LIFE CYCLE ASSESSMENT OF TWO CATALYSTS USED IN THE BIOFUEL SYNGAS CLEANING PROCESS AND ANALYSIS OF VARIABILITY IN GASIFICATION

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Abstract: Syngas known also as producer gas is the main product from biomass gasification process. This gas is considered as a renewable energy which can be converted into liquid fuels. Within syngas are significant amount of tars, syngas cannot be used directly as a clean fuel. The current method used in the syngas cleaning process is reforming tars with metal catalysts. Biochar, a co-product of gasfication, has been developed with the function of removing tars from the syngas. Compared to metal catalyst, biochar has a lower price and higher potential sustainability for the environment. Life cycle assessment (LCA) is introduced into this study to analyze the sustainability performance of producing a metal catalyst versus a dedicated biochar catalyst. The comparative LCA results indicate that biochar production has a 93% reduction in GHG emissions and requires 95.7% less energy than the metal catalyst. Biochar production also releases few impacts on human health than metal catalyst. The disadvantage of biochar in ecosystem quality is due mostly to its larger agricultural land occupation impacts. Sensitivity analysis is also carried out for identifying the effects of variability in the two production systems on environmental impacts. In the metal catalyst manufacture, the production of nickel and energy used has significant effects on the environmental impacts. The gasification process using low moisture content (9%) and high yield type (8 tons/acre) of switchgrass is suggested as possibly a more sustainable scenario to produce syngas and biochar.

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CHAPTER I

INTRODUCTION

1.1 Gasification and Syngas

Gasification is a thermochemical conversion process which can produce gaseous and liquid fuels. Biomass gasification typically converts solid biomass into combustible gases through high temperature and partial oxidation processes. Gasification using relatively dry biomass (moisture ≤10 wt.%) is typically operated at a temperature ≥700°C and 1–5 atmosphere pressure in the presence of one or more oxidizing agents such as air, steam, and oxygen [1]. Gasification of various biomass feedstocks such as switchgrass and forage sorghum has been conducted at the OSU Bioenergy labs and at other research institutions for years. The main value added product of biomass gasification is known as syngas, or producer gas, which contains a variety of gases. The raw syngas is flammable at standard atmospheric conditions and its primary mixture components are methane, hydrogen, carbon dioxide and carbon monoxide (see Table 1). The producer gas can be used for various thermal and power applications or can be further processed into liquid fuels and chemicals after cleaning and conditioning.

Tars are also generated during gasification of biomass into syngas, which contain a mixture of complex organic compounds of higher molecular weight than benzene. Although silica sand can be used as an inexpensive filter to reduce the tar formation [2], tars are still the major obstacle in using syngas directly for producing power, fuels and chemical products. The main

Table 1 Switchgrass gasification syngas [3]

Compound	Composition (% mole)
Carbon Monoxide	19.3
Carbon Dioxide	16.79
Methane	7.49
Hydrogen	5.15
Nitrogen	51.27

reason that tars are a problem is that they can condense and corrode metal surfaces. In addition, tars render process catalysts inactive [4]. Besides the harmful carbon deposition on catalyst surfaces, tar aerosols and higher complex molecules can clog fuel pipes and fuel injectors. Tars often have detrimental effects on chemical and microbial processes converting syngas into fuels [5]. As a consequence, tar removal from the syngas should be considered as a key process in the utilization of biomass generated syngas.

The traditional methods in hot syngas cleaning include water scrubbing, thermal cracking and catalytic cracking [4]. The preferred method for reducing tars is using solvents (acetone and water) or catalysts (Nickel-Alumina catalyst) which convert the tars to more useful gases. These processes avoid using higher temperatures and producing more pollutants [6]. Compared to solvent tar removal systems, catalyst-based methods can crack and reform tar compounds to produce extra gases such as carbon monoxide and hydrogen which are the main syngas components without also producing a liquid waste. The conventional catalyst used in cleaning syngas process is Ni catalysts with the most common being Ni/Al_2O_3 and $Ni/CeO_2/Al_2O_3$ [2]. However, some metal materials like nickels and wastes of these manufacturing catalysts could also have harmful impacts on environment during production and their costs are expensive. Therefore a life cycle study of the catalyst production is needed.

1.2 Biochar

Biochar, one of the co-products of gasification, has been observed to behave as a catalyst that is capable of reforming tar effectively [6]. Biochar is often simply considered as gasification waste if there is no need for the char. Therefore, the ability to reuse a waste as a valuable catalyst is appealing. For this study, the production of biochar is assumed to be a dedicated process – not a waste reuse. This allows the full accounting of the environmental impacts of producing biochar. Biochar properties that contribute to the ability of reforming tars were shown in Tables 2 and 3. The function of biochar for removing tars is related to the surface area, pore volume and carbon structure in the char [7]. Both biomass char and metal catalyst supported on biomass char can increase the contents of H_2 and CO by reforming tars in the syngas [8]. Basically, manufacture of metal catalyst consumes virgin material resources and energy in the production of syngas cleaning system and the waste of metal production will cause environmental impacts to a certain degree. Therefore, a systematic environmental sustainability assessment should be performed to show the differences of two prospective catalysts (biochar and metal catalyst) and their performances in environmental impact areas.

Table 2 Ultimate analysis of switchgrass biochar [3]

Material	Volatile Matter (wt.%)	Fixed Carbon (wt.%)	Ash (wt.%)
Biochar	18.85	63.35	17.5

Table 3 Elemental analysis of switchgrass biochar [3]

Element	C	H	N	S	O
(wt.%)	87.43	1.49	0.74	0.08	10.26

1.3 Life Cycle Analysis

Life cycle analysis (LCA) is defined by United States Environmental Protection Agency (U.S. EPA) as a methodology of assessing potential environmental impacts associated with a product or process through its entire lifetime (“cradle to grave”) [9]. The LCA technique can evaluate environmental impacts of products across several important impact areas based on their materials and energy inputs and outputs. LCA has also been applied to industries for product improvements and sustainability [10].

According to the guidelines of the International Organization of Standards ISO14040 [11], there are four basic stages included in a LCA:

- Defining goal and scope
- Developing process inventories
- Impact assessments
- Interpretation

The goal and scope of LCA stage includes the purposes for conducting the study, the intended application and the intended audience [12]. The system boundaries of the study and functional unit are also defined in the goal and scope section. The functional unit is a quantitative measure of the functions provided by the products [12]. For example, the functional unit for a biofuel LCA may be an examination of the processes to produce 1,000 MJ of liquid fuel. The functional unit and system boundaries are described in further detail later. The life cycle inventory (LCI) is a database compilation of the inputs (energy, materials) and the outputs (environmental emissions) from the product over its life-cycle [12]. The calculation of inputs and outputs is tied directly to the functional unit. The impact assessment indicates the magnitude and significance of the potential environmental impacts of the product system [12]. In the interpretation, conclusions and recommendations are given by evaluating the results of the LCA environmental impacts.

A comparative LCA is often used to identify which product has most benefits or less environmental impacts. The subjects could be same products with different construction materials and production methods or several totally different products with the same function.

Since biochar has been found capable of removing tars in the syngas, many researches are seeking to develop the biochar as a high effective catalyst. Kezhen et al. [13] had analyzed the physiochemical properties of biochar based on several feedstock and different gasification conditions in order to find the optimal biochar for catalytic function. The articles about life cycle assessment of biochar generated by gasification are limited and no study has been found conducting a comparative LCA of biochar and metal catalyst used in the biomass tar removal process. Therefore, a systematic life cycle analysis is essential for providing the best understanding of the potential environmental impacts caused by biochar and metal catalysts.

In this study, an LCA comparative analysis is used to quantify the environmental impact caused by the processes of producing metal catalyst and biochar catalyst. The study assumes that the gasification process on the biochar side is used only to produce biochar as the primary product. The LCA is performed considering raw materials to the final catalyst production. The analysis is conducted using the SimaPro 7.3.3® software to assess the environmental impacts. A sensitivity analysis is carried out to indicate that which factors affect the environmental load most heavily in each catalyst production system and how the results change by variations in the switchgrass production and gasification input parameters.

CHAPTER II

REVIEW OF LITERATURE

2.1 Development of Life Cycle Assessment

The international standards for life cycle assessment were compiled in 2006 as an updated version of ISO 14040 and ISO 14044 based on modification of the existing ISO 14040-14043 standards [14]. The aim of this effort was to remove inconsistencies and errors in the old standards and improving the readability and consistency of new standards.

The main technical content of the new standards continued using principles that were valid originating from the old standards while incorporating changes of definitions and principles [14]. For instance, the definition of system boundary was “The system should be modeled in such a manner that inputs and outputs at its boundaries are elementary flows[1]” [15]. In the new standards, the system boundary itself is related to the internal unit processes[2] of product system and doesn’t refer to the interface between the product system and the environment [14]. The definition of waste is not limited to hazardous waste within the new standards [14].

The principles of LCA have more focus on the environmental impacts than other sustainability aspects like economics and social responsibility which are the two other typical

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[1] (1) material or energy entering the system being studied, which has been drawn from the environment without previous human transformation; (2) material or energy leaving the system being studied, which is discarded into the environment without subsequent human transformation

[2] Unit process: a subsystem that has inputs and outputs

components of classical sustainability for more extensive assessments [14]. The LCA modelling methodology is more focused when considering all attributes of human health, ecosystem, climate and resources. Moreover, the new ISO standards address that LCA is used as a comparative tool [14] and results can be used as a methodology to disclose environmental impact information to the public because LCA reporting has become part of accepted policy documentations and legislation [16]. For the interpretation part, it is typically emphasized that the impact conclusions should be drawn with regard to overall study limitations. The general technique developments have made LCA more acceptable and valid as an assessment technique. However, the inherent uncertainty and variability in any assessment is still a challenging and complex problem that needs to be addressed by using more systematic and scientific methods in boundary determination, data acquisition and accuracy [17].

2.2 Life Cycle Assessments Related to Switchgrass and Gasification

The need to find a replacement for fossil fuels has focused the minds of many researchers and policy makers on bioenergy over the last few years. An estimate indicated that 98% of total US carbon dioxide emissions is attributed to fossil fuels combustion in 2002 [18]. Bioenergy crops that can take in CO_2, water, and sunlight to create biomass, which is then processed and transferred to a refinery to create fuel, has been determined to have many possible environmental benefits. The most attractive benefit is that the bioenergy has a potential in saving non-renewable energy and reducing GHG emissions to the environment. With emerging advanced biological and chemical technology, it has been estimated that the renewable energy from biomass contributes to 14% of the world total primary energy consumption in 2005 [19]. The life cycle assessment technique has been applied to analyze many energy products and systems in the environmental performance including energy consumption and global warming impacts, especially in bioenergy field [20]. It is necessary for decision makers to come up with systematic and scientific evaluation methodologies for making a policy of a challenging biomass adoption strategy. Life cycle assessment is the primary tool being examined to perform this duty.

2.2.1 LCA of Switchgrass Production

Switchgrass (*Panicum virgatum* L.), is a perennial, warm-season grass and native crop across the USA. It has attained much attention as a promising biomass used in producing bioenergy because of its capacity of growing in the dry environment [21]. The characteristics of switchgrass as a good feedstock include the high yield and consistent supply; low energy and resource inputs; low risk of invasiveness (An invasive plant has the ability to thrive and spread aggressively outside its natural range and it can increase the competition of energy intake with other plants) [22]; easy harvest processing with conventional farming equipment and potential uses of by-products [23]. Additional considerations for selecting switchgrass are its positive environmental attributes, such as low pesticide and fertilizer requirements and its perennial growth habit [24]. The environmental consequences of producing switchgrass for bioenergy have been identified by specific studies and life cycle assessments. Studies of soil carbon storage indicate that using switchgrass as a bioenergy crop can significantly contribute to carbon sequestration that will improve soil quality and nutrient contents [25, 26]. Moreover, switchgrass can play an important role in soil erosion reduction and sedimentation control under cultivation [21]. Most LCAs found reduction in GHG emissions and energy consumptions were the main benefits of substituting bioenergy for non-renewable energy [27-29]. For instance, a 35% emissions reduction in case of biofuels in Members States of the European Union [30]. Adler et al. [31] indicated that a 115% reduction in GHG emissions resulted from producing ethanol and biodiesel from switchgrass and hybrid poplar when compared with gasoline and diesel. Bai et al. [32] found a 65% reduction in GHG emissions with switchgrass ethanol fuels.

An integrated environmental, energy and economic life cycle assessment of using switchgrass as a feedstock in utility scale power generation was conducted to evaluate the environmental load and GHG emissions compared to coal [18]. The life cycle analysis of switchgrass included switchgrass preparation and power generation. For the switchgrass preparation, the study boundary began with soil preparation and ended with biomass transportation to the power plant. The preparation procedure also included fertilizer, herbicide and lime production and the fuel used in the transportation of switchgrass production. Based on the cost and GHG emissions data, Xiaoyun et al. [18] compared four models of preparing the switchgrass. The procedure including harvesting loose material for hauling, chopping, compressing and transportation was indicated as the most sustainable technology in switchgrass preparation. Meanwhile, for power production, 10% switchgrass was co-fired with coal (co-firing ratio equals 1: 9 biomass to coal on a mass basis). This combination had a better GHG reducing effect in the LCA study than switchgrass fired power production alone.

This study also applied some interacting input factors to the sensitivity analysis performed on the LCA. One of the variability assessments was to identify the effect of switchgrass co-firing ratio on the GHG emission rates. The results showed that CO_2-eq emission decreased with the increase of co-firing ratio within the co-firing ratio of 20%. The other variability assessments analyzed how the variations in combinations of co-firing ratio, hauling distance and switchgrass yield influenced the CO_2-eq emission. For making switchgrass relatively competitive to coal at price, improving the yield and reducing the hauling distance could achieve this goal [18]. Additional studies [18, 33, 34] have applied economic methodologies such as techno-economic analysis, which is used to evaluate technology viability and value on the commercial level, to bioenergy LCA studies beside the conventional methods of simply focusing on the potential environmental impacts [35].

An LCA of a biorefinery system producing bioethanol, bioenergy, and chemicals from switchgrass was conducted to assess its environmental impacts focusing on GHG and energy balances, and compared to the fossil reference system producing the same products [36]. The results evidenced that GHG emissions of biorefinery system were decreased by 79% and about 80% non-renewable energy was saved when compared to a fossil reference system. Among additional impact categories, the impacts on acidification and eutrophication of biorefinery system were higher than the same impacts of the fossil reference system [36]. An LCA approach of assessing biorefinery systems also indicated that using crop residues in a biorefinery could reduce GHG emissions by 50% and save more than 80% of nonrenewable energy, but it had more eutrophication impacts than in fossil fuel systems due to leaching of nitrates to groundwater [37]. Cherubini and Jungmeier [36] concluded that soil C sequestration was responsible for a large GHG benefit (65 kt CO_2 eq/a, for the first 20 years), while switchgrass production had the most important contributions to total GHG emissions of the biorefinery system.

The ethanol production derived from cellulosic biomass has been used for light-duty vehicle as a transportation liquid fuel. An LCA study of three switchgrass-derived transportation liquid fuels, E85 (mixture of 85% ethanol and 15% gasoline by volume), Fischer-Tropsch diesel (FTD) and dimethyl ether (DME), revealed that cellulosic biofuels as E85, FTD and DME offer significant savings in petroleum (66-93%) and fossil energy (65-88%) consumption, and 82-87% reductions in greenhouse gas emissions on a per-mile basis [38]. An additional LCA of switchgrass-derived ethanol-fueled automobiles compared its results to those of corn stover-derived ethanol and low-sulfur reformulated gasoline (RFG) based on an equivalent functional unit [39]. In this study, the average yield of switchgrass was set at 8 oven-dry Mega grams per hectare (odMg/ha) based on the best cultivation and harvesting practices in Ontario. This amount is similar to the average yield of switchgrass in the North America. The results showed that GHG emissions of an E85-fueled automobile derived from switchgrass are 57% lower than the GHG emissions of a reformulated gasoline (RFG) automobile [39]. While the GHG emissions of ethanol from corn stover is 65% lower than those of RFG due to sharing emissions with grain production [39]. The authors used a mass-based allocation method in producing ethanol system from corn stover with the assumption that 62% of the aboveground stover was used for ethanol production and 38% is left on the field [39]. In this LCA study, a mass-based allocation method is also used based on the proportion of biochar produced from switchgrass.

