

# Life cycle assessment of commodity chemical production from forest residue via fast pyrolysis

Yanan Zhang · Guiping Hu · Robert C. Brown

Received: 18 August 2013 / Accepted: 18 April 2014 / Published online: 28 May 2014  
© Springer-Verlag Berlin Heidelberg 2014

## Abstract

**Purpose** This life cycle assessment evaluates and quantifies the environmental impacts of renewable chemical production from forest residue via fast pyrolysis with hydrotreating/fluidized catalytic cracking (FCC) pathway.

**Methods** The assessment input data are taken from Aspen Plus and greenhouse gases, regulated emissions, and energy use in transportation (GREET) model. The SimaPro 7.3 software is employed to evaluate the environmental impacts.

**Results and discussion** The results indicate that the net fossil energy input is 34.8 MJ to produce 1 kg of chemicals, and the net global warming potential (GWP) is  $-0.53$  kg CO<sub>2</sub> eq. per kg chemicals produced under the proposed chemical production pathway. Sensitivity analysis indicates that bio-oil yields and chemical yields play the most important roles in the greenhouse gas footprints.

**Conclusions** Fossil energy consumption and greenhouse gas (GHG) emissions can be reduced if commodity chemicals are produced via forest residue fast pyrolysis with hydrotreating/FCC pathway in place of conventional petroleum-based production pathways.

**Keywords** Bio-oil upgrading · Commodity chemicals · Fast pyrolysis · Fossil energy · Greenhouse gas emission · Life cycle assessment

Responsible editor: Ivan Muñoz

Y. Zhang · R. C. Brown  
Department of Mechanical Engineering, Iowa State University,  
Ames, IA 50011, USA

G. Hu · R. C. Brown (✉)  
Bioeconomy Institute, Iowa State University, Ames, IA 50011, USA  
e-mail: rcbrown3@iastate.edu

G. Hu  
Industrial and Manufacturing Systems Engineering, Iowa State  
University, Ames, IA 50011, USA

## 1 Introduction

Aromatics and olefins are two main types of petrochemicals and have a wide range of applications. Aromatics can be used to produce a number of petrochemical intermediates including styrene, phenol, purified terephthalic acid (PTA), and phthalic anhydride (PA) (ICIS 2013a). The most important commercial olefins are ethylene, propylene, and butadiene, all of which can be used to manufacture rubbers, polymer resins, and other chemical intermediates (ICIS 2013b). In 2012, the aromatics production capability of the US petroleum refining sector reached 296,911 barrels per day (EIA 2012b). The demand for light olefins in the USA is expected to increase at a compounded annual growth rate (CAGR) of 3.4 % over the period 2010–2020, reaching approximately 68.4 million tons by 2020 (GBI Research 2012). Petrochemicals are generally produced from fossil feedstocks such as the refining of crude oil or the processing of natural gas. Global petrochemical feedstock consumption is projected to rise through 2025 with the greatest proportion coming from naphtha and coal, increasing about 100 million tons and 70 million tons by 2025, respectively (CHEMSYSTEMS 2013). Among all the regions, North America leads in the feedstock consumption, accounting for 17 % of world feedstock consumption in 2010 (CHEMSYSTEMS 2013). The US Energy Information Administration (EIA) has projected a 2.4 % annual increase for crude oil prices from 2010 to 2035 (EIA 2012a). The growing greenhouse gas (GHG) emissions along with projected growth in consumption of fossil feedstocks drive an increasing interest in investigating alternative feedstocks for commodity chemical production. A variety of alternative feedstocks have been under consideration, including coal, unconventional natural gas, plastic waste, tar and heavy oil, and biomass (Ren and Patel 2009; McFarlane and Robinson 2007). Feedstocks of nonfossil resources (lignocellulosic biomass, etc.) within the petrochemical industry have also gained

increasing interest (Brehmer et al. 2009; Christensen et al. 2008; Dale 2003; Gavrilescu and Chisti 2005; Schilling 1995).

Biomass can be converted into basic chemical compounds through thermochemical conversion (gasification, pyrolysis, and liquefaction/hydrothermal upgrading) or biochemical conversion (fermentation and anaerobic digestion) (Fahmi and Cremaschi 2012). The biochemical process is a complex process, and there are technical issues and challenges, such as low bulk density feedstock, high viscosity substrate, high enzymes cost, and low fermentability of some substrates (Stephanopoulos 2007; Lin and Tanaka 2006; Chen 2012). The energy use and CO<sub>2</sub> emissions for basic chemical production from biomass are fully examined by Ren and Patel (2009). The pathways examined in that study include steam cracking of naphtha derived from the Fischer-Tropsch processing (FT) of syngas derived from biomass gasification, dehydration of ethanol (ethanol is derived from biomass via syngas fermentation or via direct fermentation), and the processing of methanol to olefins (methanol is derived from biomass via syngas). For thermochemical conversion, the process of chemical production from biomass gasification is relatively slow and typically requires large, complicated, and expensive equipment (Xu et al. 2008; Salge et al. 2006).

Brehmer et al. (2009) utilized a limited energetic and exergetic analysis with life cycle assessment (LCA) to evaluate the maximum fossil fuel feedstock replacement potential and concluded that the best potential for biomass to replace fossil fuel would be as an alternative feedstock source for the petrochemical industry. Hermann et al. (2007) analyzed the CO<sub>2</sub> emissions and fossil energy use for bulk chemical production using industrial biotechnology and found that more than 100 % savings in nonrenewable energy use and greenhouse gas emissions would be possible with current state of the art biotechnology. Hipolito (2011) evaluated the environmental loads associated to the production of chemicals (phenolic compounds, acetone, polyhydroxybutyric acid, and polylactic acid) from lignocellulose biomass scenarios and compared these environmental loads to the petrochemical equivalents. Hipolito (2011) concluded that the production of chemicals from biomass could contribute to possible reductions between 37 and 48 % on greenhouse gas emissions, and up to 80 % fossil fuel can be saved while ecotoxicity indicators present much lower values for the production of chemicals from biomass. But chemicals from biomass may increase other impact categories such as eutrophication and acidification, human toxicity, photochemical oxidant formation, water depletion, and particulate matter formation. A number of other similar LCA studies discussed the environmental impacts of the production of biopolymers or bioplastics from biomass (Heyde 1998; Dornburg et al. 2003; Groot and Borén 2010; Piemonte 2011; Kim and Dale 2008; Lynd and Wang 2003). Yates and Barlow (2013) made a

