PNNL-22684



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

Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: 2012 State of Technology and Projections to 2017

SB Jones LL Snowden-Swan

February 2013



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#### PACIFIC NORTHWEST NATIONAL LABORATORY operated by BATTELLE for the UNITED STATES DEPARTMENT OF ENERGY under Contract DE-AC05-76RL01830

#### Printed in the United States of America

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# Contents

| 1.0 | Stat | e of Technology for 2012                       | 1   |
|-----|------|--|-----|
|     | 1.1  | Feedstock and Feedstock Preparation            | 1   |
|     | 1.2  | Fast Pyrolysis                                 | 1   |
|     | 1.3  | Upgrading                                      | 1   |
|     | 1.4  | Hydrocracking and Balance of Plant             | 4   |
| 2.0 | Prog | gression to 2017 Conversion Target             | 5   |
| 3.0 | Env  | ironmental Sustainability Metrics              | 9   |
|     | 3.1  | Greenhouse Gas Emissions and Fossil Energy Use | .10 |
|     | 3.2  | Fuel Yield and Carbon-to-Fuel Efficiency       | .12 |
|     | 3.3  | Water Consumption and Wastewater Generation    | .12 |
| 4.0 | Refe | erences  | .14 |

# Figures

| 1 <sup>st</sup> 350 Hours Operation 2011 versus 2012 Catalysts | 2  |
|--|--|
| 2012 Catalyst Chained Runs                                     | 3  |
| 2012 SimDis Results HT184                                      | 3  |
| Comparison of the 2011 and 2012 Flowsheets                     | 4  |
| Conversion Cost Progression                                    | 6  |
| Fossil GHGs for fast pyrolysis and upgrading1                  | 1  |
| Biogenic and fossil GHGs for fast pyrolysis and upgrading      | 2  |
|  | <ul> <li>1<sup>st</sup> 350 Hours Operation 2011 versus 2012 Catalysts</li> <li>2012 Catalyst Chained Runs</li> <li>2012 SimDis Results HT184</li> <li>Comparison of the 2011 and 2012 Flowsheets</li> <li>Conversion Cost Progression</li> <li>Fossil GHGs for fast pyrolysis and upgrading</li> <li>1</li> <li>Biogenic and fossil GHGs for fast pyrolysis and upgrading.</li> </ul> |

# Tables

| Table 1. | SOT Standalone Plant                                    | 7 |
|----------|---|---|
| Table 2. | Sustainability Metrics for Fast Pyrolysis and Upgrading | ) |

# 1.0 State of Technology for 2012

Each year, the DOE Bioenergy Technologies Office (BETO) assesses their research progress towards the goal of enabling the sustainable production of renewable fuels. Annual technical and economic targets and sustainability indicators have been established for the production of liquid transportation fuels via fast pyrolysis and upgrading of woody biomass. This report summarizes the research work completed in 2012 for fast pyrolysis oil upgrading to fuels, and compares the resultant modeled minimum selling fuel price to the 2012 target price as reported in the November 2012 Biomass Multi-Year Program Plan (DOE 2012). Research for this pathway is meant to drive towards the 2017 programmatic target of \$3/gasoline gallon equivalent.

The modeled minimum selling fuel price is based on a conceptual process design for converting biomass into liquid fuels that achieves key technical targets in a specified year, assuming n<sup>th</sup> plant modeled capital and operating costs. Thus it is not a calculation of the current commercial cost of production for the products for a pioneer plant. All economics are shown in constant 2011 U.S. dollars.

The conceptual plant (Jones et al 2009) has five main processing areas: Feed preparation, fast pyrolysis oil production, pyrolysis oil upgrading via hydrotreating, hydrocracking and the balance of plant (hydrogen generation, utilities, storage, etc.). Each area is discussed in the following sections. The 2012 conversion research is focused on upgrading the pyrolysis oil via hydrotreating.

### 1.1 Feedstock and Feedstock Preparation

INL has made significant advances in understanding feedstock preparation and its associated costs. As such, the feedstock cost projections assume pyrolysis reactor throat ready feedstock that has been dried from 30% moisture to 10% moisture and ground to 2-6 mm particles. The feedstock cost for 2012 are \$79.21/dry short ton.

