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Fast Pyrolysis and Hydrotreating: 2015 State of Technology R&D and Projections to 2017

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March 2016

Pacific Northwest
NATIONAL LABORATORY

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1.0 State of Technology R&D for 2015

The Bioenergy Technologies Office's (BETO) strategic goal is to "*develop commercially viable bioenergy and bioproducts technologies to enable the sustainable, nationwide production of biofuels that are compatible with today's transportation infrastructure, can reduce GHG emissions relative to petroleum-derived fuels, and can displace a share of petroleum-derived fuels to reduce U.S. dependence on oil and encourage the creation of a new domestic bioenergy industry*" (US DOE, 2015). As such, BETO supports research and development (R&D) activities related to conversion of terrestrial feedstocks (e.g. wood, agricultural residues, energy crops) and algal feedstocks to liquid transportation fuels.

The Conversion R&D Program sets performance goals toward a future cost target each year and measures R&D progress toward those targets by verifying that technical progress made in a given year has an impact on modeled conversion costs. Modeled scenarios, in close collaboration with researchers, are used to perform conceptual evaluations termed "design cases". These provide a detailed basis for understanding the potential of conversion technologies and help identify technical barriers where research and development could lead to significant cost improvements. There are two design cases for (non-catalytic) fast pyrolysis and catalytic upgrading to hydrocarbon fuels. First is the 2009 "Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case" (Jones *et al* 2009). This report is based on the relatively small amount of literature available at the time, particularly for the catalytic upgrading of fast pyrolysis oil and the capital costs associated with fast pyrolysis. An updated design case, "Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Fast Pyrolysis and Hydrotreating Bio-oil Pathway" (Jones *et al* 2013a), captures a better understanding of the capital and operating costs from BETO's research and development efforts and details the technical and economic targets expected to be achievable by 2017.

Each year, BETO assesses their research progress towards annual technical targets by incorporating data from their R&D portfolio into technoeconomic models, from which production costs are estimated. Published data are also used, when available, to capture the current state of the art for a given technology. The state of technology (SOT) R&D model and accompanying report reflect the minimum fuel selling price (MFSP) for the technology, modeled as an nth plant[1] obtaining a 10% internal rate of return at a net present value of zero. Economic assumptions are consistent across BETO design cases and SOTs, to allow standardization of an economic basis for technology comparisons[2]. This standardization does not account for differing levels of maturity amongst technologies under investigation, thus SOTs play an important role in documenting current thinking about data gaps and research needs. New projections for annual cost targets are then developed and documented as a reference for BETO's Multi-Year Program Plan[2]. Finally, the SOT captures the current state of sustainability indicators, based on modeled inputs and outputs for the technology in the context of an nth plant design, including greenhouse gas (GHG) emissions, fossil energy consumption, total fuel yield per ton of biomass, carbon-to-fuel efficiency, water consumption, and wastewater generation.

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[1] "nth" plant design assumptions do not account for additional first of a kind plant costs, including special financing, equipment redundancies, large contingencies and longer startup times necessary for the first few plants. For nth plant designs, it is assumed that the costs reflect a future time when the technology is mature and several plants have already been built and are operating.

[2] Current and historical economic assumptions may be found in Appendix C of BETO's Multi-Year Program Plan (US DOE 2015).

This State of Technology report documents the modeled costs that are based on experimental data for pyrolysis oil upgrading that was generated in FY15 and compares them to the projected costs for FY15. Previous year's assessments may be found in Jones *et al* (2011, 2012, 2013b, 2014, 2015).

The following sections describe each processing step and its supporting SOT data.

1.1 Feedstock Preparation and Costs

The Idaho National Laboratory (INL) has made significant advances in understanding feedstock preparation and its associated costs. The feedstock cost used in the 2015 SOT is based on their analysis of current feedstock costs associated with preprocessing at a depot. Biomass is dried and sized at the depot, and is delivered to the conversion plant in a form that is ready to use in a fast pyrolysis reactor. The 2015 SOT feedstock delivered cost as a dried and sized material to the conversion plant ready for use in the pyrolyzers is $97.34/dry ton (in 2014$) of biomass (Searcy 2015). The details of the depot system and the feedstock costs are documented in the 2014 woody-feedstock report by Cafferty *et al* (2014b). Work is ongoing to estimate the impact of processing blended feedstocks as opposed to pure feedstocks.

1.2 Fast Pyrolysis

Conventional fast pyrolysis entails rapid heating of biomass feedstock to approximately 932°F (500°C) in less than two seconds, at atmospheric pressure and without the addition of a catalyst. Pyrolysis vapors are rapidly quenched and captured. Cooled pyrolysis products comprise primarily liquid (water and organic compounds), char mixed with biomass ash, and non-condensable gases. Conventional fast pyrolysis technologies are already commercialized for production of food flavorings and heat/power applications. While some R&D efforts are focused on making fast pyrolysis more efficient, this work is fairly fundamental (as opposed to applied) and is not included in the modeling elements of this SOT. Fundamental R&D, new patents (e.g., novel processes), industrial and international fast pyrolysis efforts are captured in Section 4.

The process model used in this analysis is based on a feed rate of 2000 metric tons per day (2205 dry U.S. tons per day) of biomass. For the modeled costs, two 1000 metric ton per day pyrolyzers (dry feed basis) are assumed to be operating in parallel. The yield of pyrolysis oil from biomass is modeled at 62 wt% (dry basis). This assumed yield is based on published data for small-scale pyrolysis (1 - 20 kg/h) operating on low-ash pine feedstock (VTT 2012). Enabling national-scale implementation of fast pyrolysis predicates the need to understand broader sourcing of biomass feedstocks and feedstock blends that can be delivered reliably and at low cost. The effects of blended feedstocks are currently being explored experimentally to inform future technoeconomic efforts. Preliminary data may be found in recent literature and presentations to scientific symposia (Howe 2015, Carpenter 2014).

