PNNL-33695

A 100+RON Gasoline Blendstock for High Efficiency, Low Emission Vehicles Engines - CRADA 493 (Final Report)

November 2022

Vanessa Lebarbier Dagle

Lanza Tech, Inc

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: November 2022

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions, to be provided to PNNL Information Release who will forward to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement:

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Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, Washington 99354

CRADA number: 493

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Responsible Technical Contact at DOE Lab: Trevor Smith

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DOE Program Office: Bioenergy Technologies office

Joint Work Statement Funding Table showing DOE funding commitment:

Funding from DOE to PNNL	Project Year 1	Project Year 2	Project Year 3	Project Year 4	Project Year 5	TOTALS
	200	100	0	0	0	300

Executive Summary

This study aimed at demonstrating production of a 100+RON gasoline fraction from a linear olefins feedstock to help improve further the viability and flexibility of the Pacific Northwest National Laboratory/ LanzaTech alcohol-to-jet (ATJ) patented process that converts ethanol from LanzaTech's syngas fermentation process to low aromatic jet-range iso-paraffins. To achieve a high RON gasoline and ultimately a 100+RON, the technical approach consisted of converting the linear olefins into an iso-olefins rich mixture and then oligomerizing the iso-olefins rich mixture into high RON compounds in a single bed loaded with an acid catalyst that allows conversion at low reaction temperature.

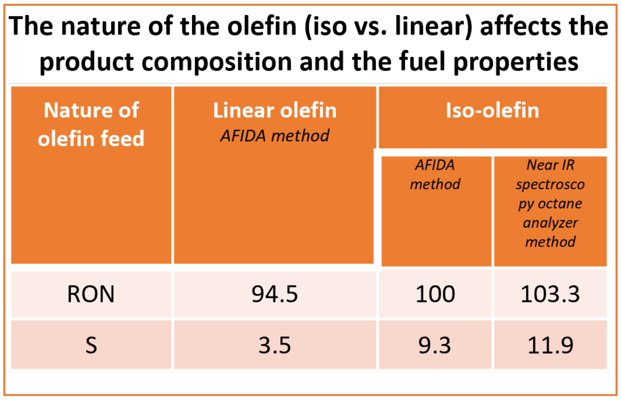
Three families of acid catalysts labeled as type A, B and C were investigated for the single-bed conversion of linear olefins into high RON gasoline range compounds. The effects of the nature of the catalyst, acid sites concentration and operating conditions were investigated. Fuel properties measurements and engine testing were conducted for the most promising catalyst. For type A catalysts, we demonstrated that the conversion increases with the increase of the Brönsted acid site concentration and that lower reaction temperature favors the formation of desired highly branched compounds. The highest dRON obtained with type A catalyst was equal to 94 (from NMR and IQT). Type B catalysts appear very effective for producing dimethyl-olefins compounds when operating at low reaction temperature (i.e., < 100°C). The highest dRON obtained with type B catalyst was equal to 92. The results suggest that type B catalysts are less favorable to internal conversion of linear olefins into iso-olefins compared to type A catalysts which leads to the formation of a gasoline blendstock with a lower dRON. A Type C catalyst that is less commonly used for production of gasoline range compounds from linear olefins was investigated due to its ability to favor conversion of linear olefins into iso-olefins. Compared to type A and type B catalyst, type C favors the formation of highly branched compounds (i.e., with 3+ methyl groups) in the gasoline range. Indeed, a gasoline blendstock containing about 33 wt.% of highly branched compounds was produced with type C catalyst while maintaining a high linear olefins conversion (i.e., 70%). A large quantity of this gasoline blendstock was produced and fuel properties measurements including engine testing for Research Octane Number (RON), Motor Octane Number (MON) and octane sensitivity (S) were conducted. A high RON = 97, MON = 82.7, S =14.3, AKI = 90 and HoV = 334.1kJ/kg were measured. While a RON of 100 was not achieved, the fuel properties of the gasoline blendstock are very acceptable as compared to current premium gasoline. Overall, these results highlight the potential for producing a high RON/ premium gasoline blendstock starting from a linear olefins feedstock.

