

DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

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

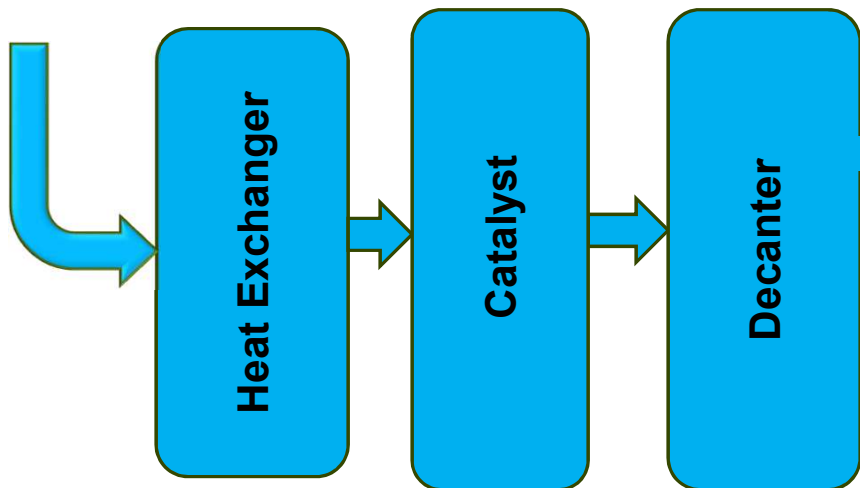
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Catalytic Upgrading

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Technology Goal: High Yields of Liquid Hydrocarbons from Ethanol at Pilot Scale to Support Commercialization



5-100%
Ethanol



Chemicals,
e.g., BTEX



Fractionation
(as needed)

Jet Fuel



Diesel



JP-8



Gasoline



Overcome ethanol blend wall and open up new ethanol markets by using it as an intermediate

Existing infrastructure

Goal Statement

○ Project Goals:

- 1) Increase Yields:** Increase hydrocarbon liquid (C5+) yields for ethanol-to-hydrocarbon catalytic technology invented at Oak Ridge National Laboratories (ORNL)
- 2) Scale-up:** Employ commercial catalyst formulations in scalable reactors to provide engineering design basis from which to directly scale-up to commercial operations,
- 3) Technology Advancement:** TRL 3 to TRL 5.

○ Project outcome:

- 1) Drastically Changes Biofuel Landscape:** Opens up ethanol to HC market
- 2) Ethanol Producer Flexibility:** Producers can now make:
 - Gasoline blend stocks that eliminate the ethanol “blend wall,”
 - Diesel and jet fuel blend stocks that expand ethanol markets, and
 - Higher value chemical coproducts (BTEX – benzene, toluene, ethylbenzene, and toluene) that can improve process economics, particularly when fuel prices are low.
- 3) Worldwide Adoption:** Sustainable conversion of cellulosic ethanol into fuels and chemicals with GHG reduction potential of +95% while significantly reducing fossil fuel dependence.

Quad Chart Overview

Timeline

- Project start date: November 15, 2015
- Project end date: May 31, 2019
- Percent complete: 90%

Barriers addressed

- Ct-F. Increasing the Yield from Catalytic Processes:
- Ot-C. Risk of Financing Large-Scale Biorefineries:

	Total Costs Pre FY17*	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	\$488k	\$594k	\$568k	\$0
Project Cost Share*	\$195k	\$239k	\$366k	\$650k

•Partners: Vertimass (25%), ORNL (15%), TechnipFMC (60%)

Objective:

Provide an economically viable ethanol upgrading platform that be scaled directly to commercial operations

End of Project Goal:

Complete conversion of ethanol to >90% liquid hydrocarbons in commercially scalable reaction system on readily available commercial catalyst form (extrudates).

1 - Project Overview

- History
 - Oak Ridge invented catalyst to convert ethanol into hydrocarbons.
 - Vertimass recognized its importance and applied for license.
 - Vertimass was awarded license in 2014 in competitive solicitation.
 - Vertimass won DOE funding to accelerate scale up.
- Among biomass derived fuels, ethanol is the major success story.
 - Now added to gasoline to meet EPA RFS requirements.
 - However, market is limited to ~10% due to “blend wall” unless flex-fuel vehicles (FFV) or E15 have greater market penetration.
- Catalytic conversion of ethanol to hydrocarbon blend stocks overcomes (or bypasses) the blend wall using ethanol as an intermediate molecule
- Employing TechnipFMC pilot plant to increase liquid yields and provide engineering data for commercial scale implementation.
- Goal is to become cost competitive with petroleum fuels.