1.3 Bio-Oil Stabilization and Catalytic Upgrading

The use of hydrotreating to upgrade pyrolysis oil constitutes a significant portion of the fuel production costs, and is therefore the main focus of the experimental work. Hydrotreating removes oxygen, nitrogen, and sulfur and saturates olefins and some aromatics. Pyrolysis oil contains hundreds of compounds of varying degrees of reactivity. Upgrading fast pyrolysis oil to hydrocarbon oil is accomplished in separate catalytic steps. Each step uses increasing severity to allow reduction of the oxygen content without causing immediate catalyst deactivation. Improved understanding of the nature of bio-oil reactivity and the conditions to successfully upgrade that oil has led to a revision in the reactor purpose and arrangement.

In the 2009 design case, pyrolysis upgrading comprises two fixed bed reactor systems in series. By 2013, pyrolysis oil upgrading transitioned to three fixed bed reactor systems in series to enable longer catalyst lifetimes. Experimentally, and as assumed in the models for the 2013 Fast Pyrolysis and Upgrading Design Case update and the 2013-2014 SOTs, the first reactor contains a ruthenium (Ru) based catalyst and operated at very mild hydrotreating conditions of 1200 psig, 284 °F (140 °C). This “stabilization reactor” reduced the reactivity of certain species that cause fouling in downstream beds when the temperature was increased. The next reactor in series, also containing a Ru-based catalyst, operated at 2000 psig, 338-392 °F (170-200 °C). The final bed contained a molybdenum (Mo) based catalyst and operated at more severe conditions of approximately 2000 psig, 788 °F (420 °C), allowing near total oxygen removal, plus a limited amount of hydrocracking. Still, longer catalyst lifetimes were needed to eliminate spare reactors. At the same time, the location of catalyst bed fouling and deactivation indicated a potential to combine the first two beds (stabilization and hydrotreating) into a single operation.

Work completed in 2015 focused on this process intensification, termed Deep Stabilization. Figure 1 shows the changes in the experimental setup. Deep stabilization of the bio-oil allows elimination of the middle bed, while increasing the catalyst life in the final bed. Deep stabilization is achieved by operating at significantly reduced space velocity, thus allowing greater conversion of sugars and carbonyls into more stable forms. This in turn delays catalyst deactivation in the final high temperature upgrading reactor.

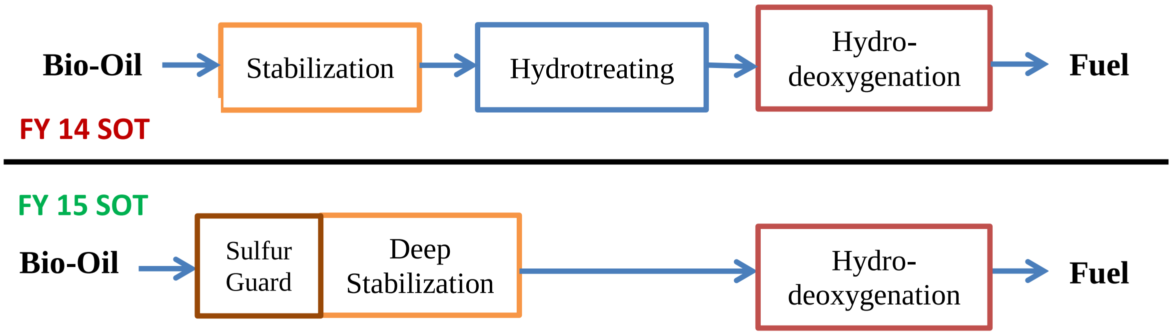

Figure 1: Box Flow Diagram of Bio-oil Upgrading Process Intensification

The process conditions used during stabilization and deep stabilization require a catalyst that is active at low temperatures, such as a precious metal. These types of metals render the catalyst extremely sensitive to sulfur poisoning. In the 2013 and 2014 SOTs, stabilization catalyst lifetimes assumed for meeting previous cost targets did not necessitate the implementation of a sulfur guard. As we move forward, catalyst lifetimes required to meet the 2015 cost target (and those beyond) require that sulfur, and possibly other inorganics, be actively managed. Catalyst regeneration methods will also become increasingly important. Experimental data for sulfur removal and catalytic upgrading was collected using continuous fixed bed reactors ranging from 30 mL to 400 mL.

The FY15 technical target was aimed at reducing capital costs contribution to the modeled minimum fuel selling price (MFSP). As shown in Table 1, this was achieved through elimination of the middle reactor, reducing the final operating pressure from 2000 psig to 1800 psig and slightly increasing the final bed space velocity.

Table 1: Reactor Conditions for the 2014 SOT and 2015 SOT

Reactor	**2014 SOT**	**2015**	**Change**
Stabilizer	LHSV = 0.5 T = 284 °F (140 °C) P =1200 psig Catalyst = Ru-based	**Deep Stabilization** LHSV = 0.23 T = 284 °F (140 °C) P = 1200 psig Catalyst = Ru-based	Deep Stabilization: operating at reduced space velocity and preceded by a sulfur scavenger Eliminated higher pressure & temperature intermediate upgrading bed #1
Upgrading Bed #1	LHSV = 0.27 T = 338-392 °F (180-200 °C) P = 2000 psig Catalyst = Ru-based		
Upgrading Bed #2	LHSV = 0.18 T = 788 °F (420 °C) P = 2000 psig Catalyst: Mo-based	LHSV = 0.22 T = 788 °F (420 °C) P = 1800 psig Catalyst: Mo-based	Increased liquid hourly space velocity, decreased operating pressure

The main research areas for conventional fast pyrolysis oil upgrading are related to catalyst life. The key results contributing to the 2015 SOT are given in Table 2.

