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One-Step High-Yield Production of Fungible Gasoline Blend Stocks and High-Value Chemical Coproduct (BTEX) from Ethanol without Added Hydrogen

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February 28, 2019

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Energy and Transportation Science Division
Materials Science and Technology Division
Environmental Sciences Division
Bioscience Division

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ABSTRACT

The overall objective of this Cooperative Research and Development Agreement (CRADA) project between Oak Ridge National Laboratory (ORNL) and Vertimass LLC is to develop data and documentation needed to support process guarantees and Engineer-Procure-Construct (EPC) packages suitable for process commercialization. The specific tasks, deliverables, and milestones are organized in such a way to this project that supplies as much information as possible about the catalyst performance, lifetime, and operating space to minimize risk upon scale-up. Vertimass LLC licensed a revolutionary new class of catalyst technology from ORNL that directly converts ethanol with or without water into gasoline, jet, and diesel fuel blendstocks and high-value chemicals (BTEX, Benzene, Toluene, Ethylbenzene, and Xylenes) without adding hydrogen. Through this CRADA project, Vertimass seeks to build from the solid baseline established by ORNL with the goal of developing the key information needed for rapid scale-up.

ORNL was responsible for: 1) technology transfer of catalyst and reactor as well as synthesizing catalysts for Vertimass LLC, 2) extended runs to determine how varying water levels impact catalyst performance and lifetime, 3) assess hydrocarbon partitioning to the water byproduct and appropriate treatment, and 4) optimize catalyst regeneration. These studies were performed in the lab-scale flow reactor at ORNL (flows typically 0.4 mL/hour ethanol). ORNL has found that the presence of water has minimal impact on the product distribution for both V-ZSM-5 and Ga-ZSM-5 though may impact catalyst deactivation. For Ga-ZSM-5 with low Si/Al ratio (20-25), the product selectivity change is very small over 200 h extended run with pure ethanol feed. When increasing the water co-feeding (reactor inlet water vapor concentration is 36%), significant product selectivity changes are observed probably due to the instability of the aluminum in this type of high aluminum zeolite. This finding provides guidance of developing high Si/Al zeolite (>50) which typically increases catalyst stability in the presence of water. We found that there were trace amounts of hydrocarbons in the water fraction (amounts ~500 ppm) and this water byproduct can be directly used for fermentation without further treatment. Vertimass

and TechnipFMC have been working together on the majority of DOE Award DE-EE0006875 in parallel to ORNL's supporting work. The team had the following major accomplishments in moving this technology towards commercialization from the original technology: 1) successful technology transfer from lab scale to pilot scale; 2) increase liquid yield from original 36% to 80+%; 3) advance from lab powder to commercial catalyst formulations.

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1. STATEMENT OF OBJECTIVES

The aim of the CRADA collaboration is to develop the data and documentation needed to support process guarantees and EPC packages suitable for process commercialization. To complete this goal, ORNL (contractor) performed several tasks, in collaboration and continuous consultation with Vertimass LLC (participant):

The participant key plans and tasks under this project include:

- Engineering design of unit operations
- Scale-up to pilot
- Operate the engineering design unit to establish long term catalyst(s) performance, regeneration strategies, and lifetime for design and further scale-up
- 1000 h catalyst test
- Validate industrially robust catalysts
- Produce more blend-stocks for blending for certification tests for gas, diesel, and jet
- Close mass and energy balances
- Perform blending to proceed into certifications for gasoline, diesel and jet fuels
- Develop partners for engineering design, catalyst manufacture, co-siting of pilot tests
- Integrate design into cellulosic ethanol refinery and compare with corn refinery

Specific Contractor (ORNL) tasks include:

- Extended runs (~200h) with varying levels of hydrous ethanol to determine water impact on performance and to perform hydrocarbon measurements in produced water to assess treatment issues
- Optimize catalyst regeneration cycle time
- The Participant will also share project data from the Participant for interpretation by the Contractor staff. The Contractor will also participate as required in DOE validation and Go/No-Go evaluations.

The focus of this work is to obtain data needed for commercialization of this technology. The specific tasks, deliverables, and milestones are organized such that this project supplies as much information as possible about the catalyst performance, life, and operating space to minimize risk upon scale-up. While investigating these parameters, it is also critical to produce renewable gasoline *Vertifuel blend-stock* to prove long-term results and produce quantities of fuel for testing.

2. BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

Successful project completion made the technology widely available for licensing to the emerging commercial cellulosic ethanol industry, eliminating the ethanol blend wall that stymies growth. It also opened new markets for ethanol in heavy-duty vehicles and air travel. Additionally, DOE funding avoided diluting management and potential distractions of the primary mission to rapidly develop, widely license, and deploy this technology to achieve widespread benefits that support DOE missions.

This proposed project can have major impacts on the renewable fuels by transforming ethanol into fungible components with conventional fuels, thereby overcoming the ethanol blend wall that limits current markets and opening new jet and diesel fuel markets. Converting ethanol to fungible hydrocarbons will help meet renewable fuel targets (Renewable Fuels Standard 2, RFS2) that are in jeopardy due to fungibility issues. The Federal Aeronautics Administration (FAA) also has a goal for use of 1 billion gallons of renewable jet fuel by 2018. Adoption of Vertimass technology promises to overcome these challenges by providing a rapidly deployable simple bolt-on operation with low capital and operating costs to produce hydrocarbons that are totally fungible with conventional fuels to assist in achieving RFS2 and FAA goals. Thus, the catalyst can accelerate market entry for worldwide ethanol production from cellulosic biomass (e.g., corn stover, poplar wood, switchgrass) without competing with current corn ethanol on cost, a potentially major barrier to the emergence of this important technology that has the potential for about 100 billion gallons in the U.S. alone. Transforming ethanol into fungible hydrocarbon fuels can also make it possible to transport the fuel through current pipelines and usage practices.

Additional benefits include:

- Allow introduction of biofuels into new fuel markets, significantly expanding its reach,
- Be widely deployable to support build-out of cellulosic ethanol,
- Provide the military with a new source of fuel that reduces their strategic vulnerability and reduce greenhouse gas emissions and oil imports from unstable regions of the world.

3. TECHNICAL DISCUSSION OF WORK PERFORMED

3.1 Background and Tasks

Vertimass LLC licensed a revolutionary new class of hetero-bimetallic catalyst technology from Oak Ridge National Labs (ORNL) that directly converts ethanol with or without water into gasoline, jet fuel, and diesel fuel blendstocks and high-value BTEX chemical coproducts without adding hydrogen. This unique catalytic technology has a technical, operational, market, and economic benefits compared to other renewable fuel technologies and previous attempts for direct alcohol conversion to hydrocarbons. Through this CRADA project, Vertimass seeks to build from the solid baseline established by ORNL with the goal of developing the key information needed for rapid commercial scale-up.

ORNL recently created a family of novel catalysts that convert 100% of ethanol with varying levels of water into gasoline, diesel, and jet fuel blendstocks at approximately 90+% of theoretical yield, with the rest being an ethylene co-product. Additionally, this was accomplished without hydrogen addition in contrast to all similar technologies. Furthermore, conversion is completed in one step versus multiple steps for competitors, operates at relatively moderate temperatures and atmospheric pressure, and produces very little light components (i.e., ethylene and C_3 compounds). All these important attributes compared with previous attempts to convert ethanol into hydrocarbon drew Vertimass to license and develop this process.

Although these catalyst improvements are novel and certainly open the door for economic conversion of ethanol to hydrocarbons, at this start of the CRADA work was still needed to further develop these catalysts, minimize scale-up risk, and certify the blend stocks for target markets. Vertimass teamed with TechnipFMC as experts in rapidly developing and scaling up novel catalytic technology. TechnipFMC is experienced in guaranteeing commercial scale-ups from EDU results, a critical step for Vertimass. Vertimass worked with both ORNL and Technip to further advance the catalysts and build the foundation for rapid scale-up.