2 – Approach (Management)

CLARIANT 

○ Project Structure

- **Vertimass:** Overall management of the project activities, schedule, and budget to achieve technical goals. TechnoEconomic Analysis (TEA) lead.
- **TechnipFMC:** Pilot scale-up experimental operations, providing technical data and scale-up expertise to reach overall technical goals.
- **Oak Ridge:** Transfer historical run data and catalyst preparation, continue development at smaller scale (e.g., effects of water co-feed)
- **Clariant:** Commercial catalyst supplier

○ Management Approach

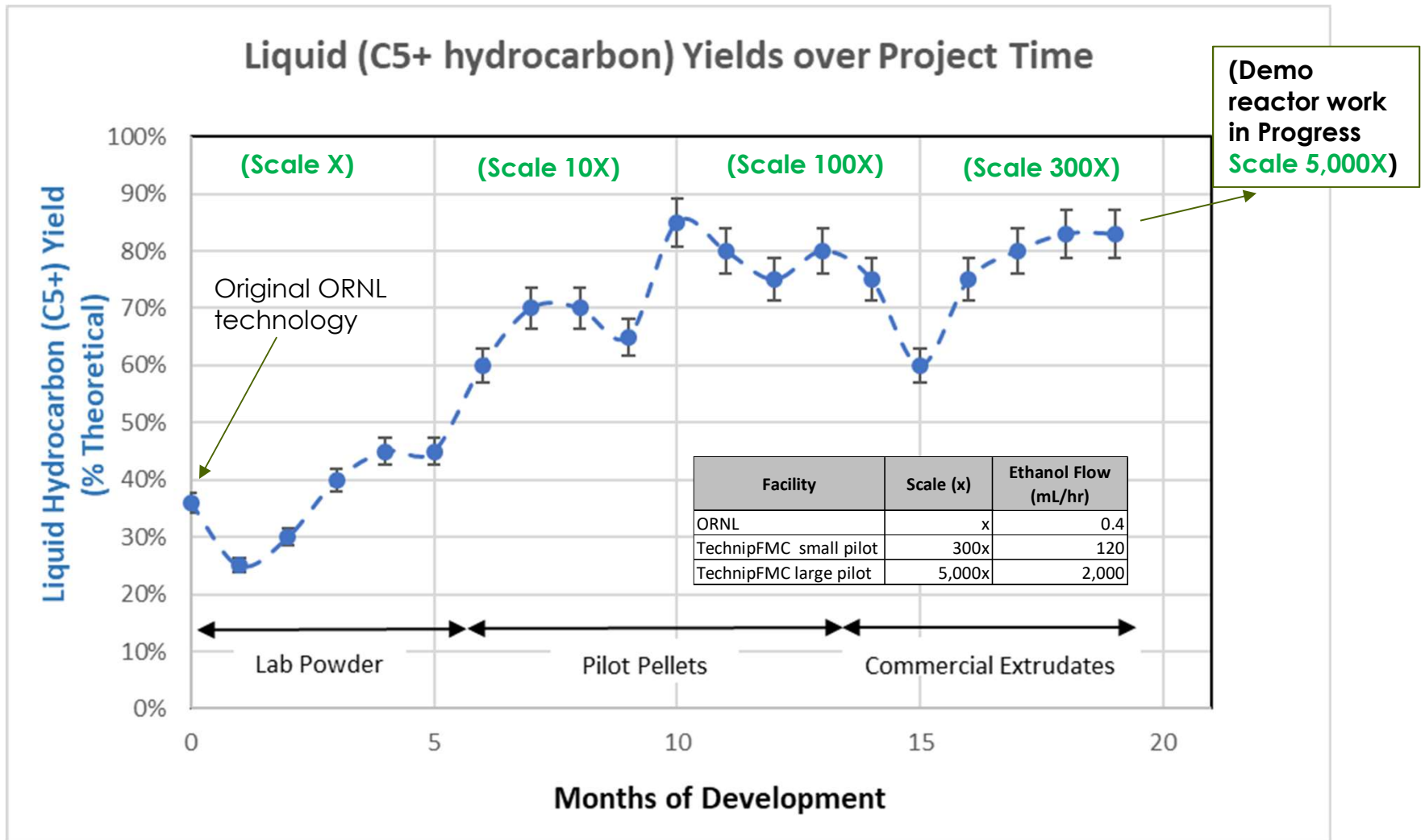
- Weekly coordination meetings with ORNL (conference), TechnipFMC (Weymouth MA pilot), and Vertimass (conference).
- Quarterly meetings with ORNL, TechnipFMC, and Vertimass.
- Monthly conference updates with DOE and quarterly reports on progress and budgets.

