

2015-01-28

Life Cycle Assessment of Using Biomass-Based Activated Carbon for Water Treatment in Oil Sands Operations in Alberta

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Parchei Esfahani, M. (2015). Life Cycle Assessment of Using Biomass-Based Activated Carbon for Water Treatment in Oil Sands Operations in Alberta (Master's thesis, University of Calgary, Calgary, Canada). Retrieved from <https://prism.ucalgary.ca>. doi:10.11575/PRISM/26759
<http://hdl.handle.net/11023/2042>

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Life Cycle Assessment of Using Biomass-Based Activated Carbon for Water Treatment in Oil
Sands Operations in Alberta

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

GRADUATE PROGRAM IN CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA

JANUARY, 2015

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Abstract

The recovery of bitumen through steam-assisted gravity drainage in Alberta produces about 2.7 m³ of water per one m³ of bitumen, resulting in about 118 million m³ of water per year having high levels of organic compounds. When this water is recycled to the boilers, the organic compounds contribute to fouling and corrosion, thus, the energy companies are interested in finding a cost-effective strategy to remove the organics before recycling the water. In mining operations, approximately 3 m³ of water are produced per one m³ of bitumen, resulting in 148 million m³ of water per year flowing into tailings ponds. While the majority of this water is reused, the organics in water can be metabolized and produce methane, a potent greenhouse gas.

Laboratory studies have shown that activated carbon from forestry residues (aspen wood) could remove the organics, create a carbon sink, reduce emissions from tailings and provide a new market for the residual biomass from the local forestry industry. This study compares the cost, energy requirement, and greenhouse gas (GHG) emissions associated with four scenarios: two scenarios for activated carbon production, pyrolysis and activation of biomass in mobile units in the field or transporting the residual biomass to a central location where it is both pyrolyzed and activated, and two scenarios for using the produced activated carbon for removal of organics from the produced water in either SAGD operations or tailings ponds in mining operations.

Field pyrolysis of biomass for both SAGD and mining operations was calculated to have lower emissions (approximately 75% lower GHG emissions), but higher economic costs (approximately 20% higher cost) compared to the centralized processing. The net emissions of the systems were calculated to be between 0 to 16 kgCO_{2e}/m³. Furthermore, at 75% removal level, the maximum feasible amount for the systems used in this study, the net emissions range

between -55 to -76 kgCO_{2e}/m³. Hence, the ultimate GHG emissions range achievable by these systems is 16 to -76 kgCO_{2e}/m³. The sensitivity analysis showed pyrolysis and activation yields as well as removal level are the main parameters that should be the focus of future research in order to reduce energy requirements, emissions, and cost of the entire process.

Acknowledgements

First and foremost, I would like to express my special gratitude to my supervisor, Dr. Josephine M. Hill, for the opportunity of working in the LECA research group and her valuable advice, encouragement, patience, and support throughout the recent two years. Without her constructive comments and continued guidance I could not have been able to accomplish this project. I would also like to thank Dr. Bergerson, Dr. Layzell, and Dr. Veksha for their professional advice and constructive comments during the course of this project.

The financial support of the Institute for Sustainable Energy, Environment, and Economy (ISEEE) is gratefully acknowledged. Financial support for conference travel was provided by the Schulich School of Engineering and the Institute for Sustainable Energy, Environment, and Economy - thank you for your assistance in funding my travel to the 2014 CSChE conference.

Special thanks to the current and past members of the Laboratory for Environmental Catalytic Applications (LECA) group and my friend, Amir Ahmad, for their continued help and support during the recent years.

And last but not least, I am deeply grateful to all my family members for their constant love, support, and encouragement. Without their love and support, this thesis would not have been possible.

Dedication

To my mother, Mitra, the infinite source of love and devotion, who devoted her life and sustained love to her children.

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List of Abbreviations

Acronym	Definition
AC	Activated Carbon
CAD	Canadian Dollar
CHP	Combined Heat and Power
CPI	Consumer Price Index
GHG	Greenhouse Gas
GWP	Global Warming Potential
IPCC	Intergovernmental Panel on Climate Change
LCA	Life Cycle Assessment
LECA	Laboratory for Environmental Catalytic Applications
NGCC	Natural Gas Combined-cycle
R&D	Research and Development
SAGD	Steam-assisted Gravity Drainage
TOC	Total Organic Carbon
USD	United States Dollar

Chapter One: Introduction

Canada has some of the world's largest oil reservoirs located in northern Alberta, which are mainly in the form of heavy oil and bitumen [1,2]. Oil sands contain mixtures of sand, clay, water and an extremely viscous substance known as *bitumen* [1]. Bitumen must be recovered and processed for removal of the sand to produce products including gasoline, diesel fuel, jet fuel, and propylene [1]. These processes are more costly than conventional oil and gas recovery. However, increasing global oil demand and recent improvements in bitumen production technologies have triggered rapid growth in this area [1,3].

In general, there are two methods for the bitumen extraction in Alberta, in-situ extraction with thermal recovery methods and surface mining. For in-situ extraction, the main process is Steam Assisted Gravity Drainage (SAGD). In this method steam is used to decrease the viscosity of bitumen by heating the reservoir. The in-situ thermal methods are employed when the oil sand reservoirs exist at a depth of more than 150 meters, which is more common for Alberta reservoirs, whereas, surface mining operations are restricted to a depths of less than 75 meters [3]. For surface mining, oil sands are mined and moved by trucks to be mixed with warm water for separating the bitumen. NaOH is usually added to improve the bitumen separation [4].

The recovery of bitumen through steam-assisted gravity drainage in Alberta produces about 2.7 L of water per L of bitumen, resulting in about 118 million m³ of water/yr having high levels of organic compounds [5]. In mining operations, about 3 L of water are produced per L bitumen, resulting in 148 million m³ of water/yr flowing into tailings ponds [5].

Despite the development of different technologies and advanced materials, production costs of SAGD operations are still influenced by fouling and corrosion of equipment [5]. SAGD

produced water contains a significant concentration of dissolved organics (typically more than 750 mg/L) as well as dissolved solids, which cause fouling in heat exchanger and steam generator tubes if recycling the produced water without removing organics [6, 7]. Although, approximately 90 percent of the produced water is usually recycled for steam generation, there is still a demand for fresh water for both mining and in-situ extraction process (2.7 L of water per L of bitumen for SAGD and 3 L of water are produced per L bitumen for mining operations) [5].

In surface mining during hot water extraction process, quality of used water for bitumen extraction is not sufficient enough to return to the environment and is stored in tailings ponds. In the tailings pond, the sand separates rapidly and sinks to the bottom. Clarified water from the upper parts of the pond is recycled to the oil sands extraction process and more than 80 percent of the water used in the extraction process is recycled. The bottom layer of the tailings pond consists of a combination of clay and water [4]. The water has a variety of harmful chemicals, including heavy metals and naphthenic acids, which damage aquatic organisms, birds and wildlife [8]. Water in the Athabasca River is expected to decline due to climate change while oil sands development expands in the future especially during the winter when flows are naturally lower [8]. Water withdrawal during this time can affect fish habitats and decrease the amount of dissolved oxygen available to fish in the winter [8]. Because the water in tailings ponds is contaminated by soluble organic compounds, based on Alberta's zero-discharge law, producers cannot return the water to the rivers. In this regard, the water must be treated and reused in the plant [9, 3].

Laboratory studies have shown that activated carbon (AC) from forestry residues (aspen wood) could remove the organics, create a carbon sink, reduce GHG emissions from tailings and provide a new market for residual biomass from the local forestry sector [5, 10, 11] .

Alberta offers considerable biomass potential including forest residues and the amount of annual forest biomass is estimated to be more than 5 million tonnes [12]. Forest biomass includes the whole tree from the forest, mill residues, dead or dying trees, stumps and harvesting residues (including branches and tops generated during the logging operation) [12]. Currently in Alberta, pulp and lumber companies cut the trees and drag the trees to the roadside [12].

Finding an effective way to use forest residues for removing organics from water would be environmentally beneficial. In this regard, using forest residue to produce activated carbon and using activated carbon for organic contents removal of water in oil sands operations can be an effective strategy. Employing this strategy reduces the demand for fresh water in oil sands operations and creates a new market for the forestry industry.

The life cycle analysis (life cycle assessment or LCA) is a methodology that allows decision makers to analyze multiple options (different scenarios) with different environmental impacts and costs. This study involves developing a detailed life cycle model which will inform decision makers in Alberta's oil sands and the forestry industry, of the environmental and economic advantages of producing and using biomass-based activated carbon for the removal of organics from produced water.

The LCA model is used for quantification of the environmental and economic implications of a number of alternatives for the treatment of produced water in oil sands operations.

Environmental variables considered are emission of greenhouse gases (GHG), energy requirement, and cost. Because biomass is not dense (less than 400 kg/m³ aspen wood [13]) transportation is an issue. If biomass is trucked in long distances (typically more than 150 to 200 km [14]) it is not economic or environmentally more beneficial, as the emissions released by fuel consumption and the money spent for satisfying the fuel demand is more than the amount that is saved by using biomass. A number of previous studies in this area reported that transportation of biomass because of its low density and high moisture content (usually more than 30%) is a serious issue [14, 15]. Whereas, another study concluded that transportation had minimal impact on emissions and energy requirement of biochar system [16].

In this study two activated carbon production systems (field and factory) are considered to indicate how converting biomass to a denser material (activated carbon) influences total emissions and cost of the sets of processes and investigating whether transportation distance in an important factor influencing the emissions and cost of the activation production systems. By using a mobile pyrolysis unit, pyrolysis and activation happens at roadside and close (3 to 6 km) to the piles of forest residues, which circumvents the necessity of transporting biomass. On the other hand, another scenario (factory) considers trucking forest residues from different regions to a central site to be pyrolyzed and activated there. Therefore, comparing these two scenarios indicates the impact of transportation on total emissions, energy requirement, and cost and evaluates scenarios in terms of economic costs and environmental impacts. Furthermore, this study investigates other parameters such as pyrolysis yield, activation yield, and moisture content that can have significant effect on emissions, energy requirement, and cost of the entire processes.

Because of the limited published research on biochar systems, the conducted research, a comprehensive comparison between two potential activated carbon production systems for water treatment in oil sands industry, performs a key role in this area. This study helps government agencies to know how to allocate funding to different research areas to direct research towards achieving a cost-effective and environmental friendly solution for removing organic compounds from water in oil sands operations. Therefore, the audience for this project include industry, policy makers, and academia.

