Life-Cycle Assessment of Pyrolysis Bio-Oil Production*

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Abstract

As part of the Consortium for Research on Renewable Industrial Materials' Phase I life-cycle assessments of biofuels, life-cycle inventory burdens from the production of bio-oil were developed and compared with measures for residual fuel oil. Bio-oil feedstock was produced using whole southern pine (*Pinus taeda*) trees, chipped, and converted into bio-oil by fast pyrolysis. Input parameters and mass and energy balances were derived with Aspen. Mass and energy balances were input to SimaPro to determine the environmental performance of bio-oil compared with residual fuel oil as a heating fuel. Equivalent functional units of 1 MJ were used for demonstrating environmental preference in impact categories, such as fossil fuel use and global warming potential. Results showed near carbon neutrality of the bio-oil. Substituting bio-oil for residual fuel oil, based on the relative carbon emissions of the two fuels, estimated a reduction in CO_2 emissions by 0.075 kg CO_2 per MJ of fuel combustion or a 70 percent reduction in emission over residual fuel oil. The bio-oil production life-cycle stage consumed 92 percent of the total cradle-to-grave energy requirements, while feedstock collection, preparation, and transportation consumed 4 percent each. This model provides a framework to better understand the major factors affecting greenhouse gas emissions related to bio-oil production and conversion to boiler fuel during fast pyrolysis.

T his report has been produced as part of the Consortium for Research on Renewable Industrial Materials (CORRIM) Phase I reports on the life-cycle inventory (LCI) and life-cycle impact assessment (LCIA) studies of biofuels. CORRIM's goal is to provide a database of information for quantifying the environmental impacts and economic costs of biofuels from woody biomass through the stages of collection, fuel conversion, and combustion in the United States.

Life-cycle assessment (LCA) has evolved as an internationally accepted way to analyze complex impacts and outputs of a product and the corresponding effects on the environment. An LCA can provide the most comprehensive method to assess net carbon emissions and their associated impacts for fossil and biofuels evaluated under similar uses. The environmental outcomes of an LCA can accurately target the source of impacts, including where, when, and how they occur throughout a product's life. The LCA process can provide characteristics such as global warming potential (GWP) and fossil fuel use that can be useful on a regional, national, or global scale. Outcomes from LCAs can be used to suggest more "environmentally friendly" products or sustainable production methods and may also provide insights regarding raw material conservation and emissions and waste output reduction. LCIA aggregates the inventory data and classifies them into the type of environmental impact to which they contribute, for example, GWP. Comparisons of the emission outputs of bio-oil with a relevant fossil fuel
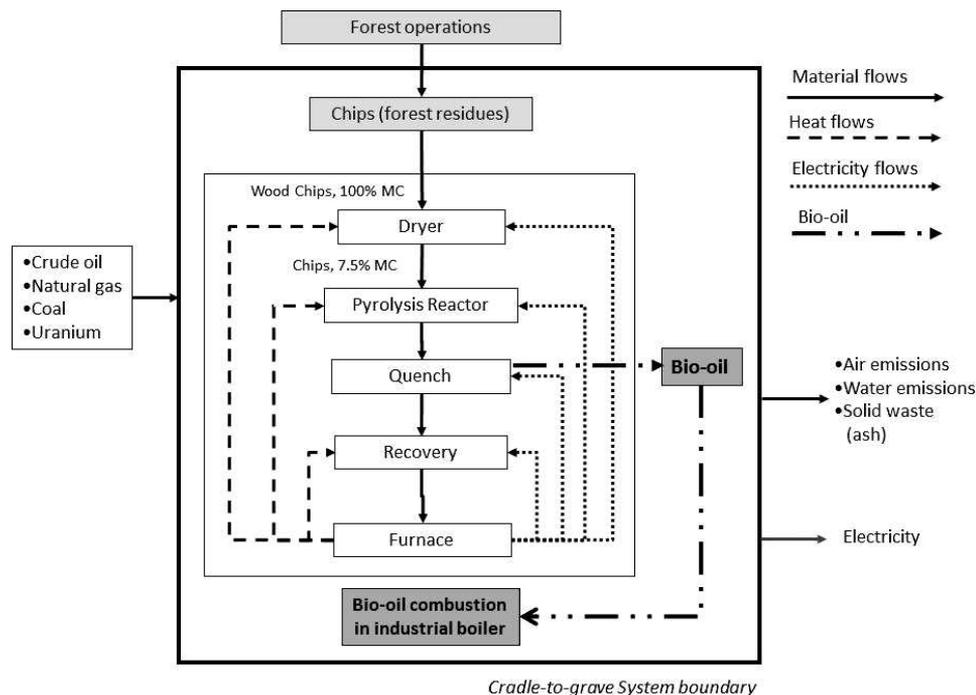
Figure 1.—Cradle-to-grave system boundary for the production of bio-oil.

(e.g., residual fuel oil [RFO]) determine the carbon benefit or mitigation performance.

The specific focus of this report is a cradle-to-grave LCI and LCIA of bio-oil produced from fast pyrolysis (Fig. 1). Feedstocks are based on noncommercial thinning in the southeastern United States. The data for this report were derived from conversion parameters incorporated into an Aspen model (Ringer et al. 2006) and the subsequent outputs produced in Aspen. Secondary data from published databases for the production of electricity, fuels, and ancillary materials have also been incorporated into this analysis (National Renewable Energy Laboratory [NREL] 2012).