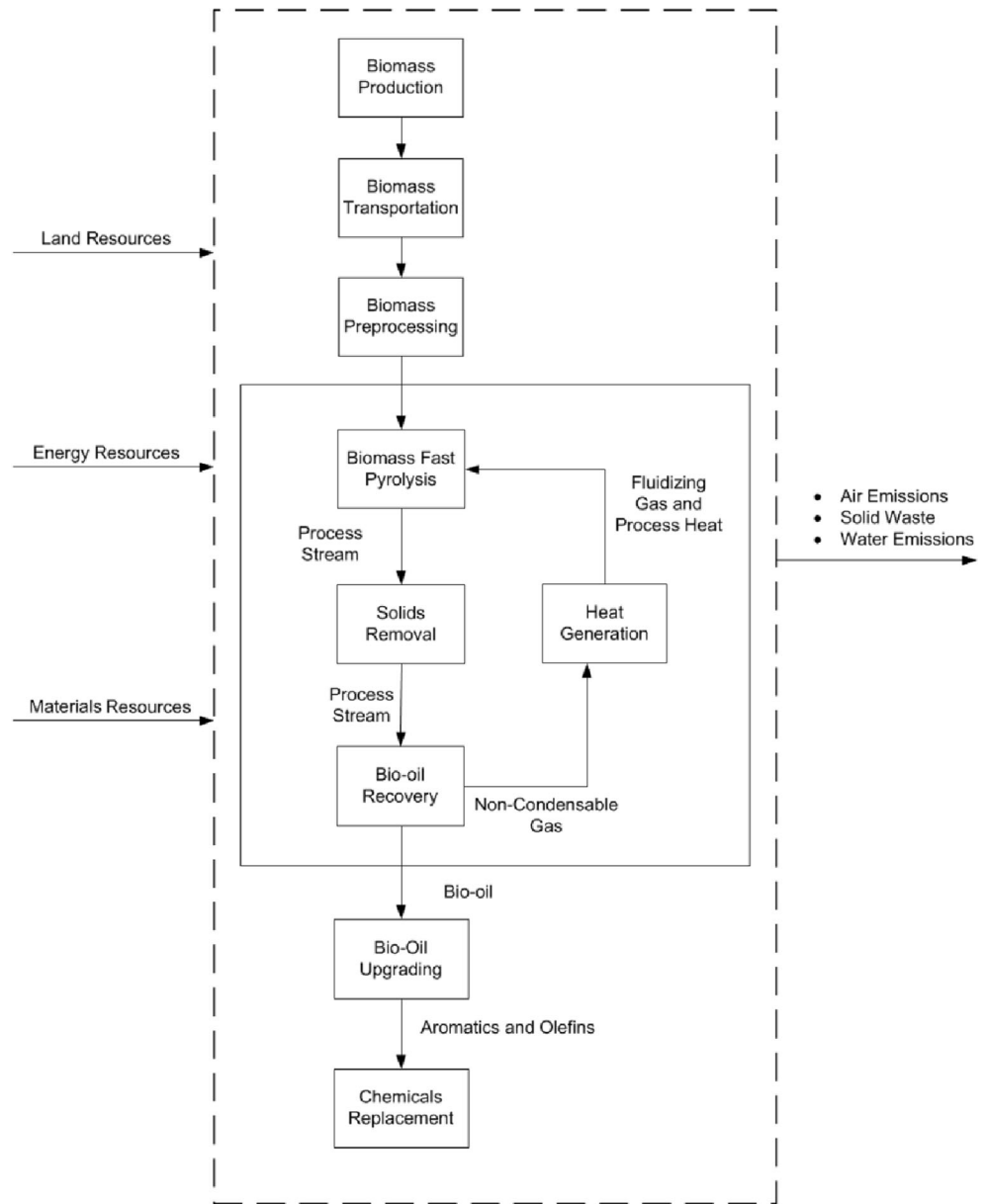
thoughtful review from these existing biopolymer production LCA studies especially for polylactic acid (PLA), polyhydroxyalkanoates (PHA), and starch-based biopolymers. It is demonstrated as well that reductions in nonrenewable energy use and GHG emissions can be achieved from biopolymer production, but higher impacts in other categories were commonly reported (Yates and Barlow 2013).

Although some LCA studies have been done on the intermediate chemicals or biopolymers, few LCA studies have been reported on basic commodity chemical (benzene, toluene, xylene, etc.) production from biomass. Recently, fast pyrolysis has attracted considerable interest as a means for converting biomass into valuable fuels or energy. With the growing interest in fast pyrolysis technology, the related economic and environmental impacts of pyrolysis-based energy systems are under extensive examination (Kauffman et al. 2011; Heracleous 2011; Zhong et al. 2010; Hsu 2012; Fan et al. 2011; Iribarren et al. 2012; Zhang et al. 2013b, c). Vispute et al. (2010) combined a two-stage hydrotreating process with FCC to form an integrated catalytic process for the high-yield production of valuable commodity chemicals (i.e., olefins and aromatics). Zhang et al. (2013c) compared this chemical production pathway with the transportation fuel production from the fast pyrolysis pathway and found that the internal rate of return (IRR) of the chemical production pathway is much higher than that of the transportation fuel production pathway. In this paper, life cycle assessment is conducted to evaluate and quantify the environmental impacts of renewable commodity chemical production via forest residue fast pyrolysis and hydrotreating/FCC upgrading. A variety of environmental impacts are evaluated, including the fossil energy input, GHG emissions, acidification, ozone depletion, ecotoxicity, smog, etc.