This thesis contains 6 chapters. Chapter 2 provides definition of the technical terms used in this study, explanation of the process of using biomass for water treatment in oil sands operations, and the previous studies in this field, the gaps, and how this study will solve the main problem by completing previous studies as well as filling these gaps will be discussed. In Chapter 3 a detailed overview of life cycle assessment and the product systems including a detailed description of all unit processes, flow diagrams, assumptions, data collection, and calculation procedures will be discussed. In Chapter 4 the total energy requirement, GHG emissions, and cost of different scenarios has been calculated and the results are presented. Furthermore, the relationships between different parameters of the Life cycle assessment system and final results are discussed in detail. The effect of changing inputs of the LCA model (e.g. pyrolysis yield, activation burn-off, biomass moisture content) on energy requirement, GHG emissions, and cost of each scenario is explored in Chapter 5 and the results of the model are discussed. Finally, in Chapter 6 draws conclusions and offers recommendations.

Chapter Two: Literature review

Pyrolysis of biomass and producing biochar to be used for different purposes has been an attractive subject in the recent years, because biochar can be used either for energy generation, or sequestration, which enhances the productivity of soil [17]. Before talking about this study in more detail, different technical terms should be defined. In the following sections of this chapter the technical terms used in this study will be explained. The process of using biomass for water treatment in oil sands operations consists of different stages such as conversion of biomass through pyrolysis and activation to activated carbon and disposal of used activated carbon. Finally, the previous studies in this field, the gaps, and how this study will solve the main problem by completing previous studies as well as filling these gaps will be discussed.

2.1 Carbonization

Conversion of a carbon-based substance into carbon or a carbon-containing material through pyrolysis is called carbonization. Carbonization is a general concept and can be named as pyrolysis or gasification depending on operating conditions and products. The pyrolysis of biomass at low temperatures and slow heating rates is a well-known process to achieve a carbon-rich solid (80 to 90 wt %) known as charcoal (biochar) [18]. Since, the carbonization stage influences the whole process from growing the biomass to the final distribution of the biochar to the users, this step is the most important in the overall process. As a rule of thumb, the carbonization step represents approximately 10% of total costs from growing and harvesting the biomass to transportation of the biochar [19]. Carbonization process has two main drawbacks. First, the pyrolysis of biomass produces toxic substances such as CO, CH₄, polycyclic aromatic hydrocarbons and oils [18]. To reduce the emissions of these substances there is a huge demand

for more complex pyrolysis equipment, which is more sophisticated and costly than the traditional ones. Secondly, storing the biochar powders in large piles can result in spontaneous ignition [18]. Moreover, commercial biomass carbonization technologies are usually slower than small scale carbonization process[20].

During the carbonization process, some volatiles are driven off the biomass and the total mass decreases. The percentage of the remaining weight over the initial weight is called *yield*, which is usually used to indicate the extent of reaction (see Equation 3-8) [2].

2.2 Pyrolysis

Pyrolysis is thermal decomposition of the carbonaceous feedstock (usually biomass) into gas, liquid, and solid in the absence of oxygen (unlike combustion). In pyrolysis large molecules are broken down into smaller ones [21, 22]. Since, this process converts waste biomass into useful liquid fuels, pyrolysis has received growing attention recently. The basic step of pyrolysis is increasing temperature of feed, which initiates the pyrolysis reactions. Initiation of pyrolysis reaction produces volatiles, char, and tar by condensation of some of the volatiles in the cooler parts of the fuel. Pyrolysis is always the first step in combustion and gasification processes, but, it can be used as a separate process for the production of fuels or chemicals [22, 23].

The pyrolysis of biomass is a useful approach for the production of solid (charcoal), liquid and gaseous products [23]. The gaseous products (including carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethylene, minor amounts of higher gaseous organics and water vapor) can be used for electricity generation. Bio-oil, a complex mixture of water (15–35% wt)

and organic chemicals (consisting of acids, alcohols, aldehydes, ketones, esters, phenols, sugars, alkenes, aromatics, etc.), is usually refined into ‘green’ gasoline and diesel [21, 24-26].

Depending on the operating conditions, the pyrolysis process can be divided into three groups: fast pyrolysis, slow pyrolysis, and mild pyrolysis (torrefaction). Fast pyrolysis requires higher heating rates and mainly produces liquid fuel (bio-oil) [22, 24]. The practical purpose of the slow pyrolysis is to produce mainly charcoal, whereas fast pyrolysis is applied to convert the biomass into a maximum quantity of liquid [24]. Torrefaction increases the energy density of the biomass and reduces its weight, in order to reduce the transportation cost [22].

Implementing mobile pyrolysis facilities reduces the energy content of forest residues delivered to a bio-fuel facility because mobile facilities use a fraction of the biomass energy content to meet thermal or electrical demands [27]. However, implementing mobile facilities is economically beneficial when using a large scale pyrolysis plant is not possible [27].

2.3 Biochar

Biomass based char intended for agricultural use is known as biochar [28]. Biochar is the solid, carbon and energy rich porous product obtained through thermal conversion processes (mostly pyrolysis or gasification) and applying biochar is recommended as an approach for storing carbon in soils because biochar contains a high content of stable carbon (typically 50–85%), resisting decay and remaining in soils for hundred years [29-31]. Moreover, some chemical and physical properties of soils can be improved when it is used as soil amendment [31, 32]. Biochar is made by heating an organic material, such as wood, biomass crops, grasses, agricultural by-

products such as cereal straw, and also from different wastes as waste plastic, food, or sewage sludge, in the absence of oxygen.

Biochar has received increasing attention recently because of reducing N₂O soil emissions and its potential to improve soil fertility and thus, reduce the need for chemical fertilizers [17, 28]. Since, biochar withdraws net carbon dioxide from the atmosphere and stores it as carbon sources in soil, use of biochar can provide a practical solution to global warming caused by emissions of greenhouse gases such as CO₂ and CH₄ [33]. However, for utilizing this potential, biochar needs to have high environmental stability. This aim can be achieved by providing suitable biochar production conditions [34]. Based on some studies, adding biochar to the soil separately or jointly with fertilizer not only can increase crop productivity, but also improves water retention and soil organic carbon stabilization [31, 35].

In general, the characteristics of biochar are prone to vary considerably depending on the feedstock and the production conditions, so that biochar is defined by its production process rather than its chemical composition or structure [29]. The chemical composition of biochar and its properties depend on the pyrolysis conditions and raw material characteristics. The temperature of pyrolysis significantly influences the chemical and physical properties of this material [31]. The most common technology used for biochar production is pyrolysis, specifically slow pyrolysis, because of the higher biochar yield than other conversion technologies [30].

Biochar has been studied as a tool to provide inexpensive adsorbents to cover the growing demand of activated carbon for various environmental applications and offers important physical

and chemical benefits as a precursor of activated carbon, such as having highly concentrated carbon (typically 60-80%), low inorganic content (mostly less than 20%), and a non-graphitizable carbon structure [29].

2.4 Activation

After carbonization, the produced biochar needs to be activated in order to extend the pores created during the carbonization, increase surface area and adsorption capacity of biochar, and produce activated carbon [2]. Physical and chemical activation are the two main methods for the production of activated carbon. For physical activation, gases such as nitrogen, steam, carbon dioxide, air or their mixtures are utilized, whereas, for chemical activation the material is mixed with a chemical agent such as, H_3PO_4 , H_2SO_4 , KOH , NaOH and ZnCl_2 , before the activation process. Physical activation is usually a two-stage process, but it can take place simultaneously as a single stage. During the first stage, carbonization, the material decomposes into chars, tars and gases at high temperatures (600–1000 °C) and under an inert atmosphere (N_2 , Ar). During the actual activation, the charred material and the activating agent (steam, CO_2 , air) are heated for a specific time (called *activation time*). Compared to N_2/CO_2 mixtures steam leads to relatively higher surface areas [36, 37]. In chemical activation a chemical agent (typically a Bronsted acid such as H_3PO_4 , a Lewis acid such as ZnCl_2 or a strong base usually KOH) is used before activation [38]. The temperature for chemical activation, can be lower (400–800 °C) and for shorter activation times. To remove residual chemicals, the material is washed with distilled water or a mild acid. The properties of the produced activated carbon depend on the type of activation (physical, chemical) and the activating agent and the process conditions (temperature,

retention time). There are a number of methods for heating materials during the activation stage such as conventional heating via an electrical furnace or with microwave heating [36, 37].

Although, chemical activation has several advantages over physical activation such as, higher yield, lower temperature of activation, shorter activation time and, higher development of porosity, and lower energy consumption, the activating agents of chemical activation are more expensive (KOH and NaOH compared to CO₂ and H₂O) and also an additional washing stage is required. Besides, these hydroxides are very corrosive [2, 39]. In general, for producing extremely pure materials, physical activation would be preferred [2, 38, 40]. Physical activation is an older process and many current activated carbon production facilities use physical activation in the industry [2, 40].

The activation process leads to weight loss; the term *burn-off* is defined as the mass of biochar removed after activation in relation to the initial mass of the biochar. The burn-off value is usually presented on an ash-free basis (see Equation 3-9) [41].

2.5 Activated Carbon

Activated carbon (AC) is a porous material mainly used for wastewater treatment and gas filters. Although activated carbon can be produced from any carbonaceous material rich in carbon, typically, coal, peat and lignite have been used for activated carbon production and in the recent years agricultural by-products and residual wastes are the main sources [36]. Activated carbon has a developed porosity and a large surface area (typically more than $800 \frac{m^2}{g}$); thus, it is considered an effective adsorbent for removing various organic and inorganic pollutants dissolved in aqueous systems or presented in gaseous environments [37].

Owing to its large micropore and mesopore volumes and thus, the high surface area, activated carbon is the most widespread used sorbent and known as a promising adsorbent for removing organics. This method has been manufactured and used since 19th century [2, 42]. Although, removing contaminants from liquids and gases had its beginning in 1550 BC when the Egyptians used charcoal to purify oils, this method has received considerable attention since the twentieth century [43].

Since, particle size is important for the subsequent handling of the material (e.g. mixing with a catalyst or impregnation), before the actual production of activated carbon, the raw materials are usually crushed, milled and sieved to an appropriate particle size. This action might also affect the properties of the subsequent activated carbon. Generally, the activated carbon production process has three steps: raw material preparation, low-temperature carbonization, and activation [42].

Among several methods, such as adsorption, reverse osmosis, and ion exchange, applied for removal of pollutants from water or wastewater, adsorption with activated carbon is considered to be one of the best technologies for removing color, nitrate, and heavy metals. On the other hand, this method raises the manufacturing costs [37]. Therefore, finding an affordable alternative precursor, such as agricultural by-products, sewage sludge or agricultural manures, for the activated carbon production is beneficial. There are various raw materials that can be used for the production of activated carbon for instance corn, rice husks, wood, coal and petroleum pitch [2, 44].