2.2.2 LCA of Gasification

Biomass can be converted into solid, liquid and gaseous product through either biological or various thermochemical processes [40, 41]. One of the promising technologies which utilizes the biomass is biomass gasification [42]. Biomass gasification is considered one of the most efficient ways of converting biomass into energy [43]. The biomass gasification process is an old but promising technology because it is typically more efficient than other thermochemical processes of converting biomass into a combustible gas [44]. Biomass gasification has many advantages over coal gasification. Since biomass is more reactive and has higher volatiles content than coal, biomass gasification needs lower temperature than coal gasification so that there are less heat loss, emissions and material problems associated with biomass gasification [45]. Using feedstock as crop residues, including straw, stalk, husk, shell, peel and bagasse can reduce the GHG emissions generally due to low sulfur and nitrogen content in there biomass [46].

An LCA of a biomass integrated gasification combined cycle with CO_2 removal was carried out to indicate that it could definitely mitigate the CO_2 emissions by 76%-79% of conventional coal integrated gasification combined cycle [47]. In this article, dry poplar with a 15% moisture content was used as a gasification feedstock associated with 31 kg/s mass flow. The gasification process was operated with an air equivalence ratio (ER) of 0.2 at a temperature of 1200°C. In the LCI, the biomass production had a yield of 13.4 ton/ha per year and was cultivated every 7 years. The data of fertilizer, herbicide and fuel consumption was also considered in order to estimate the CO_2 emissions of biomass production. The data source for the biofuel utility plant construction materials were based on an equivalent capacity (i.e.MW) coal power plant.

A comparative LCA of hydrogen production via biomass gasification was built to assess the environmental impacts of biomass gasification followed by reforming of the syngas and biomass gasification followed by electricity generation and electrolysis [48]. The results of comparison indicated that the biomass-gasification-electricity-electrolysis system had a 86% reduction in GHG emissions, while had more acidification impacts than the biomass-gasification-steam reforming system [48]. This consequence resulted from the additional electricity required in the biomass-gasification-steam reforming system due to compression requirements that involve the steam reforming and purification processes [48]. Another LCA study of biomass-based hydrogen production for usage in a fuel cell vehicle was performed associated with two different gasification systems which reacted in a downdraft gasifier (DG) and a circulating fluidized bed gasifier (CFBG) [49]. The functional unit was producing 1 MJ/s hydrogen production. The LCA results indicated that the fossil energy consumption rate (0.088 MJ/s) of DG system is less than the rate (0.175 MJ/s) of CHBG, and the GHG emissions of DG and CHBG systems are 6.27 CO_2 eq g/s and 17.13 CO_2 eq g/s, respectively [49]. These two LCAs of hydrogen production are both based on gasification technology. The first LCA compares the results of two different hydrogen production usage stages and the second LCA compares the results of two different gasification systems. Therefore, LCA results can be various due to not only various biomass cultivations but also different producing technologies and production usages.

2.2.3 LCA of Biochar Production

Biochars refer to the high carbon materials produced from the slow pyrolysis of biomass [50]. Biochar is either disposed or recycled and used as a soil amendment - which has the beneficial function of adding nutrients to the soil [51]. It is also a promising way to possibly mitigate climate change level by sequestering and distributing carbon back into the soil [52]. The utilization of biochar such as the substitution of fertilizer; sources of heat, bio-oil and gases for farm and ranch use, can bring much economic potentials to farmers and ranchers [53].

Kelli et al. conducted an LCA focusing on the energetic and climate change performances of biochar from pyrolysis systems [54]. Switchgrass with two different land-use scenarios were compared in the GHG emissions impact. Switchgrass A was grown on virgin land and switchgrass B was grown on a land diverted from the existing cropland. The results implied that the GHG emissions of switchgrass B was more than the GHG reduction and made the net GHG emissions as a positive value of 36 kg CO_2e t^{-1}. The author explained that if energy crops such as switchgrass are planted on land converted from annual food crops, the indirect land-use change impacts may lead to more GHG emissions than GHG sequestration [54]. Therefore, the conclusion indicated that it was probably not appropriate to replace food crops with fuel biomass crops such as switchgrass on the same land [54].

A life cycle assessment of biochar co-firing with coal for electricity generation in Taiwan was conducted associated with SimaPro® 7.2 software and IMPACT 2002+ impact assessment model [46]. When compared to coal-fired system, the biochar co-firing with co-firing ratio of 10% and 20% had benefits in five impact categories, including aquatic ecotoxicity, terrestrial ecotoxicity, land occupation, global warming, and non-renewable energy, but it might cause higher impacts than coal firing systems in human health impact category [46]. For evaluating the environmental impact of biochar as a soil amendment, an LCA of biochar implementation in conservation agriculture in Zambia was conducted associated with a comparison to conventional agriculture [55]. The results confirmed that the use of biochar in conservation farming was beneficial for climate change and fossil fuel consumptions [55]. However, the impacts on human health of conservation farming plus biochar from earth-mound kilns were worse than those of conservation farming without biochar addition due to particle emissions stemming from biochar production [55].

The selection of biomass feedstock for producing biochar also has a heavy influence on the environmental impacts of producing the char, especially GHG emissions. The LCA of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime was conducted for assessing the environmental impacts of slow pyrolysis system using microalgae biomass as a feedstock for generating biogas, biofuel and biochar [56]. The comparison results of biomass cultivation in microalgae biomass, soybean and canola seed released that a net reduction of 220 kg of CO_2 (eq) removed from the atmosphere in microalgae cultivation, while a net increase of 243 kg and 739 kg CO_2 (eq) emitted to the atmosphere in soybean and canola seed cultivation, respectively [56]. Moreover, the land use of microalgae is only 0.2% of the land use in soybean cultivation. However, the water use of microalgae was much more than water use of the other two crop cultivations. The non-renewable energy depletion of cultivating microalgae was nearly 10 times higher than energy used in soybean cultivation [56].

The preliminary work of a pyrolysis biochar system in Scotland suggested that for different biomass availability scenarios, a sustainable biochar strategy could achieve an abatement of GHG emission between 0.4 and 2.0 Mt (megatonne) CO_2 eq per year in 2009, and it will increase up to 1.5 and 4.8 $MtCO_2$ eq by 2050 [57]. Sohel et al. [57] indicated that growing of biomass crops on peatlands, grasslands, forest or other land uses would result in a substantial direct net carbon emission to the atmosphere. Conversely, it can be expected to enhance carbon storage that growing biomass crops in the changed land (e.g. conversion of arable land to perennial crops) [57]. Sebastian et al. [58] compared the results of GHG balance of different biochar systems (pyrolysis, gasification, hydrothermal carbonization, and flash carbonization) in peer-reviewed scientific articles, and found that the GHG emissions was between −1054 kg CO_2 eq and +123 kg CO_2 eq per t dry biomass feedstock. The authors concluded that net GHG reductions were often not achieved if dedicated energy crops were used as feedstock for the production of biochar [58]. This conclusion could be one of the reasons that why producing biochar as a catalyst does not achieve GHG abatements.

2.3 Variability and Uncertainty in LCA Studies

Uncertainty is defined as the error of the outcome caused by variability or deficient data in the model input [59]. Life cycle assessments are very dependent on the data quality and sensitive to the variability of data because the quality of an LCA is directly related to the inventory upon which it is based [60]. Although practitioners have been long aware of improving the data quality, the variability and uncertainty still exist and cannot be totally eliminated due to the inherent variations in the inventory data [61]. Many articles mentioned that the data uncertainty is caused by a general lack of accurate data values and incorrect measurement techniques [62].

The LCA variability and uncertainty can be classified as parameter uncertainty, model uncertainty, uncertainty due to choices, spatial and temporal variability, and variability between sources and objects [63]. Stochastic modelling is used to deal with parameter uncertainty and variability between sources and objects. For example, the uncertainty of the crop production unit process data developed for LCA was identified by Student's t-test distributions through the relative standard error [64]. Uncertainty due to choices can be the uncertainty caused by the choices of functional unit, allocation method and product systems. The model uncertainty can be due to the flaws of modelling method. For instance, it is assumed that ecological processes are affected by the environmental interventions in a linear manner and the thresholds of interventions are ignored [61]. Actually many ecological processes are non-linear and many releases out of the thresholds do not lead to any effects on the environment or more environmental consequences than the estimated results [65]. Spatial variability of location is due to the variations of ecological properties and human population density in different locations [66]. Moreover, the data collection such as the substance emissions of global warming potentials, ozone depletion potentials and photochemical ozone creation potentials will be different with the chosen time periods because the temporal variability in these characterization factors is caused by the difference of the substances' life-times [61]. The availability of data is also a concern for aggregating data in the impact assessment [67]. The uncertainty and variability of data obviously become limitations and constraints on using LCA studies to make precise and appropriate interpretations for results of impact assessments [68].

The sensitivity analysis is generally defined as a technique used to determine how variations in the inputs of a mathematical model or system can affect the variability of its output. The LCA sensitivity analysis is required to be performed in the ISO 14040 standards[69]. The uncertainty and variability of data is essential to analysis for making valid interpretations of the results. Therefore, more and more LCA researchers have conducted sensitivity analysis to improve the credibility of results [66].

2.3.1 Parameter Uncertainty

Among the several classified types of uncertainty, parameter uncertainty is one of the most significant origins of uncertainty and is widely present in the practice of LCAs [70]. Uncertainty and data quality actually are two different attributes. The uncertainty including the variability of data can be analyzed through sensitivity analysis. For the data quality, stochastic models are often used to enhance making valid assumptions and conclusions [71].

In the following examples sensitivity analysis and variability of input parameters were examined while performing LCAs. Several sensitivity analyses (SAs) were carried out in the life cycle assessment of a solar thermal collector in literature for sanitary warm water [62]. The SAs focused on the variations in input materials, electricity used, transport of raw materials, installation, maintenances and disposal process [62]. The sensitivity analysis of input materials investigated into three specific materials including galvanized steel, thermal fluid, aluminum and stainless steel. The overall energy consumption variability caused by the variations in input materials was estimated at about ± 20% based on the normal value of 11.0 GJ and the synthesis variation in CO_2 emission can vary from 83% to 117% based on the normal value of 700 kg CO_2 [62]. The remaining SAs examples are very similar with the mentioned variability assessments which contain uncertainty due to different chosen scenarios.

Statistical approaches such as the Monte Carlo technique has been utilized to study the uncertainty in model input parameters. Monte Carlo simulation is based on a combined statistical distribution of all parameters with multiple and replicated measurements in the analysis [59]. Usually the probability distributions of parameters are generated with the assumption of parameter independence [59]. However, the model may overestimate the final uncertainty if the correlation uncertainty between two dependent variables is not considered. In an LCA of potato production that the yield is related to the inorganic fertilizers and pesticides, Carlos and Eddie used an improvement of introducing the multivariate random distribution to the Monte Carlo simulation to reduce the correlation uncertainty between fertilizers and pesticides [59]. The results indicated a lower uncertainty level for some environmental impacts when correlation was taken into account [59]. To obtain more reliable results, selecting an appropriate stochastic modelling and incorporating correlation between parameters should be emphasized on the uncertainty analysis [72].

2.3.2 Variability between Sources and Objects and Model Uncertainty

Variability also appears between sources of the inventoried system (e.g. inherent differences in comparable technical processes) [73] and objects determining the environmental impact (e.g. variability of human characteristics such as body weight or sensitivity to toxic substances may cause variations in human toxicity potentials) [61]. The following examples of variability between sources and objects mainly focus on the variability of technical processes.

A sensitivity analysis of a typical smart phone LCA model was performed by Fredrik and Pernilla with variations in electricity mix for production and usage of the phone [74]. The three scenarios are described as below [74]:

- Reference model: LCA model for a typical smart phone.
- Scenario 1: Change of electricity mix for integrated circuits (IC) production and for the use stage resulting in more GHG emissions. Also more usage of the smart phone.
- Scenario 2: Change of electricity mix for IC production and usage but now resulting in less GHG emissions. Less usage of the smart phone.

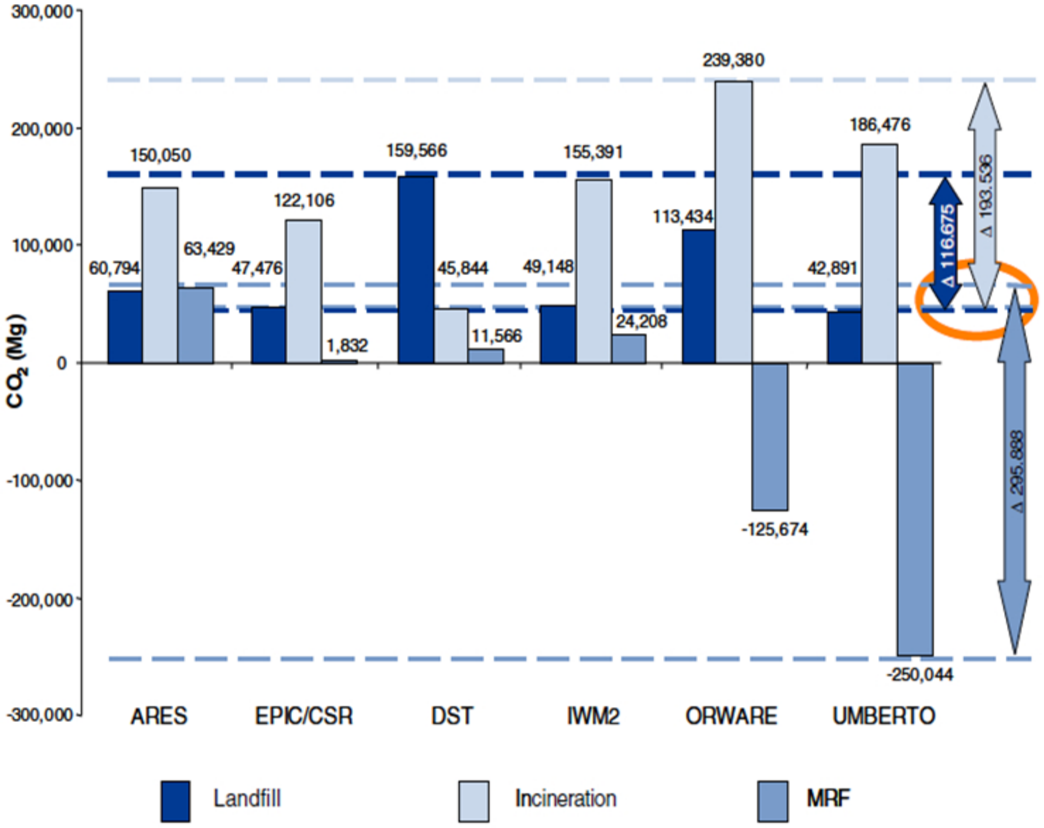
The comparable results of these two scenarios and the basic model showed that the range of variability in CO_2 emission was 70% to 180% which is associated with the range of variations in electricity use stage from 20% to 50% of the basic scenario [74].

In the next example, the LCA research of thermochemical conversion of woody biomass to mixed alcohols, the author used the variability in biomass feedstock moisture and ash contents to assess their impacts on the life cycle GHG emissions [75]. With a reduction of feedstock moisture content from 50 wt.% to 30 wt.%, the life cycle GHG emissions is cut down by more than 13%. The overall CO_2 emission is reduced by approximate 7% due to 6% wt.% loss in ash content in the feedstock [75] .

In the study of an LCA, including sensitivity analysis, of a multi-megawatt wind turbine aimed at determining the effects of variability in maintenance, manufacturing, dismantling, and blade recycling processes of a wind turbine on the environmental impacts [76]. For example, there are two scenarios of inputs of materials and energy consumed in manufacturing the wind turbine. The alternative scenario has a 10% increase in the area of materials and energy of the basic scenario. [76]. The result indicated that the scenario with 10% increase of materials and energy had an increase of 8.8% in total impact of the wind turbine [76].

Jorg and Bernd [77] assessed model uncertainty by comparing six different LCA models (ARES, EPIC/CSR, DST, IWM_2, ORWARE and UMBERTO) used for solid waste management systems for the city of Dresden, Germany. The complex waste management systems in Dresden were simplified into three theoretical cases: landfill, incineration and materials recovery facility (MFR). Most of models indicated that the most environmentally friendly scenario in GHG emissions was the MRF [77]. However, it was found (see Figure 1) that the variations in the LCA results given by the models were very high and must be addressed [77]. The main reason for the high variability of different models was that the common approach used in all models was linear modelling which cannot reflect variability of actual conditions [77]. Because of the high variability existing in the comparative results of different models, the authors can only make general conclusions based on the results estimated by these models. Therefore, the choice of a model or impact assessment methodology heavily affects the credibility of LCA.