## 2 Description for the chemical production pathway

In the chemical production pathway, the bio-oil yield is assumed to be 52 % of the dry mixed wood, based on the previous techno-economic analysis study (Zhang et al. 2013c). Bio-oil generation from the raw feedstock includes five steps: biomass preprocessing, biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation. In the biomass preprocessing step, the raw biomass is assumed to be 25 wt% moisture and chopped to a 10-mm diameter. It is dried to 7 wt% moisture and ground to 3 mm diameter particles. Steam generated in the combustion area is used to dry the biomass, and a 1 % makeup is assumed to compensate for condensate losses. In the fast pyrolysis step, biomass particles are converted into noncondensable gases, bio-oil vapors, and solid char phases in a fluidized bed reactor operating at 500 °C and ambient pressure. Bio-oil vapors are recovered using a condenser and an electrostatic precipitator. In the solids

**Fig. 1** Life cycle system boundary for the chemical production from forest residue via fast pyrolysis and upgrading



removal step, the pyrolysis products are cleaned by removing 90 % of the entrained char and solid particles through cyclones. Finally, in the combustion step, the noncondensable gases are combusted to provide the heat for the pyrolysis

process. The Aspen Plus model shows that there is enough heat available from the noncondensable gas combustion. The excess char is treated as a low-value coal substitute for local usage such as heat generation. Portions of the combusted

**Table 1** Inventory data of biomass collection

Item	Amount	Unit	Description
<b>Outputs</b>			
Collected forest residue	1	kg	
<b>Resources</b>			
Biomass energy	18	MJ	Gross calorific value, in biomass, primary forest
<b>Materials and fuels</b>			
Diesel fuel	7.38	g	Low sulfur, at regional storage/RER with US electricity
Building machine	18.4	p	RER with US electricity

“p” is one process unit in SimaPro; the process unit incorporates all input resources

**Table 2** Inventory data of biomass transportation

Item	Amount	Unit
Outputs		
Delivered forest residue	2,670	Metric ton
Input from material		
Truck 40 t	710,000	tkm
Collected forest residue	2,670	Metric ton

Transportation units in SimaPro are measured in “tkm,” which represents the transport of 1 ton of a commodity with a distance of 1 km

noncondensable gases are compressed and sent to the pyrolyzer as the carrier gases.

After bio-oil production, a two-stage hydrotreating and FCC process is employed to upgrade the aqueous phase of the bio-oil to commodity chemicals. Process configurations are based on Vispute et al. (2010). A liquid-liquid (L-L) extractor is employed to separate the whole bio-oil into the aqueous phase and the water-insoluble fraction. The aqueous phase undergoes a two-stage hydrotreating process, which consists of a low-temperature hydrotreatment and a high-temperature hydrotreatment. The low-temperature hydrotreatment stage is carried out in a hydrotreater operating at 125 °C and 100 bar pressure, and the high-temperature hydrotreatment stage is carried out at 250 °C and 100 bar pressure. After the two-stage hydrotreating process, fluidized catalytic cracking is performed on the hydrotreated aqueous phase of the bio-oil over HZSM-5 catalyst at 600 °C. The FCC process converts the aqueous phase to commodity chemicals. Natural gas is steam-reformed to produce hydrogen via a two-stage catalytic process, and the hydrogen is used for the hydroprocessing steps. Because natural gas contains enough sulfur to poison the reforming catalysts, reforming is preceded by a desulfurization step. In the first stage of reforming, steam reacts with the natural gas in a steam methane reformer (SMR) at 700–1,100 °C to yield syngas. In the second stage, low-

temperature water-gas shift (WGS) reaction occurs at about 250 °C to generate the hydrogen from the syngas. The hydrogen is separated from the syngas through a pressure swing adsorption (PSA) unit and the rest of the gas is treated as exhaust gas. The water-insoluble fraction is mainly the pyrolytic lignin, which is assumed to be a coal substitute and consumed locally.

### 3 LCA goal and scope definition

The goal of this LCA study is to analyze the environmental impacts of the chemical production from forest residue via fast pyrolysis with hydrotreating/FCC upgrading. The system for this LCA is divided into five unit processes: biomass production, biomass transportation, biomass preprocessing, bio-oil production, and bio-oil upgrading. The system boundary is illustrated in Fig. 1, which contains land, energy, and material resources consumptions as well as air emissions, solid waste, and water emissions in the process. Bio-oil production unit is a combination of biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation, which is shown as the sub-block in the system boundary diagram. The biomass fast pyrolysis and upgrading facility is assumed to be an integrated facility, where the biomass is preprocessed and converted to intermediate bio-oil that is ultimately upgraded to the commodity chemicals. Electricity usage is assumed to be medium voltage electricity produced in the USA. The indirect land-use change effects and chemical distributions are not considered in the LCA study. This study is a generic study for chemical production from forest residue fast pyrolysis and location-specific energy carriers associated with feedstocks are not considered.

The Aspen Plus model for the chemical production process is based on a previous process model of chemical production via fast pyrolysis (Brown et al. 2012; Zhang et al. 2013c). In this study, the bio-oil recovery modeling has been updated. The modified Aspen Plus model assumes an nth plant facility

**Table 3** Inventory data of biomass preprocessing

Item	Amount	Unit	Description
Outputs			
Pretreated forest residue	2,140	Metric ton	
Materials and fuels			
Delivered forest residue	2,670	Metric ton	
Steam	255	Metric ton	On-site steam average
Electricity for chopping	44,600	kWh	Medium voltage, at grid/US with US electricity
Electricity for grinding	109,000	kWh	Medium voltage, at grid/US with US electricity
Electricity for compressor	170,000	kWh	Medium voltage, at grid/US with US electricity
Emission to air			
Water	523	Metric ton	

**Table 4** Inventory data of bio-oil production

Item	Amount	Unit	Description
Outputs			
Forest residue bio-oil	1,040	Metric ton	
Char	219	Metric ton	
Avoided products			
Coal	110	Metric ton	Hard coal supply mix, at regional storage/US S
Resources			
Air	2,165	Metric ton	
Process water	9,590	Metric ton	Water, process, unspecified natural origin/kilogram
Materials and fuels			
Pretreated forest residue	2,140	Metric ton	
Electricity for pyrolysis	450,000	kWh	Medium voltage, at grid/US with US electricity
Emission to air			
N <sub>2</sub>	1,660	Metric ton	
O <sub>2</sub>	21.7	Metric ton	
CO <sub>2</sub>	928	Metric ton	
Water	432	Metric ton	
Waste or emissions to treatment			
Ash	11	Metric ton	Disposal, wood ash mixtures, pure, to sanitary landfill