Table 2: Effect of 2015 Process Changes

2015 Research	**Effect**
Substituted more severe stabilization (deep stabilization) for the previously milder stabilization, allowing elimination of the middle reactor and longer time on-stream for the remaining high temperature reactor	• Reduces capital and operating costs for the high temperature reactor section • Increases capital for stabilizer (plus guard bed)
Changed stabilizer catalyst base from carbon to titanium to allow regeneration	• Extends expensive Ru catalyst life decreasing operating costs
Installed base metal guard bed ahead of the deep stabilizer to capture sulfur. Guard bed life ~60 days, deep stabilizer (Ru catalyst) life ~100 days	• Extends expensive Ru catalyst life decreasing operating costs • Adds inexpensive base metal sulfur scavenger cost • Overall decreases the operating expenses
Deep stabilization reduces carbonyl content to the high temperature reactor, allowing longer time on stream. AOP work and partner work suggests that half a year is likely (previously 60 days)	• Reduces high temperature reactor operating costs

Overall, the process intensification achieved in 2015 results in a net decrease in both the capital and operating expenses related to bio-oil upgrading.

1.4 Fuel Finishing and Balance of Plant

Hydrocracking creates smaller molecules from larger ones and saturates alkenes and aromatics. It also converts any remaining oxygenates to hydrocarbons, such as phenolic groups which appear to be the most difficult oxygenate type to remove. While a small amount of hydrocracking is accomplished in the reactor system described in Section 1.3, there is still a significant heavier than diesel boiling fraction that could be cracked into additional gasoline and diesel. It is assumed in the 2015 modeled SOT costs that the diesel and heavier boiling range product are finished in a hydrocracker. This treatment cracks the heavier-than-diesel components back to the diesel range removes residual oxygenates and saturates some of the aromatics. No data have been published in this area as of 2015, and future research is planned to address this assumption.

The main contributor to the balance of plant costs is from hydrogen generation via conventional natural gas steam reforming. It is assumed that off-gases from the fast pyrolysis reactor and from the hydrotreaters can be used in the hydrogen plant. Verification of this assumption was not conducted in 2015 in support of this SOT, and may require future work.

2.0 Progression to 2017 Design Case

In order to be on a trajectory toward the 2017 design case, reduced capital and operating costs associated with the stabilization catalyst are needed. Deep stabilization not only allows a reduction in the number of high temperature and pressure upgraders, it also allows longer time on stream for the remaining high temperature reactor. Protecting the deep stabilizer from premature sulfur poisoning and effective regeneration methods for all catalyst are key areas of cost reduction, as is the need to:

- Optimize catalyst regeneration methods, through thermal or chemical means,
- Demonstrate catalyst time-on-stream through longer testing periods,
- Develop processes that achieve significant cost reductions, such as reactor type (e.g. ebullated bed), co-processing with petroleum in fluidized catalytic cracking to understand options for petroleum refinery integration, catalytic pyrolysis, and partial oil recycle in the upgrading reactors,
- Process scale up for both catalytic conversion and hydrocarbon fractionation to standard fuel boiling cuts and analysis of fuel characteristics, and
- Continue analysis to estimate the economic impact of processing blended feedstocks.
- Develop experimental plans to further explore gaps and opportunities for integrating partially hydrotreated bio-oil into existing petroleum refineries.

Figure 2 and Table 4 show the conversion cost (excludes feedstock cost) progression towards the 2017 target. Table 3 shows a comparison between the projected and the achieved 2015 results. All costs are in dollar year 2014 USD. The projected conversion cost for FY16 is \$3.05/gge, based on a reduction in upgrading and finishing processing costs over the 2015 SOT of \$3.80/gge.