Figure 1 Comparison of the results of CO_2 emissions for landfill, incineration and MRF scenarios [77]



No matter the kind of uncertainty and variability, the variations in the LCA results can be estimated by a reasonable range of data. There is no uniform standards to decide if the LCA results are correct or not by the range of variability. The ways to make LCA results more valid can be achieved by improving the quality of life cycle inventory, including more possible scenarios and choosing the more precise modelling method [17]. The practitioners should also make more valid conclusions based on the rational assumptions and variability [73]. The sensitivity analysis for the uncertainty becomes more and more necessary for stakeholders to make an appropriate decision [73].

CHAPTER III

METHODOLOGY

3.1 Goal and Scope

The goal of this thesis is to collect and apply available data to conduct a life cycle assessment of the commercial metal catalyst and potential biochar catalyst. Each catalyst process has detailed interpretations for its contributions to the environmental impacts. Specifically, the goal is to compare these two processes to provide a more sustainable catalyst for cleaning syngas. Additionally, sensitivity analysis of the two catalyst production and data variability of switchgrass production and gasification process are performed to identify the effects of variable parameters on the results of this study. The scope of this study is determined by the functional unit. For the metal catalyst, the scope includes all necessary production processes before the waste treatment. As biochar is a co-product of gasification process, the scope only includes the energy and materials of producing biochar without syngas production.

3.2 Functional Unit and System Boundary

The functional unit is a basic standard for the comparison of two productions. Currently the biochar production is based on the OSU gasification experiment which is a lab-scale project. Hence an industrial scale should be built in line with the metal catalyst production. The industrial amount of feedstock on a dry basis is estimated to be 2000 metric tons per day [34]. The rate of syngas yield is 2 m^3 per kg of dry biomass and the amount of tar is 4.28 g/m^3 of syngas. The functional unit is determined as the amount of catalyst needed to clean up the syngas based on an average yield of 4,000,000m^3/day. The amounts of cleaning the same quantity of syngas are different due to the two catalysts' efficiencies in removing tars. The efficiency ratio of metal catalyst to biochar is 2.404 (see Appendix 1), which was obtained by assuming toluene as a model of tars. The calculations of functional unit are as follows:

$$\text{The amount of tars} = 2000\,\frac{\text{ton}}{\text{day}} \times 1000\,\frac{\text{kg}}{\text{ton}} \times 2\,\frac{\text{m}^3}{\text{kg}} \times 4.28\,\frac{\text{g}}{\text{m}^3} = 1.712 \times 10^7\text{g/day} \tag{1}$$

$$\text{The amount of metal catalyst} = 1.712 \times \frac{10^7\text{g}}{\text{day}} \div \frac{0.87\text{g}}{\text{ml}} \times \frac{20.14\text{g}}{1000\text{ml}} \times \frac{1\text{ kg}}{1000\text{g}} = 396\text{kg/day} \tag{2}$$

$$\text{The amount of biochar} = 396\,\frac{\text{kg}}{\text{day}} \times 2.404 = 952\text{kg/day} \tag{3}$$

where 0.87g/ml is the density of toluene and 20.14g is the amount of metal catalyst used to remove 1000ml toluene.

The metal catalyst consists of nickel oxide and aluminum oxide which is a supportable base. Basically the nickel based catalyst is composed of various virgin materials. The processes of producing raw metals initially include mining, crushing and transportation. The raw materials such as nickel ore and bauxite are the main inputs of industrial metal catalyst manufacture with air, water, chemicals and energy sources. Steel is also one of the most important inputs of two catalyst production processes. The simplified process flow of aluminum oxide, nickel production and steel are given in Figures 2, 3 and 4, respectively.

Figure 2 Simplified aluminum oxide production process

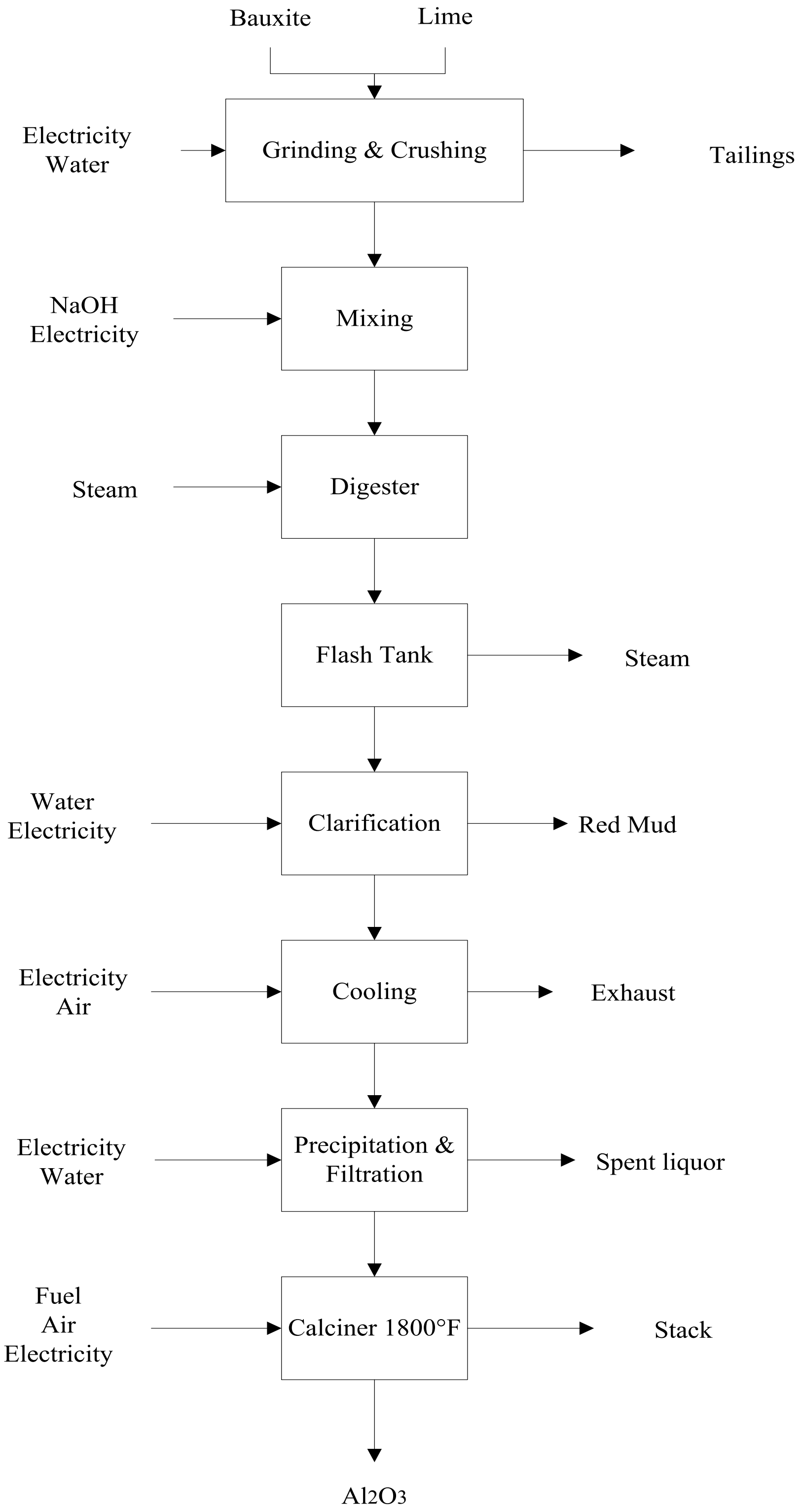


Figure 3 Simplified nickel production process [78]

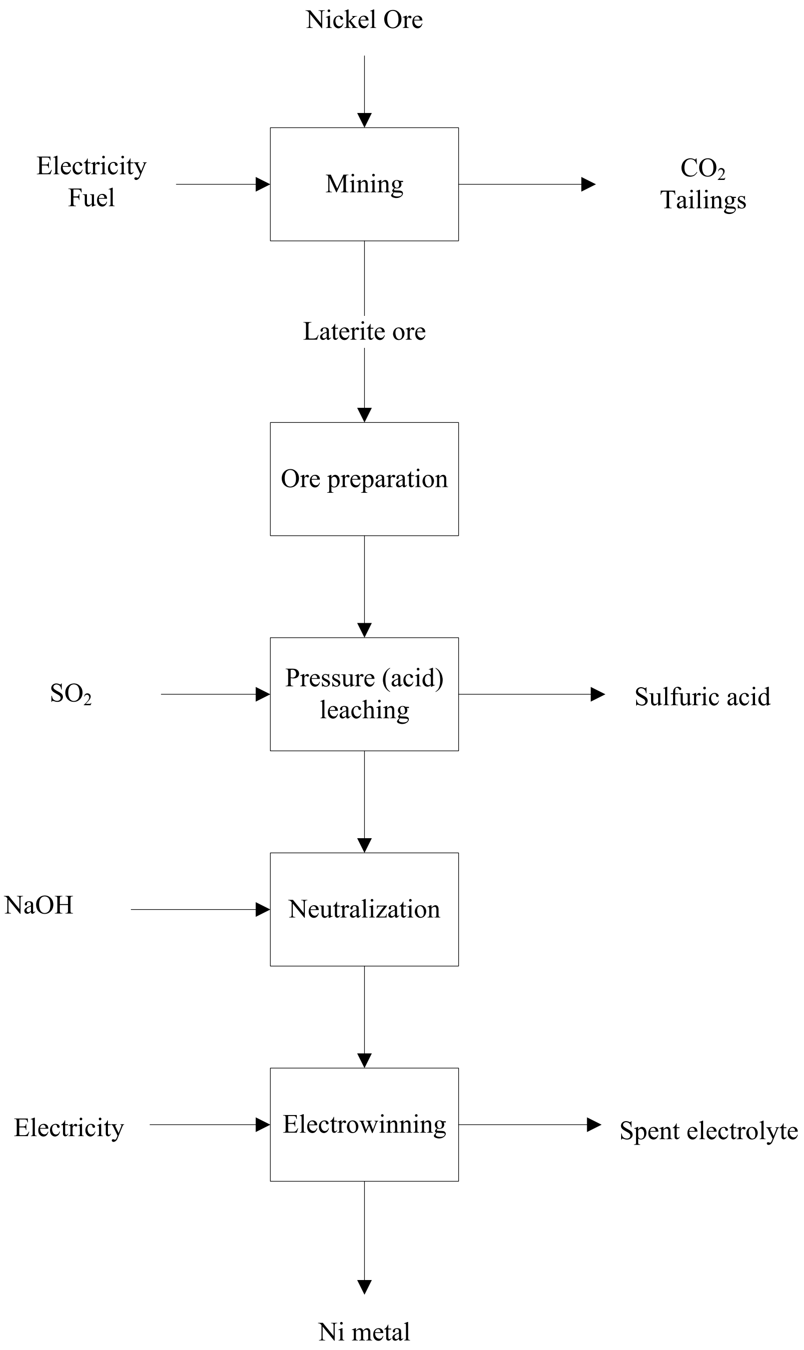
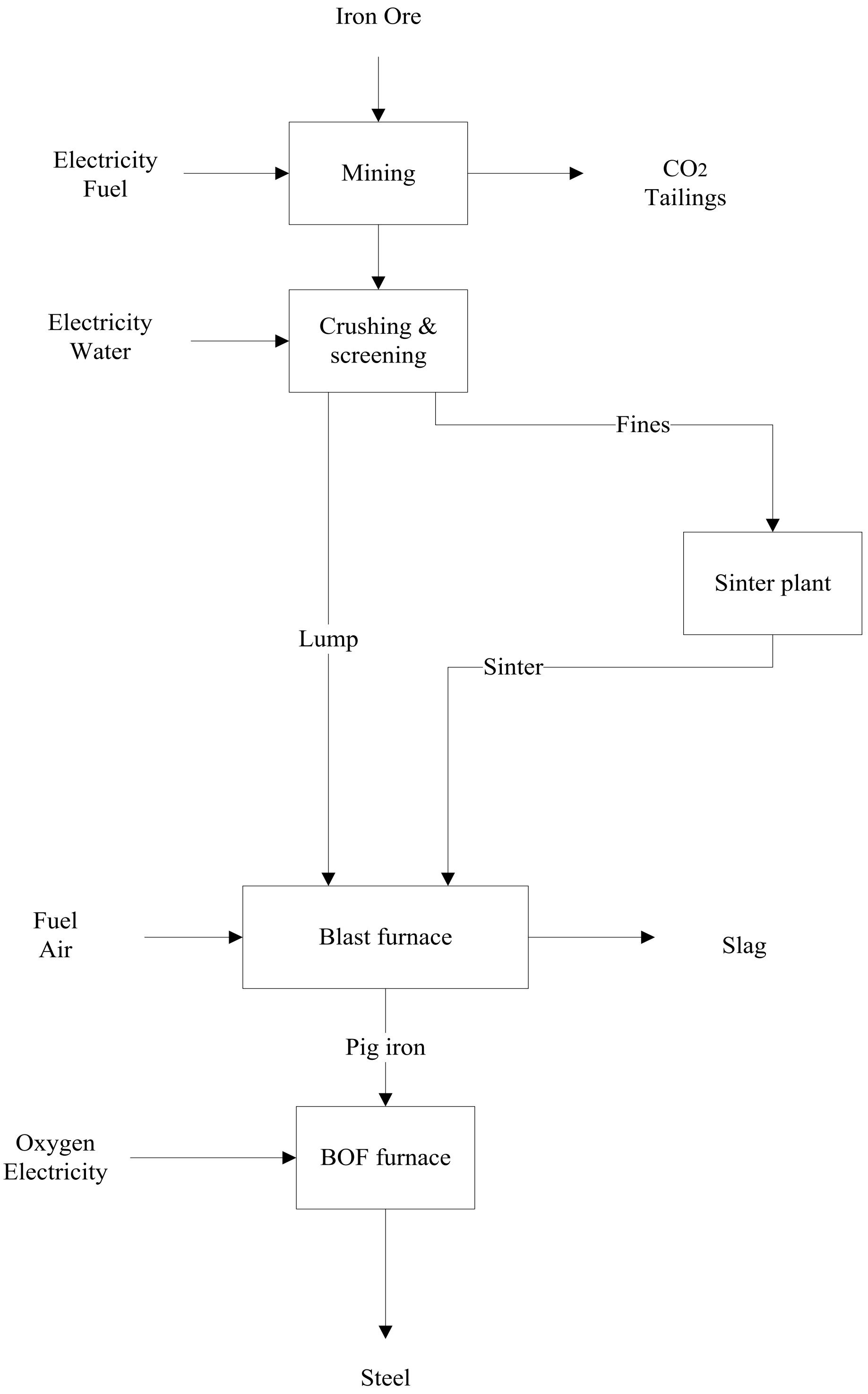
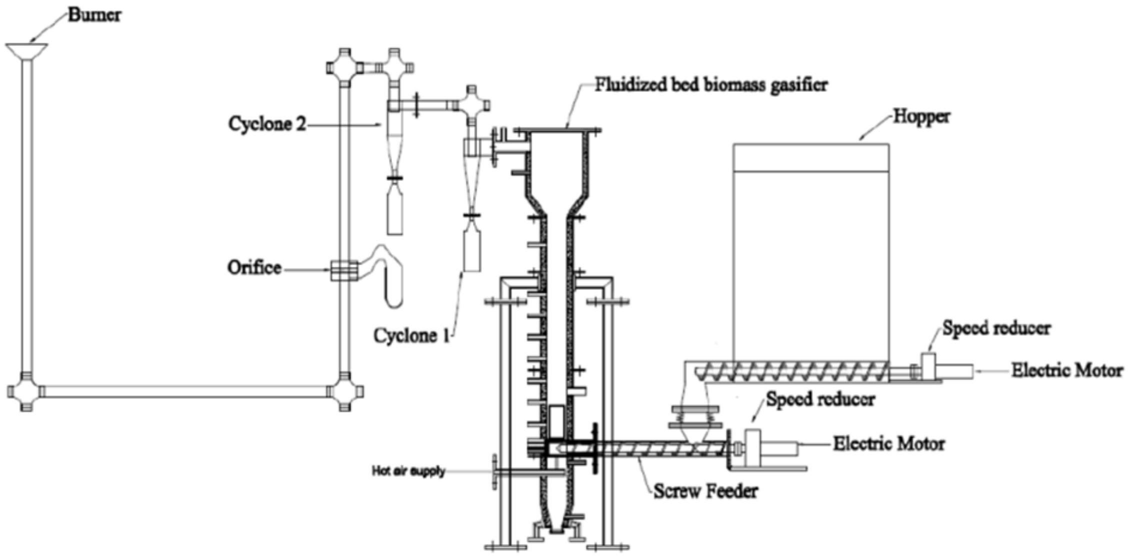


Figure 4 Simplified steel production process [78]



The second catalyst is actually a by-product of the syngas production. Biochar is naturally produced during gasification. In this study, biochar is produced by the gasification process using switchgrass as feedstock. Figure 5 is the schematic of a lab-scale fluidized bed gasifier which is built for OSU gasification experiments. Biochar is collected typically in particle cyclones (see cyclones 1 and 2 in Figure 5) from the syngas downstream of the gasifier. The process that needs to be pointed out is the recycling of biochar in the future tar removal system.