**Table 5** Inventory data of bio-oil upgrading

Item	Amount	Unit	Description
Outputs			
Chemicals	243	Metric ton	
Avoided products			
Coal	117	Metric ton	Bituminous coal, combusted in industrial boiler, NREL/US
Resources			
Air	370	Metric ton	
Process water	2,840	Metric ton	Water, cooling, unspecified natural origin/kilogram
Materials and fuels			
Bio-oil	1,040	Metric ton	
Electricity for upgrading	103,000	kWh	Medium voltage, at grid/US with US electricity
Natural gas	60	Metric ton	From onshore and offshore production including pipeline and LNG, consumption mix
Zeolite powder	0.79	Metric ton	At plant/RER S
ZnO catalyst	0.24	Metric ton	At plant/RER with electricity U
Heat	116,000	MJ	Natural gas, at industrial furnace >1,000 kW/RER U
Emission to air			
N <sub>2</sub>	284	Metric ton	
O <sub>2</sub>	14.2	Metric ton	
CO	39	Metric ton	
CO <sub>2</sub>	395	Metric ton	
Water	388	Metric ton	
Sulfur	1.56	Metric ton	
SO <sub>2</sub>	0.263	Metric ton	
Waste or emissions to treatment			
Wastewater	1,010	m <sup>3</sup>	Treatment, sewage, to wastewater treatment, class 3/with US electricity

**Table 6** Commodity chemical composition

Chemicals	Weight (%)
Ethylene	22.9
Propene	38.5
Butylene	10.2
Benzene	7.6
Toluene	14.1
Xylene	5.5
Ethylbenzene	0.7
Styrene	0.4
Indene	0.1
Naphthalene	0.1

with mature technology processing 2,000 metric tons/day of dry mixed wood feedstock. SimaPro 7.3 is used to develop and link the primary unit processes related to the current chemical production pathway. Materials and energy associated with the unit processes are collected as the inventory data which is set as primary materials and energy in SimaPro 7.3. The built-in Ecoinvent v.2.2 database in SimaPro 7.3 provides life cycle inventories for secondary materials and energy required in those primary unit processes. The required primary materials and energy inputs associated with the unit processes of the LCA are derived from this modified Aspen Plus model in combination with a greenhouse gases, regulated emissions, and energy use in transportation (GREET) model (Argone National 2011). The functional unit for interpreting the LCA results is 1 kg of chemicals. The IPCC 2007 GWP 100a method is employed to calculate the GWP. The cumulative energy demand (CED) method is used to estimate the fossil

energy input for the chemical production pathway. Other potential environmental impacts (smog, acidification, ecotoxicity, etc.) are evaluated with the TRACI 2 method.

## 4 Inventory analysis

### 4.1 Biomass collection and biomass transportation

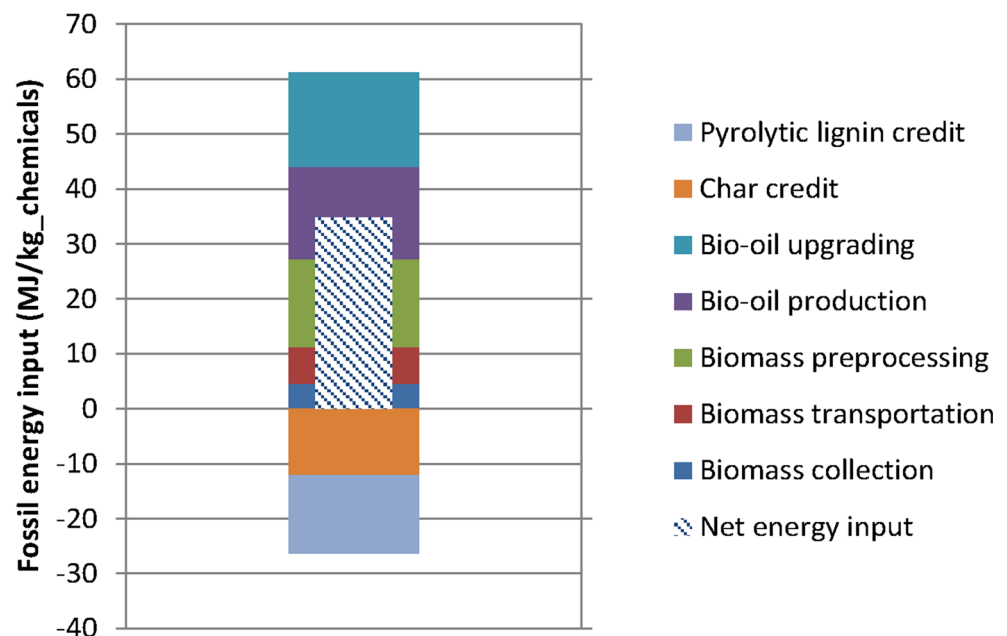
The biomass feedstock in this analysis is assumed to be forest residue. The input data for the biomass collection is detailed in Table 1 (based on data from Fan et al. (2011)). In this study, forest residue is treated as a waste product. The inputs for biomass collection include the fuel consumption associated with the forwarding and the grinding of the biomass and the equipment involved (Fan et al. 2011).

The wet forest residue, which contains 25 wt% moisture, is transported by 40-ton trucks. The total weight of the transported wet forest residue is 2,670 metric tons and the transportation distance is 150 miles one way, based on the GREET model developed by Argone National (2011). Detailed input data for the biomass transportation are summarized in Table 2.

### 4.2 Biomass preprocessing

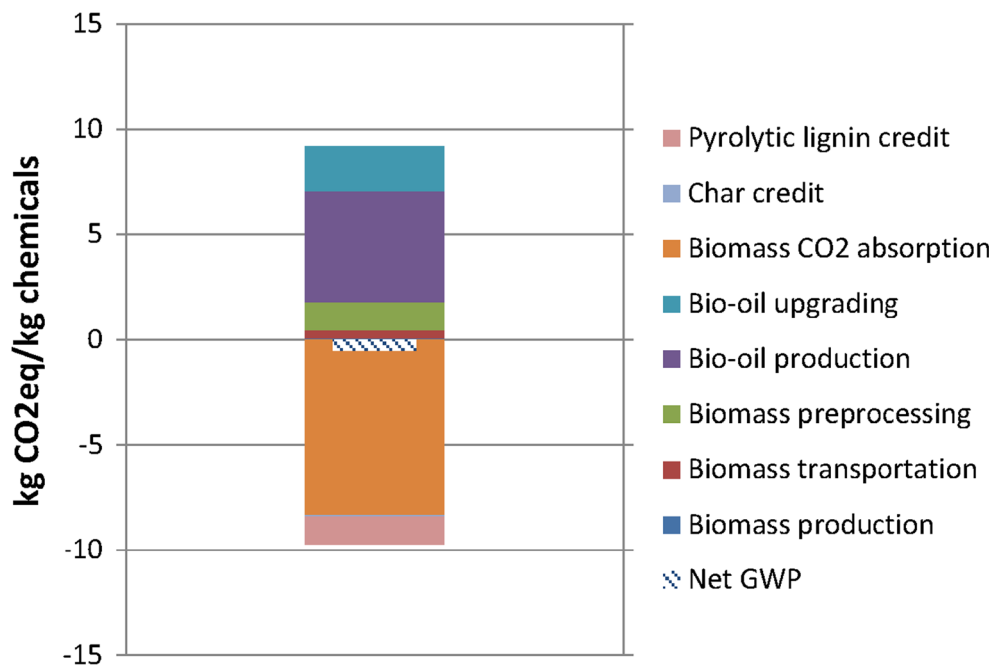
Steam is employed in the dryer to remove water from the wet forest residue. We assume a makeup of steam for biomass drying process, which is 1 % of the recycling steam. For the inventory analysis of biomass preprocessing, electricity and steam usage are considered as the material inputs. Water vapor