The significance of this study is to demonstrate a reduction in greenhouse gas (GHG) emissions by the substitution of biofuels for fossil fuels. The goals of the Energy Independence and Security Act of 2007 (EISA 2007) are to reduce GHG emissions, increase energy independence, and stimulate rural economies by mandating the production of 36 billion gallons of biofuel per year, of which 21 billion gallons must be produced by nonfood feedstock sources. This study adheres to International Organization for Standardization (ISO) 14044 (ISO 2006) and CORRIM guidelines for conducting LCIs on biofuels (CORRIM 2010).

The benefits of this study include the following:

- Developing a benchmark for potential GHG reductions from the production of bio-oil from wood biomass, specifically forest thinnings
- Producing a quantitative carbon accounting from the collection of forest thinnings through the combustion of bio-oil
- Comparing residual fuel oil for heating with the benchmark for bio-oil
- Contributing to the US LCI database (NREL 2012)

Background

Peak petroleum production has either arrived or is expected to arrive soon. There is broad, although not universal, agreement that releases of GHG from fossil fuels are warming our planet, which will have potentially serious future environmental and social consequences. Biomass used as fuel is considered carbon neutral in the sense that only the carbon absorbed from the atmosphere by the biomass is released to the atmosphere when the biomass is burned; hence, there is no net addition to carbon released into the environment. There is also recognition that our biomass resource has been largely underused for the production of fuels. Finally, with increasing fossil fuel prices and rapid technological advances in conversion processes, in conjunction with national objectives to reduce carbon emissions and improve energy independence, the interest in biofuels has been growing. Gan and Smith (2006) assessed the availability of biomass on a regional basis. They reported that most of the national available biomass was located in the eastern United States, with the Southeast accounting for 67 percent of the total growing stock (9.3 million dry tons). About 50 percent of the total growing stock together with other sources (totaling 18.1 million dry tons) has the potential to displace 8.4 million tons of carbon emitted from coal-fueled plants.

Pyrolysis technology is advancing at a rapid rate and has promising potential for the commercial conversion of biomass to fuels. New paths to the production of upgraded bio-oils for transportation fuels are being announced with increasing frequency. Universal Oil Products, LLC, and Ensyn Corporation announced in September 2008 their intention to form a joint venture to produce heating fuels (Voegele 2008). Dynamotive Energy Systems Corporation announced success in producing a hydrotreating process to produce hydrocarbon fuels for heating and transportation fuel applications (Dynamotive Energy Systems 2012). Kior,

Inc., announced the intent to build five bio-oil production and upgrading facilities in Mississippi (Biofuels Digest 2010). Thus, the commercialization of pyrolysis technology to produce biofuels is proceeding at an accelerated rate.

Pyrolysis is performed in the absence of oxygen. This process converts the organic materials in the feedstock to a complex mixture of oxygenated compounds. Three separate products are produced during pyrolysis: a condensable liquid (pyrolysis oil), a charcoal coproduct, and a mixture of noncondensable gases (syngas). Pyrolysis oil is the target product of the fast pyrolysis process with an approximate density of 10 lb/gal at 59°F (1.20 kg/liter at 15°C) with higher heating value (HHV) energy content of approximately 18 MJ/kg. In fast pyrolysis, the feedstock is rapidly heated to bring the feedstock particles to temperatures of 752°F to 1,022°F (400°C to 550°C) in less than 2 seconds. A thin particle dimension facilitates rapid heat transfer and improves pyrolysis oil yield and quality.

The development of technoeconomic models to estimate pyrolysis product costs and analyses to quantify environmental impacts provides important information to the public, policy makers, and investors for effective decision making. These models integrate the technical, economics, and engineering parameters into the model and have been invaluable tools in the development of biomass processing projects (Mullaney and Farage 2002, Renewable Oil International 2009, Badger et al. 2011)

For nearly a decade, technoeconomic analyses have been performed for pyrolysis oil production (Gregoire and Bain 1994, Mullaney and Farage 2002, Ringer et al. 2006, Badger et al. 2011). Costs to produce bio-oil differ significantly depending on the feedstock moisture content (MC), cost and chip size, size of plant, and type of analysis. Mullaney and Farage (2002) studied the environmental and economic feasibility of bio-oil from 110- and 440-ton wet wood per day (tww/d) facilities in New Hampshire. Their results showed that the bio-oil cost for the 110-tww/d facility was $1.21/gal, $0.216/MMBtu, or $0.20/GJ. The bio-oil cost for the 440-tww/d facility was $0.89/gal, $0.16/MMBtu, or $0.17/GJ, assuming a low feedstock cost of $18/tww. Ringer et al. (2006) reported a bio-oil cost of $1.12/gal, $8.04/MMBtu, or $7.62/GJ using a lower heating value method for a 606-dry ton per day (dt/d) feed facility with feedstock cost of $30.00/dt, and a bio-oil yield of approximately 77 percent. Based on HHV (18 MJ/kg), the Ringer et al. (2006) cost values were $1.20/gal, $8.44/MMBtu, or $8.91/GJ. Badger et al. (2011) produced a technoeconomic analysis for a 100-dt/d facility. Based on a feedstock cost of $50/dt, the cost of producing a gallon of bio-oil was reported to be $0.96/gal, $6.35/MMBtu, or $6.70/GJ.