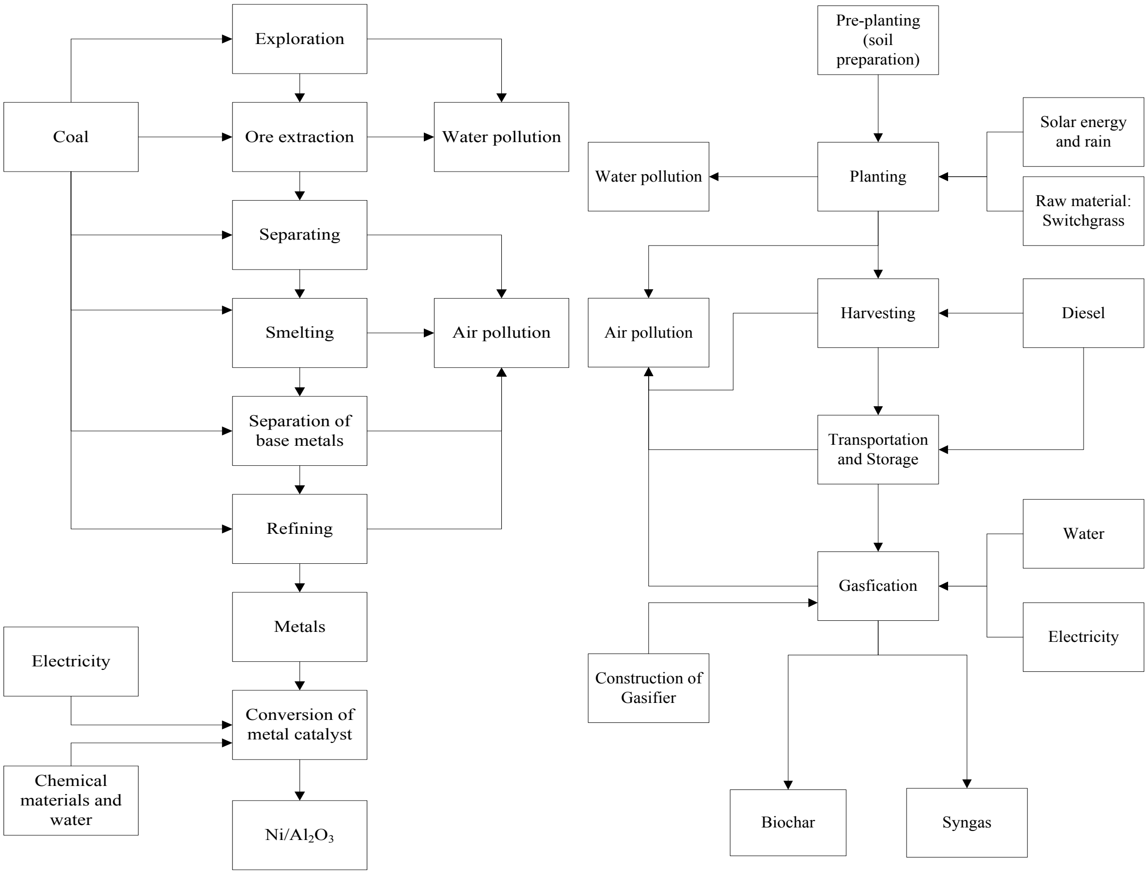
Figure 5 Schematic of fluidized bed gasifier with tar removing cyclones [79]



The boundary of the LCA is a significant step which is directly related to the data inventory and results. It is hard to guarantee that the system boundaries of two product systems are equivalent when comparing two different systems [80]. The basic principle of deciding the system boundary is provided by ISO 14040 that the inputs and outputs included in the boundary should be fundamental processes. A fundamental process is defined as a process that includes the materials and energy entering or leaving the system without human transformation.

However, the data collection of all the resources seems practically impossible. Therefore, an appropriate cutoff decision is determined to establish a reasonable boundary. Several indicators such as mass, energy and environmental matters have been introduced by the ISO standards to be considered for choosing important inputs and outputs [80]. Sometimes tiny amounts of input might be ignored but they can heavily influence the environmental impacts. Although the metal catalyst is used in the syngas cleaning system, this LCA only assesses the processes of producing each catalyst rather than syngas cleaning procedure. Therefore, both boundaries of two catalysts do not include the inputs and outputs during the cleaning system. The biochar can be recycled to the cleaning system during gasification process but the recycle process is not included in this study. Also, both catalyst systems include no disposal processes. The system boundary is described as the content in Figure 6.

Figure 6 Simplified system boundaries for metal catalyst and biochar production



Metal Catalyst System Boundary

Biochar Catalyst System Boundary

3.3 Assumptions

Assumptions are essential for an LCA since they have a strong influence on results and make the assessment fair. The sensitivity analysis is also based on assumptions. Below is a list of assumptions used in this life cycle.

- The boundary for studied systems was for the production of the catalysts only and a 0.5% cutoff used in SimaPro® for some of the database inventory
- The system boundaries include the fundamental flows such as metal mining and extraction for both catalyst processes
- The functional unit is the mass of catalyst needed to clean 4,000,000 m^3/day syngas in an industrial scale gasifier
- Biochar is considered for catalyst use only - no soil supplementation or other uses
- The inventory data from the various databases reflects actual process inventories (for study)
- Hyfuel-110(r)® is used as an analog for NiO/Al_2O_3 catalyst in the cleaning syngas experiment
- The equivalent mass of biochar to metal catalyst for gas cleaning is 2.404 to 1
- The biochar of gasification yield is 10% of the switchgrass [1]
- The mass of materials used in gasifier construction per volume of syngas produced is a linear scale-up to a gasification power plant
- No stochastic behavior is modeled at this time. Point values are used in inventory data

- The various manufacturing processes described in the reference journal articles reflect actual production
- In the industrial scale, we assume 10 years and 220 day/year which is based on an operation efficiency of 60% [81]
- The switchgrass land is prepared and mechanically harvested
- The switchgrass land is used for 10 years with two harvests per year
- The location and production of the switchgrass is a nationwide (US) average from NREL
- The database of switchgrass production doesn't include pesticide data
- The nickel oxide production database is based on the unit of 1.3 kg of Nickel Oxide (77% Nickel wt.)
- The primary energy used in the both catalyst processes are the heat from natural gas combustion
- The emissions of gasification process only include the VOC (volatile organic compounds)
- This analysis does not include waste treatment process in both catalyst systems
- The metal catalyst mixing process is based on a lab-scale experiment
- The mass ratio of nickel oxide to aluminum oxide in metal catalyst mixing is 1 to 9
- The efficiency of metal catalyst mixing reaction is 100%

3.4 Assessment Tool and Method

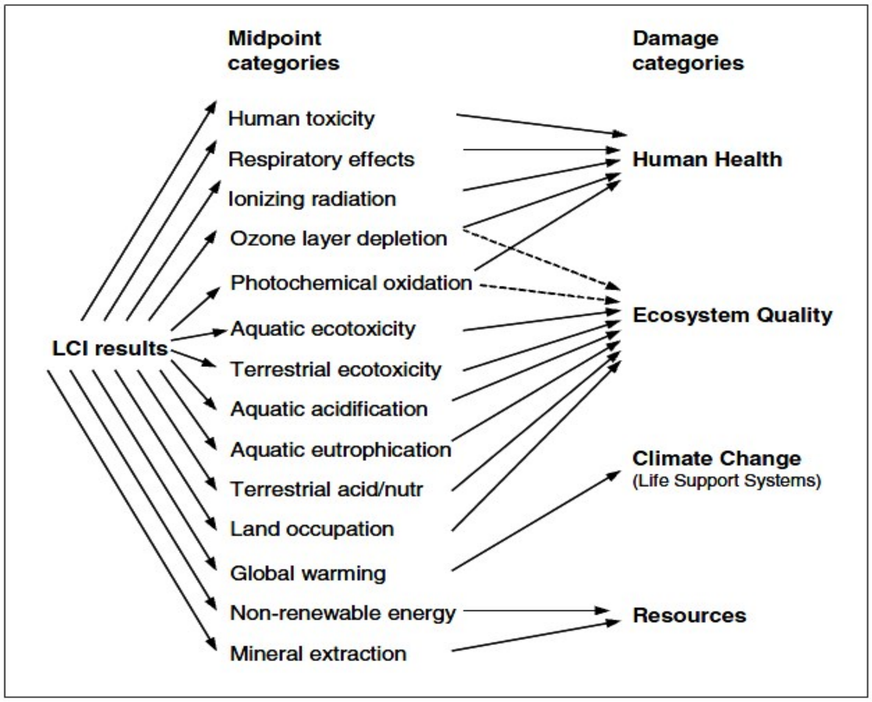
3.4.1 SimaPro® 7.3.3

The SimaPro® Life Cycle Assessment Software produced by PRé Consultants® has been widely used by industry and research institutes to make firm decisions to improve the product life cycle strategy. With large available inventory and professional tools, SimaPro® 7.3.3 is used to collect, assess and model the environmental performance of products in this study. This study will utilize a systematic way to model and compare production of two catalysts.

3.4.2 Impact Assessment

Impact assessment is clearly defined as an integral and fundamental part of life cycle assessment (ISO14044). Life cycle impact assessment (LCIA) is an evaluation of the potential environmental impacts during a product's life time. It is a better way to reflect the magnitude and significance of the product's environmental impacts [82]. The impact assessment is performed with IMPACT 2002+ method which includes midpoint and endpoint analysis in this study. A framework of this method is shown in Figure 7. A midpoint indicator is the characterization of the elementary flows and other environmental interventions contributing to the same environmental impact [83]. Midpoints are considered to be links in the cause-effect chain (environmental mechanism) of an impact category, prior to the endpoints (damage impact), at which characterization factors or indicators can be calculated to indicate the relative importance of emissions or extractions in an LCI (Life cycle inventory) [84]. The new life cycle impact assessment methodology used classical impact assessment methods to group the similar LCI results into midpoint categories such as climate change and eco-toxicity. A score of one midpoint characterization factor is given in kg-equivalents of a substance compared to a reference substance. Then damage oriented methods try to model the cause-effect chain up to the damage categories [83]. Human toxicity, land use and mineral extraction have been developed with better estimation methods which make midpoint categories more representative. Within two different product systems, a comparison of impacts is generated to determine which system is possibly more sustainable.

Figure 7 Overall scheme of the IMPACT 2002+ framework [83]



3.5 Life Cycle Inventory

The full inventory database is set on the basic existing data which is suitable for American situations in the SimaPro® 7.3.3 software. Most specific data for gasification process are provided by Dr. Kumar’s gasification and syngas conditioning experiments. The remaining data are collected from published databases and academic literature.

The structure of the database is typical in the SimaPro® 7.3.3. Each process has inputs and outputs. The inputs may contain substances and specific unit processes. Two categories are classified in the input part. If materials can be directly taken from the natural resources, they belong to the resource. The technosphere category means that the inputs are obtained from other industrial processes and not from nature such as electricity generated from coal. The outputs only contain substances that are exposed and emitted to the environment. The units of inputs and outputs are various, and they should correspond to the units of the chosen inputs in the software.

3.5.1 Metal Catalyst Inventory

For modeling the process of manufacturing the metal catalyst, the data for the primary nickel oxide (NiO) material is obtained from the Nickel Institute LCI report [85]. In this study, all inputs and outputs of 1 kg nickel included in nickel oxide (77% nickel wt.) are integrated in Table 4 and scaled up to the functional unit when modeling the final assembly. The inventory data for aluminum oxide (Al_2O_3), which is the base support material, is obtained directly from the US-EI 2.2 database [86] that is available in the SimaPro® LCA libraries. Both the metallic compounds include the data of mining and extraction processes which are the initial boundary.

The final metal catalyst production process is based on a description of the production of commercial nickel-alumina catalyst [87] in which prepared samples consist of 10 wt.% nickel oxide and 90 wt.% aluminum oxide. The matured nitrate solutions with nickel and aluminum ions are filtered and treated at 105°C in air to dry [87]. Subsequently the catalyst samples are mixed by mechanical mixer into powders at 700°C. Using standard heat transfer equations and a quantity of 1 Kg of Ni/Al_2O_3, the energy for thermally drying and treating the metal catalyst is calculated at approximately 0.5 Mega Joules per kilogram.

Table 4 Inventory data for nickel oxide production (1 kg of Ni in nickel oxide) [85]

	Category	Unit Process	Quantity
Inputs	Resource	Coal, in ground	3.1 kg
		Iron (Fe, ore)	7.4E-4 kg
		Limestone ($CaCO_3$), in ground	0.4 kg
		Natural gas, in ground	3.5 kg
		Nickel, in ground	2.5 kg
		Oil, in ground	4.5 kg
		Uranium (U, ore)	2.5E-5 kg
		Total water used	309 liter

	Technosphere	Total primary energy	455 MJ
Outputs	Emission to air	Carbon dioxide	26337 g
		Carbon monoxide	62 g
		Nitrogen oxides, NO_x as NO_2	85 g
		Nitrous oxide	2.0 g
		Particulates	74 g
		Sulfur oxides, SO_x as SO_2	2205 g
		Methane	47 g
		Hydrocarbons	22 g
		Nickel	6.1 g
		Chromium	3.3E-3 g
		Arsenic	1.0 g
		Copper	1.2 g
		Cobalt	5.6E-2 g
		Zinc	0.19 g
		Lead	0.53 g
		Cadmium	3.7E-3 g
		Mercury	3.6E-2 g
		Silver	1.1 g
		Metals	0.23 g
		Ammonia	4.7 g
		Chloride	1.3E-3 g
		Dioxins	4.4E-7 g
		Volatile organic compounds	2.7 g
		Hydrogen chloride	0.98 g
		Hydrogen cyanide	3.9E-5 g
		Hydrogen fluoride	5.9E-2 g
		Hydrogen sulfide	4.6E-2 g
		Sulfuric acid	40 g
	Emission to water	Biochemical oxygen demand	1.1 g
		Chemical oxygen demand	8.7 g
		Sulfates	186 g
		Nitrogenous matter, as N	269 g
		Phosphates, as P	9.9E-3 g
		Total organic compounds	0.43 g
		Arsenic	6.0E-4 g
		Nickel	0.14 g
		Copper	8.7E-3 g
		Zinc	1.3E-3 g
		Lead	4.1E-2 g
		Mercury	4.0E-5 g
		Silver	1.8E-4 g
		Cadmium	4.2E-5 g
		Chromium	3.3E-4 g
		Acids	1.4E-2 g
	Emission to soil	Waste rock and backfill	175 kg
		Tailing and other process residues	187 kg
		Other solid materials	1.8 kg

3.5.2 Biochar Catalyst Inventory

For the biochar production description, the data of the biomass feed material (switchgrass) is obtained from the Switchgrass LCI report of National Renewable Energy Laboratory [88]. This database includes the processes of soil preparation, planting, harvesting, storage, transportation and pretreating. The land use is based on an estimate of 10 years of life considering the average switchgrass yield of 14,800 kg/ha [88]. The detailed data in the switchgrass production is shown in Table 5.

The data of biochar production from switchgrass gasification is based on earlier experiments at the Oklahoma State University Bioenergy Center. For the gasification process, the operating lifetime of the gasifier is assumed to be 10 years. The metal used to construct the gasifier includes steel pipes and steel plates. Since the functional unit is based on an industrial scale, the total mass of steel needs to match the demand of building an industrial scale gasifier. An LCA of a gasification power plant with a 407.1 MW [89] capacity and 42% efficiency [81] is introduced into estimating the inputs of gasifier. The calculations are shown in Appendices 2 and 3. Finally, the materials' mass of a larger gasifier for this case are 6,099 tons of steel, 6,099 tons of cement and 36,660 tons of aggregates.

In the laboratory-scale experiment, optimal operating conditions for the gasifier is observed to be a dry switchgrass biomass feed rate of 3.4 kg per hour and an air equivalence ratio[3] of 0.32 [79]. Typically, the experiment continues for 2.5 hours. The gas yield, low heating value and air input are 21.25 m^3, 144 MJ and 16.25 kg, respectively. The heat waste of gasification is calculated to be 7.9 MJ by assuming that the outside gasifier surface temperature is roughly 200 °C. The inside of the gasifier tube is insulated with refractory material.