# 1.2 Fast Pyrolysis

Conventional non-catalyzed fast pyrolysis is already commercialized on a small scale. The 2012 case assumes a single 2000 dry metric tpd pyrolyzer. Heat transfer limitations may make this degree of scale-up difficult to achieve and evaluation of multiple parallel units will be considered in future work. The assumed yield of pyrolysis oil is unchanged from 2011 (71 lb wet oil/100 lb of dry wood, of which, water is 15 wt%).

# 1.3 Upgrading

Hydrotreating removes oxygen, nitrogen, sulfur and saturates olefins and aromatics. Upgrading fast pyrolysis oil to stable hydrocarbon oil occurs in two steps. The first reactor step uses mild hydrotreating conditions to remove some of the oxygen and prevents secondary reactions (such as polymerization) that lead to catalyst occlusion. The second reactor operates at greater severity than the first; it uses higher temperatures and/or lower space velocities to achieve low levels of oxygen (<1 wt %). However, catalyst life has proved to be limited for both beds.

The 2012 research efforts were directed towards lengthening the amount of time before the catalysts in both beds required complete replacement. Previously, the reactors could only stay on line for a few days before the pressure drop increased to a point where shut-down was required. This indicated coking between the beds which was alleviated by dumping the catalyst, removing the plugged portion and then topping up (~10% of the whole) with fresh catalyst. Associated with the plugging was decreased catalyst activity which was monitored by the rise in product density. This type of operation resulted in complete catalyst replacement that corresponded to one month's life.

In 2012, catalyst maintenance significantly improved. This can be attributed to two enhancements. The first is the addition of a stabilizer reactor ahead of the 1<sup>st</sup> and 2<sup>nd</sup> stage hydrotreaters operating at 1400 psig, 180 °C and a weight hourly space velocity of 1.5 grams/hour feed/ gram catalyst. The second is the use of a more robust NiMo/alumina catalyst in the 2<sup>nd</sup> HDO reactor. This resulted in no pressure increase or accelerated product quality decline as measured by a rise in specific gravity. The difference between the 2011 and the 2012 HDO runs are shown in Figure 1. The blue line (2011 operation) shows frequent plugging and product specific gravity values above 0.9, which is a good indication of loss of catalyst was removed or added during the entire course of the run. Shut downs and restarts (spikes and dips) for the 2012 data are not the result of plugging, but merely the effect of required shut downs and restarts to allow operating personnel to work on other projects.



**Figure 1.** 1<sup>st</sup> 350 Hours Operation 2011 versus 2012 Catalysts

Figure 2 shows the complete results for the 2012 chained runs (runs that were paused, then restarted). 700 hours were accumulated without need for any catalyst replacement. The extension of the specific gravity trend line indicates that 40 hours is achievable before significant product degradation (specific gravity  $\geq 0.89$ ) requiring complete catalyst change out.





SimDis data in Figure 3 shows the boiling range for the product remains reasonably consistent over the length of run HT184. The product is fairly split between the gasoline range and diesel range, with a small heavier than diesel fraction.



Figure 3. 2012 SimDis Results HT184

The process simulation and associated Chemcad cost model were updated to include the cost for the stabilizer bed and associated equipment. This increased the overall capital cost for the system. This cost was mitigated by revising the flowsheet heat recovery to require less fuel gas for the HDO reactor trim heaters. This in turn resulted in more offgas to the hydrogen plant which displaced some of the

supplemental natural gas needed for hydrogen production. The 2011 and 2012 flowsheets are shown in Figure 4 for comparison.



Figure 4. Comparison of the 2011 and 2012 Flowsheets

The key research areas for conventional fast pyrolysis oil upgrading are catalyst life, efficient usage of hydrogen, and product quality.

### 1.4 Hydrocracking and Balance of Plant

Hydrocracking creates smaller chain components from larger ones and saturates alkenes and aromatics. It also removes any remaining oxygenates, such as the phenolic type groups which appears to be the most difficult oxygenate type to remove. The 2012 SOT case requires that all of the diesel and heavier boiling range product be finished in a hydrocracker. This treatment cracks the heavier-than-diesel components back to the diesel range and removes residual olefins and oxygenates and saturates some of the aromatics. No research in 2012 was conducted in this area.

The main area of the balance of plant is 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 2012.