**Fig. 2** Fossil energy input for various unit processes per kilogram chemical production (Note: Product credits are treated as negative fossil energy input)





**Fig. 3** Contributions of unit process to GWP reported per kilogram of chemical production per kilogram chemical production (Note: Biomass CO<sub>2</sub> absorption and the product credits are treated as negative contributions to total GWP)



from the drying process is treated as an emission to the environment. Detailed inventory data are shown in Table 3.

#### 4.3 Bio-oil production

The inventory analysis for bio-oil production is shown in Table 4. Noncondensable gases generated during fast pyrolysis process are combusted to provide sufficient heat for the pyrolyzer. Char generated in pyrolysis is treated as coal substitute with an assumed heating value that is 50 % of the displaced coal. Electricity, air, and process water are considered to be inputs, while bio-oil and char are considered to be outputs. Process water is mainly used in bio-oil recovery and air is employed to support combustion of noncondensable gases. Emissions from bio-oil production include carbon oxides, hydrocarbons, nitrogen oxides, sulfide, and ash. Ash separated from the cyclones is used in sanitary landfills as waste treatment.

#### 4.4 Bio-oil upgrading

The final products from the hydrotreating/FCC pathway are aromatics and olefins. The total yield of chemicals is 243 metric tons/day. Pyrolytic lignin generated from bio-oil separation is treated as coal substitute with an assumed heating value that is 50 % of the displaced coal. The inventory inputs involved in this step are as follows: air, catalysts, process water, electricity, natural gas, and bio-oil. Natural gas is used to produce the hydrogen for the two-stage hydrotreating processes. Process water includes the water used for gas cooling and separation processes. Wastewater from bio-oil upgrading is assumed to be sent to a wastewater treatment plant. Details of the inventory analysis are shown in Table 5. Chemical products include

aromatics and olefins like benzene, toluene, and xylene. Table 6 details the composition of the commodity chemical.

## 5 Results and discussion

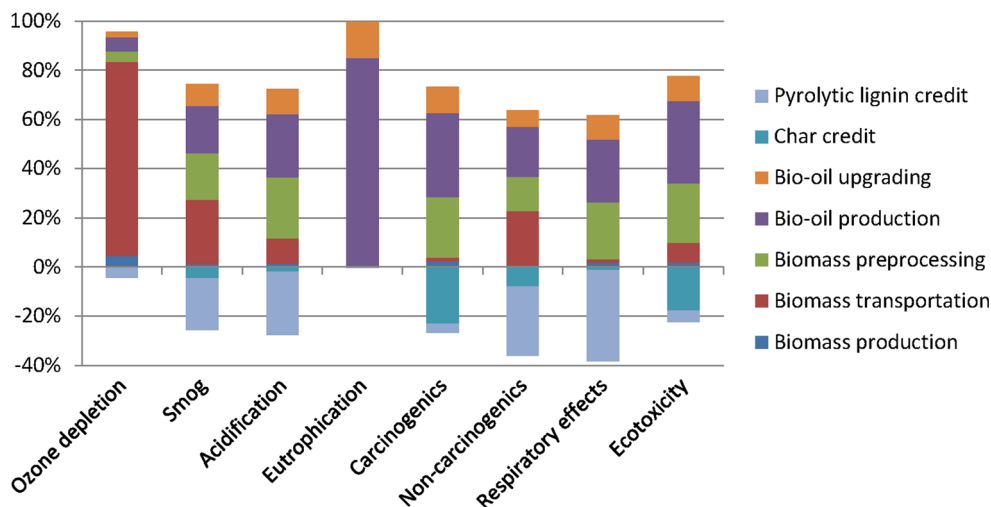
### 5.1 Fossil energy

Figure 2 includes the breakdown of fossil energy input for individual unit processes for chemical production. Fossil energy input is separated into two parts: required fossil energy and product credits (shown as negative fossil energy input). The bio-oil production and bio-oil upgrading steps consume the largest portion of the required fossil energy, each representing 28 % of the total fossil energy. Biomass transportation and biomass production consume relatively smaller portions, 11 and 7 % of the total required fossil energy input, respectively.

**Table 7** Environmental impacts (kg\_chemicals)

Impact category	Unit	Data
Ozone depletion	kg CFC-11 eq.	1.05E-06
Smog	kg O <sub>3</sub> eq.	0.243
Acidification	mol H+eq.	1.38
Eutrophication	kg N eq.	1.21
Carcinogenics	CTUh	1.17E-07
Noncarcinogenics	CTUh	5.16E-07
Respiratory effects	kg PM10 eq.	0.0037
Ecotoxicity	CTUe	2.38

**Fig. 4** Potential environmental impacts for various impact categories per kilogram chemical production



Conventional chemicals are petroleum-based products. In this study, chemicals are produced from renewable feedstocks and treated as substitutes for petroleum-based chemicals. Biochar generated in pyrolysis contributes as a credit, which reduces fossil energy input by 12.1 MJ per kg chemical production. Pyrolytic lignin generated in bio-oil upgrading process also contributes as a credit, which reduces fossil energy input by 14.3 MJ per kg chemical production. Accounting for all fossil energy inputs and credits, net fossil energy input is 34.8 MJ per kg chemical production.