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[3] Equivalence ratio (ER) is the fraction of actual air to stoichiometric air of fuel complete combustion.

Table 5 Inventory data for 1 ton swtichgrass feedstock [88]

	Category	Unit Process	Quantity
Input	Resource	Carbon dioxide	1.5E+3 kg
		Energy, from biomass	1.5E+4 MJ
		Occupation, pasture and meadow	0.68 ha
		Transformation from permanent crop	2.25E-2 ha
		from pasture and meadow	2.25E-2 ha
		from arable	2.25E-2 ha
	Technosphere	Tillage, rotary cultivator and rolling	6.8E-3 ha
		Fertilizer	0.068 ha
		Planting	0.068ha
		Mowing, by rotary mower	9.33E-2 ha
		Baling	9.33E-2 ha
		Dried roughage store, non-ventilated	9.57E-8 m^3
		Conveyor belt, at plant	3.47E-5 m
		Fodder loading, by self-loading trailer	2.2654 m^3
		Maize drying	50 kg
		Grinding	0.97 tn.sh
		Loading bales	1.43 p
		Agricultural machinery	0.9 kg
		Electricity, at grid	63.93 kWh
		Transport, tractor and trailer	7.42 tkm
		combination truck	182.6 tkm
		Train	200 tkm
		Barge	11.3 tkm
Output	Emission to air	Carbon dioxide, biogenic	295 kg
		Water	333 kg

3.5.3 Allocation Method

Many processes can produce more than one product and the total environmental impacts of that system should be allocated over the various outputs. It has been recommended in the ISO 1997 that allocation can be avoided by splitting a huge and complex process into separate processes or expanding the system boundaries in order to cover the co-products. If it is not possible, the ISO standards advise that the allocation method should be used to identify the environmental load of co-products [82]. For the biochar production database, an allocation value is used to quantify the accurate impacts of switchgrass and gasification process since biochar is a co-product of gasification. As mentioned above, biochar is generated along with syngas during the gasification process. Generally, there are three methods of allocation: mass-based allocation, economic-based allocation and system expansion allocation [90]. In this scenario, the allocation value should be evaluated as the yield of biochar compared to the total mass of switchgrass feedstock. The biochar of gasification yield is around 5-10% of the feedstock mass [1]. It means that all the impacts from biochar production take 5-10% of the total impacts of switchgrass production and gasification process.

3.6 Sensitivity Analysis

The sensitivity to every impact category is significantly various with different process parameters. Meanwhile, the sensitivity analysis is conducted based on some assumptions that may affect the consequences intensively with the modification. There are three factors introduced to the sensitivity analysis in this study. Each parameter is changed independent of all others so that the magnitude of its effect on the base case could be identified.

3.6.1 Fraction of Nickel Oxide in Metallic Catalyst

Nickel oxide is widely used as a catalyst in steam reforming and syngas production processes. It has a strong reactivity with the support materials. The component is one of the factors that influences the activity and stability of the metallic catalyst [87]. The mass fraction of nickel oxide in the metal catalyst is adjusted as 5, 10 and 20 wt.%. This analysis uses 10 wt.% nickel oxide and 90 wt.% aluminum oxide as a basic fraction. The overall environmental impacts of the metal catalyst are determined by both nickel oxide and aluminum oxide. For instance, the metal catalyst with the lowest fraction of nickel oxide may reduce nickel oxide's contributions to environmental impacts but the total environmental impacts of the metal catalyst are likely to increase due to the highest fraction of aluminum oxide is used.

3.6.2 Energy Used in Nickel Oxide Production

Non-renewable energy is one of the most important indicators that assesses the life cycle performance of a process or product. Since the metal catalyst system includes many processes that need lots of energy consumption, such as mining and crushing, the energy used in the manufacture of metal catalyst is applied to a second sensitivity analysis. According to the various amounts of energy used in different industrial scale manufacture of nickel oxide with different technologies, the primary energy is reduced by 50% and increased by 50% of the basic energy, respectively.

3.6.3 Land Use in Switchgrass Production

The land occupation of biochar production is mainly used for cultivating and harvesting switchgrass. In the switchgrass database, one hectare soil land can harvest 14,800 kg switchgrass. A good cropping system and space management can not only keep the high yield but also save the arable land. A 20% reduce and 50% increase of the given switchgrass field in this LCA are applied to another sensitivity analysis to find how land occupation of switchgrass varies the environmental impacts.

3.7 Variability of Switchgrass and Gasification

In the practical manufacture procedures, uncertainty will be caused by the choices of various product systems for the same product e.g. different scenarios of gasification process. Based on the practical data, multiple representative factors can be estimated in order to indicate how variations in the switchgrass production and gasification process influence the LCA results. In theory, variations in operation processes of gasification can cause huge differences in the biochar properties which decide the efficiency of reforming tars in the syngas. Since the limited data about the catalytic efficiency of different biochar, the functional unit is changed to producing $1m^3$ syngas in the gasification process. The variations in switchgrass production yield, the equivalence ratio (ER), and biomass moisture content (MC) are considered valuable units of changing the consequences for LCA in syngas production.

3.7.1 Variations in the Switchgrass Production Yield

The types of switchgrass are various and their yields are heavily dependent on several environmental factors such as soil quality, the availability of water and nutrients, and the weather. Switchgrass is basically classified into two main types by their growing geographic location. The upland species can grow 5 to 6 feet tall with an average yield of 8.7 ± 4.2 metric ton ha^{-1} [91] and lowland species usually grow 7 to 10 feet tall with an average 12.9 ± 5.9 metric ton ha^{-1}. A commercial guide provided by Blade Energy Crops company reported that the typical yields of switchgrass in the northern range, midrange and southern range are 2 to 6 tons/acre, 4 to 8 tons/acre and 6 to 10 tons/acre, respectively [92]. The yield data of switchgrass production in ten years indicated that Cave-in-Rock is the best commercial type for northern range, Kanlow for midrange and Alamo for southern range [93]. The energy (HHV) in switchgrass also varies roughly from 7750 BTU/Ib (18.03 MJ/kg) to 8250 BTU/Ib (19.19 MJ/kg) [92]. Moreover, the harvest time makes no significant change in the net energy of switchgrass [94] and no appreciable difference in energy value has been found with degrading after harvest in OSU Biosystems and Agricultural Engineering lab studies so far. The variability of switchgrass yield is presented in Table 6.

Table 6 Variations in switchgrass production yield

Variety of Switchgrass in U.S.	Average Yield (tons/acre)
Northern range	4
Midrange	6
Southern range	8

3.7.2 Variations in the Equivalence Ratio

For gasification technology, many process conditions should be controlled to optimize the syngas product. The higher heat value (HHV) is considered an indicator of the optimum syngas and can be affected by biomass type, biomass moisture, reaction temperature, reactor type etc.[95]. Some process parameters, such as feedstock size and equivalence ratio, are designed diversely based on specific reaction sets. In this study, the variations in biomass moisture content and equivalence ratio of air are investigated to evaluate the results in LCA.

The equivalence ratio of air is an essential parameter and usually adapted to a certain range in order to achieve the optimum syngas. With an air blown auto-thermal gasifier, the HHV of syngas has a range of 5.5MJ/m^3- 6.3MJ/m^3 [95]. As mentioned in Dr. Kumar's gasification experiments, an air blown fluidized bed gasifier was used to produce syngas. The ER varied from 0.2 to 0.45 associated with airflow and feedstock rate. Table 7 shows various gas yields and energy values in the syngas resulted from different ERs. In this case, there are five scenarios of the gasification process with different operation parameters. The variations in the inputs of producing 1m^3 syngas are shown in Table 8.

Table 7 Variations in process parameters with different ERs

	Equivalence Ratio				
Parameter	0.20	0.29	0.32	0.40	0.45
Airflow rate (kg h^{-1})	4.5	6.8	6.8	6.4	10
Feedstock rate (kg h^{-1})	3.9	4.2	3.4	2.9	3.7
Gas yield (Nm^3 kg^{-1} d.b)	1.2	1.7	2	2.2	2.5
HHV of dry gas (MJ Nm^3)	5.3	6.2	6.6	5.5	3.4

Table 8 Variations in inputs of producing 1 m^3 syngas

`	Equivalence Ratio				
Input	0.20	0.29	0.32	0.40	0.45
Air (kg)	0.96	0.95	0.956	1	1.08
Biomass Energy (MJ)	15.7	11	9.45	8.56	7.53
Biomass mass (kg)	0.83	0.59	0.5	0.45	0.4

3.7.3 Variations in the Biomass Moisture Content

Typically the biomass moisture content (MC) is suggested at 10%-20% of wet basis weight [95]. More moisture content will reduce the reaction temperature and produce less syngas gas with lower energy value [95] due to the change of gas composition. Dr.Cateni used switchgrass with different level moisture content in the fluidized bed gasifier to identify the effect of moist biomass on the syngas composition [96]. The conclusions of his experiment indicated that the observed decreases of gas composition were found in CO and H_2 by 30%-40% with 20% increase in the moisture content. Meanwhile, the reactor bed temperature could decrease and not be maintained at 800°C with higher moisture content than 19%. The heat waste is due to more water evaporation, and heating the input air can fix the operation temperature decrease [96]. Based on Dr. Cateni's data, three moisture content levels including 9%, 19% and 29% were chosen as variations in moist switchgrass. Table 9 is given to show the analysis of gas composition corresponding to each MC under an equivalence ratio range of 0.27-0.3.

Table 9 Gasification products at various levels of switchgrass moisture content [96].

M.C.	Gasification Products (% Feed Weight)						
(% w.b.)	H_2	CO	CH_4	CO_2	H_2O	Tar	Ash
9	0.90	37.91	5.74	55.92	17.71	2.81	8.94
19	0.59	34.54	4.62	51.07	20.26	2.14	8.47
29	0.43	29.42	3.41	50.01	21.06	1.62	8.28

The HHV of every syngas cannot be obtained directly according to these data. Therefore, the results of HHV of syngas were estimated by using the combination of Dr. Kumar's and Dr. Cateni's data. The following equation [79] was used to calculate the HHV of syngas in Dr. Kumar's experiment:

$$HHV = (13.6\times H_2\%) + (13.4\times CO\%) + (42.3\times CH_4\%) + (61.7\times C_2H_2\%) + (67\times C_2H_4\%) + (74.1\times C_2H_6\%) \quad (4)$$

where $H_2\%$, $CO\%$, $CH_4\%$, $C_2H_2\%$, $C_2H_4\%$, and $C_2H_6\%$ represent the volumetric percentages of H_2, CO, CH_4, C_2H_2, C_2H_4, and C_2H_6, respectively. Since the contents of CH_4, C_2H_2, C_2H_4 and C_2H_6 are much lower than other gases and don't vary too much with at different levels of ER, it is assumed that the total HHV of syngas is mainly changed by the sum HHV of hydrogen and carbon monoxide.

As the results of gas composition in moist feedstock were measured at the ER of 0.27-0.3, the data of gas composition at ER of 0.29 in Dr. Kumar's experiment were used to indicate the fraction for the HHV of hydrogen and carbon monoxide to the total HHV of dry gas.

$$\frac{\text{HHV of }(H_2+CO)}{\text{Total HHV of gas}} = \frac{13.6\times 9.2\%+13.4\times 16\%}{6.2} = 54.8\% \quad (5)$$

where 9.2% and 16% are the volumetric percentages of H_2 and CO, respectively [79].

At ER=0.29, $1m^3$ syngas needs 0.59 kg switchgrass, the HHV of hydrogen is 142 MJ/kg and HHV of carbon monoxide is 10.16 MJ/kg.

$$\text{The HHV of dry gas in 9\% MC} = \frac{(0.90\%\times 142MJ/kg+37.91\%\times 10.16MJ/kg)\times 0.59kg/m^3}{54.8\%} = 5.5MJ/m^3 \quad (6)$$

$$\text{The HHV of dry gas in 19\% MC} = \frac{(0.59\%\times 142MJ/kg+34.54\%\times 10.16MJ/kg)\times 0.59kg/m^3}{54.8\%} = 4.7MJ/m^3 \quad (7)$$

$$\text{The HHV of dry gas in 29\% MC} = \frac{(0.43\%\times 142MJ/kg+29.42\%\times 10.16MJ/kg)\times 0.59kg/m^3}{54.8\%} = 3.9MJ/m^3 \quad (8)$$

The input air was heated to 350°C to maintain the reaction at a normal temperature at 800°C when the moisture content is at 19%. The external heat is calculated as below:

$$\mathrm{Q} = \mathrm{mC_p}\Delta\mathrm{T} = \frac{0.95\mathrm{kg}}{\mathrm{m}^3} \times \frac{1.0\mathrm{kJ}}{\mathrm{kg{\cdot}K}} \times (350 - 25)\mathrm{K} = 0.3\mathrm{MJ/m}^3 \quad (9)$$

For moisture content of 29%, the external heat is 0.6 MJ/m^3. Table 10 shows the parameters of various moisture contents.

Table 10 Parameters of various moisture contents

M.C. (% w.b.)	HHV of dry gas (MJ/m^3)	External heat (MJ/m^3)
9%	5.5	0
19%	4.7	0.3
29%	3.9	0.6

CHAPTER IV

FINDINGS

4.1 Interpretation of Process Results

The assessment results show the evaluated environmental impacts of different substances in midpoint categories. Results of the metal catalyst production system are shown in Table 11. Nickel oxide manufacture process takes approximately 82% of the global warming impact. This contribution mainly results from the CO_2 emissions of exploring, mining and producing nickel. The combustions of the natural gas, coal and oil which lead to greenhouse gas emissions are used to supply the energy of manufacture and transportation. In this study, the average CO_2 emission rate of nickel is 47.2 kg CO_2 eq/kg Ni and it is a little higher than the result of CO_2 emission (44.8 kg CO_2 eq/kg Ni) [97] in nickel laterite processing. The difference may be due to various technologies that are used for producing nickel. Although the process of aluminum oxide production has less impact on global warming than nickel oxide, the resources of CO_2 emissions are the same with nickel oxide.

As for the depletion of non-renewable energy category, nickel oxide production process also consumes more energy such as natural gas and coal than aluminum oxide production process. The primary energy input of nickel oxide in this study is 350 MJ/kg which is close to the value of 370 MJ/kg estimated by Matthew [98] in an LCA study of global nickel industry. The total non-renewable energy usage is 3,970 MJ/kg NiO calculated by IMPACT 2002+ method, which is 10 times more than the primary input energy. The reason could be all the primary input energy used in the nickel oxide database is natural gas and no renewable energy is used for the primary energy. The impacts on carcinogens and non-carcinogens categories in nickel oxide production are four times as much as the impacts of aluminum oxide production. These results are due to the fact that nickel compounds have a higher level of toxicity and carcinogenicity than aluminum oxide when they are exposed to the environment [99]. Respiratory inorganics are air pollutants such as tiny particles that affect human lungs. These pollutants are released by heavy industries such as natural gas combustion and road traffic [100]. Aluminum oxide production only has more impacts on ionizing radiation, ozone layer depletion and land occupation than nickel oxide production. The ionizing radiation impact is caused by uranium tailings from uranium usage in the nuclear reaction [101]. The ozone layer is destroyed by greenhouse gas from fossil fuels and chlorofluorocarbons (CFCs) emissions from transportation. The extraction of both metals is responsible for almost the whole impact of mineral extraction category. According to the analysis of single score (see Figure 9), the impacts on remaining midpoint categories in the metal catalyst production are much less significant than the impacts on carcinogens and non-carcinogens, respiratory inorganics, global warming and non-renewable energy. Compared to nickel oxide and aluminum oxide production processes, the procedure of mixing two materials into the metal catalyst has insignificant impacts on the characterized categories.