2 – Approach (Technical)

- Technical Approach
 - **Scale-up Experts:** Capitalizing on TechnipFMC's 40+ years experience in scale-up from their pilot plant (Weymouth, MA) to commercial operations
 - **Commercial Catalyst Experts:** Utilizing Clariant's experience to define most effective catalyst formulations
 - **Parametric Examination:** Varying temperature, pressure, space velocity and catalyst formulations to maximize yields of liquid hydrocarbon blend stocks from ethanol at pilot scale.
 - **TechnoEconomic Model:** Follow cost impacts of technical advancements (highly dependent on liquid yields)
- Top 3 challenges to commercial success
 - Achieving high liquid yields with commercial catalyst formulation
 - Qualifying product suitable for blending with gasoline
 - Confirming commercial catalyst durability
- Critical success factors
 - High liquid yields with commercial catalyst formulation.
 - Engineering design basis for integration into ethanol plant.
 - Partnerships with first adopters

3 – Technical Accomplishments

(From original ORNL technology through this project)



3 – Technical Accomplishments

(From original ORNL technology through this project)

- **Stoichiometric conversion:** Maintained 100% conversion of ethanol to hydrocarbons and water throughout scale-up
- **Increased Liquid Yields:** Liquid hydrocarbon yields (C5+) improved from 36% (initial validation) to >80%
- **Scale-up:** 300x scale-up in 15 months while increasing yields (on way to final 5,000x scale-up)
- **Catalyst Form:** Moved from catalyst powder to pilot pellets to commercial extrudates
- **Maintain Mild Conditions:** Relatively low temperature (350 °C) and pressure operations (60 psi) operation.
- **Utilizing wet ethanol feedstock:** 20-100% ethanol concentrations have minimal effect on product distribution while buffering exotherm.

3 – Technical Accomplishments (cont)

Progress on Key Technical Targets (to drive costs lower)

Key Performance Indicator (KPI)	Units	Initial Validation	Intermediate Target	Current		Final Target
Total Hydrocarbon Yield (HC _T)	g total hydrocarbons / g EtOH	0.55	0.55	0.55	✓	0.55
Hydrocarbon Liquid Yield (HC _L)	g C5+ hydrocarbons/g EtOH	0.22	0.44	0.46	✓	0.50
Hydrocarbon Gas Yield (HC _G)	g C1-C4 hydrocarbons/g EtOH	0.33	0.05	0.09	✓	0.06
Scale of Operations	mL EtOH / hr	0.40	120	120-300	✓	5000
Temperature	Degrees Celsius (C)	350	325-375	350	✓	350
Space Velocity	LHSV (1/hr)	1.20	1.20	1.6-2.0	✓	2.0
Catalyst Loading level	g catalyst / mL/hr EtOH	0.50	0.50	0.50	✓	0.50
Stability	hours on stream before regen	6.0	16	15-20	✓	24
Regen Method	Air / Oxygen	Air	Air	Air	✓	Air

Progress on Key Milestones

- Determine effects of water cofeed & evaluate water product at lab scale ✓
- Optimize catalyst regeneration cycle times ✓
- Isothermal operation for process and catalyst characterization ✓

Final Validation – Targeting April / May 2019 timeframe

- Development and validation of robust industrial catalysts (In progress)
- Adiabatic operation and prepare Design Basis Memorandum (In progress)
- Integrate catalyst into ethanol production and optimize cost estimates via TechnoEconomics and Life Cycle Analysis (In progress)

3 – Technical Accomplishments (cont)

- **Key Finding 1:** Initial technology / catalyst (M1 Zeolite) maximum liquid yields plateaued at 60% one pass, 70% with recycle. Thus needed another solution.
- **Key Finding 2:** Moved to different licensed catalyst formulation (M2 Zeolite) that offered higher yields: reached >80% one pass
- **Key Finding 3:** M2 Zeolite can increase BTEX yields compared to M1 Zeolite at defined conditions
 - BTEX commands a premium over fuels (~70-80% higher value per unit volume).
 - This valuable co-product can be very important to reducing overall blend stock costs and improving competitiveness at low petroleum prices.
- **Key Finding 4:** Decrease metal loading for M2 Zeolite lowers catalyst costs while maintaining performance