Summary of Research Results

"This product contains Protected CRADA Information, which was produced on [May 2021-September 2022] under CRADA No. [493] and is not to be further disclosed for a period of five (5) years from the date it was produced except as expressly provided for in the CRADA."

Background

The Pacific Northwest National Laboratory (PNNL)/ LanzaTech alcohol-to-jet (ATJ) patented process converts ethanol from LanzaTech's syngas fermentation process to low aromatic jet-range iso-paraffins. The process produces compounds with a wide range of boiling points. Demonstrating production of a high RON/ premium gasoline fraction could help improve further the viability and flexibility of the ATJ process. To achieve a high Research Octane Number (RON) gasoline range blendstock, production of highly branched compounds from light olefins oligomerization is needed. Previously, PNNL demonstrated that a 100 RON gasoline product can be obtained from oligomerization of an iso-olefin feed (see Figure 1). However, a RON of only 94.5 was obtained using a linear olefin feedstock in prior work by PNNL.



The nature of the olefin (iso vs. linear) affects the product composition and the fuel properties

Nature of olefin feed	Linear olefin *AFIDA method*	Iso-olefin	
		AFIDA method	*Near IR spectroscopy octane analyzer method*
RON	94.5	100	103.3
S	3.5	9.3	11.9

Figure 1. RON and octane sensitivity (S) of gasoline range mixtures from iso-olefin and linear olefin feedstock. S = RON-MON.

Approach

To achieve a high RON gasoline and ultimately a 100+RON, the technical approach consisted of converting the linear olefins into an iso-olefins rich mixture and then oligomerizing the iso-olefins rich mixture into high RON compounds in a single reactor loaded with a single catalyst. Single-bed, continuous flow processing studies were performed using acid catalysts at low reaction temperature. Indeed, a previous study from PNNL had found that decreasing the reaction temperature favors conversion of linear olefins into iso-olefins which leads to an increase of the RON at the expense of a conversion loss. At low reaction temperature, the challenge is to obtain a high RON (target 100+RON) gasoline blendstock at reasonable single pass conversion for the process to be carbon efficient.

Results

Three families of acid catalysts labeled as type A, B and C were investigated for the single-bed conversion of linear olefins into high RON gasoline range compounds. The effects of the nature of the catalyst and operating conditions were investigated. Fuel properties measurements and engine testing were conducted for the most promising catalyst. Here, we report the results obtained for each type of catalyst.

A. Type A catalyst

Impact of the acidity on the olefins conversion

The reaction for conversion of linear olefins into gasoline range compounds is catalyzed by acid sites. Both the type of acid (Brönsted vs. Lewis) and the concentration of the acid sites can impact catalyst performance. Thus, we measured the acidity of catalysts using lutidine (i.e., 2,6 dimethylpyridine) adsorption/desorption followed by Fourier Transform Infrared spectroscopy (FTIR). Figure 2 presents the infrared spectra recorded for each catalyst after desorption of lutidine at 350°C between 1670–1500 cm^{-1}. One doublet at 1644 and 1636 cm^{-1} and a band at 1551 cm^{-1} characteristic of protonated lutidine are seen but no bands characteristic of coordinated lutidine at ~1602cm^{-1}, ~1595 cm^{-1}, and ~1580 cm^{-1} are detected.[1]