To build the foundation from which to next design and build commercial operations, Vertimass contracted with ORNL to 1) perform extended runs to determine how varying water levels impact catalyst performance and lifetime, 2) optimize catalyst regeneration cycle times, and 3) assess hydrocarbon partitioning to the water byproduct and appropriate treatment. Here is the work breakdown structure of the tasks.

Task 1: Perform extended runs with varying levels of water in ethanol to determine how water impacts catalyst performance and soluble fuel losses. (ORNL)

The goal of this task was to do extended runs with varying levels of hydrous ethanol to establish how the amount of water impacts catalyst performance and hydrocarbon losses in the water to support scale-up and evaluate feed locations for Vertimass bolt-on. Basically, this task included the following work.

- Extended runs with varying levels of water in ethanol feed: water impact on V-ZSM-5 and Ga-ZSM-5 (impact on product distribution, and catalyst stability)
- Measurement of hydrocarbons within the produced water phase (this determined the potential impact for hydrocarbon loss in produced water)
- Confirmation testing of vendor-supplied catalysts: this subtask tests the vendor supplied catalysts to confirm the product yields, product distributions and water effect on these catalysts.

Task 2: Optimize the catalyst regeneration cycle times. (ORNL)

The goal of this task was to optimize the catalyst regeneration times to maximize product outputs and overall returns in conjunction with the techno-economic model.

Task 3: Isothermal operation for process and catalyst characterization. (TechnipFMC)

The goal of this task was to employ an isothermal Engineering Development Unit (EDU) to develop baseline data that will facilitate the definition of industrially relevant operating conditions, catalyst features and loadings, regeneration strategies, and reactor configurations.

Task 4: Development and validation of robust industrial catalysts (TechnipFMC)

The goal of this task was to focus on working with a commercial catalyst manufacturer to develop and provide catalyst samples and prove it is robust for operation at industrial conditions.

Task 5: Complete adiabatic EDU operation to establish long-term catalyst performance, regeneration strategies, and lifetime and employ data for Design Basis Memorandum scale-up the platform. (TechnipFMC)

This task focused on developing key data in TechnipFMC's adiabatic reactors using the industrially robust catalyst developed in Task 4 to support specification of commercial reaction conditions that can be employed to scale up the technology to commercial operations.

Task 6: Integrate catalyst into ethanol production and optimize cost (Vertimass)

The results from Tasks 1-5 were used to determine how to best fit the catalytic operation into an ethanol plant.

3.2 Relevance and outcomes

Application of the technology is outlined in Figure 1 (left side). Ethanol from starch, cane sugar, or cellulosic biomass is currently recovered and purified by distillation and dehydration to remove water and other fermentation components. The ethanol concentration increases as it moves up a distillation column until it nears the azeotrope of about 94% ethanol in water. At that point, the mixture is sent to a molecular sieve dehydration unit to remove remaining water and achieve "fuel grade" specifications of 1% or less residual water.

Ethanol produced from corn starch, cane sugar, or cellulosic biomass is recovered and purified for fuel by distillation and dehydration, as shown on the left. The new catalytic technology would convert wet ethanol into fungible hydrocarbon fuel components and eliminate the need for ethanol dehydration and possibly some of the distillation column. The right side of Figure 1 illustrates how this novel Vertimass technology can be bolted on to an ethanol process in place of the dehydration unit and converts azeotropic ethanol to hydrocarbon fuel components for blending with jet, diesel, and gasoline. Thus, part of the distillation operation could be eliminated for new Greenfield plants. Alternatively, because the catalyst can function well with even higher water levels, the catalytic reactor could replace part of the rectification column, thereby reducing its size if the satisfactory heat exchanger is employed. The small size and simplicity of the catalytic unit result in low capital and operating costs that realize high returns on capital investment. Furthermore, there will be energy savings at the plants.

This unique technology has many important technical, operational, and economic benefits compared to other renewable fuel technologies and previous attempts for direct alcohol conversion to hydrocarbons. As noted in the discussion above and Figure 1, the catalyst could eliminate the dehydration unit and possibly part of distillation for new Greenfield plants. And the bolt-on configuration of a preheat exchanger, catalytic converter, and decanter to phase separate the products results in low capital and operating costs. Because Vertimass now has 3 distinct catalysts to convert renewable ethanol into gasoline, jet fuel, or diesel blendstocks. This bolt-on provides the renewable ethanol producers the optionality to make 3 fuel products plus ethanol and quickly shift among them to meet market demands and maximize financial returns. The ability to cost-effectively convert ethanol to other renewable fuels would overcome the ethanol blend wall barrier and allow much greater production of renewable biofuels in the US that directly address BETO goals. Vertimass licensed this novel technology because we believe it provides the lowest cost route to sustainable hydrocarbon fuels compared to other options and has the potential to lower plant energy usages and water demands.

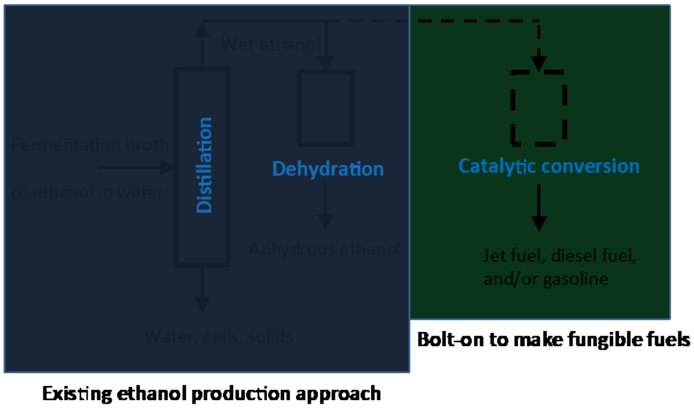


Figure 1: Schematic diagram of the production of ethanol from corn starch, cane sugar or cellulosic biomass.

4. RESULTS

4.1. Task 1: Extended run

4.1.1 Water impact on product distributions and catalyst stability

In this task, ORNL has performed extended runs to determine how water impacts the catalyst performance and soluble fuel losses. All studied catalysts were synthesized with H-ZSM-5 of Si/Al ratio 11.5, high Al content. First of all, impacts on product distribution due to the presence of water were studied by varying the concentrations of water in the stream.

~~(Protected CRADA Information)~~

Table 1: Water impacts on product distributions for V-ZSM-5. Conditions: V-ZSM-5 and temperature 350 °C. The ethanol flow rate was kept constant by varying water concentration. The total inert flow was maintained at 50 ml/min (He balance with vapor H_2O). LHSV= liquid hourly space velocity

%v/v	**%v/v**	**LHSV**				**Based on Liquid C5+, %**		
H_2O	**EtOH**	**h^{-1}**	**C3-C11**	C2	**Liquid**	**Paraffin**	**Olefin**	**Aromatic**
0	100	2.4	89	11	35	24	20	56
10	90	2.4	88	11	35	27	19	56
20	80	2.4	90	9	37	25	17	58
30	70	2.4	88	11	35	25	19	56
40	60	2.4	92	7	38	33	15	58
60	40	2.4	95	4	38	35	14	51

Table 1 summarizes the water impact on product distributions over V-ZSM-5. It is noticed that water content (0-60 %) does not have a significant impact on product distribution. The amounts of liquid C5+ yield is similar. The liquid composition (paraffin, olefins and aromatics selectivity) also remains similar for water content up to 30 v%. As water content increased above 40%, we observed a slight increase in paraffin, a decrease of olefins and aromatics.

We also performed extended runs to understand water impact on catalyst stability. Even though no water was co-fed with ethanol, one ethanol converted generates one water, so there is significant water in the catalyst bed (water vapor concentrations at the end of catalyst bed are ~3%, ~7%, ~16% for LHSV of 0.8, 1.6 and 3.9 respectively) with water vapor concentration increasing along the catalyst bed. Figure 2 shows the extended runs for V-ZSM-5 at three different LHSV with different water vapor concentrations in the catalyst bed. As shown in Figure 2, water does not have a significant impact on catalyst stability and regenerability at 350 ºC in the presence of different water vapor concentrations.