The ASTM ''Standard Specification for Pyrolysis Liquid Biofuel,'' ASTM D7544-10 (ASTM International 2010), provides grades for pyrolysis liquid biofuels from biomass for combustion in industrial burners. This standard provides a means to rate bio-oils meant to be combusted as boiler fuels with regard to quality for that purpose. Although no commercial market for boiler fuels produced from bio-oil has developed to date, this standard will provide an underpinning that will allow for future rational trading in combustible bio-oils by quality. ASTM D7544-10 is a performance standard with no specification as to the methods of production for the graded products. The grades of boiler fuel are determined by levels of gross heat of combustion, magnitude of water content, solids content, kinematic viscosity, density, sulfur content, ash content, flash point, and pour point.

Red Arrow Products, a Wisconsin company that manufactures liquid smoke flavorings from bio-oil, combusts the pyroligneous byproduct of their process, combined with char and noncondensable exit gases, to provide their process heat. The bio-oil is combusted at an air-atomizing nozzle, with the char and gas input separately. This combustion boiler has successfully operated in this mode for many years (Czernik and Bridgewater 2005). Finnish researchers have performed considerable research on boiler combustion of bio-oil. A dual-fuel boiler was tested with various fuel oil–to–bio-oil proportions including without the cofuel. A second set of tests was performed with raw bio-oil, using an 8-MW furnace operated at 4 MW. The results of these tests showed that some minor modifications of burner and boiler are required to replace petroleum fuels with bio-oil. A petroleum fuel was required for ignition. All emissions were lower from the bio-oil except particulates (Czernik and Bridgewater 2005).

Although several prior technoeconomic analyses have been performed to determine the cost of producing fast pyrolysis bio-oil, none of these models included an LCA to estimate environmental impacts from bio-oil production. This study includes an LCA of the production of bio-oil from fast pyrolysis, with char and syngas as coproducts used to offset the need for fossil fuels for energy and heat generation.

Methods

Aspen model

The Aspen-Plus (Aspen) model used was previously developed by Ringer et al. (2006). This model was used to estimate mass and energy flows and the cost of production of bio-oil by a fluidized bed reactor. For this analysis, the reactor size assumed was modified from 606 to 2,000 dt/d input feed. Feedstock cost was assumed to be $50/dt. The mass and energy balance output data from the Ringer Aspen model were provided as an input into the LCA model to allow estimates of environmental impacts in the form of emissions, fossil fuel use, resource consumption, and global warming impacts.

Life-cycle assessment model

This study included both an LCI and an LCIA of bio-oil and RFO. LCIs quantify emissions associated with all activities, from the initial resource collection and fuel production through the use of fuels, including for the transportation and distribution stages. Emissions related to the production of inputs were included based on their cradle-to-grave activities. There are several guidelines published for conducting LCAs. This study followed the methods set forth in the ISO 14000 series of standards (ISO 2006).

The LCI of bio-oil integrated a chemical engineering simulation tool (Aspen-Plus) with an LCA tool. SimaPro (PRé Consultants 2011), an LCA model, was used to document the environmental impacts of bio-oil production from cradle to grave. The mass and energy balances produced from the Aspen model, together with environmental releases, comprised the input and output parameters in the SimaPro model. The GWP of producing and using bio-oil from pine chips was assessed relative to that of an RFO. Comparison was performed on a per megajoule of fuel equivalent basis.

Goal, scope, and system boundaries

The scope of this report encompasses three life-cycle stages: (1) collection of forest biomass from the southeastern United States, (2) bio-oil production from fast pyrolysis, and (3) combustion of bio-oil in industrial boilers. The system boundaries are commonly referred to as a cradle-to-grave analysis. This report is confined to collection of biomass, bio-oil production, transportation of resources and fuels, production of fuels and electricity, and combustion of fuels (Fig. 1). Biomass collection for harvesting whole trees, chipping, and loading feedstock (Johnson et al. 2012) was combined with Aspen process data to develop the cradle-to-grave impact analysis for bio-oil production.

With SimaPro modeling the different life-cycle stages of bio-oil production, the production of bio-oil was further divided into five unit processes, consisting of feedstock preparation and drying, a pyrolysis reactor, quench condenser, char recovery, and a furnace process (heat/energy generation). The rationale for this approach was that a multiunit model would be most useful in analyzing ways to improve process efficiency, optimize operations, and provide a realistic assignment of environmental burdens in order to optimize environmental improvements. This approach also provided opportunities for one unit process to be used for modeling other products.

The functional unit was 1 MJ of energy for comparing bio-oil with RFO. All data were model generated based on highly defensible parameters for bio-oil production. Data for RFO, transportation, electricity use, and other fuels were obtained from the US LCI database (NREL 2012). The following assumptions were used for the comparison between bio-oil and RFO:

- All feedstock was obtained from whole-tree chipping as is practiced during harvest of underused material in southern pine (*Pinus taeda*) forests and may include bark (Johnson et al. 2012).
- All reported weights were oven dry.
- Green wood MC was 50 percent wet basis; 100 percent dry basis.
- The process model for syngas used a combustion process for natural gas based on equivalent energy outputs (US Environmental Protection Agency [US EPA] 1998). Adjustments were made to reflect the lower energy content of the syngas, as well as to some of the air emissions to reflect those emitted by a biogenic fuel versus a fossil fuel.[1]
- All heat energy and electricity necessary for the production of the bio-oil was self-generated (closed loop, Fig. 1). Char was fed through a ''char recovery'' process; together with the syngas produced during pyrolysis, these two fuels were then used as inputs into a furnace (heat energy generation) and then used by the dryer and pyrolysis reactor.
- The HHV for RFO = 43.41 MJ/kg.