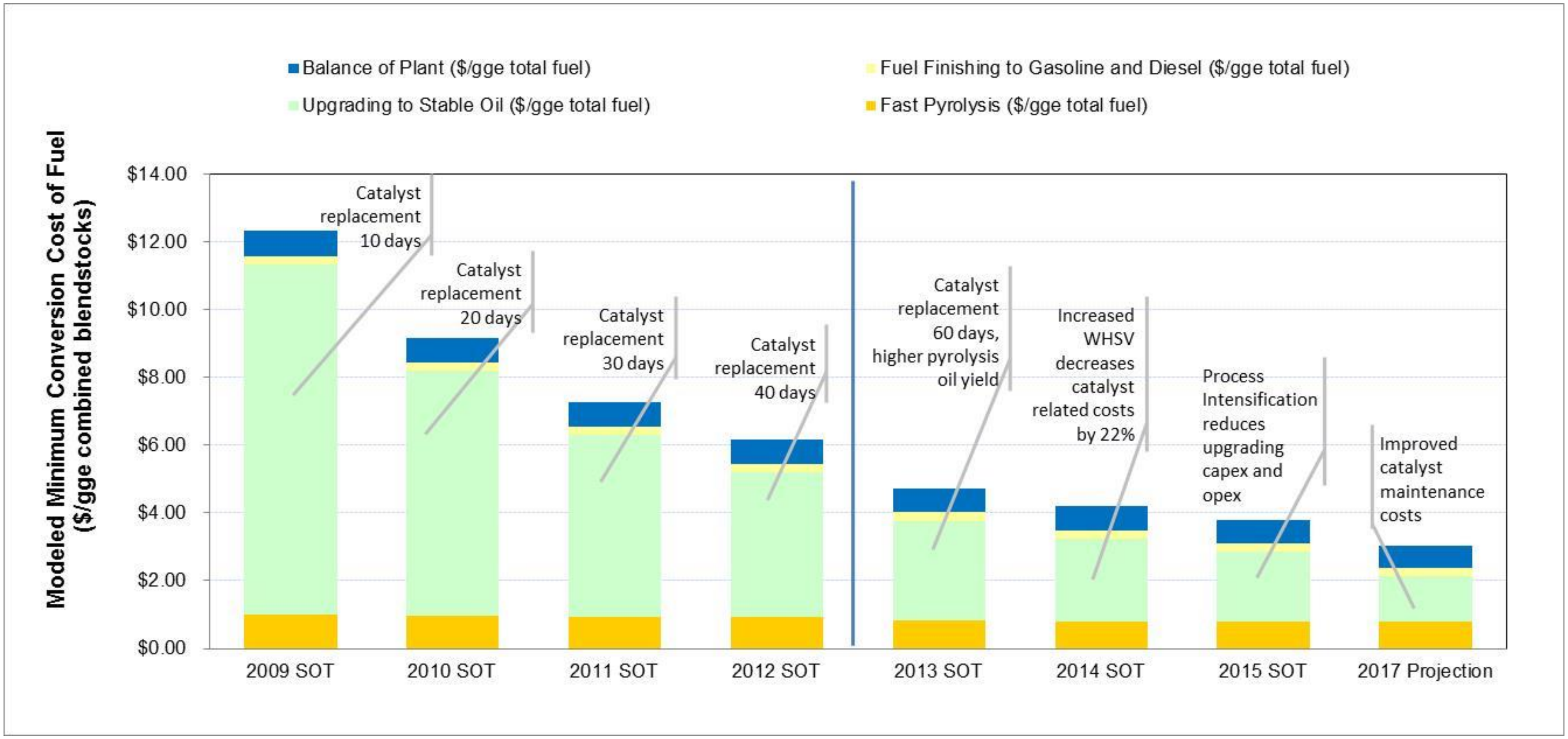

Figure 2: Conversion Cost Progression (2014 USD)

Table 3: Comparison of 2015 SOT and Projection (2014 USD)

Processing Area Cost Contributions & Key Technical Parameters	**Metric**	**2015 Projected**	**2015 SOT**
Conversion Contribution	$/gal gasoline blendstock	$3.73	$3.73
	$/gal diesel blendstock	$4.15	$4.16
Conversion Contribution, Combined Blendstocks	$/GGE	$3.80	$3.80
Perfomance Goal			
Combined Fuel Selling Price	$/GGE	$4.92	$4.92
Production Gasoline Blendstock	mm gallons/yr	29	29
Production Diesel Blendstock	mm gallons/yr	32	32
Yield Combined Blendstocks	GGE/dry US ton	87	87
Yield Combined Blendstocks	mmBTU/dry US ton	10	10
Natural Gas Usage	scf/dry US ton	1,685	1,774
Feedstock			
Total Cost Contribution	$/gge fuel	$1.12	$1.12
Capital Cost Contribution	$/gge fuel	$0.00	$0.00
Operating Cost Contribution	$/gge fuel	$1.12	$1.12
Feedstock Cost	$/dry US ton	$97.34	$97.34
Fast Pyrolysis			
Total Cost Contribution	$/gge fuel	$0.80	$0.80
Capital Cost Contribution	$/gge fuel	$0.68	$0.68
Operating Cost Contribution	$/gge fuel	$0.12	$0.12
Pyrolysis Oil Yield (dry)	lb organics/lb dry wood	0.62	0.62
Upgrading to Stable Oil via Multi-Step Hydrodeoxygenation/Hydrocracking			
Total Cost Contribution	$/gge fuel	$2.07	$2.07
Capital Cost Contribution	$/gge fuel	$0.53	$0.49
Operating Cost Contribution	$/gge fuel	$1.54	$1.57
Annual Upgrading Catalyst Cost, mm$/year	Annual cost is a function of: WHSV^2, number of reactors, catalyst replacement rate & $/lb	83	82
Upgraded Oil Carbon Efficiency on Pyrolysis Oil	wt%	68%	68%
Fuel Finishing to Gasoline and Diesel via Hydrocracking and Distillation			
Total Cost Contribution	$/gge fuel	$0.25	$0.24
Capital Cost Contribution	$/gge fuel	$0.17	$0.16
Operating Cost Contribution	$/gge fuel	$0.08	$0.08
Balance of Plant			
Total Cost Contribution	$/gge fuel	$0.68	$0.69
Capital Cost Contribution	$/gge fuel	$0.31	$0.31
Operating Cost Contribution	$/gge fuel	$0.38	$0.38
Models: Case References		2015 P 123013 $14	2015 SOT 123015 $14

Table 4: SOT and Projections for 2009 – 2017 (2014 USD)