## 5.2 GHG emissions

The contributions of the unit processes to GWP are shown in Fig. 3. Contributions to GWP have two parts: positive GWP and negative GWP. Positive GWP contributions come from biomass production, biomass transportation, biomass preprocessing, bio-oil production, and bio-oil upgrading. Negative GWP contributions come from carbon fixation by biomass, char credit, and pyrolytic lignin credit. For biomass absorption, it is assumed that the atmosphere can take up

0.942 kg CO<sub>2</sub> per kg of forest residue during the biomass growth (Hsu et al. 2010). Biochar and pyrolytic lignin are treated as credits since they are used as coal substitute.

Total positive GWP is 9.2 kg CO<sub>2</sub> eq. per kg chemical production. Among all of the unit processes, bio-oil production step has the largest GHG emissions, contributing 57 % of the total positive GWP. Bio-oil upgrading and biomass preprocessing steps represent 23 and 14 % of the total positive GWP, respectively. Biomass transportation contributes 5 % of the total positive GWP, and biomass production makes the smallest contribution (0.6 %) to GHG emissions.

Total CO<sub>2</sub> absorption by the forest residue is 8.33 kg CO<sub>2</sub> eq. per kg of chemicals. Biochar and pyrolytic lignin save 0.076 and 1.33 kg CO<sub>2</sub> eq. per kg chemicals, respectively. As a result, net GWP is -0.53 kg CO<sub>2</sub> eq. per kg chemicals.

## 5.3 Other impact categories

Table 7 presents the potential environmental impacts evaluated with the TRACI 2 method, and the relative contributions of individual unit processes to potential environmental impacts

**Table 8** Descriptions for compared chemical production pathways

Compared pathways	Descriptions
Oil byproduct CC	Fluidized catalytic cracking of byproducts derived from crude oil
Oil naphtha SC	Steam cracking of naphtha derived from crude oil
Waste naphtha SC	Steam cracking of naphtha derived from plastic waste gasification
Ethane SC	Steam cracking of ethane derived from natural gas
Methane FT naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from gas-to-liquid process of methane
Ligno FT naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from biomass gasification
Coal-ligno FT naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from coal and biomass gasification
Coal FT naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from coal gasification
Coal direct naphtha SC	Steam cracking of naphtha derived from direct liquefaction of coal

All of the abbreviations of the pathways are adopted from the study of Ren and Patel (2009)



**Table 9** Comparison results of different chemical production pathways

Pathways	GHG emissions (kg CO <sub>2</sub> eq./kg chemicals)	Fossil energy input (MJ/kg chemicals)
Current study	-0.53	34.8
Compared pathways		
Oil byproduct CC	1	11
Oil naphtha SC	0.9	10.3
Waste naphtha SC	1.2	20
Ethane SC	1	11.4
Methane FT naphtha SC	1	28.7
Ligno FT naphtha SC I	-3.5	-6
Ligno FT naphtha SC II	-7.1	-72
Coal-ligno FT naphtha SC	-1	76.7
Coal FT naphtha SC I	5.1	46
Coal FT naphtha SC II	7.8	84.7
Coal direct naphtha SC	6.5	77.1

The fossil energy input and GHG emissions data are calculated based on Tables 2, 3, 4, 5, 6, and 7 and Figs. 3 and 4 in Ren and Patel (2009)

are presented in Fig. 4. Biomass transportation has the largest impact on ozone depletion, contributing 86 % of the total impact. Bio-oil production has the greatest impact on eutrophication, contributing 85 % to the total impact. Bio-oil upgrading contributes almost the rest of the 15 % of the eutrophication. During the bio-oil production and bio-oil upgrading processes, nitrogen gases are emitted which results in the large eutrophication impacts. Char has larger contributions to reductions of ecotoxicity and carcinogenics compared to other environmental impacts due to offsetting fossil energy input.

#### 5.4 Comparison to other chemical production pathways

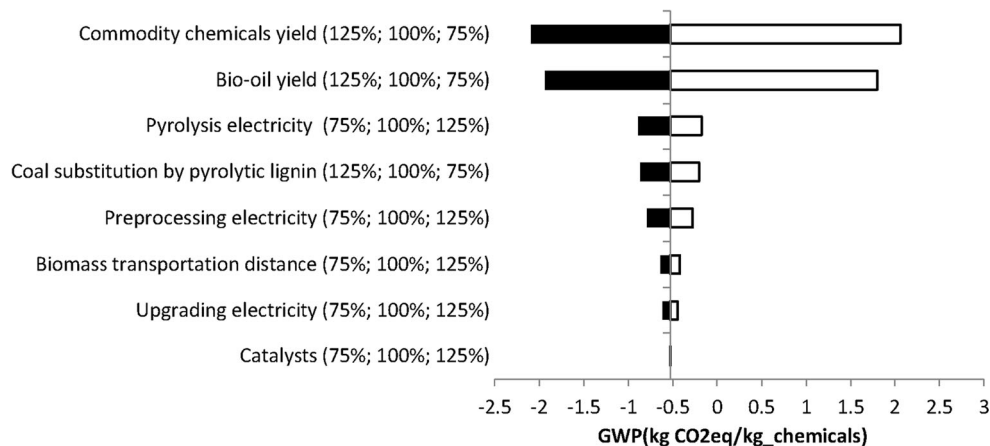
Table 8 describes several pathways selected for comparison. Generally, steam cracking is considered the key petrochemical conversion pathway (IEA 2004). Naphtha steam cracking

routes based on Ren and Patel (2009) are selected for comparison. In these pathways, a variety of energy sources, including crude oil, natural gas, coal, and lignocellulosic biomass, are considered for the chemical production. Table 9 compares the GHG emissions and fossil energy input in this study to the results from other production pathways.

As indicated in Table 9, among all of the pathways, coal-based pathways (coal FT naphtha SC I, coal FT naphtha SC II, and coal direct naphtha SC) have the greatest GHG emissions and fossil energy inputs. Coal-based pathways produce chemicals via steam cracking of coal-derived naphtha. Coal-based pathways can consume three to eight times more fossil energy and release five to eight times more GHG emissions than other petroleum-based (oil, natural gas, etc.) pathways. Lignocellulose biomass-derived chemicals have negative GHG emissions (included the carbon fixation from biomass growth) and negative fossil energy input. Ligno FT naphtha pathways produce chemicals via steam cracking of FT naphtha derived from biomass gasification. Ligno FT naphtha II represents the maximum co-generation of electricity and the minimum output of FT liquids, and it has the largest saving of GHG emissions and fossil energy input. Ligno FT naphtha I, on the other hand, represents the minimum co-generation of electricity and the maximum output of FT liquids. This indicates that electricity production from biomass-derived synthesis gas could save larger GHG emissions as well as fossil energy. Other petroleum-based pathways (oil, natural gas, etc.) have comparable smaller GHG emissions and fossil energy than coal-based pathways but larger GHG emissions and fossil energy than lignocellulose biomass-based pathways.