Much of the data used in the Aspen model were derived from actual measured assessments. The following values were based on actual measurements:

- HHV for bio-oil = 18 MJ/kg.
- Density of bio-oil = 1.2 kg/liter (10 lb/gal).
- MC of chips after drying = 7.5 percent, ovendry basis.

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[1] Substitutions like this are allowed within the ISO standards for performing life-cycle assessments (ISO 2006).

Feedstock properties

Bio-oil feedstock.—Whole southern pine trees were either harvested from forest stands that were being converted to more intensively managed stands or thinned from stands where the remaining trees were to later be harvested for saw logs or pulpwood before reforestation. This process involved felling, skidding, and whole-tree chipping of harvested trees. The product was chips ready for transport and input into the pyrolysis process. The impacts associated with forest growth and management were not included because they are considered an integral part of the management of the forest to produce merchantable solid wood products. The ''cradle'' thus began with the harvesting of the thinned trees that were then chipped. Carbon dioxide absorbed during growth was included for the mass of chips collected. The biomass collection process used diesel fuel and lubricants for all equipment.

Feedstocks determine the type of preprocessing equipment required for particle size reduction and the amount of drying required. For this study, it was assumed that the chips collected from whole-tree chipping were of adequate size for regrinding. Incoming chips have an average MC of 50 percent (wet basis; 100% ovendry basis). Transportation of chips on trucks to the bio-oil processing facility was assumed to be 50 miles (one way). The chips were dried from 100 percent MC (ovendry basis) to 7.5 percent MC (ovendry basis). This process consumed both electricity and self-generated heat energy. Dryer efficiencies are built into the Aspen model, since the inputs and outputs are based on energy consumption, not the mass of the fuel. Outputs included dry chips, water vapor, and air emissions. The electricity consumed for drying was the combined power used for drying and transport by conveyors. Following drying, particle size was again reduced to 3 mm or less. Input parameters for the Aspen process model for the feedstock are shown in Table 1.

RFO feedstock.—RFO is a coproduct from the oil refineries where the primary products are gasoline and diesel fuel (transportation fuel). Other coproducts might include liquefied petroleum gas, kerosene, petroleum coke, and gases. The RFO LCI data obtained were from the US LCI database (NREL 2012), where RFO represented 4.89 percent of the products produced. Therefore 4.89 percent of the burdens of all upstream processes (extraction and transportation) and the refinery process were assigned to the RFO.

Bio-oil conversion technology

The products and coproducts generated during pyrolysis of biomass were liquid bio-oil, char, ash, and syngas. Bio-oil composition from the pyrolysis process is shown in Table 2. Pyrolysis input parameters for the bio-oil process model in Aspen are shown in Table 3. Bio-oils are known to contain hundreds of compounds, but some major compounds can be identified that largely determine the nature of each bio-oil. Ringer et al. (2006) provide a detailed description of the chemistry of the bio-oil assumed to be produced by their Aspen-modeled fast pyrolysis reactor.

The char entered the char recovery directly from the pyrolysis process. All of the char produced during pyrolysis was used for heat generation. After the char was processed through the recovery process, it was funneled directly to the furnace for energy generation.

The energy available in the pyrolysis reactor exit gas contains combustible components that are used as an energy

Table 1.—Aspen feedstock input parameters for the bio-oil process model from pine chips.

Process area	Parameter (unit)	Value
Feedstock	Type/species	Wood chips/pine
	Moisture content (%)	50
	Cost ($/dry ton)	30
	Throughput (dry tons/day)	2,000
	Particle size (mm)	<3
Feedstock composition (wt%, dry)	Carbon (%)	50.93
	Hydrogen (%)	6.05
	Oxygen (%)	41.93
	Nitrogen (%)	0.17
	Sulfur (%)	0.00
	Chlorine (%)	0.00
	Ash (%)	0.92

Table 2.—Bio-oil composition from pyrolysis of pine chips.

Property (unit)	Value
pH	2.4
Density (kg/m^3)	1.2
Viscosity, cSt at 50°C	28
Lower heating value (MJ/kg)	17.2
Solids (wt%)	0.03
Water (wt%)	17.00
Ash (wt%)	0.03
Conradson carbon residue (wt%)	16.00
Carbon (wt%)	45.70
Hydrogen (wt%)	7.00
Nitrogen (wt%)	<0.10
Sulfur (wt%)	0.02
Oxygen (wt%)	47.00
Sodium + potassium (ppm)	22
Calcium (ppm)	23
Magnesium (ppm)	5
Flash point (°C)	95
Pour point (°C)	−19

source for the production of either pyrolysis heat or feedstock drying heat. The syngas produced (13% by weight) during the pyrolysis process was piped to a furnace associated with the plant and burned along with the char for process heat.

Bio-oil distribution

Bio-oil is transported from the pyrolysis plant to a regional storage facility. The transportation mode was assumed to be diesel truck. Total transportation distance for bio-oil distribution (including transport from the biorefinery to the blending terminal, from the latter to regional storage, and from there to a refueling station) was assumed to be 100 miles round trip. Infrastructure needed for bio-oil production or use is not within the scope of this study. The materials used for infrastructure are generally considered to be a negligible share of the output product environmental burden assuming amortization over a long plant life.