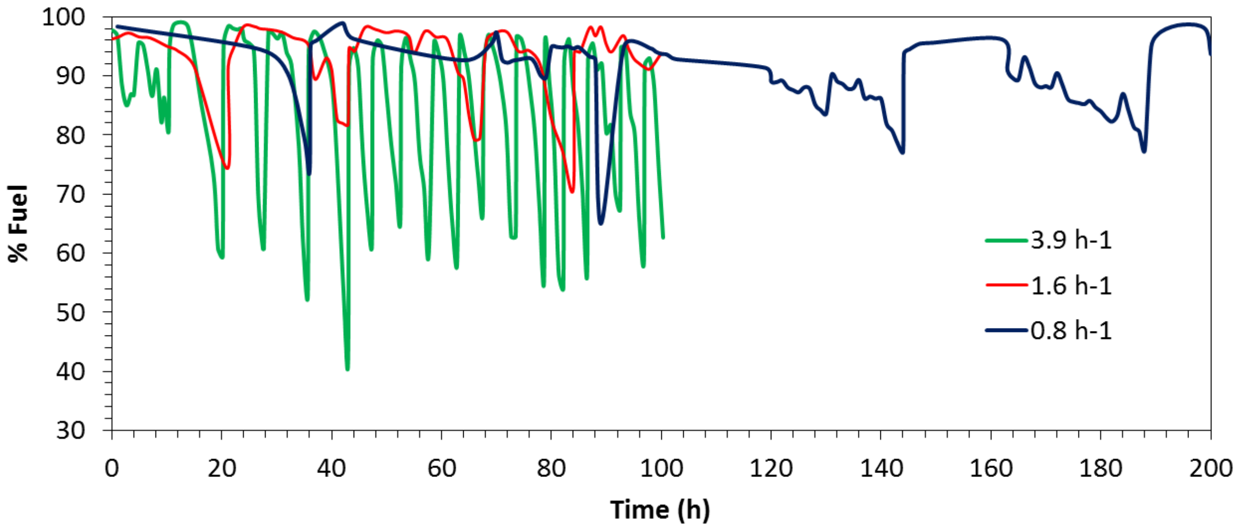


Figure 2: Water impact on the extended run for V-ZSM-5. Conditions: V-ZSM-5 and temperature 350 °C. Reactants: ethanol with 50 ccm Helium. LHSV at 0.8, 1.6 and 3.9 h^{-1}.

Since only 36% of the hydrocarbon product was C5+ and because V-ZSM-5 could not further convert the light gases into heavier MW hydrocarbons, Vertimass had to shift catalyst focus from V-ZSM-5 to Ga-ZSM-5 which was active on light gases. ORNL's study then also focused on extensive studies of water impact on Ga-ZSM-5 catalyst performance. Table 2 summarizes the water impact on product distributions for Ga-ZSM-5. As seen in Table 2, as water vapor concentration in the reactor inlet varied from 0% to 36%, the product yield doesn't change very much. There are only small changes in the liquid hydrocarbon composition. As increasing the water vapor concentration, paraffin increases slightly, but aromatics decrease, which is consistent with the observation from V-ZSM-5.

Table 2: Water impacts on product distributions for Ga-ZSM-5. Conditions: Ga-ZSM-5 and temperature 375 °C. The ethanol flow rate was kept constant by varying water content in the liquid feed. All the data were recorded at 10 h of time of stream. WHSV= weight hourly space velocity

H$_2$O vapor conc.	**WHSV h^{-1}**	**C3-C11**	**C2**	**Liquid C5+**	**Based on Liquid C5+, %**		
					Paraffin	**Olefin**	**Aromatic**
0	1.6	91	7	42	19	10	71
10	1.6	90	8	38	23	12	65
36	1.6	86	5	40	25	9	66

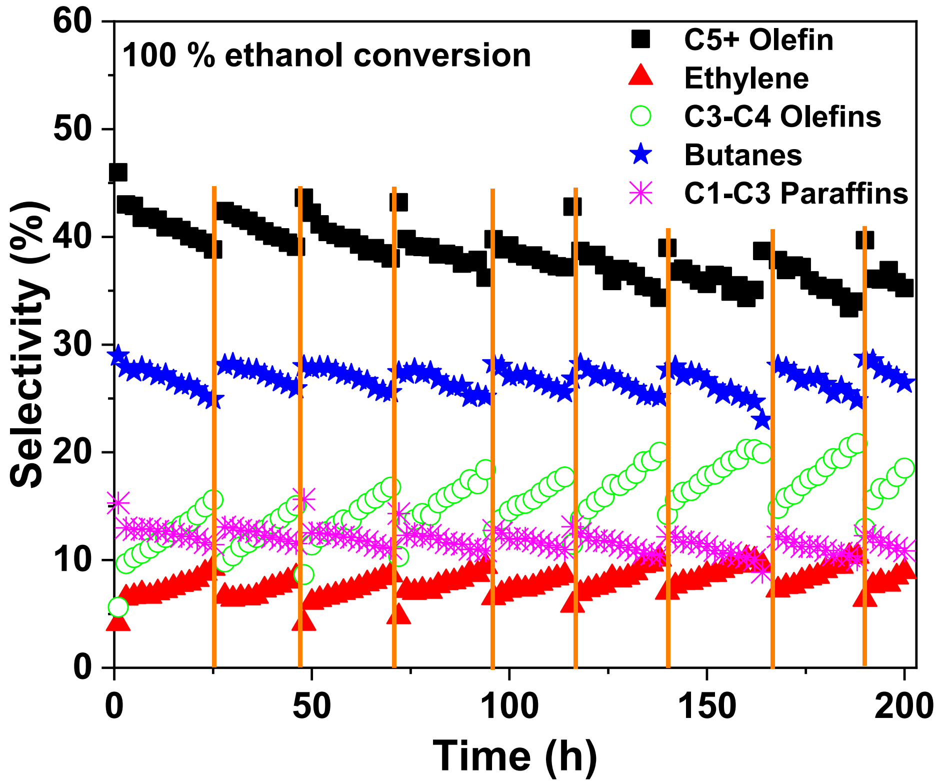


Figure 3: Extended run of Ga-ZSM-5 with water vapor concentration at the reactor inlet of 0%. Conditions: Temperature, 375 °C; pressure, 1 atm; WHSV, 1.6 h^{-1}. The orange vertical lines indicate where the regenerations were performed.

