. These changes in conversion are due to catalyst coking, which tends to be faster under increased flow of light gas hydrocarbons. Isobutane also does not convert to C₅₊, and the product stream shows more isobutane than the input stream (Figure S2 of the Supporting Information). For pure ethanol feed, the amount of *n*-butane stays at ~6% but isobutane is 23% at the beginning and gradually decreases to 19% over 12 h (Figure S2 of the Supporting Information). The total butanes in the products are ~25% at 12 h. As discussed in the Introduction, propane and butanes are desirable products that can be mixed in gasoline to achieve the required Reid vapor pressure. Thus, a fraction of

these butanes can still be added to the liquid hydrocarbon blendstock, and excess butanes could be further converted to liquid hydrocarbons, which will be discussed later.

The C₄ olefins, isobutylene and 2-butene, exhibit 88 and 75% conversion at 0.027 mol g⁻¹ h⁻¹ feed rate and then decrease to 74 and 48% over 10 h (Figure 5a). At the feed rate of 0.053 mol g⁻¹ h⁻¹, the conversions for isobutylene and 2-butene are 86 and 72%, which decrease to 69 and 38% over 10 h (Figure 5b).

3.3. Impact of LGR on Liquid Hydrocarbon (C₅₊) Composition.

The changes in paraffins, olefins, aromatics, and benzene content in the liquid stream from ethanol, light gas stream, and LGR with ethanol from fresh catalyst to 10 h TOS are summarized in Table S2 of the Supporting Information. Paraffins do not vary much, while olefins and aromatics are sensitive to the feed streams. The conversion of pure ethanol over V-ZSM-5 produces liquid hydrocarbons containing 24% paraffins, 9% olefins, and 68% aromatics that change to 24, 15, and 61%, respectively, over 12 h (average of 24% paraffins, 12% olefins, and 65% aromatics) (Figure 6). Normally gasoline contains 26–32% aromatics and less than 9–11% olefin.²⁶ If this ethanol-derived hydrocarbon blendstock is to be blended to produce gasoline, it will require petroleum-derived paraffins in an approximately 1:1 ratio to meet the gasoline regulatory

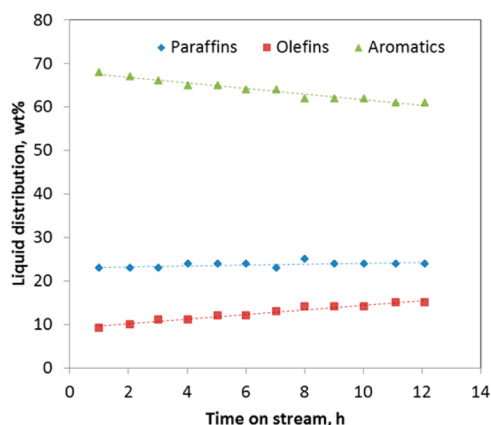


Figure 6. Liquid hydrocarbon composition with only ethanol ($0.034 \text{ mol g}^{-1} \text{ h}^{-1}$) as the feed over V-ZSM-5 at 350°C .

requirements. A fraction of C_3 and C_4 paraffins from ethanol conversion can be mixed in the 2–10% range to achieve the correct Reid vapor pressure for summer or winter blends.^{18,20}

For $0.027 \text{ mol g}^{-1} \text{ h}^{-1}$ light gas co-feeding, paraffins are in the 25–28% range, olefins increase from 15 to 30% (average of 22.5%), and aromatics decrease from 58 to 45% (average of 51.5%) (Figure 7a). In comparison to ethanol only as feed, the average olefin yield increases from 12 to 22.5% and the average aromatic yield decreases to 51.5% (21% decrease). For $0.053 \text{ mol g}^{-1} \text{ h}^{-1}$ light gas mixture co-feeding, paraffins remained in the 20–26% range over 11 h. The increase in olefins from 18 to 53% (average of 35.5%) is accompanied by a concurrent decrease in aromatics from 59 to 26% (average of 42.5%) (Figure 7b).

Another important consideration is the benzene concentration in the product stream, which is now subject to regulatory limits of 0.66–1.0% in most of the countries.²⁷ The benzene concentration in the C_{5+} stream from ethanol is 4.7%, which decreases to 2.8% over 12 h (average value of 3.75%) (Figure 8). A 5.6 times dilution with petroleum stream is needed (4.6:1 petroleum/ethanol-derived hydrocarbons) to meet benzene regulatory requirements. Thus, the benzene-based blend wall (defined in eq 3) for ethanol-derived hydrocarbon blendstock will be $\sim 18\%$.