End use

The application for bio-oils depends on the quality of the bio-oil and the cost of alternatives. The primary limitation to its use has been the low cost of fossil fuels. Bio-oil can be upgraded to be used as transportation fuels or can be

Table 3.—Aspen pyrolysis reactor input parameters for the bio-oil process model from pine chips.

Parameter (unit)	Value
Pyrolysis type	Fluidized bed pyrolysis feed
Temperature (°C)	500
Air carrier ratio (lb air/lb)	2.75
Feed moisture content (%)	7
Ground particle size (mm)	<3

combusted as boiler fuel. For the purpose of this study, bio-oil was assumed to be used as heat energy and combusted in an industrial boiler. It has been reported that NO_x, CO, and particulate emissions can be higher for bio-oil than for petroleum heating fuels. Emissions associated with the combustion of bio-oil in boilers were not available. For this analysis, the emissions associated with the combustion of bio-oil were assumed to be equivalent to the emissions of the combustion of RFO for equal heat outputs (1 MJ). Emissions specific to biogenic fuel sources (CO_2, CO, CH_4) were relabeled to reflect the biofuel and used accordingly in the LCIA (Bare et al. 2003, US EPA 2011). Fuel combustion data for industrial boilers were obtained from the US LCI database (NREL 2012).

Results and Discussion

Product yields

At an input feed of 2,000 dt/d (81,000 kg/h), the modeled pyrolysis reactor produced 48,345 kg/h bio-oil, 10,496 kg/h syngas, 12,377 kg/h char, and 745 kg/h ash. Water removed was released as vapor and accounted for 11.2 percent of the total input mass on an ovendry basis (Table 4). The total mass balance flow for bio-oil production including all coproducts is shown in Table 4. The recovery efficiency of bio-oil from ovendry wood chips was 59.7 percent. Other yields for char, ash, and syngas were 15.3, 0.9, and 13.0 percent, respectively.

The char produced had a high (73%) carbon content and was similar in properties to bituminous coal. The economic production of bio-oil will depend on the use of the char as an energy source for production of pyrolysis heat or for drying of feedstocks. The use of the char for heat generation can significantly offset carbon impacts by displacing fossil fuels. Ash was a by-product of the char conversion to pyrolysis energy.

Table 4.—Mass balance for bio-oil production for a 2,000 dry tons per day input feed.

	Amount (kg/h)	Yield (%)
Inputs		
Forest residues, oven dry	81,000	
Outputs		
Bio-oil	48,345	59.7
Syngas	10,496	13.0
Char	12,377	15.3
Ash	745	0.9
Water vapor lost during conversion	9,037	11.2
Total	81,000	100.0

Fuel type	Bio-oil (MJ/MJ)	Breakdown (%)	RFO (MJ/MJ)	Breakdown (%)
Coal	0.0022	0	0.0466	3
Natural gas	0.0033	1	0.0992	7
Crude oil	0.0709	14	1.3342	89
Uranium oxide	0.0008	0	0.0162	1
Char	0.3107	59	0	0
Syngas	0.1371	26	0	0
Total	0.5249	100	1.4962	100

[a] Energy totals include required fuels for extraction/harvesting, fuel production, and all transportation. Energy content of the final product fuel is not included.

Energy consumption

A total energy of 0.52 MJ/MJ was required from cradle to grave for the production and use of bio-oil (Table 5). Table 5 shows the total energy resources (fossil and nonfossil fuels) consumed for the production of 1 MJ of each fuel. The total resource energy for the production of bio-oil was nearly three times lower than the energy required to produce the energy equivalent of RFO, which consumed 1.5 MJ/MJ. Most of the resource energy needed to produce RFO occurred during the extraction life-cycle stage (Fig. 2). On the other hand, the production life-cycle stage for bio-oil required the greatest amount of energy (92%). When the self-generated energy consumed during bio-oil production is shown as an "avoided product" (avoiding the use of fossil fuels), the overall energy use for bio-oil was negative (Fig. 2). A small amount (1%) of excess energy was generated during the pyrolysis process (not shown) and was sold as electricity.

Heat energy from syngas represented 31 percent of the total heat required by the system. The use of syngas for process heat offset the consumption of fossil-based energy. All of the char (12,377 kg/h) produced was combusted for process heat for the plant, and it represented 69 percent of

the total energy produced in the furnace. A total of 456,915 MJ/h were produced in the furnace. The dryer consumed 116,519 MJ, or 27 percent, and the pyrolysis reactor required 288,947 MJ, or 67 percent, of total energy. Char recovery also consumed a small portion of heat energy, 27,509 MJ, or 6 percent. It was assumed that the combustion of the syngas is similar to that of natural gas (US EPA 1998, Badger et al. 2011). Some emissions were renamed to associate them with biomass fuel combustion rather than fossil fuel combustion.

Life-cycle inventory results

Environmental releases in the form of air emissions, water effluents, and waste to landfills can be sourced from a variety of activities: harvesting equipment, transportation of feedstocks and other raw materials, electricity production, fuel production, and fuel combustion. Tables 6 and 7 represent a condensed version of air and water emissions from the LCI for bio-oil production.