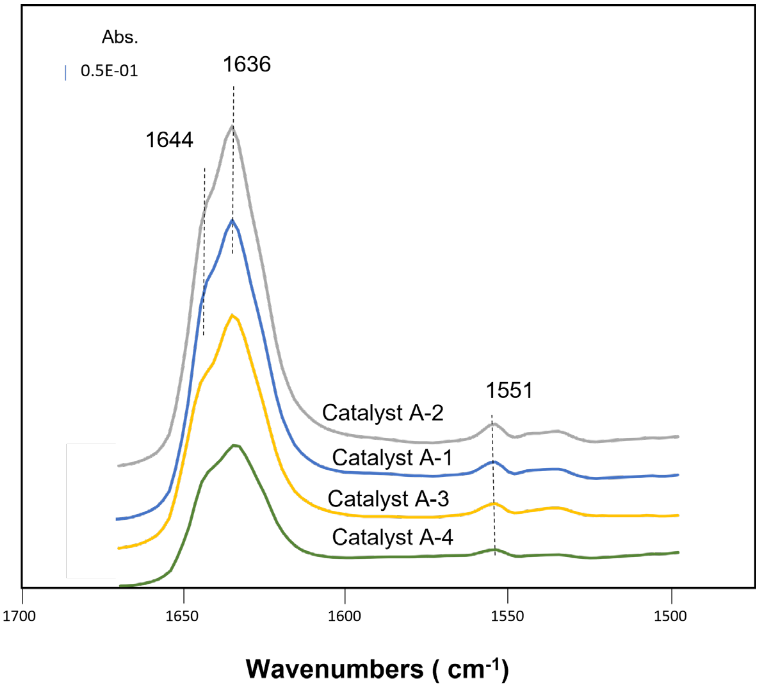


Figure 2. Infrared spectra recorded after lutidine desorption at 350°C between 1670–1500 cm^{-1}. Spectra are normalized to a 20 mg pellet with a surface of 2 cm^2.

The concentration of the Brönsted acid sites was measured using Beer Lambert-law (i.e., A = Ɛlc) with Ɛ = 6.8 cm/μmole.[2] The results presented in Table 1 show that the concentration of the acid sites increases as follows: A-4< A-3< A-1< A-2.

Table 1. Concentration of Brönsted acid sites for A-1, A-2, A-3 and A-4

Catalyst	Brönsted acid sites concentration after lutidine desorption at 350°C (μmoles. g^{-1})
A-1	98.3
A-2	114.1
A-3	79.5
A-4	48.6

Operating at low reaction temperature is critical to favor internal conversion of linear olefins into iso-olefins prior to oligomerization to desired high-RON olefins in one single step/ reactor. However, the conversion level needs to remain as high as possible when decreasing the reaction temperature. Hence, we tested the reactivity of the 4 catalysts to identify catalyst(s) that would allow reasonable conversion while operating at relatively low temperature (i.e., < 140°C). As shown in Figure 3, catalysts A-1 and A-2 present high conversion (i.e., 50-60%) as compared to catalysts A-3 and A-4 for which conversion is < 15%. The four catalysts present high selectivity to dimethyl-olefins (i.e., 68–90%). However, the selectivity to the most desired highly branched olefins (3+ methyl groups) is below 6%. The selectivity to di-alkyl olefins is the highest for catalyst A-1 and A-3 and equal to 12-15%.