Using activated carbon for removing organics from water in oil sands operations is a potential solution, which has received growing attention during the recent years [5]. However, this method is not currently being used. In the following sections different oil sands technologies and major environmental issues associated with their produced water are discussed.

2.6 Oil sands technologies

Bitumen is extracted from the oil sands using two technologies, in situ recovery or surface mining. In the following paragraphs each technology is explained.

2.6.1 Steam-assisted gravity drainage

Roger Butler and his colleagues in Imperial Oil designed and developed SAGD in the late 1970s [47]. Steam-assisted gravity drainage is a thermal in-situ heavy oil recovery process, in which two horizontal wells with the length of 500 to 1000 meters and the vertical separation of 4 to 10 meters are drilled parallel to each other and near the bottom of the reservoir. The upper and lower wells are called the “injection well” and the “production well”, respectively [45, 46]. The top horizontal well (injection well) is used to inject steam, whereas, the bottom one (production well) is used to flow reservoir fluids [46]. The reason that wells are drilled horizontally and steam is injected in injection well is that the gravity force is not enough effective to move heated bitumen to a conventional well at an economic rate [47]. The SAGD process begins by circulating steam in both production and injection wells in order to heat the bitumen or crude oil between the well pair (raise the temperature of the bitumen to more than 200°C) and reduce the viscosity (to less than 0.010 Pa.s for Athabasca bitumen), which allows bitumen to flow down into the production well. The injected steam forms a "steam chamber" that grows vertically and

horizontally and heats and drains bitumen. Then, steam is injected into the upper injection well only instead of circulating in both wells. The injection well injects steam, and the production one collects the heated crude oil or bitumen, along with water produced from condensation of steam. Because of the low density, the steam and gases such as methane, carbon dioxide, and hydrogen sulfide rise in the well. The condensed water and crude oil or bitumen are returned to the ground surface by pumps [45, 48].

SAGD retains several advantages over conventional surface mining extraction techniques and steam flooding and alternate thermal recovery methods, such as providing greater per well production rates and reservoir recoveries and reducing cost of water treating [45, 46]. However, a number of researchers have pointed out some limitations of SAGD. For instance, absence of oil saturation in the steam chamber and being residual instead, and high operating costs. Apart from these limitations, the high viscosity of bitumen at reservoir temperature is one of the formidable challenges for the recovery process [46, 47]. Steam-assisted gravity drainage among all of the thermal methods has received increasing attention in recent decades, especially for bitumen recovery [46]. Therefore, existence of organic compounds in produced water of SAGD operations will raise several environmental issues in the future.

Cleaning and clarifying the produced water in order to make it suitable for steam generation is vital for SAGD operations. When oil is separated from water and before recycling it as steam, the remaining water needs to be treated to remove organic and inorganic contaminations. The water clarification is usually developed for removing color and total organic content (TOC), and reducing the sludge volume [49]. One potential approach for cleaning and clarifying produced water is using activated carbon for adsorption and removal of organics.

2.6.2 Surface Mining

Surface mining technique removes the oil sand deposits by truck and shovel and extracts the bitumen with a hot water process (Clarke hot water extraction process) by mixing the oil sand with water warmed using natural gas [9, 50]. Unlike in situ method, surface mining is used for shallower reservoirs (generally less than 75 m below the surface) [51].

After identifying the potential source of bitumen, the area is cleaned to be ready to mine. The first step is collecting oil sands ore from the ground and transporting it to a crushing facility by shovels and trucks [52]. Then hot water is added to the crushed oil sands ore and the ore is pumped to the extraction plant. At the extraction plant more hot water is added to this slurry of sand, clay, bitumen. By settling the slurry, bitumen froth (containing bitumen, clay and trapped water) rises to the surface and sediments (rocks, clay, and sand) settle to the bottom [52].

Froth treatment reduces the water and solid waste going to the upgrader. The purpose of upgrading is transforming bitumen into synthetic crude oil, which can be refined to produce commercial products such as diesel and gasoline fuels [52]. At the end of the froth treatment, a mixture of clays, water, sand and traces of bitumen combined with different chemicals, known as tailings, is pumped out to settling ponds (known as tailing ponds) and recovered bitumen is sent to the upgrader [52]. Although, a significant portion of water released to tailing ponds is recycled after undergoing further treatment, the residual tailings mixture remains in ponds [52].

After using activated carbon for removing organics from water the spent activated carbon needs to be disposed. A practical solution for waste management is landfilling activated carbon.

2.7 Landfilling

Disposal of waste materials by burial under the ground is the oldest form of waste treatment and is known as landfilling [53]. When biomass such as food scraps, yard trimmings, paper and wood are landfilled, anaerobic bacteria degrade the materials and produce methane and carbon dioxide [54].

Cellulose and hemicellulose are the major biodegradable components of municipal solid waste in landfills [55]. The type of released gas from biodegradation is important because CH_4 is a greenhouse gas with an infrared activity 25 times that of CO_2 for a 100 year time horizon [56]. After capturing CH_4 , this gas can be flared and converted to CO_2 and produce energy in the form of steam or electricity, which offsets the utilization of fossil fuels and the resulting emissions [55].

There are several factors limiting the decomposition of cellulose and hemicellulose in landfills, including environmental conditions such as moisture, pH, and temperature, as well as the availability of these substrates to microorganisms [53]. Thus, although significant decomposition of these materials occurs, the complete conversion of cellulose and hemicellulose buried in landfills would not be feasible and the organic carbon that does not biodegrade is sequestered [55].

Carbon sequestration is the removal of carbon from the atmosphere [57]. In landfills, some of the carbon, including wood, paper, food waste, and green waste, is not degraded after disposal and permanently stored (or sequestered) in the landfill [55].

2.8 Life cycle assessment

Doing Life Cycle Assessments began in the 1960's when the limitations of raw materials and energy resources forced researchers to account for increasing energy consumption and to address new resource for the future [58]. Life cycle assessment is a "cradle-to-grave" approach for assessing the environmental aspects and potential impacts associated with a product, process, or service [59]. This method makes an inventory of all inputs and outputs related to a product system to evaluate the potential impacts associated with those inputs and outputs. Finally, interpreting the results of the inventory analysis and impact assessment stages with regard to the goals of the study to draw conclusions [59]. "Cradle-to-grave" means that first all raw materials are gathered from the earth to create the product or provide a service and reused or returned to the earth at the end. Every product has a life, beginning with the product design and development, followed by extraction of resource, production, and consumption and ending with end-of-life activities such as reuse or recycling [58, 59]. LCA can provide a comprehensive view of the environmental aspects of the product or process by considering the associated impacts throughout the product life cycle.

An LCA model can help to find the ways to improve the environmental aspects of products and make conscious decisions in industry, governmental or non-governmental organizations. Generally, the results of an LCA study are used as part of a more comprehensive decision process regarding this fact that a LCA usually cannot provide all the information required for decision making separately and is mostly used as a tool to help decision makers [55, 58].

LCA is usually used to make comparisons either between competing products fulfilling the same function or in evaluating modifications to a product to result less negative environmental impacts [60]. An LCA helps decision-makers select an environmentally friendly process and allows them to study an entire product system, which avoids *sub-optimization*. For instance, when a company wants to select between two rival products, it may appear that process A is better because it generates less hazardous waste than process B. However, after performing an LCA it might be understood that the first option actually has bigger cradle-to-grave environmental impacts. Therefore, the second product (that produces more hazardous waste) may be recognized as better process than the first technology because of its lower chemical emissions. This information can be used with other factors, such as cost data to select the best product or process [58].

Aside from the benefits and applications, LCA has some inherent limitations. First, the accuracy of the results depends on the quality and the availability of the required data. In addition, the results of such studies are focused on regional level and they might not be suitable for national applications. Furthermore, LCA usually focuses more on the environmental aspects of products compared to their social and other characteristics [61]. Generally, performing an LCA can be resource and time intensive.

The LCA process consists of four stages:

1. *Goal and scope definition* – stating the application of study and the reason for performing it, defining the system boundaries and level of details in the study and to whom the results are intended to be communicated.

2. *Inventory Analysis* – collecting data including inputs and outputs of all activities according to the requirements of the goal and scope definition, identifying and quantifying energy usage and environmental releases, constructing the flow diagram of the entire system.

3. *Impact Assessment* - Assessing the potential effects of energy, water, and material usage and the environmental releases identified in the inventory analysis and converting the inventory results into more environmentally relevant and helpful information.

4. *Interpretation* – Evaluating and interpreting the results of the inventory analysis and impact assessment to select the preferred product, process or service with an investigation of the uncertainties in order to reach conclusions and recommendations [58, 62].

Environmental impacts include emissions into the environment, consumption of resources and other interventions (e.g. land use) associated with providing products. These emissions and consumptions lead to different kinds of impacts, such as climate change, stratospheric ozone depletion, eutrophication, acidification, toxicological stress on human health and ecosystems, and the depletion of resources [59].

2.9 Previous LCA studies

A number of researchers have analyzed economic and climate change potential of biochar production and sequestration by conducting a life cycle analysis for different biomass sources (e.g. switchgrass and stover) [16, 17, 63]. They concluded that stover requires the least energy, yard waste offers the highest benefit for emission reduction, and switchgrass is the most economical biomass source for this purpose [17]. In terms of mitigation of climate change a strategy that combines pyrolysis for bioenergy production with application of biochar to soil is

more effective than producing solely bioenergy [63]. Moreover, gasification (as opposed to slow pyrolysis) is associated with the largest energy and GHG emissions benefits [16]. Kimetu et al. explored the potential of using biomass residues to treat produced water in oil sands operation in Alberta and compared two alternatives for waste scenario: landfilling spent AC and using as a source of energy [5]. They concluded that using activated carbon for removal of organics is more environmentally beneficial when spent activated carbon is landfilled and use of activated carbon for organics removal not only has GHG benefits, but also might be one of the best approaches for water treatment in oil sands operations [5]. These studies suggested biomass type is the factory strongly affects cost, emissions, and energy requirement of biochar systems. Table 2-1 shows energy requirement, emissions, and cost of different feedstock in a biochar system [17].

Table 2-1 Energy requirement, emissions, and cost of different feedstock in a biochar system.

Feedstock	Energy requirement (MJ/tonnes dry feedstock)	Emissions (kg CO_{2eq}/tonnes dry feedstock)	Energy requirement (\$/tonnes dry feedstock)
Stover	4116	-864	-17 to 35
Switchgrass	4899	-442	-18 to 8
Yard waste	4043	-885	16 to 69

Furthermore, some researchers have compared in-situ operations with mining and concluded that although, SAGD is more environmental friendly compared to surface mining and it has a higher overall cost and thus, surface mining is more economical [50, 64].