Air emissions

Carbon dioxide emissions were greater than all other emissions over all bio-oil life-cycle stages (Table 6). A total of 0.19 kg/MJ CO_2 emissions were released from cradle to gate for the production of bio-oil, representing 67 percent of the total emissions to air by mass. Steam released during the drying of wood chips was the second highest emission, representing 32 percent by mass.

Some emissions substances are given special designators to better indicate their source: for example, emissions resulting from the combustion of biomass would be assigned a "biogenic" designation and fossil-based fuels a "fossil" designation. These substances are "equal" in terms of output, but when used in an impact assessments method, they might be weighted differently or not included based on this designation. Since the scope of this study was to produce a net GWP for bio-oil and RFO, we considered carbon to be
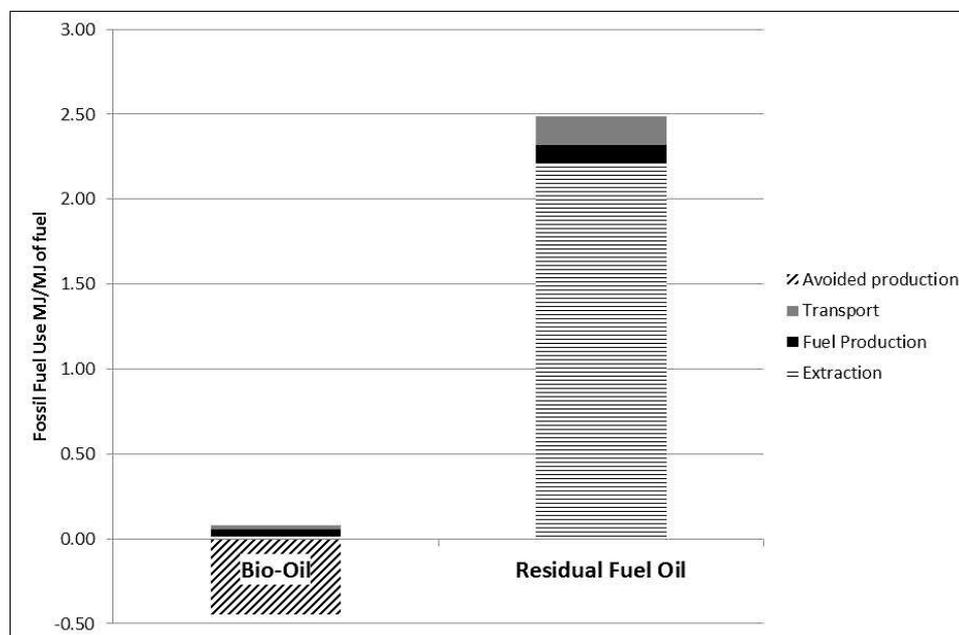

Figure 2.—Cradle-to-grave fossil energy requirement for bio-oil and residual fuel oil for each life-cycle stage.

Table 6.—Cradle-to-grave air emissions (kg/MJ) for the production of 1 MJ of bio-oil.

Substance	Total	Biomass collection	Bio-oil production	Bio-oil combustion	Transport
Carbon dioxide, biogenic	1.87E−01	9.53E−07	4.05E−02	1.46E−01	9.40E−07
Carbon dioxide, fossil	2.69E−03	1.30E−03	0.00E+00	0.00E+00	1.38E−03
Carbon monoxide, biogenic	2.97E−04	0.00E+00	2.68E−04	2.87E−05	0.00E+00
Carbon monoxide, fossil	1.86E−05	1.13E−05	0.00E+00	0.00E+00	7.24E−06
Hazardous air pollutants	7.51E−05	0.00E+00	7.51E−05	0.00E+00	0.00E+00
Hydrogen chloride	3.79E−06	1.22E−08	0.00E+00	3.76E−06	1.20E−08
Methane	9.09E−06	1.69E−06	0.00E+00	5.74E−06	1.66E−06
Nitrogen oxides	4.67E−04	2.38E−05	1.19E−04	3.16E−04	9.40E−06
Nonmethane volatile organic compounds	1.58E−06	7.93E−07	0.00E+00	0.00E+00	7.82E−07
Particulates	1.03E−04	7.33E−07	9.14E−05	1.09E−05	1.69E−07
Sulfur dioxide	1.32E−06	6.64E−07	0.00E+00	0.00E+00	6.55E−07
Sulfur oxides	2.33E−04	1.32E−06	2.09E−07	2.30E−04	1.32E−06
Volatile organic compounds	1.47E−05	6.24E−07	1.20E−05	1.61E−06	4.52E−07
Water	9.12E−02	0.00E+00	9.12E−02	0.00E+00	0.00E+00

Table 7.—Cradle-to-grave emissions to water (kg/MJ) for the production of 1 MJ of bio-oil.

Substance	Total	Biomass collection	Bio-oil production	Bio-oil combustion	Transport
Dissolved solids	1.33E−04	6.69E−05	0.00E+00	0.00E+00	6.60E−05
Chloride	1.08E−04	5.43E−05	0.00E+00	3.85E−10	5.35E−05
Sodium, ion	3.04E−05	1.53E−05	0.00E+00	0.00E+00	1.51E−05
Calcium, ion	9.59E−06	4.83E−06	0.00E+00	0.00E+00	4.76E−06
Suspended solids, unspecified	7.99E−06	3.99E−06	0.00E+00	5.78E−08	3.94E−06
Barium	3.53E−06	1.78E−06	0.00E+00	0.00E+00	1.75E−06
Magnesium	1.87E−06	9.43E−07	0.00E+00	0.00E+00	9.31E−07
Chemical oxygen demand	1.04E−06	5.22E−07	0.00E+00	0.00E+00	5.15E−07

carbon no matter the source (biogenic or fossil) and included all of these in the impact assessment described below.