Table 11 Characterization LCIA results of metal catalyst production

Impact category	Unit	Total	Nickel oxide production (%)	Alumina production (%)	Mixing process (%)
Carcinogens	kg $C_2H_3Cl_{(eq)}$	3.51E3	92.9	5.1	1.32
Non-carcinogens	kg $C_2H_3Cl_{(eq)}$	697	86.4	13.1	0.449
Respiratory inorganics	kg $PM_{2.5\ (eq)}$	11.7	93.1	6.27	0.647
Ionizing radiation	Bq C-14 $_{(eq)}$	4.19E3	17	82.7	0.243
Ozone layer depletion	kg CFC-11 $_{(eq)}$	7.15E-5	29.3	70.3	0.418
Respiratory organics	kg $C_2H_{4\ (eq)}$	2.59	88.4	10.3	1.24
Aquatic ecotoxicity	kg TEG water	1.37E6	88.7	10.2	1.11
Terrestrial ecotoxicity	kg TEG soil	1.87E5	93.4	6.56	0.0143
Terrestrial acid/nutri	kg $SO_{2\ (eq)}$	167	91.7	7.67	0.598
Land occupation	m^2org.arable	2.16	15.4	84.4	0.22
Aquatic acidification	kg $SO_{2\ (eq)}$	144	95.3	4.08	0.665
Aquatic eutrophication	kg $PO_{4\ (P\text{-}lim)}$	0.14	62.8	36.4	0.835
Global warming	kg $CO_{2\ (eq)}$	2.95E3	82.3	16.9	0.776
Non-renewable energy	MJ primary	1.73E5	90.9	7.91	1.19
Mineral extraction	MJ surplus	2.34E3	78	22	0.00821

Table 12 shows the environmental impacts of biochar production process. Most contributions to the global warming impact are from switchgrass production. The fertilizer (N and P) for planting switchgrass plays an important role in increasing nitrous oxide emission which is a major factor contributing to climate change. This result corresponds to the evidences that N_2O emissions are the largest GHG source [32]. Another main reason is the electricity and fuel oil used in planting and transportation. Kelli et al. [54] estimated that the net climate change impact was 36 kg CO_2 eq/t dry feedstock in biochar system using switchgrass as a feedstock. The net GHG emission is 21.6 kg CO_2 eq/t dry feedstock in the biochar catalyst system, which is lower than the previous investigated result. Both results are estimated based on cultivating switchgrass with land-use change, but with different biochar system (slow pyrolysis and gasification). Several studies have found that the GHG emissions stemming from converting virgin natural land to agricultural land may be severe [102, 103]. In the carcinogens impact category, gasification process takes approximately 94% of the total impact due to the energy generated from natural gas. The gasification process produces many volatile organic compounds that contribute to respiratory organics impact. Due to an industrial scale gasifier is included in the gasification process, more non-renewable energy such as natural gas is consumed and more carcinogens are generated when compared to the switchgrass cultivation. The impact on respiratory inorganics of gasification process is a little higher than the same impact of switchgrass production. The sources of impacts on respiratory inorganics for these two integrated processes are from natural gas industry and electricity generated by coal, and the application of fertilizer in switchgrass production also has a little impacts on respiratory inorganics. The land use and transformation of pasture and meadow in planting switchgrass are responsible for impacts of land occupation, aquatic and terrestrial ecotoxicity [104]. Andres et al. [105] estimated that 1.67MJ energy was consumed to produce 1 kg switchgrass production. The energy used for producing switchgrass in this study is 2.19 MJ/kg which is a little higher than 1.67 MJ/kg, but this result is consistent with the published values (1.67 MJ/kg – 2.31 MJ/kg) [106]. The energy used in a biochar system with switchgrass was approximately 888 MJ t^{-1} dry feedstock [54], and it is a little higher than the energy used (793 MJ t^{-1} dry feedstock) for biochar production in this study. The reason for this result could be disposal processes such as composting were included in the reference study. The aquatic eutrophication impact of switchgrass production is 5.53E-6 kg PO_4 eq/kg, and it is much lower when compared to the result of 3.5E-4 kg PO_4 eq/kg [105] from switchgrass cultivation. The yields of switchgrass in the reference article and this study are 10 t/ha and 14.8 t/ha, respectively. The various yields of switchgrass may cause different land occupation impacts which are related to aquatic eutrophication impact. The single score (see Figure 9) indicates that land occupation, carcinogens, non-renewable and respiratory inorganics are the most relevant of the potential environmental impacts for biochar production.

Table 12 Characterization LCIA results of biochar production

Impact category	Unit	Total	Switchgrass production (%)	Gasification process (%)
Carcinogens	kg $C_2H_3Cl_{(eq)}$	130	6.25	93.8
Non-carcinogens	kg $C_2H_3Cl_{(eq)}$	12.4	33.1	66.9
Respiratory inorganics	kg $PM_{2.5\ (eq)}$	0.344	41.5	58.5
Ionizing radiation	Bq C-14 $_{(eq)}$	283	73.5	26.5
Ozone layer depletion	kg CFC-11 $_{(eq)}$	4.85E-6	80.7	19.3
Respiratory organics	kg $C_2H_4\ _{(eq)}$	5.6	1.14	98.9
Aquatic ecotoxicity	kg TEG water	5.32E4	23.8	76.2
Terrestrial ecotoxicity	kg TEG soil	4820	96.7	3.3
Terrestrial acid/nutri	kg $SO_2\ _{(eq)}$	7.19	62.7	37.3
Land occupation	m^2org.arable	8300	100	5.84E-4
Aquatic acidification	kg $SO_2\ _{(eq)}$	3.67	31	69
Aquatic eutrophication	kg $PO_4\ _{(P\text{-}lim)}$	8.89E-3	59.3	40.7
Global warming	kg $CO_2\ _{(eq)}$	206	69.3	30.7
Non-renewable energy	MJ primary	7550	27.6	72.4
Mineral extraction	MJ surplus	2.7	70.8	29.2

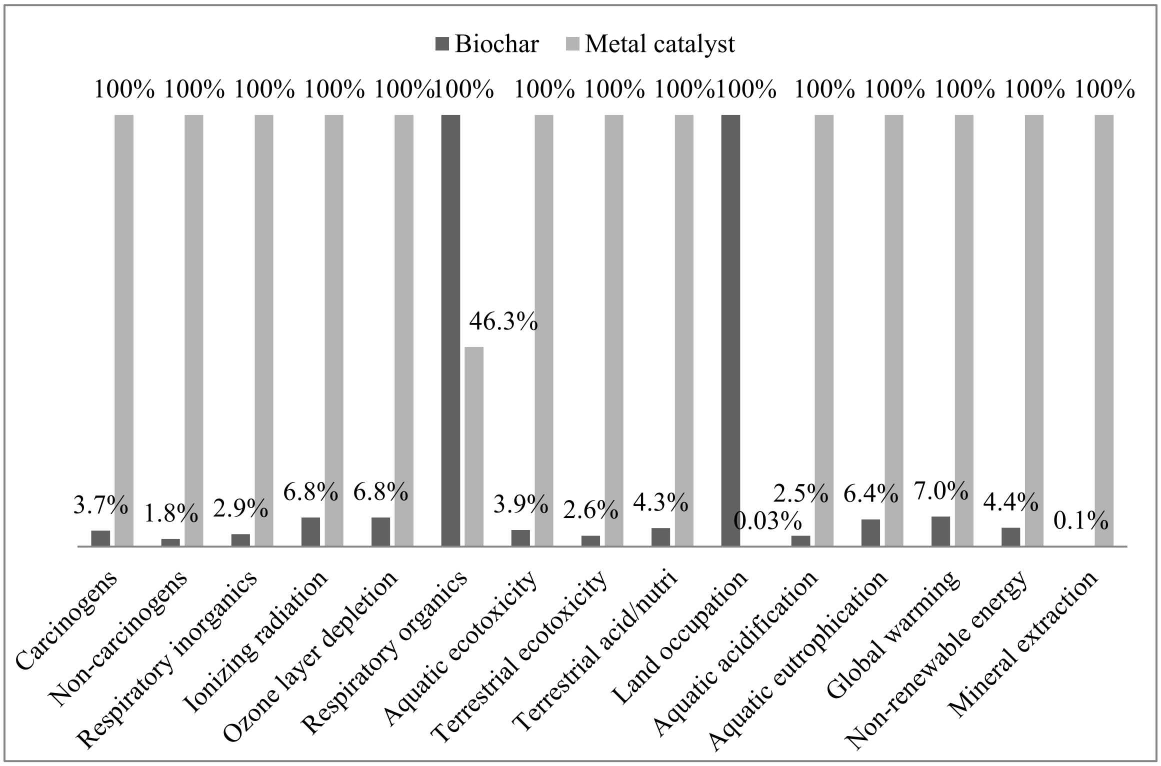
4.2 Comparison Analysis Results

Table 13 reports the comparison results in different impact categories. The results which should be highlighted are that only the respiratory organics and land occupation impacts of biochar production are much higher than the same impacts of the metal catalyst production. The percentages in Figure 8 are the proportions of lower value to higher value in different impact categories, and each impact category includes two different columns representing the biochar and metal catalyst, scaling up the higher value to 100% for ease of comparison. In the same functional unit condition, the metal catalyst production process produces 30 times more carcinogens and non-carcinogens than the biochar production process. The potential global warming and non-renewable energy impacts of biochar production are 7% and 4.4% of the metal catalyst production, respectively. The reduction in GHG emissions of biochar production is due to soil organic carbon change by switchgrass production [107].

Table 13 Characterized LCA comparison results

Impact category	Unit	Total value	
		396 kg metal catalyst	953 kg biochar catalyst
Carcinogens	kg $C_2H_3Cl_{(eq)}$	3.51E3	130
Non-carcinogens	kg $C_2H_3Cl_{(eq)}$	697	12.4
Respiratory inorganics	kg $PM_{2.5\,(eq)}$	11.7	0.344
Ionizing radiation	Bq C-14 $_{(eq)}$	4.19E3	283
Ozone layer depletion	kg CFC-11 $_{(eq)}$	7.15E-5	4.85E-6
Respiratory organics	kg $C_2H_{4\,(eq)}$	2.59	5.6
Aquatic ecotoxicity	kg TEG water	1.37E6	5.32E4
Terrestrial ecotoxicity	kg TEG soil	1.87E5	4820
Terrestrial acid/nutri	kg $SO_{2\,(eq)}$	167	7.19
Land occupation	m^2org.arable	2.16	8300
Aquatic acidification	kg $SO_{2\,(eq)}$	144	3.67
Aquatic eutrophication	kg $PO_{4\,(P\text{-}lim)}$	0.14	8.89E-3
Global warming	kg $CO_{2\,(eq)}$	2.95E3	206
Non-renewable energy	MJ primary	1.73E5	7550
Mineral extraction	MJ surplus	2.34E3	2.7

Figure 8 Characterized LCA comparison results



The environmental performance of two catalysts in every impact category is given in a single score in Figure 9. The single score is calculated by applying weighting factors of every impact category to normalization scores of damage assessment results [108]. In terms of absolute value, every impact category may appear to be significant. However, when considering the total impact, each impact category could have a minor magnitude. The weighting factor which is determined by a panel, based on subjective opinions, reflects the importance of the category. The total score is the sum of all impact categories' scores. Therefore, the total score of biochar production is 0.827 Pt, and the total score of metal catalyst production is 4.4 Pt. The environmental damage of metal catalyst is mainly caused by the impacts on carcinogens (31.6%), non-renewable (26%), respiratory inorganics (26%), global warming (6.8%) and non-carcinogens (6.3%) categories. The environmental damage of biochar is mostly due to the impacts on land occupation (80%), carcinogens (6.2%), non-renewable (6.0%) and respiratory inorganics (4.1%) categories. In both catalysts systems, the impacts on ionizing radiation, ozone layer depletion, respiratory organics, aquatic ecotoxicity, terrestrial acidification/nutrition and mineral extraction categories are relatively much lower than other categories' impacts. The normalization factors of aquatic acidification and aquatic eutrophication are not well-developed in the IMPACT 2002+ method so they do not have relative scores [83].

Figure 9 Characterized LCA comparison results expressed as single scores (Pt)