The study conducted in 2013 in collaboration with the Faculty of Civil Engineering of University of Calgary and the Institute for Sustainable, Energy, Environment, and Economy (ISEEE), by Claudia Bess-Ouko, developed an LCA model to estimate the environmental and economic impacts of using different sources of biomass for water treatment in SAGD operations [16]. This

study showed that producing biochar through different carbonization processes for biochar production (pyrolysis and gasification) and using it for produced water treatment in SAGD operations is environmentally beneficial. However, the activation process for producing activated carbon and using activated carbon for water treatment was not considered in this study.

By considering all studies conducted in this field, a comprehensive economic and environmental analysis of biochar system including biomass preparation, carbonization, activation and sequestration appears to be crucial. Although there are a few economic and environmental studies that examine the potential of biochar production and sequestration [16,17,63], they did not consider activation of biochar and using it for water treatment. Kimetu et al. [5] explored the feasibility of using AC for water treatment, however, they did not focus on different unit processes and their study is based on a macro insight, which increases the uncertainty of results. Furthermore, this study did not consider different processes (e.g. biomass preparation) in detail and their results are rough estimation of GHG emissions and cost of each method. Therefore, the necessity of a life cycle assessment considering different unit processes and comparing different alternatives (e.g. SAGD vs mining and field preparation vs factory preparation) is clear for making better and more precise decisions.

Chapter Three: Methodology

In this chapter a detailed overview of life cycle assessment and the product systems including a detailed description of all unit processes, flow diagrams, assumptions, data collection, and calculation procedures will be discussed. As it was discussed in the previous chapters, the LCA procedure includes identifying the goal and scope of the work, conducting an inventory analysis and building a model based on the defined goal and scope, and identifying the potential environmental impact of systems or processes. In this regard, this study involves the development of an LCA model to evaluate the environmental impacts, costs of the production, and use of biochar in the remediation of SAGD and mining produced water.

There are two potential methods for producing activated carbon from forest residues to be used for water treatment in oil sands operations. First, field pyrolysis and activation of biomass to biochar at roadside (field) and then transporting it to the oil sands operations for removal of organics (field scenario). Second, collecting and transporting the residual biomass from different locations to a central location where it is both pyrolyzed and activated (factory scenario). Generally, there are two methods for the bitumen extraction in Alberta, in-situ extraction with thermal recovery methods and surface mining. In both methods at the end the process water needs to be treated to remove organic contaminants and thus, mitigate environmental impacts of produced water.

Each of these two biomass preparation scenarios can be used for water treatment in either SAGD, or mining operations. Therefore, there are four scenarios for using forest residues for removal of organics from water in oil sands operations (see Figure 3-1).

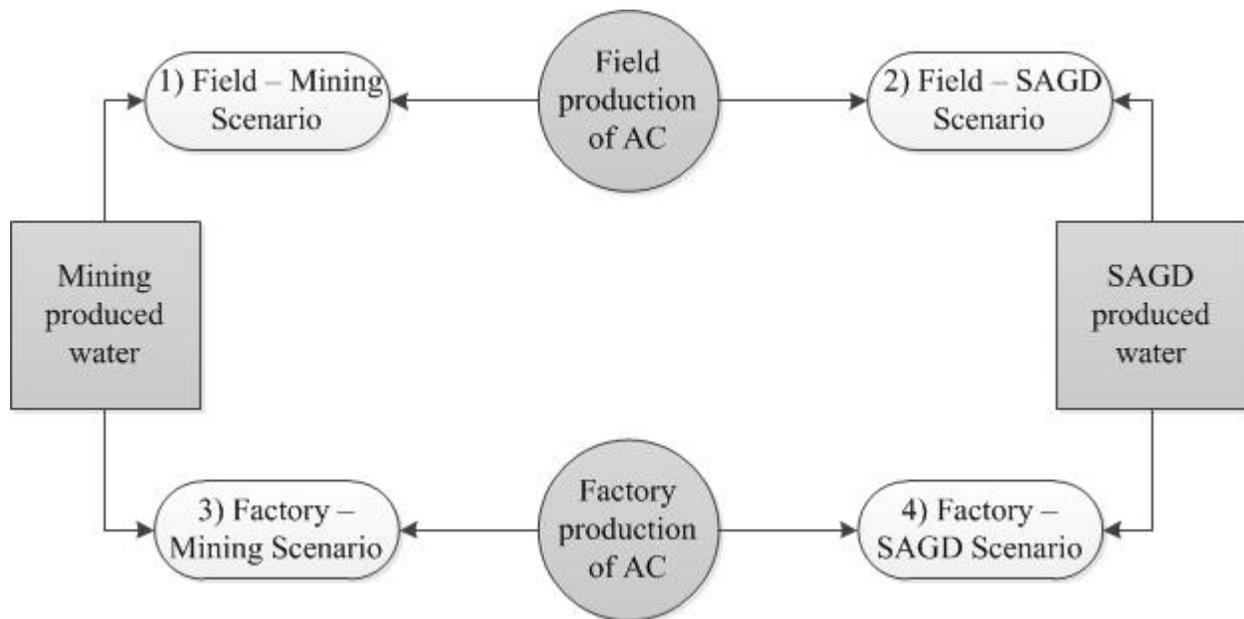


Figure 3-1 Four scenarios for using forest residues for water treatment in oil sands operations.

3.1 Product Systems

The process of using forest residues for removal of organic compounds from water in oil sands operations from cradle to grave (from biomass preparation to adsorption and landfilling) consists of two systems:

Activated carbon production system includes production process of biochar from biomass. Biomass is collected and transported to the pyrolysis and carbonization facility where it is transformed into biochar and its by-products. The carbonization process for the production of the biochar is slow pyrolysis, as this process maximizes biochar production.

Adsorption and landfilling system includes using the produced activated carbon for removal of organics and landfilling spent activated carbon as a waste management scenario (the possible decisions for the end of life management of the spent activated carbon).

3.2 Field production of activated carbon

In the field preparation scenario, forest residues are collected and transported from different regions to a nearby central region and used for activated carbon production on a small scale (25 Mg biomass/day, the maximum capacity of a typical mobile pyrolysis is between 20 to 30 Mg biomass/day [65]). The technology of mobile pyrolysis suits this scenario because, instead of transporting biomass from different regions to the pyrolysis site, which increases the cost of transportation and emissions, the pyrolysis site is brought to different regions. When activated carbon is produced by activation, it is transported to the adsorption site, which is assumed to be near oil sands operations. The lifetime of the entire plant including pyrolysis and activation units, combustor, steam turbine, and off-gas capture unit is 5 years as the lifetime of a mobile pyrolysis unit is typically less than 10 years [66].

Figures 3-2 and 3-3 show flow diagrams of the field preparation scenario for water treatment in different oil sands technologies. The activated carbon production system is the same for both of these scenarios and the difference is the adsorption unit in adsorption and landfilling system (filled in black).

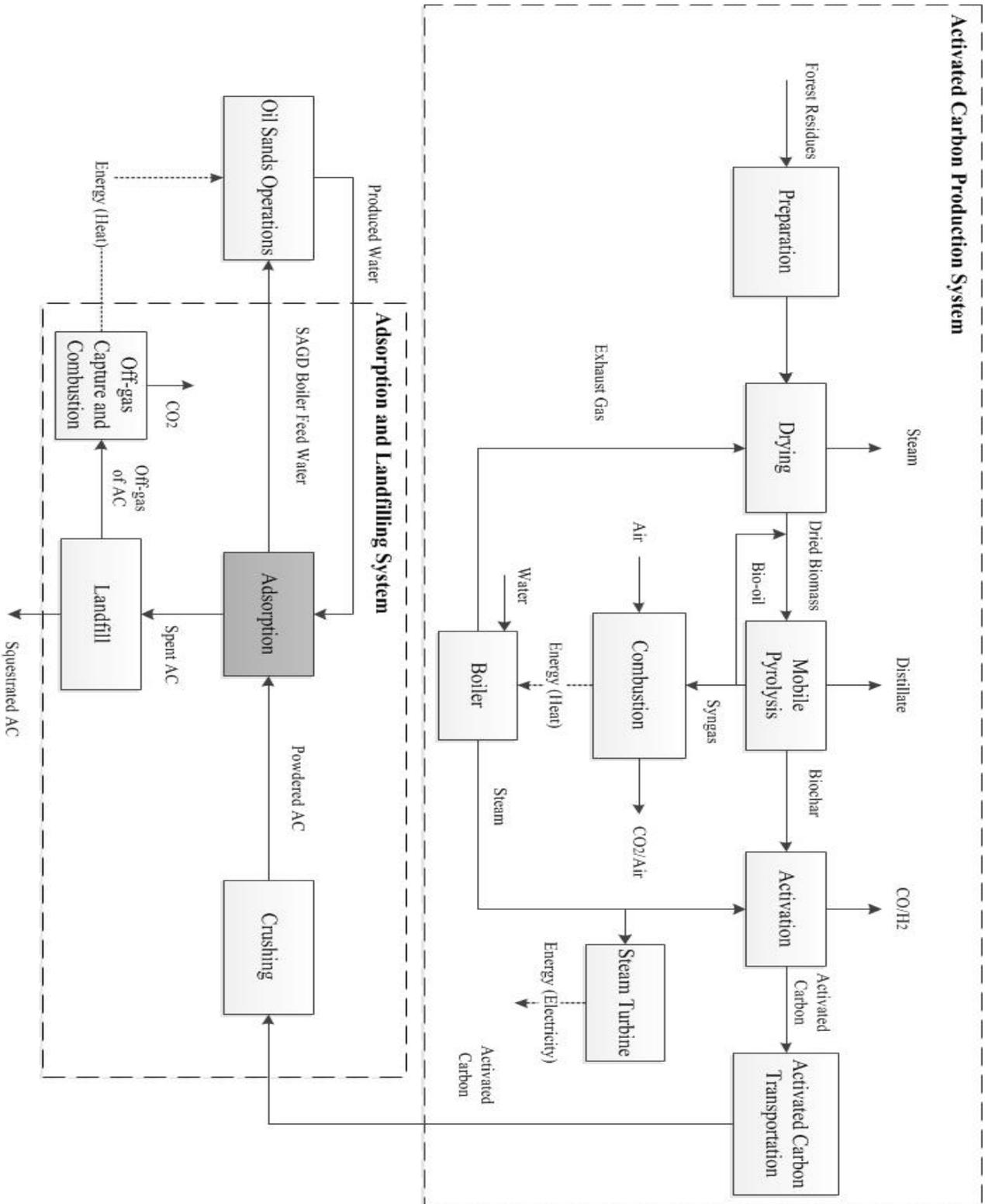


Figure 3-2 Flow diagram of field preparation scenario for water treatment in SAGD operations.