Ninety-nine percent of the total CO_2 was classified as biogenic and was released by the combustion of biomass-generated fuel (bio-oil, syngas, char). The combustion of the bio-oil released the majority of the biogenic CO_2, while the biomass collection process and the transportation of the feedstock represented 100 percent of the fossil-based CO_2. Particulate emissions were negligible over the entire life cycle, while the production process for producing bio-oil released 89 percent of the total particulates. Combustion of the biofuel released 11 percent of the total particulates. The top 14 air emissions are reported in Table 6.

Water emissions

The bio-oil production process is a closed system, with the exception of the releases to air. Water effluents leaving the system originated in other upstream processes, such as fossil fuel production and electricity production. Therefore, the water emissions were limited to the biomass collection and transportation life-cycle stages (Table 7).

Life-cycle impact assessment

The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), version 3 (Bare et al. 2003), was used to perform LCIAs. This tool is a midpoint-oriented LCIA methodology developed by the US EPA specifically for the United States using input parameters consistent with US locations. Cradle-to-grave impact assessment comparisons were conducted between the bio-oil and RFO. The environmental impact measures applied consistently to each product were as follows: GWP, acidification potential, human respiratory effects (particu-

lates), aquatic eutrophication potential, smog formation potential, and ozone depletion (Table 8).

Bio-oil outperformed RFO in four of the seven impact categories: net global warming, respiratory effects, ozone depletion, and total energy consumption (Fig. 3). In each set of bars in Figure 3, the product with the highest impact in that category is the benchmark (100%), and the other products are shown as a percentage relative to the benchmark. The values are relative to the benchmark and not absolute values.

For acidification, bio-oil showed the greater impact over RFO. The higher values were consistent over all life-cycle stages, indicating that the driving force is the heat value of bio-oil, which is about half of the value for RFO; therefore, bio-oil required nearly double the resources to produce an equivalent megajoule of energy. The bio-oil production stage contributed nearly double the eutrophication potential of RFO, but for both acidification and eutrophication, RFO contributed 80 percent of the benchmark to the impact.

Particulate matter (PM) has always been an unfavorable emission in the wood product industry. Total PM (>2.5

Table 8.—Factors for calculating the selected environmental impacts.

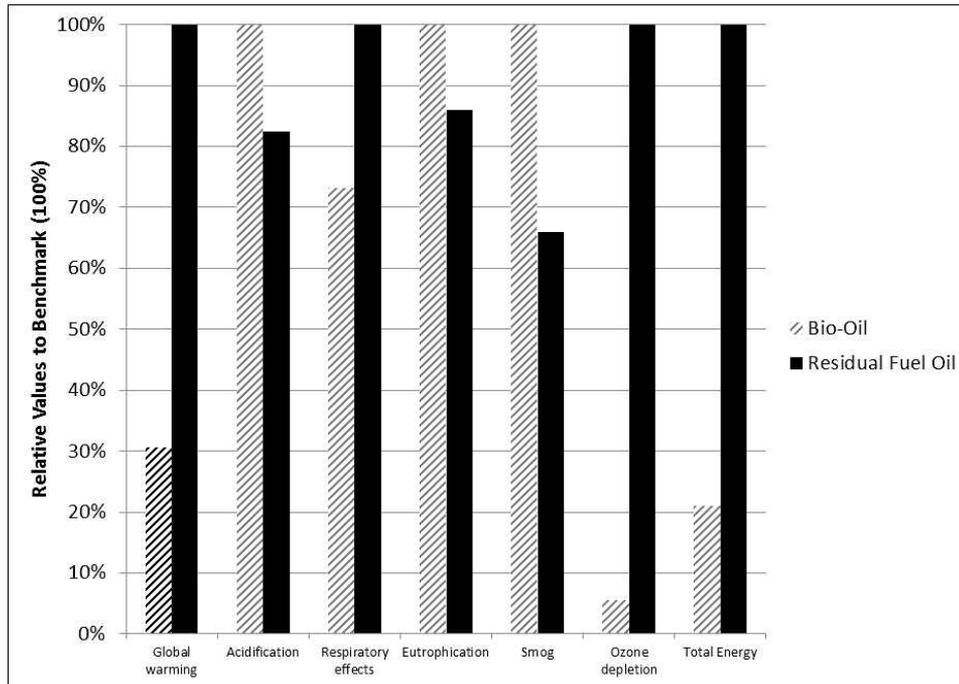| Impact category	Unit
Global warming potential	kg CO_2 eq
Acidification	H^+ moles eq
Respiratory effects	kg PM 2.5 eq
Eutrophication	kg N eq
Smog	g NO_x eq
Ozone depletion	kg CFC-11 eq