Light gas co-feeding ($0.027 \text{ mol g}^{-1} \text{ h}^{-1}$) decreases the benzene concentration to 2.1% at 1 h TOS, which gradually

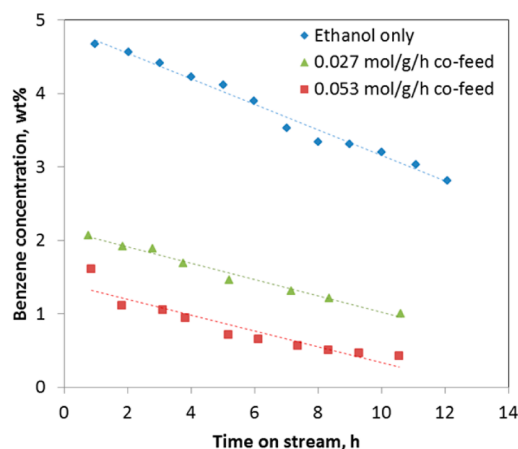


Figure 8. Benzene concentration in the liquid (C_{5+}) hydrocarbon for ethanol only, $0.027 \text{ mol g}^{-1} \text{ h}^{-1}$ and $0.053 \text{ mol g}^{-1} \text{ h}^{-1}$ light gas co-feeding with $0.034 \text{ mol g}^{-1} \text{ h}^{-1}$ ethanol on V-ZSM-5 at 350°C .

decreases to 1.0% at 10.6 h TOS (average of 1.5%). This decrease in benzene moves the blend wall for the ethanol-derived blendstock from ~ 18 to 43%. When $0.053 \text{ mol g}^{-1} \text{ h}^{-1}$ light gas is co-fed, the benzene concentration drops below 0.6% from 1.6% at the start of the run after 7 h TOS (average of 1.0%). However, olefins become another limiting factor (average olefins of 35.5%), and the ethanol-derived hydrocarbon blend wall decreases to $\sim 25\%$. As a result of the ease of olefin hydrogenation, this hydrocarbon blendstock can be easily hydrogenated to increase the paraffin content and increase the blending ratio.

The alkylation of benzene and toluene appears to be responsible for the decrease in the benzene concentration in the blendstock, which occurs with a concurrent decrease of toluene and an increase in C_{9+} aromatics (Table 1) because co-feeding operating conditions match well with alkylation conditions reported in the literature.²⁸ For example, Panagiotis and Eli²⁸ have shown that gas-phase alkylation of benzene and toluene with ethylene over ZSM-5 can occur between 200 and 470°C at ambient pressure. At 350°C , benzene and ethylene showed 65.7 and 94.8% conversion at WHSV of 4.3 h^{-1} . Alkylation of benzene with propylene to produce cumene has also been demonstrated on the ZSM-5 catalyst.¹⁶

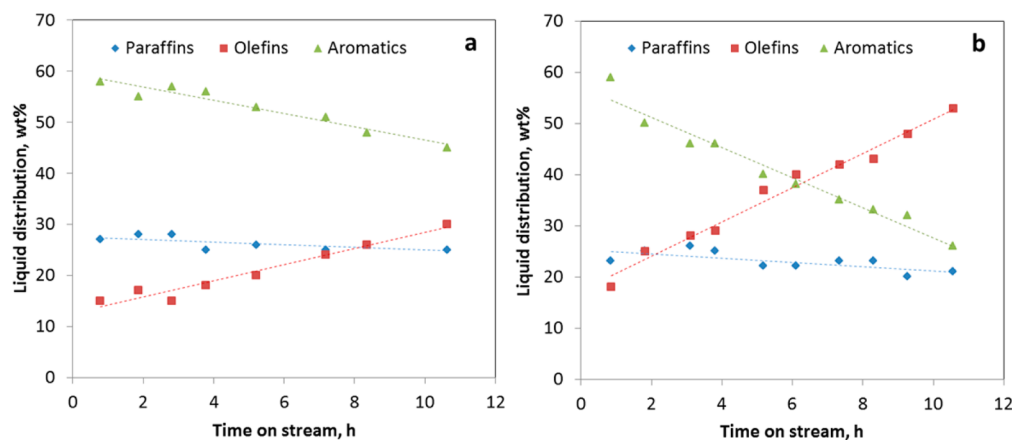


Figure 7. Liquid hydrocarbon composition for (a) $0.027 \text{ mol g}^{-1} \text{ h}^{-1}$ light gas and (b) $0.053 \text{ mol g}^{-1} \text{ h}^{-1}$ light gas co-feeding with $0.034 \text{ mol g}^{-1} \text{ h}^{-1}$ ethanol on V-ZSM-5 at 350°C .

Table 1. Aromatic Distributions in Total Liquid Hydrocarbons at 1 h TOS

	ethanol only	light gas co-feeding	
	0.034 mol g ⁻¹ h ⁻¹	0.027 mol g ⁻¹ h ⁻¹	0.053 mol g ⁻¹ h ⁻¹
benzene (wt %)	4.68	2.1	1.6
toluene (wt %)	24.0	15.3	13.4
ethylbenzene (wt %)	3.0	3.5	3.3
xylene (wt %)	24.0	20.2	21.2
C ₉₊ (wt %)	12.4	17.5	19.1

Thus, light gas co-feeding with ethanol not only improves the liquid yield but also leads to decreased aromatics and benzene, thereby changing the blend wall for the liquid hydrocarbons to 43%. However, the product stream contains a higher concentration of C₃–C₄ paraffins than necessary for adjusting the Reid vapor pressure. The conversion of excess paraffins to C₅₊ hydrocarbons is described in the following section.