Processing Area Cost Contributions & Key Technical Parameters	**Metric**	**2009 SOT**	**2010 SOT**	**2011 SOT**	**2012 SOT**	**2013 SOT**	**2014 SOT**	**2015 SOT**	**2016 Projected**	**2017 Projection**
Conversion Contribution	$/gal gasoline blendstock	$12.71	$9.45	$7.50	$6.36	$4.62	$4.12	$3.73	$2.99	$2.49
	$/gal diesel blendstock	$13.36	$9.93	$7.88	$6.68	$5.14	$4.58	$4.16	$3.32	$2.76
Conversion Contribution, Combined Blendstocks	$/GGE	$12.33	$9.17	$7.27	$6.17	$4.71	$4.19	$3.80	$3.05	$2.53
Perfomance Goal										$3
Combined Fuel Selling Price	$/GGE	$13.78	$10.57	$8.50	$7.25	$5.95	$5.42	$4.92	$4.10	$3.50
Production Gasoline Blendstock	mm gallons/yr	30	30	30	30	29	29	29	29	29
Production Diesel Blendstock	mm gallons/yr	23	23	23	23	32	32	32	32	32
Yield Combined Blendstocks	GGE/dry US ton	78	78	78	78	87	87	87	87	87
Yield Combined Blendstocks	mmBTU/dry US ton	9	9	9	9	10	10	10	10	10
Natural Gas Usage	scf/dry US ton	1,115	1,115	1,115	1,115	1,685	1,742	1,774	1,685	1,685
Feedstock										
Total Cost Contribution	$/gge fuel	$1.45	$1.40	$1.23	$1.08	$1.24	$1.23	$1.12	$1.05	$0.97
Capital Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00
Operating Cost Contribution	$/gge fuel	$1.45	$1.40	$1.23	$1.08	$1.24	$1.23	$1.12	$1.05	$0.97
Feedstock Cost	$/dry US ton	$112.86	$108.68	$95.60	$84.14	$107.80	$107.09	$97.34	$91.54	$84.45
Fast Pyrolysis										
Total Cost Contribution	$/gge fuel	$1.00	$0.97	$0.95	$0.93	$0.81	$0.81	$0.80	$0.79	$0.78
Capital Cost Contribution	$/gge fuel	$0.85	$0.82	$0.80	$0.78	$0.69	$0.68	$0.68	$0.67	$0.67
Operating Cost Contribution	$/gge fuel	$0.15	$0.15	$0.15	$0.15	$0.12	$0.12	$0.12	$0.12	$0.11
Pyrolysis Oil Yield (dry)	lb organics/lb dry wood	0.60	0.60	0.60	0.60	0.62	0.62	0.62	0.62	0.62
Upgrading to Stable Oil via Multi-Step Hydrodeoxygenation/Hydrocracking										
Total Cost Contribution	$/gge fuel	$10.32	$7.21	$5.36	$4.27	$2.95	$2.45	$2.07	$1.34	$0.96
Capital Cost Contribution	$/gge fuel	$0.72	$0.69	$0.68	$0.67	$0.60	$0.63	$0.49	$0.46	$0.43
Operating Cost Contribution	$/gge fuel	$9.59	$6.52	$4.68	$3.60	$2.34	$1.82	$1.57	$0.88	$0.53
Annual Upgrading Catalyst Cost, mm$/year	Annual cost is a function of: WHSV[2], number of reactors, catalyst replacement rate & $/lb	525	352	249	188	133	100	82	41	19
Upgraded Oil Carbon Efficiency on Pyrolysis Oil	wt%	65%	65%	65%	65%	68%	68%	68%	68%	68%
Fuel Finishing to Gasoline and Diesel via Hydrocracking and Distillation										
Total Cost Contribution	$/gge fuel	$0.25	$0.25	$0.24	$0.24	$0.25	$0.24	$0.24	$0.25	$0.14
Capital Cost Contribution	$/gge fuel	$0.16	$0.16	$0.15	$0.15	$0.17	$0.16	$0.16	$0.16	$0.07
Operating Cost Contribution	$/gge fuel	$0.09	$0.09	$0.09	$0.09	$0.09	$0.09	$0.08	$0.08	$0.07
Balance of Plant										
Total Cost Contribution	$/gge fuel	$0.75	$0.74	$0.73	$0.72	$0.70	$0.70	$0.69	$0.67	$0.64
Capital Cost Contribution	$/gge fuel	$0.38	$0.36	$0.35	$0.35	$0.31	$0.31	$0.31	$0.31	$0.30
Operating Cost Contribution	$/gge fuel	$0.38	$0.38	$0.38	$0.38	$0.38	$0.38	$0.38	$0.37	$0.34
Models: Case References		2009 SOT 090913 14$	2010 SOT 090913 14$	2012 SOT 090913 $14	2012 SOT 090913 $14	2013 SOT 122013 $14	2014SOT HT213 $14	2015 SOT 123015 $14	2016 P 121913 $14	2017 P 090913 $14

[1] Note: The table may contain very small (≤ $0.01) rounding errors due to the difference between the way that Microsoft Excel™ displays and calculates rounded values.

[2] WHSV is weight hourly space velocity: weight of oil feed per hour per weight of catalyst.

3.0 Environmental Sustainability Metrics

BETO evaluates both economic and environmental performance of conversion pathways. The following environmental considerations are currently being assessed: greenhouse gas (GHG) emissions, fossil energy consumption, fuel yield, carbon-to-fuel efficiency, water consumption, and wastewater generation. Shown in Table 5 are the estimated metric values for the 2009 and 2012 to 2015 SOT cases and the 2017 projected case for the fast pyrolysis and oil upgrading pathway. The cases shown align with the corresponding cost year scenarios presented in Table 4, the models for which are based on the 2013 design case (Jones et al 2013). Metrics for the 2010 and 2011 are not shown because they only differ from the 2009 and 2012 cases by catalyst lifetime, resulting in only slight changes in GHGs and fossil energy. The GHGs and fossil energy increased for the 2015 SOT as compared to the 2014 SOT as a result of slightly higher natural gas and power consumption and the addition of base metal sulfur guard bed, and chemicals used for catalyst regeneration (see Appendix for more detail).

Table 5: Sustainability Metrics for Fast Pyrolysis and Upgrading Conversion

Sustainability Metric	2009 SOT[1]	2012 SOT	2013 SOT	2014 SOT	2015 SOT	2017 Projected
Fossil GHGs (g CO_2-e/MJ fuel)	22.1	19.8	20.5	19.4	22.2	18.9
Fossil Energy Consumption (MJ fossil energy/MJ fuel)[2]	0.326	0.294	0.321	0.310	0.359	0.301
Total Fuel Yield (gal/dry ton wood; gge/dry ton wood)	74; 78	74; 78	84; 87	84; 87	83; 87	84; 87
Carbon-to-Fuel Efficiency (C in fuel/C in biomass)	38%	38%	47%	47%	48%	47%
Water Consumption (m^3/day; gal/GGE fuel)[3]	998; 1.5	998; 1.5	1124; 1.5	1088; 1.5	1125; 1.6	1050; 1.4
Wastewater Generation (m^3/day; gal/GGE fuel)[3,4]	917; 1.4	917; 1.4	948; 1.3	975; 1.3	1800; 2.5	932; 1.3

Table Notes:

1. The only difference between the 2009 and 2012 SOT cases is a decrease in hydrotreating catalyst consumption for the 2012 SOT.
2. Fossil energy consumption does not include grinding of the feedstock prior to the pyrolysis step.
3. Water consumption and wastewater generation include only direct use/emissions and do not include water associated with upstream production of materials and energy used at the plant.
4. Wastewater generation includes both wastewater from hydrotreating and blowdown from the cooling towers.

The metrics for GHG emissions and fossil energy consumption include both direct effects at the plant and upstream effects associated with the production and distribution of materials and energy for the plant operations, i.e., these are the life cycle emissions and energy usage for the conversion stage of the fuel supply chain. The SimaPro software (2014) is used to model and calculate cumulative GHGs and energy use for the conversion process. Mass and energy balance information from the process model, along with life cycle inventory data from the Ecoinvent (2011) and U.S. Life Cycle Inventory (2012) databases is used to populate the model. For a list of inventory data and additional assumptions, see Appendix A. Water consumption and wastewater generation values consider only direct water inputs and wastewater generation at the plant, and therefore do not include the effects of water use and discharge associated with production and distribution of energy and materials used at the plant.