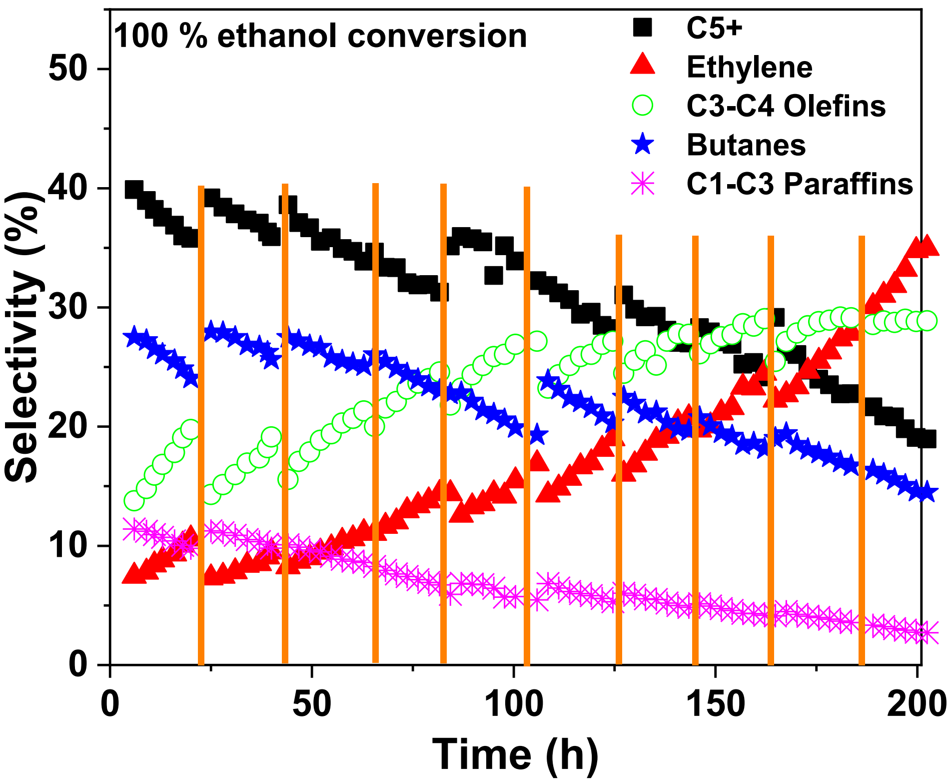


Figure 4: Extended run of Ga-ZSM-5 with water vapor concentration at the reactor inlet of 10%. Conditions: Temperature, 375 °C; pressure, 1 atm; WHSV, 1.6 h^{-1}. The orange vertical lines indicate where the regenerations were performed.

Figure 3 shows an extended run of Ga-ZSM-5 catalyst without water co-feeding (i.e. 100 % ethanol) at 375 °C. Since water is regenerated from ethanol conversion, significant water is still present in the catalyst bed (~5% water vapor concentration at the end of catalyst bed). The catalyst was regenerated in every ~20 hours of reaction using air calcination at 550 °C. As shown in Figure 3, ethanol conversion remains 100% all the time, either during each reaction cycle or between regenerations. The liquid C5+ product selectivity decreases in each cycle. All the light paraffin (C1-C3 paraffin, butanes) all decrease in each cycle with increasing of ethylene and C3-C4 olefins. There are only small changes of C5+ yield (40% to 38%, a 12% decrease) after 200 h run. The C2-C4 olefins increased while all the light paraffins also slightly decreased. This is very beneficial as the olefins are much easier to be further converted in the 2nd bed than the light paraffin.

To understand the water impact on the catalyst's performance and selectivity, this catalyst was also run in the presence of different amounts of water. Figure 4 and Figure 5 show the extended runs for Ga-ZSM-5 catalysts in the presence of 10% water vapor and 36% water vapor respectively. Both the runs were done at 375 °C. The conversion of ethanol remains at 100 % in both cases throughout the 200-hour run time, however, the product selectivity changes differently with different amount of water vapor in the stream. When comparing Figure 3, 4 and 5 (all runs at 375 °C), the increase of water vapor concentration in the stream affects the product selectivity significantly. At the 10th cycle, only 13% decrease of C5+ yield is observed with a small increase in ethylene and C3-C4 olefins in the case of the run without water feeding (Figure 3). When the reactor inlet water vapor concentration increases to 10%, the C5+ decreases 43% (from 40% to 23%) at the 10th cycle (Figure 4), compared with the 1st cycle. When the water vapor concentration is further increased to 36%, the amount of C5+ drops by 95% (from 43% to 2%) after the 10th cycle (Figure 5). Ethylene becomes the dominant product. The selectivities of the light C1-C3 paraffin and butanes continue to go down, while the C3-C4 olefins reach a maximum at the 4th cycle. All of these suggest the regeneration is not able to regenerate this catalyst with low Si/Al at this condition due to water impact. The characterizations performed in the other BETO funded CRADA project (WBS) have indicated dealumination is the primary reason for these irreversible changes. This is due to the instability of the aluminum in ZSM-5 with low Si/Al ratio. H-ZSM-5 with higher Si/Al ratio could help to address this issue.

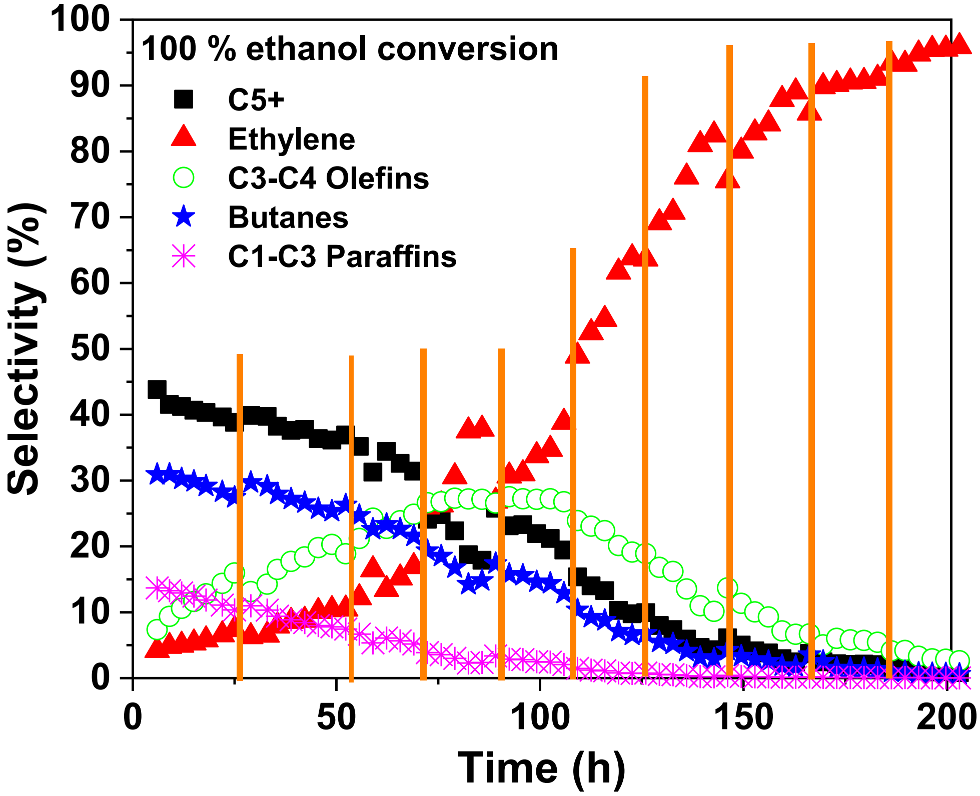


Figure 5: Extended run of Ga-ZSM-5 with water vapor concentration at the reactor inlet of 36%. Conditions: Temperature, 375 °C; pressure, 1 atm; WHSV, 1.6 h^{-1}. The orange vertical lines indicate where the regenerations were performed. ~~(Protected CRADA Information)~~

In addition to running at the same temperature (375 °C), ORNL also performed the water impact test for this catalyst (Ga-ZSM-5) at a lower temperature (350 °C) as well as keeping the same water vapor concentration (10%) to understand the temperature effect. Figure 6 shows the extended run of Ga-ZSM-5 with 10% of water vapor concentration at 350 ºC. After the 10th cycle, the product selectivity for C5+ decreases from 40% to 35% (a 13% decrease) in the case of 350 ºC (Figure 6), while it decreases by 43% (from 40% to 23%) in the case of run at 375 ºC (Figure 4). Similarly, ethylene production increases from 11% to 19% in the run at 350 ºC, while it increases from 17% to 31% in the case of run at 375 ºC. Similar results can be seen for butanes, C1-C3 paraffin, and C3-C4 olefins. All these results suggest that even small temperature changes in the presence of 10% water vapor could affect the product selectivity in the extended runs for this type of low Si/Al catalyst though while still maintaining 100% conversion of ethanol