3.4. Light Gas Conversion over Ga-ZSM-5. As discussed in the preceding section, even though C₃ and C₄ alkanes are valuable for preparing gasoline blends, it is still desirable to decrease the C₃–C₄ alkanes to <10%, which is the upper limit of light alkanes needed for gasoline blends. We find that both alkenes and alkanes can be converted to C₅₊ hydrocarbons over Ga-ZSM-5, which has been reported to be an active catalyst for light paraffin (propane, ethane, etc.) conversion.^{29,30} For our work, we carried out light gas conversion with a feed rate of 0.013 mol g⁻¹ h⁻¹ at 500 °C and ambient pressure for 4 h. The conversion of various components in the light gas feed is summarized in Table 2. Even after 4 h on stream, the

Table 2. Light Gas Mixture Conversion with 0.2 g of Ga-ZSM-5 (6.8% Ga Loading), 0.013 mol g⁻¹ h⁻¹ Light Gas Mixture Flow at 500 °C

TOS (h)	conversion (%)					
	ethylene	propene	propane	isobutane	2-butene	isobutylene
0.4	86	94	91	100	100	100
1.9	75	87	81	90	100	100
4.0	52	73	42	96	99	99

conversion of C₄ remains high but the conversion of ethylene drops from 95 to 52% and that of propene drops from 94 to 73%. Thus, a second catalytic reactor with Ga-ZSM-5 can be used to convert light paraffins and residual olefins into liquid hydrocarbons (R2 in Figure 1), leading to an increased total liquid hydrocarbon yield and a decreased light gas fraction.

The liquid product stream from light gas conversion over Ga-ZSM-5 is primarily aromatics, with benzene and toluene being the dominant fractions (Table 3). Both xylenes and C₉₊ increase with an increase in TOS. This liquid hydrocarbon stream is obviously not suitable for direct blending with

Table 3. Liquid Hydrocarbon Composition with 0.2 g of Ga-ZSM-5 (6.8% Ga Loading), 0.013 mol g⁻¹ h⁻¹ Light Gas Mixture Flow at 500 °C

TOS (h)	liquid composition (wt %)			
	benzene	toluene	xylenes	C ₉₊
0.4	47	41	7	6
1.9	35	38	24	4
4.0	30	39	11	21

petroleum stream to make fuels without distillation to separate benzene but can be used to produce more valuable BTX products.

3.5. Advantages of LGR. The primary advantage of LGR is that it increases the liquid hydrocarbon yield and improves the quality of the hydrocarbon blendstock. On the basis of 60% liquid yield, 36.6 kg of C₅₊ hydrocarbons can be obtained from 100 kg of ethanol using the first reactor with recirculation (Figure S3a of the Supporting Information). The rest of the carbon is converted to lights (C₂–C₄ olefins and paraffins). Water (39 kg) is produced as a byproduct. The second reactor (R2 in Figure S3a of the Supporting Information) can produce an additional 17 kg of BTX by employing Ga-ZSM-5 and can reduce lights to 7.4 kg.

Without LGR, 220 kg of ethanol is needed to produce 53.6 kg of C₅₊ hydrocarbon blendstock over V-ZSM-5 (on the basis of 40% liquid yield) (Figure S3b of the Supporting Information). To accommodate more than twice the feed rate, the size of R1 and column 1 will need to be increased 2-fold, leading to increased capital, input stream, and operating cost. For LGR, the second reactor, R2, will be rather small because 75% of products (C₅₊ hydrocarbons and water) from ethanol are collected after R1.

A second benefit of LGR is that superior hydrocarbon blendstocks can be produced. The first hydrocarbon stream has a proper aromatic and benzene level, which allows for much higher blending into gasoline. The second stream is concentrated in BTX, which, after separation, will be valuable commodity chemicals. However, without LGR, the liquid hydrocarbon blendstock is constrained by high benzene content, high aromatics, and low paraffins, limiting the blending level in gasoline. Overall, the LGR presents a cost-effective technology to produce a high liquid yield with better quality.

4. CONCLUSION

We have demonstrated that the LGR could significantly improve the liquid hydrocarbon yield, with most of the light olefins being converted to liquid hydrocarbons. At 0.053 mol g⁻¹ h⁻¹ light gas co-feeding rate, the maximum liquid yield reaches 80%, which is twice that of the liquid products from pure ethanol. Furthermore, the LGR also decreases benzene and aromatic contents, thereby bringing the blendstock closer to gasoline requirements. Overall, the compositions of the liquid hydrocarbons obtained from the co-feeding experiments are significantly different from those obtained from pure ethanol feed or light gas, with higher paraffins and olefins and lower aromatics and benzene. The blend wall for the produced blendstock is ~43%, which is much higher than the current blend wall for ethanol at 10–15%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b02562.

Additional data, including liquid composition from light gas conversion (Table S1), ethanol conversion (Figure S1), isobutane yield (Figure S2), liquid composition from different feeds (Table S2), and overall mass balance comparison (Figure S3) (PDF)

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Notes

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The authors declare the following competing financial interest(s): The technology described in this work is licensed to Vertimass, LLC, and two of the authors (Chaitanya K. Narula and Brian H. Davison) are minority owners of Vertimass, LLC.

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