4.0 Overall State of Technology

Pyrolysis and upgrading in various forms continues to be the subject of much research. Research, patents and commercialization related to uncatalyzed pyrolysis and condensed phase upgrading were surveyed during 2015 and summarized here.

Universities

Slovenian researchers studied novel upgrading catalysts with improved performance over conventional HDO catalysts. Čelič et al (2015) employed nickel containing Metal-Organic Framework (MOF) to generate nanoparticles in situ. The resulting HDO activity was more than ten times higher compared to commercial catalysts. Iranian researchers (Taghvaei 2015) used a novel catalytic reactor with electric arc discharge to deoxygenate 4-methylanisole (model compound), resulting in different product slates depending upon the type of catalyst used. In China, Wang et al (2015) used a sequence of zeolite cracking, ionic liquids and Pd/C to produce good quality jet fuel from rice straw bio-oil.

Precious metal and base metal upgrading catalysts performance continues to be an area of research interest. Sanna et al (2015) using continuous flow reactors, found that the order of reactions are levoglucosan > hydroxyacetaldehyde > catechol > acetic acid > hydroxyacetone > and glucose as the temperature rises. At 125°C levoglucosan becomes hydroxyacetone, furfural and 5-HMF. At 150°C polymerization and condensation causes sugars to form coke. South Korean researchers (Oh 2015) investigated ethanol and bio-oil mixtures over Ru/C and Pt/C in batch reactions. Ethanol reduced coke formation relative to neat processing. Yao et al (2015) studied Rh, Pt, Pd, Ru catalysts over various supports to convert a model compound, diphenyl ether, to a variety of oxygenated and non-oxygenate products. Catalyst and temperature affected the selectivity. Ying et al (2015) demonstrated that methanol when combined with bio-oil over Raney nickel could be a hydrogen substitute. Leiva et al (2015) studied HDO of 2-methoxyphenol over Re active phases on SiO_2. The $ReOx/SiO_2$ was the most active and sulfiding was not required. Shafaghat et al (2015), in a model compound study with phenol, cresol, guaiacol HDO over mixed Pd/C and zeolite found that strong acid site favor cycloketones, while weak acid sites favor cyclohexane.

Upgrading phase separated fractions also received attention. Sharifzaden et al (2015) at Imperial College in London water separated bio-oil, and then applied HTL to the predominately aqueous fraction and HDO to the predominately organic fraction. Researchers at the University of the Basque Country (Valle 2015) performed HDO studies on whole and phase separated bio-oil, The HDO test were preceded by thermal treatments at various temperatures, with the whole oil performing better than the phase separated oil.

Studies at Mississippi State University oxidized bio-oil as a pretreatment step and noted its effect on subsequent upgrading (Parapti 2015; Tanneru 2015). Rover et al (2015) at Iowa State University condensed pyrolysis vapors into several separate fractions. Stabilization of the phenol rich fraction over Pd/C at nearly ambient conditions appeared to reduced bio-oil viscosity.

Co-product opportunities associated with pyrolysis include studies by Hosseinnezhad (bio-adhesives), Kim (phenols), and Li (sustainable aromatics).

Three reviews appeared. Researchers at the Hungarian Academy of Sciences and Slovak University of Technology (Badari et al, 2015) published a mini-review of upgrading via ketonization, aldol condensation, HDO, and esterification over solid acid catalysts. Sudipta et al, (2015) reviewed HDO processes and the conversion of platform chemicals (HMF, furfural, levulinic acid, lignin) into hydrocarbon fuels. Arun et al (2015) from the University of Saskatchewan reviewed major developments in the design of HDO catalysts.

Modeling and Techno-economic studies include Gollakota et al (2015) who modeled an ebullated bed using CFD, based on experimental results with three types of alumina supported catalysts: Pt, NiMo and CoMo. Pt produces more gas, while phenol formation is more prevalent with NiMo and CoMo catalysts. Pyrolysis and upgrading analyses appearing in 2015 include Brown (thermochemical processes), Bittner (aviation fuels), Peters (exergy and LCA), Shemfe (power generation), Sharifzadeh (decarbonization of olefin processes using pyrolysis oil and upgraded oils).

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Doug Elliott at PNNL updated his seminal 2007 review to survey HDO developments from 2008 onwards (Elliott 2015). Key to understanding upgrading issues are knowledge of the source bio-oil (conditions and characterization), the impact of sulfide versus non-sulfided catalysts, and as batch HDO studies are of limited use, more research emphasis should be placed on continuous-flow reactor systems.

French et al (2015) at NREL studied effects of $NiMo/Al_2O_3$, Pd/C and Pt/C to upgrade pyrolytic lignin produced from water separated bio-oil. NMR suggests that only phenols remain when HDO is taken to 5% remaining oxygen content.

PNNL and Iowa State University (Elliott 2015) hydroprocessed phenolic oils fractionated from oak and corn stover bio-oils. Precious metal catalyst produced more saturated products than base metal catalysts.

Panisko et al (2015) at PNNL characterized the aqueous fraction derived from complete deoxygenation of pyrolysis oil. Very little carbon (<0.2 wt %) is lost to the aqueous phase. Most of the inorganic material (by ICP) is below detection except for Na, Si and S, which were present in the hundreds of ppm or less.

ORNL researcher (Connaster 2015) measured the corrosive species of a variety of bio-oils from seven different sources with polarity-matched analytics. A modified TAN method, AMTAN, was developed to meet the specific needs of such oils.

VTT and PNNL published norms and standards for pyrolysis oil (Oasmaa 2015). VTT researchers also published a study of co-processing of dry bio-oil, catalytic pyrolysis oil and hydrotreated pyrolysis in a micro activity test unit. Catalytic pyrolysis oil is more aromatic than HDO oils. Co-processing with vacuum gas oil in the MAT unit indicated increased rates of coking with increased concentration of bio-oil (Lindfors 2015).