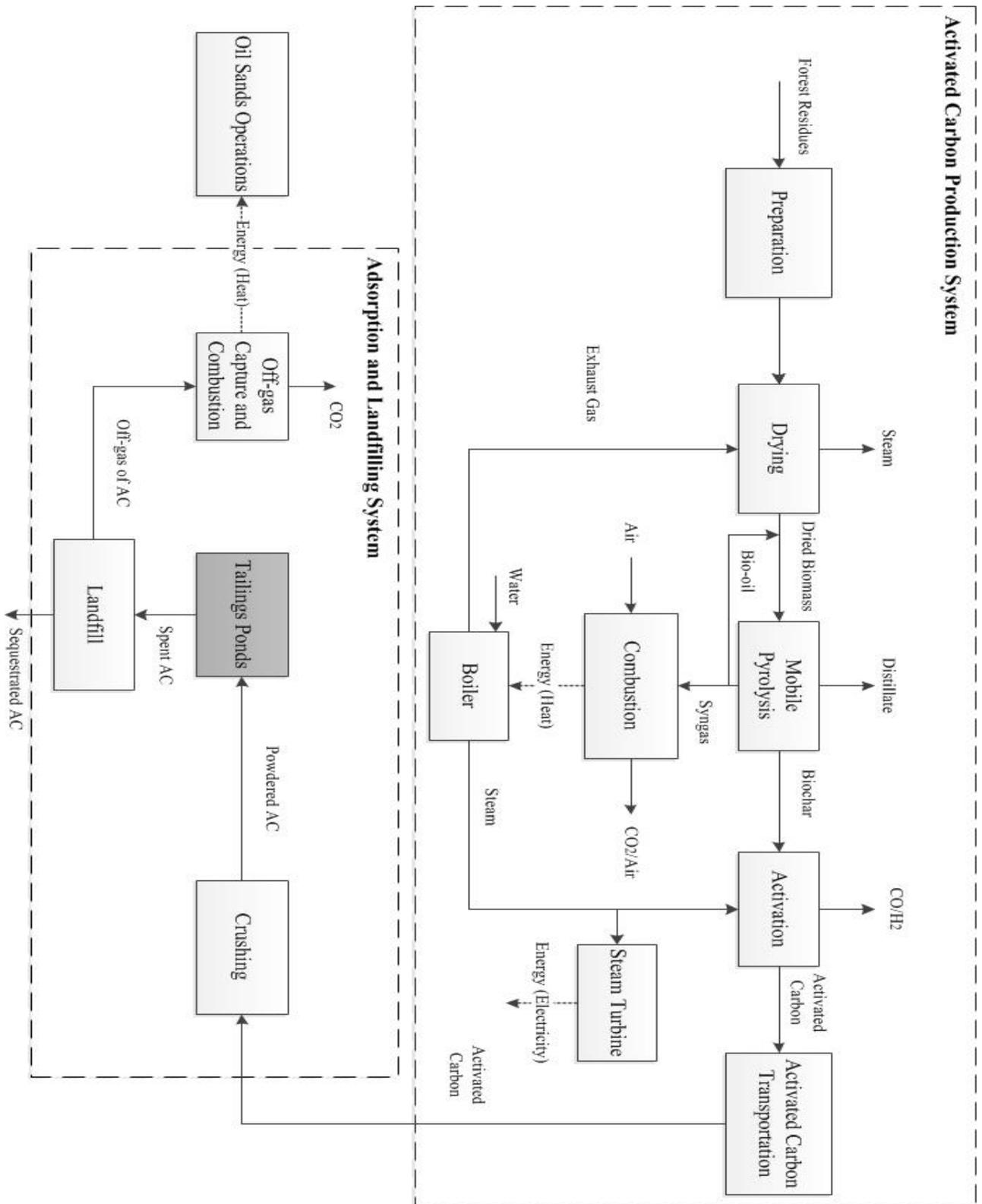


Figure 3-3 Flow diagram of field preparation scenario for water treatment in mining operations.

3.2.1 Activated carbon production system

After collecting air-dried biomass, forest residues are stored in piles and chipped. Chipped biomass is brought to the dryer, which reduces the moisture content of forest residues. Exhaust hot gas from the boiler is used to dry biomass.

Dried biomass is converted to biochar, syngas, and bio-oil in the pyrolysis unit, which works at 650°C. Bio-oil is recycled and added to biomass to increase the pyrolysis yield up to 31% [10]. Syngas is used as fuel for combustion to produce heat for the boiler. Biochar is brought to the activation site by truck.

Biochar is activated in steam activation unit and converted to activated carbon. Steam comes from the boiler unit, which uses the produced heat of syngas combustion and converts water to the steam. The main reaction in steam activation is:



Burn-off is assumed to be 30% (70% of biochar converts to AC) and excess steam is used for activation. Because a reliable source of data for energy requirement, cost, and amount of released emissions for the activation site was not found, it is assumed that the activation unit is the same as the mobile pyrolysis unit (see Section 3-5).

As Figures 3-2 and 3-3 show for steam activation of biochar a water supply is necessary in the field. Because in all fields it is not possible to fulfill the water demand by water wells or natural water resources (e.g. surface water or frozen water), the water should be transported to the field, which is associated with GHG emissions and cost. The energy requirement, emissions, and cost of transportation of water to the fields are not considered in this study and it is assumed that

sufficient amount of water is available in the fields to be used as steam in the activation unit process.

By using produced steam from the boiler site, steam turbine generates electricity. The power efficiency is assumed to be 35% [67]. Generated electricity is used on site for lighting or heating the mobile unit.

3.2.2 Adsorption and landfilling system

In SAGD operations, organic compounds are removed from the SAGD produced water in the adsorption unit by the produced activated carbon, and treated water returns to the oil sands operations as the boiler feed. Concentration of organics in the produced water is 1020 mg/L and removal level is assumed to be 50%. In mining operations, concentration of organics in the produced water is 75 mg/L and removal level is assumed to be 50%.

Landfilling spent activated carbon is the waste scenario of this study. Spent activated carbon is applied to the landfill field, which is assumed to be next to the oil sands operations (transportation of spent activated carbon is omitted). With reference to the previous studies in this area [17], the spent activated carbon is assumed to be applied to the field at a rate of 5 tonnes of carbon per hectare (application rates as high as 50 tonnes of carbon per hectare have shown improvement in soil fertility [17]). The energy consumption of activated carbon application equipment is assumed to be the same as energy requirement for biochar application, as energy requirement of carbon application mostly depends on the mass and volume (and thus, density) of the material and biochar and activated carbon are similar in terms of physical properties [17, 68]. Diesel is used as fuel to satisfy the energy demand of the truck used for activated carbon application. In addition, the embodied energy in manufacturing and repair of machinery is

included in the energy requirement of landfill unit process. However, the landfill facilities are not considered in details and aggregate values are used for the cost and energy requirement of this unit process.

It is assumed that 85% of the carbon is retained in soil and 90% of activated carbon is carbon (the remaining 10% chiefly consists of H and N - see Sections 2.5 and 2.7) [68]. The organics removed by activated carbon along with a 15% of activated carbon are converted to methane and carbon dioxide due to anaerobic metabolism. Thus, landfilled spent AC leads to emissions of greenhouse gases (chiefly CH₄ and CO₂) [5]. 50% of CH₄ is assumed to be oxidized to CO₂ by microorganisms to produce the off-gas with the composition of 67.2% CH₄ and 32.8% CO₂ [5]. Capturing and combusting off-gas not only produces energy but also, by converting methane to carbon dioxide reduces the global warming potential of emissions by almost 25 times [56]. The produced heat is used in oil sands operations. The production rate of off-gas (m³ of off-gas/year) is affected by waste composition and landfill geometry, but typically, it takes between one to seven years to reach the amount that an off-gas capture unit can collect (this time limit depends on the facility) as anaerobic metabolism is a slow process [69, 70].

The following equations are used for calculating the mass of produced water, spent AC, treated water, and removed total organic compounds (TOC):

$$\text{Mass of produced water (Mg)} = \frac{\text{Removal amount} \left(\frac{\text{g org}}{\text{kg AC}} \right) \times 1000 \times \text{Mass of AC (Mg)}}{C_i - C_f} \times \rho_{\text{water}} \quad 3-2$$

where C_i and C_f are produced water organics concentration (mg/L) and treated water concentration (mg/L), respectively and ρ_{water} is density of water (Mg/m³).

$$\text{Mass of spent AC (Mg)} = \text{Mass of AC (Mg)} + \text{Mass of removed organics compounds (Mg)} \quad 3-3$$

$$\text{Mass of removed organic compounds (Mg)} = \frac{\text{Removal amount} \left(\frac{\text{g ORG}}{\text{kg AC}} \right) \times \text{Mass of AC (Mg)}}{1000} \quad 3-4$$

$$\text{Mass of treated water} = \text{Mass of produced water} - \text{Mass of removed organic compounds} \quad 3-5$$

Figures 3-4 and 3-5 show flow diagrams of the factory preparation scenario for water treatment in different oil sands technologies. The activated carbon production system is the same for both of these scenarios and the difference is the adsorption unit in adsorption and landfilling system (filled in black).