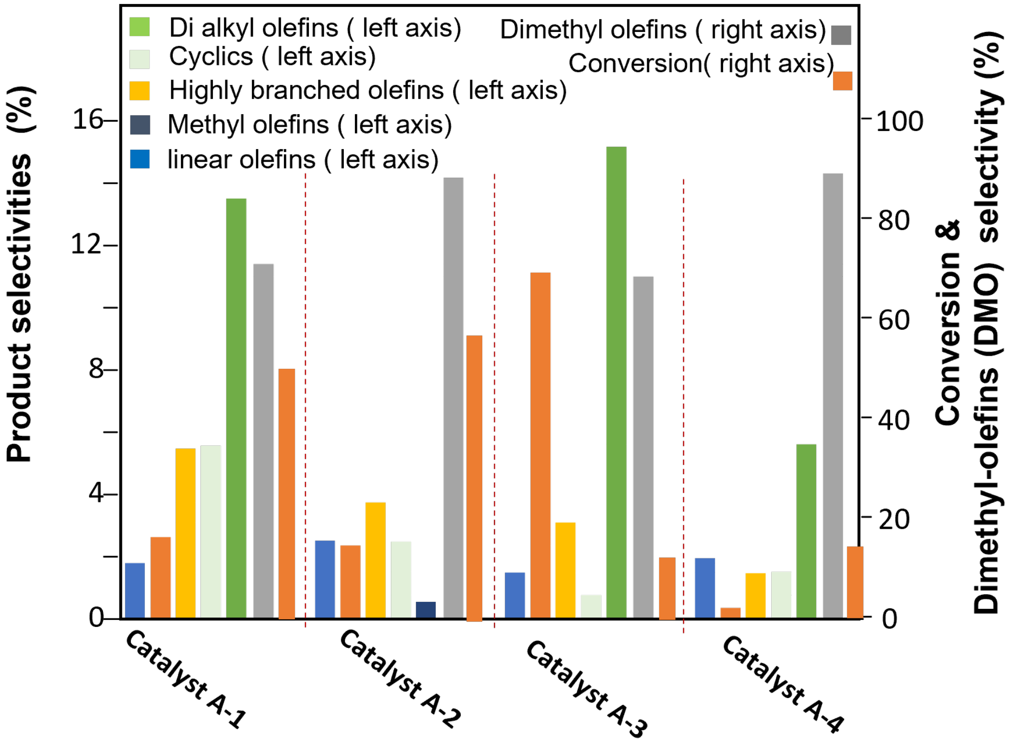


Figure 3. Conversion and products selectivity for linear olefins conversion over type A catalysts. All catalysts were tested under the same temperature, pressure, and space velocity.

Establishing the relationship between olefins conversion and acidity can be used as a tool to understand surface property requirements and help identify a preferred catalyst. Figure 4 presents the evolution of the conversion with the Brönsted acid site concentrations. As can be seen, the conversion is directly related to the number of acid sites and higher concentrations of Brönsted acid sites is beneficial. These results indicate that to further increase the conversion while operating at low temperature (<140°C) a type A catalyst with a Brönsted acid site concentration >120 μmoles g^{-1} is needed.

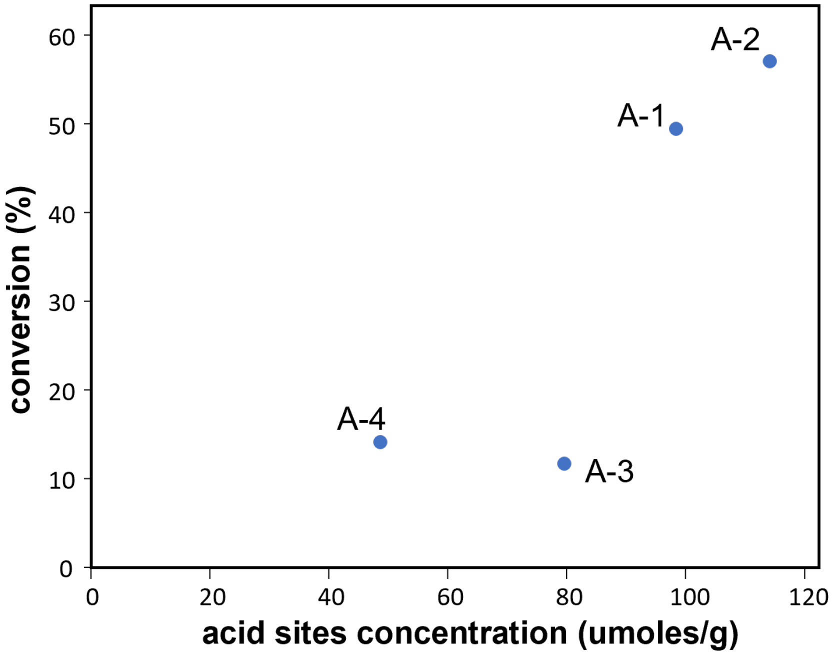


Figure 4. Evolution of linear olefins conversion as a function of the Brönsted acid site concentrations.

Given that catalyst A-1 presents high conversion and highest selectivity to the most desired compounds it was selected for additional testing where the reaction temperature was varied.

Effect of the reaction temperature on the product distribution and RON

The catalytic performance of catalyst A-1 was measured at four reaction temperatures T1, T2, T3 and T4 (<140°C), at same pressure and same space velocity. The initial conversion (i.e., Time on stream, TOS = 24 hours) decreases with the decrease of temperature from 44.8% at T1 to 22.9% at T3. We note that no conversion was detected at T4. After ≥ 70 hours on stream, the conversion at T1 is about twice higher than that at T2 and T3. Interestingly, the conversion at T2 and T3 is quite similar and equal to ~18%.