Compared to the pathways in the literature and practice, the GHG emissions related to the current pathway are smaller than all the petroleum-based chemical production pathways (coal, natural gas, oil, etc.). This is because carbon fixation from biomass growth for current production pathway significantly reduces the GHG emissions compared to petroleum-based pathways. Also, the fossil energy input for the current

**Fig. 5** Sensitivity of GWP to operating conditions for chemical production from forest residue (changes in operating parameters expressed as a percentage of the baseline case)



pathway is smaller than the coal-based pathways. But compared to chemical production via steam cracking of biomass-derived naphtha pathways, the fast pyrolysis process has larger GHG emissions and fossil energy input.

### 5.5 Sensitivity analysis

We select bio-oil yield, chemicals yield, electricity consumption, biomass transportation distances, and catalysts as the operating parameters for sensitivity analysis according to the previous techno-economic analysis (Zhang et al. 2013a) as well as their contributions in the inventory input. Each of these operating parameters is changed by a prescribed amount in relation to the baseline operating conditions (expressed as a percentage of the baseline case ranging from 75 to 125 %) to analyze the impact on GHG emissions.

The overall GWP ranges from  $-2.1$  to  $2.1$  kg CO<sub>2</sub> eq., as indicated in Fig. 5. Commodity chemicals are the main products, so the yield of commodity chemicals has the most significant impact on the GHG emissions. The increase of bio-oil yield could increase the final yields of chemicals so it is also a significant parameter for GHG emissions. A variation of bio-oil yield from 125 to 75 % results in a  $-1.9$ - to  $1.8$ -kg CO<sub>2</sub> eq. kg chemical range of GWP. Electricity consumption for biomass pyrolysis and bio-oil preprocessing and coal substitution by pyrolytic lignin are the secondary important parameters for GHG emissions. This is because electricity consumption for biomass pyrolysis and preprocessing occupies the majority of inventory inputs. Pyrolytic lignin yield is considerable so the effect of coal substitute from pyrolytic lignin is important for GHG emissions. If electricity consumption for biomass pyrolysis or pyrolytic lignin has a variation of  $\pm 25$  % on the baseline, GWP varies from  $-0.9$  to  $-0.2$  kg CO<sub>2</sub> eq. per kg chemicals. Biomass upgrading electricity consumption and transportation distance have comparably smaller impact on the GHG emissions. A variation of  $\pm 25$  % in biomass upgrading electricity consumption and transportation distance results in a  $-0.6$ - to  $-0.5$ -kg CO<sub>2</sub> eq. per kg chemical range of GWP. Quantity of catalysts used has very little impact on GWP.

The results of sensitivity analysis show that chemical yield and bio-oil yield are the most sensitive GHG emission factors which indicates the increase of plant efficiency for the pyrolysis process or bio-oil upgrading to chemicals process could largely improve the GHG emissions. In addition, the reduction of electricity consumptions related to the production processes could also reduce the carbon footprints.

## 6 Conclusions

The life cycle assessment of chemical production via forest residue fast pyrolysis and hydrotreating/FCC upgrading is examined in this study. Renewable chemicals are evaluated

as substitutes for fossil-based chemicals and char is treated as a substitute for coal. Among the production processes, bio-oil production is the key driver of the fossil energy input and GHG emissions. Bio-oil production contributes the largest GHG footprint (57 % of total positive GWP) and the largest fossil energy demand (28 % of the total required fossil energy) among all unit processes. Total fossil energy input is 34.8 MJ per kg chemicals and GWP is  $-0.53$  kg CO<sub>2</sub> eq. per kg chemicals. In contrast to conventional petrochemical production pathways, fossil energy input and GWP are smaller, which indicates that fossil energy consumption and GHG emissions could be reduced if commodity chemicals are produced via forest residue fast pyrolysis with hydrotreating/FCC upgrading processes. Biomass transportation makes the largest contribution to ozone depletion, and bio-oil production makes the largest contribution to eutrophication. Sensitivity analysis indicates that bio-oil yield and chemical yields play the most important roles in determining GHG emissions.

**Acknowledgments** The authors would like to acknowledge the financial support of the Bioeconomy Institute and the Biobased Industry Center of Iowa State University.

## References

- Argonne National Laboratory (2011) The greenhouse gases, regulated emissions, and energy use in transportation (GREET) model. <http://greet.es.anl.gov/> Accessed Aug 2013
- Brehmer B, Boom RM, Sanders J (2009) Maximum fossil fuel feedstock replacement potential of petrochemicals via biorefineries. *Chem Eng Res Des* 87(9):1103–1119
- Brown TR, Zhang Y, Hu G, Brown RC (2012) Techno-economic analysis of biobased chemicals production via integrated catalytic processing. *Biofuels Bioprod Biorefin* 6(1):73–87
- CHEMSYSTEMS (2013) Feedstock options for the petrochemical industry. <http://www.chemsystems.com/about/cs/news/items/PPE%20PCMD%20Feedstocks%202011.cfm> Accessed Aug 2013
- Chen Y (2012) Biomass to fuels: thermo-chemical or bio-chemical conversion? *Ferment Technol* 1 (2):e104. <http://www.omicsgroup.org/journals/2167-7972/2167-7972-1-e104.pdf>
- Christensen CH, Rass-Hansen J, Marsden CC, Taarning E, Egeblad K (2008) The renewable chemicals industry. *ChemSusChem* 1(4): 283–289
- Dale BE (2003) ‘Greening’ the chemical industry: research and development priorities for biobased industrial products. *J Chem Technol Biotechnol* 78(10):1093–1103
- Dornburg V, Lewandowski I, Patel M (2003) Comparing the land requirements, energy savings, and greenhouse gas emissions reduction of biobased polymers and bioenergy. *J Ind Ecol* 7(3–4):93–116
- EIA (2012a) Annual energy outlook. <http://www.eia.gov/> Accessed Aug 2013
- EIA (2012b) Production capacity of operable petroleum refineries. [http://www.eia.gov/dnav/pet/PET\\_PNP\\_CAPPROD\\_A\\_\(NA\)\\_8PR\\_BSD\\_A.htm](http://www.eia.gov/dnav/pet/PET_PNP_CAPPROD_A_(NA)_8PR_BSD_A.htm) Accessed Aug 2013
- Fahmi I, Cremaschi S (2012) Stage-gate representation of feedstock development for chemical process industry. *Foundations of Computer-Aided Process Operations*. <http://focapo.cheme.cmu.edu/2012/proceedings/data/papers/012.pdf>