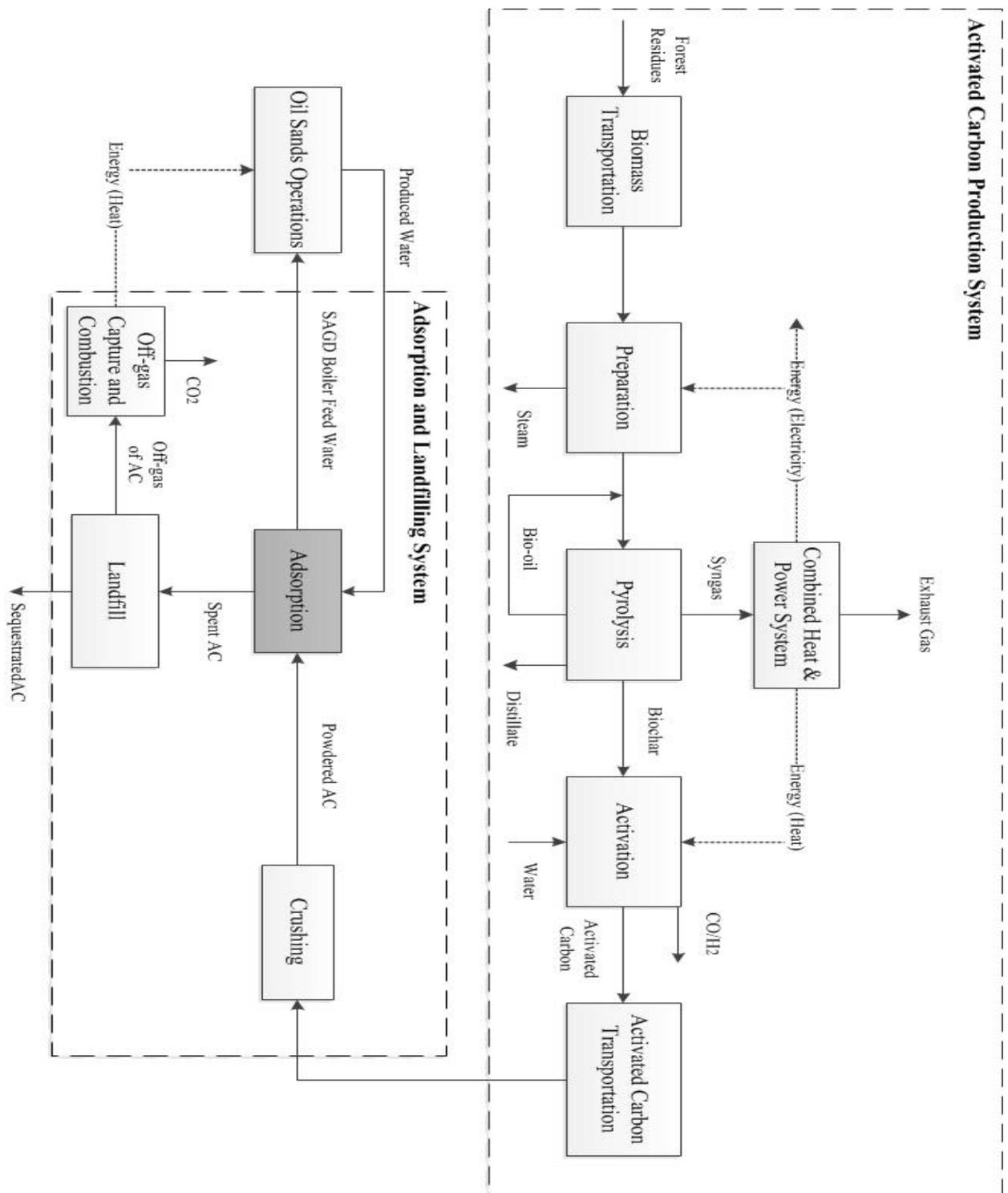


Figure 3-4 Flow diagram of factory preparation scenario for water treatment in SAGD operations.

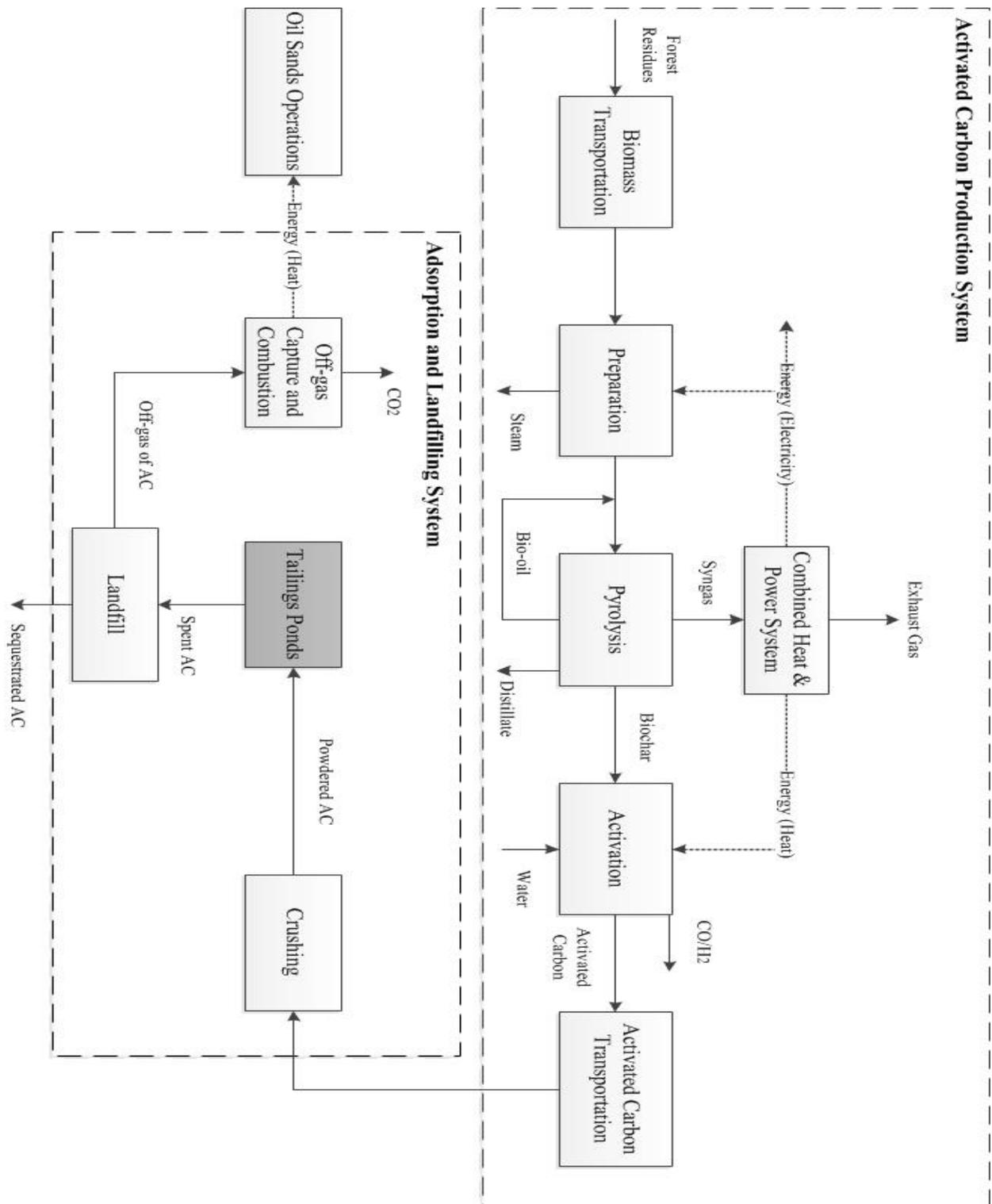


Figure 3-5 Flow diagram of factory preparation scenario for water treatment in mining operations.

3.3 Factory production of activated carbon

In the factory preparation scenario, forest residues are collected and transported from different regions to the biomass preparation site, which is in the central region the same as the pyrolysis and activation site and is used for activated carbon production on a large scale (500 Mg biomass/day, the maximum capacity of an industrial-scale biomass pyrolysis facility [71]). When activated carbon is produced by activation, it is transported to the adsorption site, which is in the oil sands operations. It is assumed that trucks used for biomass transportation are used again for transporting activated carbon (different route). The lifetime of the entire plant including pyrolysis unit, activation unit, and off-gas capture unit is 25 years as the lifetime for a typical pyrolysis unit is between 20 to 30 years [72].

Similar to the field production of activated carbon, slow pyrolysis converts the dried biomass to biochar, bio-oil, and syngas. Bio-oil is recycled and added to biomass to increase the pyrolysis yield up to 31% [10]. Syngas is used as fuel for heat and power cogeneration by the combined heat and power unit (CHP) and biochar is brought to the activation site. By using produced syngas from pyrolysis site as fuel, the combined heat and power unit generates heat and electricity. The power efficiency and heat-power ratio of CHP are assumed to be 35% and 0.5, respectively [73, 74]. Part of the generated electricity is used for biomass preparation and the remaining part can be either used on site for lighting and heating or sold to the grid.

By steam activation biochar is converted to activated carbon. Burn-off is assumed to be 30% (biochar mass basis) [10]. Because a reliable source of data for energy requirement, cost and

amount of released emissions for activation site was not found, it is assumed that the activation unit is the same as the pyrolysis unit (see section 3-5).

All other units of this scenario, including adsorption, sequestration, landfill capture and utilization, are the same as the field biomass preparation scenario (see Section 3.2.1 and 3.2.2).

Comparing flow diagrams of the field and factory scenarios indicates that in all the scenarios syngas is one of the by-products of the pyrolysis unit process. In the factory scenarios syngas is used in a combined heat and power system to produce both heat and electricity, however, in the field scenarios syngas is combusted in a combustor to produce heat for the boiler. In the factory scenarios forest residues are collected and transported to a central location to be pyrolyzed and activated. While, in the field scenarios biomass is pyrolyzed and activated in mobile units in the field. Because the field unit is 20 times smaller than the centralized factory, in the factory scenarios the amount of produced syngas is larger. Consequently, the use of the produced syngas in the field and factory scenarios will be different. The centralized facility can make use of the combined heat and power system, while, using a combined heat and power system in this small scale is not economically beneficial due to the smaller amount of syngas [37]. Hence, in the field scenarios syngas is combusted in the combustor to produce heat and heat is used in the boiler to satisfy the demand for steam for activation of biochar. Because the amount of produced steam in the boiler exceeds the demand of activation unit process, (see Chapter 5) the extra amount of steam is used in the steam turbine to produce electricity, which can be used in the field for lighting or heating purposes.

3.4 Life cycle assessment model

LCA model is used to identify the impacts of a product on the environment throughout its entire life cycle including the extraction of raw materials, the processing of raw materials, transportation and distribution of the product to the consumer, use of the product by the consumer, and disposal of the materials. LCA involve collection, validation, verification, assessment and interpretation of environmental data [16].

Developing an LCA starts with defining a functional unit for doing the calculations. A functional unit is a quantified description of the performance of the product systems, which is used as a basis of calculation. The functional unit is the central part of any life cycle assessment, as it provides a reference that normalizes all other data in the assessment process [75]. In this study, the capacity of the factory biomass preparation scenarios is 500 Mg biomass/day with a lifetime of 25 years (large scale). For the field biomass preparation scenarios the capacity is 25 Mg biomass/day with the lifetime of 5 years (small scale). The functional unit is one m³ of treated water.

Allocation is necessary when more than one material flow enters or leaves a process or when a specific product has different functions (different products or one product with different functions). In these cases it is necessary to distribute the required energy and material inputs and outputs [76]. In this study, the allocation for pyrolysis unit is 31% (wt/wt) biochar yield, syngas yield 30% (wt/wt), and distillate yield 34% (wt/wt) and for activation unit burn-off is 30% (wt/wt) activated carbon [10]. These values are the basis for the calculations. The effect of changing biochar and activation yields will be examined in the sensitivity analysis.