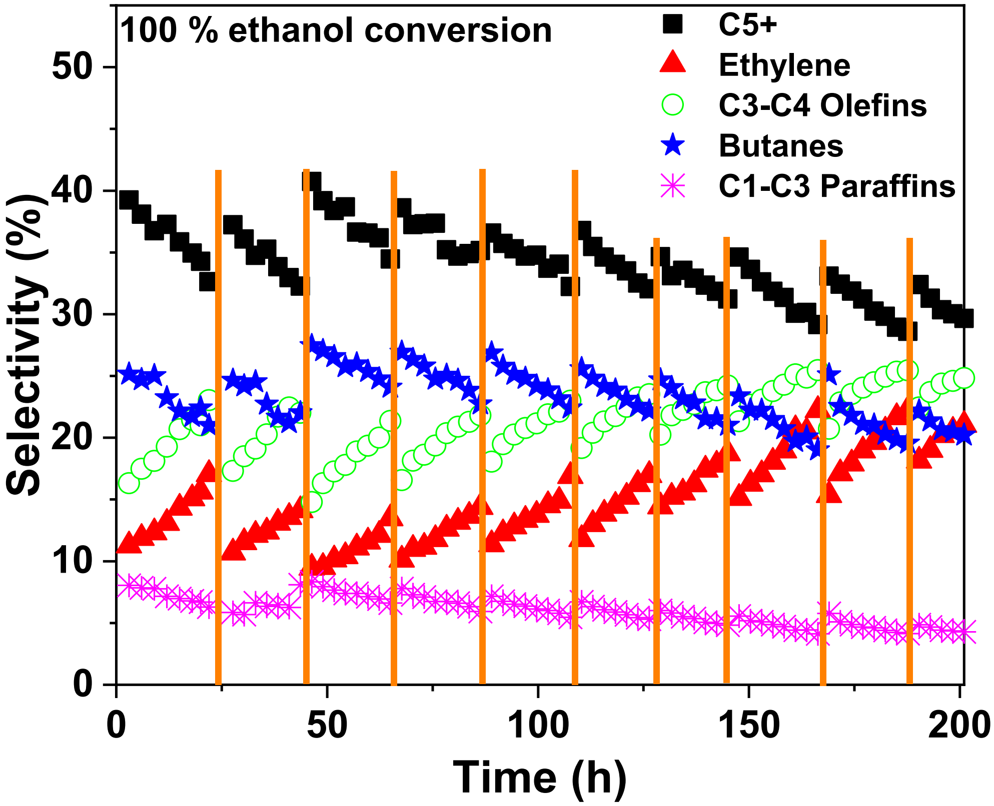


Figure 6: Extended run of Ga-ZSM-5 with water vapor concentration at the reactor inlet of 10%. Conditions: Temperature, 350 °C; pressure, 1 atm; WHSV, 1.6 h^{-1}. The orange vertical lines indicate where the regenerations were performed.

ORNL also performed studies at a higher temperature (400 and 450 ºC) without water feeding. Figure 7 shows the extended run for Ga-ZSM-5 at 400 ºC. If we compare this with the run at a lower temperature (375 ºC), we can clearly see that higher temperature run has totally different product selectivity trend (compare Figure 7 with Figure 3). C5+ selectivity at the 10th cycle is drastically decreased by 41% (from 46% to 27%) in the case of higher temperature run (400 ºC) while only decrease by 13% in the case of lower temperature run (375 ºC). Similar changes can be seen in ethylene, butane, and other product selectivities. On the other hand, if the reaction is further increased to 450 ºC, the change of product selectivity further increased. The selectivity for C5+

changes by 24% (from 55% to 42%) within 25 hours of reaction (Figure 8) while the run at 375 °C doesn't have any changes within the first 4 cycles (Figure 3). These results suggest that higher temperature could accelerate the product selectivity changes with 100% conversion of ethanol.

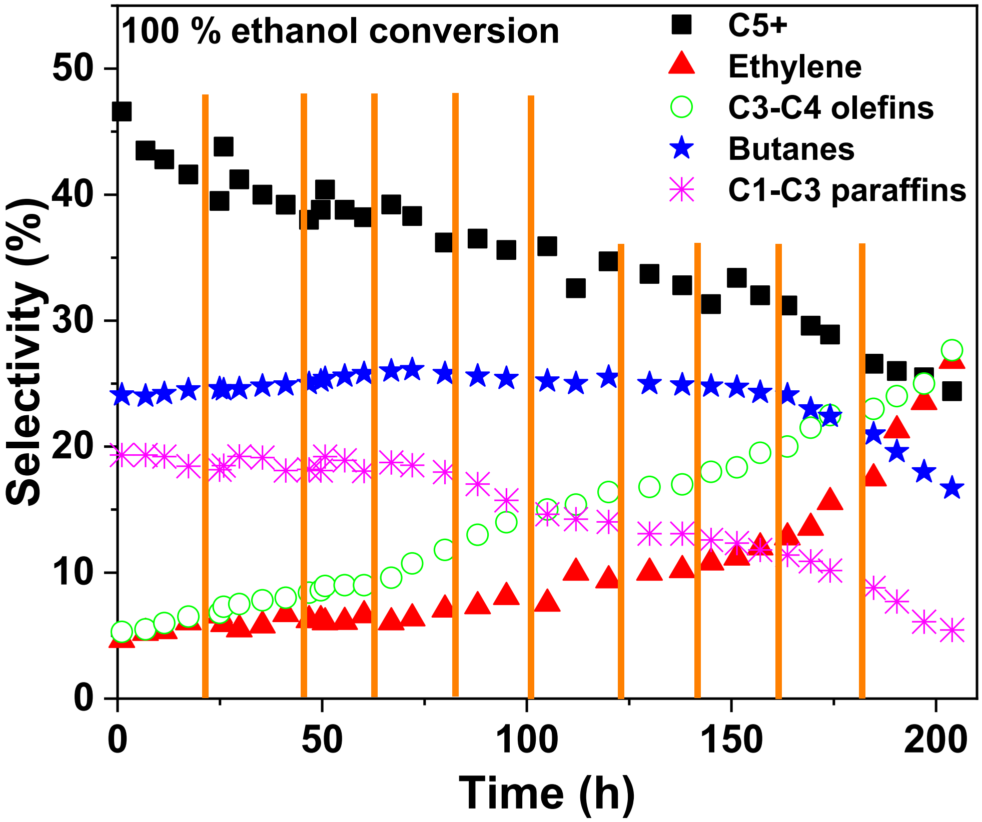


Figure 7: Extended run of Ga-ZSM-5 with water vapor concentration at the reactor inlet of 0%. Conditions: Temperature, 400 °C; pressure, 1 atm; WHSV, 1.6 h^{-1}. The orange vertical lines indicate where the regenerations were performed. ~~(Protected CRADA Information)~~