# 2.0 Progression to 2017 Conversion Target

It is possible to meet individual targets separately, such as good gasoline octane, or low hydrogen consumption or low oxygen content. However, the research challenges are to <u>simultaneously</u> make good quality gasoline and diesel blendstocks, while balancing hydrogen consumption with yield, and maximizing upgrading catalyst life. Figure 5 shows the conversion cost progression to 2017. Table 1 shows the research targets needed to advance from the current SOT to the 2017 goal.

FY13 will focus on updating the pyrolysis and upgrading design case (Jones *et al* 2009) to incorporate research from the core pyrolysis and upgrading work, the National Advanced Biofuels Consortium, the pyrolysis oil upgrading solicitation work, and other published work on this topic, such as that funded by other agencies and departments of DOE.

In order to be on a trajectory to future technical and economic targets, increased yields and improved product quality is needed. Specifically, additional research is needed to:

- Improve hydrotreated oil yields through reduced cracking,
- Develop the means to extend the life of the pyrolysis oil hydrotreating catalysts,
  - Conduct catalyst deactivation studies to understand the mechanisms responsible for short upgrading catalyst life,
  - The effect of catalyst type and support affect product quality and yield, e.g. conventional hydrotreating catalysts versus palladium or ruthenium, alumina supports versus carbon,
  - Catalyst deactivation mechanisms, which likely are a combination of coke formation, catalyst sintering, and catalyst poisoning or occlusion,
  - Develop reaction kinetics to allow improved reactor design and potential reduction in capital expenditure together with control of competing mechanisms in order to improve selectivity towards desired products,
  - o Understanding how startup and shutdown procedures affect catalyst life,
  - Determine relative reaction rates of different functional groups within the bio-oil as it relates to the catalyst, the reactants and on the reactor surface,
- Improve hydrotreated product quality and consistency,
  - Determine compound types (e.g., % oxygenates, aromatics, naphthenes, olefins and saturates) within each of the product cuts for both the raw oil feed and the hydrotreated products,
  - Determine stable oil and product fuel specifications for oil refinery acceptance and how to maximize cuts or blends of upgraded fuels to balance production in existing refineries,
  - How upgrading conditions affect product quality, e.g. temperature, pressure, space velocity, hydrogen partial pressure at the reactor outlet.