3.5 Data collection and limitations

The data that is collected on site (e.g. measurement, interviews, annual reports, from company) is called primary data, while, secondary data are from generic sources (e.g. LCA databases, previous LCA studies). For this study on-site source of data (primary data) was not available as it requires receiving data from industry and companies are usually not willing to provide detailed data of different unit processes. Moreover, because these sets of processes either for the field, or factory scenarios are new and these methods have not been employed so far, it is not possible to have access to on-site source of data. Therefore, for conducting this study secondary data from generic sources including LCA databases, previous LCA studies, published papers and theses, and official reports is used. Obtaining the most related and reliable data from different databases is always the goal. However, because a reliable source of data for energy requirement, cost and the amount of released emissions for activation unit was not found, it is assumed that the activation unit is the same as mobile pyrolysis unit with the same capacity for all the scenarios. This assumption seems logical as usually the same reactor is used for both pyrolysis and activation processes and the difference is usually the operating conditions (e.g. temperature and gas flow rate) [77]. Moreover, in some studies pyrolysis and activation are combined [78, 79].

The sets of unit processes in Figures 3-2 to 3-5 are the proposed methods for activating forest residues to produce activated carbon and using activated carbon for water treatment in oil sands operations. For choosing different unit processes the feedstock, products, and their performance are considered. For each unit process the next unit process is chosen based on the products of the previous unit process to use all by-products and minimize the energy requirement of the entire system. For instance in the field scenarios the produced syngas obtained from pyrolysis unit

process is combusted in the combustor to produce heat and the heat is used in the boiler to convert water to steam, which is required for activation unit process. Since, the amount of produced steam is more than what is required in activation unit the extra amount of steam is used in the steam turbine to produce electricity, which can be used in the field for lighting or heating purposes. In the factory scenarios the produced syngas obtain from pyrolysis unit process is used in the combined heat and power system to produce both heat and power. The generated heat and power are used in the biomass preparation and activation unit processes.

Although, for designing these sets of unit processes the adaptability of each unit process to its next and previous units is considered, technical feasibility of these methods has not been studied yet, which means the combination of unit processes shown in Figures 3-2 to 3-5 might not be technically feasible. Furthermore, some of the products can be used in different ways. As an example, syngas can be either combusted in a combustor, or used as a fuel in a combined heat and power generation unit, or any other unit process producing electricity. Although, in some cases there are some limitations that one unit process can be used but another unit process cannot be used (e.g. using syngas in different unit processes in the field and factory scenarios – see Section 3-3), mostly the alternatives are similar in terms of performance and efficiency. Therefore, the set of unit processes considered in these systems is one among a number of the possible sets that can be used to use the by-products and minimize the energy requirement of the entire system and there are alternative ways to fulfill this aim. These alternative sets of unit processes should be considered in the future studies in this area to define the best sets of unit processes.

The operating conditions for each unit process is chosen based on the literature and the experiments have been conducted in this area by my colleagues, Andrei Veksha and Waheed Zaman and other operating conditions are considered in the sensitivity analysis. For instance, the temperature of the pyrolysis unit is chosen to be 650°C as a number of researchers reported that the temperature should be chosen between 600°C to 750°C to optimize the amount of resulting biochar [96-98] (see Section 5-5).

The collected data will determine the amount of energy required, greenhouse gas emissions, and cost of using the specific amount of forest residues to produce biochar and meet the proposed removal limit of organics from water, applicable end-of-life disposal methods for the spent activated carbon after adsorption, and what are the most sensitive factors.

This study aims to develop an LCA model to estimate and quantify total energy requirement, GHG emissions, and cost of four scenarios including: factory–SAGD, field–SAGD, factory–mining, and field–mining. In order to compare the field biomass preparation scenario to the factory biomass preparation and SAGD produced water treatment with mining. The values of the main inputs (assumptions) of this model are listed in Table 3-1.

Table 3-1 The values of the main inputs of the field and factory scenarios.

Parameter	Value (field scenarios)	Value (factory scenarios)	Source
Diesel price (\$/MJ) March 2014	0.038	0.038	[46]
Diesel emissions (kg CO _{2e} /MJ)	0.070	0.070	[80]
Chipping cost (\$/Mg)	7.14	3.57	[81]
Transportation emissions (kg CO ₂ /Mg)	0.338	0.338	[82]
Pyrolysis yield (%) per 1 Mg biomass	31	31	[10]
Syngas yield (%) per 1 Mg biomass	30	30	[10]
Distillate yield (%) per 1 Mg biomass	34	34	[10]
Efficiency of steam turbine (%)	35	-	[67]
Steam-power ratio (kg steam/ hr. kWe)	17.65	-	[83]
Natural gas price (\$/MJ) - March 2014	0.006	-	[84]
Burn-off (%) – per 1 Mg biochar	30	30	[10]
SAGD produced water organics average concentration (mg/L)	1020	1020	* ¹
Organics removal level (%) - SAGD	50	50	*
Organics removal capacity (g org/ kg AC) - SAGD	50	50	*
Tailing water organics average concentration (mg/L)	75	75	[5]
Organics removal level (%) – mining average amount	50	50	[5]
Organics removal capacity (g org/ kg AC) – mining average amount	50	50	[5]
C offset by landfilling (\$/Mg CO _{2e})	28	28	[5]
C content of activated carbon (%) – mass basis	85	85	[68]
Landfilling avoided N ₂ O (kg N ₂ O/Mg AC)	0.394	0.394	[17]
Off-gas capture efficiency (%)	75	75	[85]
CH ₄ in biogas (%) – mass basis	67.2	67.2	[5]
CO ₂ in biogas (%) – mass basis	32.8	32.8	[5]
CH ₄ conversion to CO ₂ (%) – mass basis	50	50	[5]
Labor working hours (h/day)	12	8	
Labor average annual income (\$/person)	120,000	80,000	[86]
Carbon application to soil rate (Mg C/ha)	5	5	[17]
C retained in storage (%)	85	85	[17]

*¹ The results are obtained through a set of experiments conducted by my colleagues, Andrei Veksha and Waheed Zaman.

3.6 Calculation procedure

The model is developed in Microsoft Excel 2013. The LCA model employs a life cycle inventory methodology used to quantify the energy in MJ/day, MJ/day.Mg dry biomass, and MJ/day. m³ of treated water; GHG emissions in kg CO_{2e} /day, kg CO_{2e} /day.Mg dry biomass, and kg CO_{2e} /day. m³ of treated water: and cost in CAD/day, CAD/day.Mg dry biomass, and CAD/day. m³ of treated water. Figure 3-6 shows how the LCA model works:

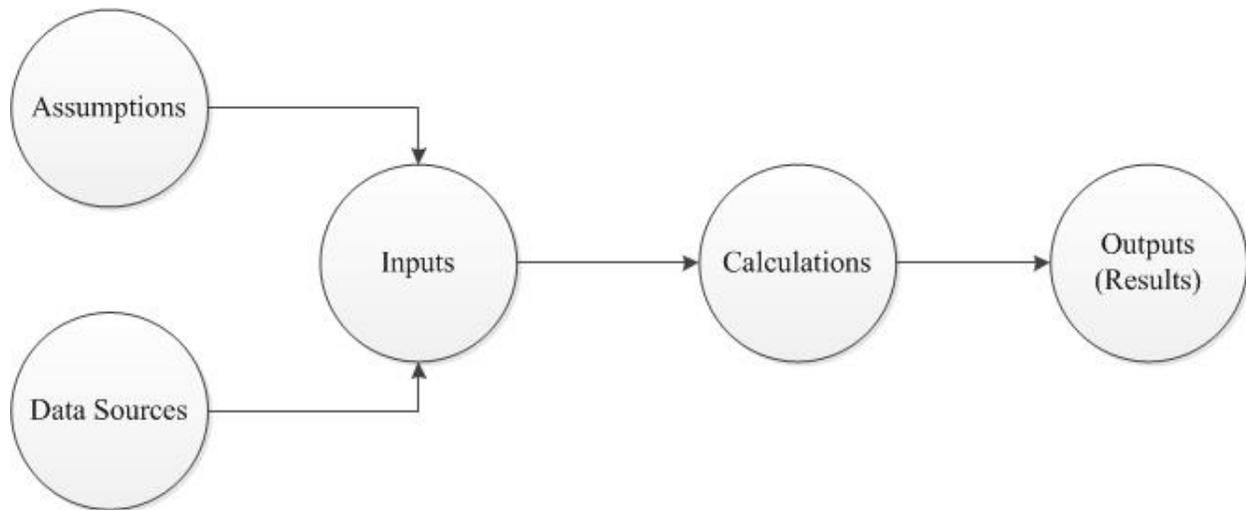


Figure 3-6 Different stages of the LCA model.

As this figure shows the inputs of the LCA model are obtained from data sources and assumptions. The model receives inputs, does calculations and provides outputs, which are results of the study.

The amount of emissions for each unit process is calculated based on collected data and by employing mass balances when the chemical reactions happened in the unit process are known. Likewise, the energy requirements of each unit process are calculated based on the collected data

and applying energy balances. For some of the unit processes such as pyrolysis and activation energy requirement and emissions are directly extracted from the literature, while, for others such as combined heat and power unit the energy requirement is calculated by applying energy balance and based on data in literature. In this study, energy requirement is the amount of energy provided by external sources of energy such as fuels and if a unit process satisfies the energy demand of another unit process (e.g. the combined heat and power unit uses the syngas produced by pyrolysis unit as a source of energy) this amount is not considered as energy requirement of the unit process. As Figures 3-2 to 3-5 show a number of unit processes produce energy (e.g. CHP and steam turbine). This means that they fulfill the demand for fossil fuel sources (mainly natural gas) for energy generation. For these units the energy offset is subtracted from the total cost. The value for energy offset is calculated by multiplying the amount of produced energy by the price of natural gas per unit of energy (see Table 3-1 and Appendix A) showing the amount of money should be paid to produce the amount of energy produced by these units (natural gas as fuel see Equation 3-10). In order to measure changes in the price level of fuels or convert Canadian dollars in previous years into 2014 Canadian dollar, *consumer price indexes* (CPI) are used. There are several ways to measure price changes, among these methods, CPI is one of the most straightforward ones and has wide-spread use [87]. Equation 3-5 shows how price of a good in one year can be converted to the price of the same good in another year:

$$\frac{CPI_{year1}}{CPI_{year2}} = \frac{Price_{year1}}{Price_{year2}} \tag{3-5}$$

The CPI in Canadian dollar for different years can be found on the website of Bank of Canada [88].