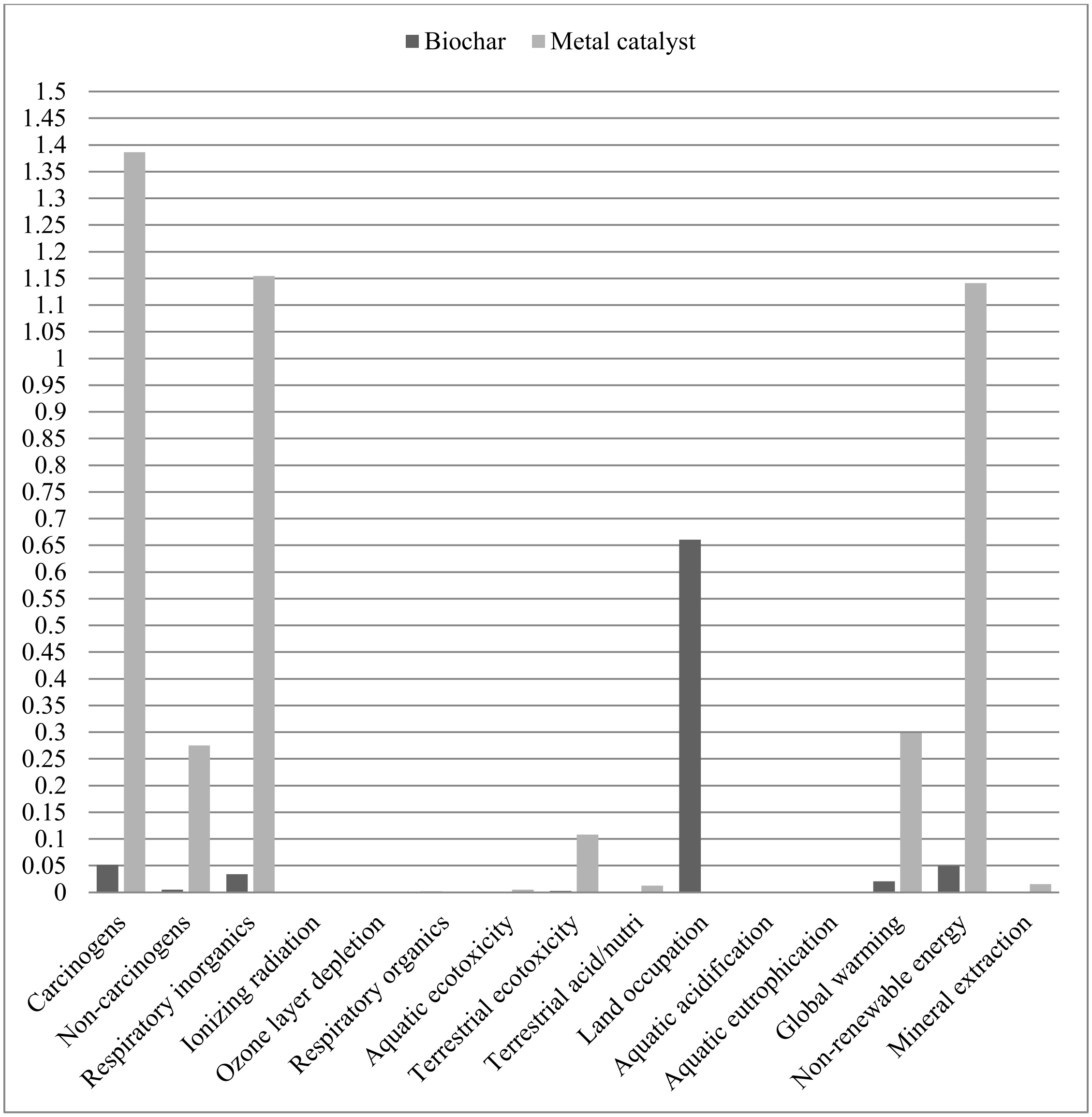


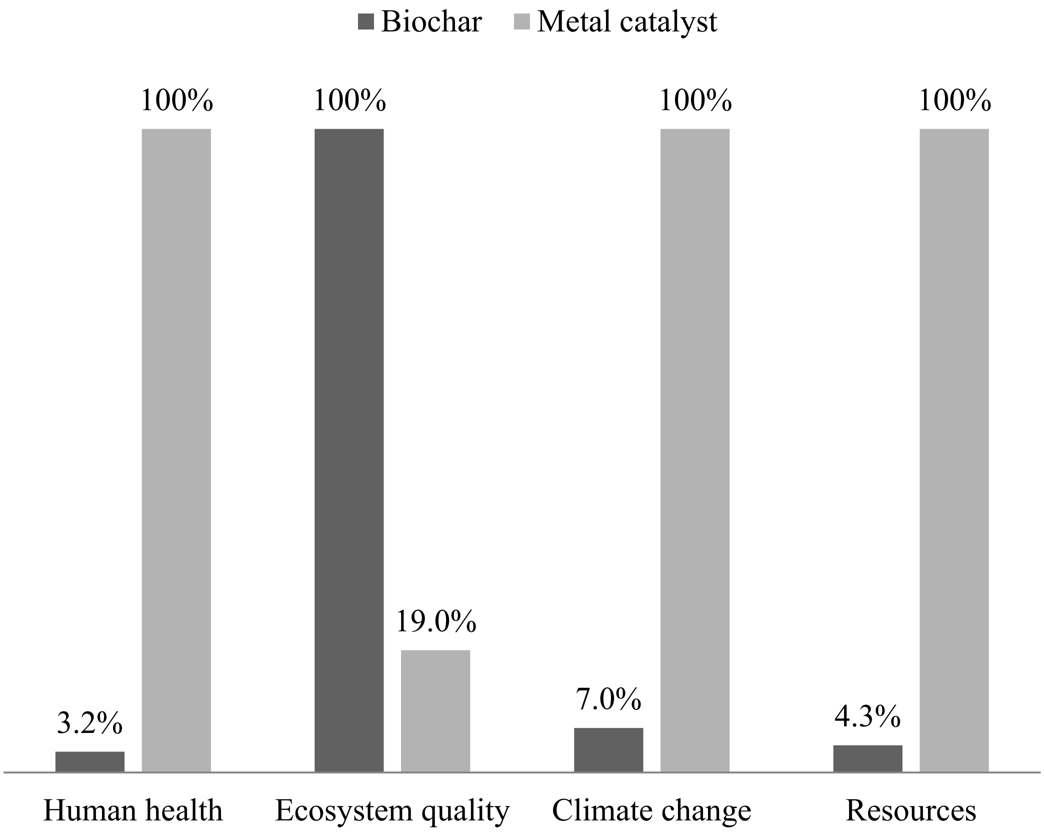
Table 14 corresponding to Figure 10 indicates the damage category impacts of two systems. For instance, 206 kg CO_2 eq is 7% of 2,960 kg CO_2 eq and so the climate change value of metal catalyst is set to 100%. The metal catalyst production has more impacts on human health than biochar production because of its carcinogens and non-carcinogens impacts. The total energy required for the estimated amount of metal catalyst and biochar are 177,000 MJ and 7,560 MJ, respectively. The energy used of biochar catalyst is roughly 4.3% of energy used in metal catalyst. The total greenhouse gas emission of metal catalyst is 2,960 kg CO_2 equivalents and ratio of biochar to metal catalyst is 7%. Compared to the LCA study of biochar production through slow pyrolysis of biomass feedstocks such as yard waste and switchgrass [54], a GHG emission rate of 0.22 kg CO_2 eq/ kg in biochar production indicates that it does not achieve a net reduction in global warming impact. The reason is that the biochar is used as a catalyst instead of a soil amendment, which means C sequestration of biochar is not taken into account through application of biochar to soil. It has been reported that biochar can contribute to a reduction in GHG emissions by 2.6–16 kg CO_2 eq/kg when applied to soil [109]. The GHG emission rate of biochar produced by slow pyrolysis using microalgae biomass is 0.4-0.66 kg CO_2 eq/ kg [56], that is higher than the rate in this study. This result may be caused by more energy used in microalgae cultivation, and the slow pyrolysis is not effective as gasification process for bioenergy production.

Although the climate change and resource impacts of biochar production are both lower than the impacts of metal catalyst, the biochar production has more environmental load than metal catalyst production in ecosystem quality impact, which is related to land occupation, aquatic ecotoxicity and terrestrial ecotoxicity impacts. The ecosystem quality impact of biochar production is approximately five times higher than metal catalyst production. The reason for this result can be that more lands are transformed from meadow and pasture to arable crop fields by human managements such as tillage and pest control. The ecosystem quality score of producing 1 kg biochar is 9.5, which implies the loss of 950% of species on 1 m^2 of earth surface during one year. This ecosystem quality impact is equivalent to the impact caused by producing 0.015 kg advertising folders [110], or the impact caused by 354 MJ electricity generated by 10 % co-firing with rice straw [46]. Although mining factories occupy large land areas, it does not destroy the soil and the creatures under the ground as much as agriculture. Reducing the diversity of environment is another possible factor that affects the ecosystem quality in planting switchgrass [111].

Table 14 Results of damage assessment

Damage category	396 kg metal catalyst production	953 kg biochar production
Human health (DALY[4])	0.0201	6.53E-4
Ecosystem quality (PDF* m^2*yr^5)	1.73E3	9.09E3
Climate change (kg CO_2 (eq))	2.96E3	206
Resources (MJ primary)	1.77E5	7.56E3

Figure 10 Comparative results of damage assessment



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[4] The unit DALY means Disability Adjusted Life Years, a measure of overall disease burden, expressed as the number of years lost due to ill-health, disability or early death.

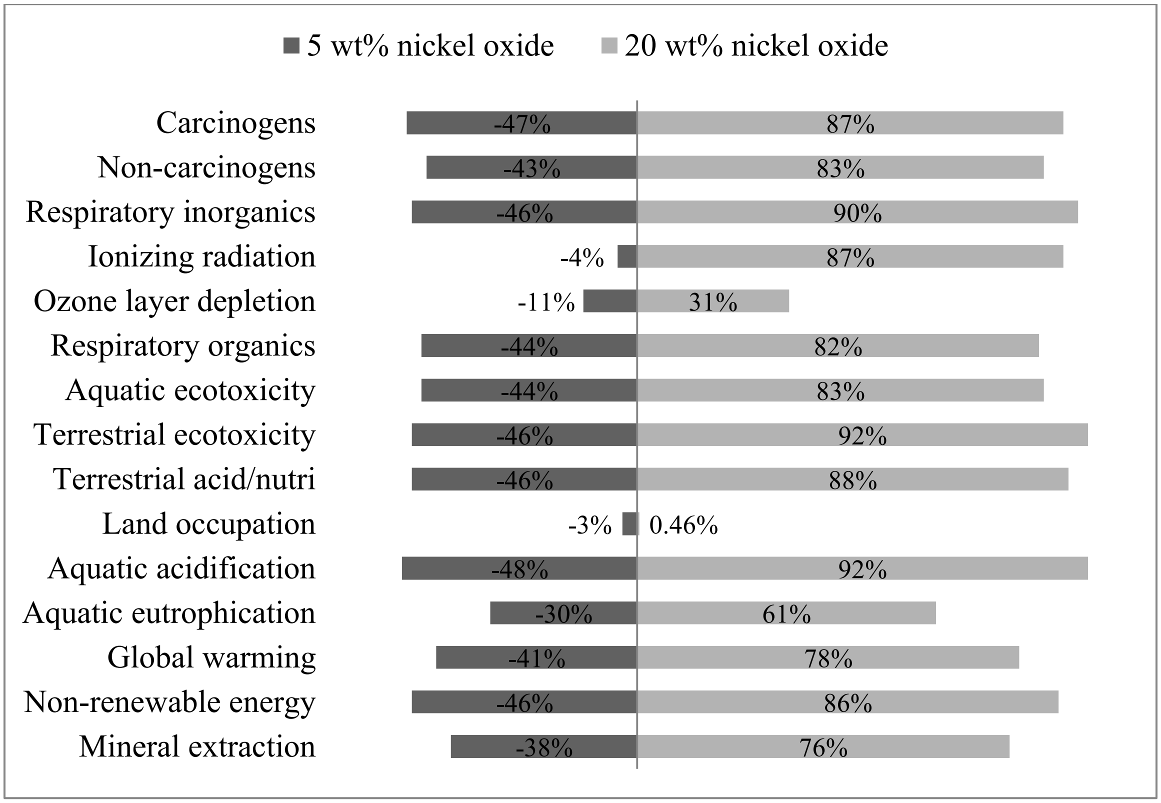
[5] The unit PDF · m^2· yr is potentially disappeared fraction of plant species, over a certain area and during a certain time

4.3 Sensitivity Analysis Results

4.3.1 Variations in the Results Affected by Fraction of Nickel Oxide

By changing the weight fraction of nickel oxide, a sensitivity analysis result is performed in Figure 11. Most impact categories increase by 61% - 92% associated with the highest nickel oxide fraction. For the highest fraction, the ionizing radiation impact increases by 87% while it reduces by only 4% in the lowest fraction. This difference between increasing and reducing indicates that a small amount of nickel oxide has large potential in the ionizing radiation harm. It heavily affects the ionizing radiation aspect when increasing nickel oxide's mass due to the more nuclear energy needed to be used. The ozone layer depletion impact does not increase and decrease as much as most impact categories in the highest and lowest fraction, respectively. Moreover, the land occupation impact has little variety when changing the mass fraction of nickel oxide and the decrease of lowest fraction is even more than the increase of highest fraction. This result reflects that the nickel oxide production has little contribution to ozone layer depletion and the land use, and it can be identified from Table 6 that aluminum oxide has more bad effects than nickel oxide on the ozone layer depletion and land occupation impacts. Overall, the mass of nickel oxide in the metal catalyst can make a huge difference in the environmental impacts except land occupation. An appropriate amount of nickel oxide is necessary to match the high efficiency and lower environmental load of metal catalyst.

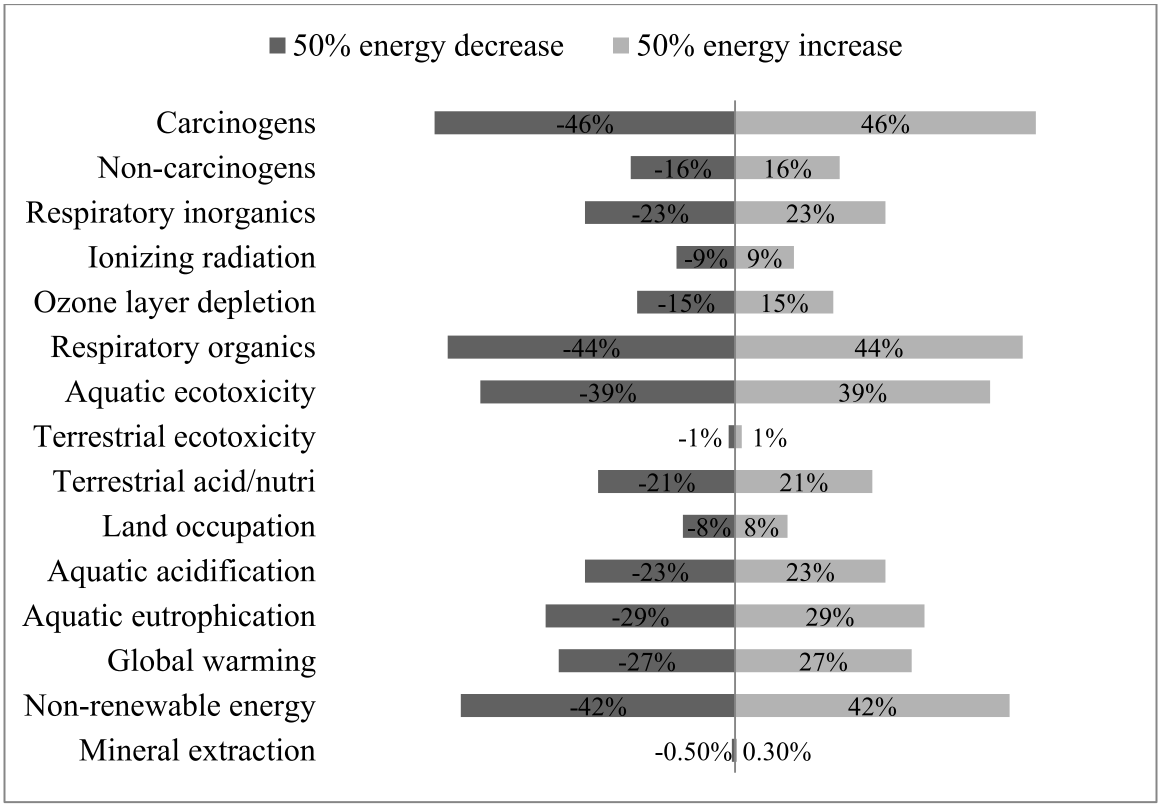
Figure 11 Fraction adjustment of nickel oxide in the metal catalyst



4.3.2 Variations in the Results Affected by Energy Used in Nickel Oxide

A symmetrical sensitivity result is shown in the Figure 12. The decrease and increase in each category have the same percentage and only mineral extraction impact has a 0.2% difference. The energy used in the nickel oxide has more influences on the carcinogens, respiratory organics and non-renewable energy than other categories. The energy adjustment hardly changes the impacts of terrestrial ecotoxicity and mineral extraction which are directly affected by land use and mining process. Basically the energy utilization in nickel oxide can have a significant effect on both human health and energy resources.

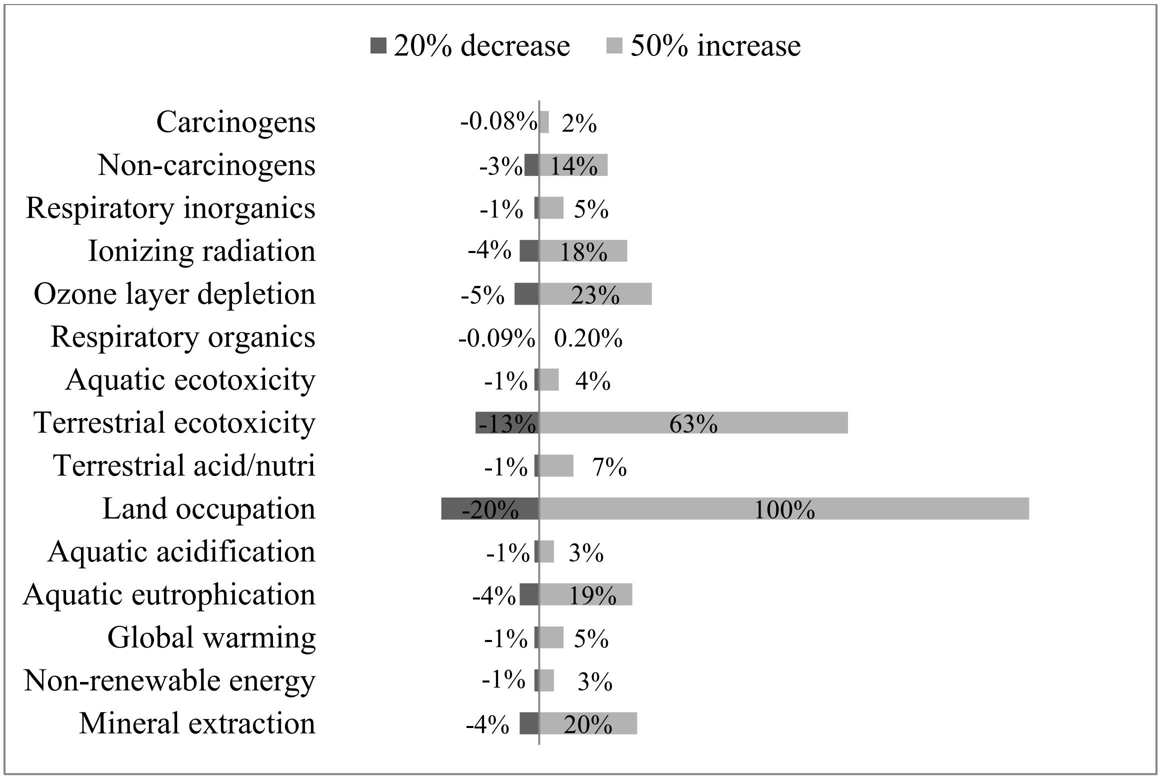
Figure 12 Energy used adjustment in nickel oxide production



4.3.3 Variations in the Results Affected by Land Use in Switchgrass

The results shown in Figure 13 have a large change in both land occupation and terrestrial ecotoxicity bars. Increasing 50% of the basic land contributes to one time increase of environmental impact on the land occupation. Using more land can lead to more potential damage on the nature ecosystem by destroying soil and microorganism under the ground. The change in land use also determines the amount of pesticide and fertilizer used which can contribute to the impact of terrestrial ecotoxicity. In contrast, the carcinogens and respiratory organics are relatively insensitive to the change in the land use. Generally the ecosystem quality of biochar is a weakness compared to the metal catalyst, and land used should be considered as an indicator when making a more sustainable decision about planting switchgrass.