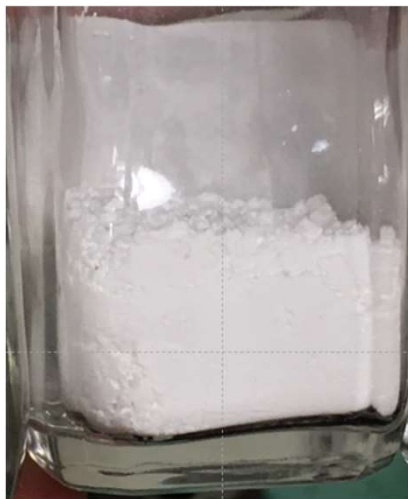
3 – Technical Accomplishments (cont)

Challenge

- 1) Needed more catalyst than ORNL could deliver
- 2) Reaching liquid yield targets
- 3) Powder catalyst channeling, high pressure drop
- 4) Required commercial catalyst forms (extrudates)

Mitigation/Solution

- 1) Transferred catalyst production to TechnipFMC (accelerated production)
- 2) Parametric investigation boosted liquid product
- 3) Pelletized catalyst
- 4) Successful in transferring technology to commercial extrudates with partners



Lab Powder



Pilot Pellets



Commercial Extrudates

3 –Accomplishments / Relevance

Pathway to Commercialization

- **Complete final scale-up:** In progress. Demonstration reactor at TechnipFMC with commercial catalyst form allows for direct scale-up to commercial operations. Determine and extend catalyst life.
- **Ethanol engineering firm:** Working with experienced engineering firm to define how Vertimass bolt-on can best integrate into starch and cellulosic ethanol facilities (e.g., heat integration, water usage).
- **First Ethanol Adopter:** LOI with commercial ethanol producer for first Vertimass commercial bolt-on.
- **Life-Cycle Analysis (LCA):** Life Cycle Associates (Stefan Unnasch) initial LCA of our process showed CO₂ sequestering potential with high carbon intensive BTEX products – this could shift starch ethanol producers into 50%+ GHG reduction (conventional to advanced fuels) *(Preliminary results and subject to EPA review)*

4 – Relevance

- **Project Goals:**

- 1) **Increase Yields:** Increase hydrocarbon liquid (C5+) yields for ethanol-to-hydrocarbon catalytic technology initially developed by Oak Ridge National Laboratories (ORNL)

- 2) **Scale-up:** Utilize scalable demonstration reactors with commercial catalyst formulations for engineering design basis from which to scale-up to commercial operations,

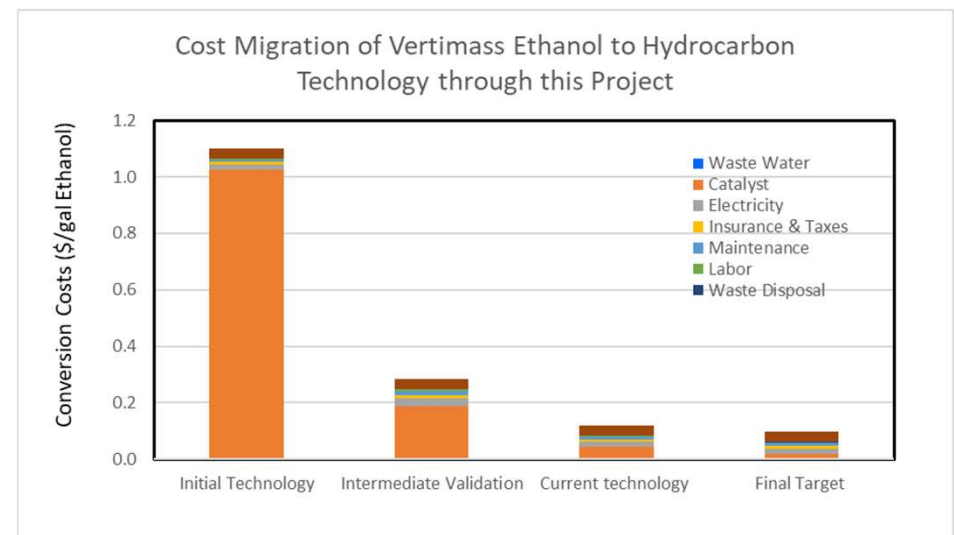
- 3) **Technology Advancement:** TRL 3 to TRL 5.