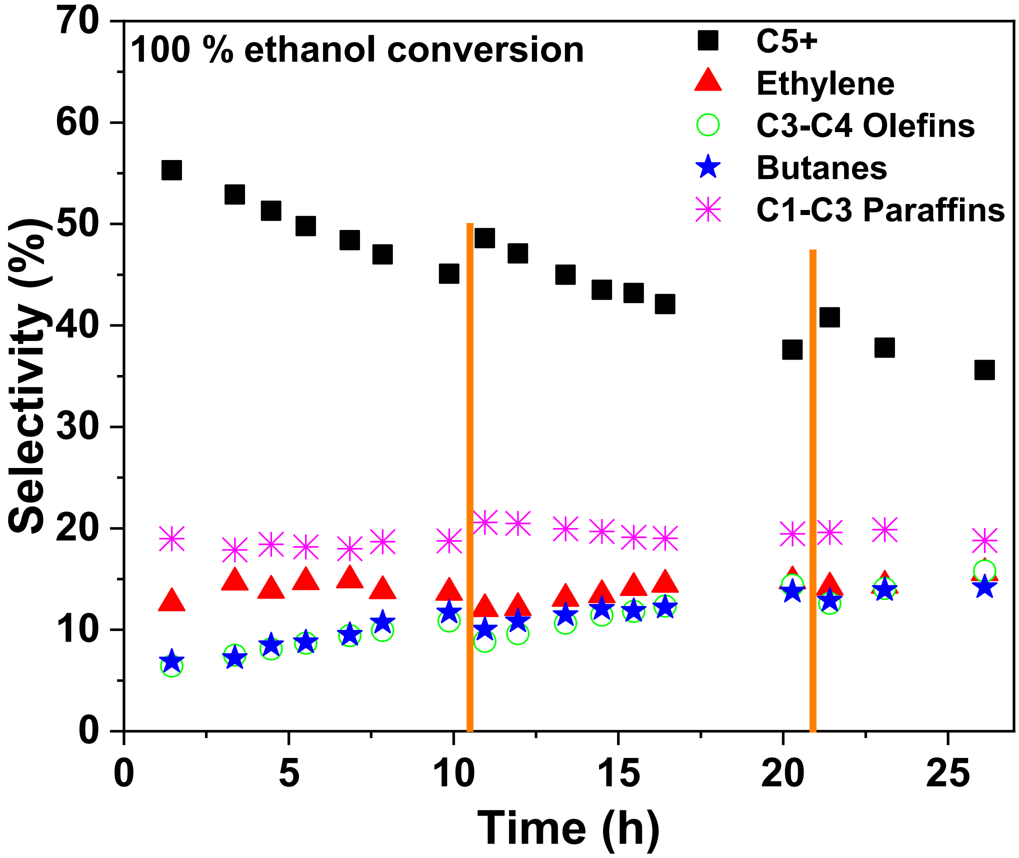


Figure 8: Extended run of Ga-ZSM-5 with water vapor concentration at the reactor inlet of 0%. Conditions: Temperature, 450 °C; pressure, 1 atm; WHSV, 1.6 h^{-1}. The orange vertical lines indicate where the regenerations were performed. ~~(Protected CRADA Information)~~

4.1.2 Hydrocarbons present in water

ORNL has also analyzed the hydrocarbon present in the water byproduct. V-ZSM-5 catalyst was run in the medium reactor and the products were collected. The water phase was separated from the hydrocarbon fraction via decanting and collected for total organic carbon analysis and Gas chromatography–mass spectrometry (GCMS) analysis. Based on the total organic carbon analysis, we found that the hydrocarbon concentration in water is around 0.08-0.16%. Based on the GCMS analysis, we observed formic acid, acetone, butanone, acetic acid, benzene, 2-pentanone, toluene, p-xylene, m-xylene, benzene, 1-ethyl,3-methyl, 1-ethyl,4-methylbenzene, 1,4-diethyl benzene, 1,3-diethyl benzene (Figure 9). The trace amount of oxygenates (e.g., formic acid, acetone, acetic acid) were only captured in the aqueous phase, while we didn't observe these compounds in the hydrocarbon phase probably due to the very low concentration (below the GC detection limit).

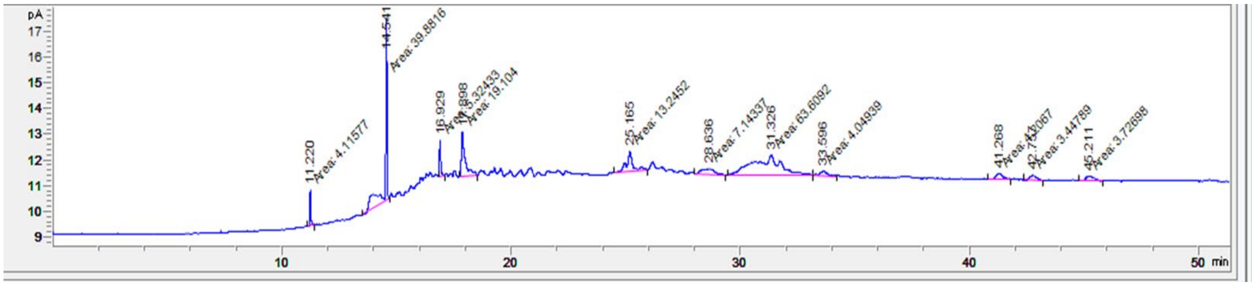


Figure 9: GC/MS analysis of the water sample after the reaction. Medium reactor, Conditions: 5 g V-ZSM-5 and temperature 350 °C. Reactants: pure ethanol with 50 ccm He flow. WHSV at 2.4 h^{-1}. The peaks correspond to formic acid, acetone, butanone, acetic acid, benzene, 2-pentanone, toluene, p-xylene, m-xylene, benzene, 1-ethyl,3-methyl, 1-ethyl,4-methylbenzene, 1,4-diethyl benzene, 1,3-diethyl benzene, respectively.

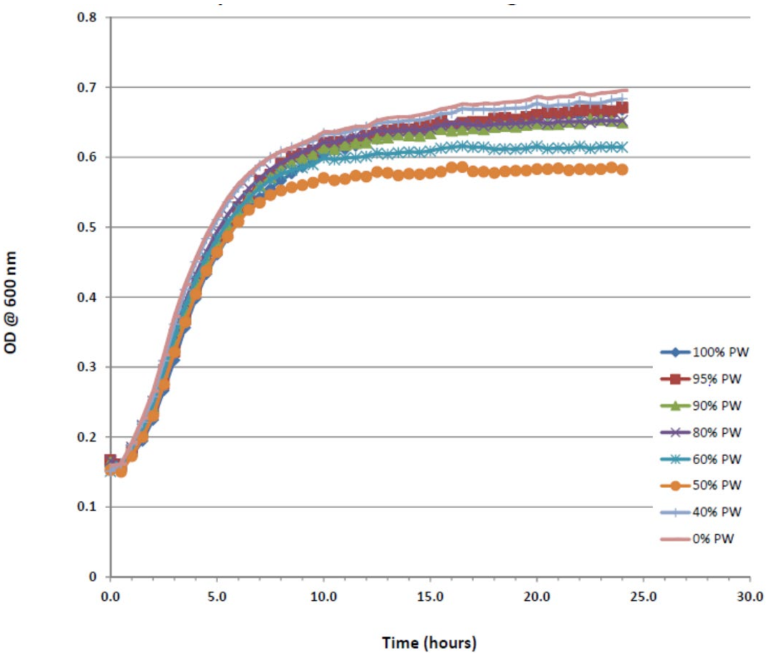


Figure 10: Yeast growth experiment using different amounts of produced water (PW) on diluted rich media with glucose, yeast extract, and peptone. The growth of *Saccharomyces cerevisiae* D5A was performed in produced water containing 0.1xYPD medium (yeast peptone dextrose).

Even though only very small amounts of organics were observed in the water phase, we evaluated the feasibility of direct reuse of the water for ethanol fermentation without wastewater treatment. Figure 10 shows the yeast growth with different amounts of water samples generated from ethanol conversion. The yeast growth experiment in presence of 0-100 % produced water on a diluted rich media shows no major inhibition of yeast due to a small number of hydrocarbons in the produced water. These results suggest we can directly recycle the water generated from ethanol upgrading for the fermentation process, which will significantly reduce the cost of wastewater treatment and also significantly reduce the amount of water input to ethanol production processes.

4.1.3 Confirmation testing of vendor-supplied catalysts

ORNL has performed studies on metal doped vendor supplied catalysts and compared with metal doped lab-based powder catalysts to understand the difference (if any) of the catalyst performance. Figure 11 shows an example comparison of pelletized Ga-ZSM-5 provided by TechnipFMC and the lab-scale powder Ga-ZSM-5. These two catalysts show similar selectivity of C5+ within the temperature range of 300-500 ºC. The other products are also similar from 350 to 450 ºC. Only some differences are observed at 300 ºC and 500 ºC for these products.