Boateng et al (2015) at the USDA pyrolyzed the woody desert shrub, guayule, to product a high quality bio-oil that can be distilled. Continuous HDO with three different catalysts (Pd/C, Ru/C and Pt/C) at LHSV of 0.4 to 0.6 resulted in products with 4 wt% oxygen content. Detailed product characterization was given.

Patents and Applications

Ensyn Renewable Inc. patent application (US 2015/0004062 A1) addresses a system to co-process bio-oil and petroleum in a petroleum refinery in the presence of a catalyst.

UOP was granted a patent (US 9,068,126 B2) which combines raw bio-oil with a heated low-oxygen bio-oil as diluent to form a heated, diluted feed, allowing heating to >150°C without plugging. UOP has three applications (US 2015/0159093 A1, 01669001 A1, 0175896 A1) for bio-oil deoxygenation employing a recycle column, HDO with neutral support catalysts, and HDO with TiO_2, SiO_2, ZrO_2 and Nb_2O_5 catalyst supports.

Shell Oil Company (US 2014/0121428 A1) patent application covers partial HDO oil co-processed in an FCC unit.

Total Raffinage Marketing was granted US 9,193,919 B2 for a process that includes fractional injection of hydrogen into a catalytic bed (using either raw bio-oil or phase separated bio-oil) to control temperature followed by phase separation and optional recycle the largely organic phase.

The following patents and applications address fast pyrolysis: American Bio Energy Converting Corp (US 9,217,110 B1) pyrolysis system co-located at sawmill to produce oil and char; Phillips 66 (US 2014/0073823 A1) auger reactor with vapor upgrading; Michigan State University (US 2014/0110268 A1) electro catalytic HDO; Ensyn (US 2015/0004062 A1) systems for fuels from biomass; Battelle Columbus (WO 2014/19031 A1) falling bed pyrolysis reactor; Battelle Columbus (WO 2015/179798 A1) downflow bed pyrolysis reactor; Albermarle Europe (US 2015/0190788 A1) pyrolysis catalyst preparation and use.

Commercial

Commercial and demonstration news highlights from 2015 are as follows:

- **Ensyn** has received key regulatory approval for its renewable gasoline RFGasoline created by co-processing pyrolysis derived Renewable Fuel Oil (RFO) with petroleum feedstocks. http://www.ensyn.com/wp-content/uploads/2015/11/Part-79-Gasoline-Press-Release-as-Issued-rev.pdf In November 2015, Ensyn signed an agreement with Youngstown Thermal to supply up to 2.5 million gallons of RFO per year. http://www.ensyn.com/2015/06/03/ensyn-and-youngstown-thermal-sign-rfo-biofuel-supply-agreement/
- **bioliq** (Biomsas to Liquid Karlsruhe) announced the startup of their pilot plant last December in Germany. The first stage is to produce fast pyrolysis oil that is then gasified for subsequent processing to fuels. https://www.airliquide.com/media/germany-start-second-generation-biofuel-production-through-bioliqtm-project
- **Battelle Columbus** demonstrated 1000 hours of bio-oil hydrotreatment on a single catalyst charge with plant to extend that to 4000 hours. (http://www.battelle.org/media/press-releases/battelle-team-passes-important-department-of-energy-pyrolysis-milestone)
- **BTG (**Biomass Technology Group) has initiated the development of the **Empyro pyrolysis** plant in Hengelo (the Netherlands) that will produce 20 million liters of pyrolysis oil annually. http://www.btgworld.com/en/news/article?id=134
- **Renergi** Pty. Ltd. operates a 100 kg/h demonstration scale pyrolysis plant in Western Australia and developed non-noble metal catalyst for upgrading to fuels. They are partnered with ARENA to design a 20 L/hr plant (http://arena.gov.au/project/a-low-emission-biofuel-technology/)
- **Amaron Energy** demonstrated their 20 tpd mobile pyrolysis unit in Cle Elum Wa. http://www.pyne.co.uk/Resources/user/PyNe%20Newsletter%2036%20FINAL%202015.pdf

Last August, Biofuels Digest published a detailed summary of key pyrolysis related industrial entities. http://www.biofuelsdigest.com/bdigest/2015/08/03/the-pyromaniax-class-of-2015-the-top-10-pyrolysis-projects-in-renewable-fuels/

Publically Available Information and Links

IEA Task 34 (http://www.pyne.co.uk) Pyrolysis January, July and December 2015 newsletters summarized current fast pyrolysis status around the world. The July newsletter lists known pyrolysis plants and scales. The website also includes a pyrolysis demo plant database of pyrolysis and their TRL levels.

“Biomass and Waste Pyrolysis: A Guide to UK Capabilities” detailing research and commercial activities (http://www.pyne.co.uk/Resources/user/UK%20Biomass%20and%20Waste%20Pyrolysis%20Guide%202015%20081015.pdf was published by Aston University.

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Appendix A – Methodology for GHG and Fossil Energy Calculations

The life cycle modeling software, SimaPro, is used to model the conversion stage of the fuel life cycle. Table A. 1 lists the process inventory data used in SimaPro for GHG and energy estimates for the SOT and projected cases (see Table 4). The comments column gives additional parameters such as fuel heating values and further detail on the methodology. The inventory is based on material and energy balances from the process models. Data from the Ecoinvent database (2011) and the U.S. Life Cycle Inventory Database (2012) is used for estimating energy and emissions associated with the production and distribution of materials and energy used at the plant (natural gas, electricity, catalyst, maintenance chemicals) and with waste treatment/disposal. Emissions and energy consumption for the U.S. average grid mix of electricity is assumed. The IPCC 2007 GWP 100a V1.02 inventory method and the Cumulative Energy Demand V1.07 inventory method (both included in the SimaPro package) are used to calculate the cumulative GHG emissions and fossil energy use, respectively. Due to a lack of available data on catalyst manufacture, recycling and reclamation processes, this component is approximated with a zeolite product from the Ecoinvent database.