- **Importance:** Potential to drastically change biofuel landscape. Commercialization eliminates ethanol blend wall, expands ethanol markets to fungible diesel and jet hydrocarbon blend stocks, further diversifies product slate to chemicals, and reduces GHGs.

- **Relevance to BETO Multi-Year Program Plan:** Technology directly addresses relevant barriers and overall MYPP goals

- **Relevant to the bioenergy industry:** Vertifuel eliminates blend wall and expands ethanol penetration to massive fuel and chemical markets.

- **Advances to state of technology:** Low temperature and pressure operation, no external hydrogen, low % light products, high liquid yields.



5 – Future Work

- Complete Demo reactor with commercial catalyst to provide engineering basis for commercial scale-up (TechnipFMC can guarantee commercial scale-up from their large pilot).
- Key Milestones
 - Demo reactor completion
 - Determine / Extend catalyst life
- Upcoming Go/No-Go Points:
 - Complete Design Basis Memorandum
 - Final Validation (Q2-Q3 2019)
- Remaining budget: DOE funds and Vertimass cost share have been completed (remaining DOE \$0k, Cost share \$0k).
- Additional \$650k cost share to complete project.

Facility	Scale (x)
ORNL	x
TechnipFMC Pilot	300x
TechnipFMC Demo	5,000x
Commercial	67,000,000x



Summary

Key results for Vertimass development of ethanol to hydrocarbon conversion technology

- 1) Major technology improvements over the last year
 - Boosted Liquid Yields from 36% to >80%
 - Scaled-up 300x to date (on way to 5000x)
 - Reduced catalyst costs by using commercial extrudates and less expensive doping techniques
- 2) Industry Acceptance: LOI with ethanol producer for commercial plant
- 3) Future Work: Complete final Demonstration reactor to establish commercial scale-up platform
- 4) Potential to drastically change biofuel landscape

Additional Slides

Patents & Presentations

○ Patents (applications) through this work

- 1) US20160362612A1: “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) 62/315889: “Systems and methods for improving yields of high molecular weight hydrocarbons from alcohols”
- 4) 62/255022: “Systems and methods for improving yields of hydrocarbon fuels from alcohols”

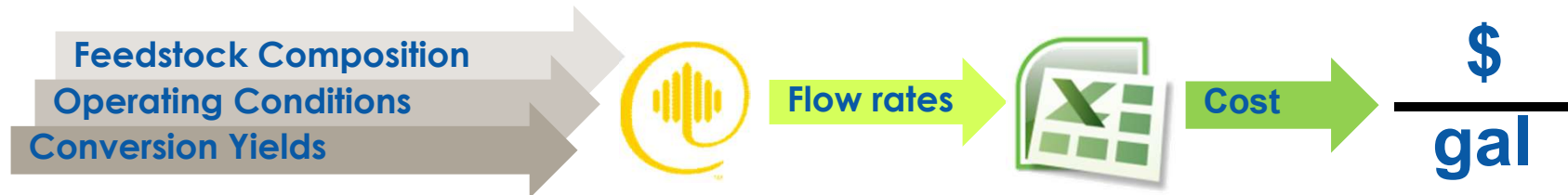
○ Presentations

- 1) “Novel Vertimass Catalyst for Conversion of Ethanol into Renewable Jet Fuel and High Value Co-Products” Lux Executive Summit Americas, May 9-11 2016
- 2) “Single Step Ethanol Conversion to BTEX and Jet, Diesel, and Gasoline Blending Components” International Fuel Ethanol Workshop & Expo 2016