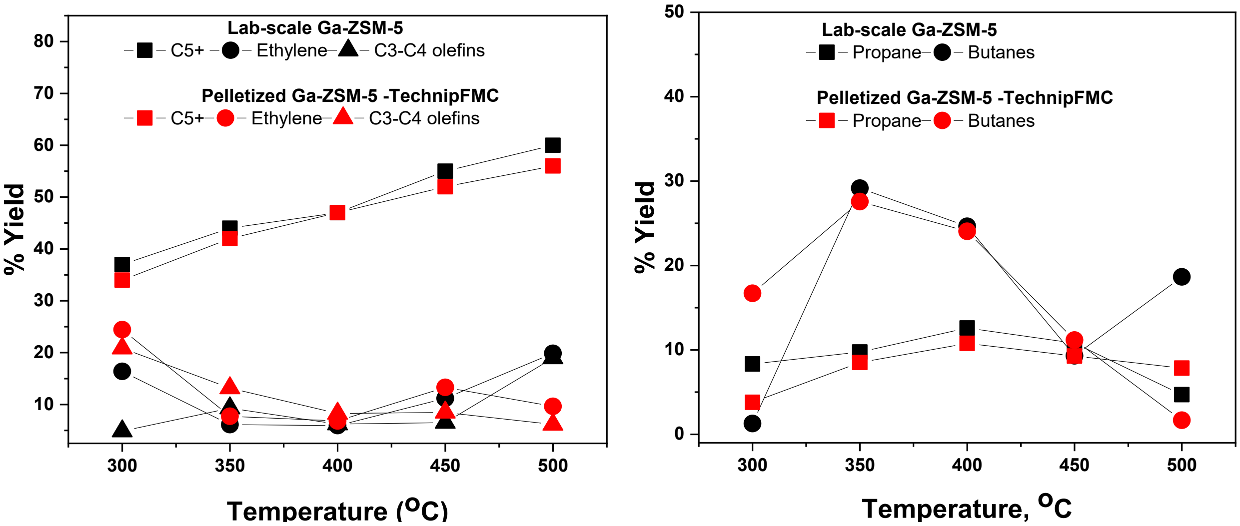


Figure 11: Comparison of pelletized Ga-ZSM-5 provided by TechnipFMC and lab-scale powder catalyst regarding the product selectivity at different temperatures. Conditions: pressure, 1 atm; WHSV, 1.6 h^{-1}.

4.2 Task 2: Catalyst regeneration

In this task, ORNL has studied the regeneration to optimize the regeneration time and conditions, particularly focusing on Ga-ZSM-5. Thermogravimetric analysis (TGA) was applied to the spent sample to find out the regeneration temperature. Figure 12 shows the thermogravimetric analysis of used Ga-ZSM-5 catalyst. The initial weight loss (~ 4 %) before 180 ºC is due to water removal. Coke removal starts at 320 °C and the decoking rate reaches a maximum at ~500 °C based on the derivative weight changes, so this temperature is used as our regeneration temperature.

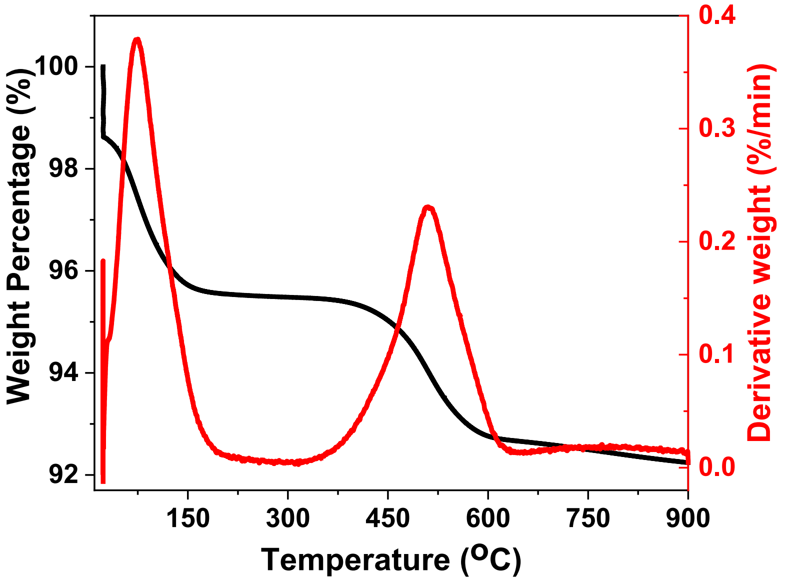


Figure 12: Thermogravimetric analysis (TGA) of the used Ga-ZSM-5 with temperature ramping up from 35-900 °C at 10 °C/min in the presence of air.

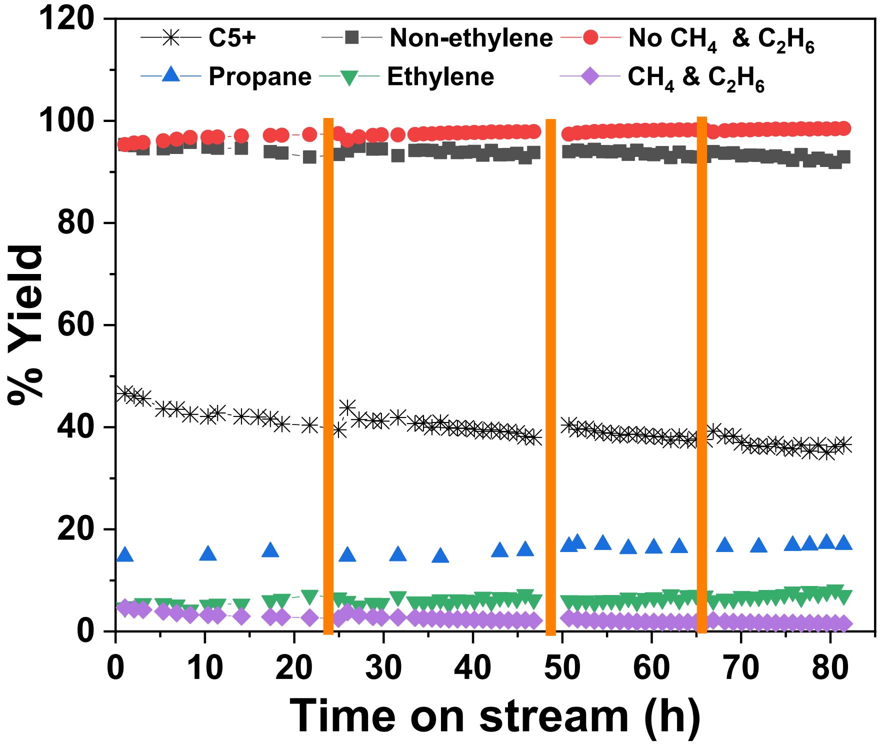


Figure 13: Regeneration test for Ga-ZSM-5. Conditions: 0.2 g Ga-ZSM-5 and temperature 400 °C. WHSV at 1.6 h^{-1}. Regeneration at 550 °C for 12, 2.5 and 6 h

We further examined the regeneration time needed by doing extended runs and varying the regeneration time between each cycle. As shown in Figure 13, shows the product distribution for the Ga -ZSM-5 catalyst to understanding the effects of regeneration. As shown in Figure 13, three different regeneration times were used (12, 2.5 and 6 h). No significant difference is observed, so a minimum regeneration of 2.5 h was used.