Figure 5. Conversion Cost Progression

#### Table 1. SOT Standalone Plant

| Processing Area Cost Contributions |                   |           |          |          | 2012       |          | 2013        | 2014       | 2015       | 2016       | 2017        |
|------------------------------------|-------------------|-----------|----------|----------|------------|----------|-------------|------------|------------|------------|-------------|
| & Key Technical Parameters         | Metric            | 2009 SOT  | 2010 SOT | 2011 SOT | Projection | 2012 SOT | Projection2 | Projection | Projection | Projection | Projection3 |
| Conversion Contribution            | \$/gal gasoline   | \$7.55    | \$5.86   | \$4.73   | \$4.14     | \$4.15   | \$3.33      | \$2.82     | \$2.65     | \$2.12     | \$1.83      |
| conversion contribution            | \$/gal diesel     | \$7.61    | \$5.92   | \$4.78   | \$4.19     | \$4.20   | \$3.39      | \$2.88     | \$2.71     | \$2.18     | \$1.83      |
| Conversion Contribution, combined  |                   |           |          |          |            |          |             |            |            |            |             |
| fuel                               | \$/gge            | \$7.19    | \$5.59   | \$4.51   | \$3.95     | \$3.95   | \$3.18      | \$2.70     | \$2.54     | \$2.04     | \$1.73      |
| Year \$ basis                      |                   | 2011      | 2011     | 2011     | 2011       | 2011     | 2011        | 2011       | 2011       | 2011       | 2011        |
| Programmatic Target                | \$/gal            |           |          |          |            |          |             |            |            |            | \$3         |
| Minimum Gasoline Selling Price     | \$/gal gasoline   | \$9.01    | \$7.27   | \$5.97   | \$5.23     | \$5.23   | \$4.36      | \$3.83     | \$3.57     | \$2.95     | \$2.59      |
| Minimum Diesel Selling Price       | \$/gal diesel     | \$9.09    | \$7.35   | \$6.04   | \$5.30     | \$5.29   | \$4.44      | \$3.91     | \$3.64     | \$3.03     | \$2.59      |
| Production Gasoline + Diesel       | mm gallons/yr     | 53        | 53       | 53       | 53         | 53       | 61          | 61         | 66         | 70         | 76          |
| Yield (Gasoline + Diesel)          | gal/dry ton wood  | 73        | 73       | 73       | 73         | 74       | 84          | 84         | 91         | 98         | 106         |
| Natural Gas Consumption            | SCF/dry ton wood  | 1,160     | 1,160    | 1,040    | 1,040      | 901      | 1,820       | 1,820      | 2,300      | 2,700      | 3,120       |
| Feedstock                          |                   |           |          |          |            |          |             |            |            |            |             |
| Total Cost Contribution            | \$/gal total fuel | \$1.46    | \$1.41   | \$1.24   | \$1.09     | \$1.08   | \$1.05      | \$1.03     | \$0.93     | \$0.84     | \$0.76      |
| Capital Cost Contribution          | \$/gal total fuel | \$0.31    | \$0.29   | \$0.29   | \$0.24     | \$0.24   | \$0.20      | \$0.19     | \$0.17     | \$0.16     | \$0.14      |
| Operating Cost Contribution        | \$/gal total fuel | \$1.16    | \$1.12   | \$0.96   | \$0.85     | \$0.84   | \$0.85      | \$0.83     | \$0.75     | \$0.68     | \$0.63      |
| Feedstock Cost                     | \$/dry US ton     | \$106.92  | \$102.96 | \$90.57  | \$79.71    | \$79.71  | \$88.10     | \$86.26    | \$84.43    | \$82.59    | \$80.75     |
| Energy Content (LHV, dry basis)    | BTU/lb            | 7603      | 7603     | 7603     | 7603       | 7603     | 7603        | 7603       | 7603       | 7603       | 7603        |
| Fast Pyrolysis                     |                   |           |          |          |            |          |             |            |            |            |             |
| Total Cost Contribution            | \$/gal total fuel | \$0.62    | \$0.61   | \$0.60   | \$0.60     | \$0.59   | \$0.51      | \$0.51     | \$0.47     | \$0.44     | \$0.39      |
| Capital Cost Contribution          | \$/gal total fuel | \$0.38    | \$0.37   | \$0.36   | \$0.36     | \$0.35   | \$0.30      | \$0.30     | \$0.28     | \$0.26     | \$0.24      |
| Operating Cost Contribution        | \$/gal total fuel | \$0.24    | \$0.24   | \$0.24   | \$0.24     | \$0.24   | \$0.21      | \$0.21     | \$0.19     | \$0.18     | \$0.15      |
|                                    |                   |           |          |          |            |          |             |            |            |            |             |
| Feed Moisture Content to FP        | %                 | 10%       | 10%      | 10%      | 10%        | 10%      | 10%         | 10%        | 10%        | 10%        | 10%         |
| Number Fast Pyrolysis Units        |                   | no filter | filter   | filter   | w filter   | w filter | filter      | wfilter    | filter     | filter     | filter      |
| Pyrolysis Oil Yield (dry)          | lb/lb dry wood    | 0.60      | 0.60     | 0.60     | 0.60       | 0.60     | 0.62        | 0.62       | 0.63       | 0.64       | 0.65        |
| Ash Content                        | ppm               | <500      | <500     | <500     | <500       | <500     | <500        | <500       | <500       | <500       | <500        |
| Char                               | ppm               | <500      | <500     | <500     | <500       | <500     | <500        | <500       | <500       | <500       | <500        |
| Corrosivity, TBD                   | TBD               | TBD       | TBD      | TBD      | TBD        | TBD      | TBD         | TBD        | TBD        | TBD        | TBD         |