Vertimass Licensed Patents from UT-Battelle

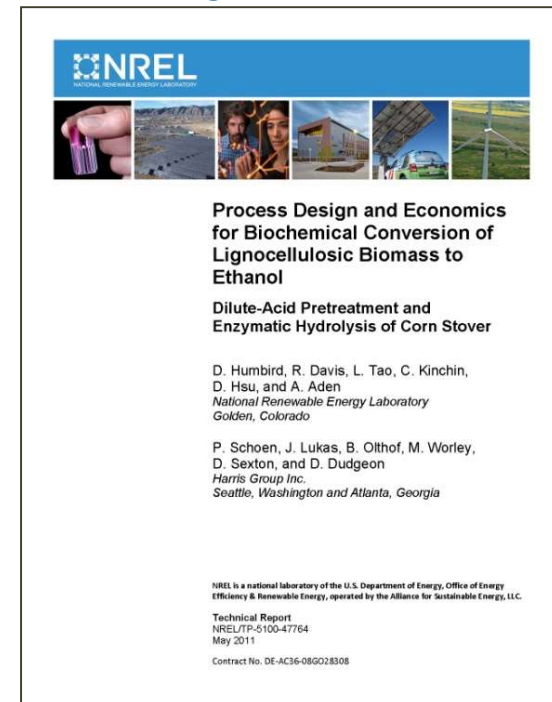
Patent #	Patent Name	Issued Patent # / Application #
1	Zeolite-based SCR catalysts and their use in diesel engine emission treatment	US 8987161 B2
2	Hydrothermally stable, low temperature NOx reduction NH3-SCR catalyst	US 8987162 B2
3	Zeolitic catalytic conversion of alcohols to hydrocarbons	US 9533921 B2
4	Catalytic conversion of alcohols having at least 3 carbon atoms to hydrocarbon blendstock	US 9181493 B2
5	Catalytic conversion of alcohols to hydrocarbons with low benzene content	US 9434658 B2, US 9278892 B2

TechnoEconomic Base Model



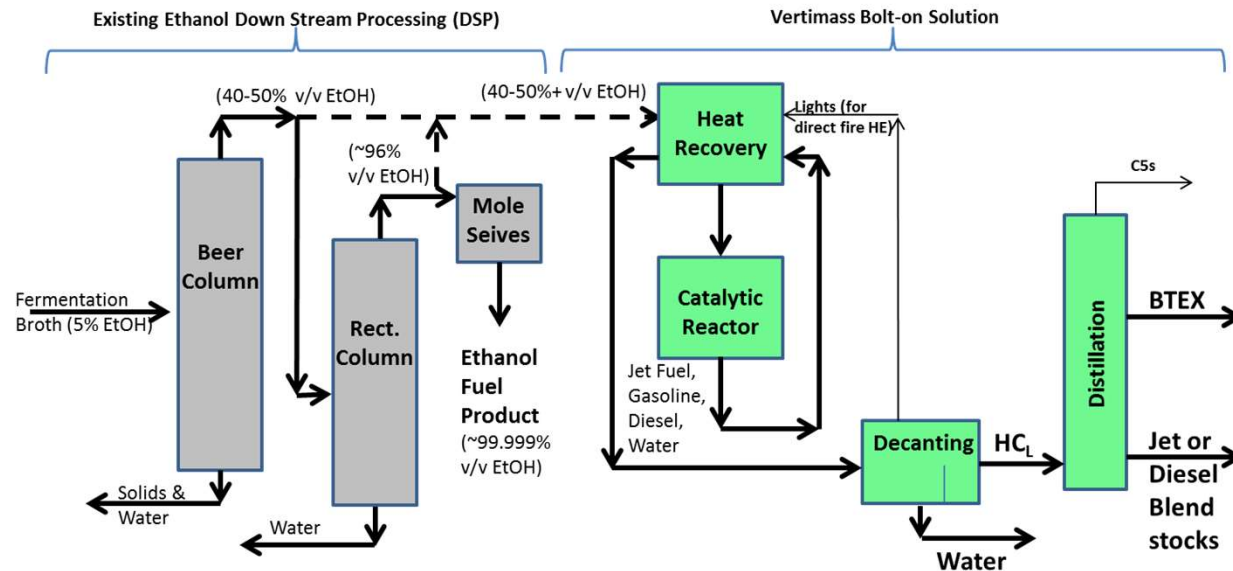
- Economics based on NREL biomass to ethanol TEA (2011 Biochemical Design Report Update), ORNL results on ethanol to hydrocarbon step
- Assumed n^{th} -plant project cost factors and financing (does not include first-of-a-kind risk)
- Discounted cash-flow ROR calculation applies 10% IRR, interest, and income taxes
- Determines the plant-gate minimum product selling price
- NREL baseline ethanol selling price is \$2.15/gal ethanol (2007\$) or \$3.27/gal gasoline eq.
- Modeled conversions are based on anticipated pilot-scale performance in 2015

2011 Design Report Update



<http://www.nrel.gov/docs/fy11osti/47764.pdf>

TechnoEconomic Vertimass Model



- Excel spreadsheet model
- Assumes takeoff at rectification column feeds Vertimass bolt-on
- Includes heat integration of Vertifuel products into ethanol facility
- Capital costs for Vertimass bolt-on estimated
- Operating Costs (added to ethanol production costs) include catalyst replacement, energy use, insurance, taxes, maintenance, and labor.