- Fan J, Kalnes TN, Alward M, Klinger J, Sadehvandi A, Shonnard DR (2011) Life cycle assessment of electricity generation using fast pyrolysis bio-oil. *Renew Energy* 36(2):632–641
- Gavrilescu M, Chisti Y (2005) Biotechnology—a sustainable alternative for chemical industry. *Biotechnol Adv* 23(7–8):471–499
- GBI Research (2012) Light Olefins Americas Market to 2020—cost effective ethylene from shale gas-derived ethane and on-purpose technology for propylene to promote industry growth. <http://www.marketresearch.com/GBI-Research-v3759/Light-Olefins-Americas-Cost-Effective-6744067/> Accessed Aug 2013
- Groot W, Borén T (2010) Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand. *Int J Life Cycle Assess* 15(9):970–984
- Heracleous E (2011) Well-to-wheels analysis of hydrogen production from bio-oil reforming for use in internal combustion engines. *Int J Hydrogen Energy* 36(18):11501–11511
- Hermann BG, Blok K, Patel MK (2007) Producing bio-based bulk chemicals using industrial biotechnology saves energy and combats climate change. *Environ Sci Technol* 41(22):7915–7921
- Heyde M (1998) Ecological considerations on the use and production of biosynthetic and synthetic biodegradable polymers. *Polym Degrad Stab* 59(1–3):3–6
- Hipolito MG (2011) Life cycle assessment of platform chemicals from fossil and lignocellulosic biomass scenarios. <http://www.diva-portal.org/smash/get/diva2:458493/FULLTEXT01.pdf>
- Hsu DD (2012) Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing. *Biomass Bioenergy* 45:41–47
- Hsu DD, Inman D, Heath GA, Wolfrum EJ, Mann MK, Aden A (2010) Life cycle environmental impacts of selected U.S. ethanol production and use pathways in 2022. *Environ Sci Technol* 44(13):5289–5297
- ICIS (2013a) Aromatics & aromatic chemicals information from ICIS. [http://www.icis.com/v2/chemicals/petrochemicals\\_aromatics.aspx](http://www.icis.com/v2/chemicals/petrochemicals_aromatics.aspx) Accessed Aug 2013
- ICIS (2013b) Olefins & olefin chemicals information from ICIS. [http://www.icis.com/V2/chemicals/petrochemicals\\_olefins.aspx](http://www.icis.com/V2/chemicals/petrochemicals_olefins.aspx) Accessed Aug 2013
- IEA (2004) Energy statistic manual. <http://www.iea.org/training/toolsandresources/energystatisticsmanual/> Accessed Aug 2013
- Iribarren D, Peters JF, Dufour J (2012) Life cycle assessment of transportation fuels from biomass pyrolysis. *Fuel* 97:812–821
- Kauffman N, Hayes D, Brown R (2011) A life cycle assessment of advanced biofuel production from a hectare of corn. *Fuel* 90(11):3306–3314
- Kim S, Dale BE (2008) Energy and greenhouse gas profiles of polyhydroxybutyrates derived from corn grain: a life cycle perspective. *Environ Sci Technol* 42(20):7690–7695
- Lin Y, Tanaka S (2006) Ethanol fermentation from biomass resources: current state and prospects. *Appl Microbiol Biotechnol* 69(6):627–642
- Lynd LR, Wang MQ (2003) A product-nonspecific framework for evaluating the potential of biomass-based products to displace fossil fuels. *J Ind Ecol* 7(3–4):17–32
- McFarlane J, Robinson S (2007) Survey of alternative feedstocks for commodity chemical manufacturing. Oak Ridge National Laboratory Report No. ORNL/TM-2007/28 <http://info.ornl.gov/sites/publications/files/Pub8760.pdf>
- Piemonte V (2011) Bioplastic wastes: the best final disposition for energy saving. *J Polym Environ* 19(4):988–994
- Ren T, Patel MK (2009) Basic petrochemicals from natural gas, coal and biomass: energy use and CO<sub>2</sub> emissions. *Resour Conserv Recycl* 53(9):513–528
- Salge JR, Dreyer BJ, Dauenhauer PJ, Schmidt LD (2006) New process to produce completely renewable fuels and chemicals. [http://scitizen.com/future-energies/new-process-to-produce-completely-renewable-fuels-and-chemicals\\_a-14-235.html](http://scitizen.com/future-energies/new-process-to-produce-completely-renewable-fuels-and-chemicals_a-14-235.html) Accessed Aug 2013
- Schilling LB (1995) Chemicals from alternative feedstocks in the United States. *FEMS Microbiol Rev* 16(2–3):101–110
- Stephanopoulos G (2007) Challenges in engineering microbes for biofuels production. *Science* 315(5813):801–804
- Vispute TP, Zhang H, Sanna A, Xiao R, Huber GW (2010) Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. *Science* 330(6008):1222–1227
- Xu Y, Hanna MA, Isom L (2008) “Green” chemicals from renewable agricultural biomass—a mini review. <http://www.benthamscience.com/open/toasj/articles/V002/54TOASJ.pdf>
- Yates MR, Barlow CY (2013) Life cycle assessments of biodegradable, commercial biopolymers—a critical review. *Resour Conserv Recycl* 78:54–66
- Zhang Y, Brown TR, Hu G, Brown RC (2013a) Comparative techno-economic analysis of biohydrogen production via bio-oil gasification and bio-oil reforming. *Biomass Bioenergy* 51:99–108
- Zhang Y, Brown TR, Hu G, Brown RC (2013b) Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose. *Bioresour Technol* 127:358–365
- Zhang Y, Brown TR, Hu G, Brown RC (2013c) Techno-economic analysis of two bio-oil upgrading pathways. *Chem Eng J* 225:895–904
- Zhong ZW, Song B, Zaki MBM (2010) Life-cycle assessment of flash pyrolysis of wood waste. *J Clean Prod* 18(12):1177–1183