| Processing Area Cost Contributions           |                      |                |               |            | 2012        |            | 2013        | 2014        | 2015        | 2016        | 2017        |
|--|----------------------|----------------|---------------|------------|-------------|------------|-------------|-------------|-------------|-------------|-------------|
| & Key Technical Parameters                   | Metric               | 2009 SOT       | 2010 SOT      | 2011 SOT   | Projection  | 2012 SOT   | Projection2 | Projection  | Projection  | Projection  | Projection3 |
| Upgrading to Stable Oil via Multi-Ste        | n                    |                |               |            |             |            |             |             |             |             |             |
| Total Cost Contribution                      | \$/gal total fuel    | \$5.70         | \$4.05        | \$3.00     | \$2.42      | \$2.62     | \$1.59      | \$1.09      | \$1.01      | \$0.56      | \$0.55      |
| Capital Cost Contribution                    | \$/gal total fuel    | \$0.53         | \$0.51        | \$0.47     | \$0.47      | \$0.66     | \$0.40      | \$0.39      | \$0.36      | \$0.22      | \$0.21      |
| Operating Cost Contribution                  | \$/gal total fuel    | \$5.18         | \$3.54        | \$2.52     | \$1.95      | \$1.96     | \$1.19      | \$0.69      | \$0.64      | \$0.34      | \$0.34      |
|  |                      | 2x100% w       | 2x100% w      | 2x100% no  | 2x100% no   | 2x100% no  | 2x100% no   | 2x100% no   | 2x100% no   | 1x100% no   | 1x100% no   |
| Number of Parallel Hydrotreaters             |                      | guard bed      | guard bed     | guard bed  | guard bed   | guard bed  | guard bed   | guard bed   | guard bed   | guard bed   | guard bed   |
| Catalyst Life                                | operating days       | 14             | 21            | 30         | 40          | 40         | 60          | 120         | 120         | 329         | 329         |
| Catalyst Regeneration Frequency              | days                 | 0              | 0             | 0          | 0           | 0          | 0           | 0           | 0           | 6           | 1           |
| Catalyst Base                                |                      | carbon         | carbon        | carbon     | carbon      | carbon     | carbon      | carbon      | carbon      | carbon      | carbon      |
| Stable Oil Yield                             | lb/lb dry FP oil     | 0.40           | 0.40          | 0.40       | 0.40        | 0.40       | 0.45        | 0.45        | 0.47        | 0.50        | 0.55        |
| Corrosivity, TBD                             | TBD                  | TBD            | TBD           | TBD        | TBD         | TBD        | TBD         | TBD         | TBD         | TBD         | TBD         |
| Sulfur                                       | ppm                  | <40            | <40           | <40        | <40         | <40        | <40         | <30         | <30         | <20         | <15         |
| Nitrogen                                     | ppm                  | <40            | <40           | <40        | <40         | <40        | <40         | <40         | <40         | <40         | <40         |
| Chlorine                                     | ppm                  | <50            | <50           | <50        | <50         | <50        | <50         | <50         | <50         | <50         | <50         |
| Alkali Compounds                             | ppm                  | <10            | <10           | <10        | <10         | <10        | <10         | <10         | <10         | <10         | <10         |
| Gasoline, Octane Number                      |                      | ~89            | ~89           | ~89        | ~89         | ~89        | ~89         | ~89         | ~89         | ~89         | ~89         |
| Diesel, Cetane Index                         |                      | ~32            | ~32           | ~32        | ~32         | ~32        | ~32         | ~32         | ~32         | ~32         | >40         |
| Hydrogen Partial Pressure Reactor            | psia                 | ~1750          | ~1750         | ~1600      | ~1600       | ~1600      | ~1600       | ~1600       | ~1600       | ~1600       | ~1600       |
| Fuel Finishing to Gasoline and Diesel        | via Hydrocracking an | d Distillation |               |            |             |            |             |             |             |             |             |
| Total Cost Contribution                      | \$/gal total fuel    | \$0.35         | \$0.34        | \$0.33     | \$0.33      | \$0.31     | \$0.31      | \$0.30      | \$0.29      | \$0.28      | \$0.13      |
| Capital Cost Contribution                    | \$/gal total fuel    | \$0.25         | \$0.24        | \$0.24     | \$0.23      | \$0.21     | \$0.22      | \$0.22      | \$0.21      | \$0.21      | \$0.08      |
| Operating Cost Contribution                  | \$/gal total fuel    | \$0.10         | \$0.10        | \$0.10     | \$0.10      | \$0.10     | \$0.09      | \$0.09      | \$0.08      | \$0.07      | \$0.05      |
|  |                      | diesel and     | diesel and    | diesel and | diesel and  | diesel and | diesel and  | diesel and  | diesel and  | diesel and  | diesel and  |
| Extent of Hydrocracking/treating             |                      | heavier        | heavier       | heavier    | heavier     | heavier    | heavier     | heavier     | heavier     | heavier     | heavier     |
| Balance of Plant: Hydrogen Generation & OSBL |                      |                |               |            |             |            |             |             |             |             |             |
| Total Cost Contribution                      | \$/gal total fuel    | \$0.91         | \$0.89        | \$0.83     | \$0.82      | \$0.65     | \$0.95      | \$0.95      | \$0.91      | \$0.87      | \$0.75      |
| Capital Cost Contribution                    | \$/gal total fuel    | \$0.46         | \$0.45        | \$0.42     | \$0.41      | \$0.43     | \$0.36      | \$0.35      | \$0.33      | \$0.31      | \$0.25      |
| Operating Cost Contribution                  | \$/gal total fuel    | \$0.44         | \$0.44        | \$0.41     | \$0.41      | \$0.23     | \$0.60      | \$0.60      | \$0.58      | \$0.57      | \$0.50      |
| Models: Case References                      |                      | 2009 SOT-      | 2010 SOT-0912 | 2011 SOT-  | 2012 P-0912 | 2012 SOT   | 2013 P-0912 | 2014 P-0912 | 2015 P-0912 | 2016 P-0912 | 2017 Design |
| Models. Case helefelices                     |                      | 0912 HL        | HL            | 0912 HL    | HL          | 2012 501   | HL          | HL          | HL          | HL          | 0912 HL     |