Table 2. Effect of the reaction temperature on the conversion of linear olefins to gasoline range compounds. Same pressure and same space velocity over catalyst A-1.

sample	Temperature (°C)	Initial conversion (%) TOS = 24 hours	Average conversion T = 70-120 hours	dRON	
				NMR	IQT
OL-T1	T1	44.8	42.6	92.3	91.7
OL-T2	T2	31.5	18.0	94.1	93.3
OL-T3	T3	22.9	18.3	94.3	94.0
	T4	No conversion	No conversion		

The analytical composition of each gasoline cut (i.e., OL-T1, OL-T2, and OL-T3) obtained after distillation was examined using gas chromatography-mass spectrometry. The composition of the gasoline blendstock obtained at T2 and T3 (see Figure 5) is quite similar. The gasoline blendstock obtained at T1 distinguishes itself from the others due to a slightly higher amount of moderately branched olefins (i.e., dimethyl olefins) of 90% as opposed to 86-87% and a lower amount of highly branched olefins of 86% as opposed to 89-90% for the gasoline blendstock obtained at T2 and T3. The derived RON (dRON) estimated from nuclear magnetic resonance and IQT is higher for sample OL-T2 and OL-T3 and equal to about 94 as compared to 92 for sample OL-T1. Hence, the decrease in reaction temperature for A-1 catalyst favors the formation of highly branched compounds leading to an increase of the RON.

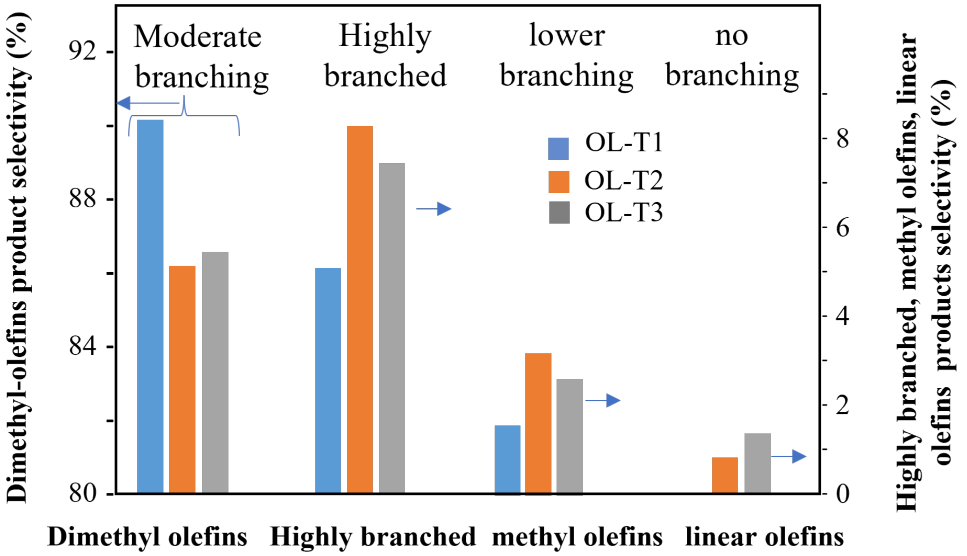


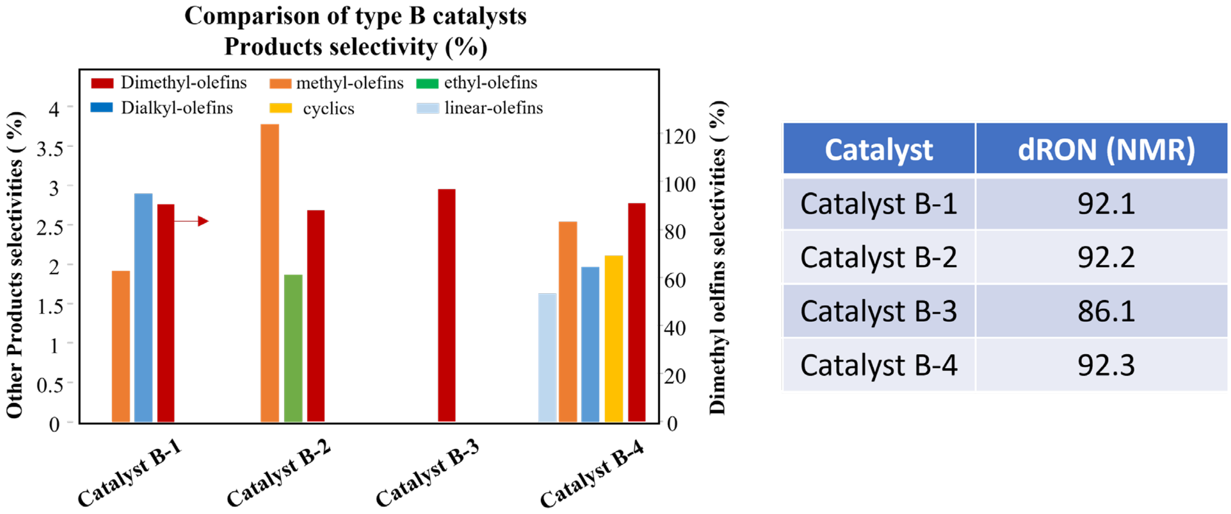
Figure 5. Composition of the gasoline range samples obtained from conversion of linear olefins into gasoline range compounds (after distillation) at different temperatures.