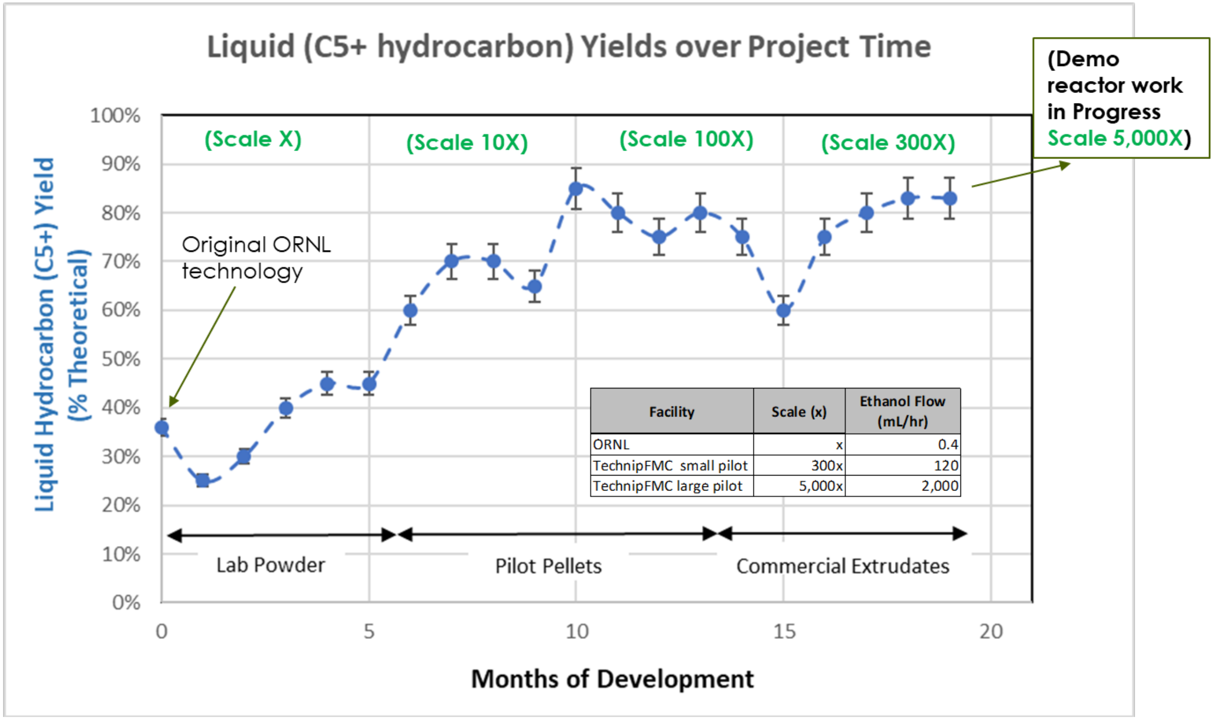
4.3 Tasks 3-6: Technical Accomplishments from Vertimass / TechnipFMC

Vertimass LLC and TechnipFMC have been working together on the majority of DOE Award DE-EE0006875 in parallel to Oak Ridge's supporting work. The team had the following major accomplishments in moving this technology towards commercialization from the original technology.

1. <u>Successful technology transfer</u>: ORNL original technology was operated in a microreactor with ethanol flow rates ~0.4 mL/hour and catalyst at 0.2 grams on the powdered (expensive) catalyst with 100% conversion of ethanol to hydrocarbons but with only 36% liquid hydrocarbon yields. Higher liquid hydrocarbon yields are desired over gaseous hydrocarbon yields as they command a significant premium in value (4-5x). TechnipFMC successfully transferred the technology over 2-3 months to consistently repeat results above in their smallest reactor representing a 10x scale-up (4 mL/hour and 2 grams of catalyst).
2. <u>Increase in Liquid yields</u>: TechnipFMC was able to increase liquid yields from original 36% to 80%+ over 8 months through a systematic study of changing flow rates, pressure, temperatures, and reactor configurations. This was a major advance which lowered the operating costs and advanced the technology to the highest liquid yields we have seen in ethanol to hydrocarbon catalytic technologies. It is also important to note that this was also accomplished by removing the nitrogen and/or Helium diluent (90% wt.) used in the original technology which was required at microreactor scale but obviously not cost effective in moving toward commercial operations.
3. <u>Commercial catalyst forms</u>: Vertimass and TechnipFMC worked together to first produce pilot pellets from the powdered catalysts to mitigate pressure drop and channeling that becomes evident with powdered catalysts upon scale-up. The doped powdered catalysts were pressed, crushed, and sieved to various sizes (usually 250-500 microns) and used in the scaled-up reactors. These new pilot pellets minimized ethylene production, reduced pressure drop (almost negligible) and distributed flow. As we scaled up even further (300x), we needed to use commercial catalysts as making pilot pellets became expensive and time-consuming. Thus, Vertimass and TechnipFMC worked with Clariant to both provide commercial extrudates and to produce extrudates from doped powder. Both worked effectively in repeating or even increasing catalyst performance over time. Using commercially available extrudates represented another significant decrease in catalyst unit costs ($/kg) versus using laboratory powder.

4. Catalyst advance: We made one final advance in lowering the catalyst unit cost by lowering the catalyst doping amount and using a more durable (in the presence of water) Clariant catalyst. This last advance was outside the scope of our project but was critical in cost-effectively advancing this technology to commercialization.

   The below figure tracks many of the advances we encountered through the project life.



Facility	Scale (x)	Ethanol Flow (mL/hr)
ORNL	x	0.4
TechnipFMC small pilot	300x	120
TechnipFMC large pilot	5,000x	2,000

Figure 14: Timeline to show the advancement in this project.

5. SUBJECT INVENTIONS

Here are some of the specific inventions through this project

1. US 20160362612 A1 "*Systems and methods for reducing energy consumption in production of ethanol fuel by conversion to hydrocarbon fuels*"
2. US 20160362612 A1 "*Systems and methods for reducing water consumption in production of ethanol fuel by conversion to hydrocarbon fuels*"
3. US 62/255502 "*Systems and methods for improving yields of high molecular weight hydrocarbons from alcohols*"
4. US 62/315889 "*Systems and methods for improving yields of hydrocarbon fuels from alcohols*"

6. COMMERCIALIZATION POSSIBILITIES

Vertimass has been in discussion with 7 different ethanol producers in the US and 5 international that have expressed interest in adopting this technology at their facilities. This conversion technology allows the ethanol producer the flexibility to produce other products to maximize profits in various market conditions. For example, during low ethanol prices and high oil price environments (high gasoline, diesel, and jet fuel prices), the producer can direct the ethanol to make these higher value renewable hydrocarbons. Some producers also can increase the throughput of their plant by debottlenecking their process which has very short paybacks.

7. PLANS FOR FUTURE COLLABORATION

Vertimass LLC and ORNL have identified areas that could further benefit the commercialization of this ethanol upgrading technology, e.g., further optimize the catalyst for better stability at more severe conditions, increase the distillate fraction, etc. We will look for further funding opportunities to collaborate in these areas. We will also explore other collaboration opportunities in biofuels and biochemicals production.

8. CONCLUSIONS

The data obtained in this CRADA project is very important for scale-up and commercialization of the ethanol upgrading technology. ORNL has performed: 1) extended runs to determine how varying water levels impact catalyst performance and lifetime, 2) assessing hydrocarbon partitioning to the water byproduct and appropriate treatment, and 3) optimization of the catalyst regeneration. These studies have provided useful information to understand catalyst operation in the presence of different amount of water in the feed, which offers important information for further catalyst optimization and proper process development. ORNL has found that the presence of water has minimal impact on the product distribution for both V-ZSM-5 and Ga-ZSM-5. For Ga-ZSM-5 with low Si/Al ratio, the product selectivity change is very small over 200 h extended run with pure ethanol feed. When increasing the water co-feeding (reactor inlet water vapor concentration to 36%), significant product selectivity changes are observed probably due to the instability of the aluminum in this type of high aluminum zeolite. This finding provides guidance of developing high Si/Al zeolite for enhanced catalyst stability. We also found that there were trace amounts of hydrocarbons in the water fraction and that this water byproduct can be directly used for fermentation without further treatment reducing water input costs. Vertimass and TechnipFMC have been working together on the majority of this CRADA project in parallel to Oak Ridge's supporting work. The team had the following major accomplishments in moving this technology towards commercialization from the original technology: 1) successful technology transfer from lab scale (x) to pilot scale (300x) with 5000x scale-up underway; 2) increase liquid yield from original 36% to 80+%, and 3) advanced catalyst form from lab powder to commercial catalysts.

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