Table A.1. Inventory Data for Conversion GHG and Energy Estimates

		2009 SOT	2012 SOT	2013 SOT	2014 SOT	2015 SOT	2017 Projected	
Products	Units	Quantity						Comments
Gasoline	Btu/hr	454500875.2	454500875.2	420538581.8	417937549.1	417937583.4	420214996.5	
Gasoline LHV	Btu/lb	18530	18530	18940	18800	18800	18900	
Diesel	Btu/hr	373358106.2	373358106.2	509575635.5	507856148.5	507858078.9	509220020.0	
Diesel LHV	Btu/lb	17950	17950	17880	17820	17820	17930	
Resources								
Water, unspecified natural origin/kg	lb/hr	91668	91668	103235	121004	103210	96410	Cooling makeup and boiler feedwater makeup
Air	lb/hr	847000	847000	789400	809900	621400	785400	Air for burners
Energy, output, from gasoline	Btu/hr	827858981.5	827858981.5	930114217.3	925793697.7	925795662.3	929435016.6	Gasoline and diesel LHV together
Materials/fuels (process used in SimaPro)								
Natural gas, high pressure, at consumer/RER WITH US ELECTRICITY U	Btu	107114960	107114960	161840067	167343519	170481269	161840067	NG for steam reforming. Calculated from NG flowrate and HHV of 23,120 Btu/lb from ChemCad model
Electricity, medium voltage, at grid/US WITH US ELECTRICITY U	MWh	11.50	11.50	10.96	9.25	10.30	9.79	Includes power from steam turbines
Zeolite, powder, at plant/RER WITH US ELECTRICITY U	lb/hr					366.2		Placeholder for sulfur guard bed fill
Zeolite, powder, at plant/RER WITH US ELECTRICITY U	lb/hr	13.4	13.4	13.4	14.0	249.38	14.0	Placeholder for stabilizer catalyst
Zeolite, powder, at plant/RER WITH US ELECTRICITY U	lb/hr	1645.6	576.0	400.0	289.4	43.4	54.9	Placeholder for hydrotreating catalyst
Zeolite, powder, at plant/RER WITH US ELECTRICITY U	lb/hr	2.0	2.0	3.0	2.6	2.6	0.7	Placeholder for hydrocracking catalyst
Zeolite, powder, at plant/RER WITH US ELECTRICITY U	lb/hr	1.7	1.7	1.8	1.8	1.8	1.8	Placeholder for hydrogen plant catalyst. Estimates from Matros Technologies Steam Reforming. catalyst life 3 yr; density 58 lb/ft3, and scaling with methane flow rate
Acetone, liquid, at plant/RER WITH US ELECTRICITY U	lb/hr					95.8		Regen of sulfur guard bed and stabilizer catalyst
Sodium formate, reaction of formaldehyde with acetaldehyde, at plant/RER WITH US ELECTRICITY U	lb/hr					3251.6		Regen of sulfur guard bed and stabilizer catalyst

		2009 SOT	2012 SOT	2013 SOT	2014 SOT	2015 SOT	2017 Projected	
Hydrochloric acid, 30% in H2O, at plant/RER WITH US ELECTRICITY U	lb/hr	0.19	0.19	0.19	0.19	0.19	0.19	Boiler chemicals
Sulphite, at plant/RER WITH US ELECTRICITY U	lb/hr	0.19	0.19	0.19	0.19	0.19	0.19	Boiler chemicals
Sodium hydroxide, 50% in H2O, production mix, at plant/RER WITH US ELECTRICITY U	lb/hr	0.19	0.19	0.19	0.19	0.19	0.19	Boiler chemicals
Chemicals inorganic, at plant/GLO WITH US ELECTRICITY U	lb/hr	0.13	0.13	0.34	0.34	0.32	0.25	Cooling system maintenance chemicals
Refinery/RER/I WITH US ELECTRICITY U	p/hr	0.0000031	0.0000031	0.0000032	0.0000032	0.0000032	0.0000032	Equipment for bio-oil refinery. Scaled based on conventional refinery of 1 million tonne crude oil/year.
Thermochemical Conversion Plant	p/hr	0.0000063	0.0000063	0.0000063	0.0000063	0.0000063	0.0000063	Equipment for pyrolysis oil plant. Based on NREL thermochem ethanol plant (2000 MTPD)
Dimethyl sulfoxide, at plant/RER WITH US ELECTRICITY U	lb/hr	60	60	50	50	50	50	Dimethyl sulfoxide used as proxy for dimethyl sulfide, sulfiding agent used for hydrotreating catalysts. Conservative estimate because more processing is required than for dimethyl sulfide)
Emissions to air								
Carbon dioxide, fossil	lb/hr	12537.90	12537.90	18943.51	19587.60	19954.98	18943.51	Emissions from steam reforming of NG
Carbon dioxide, biogenic	lb/hr	199672.09	199672.09	183158.14	183685.48	183222.07	183598.68	
Water	lb/hr	124222.83	124222.83	120187.49	120871.98	122395.86	119679.01	Burner/reboiler exhaust
Water	lb/hr	34027	34027	41533	36865	40517	36940	Evaporation and drift from cooling towers.
Hydrogen sulfide	lb/hr	14.66	14.66	12.54	12.54	3.52	12.29	
Sulfur dioxide	lb/hr	100.25	100.25	100.23	100.23	100.23	100.23	
Carbon monoxide	lb/hr	0.04	0.04	0.04	1.76	1.66	0.30	
Methane, biogenic	lb/hr	2.55	2.55	2.57	6.31	5.87	2.61	Wastewater and reformer burner exhaust
Waste to treatment								
Treatment, sewage, unpolluted, to wastewater treatment, class 3/CH WITH US ELECTRICITY U	m3/hr	38.2	38.2	39.5	40.6	75.0	38.8	From upgrading and blowdown. Assume boiler blowdown is recycled to cooling system and cooling blowdown goes to WWT.
Disposal, wood ash mixture, pure, 0% water, to sanitary landfill/CH WITH US ELECTRICITY U	lb/hr	1975	1975	1975	1975	1975	1975	Ash from fast pyrolysis

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