For type A catalysts, we demonstrated that the conversion increases with the increase of the Brönsted acid site concentration and that lower reaction temperature favors the formation of desired highly branched compounds. The highest dRON obtained with type A catalyst was equal to 94 (from NMR and IQT).

B. Type B catalyst

Given that operating at low reaction temperature appeared to increase the RON for type A catalysts, a series of 4 type B catalysts typically active at low reaction temperature (i.e., ≤ 100°C) were tested for linear olefins conversion to gasoline range compounds. Compared to type A catalysts, type B catalysts did not favor the formation of the highly branched compounds. As shown in Figure 6, highly branched compounds (with 3+ methyl groups) were not detected and di-alkyl olefins selectivity remained below < 4%. The dRON estimated via NMR was equal to ~92 for all catalysts expect B-3 for which the dRON was equal to ~86.

Overall, type B catalysts appear very effective for producing dimethyl-olefins (mainly dimethyl-hexenes) compounds when operating at low reaction temperature (i.e., < 100°C). The results suggest that they are less favorable to internal conversion of linear olefins into iso-olefins compared to type A catalysts.



Catalyst	dRON (NMR)
Catalyst B-1	92.1
Catalyst B-2	92.2
Catalyst B-3	86.1
Catalyst B-4	92.3

Figure 6. Product selectivity obtained for type B catalysts operated under the same reaction conditions (temperature, pressure and space velocity) and dRON estimated using NMR.

C. Type C catalyst

Type C catalyst is not commonly used for production of gasoline range compounds from linear olefins as compared to type A or type B catalysts but its ability to favor conversion of linear olefins into iso-olefins is well known. The stability profile shown in Figure 7 demonstrates the robustness of type C catalyst since no deactivation was observed for 200 hours on stream. The conversion for type C catalyst is relatively high and equal to ~70% when operated at temperature < 200°C.