## 3.0 Environmental Sustainability Metrics

In addition to setting technical and economic targets for the conversion pathways included in the MYPP, BETO has begun the process of setting baselines and targets for environmental sustainability metrics. Sustainability is a cross-cutting element of the Bioenergy Technologies Office whose overarching goal is to "understand and promote the positive economic, social, and environmental effects and reduce the potential negative impacts of biofuels production activities". A specific goal of the sustainability element is to identify metrics and set targets for at least one conversion pathway by 2013. To reach this goal, BETO, DOE National Laboratories and others have worked together to develop an initial set of important sustainability metrics for the conversion stage of the biofuel life cycle: greenhouse gas (GHG) emissions, fossil energy consumption, fuel yield, carbon-to-fuel efficiency, water consumption, and wastewater generation. Shown in Table 2 are the estimated metric values for the SOT and projected cases for the fast pyrolysis and oil upgrading pathway. The 2013 and 2014 projected cases are grouped together, as the only difference between these cases is slightly increased catalyst lifetime. It is important to note that the updated assumptions used for the 2012 SOT were not integrated into the other models (i.e., no back-casting or forecasting done).

| Sustainability Metric  | 2011 SOT        | 2012 SOT        | 2013-14<br>Projected | 2017 Projected |
|--|-----------------|-----------------|----------------------|----------------|
| GHGs (g CO <sub>2</sub> -e/MJ fuel) – (fossil<br>emission; biogenic emissions)         | 17; 104         | 15; 102         | 20; 78               | 22; 46         |
| Fossil Energy Consumption (MJ fossil energy/MJ fuel) <sup>2</sup>                      | 0.25            | 0.23            | 0.32                 | 0.38           |
| Total Fuel Yield (gal/dry ton wood)  | 73              | 74              | 84                   | 106            |
| Carbon-to-Fuel Efficiency (% of<br>biomass carbon ending up in liquid<br>fuel product) | 42 <sup>3</sup> | 41 <sup>3</sup> | 49                   | 62             |
| Water Consumption (m <sup>3</sup> /day; gal/gal fuel) <sup>4</sup>                     | 3330; 5.5       | 3160; 5.1       | 3510; 5.0            | 3270; 3.7      |
| Wastewater Generation (m <sup>3</sup> /day; gal/gal fuel) <sup>4,5</sup>               | 1320; 2.2       | 1310; 2.1       | 1370; 2.0            | 1340; 1.5      |

| Table 2. | Sustainability       | Metrics f | for Fast I | Pvrolvsis | and Up | grading |
|----------|----------------------|-----------|------------|-----------|--------|---------|
|          | S distantities integ | 1.1001100 |            |           | and op |         |

Table Notes:

- 1. Fossil energy consumption does not include grinding of the feedstock prior to the pyrolysis step.
- 2. The carbon-to-fuel efficiency for the 2011 SOT projected cases and the 2012 SOT is 41.6% and 41.3%, respectively. The 2012 SOT case has slightly higher gasoline yield and lower gasoline carbon content than the 2011 SOT case (83% for 2012 SOT; 87% for 2011SOT).
- 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 indirect effects associated with the production and distribution of materials and energy for the plant operations, i.e., these are the lifecycle emissions and energy usage for the conversion stage of the fuel

supply chain. Water consumption and wastewater generation values consider only direct water inputs and wastewater generation at the plant.