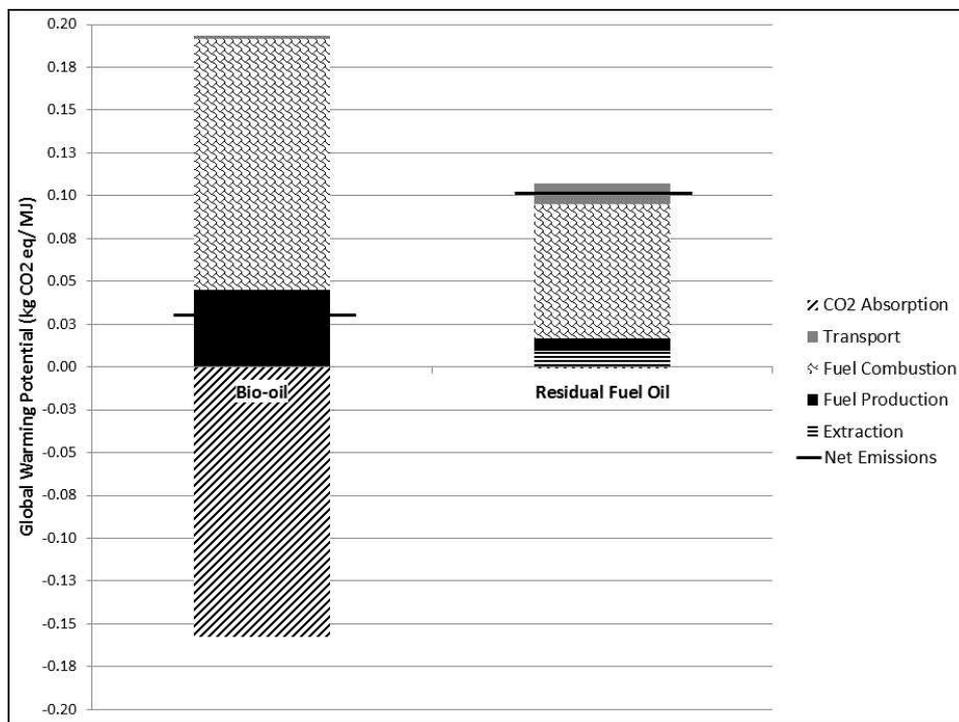Figure 3.—Life-cycle impact categories for the cradle-to-grave production of 1 MJ of bio-oil and residual fuel oil.

Figure 4.—Cradle-to-grave global warming potential for bio-oil and residual fuel oil for each life-cycle stage.

and <10 μm) for the production of 1 MJ bio-oil (Table 6) was 0.00010 kg/MJ, while for RFO, it was 0.00002 kg/MJ. Respiratory effects captured emissions particulates and other associated air emissions (SO_2, PM < 2.5 μm, PM >10 μm, and NO_2) and weighed them to PM 2.5 eq. RFO contributed 32 percent more to this impact than did bio-oil—not from the release of particulates, but from the

release of SO_2, which was 96 percent higher for RFO from cradle to grave than for bio-oil (Fig. 3).

Global warming potential

It is known that tree growth, wood products production, combustion, and final disposal result in various fluxes of biogenic CO_2. The appropriate methodology for capturing these biogenic fluxes is GWP. This indicator reflects the

relative effect of a GHG in terms of climate change over a fixed time period, commonly 20, 100, or 500 years. It is expressed as a factor of carbon dioxide (CO_2). For example, the 20-year GWP of methane (CH_4) is 56, which means if the same weights of CH_4 and CO_2 were introduced into the atmosphere, CH_4 will trap 56 times more heat than CO_2 over the next 20 years. TRACI uses a 100-year time frame.

One of the major environmental benefits of using sustainably produced forest products for energy is the positive impact in mitigating long-term climate change. The forest absorbs CO_2 from the atmosphere and stores carbon in wood. When trees are harvested and ''forest residuals'' (branches and other woody debris normally left in the forest) are collected, chipped, transported, possibly converted to a liquid fuel, and burned, the carbon is released back into the atmosphere as CO_2. When fossil fuels are combusted, the fuel carbon is released back into the atmosphere and is not part of a natural process.

We validate this natural process for wood energy and ''carbon neutrality'' for bio-oil compared with RFO by using GWP as the metric (Fig. 4). The bars in Figure 4 show the total GWP between RFO and bio-oil by life-cycle stage (harvesting/extraction, fuel production, combustion, and transport). In addition, we show a negative GWP for CO_2 absorption. The net result is not a perfect ''carbon neutrality,'' but a net GWP for bio-oil of 0.0323 kg CO_2 eq per MJ and a net GWP of 0.107 kg CO_2 eq per MJ for RFO. Substituting bio-oil for RFO would reduce CO_2 emissions by 0.0749 kg CO_2 eq per MJ of fuel energy used. This represents a 70 percent reduction in GWP emissions, which exceeds the 60 percent reduction of GHG in accordance with the Energy Independence and Security Act of 2007 (EISA 2007).

Conclusions

An LCA for the production of bio-oil was developed to analyze resource use and energy consumption inputs and emissions to air and water and to determine life-cycle impacts for bio-oil compared with RFO. Bio-oil from pine chips showed much improved GWP, fossil fuel use, and total energy consumption compared with RFO. Results showed near carbon neutrality of the bio-oil. Substituting bio-oil for RFO, based on the relative carbon emissions of the two fuels, reduced CO_2 emissions by 0.0749 kg CO_2 per MJ of fuel consumption. Producing bio-oil consumed 92 percent of the total energy from cradle to grave, while 89 percent of this energy was sourced from self-generated renewable fuels produced during manufacturing. On the other hand, RFO consumed 94 percent of the energy for its production from nonrenewable crude oil. This model provides a framework to better understand the major factors affecting GHG emissions related to bio-oil production.

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