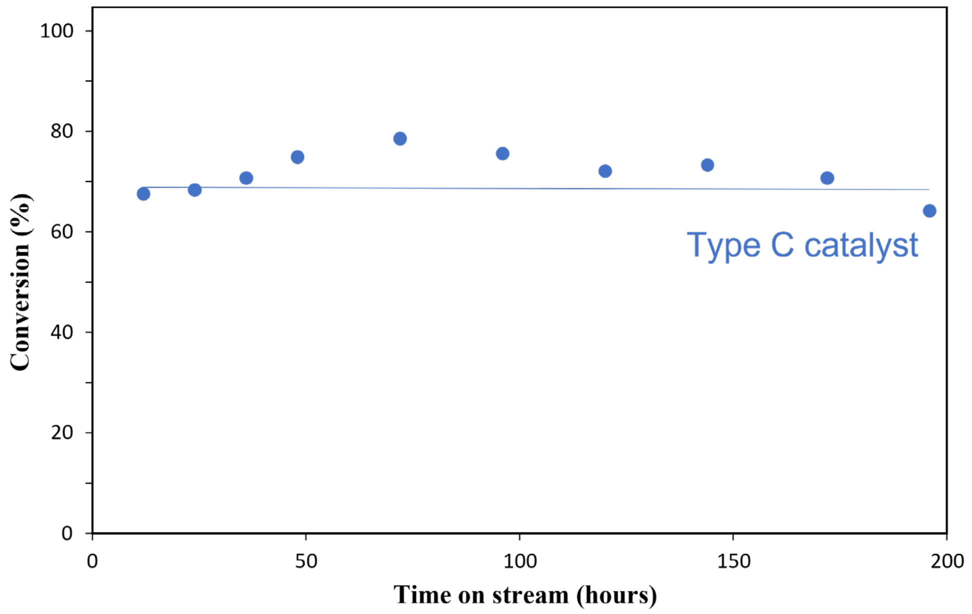
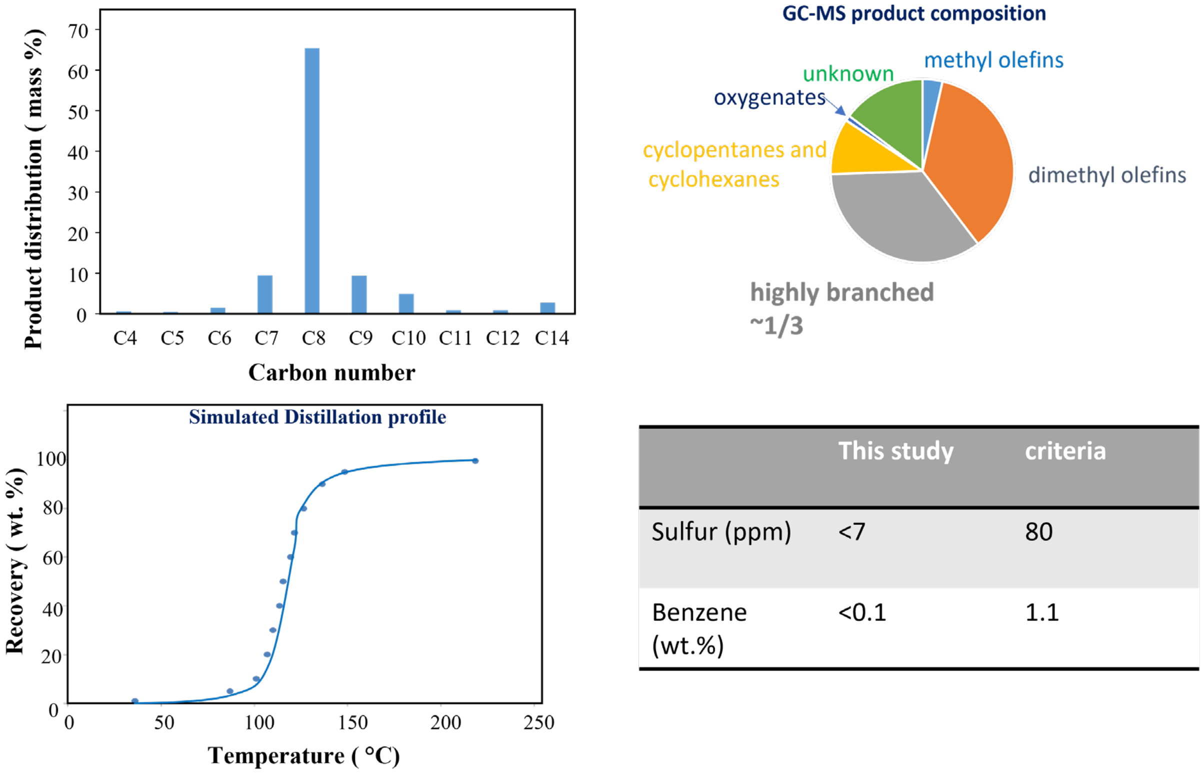


Figure 7. Stability profile for linear olefins conversion over type C catalyst.

After distillation, the composition of the gasoline blendstock was examined by GC-MS. The results displayed in Figure 8 indicate that the product is rich in C_8 and contains about 1/3 of highly branched compounds (i.e., high RON compounds). The fraction of highly branched compounds is significantly higher than that produced over type A and type B catalysts. These results suggest that type C catalyst favors the internal conversion of linear olefins to iso-olefins prior to oligomerization.