The following sections provide more detailed description of the sustainability metrics and a discussion of the results.

### 3.1 Greenhouse Gas Emissions and Fossil Energy Use

The Bioenergy Technologies Office is developing technologies that will facilitate the volumetric requirements of the national Renewable Fuel Standard (RFS(2)), as legislated by the Energy Independence and Security Act of 2007. Reducing fossil energy use and GHG emissions are integral to the RFS(2). In order to be eligible for the RFS(2) program, fuels made from renewable biomass must meet the renewable fuels categories definitions, which includes having lifecycle GHG emissions that are 50% (advanced biofuel) or 60% (cellulosic biofuel) less than the petroleum baseline. While RFS mandates the EPA to conduct its own LCA to determine fuel qualification, it is essential that lifecycle analysis be performed during the development of these pathways in order to predict and facilitate improvement of environmental performance. In many ways, this approach is analogous to that of the techno-economic analyses, allowing continual evaluation and improvement of the design throughout the technology research and development phase.

Conversion processes generate fossil-based GHG emissions stemming from fossil fuel consumption at the plant (e.g., natural gas) and from upstream production and distribution of materials and energy that are used at the plant (e.g., natural gas, grid electricity, chemicals, catalyst). Conversion GHGs consist primarily of  $CO_2$  (95%), with the remainder being methane released during natural gas production and distribution. Conversion processes also result in direct biogenic  $CO_2$  emissions from pyrolysis, char combustion, and oil upgrading processes, as well as off-gas reforming and combustion. The design is heat integrated and therefore any light gases that are produced at the plant are completely combusted for heat. Apart from land use change impacts for certain feedstocks, biomass is generally regarded as a carbon-neutral feedstock (i.e., carbon absorbed during growth equals carbon emitted during processing and final use), and therefore fossil energy use and emissions receive the majority of attention.

Conversion GHG and fossil energy metrics were developed based on material and energy balances from the process models, along with information from the Ecoinvent database (2011) and U.S. LCI database (2012). Emissions and energy consumption for the U.S. average grid mix of electricity is used. The lifecycle modeling software, SimaPro, was used to calculate the cumulative GHG emissions and fossil energy usage. Due to a lack of available data on catalyst manufacture, recycling and reclamation processes, this component has been approximated with a zeolite product from the Ecoinvent database. Future work on development of energy and material inventory data for the catalysts is necessary to fill this data gap. It is likely that catalyst will not contribute significantly if target economic catalyst lifetimes are achieved (i.e., at least 1 year). However, estimation of the catalyst impact is necessary to be able to confirm this assumption. Also, the use of precious metal or platinum group metals for catalysts may result in significantly different GHGs compared to Ni-Mo or Co-Mo catalysts.

Table 2 shows that there is an increasing trend in fossil energy use and resulting GHG emissions in going from the 2011 SOT case out to the 2017 projected case. Figure 6 shows the breakdown of contributing factors to the total fossil GHGs for the conversion plant and helps explain this trend. As fuel yields increase

over time with advances in the technology, more biomass carbon is put into the final fuel product. As a result, there is less biomass off gas to use for steam reforming into hydrogen, increasing the need for natural gas. This is the tradeoff that exists for achieving better fuel yields (and economics) when producing intermediate products that require hydrogen upgrading. Using more renewable sources of hydrogen at the plant (e.g., pyrolysis oil or adjusting gas production in pyrolysis to meet hydrogen needs) would reduce the carbon footprint of the conversion plant, however, the technical feasibility of these options as well as the impact on economics would also need to be determined. While the full supply chain is not covered here, it is important to note that improvements in fuel yield, while increasing the need for natural gas, also reduce the GHGs associated with production and transportation of feedstock.

The 2012 SOT case has slightly lower GHGs than the 2011 SOT projected case because of the factors listed below.