Figure 13 Land use adjustment in switchgrass

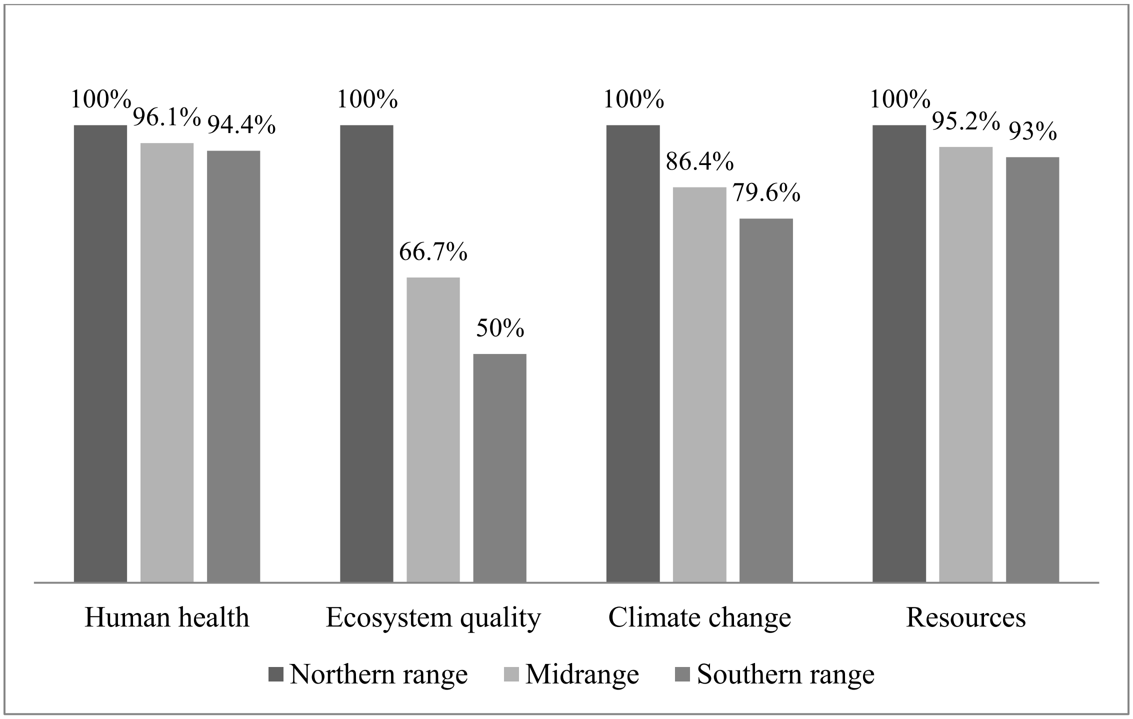


4.4 Results of Variability between Switchgrass and Gasification

4.4.1 Variations in the Results Affected by Switchgrass Yield

In the switchgrass database, the average yield is 14,800 kg/ha that equals to 6 tons/acre. Therefore, the switchgrass used in this study can be classified as a midrange type. The other two types in the northern range and southern range have an average yield of 9,866.67 kg/ha and 19,733.33 kg/ha. The damage assessment related to producing syngas with various yields of switchgrass is given in Figure 14. The percentages of these three types in ecosystem quality category correspond to the relationship of their specific yields. The variation range in the ecosystem quality is from 50% to 150% of the reference value in midrange type. The land occupation impact has a direct influence on the ecosystem quality, and the result can be explained that a higher yield biomass takes less land area than the lower yield one under the same total harvest demand. The differences of these three types in the human health and resources are not too huge, and they result from the energy used in both switchgrass production and gasification process. The climate change category mainly comes from the nitrogen fertilizer used in the switchgrass, so the biomass with higher yield has less impact on the GHG emissions.

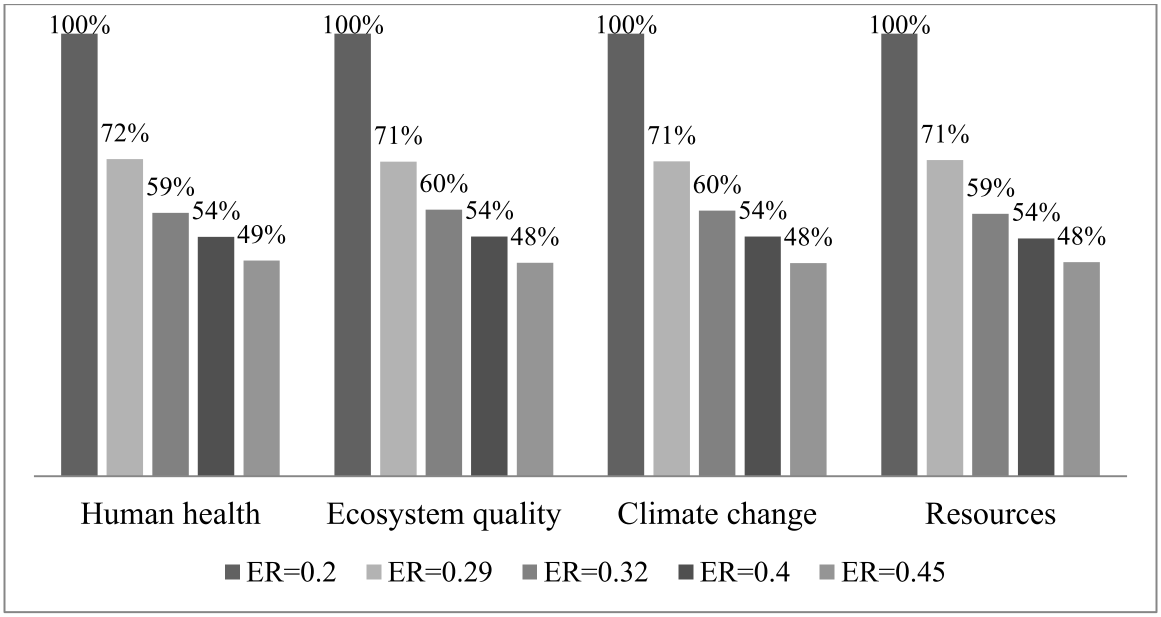
Figure 14 Damage assessment of producing syngas with various yields of switchgrass



4.4.2 Variations in the Results Affected by Equivalence Ratio

The results in Figure 15 show that the highest damage impact occurs at the lowest ER and the percentages of various ERs in every damage category are so uniform. The damage impact results can vary from 48% to 71% of the basic value in ER=0.2. The differences among these various ERs in the damage categories are caused by the input amount of biomass energy and mass. The inputs of biomass energy and mass in ER=0.2 are two times of the ones in ER=0.45, and they lead the results of ER=0.2 to be two times of ER=0.45 on the damage impacts. Variations in HHV of syngas which can affect the inputs of industrial scale gasifier and allocation value have been taken into account in this case. With higher HHV of syngas production, a bigger gasifier is needed to meet a related energy capacity. However, the effects made by HHV of syngas on the gasifier construction are too little when compared to the inputs of biomass for producing 1m^3 syngas. In the end, the variations in HHV of syngas show no obvious changes on the LCA results.

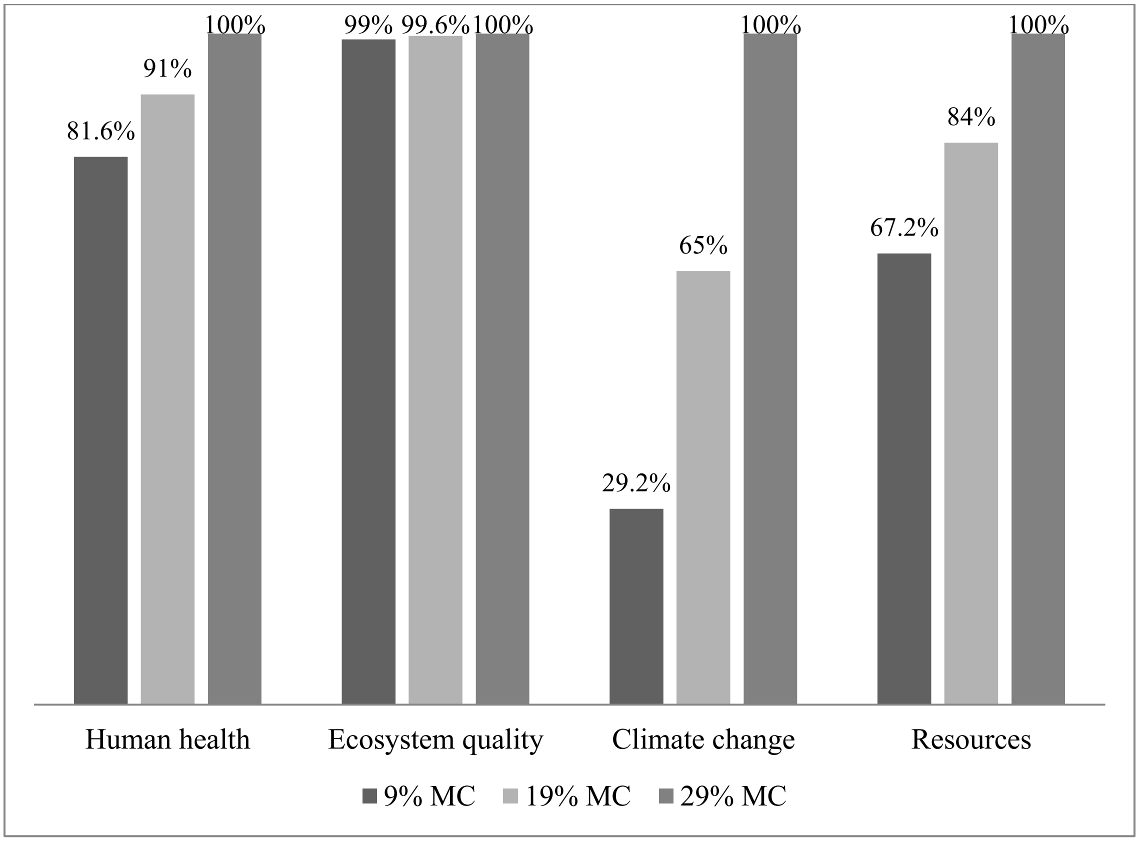
Figure 15 Damage assessment of producing syngas with various ERs



4.4.3 Variations in the Results Affected by Biomass Moisture Content

The results in Figure 16 reflect the effects of variations in biomass moisture content and HHV of syngas on the damage impacts. The highest variation occurs in the climate change with an increasing range from 120% to 240% based on the value of 9% MC. This difference in the climate change is due to extra heat added to the gasification process with higher moisture content in the switchgrass. For instance, the climate change impact in 19% MC is 65% of the value in 29% MC that has double external heat added to the air. The ecosystem quality mostly does not change because of little variations in the switchgrass production. The human health and resources categories are affected by moisture content and HHV of syngas, but it is similar with the situation of ERs that the damage impacts are more sensitive to the variations in the moisture content than the variations in the HHV of syngas. In conclusion, lower moisture content in biomass is beneficial for the syngas production and the environmental impacts.

Figure 16 Damage assessment of producing syngas with various MC in switchgrass



CHAPTER V

CONCLUSION

5.1 Conclusions

A comparative life cycle assessment is applied to model the environmental impact of producing metal catalyst versus biochar as a catalyst used in the syngas cleaning system. Each product system is conducted based on the same functional unit in SimaPro® 7.3.3. According to the comparative results of impact assessment, the biochar production provided by gasification using switchgrass as a feedstock requires 95.7% less energy than the metal catalyst which is the mixture of nickel oxide and aluminum oxide. Producing biochar as a catalyst has a potential in reducing 93% GHG emissions when compared to producing a metal catalyst. Although biochar production system has more potential impacts on ecosystem quality, it has less negative impacts on human health than the manufacture of metal catalyst production. If biochar is examined as recycling a waste from gasification, its ecological aspects will be much less. Since most of the environmental impacts of metal catalyst are from nickel oxide production, it can be concluded that current industrial extraction of metal such as mining and crushing bring in too much negative impacts on the environment. For more sustainable industrial ecosystem, every process of metal catalyst manufacture can reduce the waste materials, and the waste treatment of metal can be developed with less toxic waste distribution to the environment. Overall, biochar production can offer more environmental benefits in global warming potentials and resource consumption. The improvement of biochar production can be fixed by mitigating land occupation such as growing a higher yield switchgrass in the southern range. For gasification process, the design of an optimum ER should take into account not only higher syngas HHV but also less input of feedstock. Moreover, the moisture content in the biomass heavily affects the gasification process, especially for the energy used and HHV of syngas. The ideal syngas production is produced by gasification process with less moisture in biomass.

5.2 Recommendations for Future Work

Life cycle assessment is considered as it is not an exact scientific technique, but a science-based assessment methodology for indicating the performance of a product or a system on the environmental loads [77]. Therefore, there are still some shortcomings and limitations in this LCA. For improving the rationality of this study, the following works are suggested to be continued:

1. Including more available data in the gasification process

   The data of gasification process in the biochar production is relatively limited when compared to the data of metal catalyst, especially the sources of the emissions during gasification. The compilation of the inventory of actual industrial scale gasification process should be added into future work.

2. Combing with economic analysis to select system boundary and assess the LCA results

   A hybrid approach of combing process analysis with economic analysis can be carried out in selection of system boundary and compilation of LCI. Moreover, the LCA results can be more valid and comprehensive for stakeholders to make a profitable decision easily.

3. Accessing the uncertainty of LCI

   Since the results of LCA are very sensitive to the inventory, the variability of practical manufactures should be fixed by the sensitivity analysis. Although some data are obtained from practical measurements, a stochastic modelling such as the Monte Carlo simulation should be carried out to access the parameter uncertainty.

4. Model the biochar LCA as utilizing a waste product of gasification

   The current study assigns full impacts to the production of biochar as a dedicated catalyst product. If the biochar is examined as an inevitable consequence of the gasification of switchgrass and is a recoverable waste product, the ecological impacts should be tremendously minimized.

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APPENDICES

A.1 Ratio of Conversion Efficiency of Metal Catalyst to Biochar

An amount of 1000 ml of toluene is assumed as a model tar in the experiment of testing the conversion efficiency of Hifuel and biochar. The average toluene conversion for Hifuel (0.15g used) and Biochar (0.3g used) are 97.17% and 80.83%, respectively. Total toluene supplied within this time was:

$$230 \text{ min} \times \frac{2}{60} \text{ ml/min} = 7.667 \text{ ml}$$

The amount of toluene converted in 230 min is:

For Hifuel, $7.667\text{ml} \times 97.17\% = 7.45\text{ml}$ For biochar, $7.667\text{ml} \times 80.83\% = 6.20\text{ml}$

So, for cracking 1000 ml toluene, the amount of catalysts needed is:

For Hifuel, $0.15\text{g} \times \frac{1000\text{ml}}{7.45\text{ml}} = 20.14\text{g}$ For biochar, $0.3\text{g} \times \frac{1000\text{ml}}{6.20\text{ml}} = 48.14\text{g}$

The ratio of conversion efficiency of metal catalyst to biochar is:

$$\text{The ratio} = \frac{\text{Metal catalyst}}{\text{Biochar}} = \frac{48.14\text{g}}{20.14\text{g}} = 2.404$$

A.2 Materials of Building an Industrial Scale Gasifier

The basic data of construction materials of an industrial scale gasifier was obtained from a gasification-based power plant with coal as a feedstock. The power plant has a capacity of 407.1MW with a conversion efficiency of 42%. The total energy of coal input into the power plant is:

$$\frac{407.1\text{MW}}{42\%} = 969.3\text{MW}$$

$$969.3\text{MW} \times 24\text{hr/day} \times \frac{3.6\text{MJ}}{\text{kWh}} = 8.375 \times 10^{7}\text{MJ/day}$$

For the biomass gasification power plant, the total energy of syngas used to generate fuels is:

$$\frac{6.6\text{MJ}}{\text{m}^3} \times \frac{2000{,}000\text{kg}}{\text{day}} \times \frac{2\text{m}^3}{\text{kg}} = 2.64 \times 10^{7}\text{MJ/day}$$

The equilibrium ratio of input energy is:

$$\frac{2.64 \times 10^{7}\text{MJ/day}}{8.375 \times 10^{7}\text{MJ/day}} = 0.315$$

The construction materials contain large amounts of steel, cement and aggregates, also relatively smaller amounts of aluminum, copper, glass and iron which can be ignored. The steel, cement and aggregates used in that gasifier were 19,363 tonnes, 19,363 tonnes and 116,381 tonnes, respectively. So the relative materials used in this gasifier are:

Steel: $19363 \text{ tonnes} \times 0.315 = 6099 \text{ tonnes}$

Cement: $19363 \text{ tonnes} \times 0.315 = 6099 \text{ tonnes}$

Aggregates: $116381 \times 0.315 = 36660 \text{ tonnes}$

A.3 Allocation Value Used in the Gasifier

The industrial scale gasifier is assumed that it can run normally 10 years and with an operating capacity factor of 60%. As a result, the total amount of syngas produced by this gasifier is:

$$10\text{yr} \times \frac{365\text{day}}{\text{yr}} \times 60\% \times 4000{,}000\frac{\text{m}^3}{\text{day}} = 8.76 \times 10^{9}\text{m}^3$$

The allocation value for 1m^3 syngas is:

$$\frac{1}{8.76 \times 10^{9}\text{m}^3} = 1.1 \times 10^{-10}$$

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