Sulfur contributes to air pollution, it is a precursor of acid rain and it produces large molecules in the air that trigger asthma. Given the negative impacts of sulfur, its level is regulated, and currently the maximum level allowed is 80 ppm at refinery (ASTM D4814-21c). The sulfur content of the gasoline blendstock measured by Inductively Coupled Plasma Mass Spectroscopy was found to be lower than 7ppm which is well below the maximum requirement. This result is not surprising because the olefins feed is of high purity. Benzene is typically added to gasoline to increase its octane rating but its concentration in the gasoline fuel must be limited (< 1.3 vol.%, equivalent to 1.1 wt.%) due to its toxicity. Thus, it would be beneficial to obtain a high RON gasoline blendstock without benzene addition. In the present study, the aromatic content presented in Figure 8 is below 0.1 wt. % which is well below the maximum limit.



	This study	criteria
Sulfur (ppm)	<7	80
Benzene (wt.%)	<0.1	1.1

Figure 8. Composition of the gasoline range product in weight % obtained from linear olefins conversion over type C catalyst.

The RON estimated via IQT was equal to 98 which is attributed to the high concentration of highly branched compounds. Given the high RON obtained with type C catalyst a larger quantity of gasoline blendstock was produced to conduct engine testing and measure the RON, MON (motor octane number), AKI ([RON+MON]/2) and S (RON-MON). The heat of vaporization was also determined because it was identified as a one of the 3 most critical parameters (along with RON and S) indicative of the performance and efficiency of a gasoline range fuel for combustion engines. This is illustrated in Figure 9 copied from reference [3].

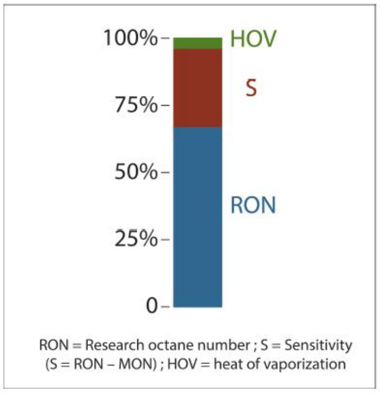


Figure 9. Average contribution to the merit function for the eight highest scoring Tier 2 blendstocks from reference [3]

Table 3 presents the fuel properties results in comparison with a conventional premium gasoline. While a RON of 100 was not achieved, the RON is still high and equal to 97 (engine). The MON is lower (i.e., 82.7) and the resulting S is high and equal to 14.3. The gasoline blendstock presents an AKI = 90 and is thus within specifications (ASTM D4814-10b). The HoV measured at 25°C is equal to 334.1kJ/kg and is comparable to the one for conventional gasoline. [3,4]

Table 3. RON, MON, S, AKI and HoV for the gasoline blendstock produced from n-butene oligomerization over Type C catalyst compared with conventional premium winter gasoline [3].

Grade	**This study**	Conventional Premium winter
RON	97 (engine) 98 (IQT)	93.7
MON	82.7	87.3
AKI (RON+MON)/2	90	90.5
S (RON-MON)	14.3	6.4
HoV (kJ/kg)	334.1	346.7
Density (g/mL)	NA	0.727

According to the merit function estimates from reference [5] a blendstock with RON = 98 and S = 12 can potentially contribute to about 7.5% fuel economy. Thus, the gasoline blendstock (RON = 97, S -14.3) obtained with catalyst type C has potential for improving the engine efficiency and the fuel economy.

Conclusion

Three type of acid catalysts were investigated for conversion of linear olefins into high RON gasoline blendstock. It was found that the production of highly branched/ high RON compounds varies greatly depending on the nature of the catalyst, the concentration of the acid sites and the reaction temperature. A preferred acidic catalyst that favors the formation of highly branched compounds (i.e., with 3+ methyl groups) in the gasoline range was identified. A large quantity of gasoline blendstock containing about ~ 30% of highly branched compounds was produced using this preferred catalyst and fuel properties measurements including engine testing for RON, MON and S were conducted. A RON= 97, MON = 82.7, S =14.3, AKI = 90 and HoV = 334.1kJ/kg were measured. While a RON of 100 was not achieved, these results highlight the potential for producing a high RON/ premium gasoline blendstock starting from a linear olefins feedstock.

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