- Reduction of fuel gas usage in the fired heaters allowed more offgas to the hydrogen plant, thus displacing natural gas
- Slight increase in product yield
- Slight reduction in hydrogen consumption (6.5 lb H2/100 lb dry pyrolysis oil versus 6.7 projected)

In addition, the catalyst lifetime used for the 2012 SOT (40 day lifetime) is longer than that assumed for the 2011 SOT (30 day lifetime), resulting in lower GHGs associated with catalyst consumption for the process.



Figure 6. Fossil GHGs for fast pyrolysis and upgrading

Figure 7 includes direct biogenic GHG emissions at the conversion plant as well as fossil emissions. As shown, biogenic emissions constitute the majority of GHGs for the conversion plant and decrease in moving from the SOT cases out to the goal case, as more biomass carbon is integrated into the fuel and less is released during conversion processes.



Figure 7. Biogenic and fossil GHGs for fast pyrolysis and upgrading.

#### 3.2 Fuel Yield and Carbon-to-Fuel Efficiency

An overarching goal of BETO is to enable technologies that produce transportation biofuels in a sustainable way. Fuel yield and carbon-to-fuel efficiency are important measures of natural resource utilization and are inherent to biofuel sustainability. As shown in Table 2 and discussed in Section 3.1 with respect to GHGs, there is an important tradeoff that exists between the fuel yield and natural gas requirement for this pathway and others that similarly produce intermediate products requiring hydrogen-based upgrading. Fuel yield and carbon-to-fuel efficiency are measures of how efficient the technology is at producing liquid fuel. Therefore, when comparing fuel options, it is important to present these metrics alongside GHGs to provide a more comprehensive representation of the overall performance of the conversion process and the balance between these metrics. For example, a conversion process may have very low (or negative) GHGs, but this may be due to the majority of its biomass carbon going to electricity production (and thus producing a large GHG credit).

#### 3.3 Water Consumption and Wastewater Generation

Protection and conservation of water resources is a global concern as the potential impacts of climate change, growing population, and energy demand become increasingly evident. Energy production is a leading consumer of water within the industrial sector and the effect of biofuel production on water resources is an important sustainability concern. Consumptive water use associated with fast pyrolysis and upgrading consists of makeup water for the boiler and cooling systems. Boiler feed water makeup is needed to replace steam consumed in the hydrogen plant. Fresh cooling water is needed to make up for losses at the cooling tower (e. g, evaporation and drift) and blow down for maintenance of the recirculating

cooling system. Cooling water makeup is approximately 80% of the total water consumption for the process. The raw pyrolysis oil vapor quench requires the majority of cooling water for the plant, using about 97% of the total. While the water consumption values presented in Table 2 are likely in the approximate range of an actual biorefinery using this technology, there is much uncertainty around the quench process, specifically the flow rate of oil needed to provide the direct quench and the associated temperature. In addition, bio-oil yield and composition (and associated enthalpies), fluidized gas rate for the pyrolysis reactor, and quench temperature are all inter-related variables and can have a significant effect on cooling water consumption for the quench process. These differences in assumptions between the SOT and projected models, therefore, make it difficult to definitively comment on any trends in the water metrics at this time. Also, values could change significantly with the collection of more recent literature data as part of the pathway redesign during FY13.

Wastewater quantity and composition are important sustainability metrics, as facility wastewater is ultimately discharged to streams or lakes in the region and both of these factors can affect the health of local water resources. In addition, wastewater treatment, whether located onsite or offsite at a publicly owned treatment works, requires additional energy and materials. The primary wastewater streams generated from fast pyrolysis and bio-oil upgrading processes are cooling tower blow down and water separated from the stabilized bio-oil after hydrotreating. Water separated from the hydrotreated bio-oil stream originates from biomass moisture introduced into the system and water produced during the pyrolysis and hydrotreating reactions. This stream accounts for 60-65% of the total wastewater generated for the plant. Cooling system blowdown accounts for the remainder of the total plant wastewater. Efforts are underway to characterize the hydrotreater wastewater to determine treatment needs and specifications. Also, research is in progress to explore utilization of organics in this stream for production of additional fuels, chemicals, or hydrogen, the outcome of which may significantly change this portion of the pathway design and the final wastewater composition. Similar to water consumption, because there are several assumptions that affect water generation in the system, including bio-oil yield, bio-oil composition, and hydrotreating stage reactions, it is difficult to make specific conclusions as to any trends seen in the wastewater results for the different cases.

### 4.0 References

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