The energy requirement of each unit process is calculated by the Equation 3-6:

$$\text{Energy requirement} = \text{Energy}_{\text{input}} - \text{Energy}_{\text{output}} \quad 3-6$$

The GHG emissions of unit processes are calculated by using the Equation 3-7:

$$\text{Emissions (Mg CO}_{2\text{eq})} = \sum_i (M_i \times GWP_i) \quad 3-7$$

where M_i is mass of component i (kg) and GWP_i is its global warming potential ($\frac{\text{kg CO}_{2\text{eq}}}{\text{kg}_i}$). A

sample of calculation for energy requirement, emissions, and cost is in Appendix A.

Pyrolysis yield is defined as the percentage of the remaining mass after pyrolysis over the initial mass of biomass:

$$\text{Pyrolysis yield (\%)} = \frac{\text{mass of biochar}}{\text{mass of biomass}} \times 100 \quad 3-8$$

Activation burn-off is defined as the mass removed from biochar during the activation in relation to the initial mass of biochar [2]:

$$\text{Activation burn - off(\%)} = \frac{\text{mass of biochar} - \text{mass of activated carbon}}{\text{mass of biochar}} \times 100 = 100 - \text{Activation yield (\%)} \quad 3-9$$

Total yield is defined as the mass of biomass converted to the activated carbon:

$$\text{Total yield} = \frac{\text{mass of AC}}{\text{mass of biomass}} \times 100 \quad 3-10$$

$$\text{Cost} = \text{Capital cost} + \text{Operation cost} - \text{Carbon offset} - \text{Energy offset} \quad 3-11$$

where, carbon offset is for a unit process that reduces the emissions (e.g. sequestration) and energy offset is for a unit process which produces energy (e.g. CHP and steam turbine).

A sensitivity analysis is required to find out how the uncertainty in different inputs (e.g. pyrolysis and activation yields, biomass moisture content) can change the results (output) of the model conducting a sensitivity analysis is crucial. Sensitivity analysis is the study of how uncertainty in the outputs can be related to different sources of uncertainty in the inputs of model, which helps research and development to focus on improving these factors to achieve desired results [89]. Thus, the purpose of conducting a sensitivity analysis is finding out which parameters need to be considered to reduce total energy requirement, GHG emissions, and cost of different scenarios.

Chapter Four: Results

In this chapter the total energy requirement, GHG emissions, and cost of different scenarios has been calculated and the results are compared with the previous studies conducted in this area. The relationships between different parameters of the LCA system and final results are discussed in detail. The discussion will begin with the relationship between burn-off and adsorption capacity. By finding this relationship and using it along with all assumptions as inputs of the LCA model, the outputs (energy requirement, emissions, and cost) have been calculated. In this chapter results are shown in two ways: for each unit process and the total amount.

4.1 Burn-off versus adsorption capacity

A laboratory study conducted by my colleagues, Andrei Veksha and Waheed Zaman, in Laboratory for Environmental Catalytic Applications (LECA) research group has found a relationship between burn-off and adsorption capacity for the AC prepared from biomass in our laboratory (see Figure 4-1). As this method is scaled up and/or other methods developed, the relationship between burn-off and adsorption capacity may change. Thus this relationship is given just to show what is currently possible. The experimental procedure to determine this relationship is explained below:

At room temperature, 1.5 g biochar was purged in reactor with N₂ with gas flow rate of 100 ml/min for one hour. After one hour sample was heated to 800°C at 10°C/min. Then, nitrogen gas is switched to CO₂ (also 100 ml/min) for activation times of 0.3, 1.0, 1.8, and 3.6 h. After activation, the gas is switched to N₂ and the reactor is cooled to 70°C. Non-activated biochar was prepared at same temperature (800°C) by holding the sample at 800°C for 1 h in N₂ flow (instead

of CO₂). The samples washed with 1 M HCl and washed samples are filtered with deionized water to reach pH \cong 5.5. Then they are heated with heating rate of 10°C/min in N₂ flow with flow rate of 300 ml/min until 900°C and hold for one hour at this temperature. Finally, samples are weighed, stored in sealed bags, and characterized.

Figure 4-1 shows how changing activation burn-off influences adsorption capacity. By curve fitting an equation showing the approximate relationship between burn-off and adsorption capacity can be found (Equation 4-1). This equation was used as an input for the LCA model. The impact of activation yield (and thus, burn-off) and removal level on the final results will be tested later in this chapter and in the sensitivity analysis (see Chapter 5).

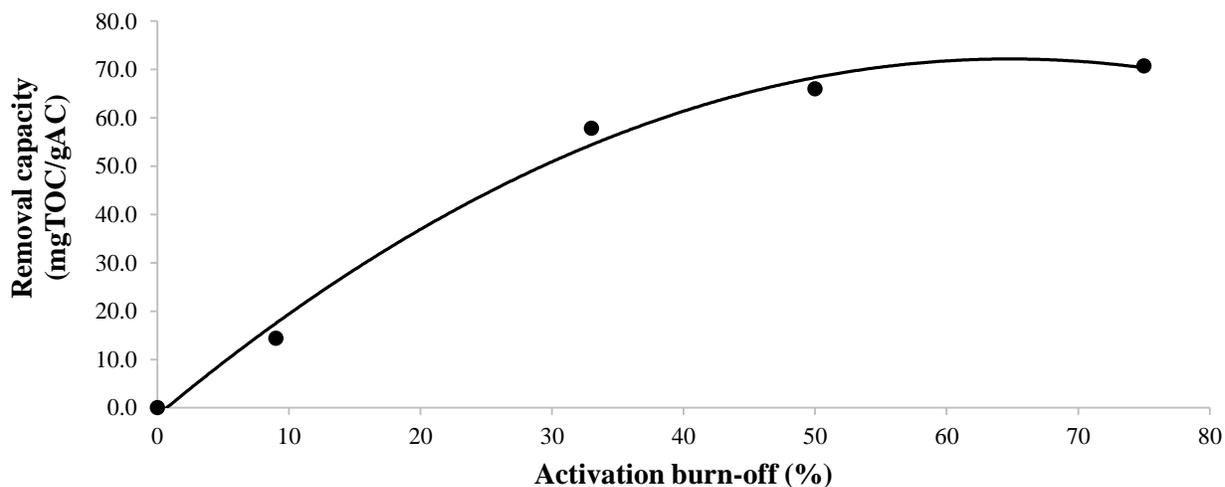


Figure 4-1 Effect of changing activation burn-off on adsorption of organics on activated carbon at room temperature.

In Figure 4-1 markers are data and line is the polynomial fit. The equations indicating the relationship between removal capacity (mg TOC/g AC) and burn-off, which are obtained by curve fitting are:

$$\text{Removal} \left(\frac{\text{mg TOC}}{\text{g AC}} \right) = -0.02(\text{burn} - \text{off}(\%))^2 + 2.3(\text{burn} - \text{off}(\%)) - 1.6 \quad 4-1$$

Equation 4-2 shows the relationship between burn-off and pyrolysis yield:

$$\text{Activation burn} - \text{off} (\%) = \frac{\text{Pyrolysis yield}(\%) - \text{Yield}_{\text{AC}}(\%)}{\text{Pyrolysis yield}(\%)} \quad 4-2$$

$$\text{Yield}_{\text{AC}}(\%) = \frac{\text{mass of AC}}{\text{mass of biomass}} \times 100 \quad 4-3$$

Because activation burn-off (and thus, activation yield) and adsorption capacity are directly related, the effect of adsorption capacity on final results is not required as it is explored while examining the effect of changing activation yield on results (see Chapter 5).

4.2 Outputs of the LCA model

Total costs, energy requirement, and emissions of different unit processes of the field and factory scenarios are shown in Figures 4-3 to 4-8. The category named “other” in the field scenarios includes drying, crushing and syngas combustion and in the factory scenarios includes transportation, off-gas capture and crushing. The capacities of mobile pyrolysis (field scenario) and pyrolysis plant (factory scenario) are assumed to be 25 and 500 Mg wet biomass per day with lifetimes of 5 and 25 years, respectively (see Chapter 3). The capital cost for each scenario is divided throughout its lifetime instead of paying the entire amount at the beginning in order to compare the results more easily as capacities are daily (because, the capacity is Mg/day all amount are daily). The cost is in 2014 Canadian dollar (CAD) and IPCC 2007 [56] was used as

an impact assessment method. The impact assessment category is global warming for a time horizon of 100 years. Labor cost in the following sections is assumed to be only labor income and their benefit or any other type of cost is not considered as it usually depends on the employer and the company they are working for. However, in the Discussion (Section 5-5) it is discussed whether addition of benefits on top of the salary will make a significant change in the results.

Figures 4-2 (a) to (c) represent total energy requirement, GHG emissions, and cost of the field scenarios for different unit processes per m³ of treated water.

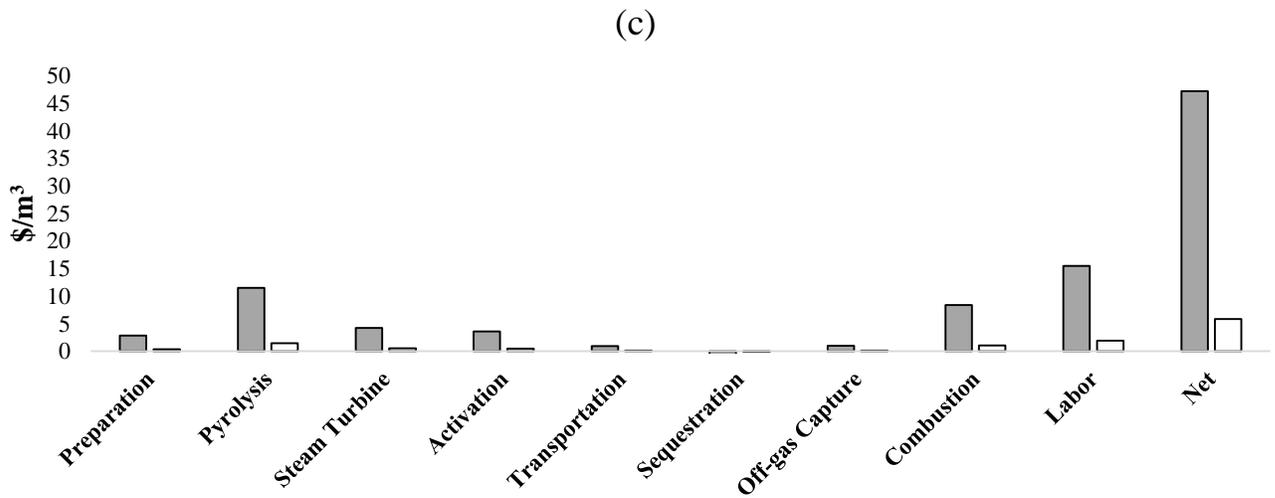
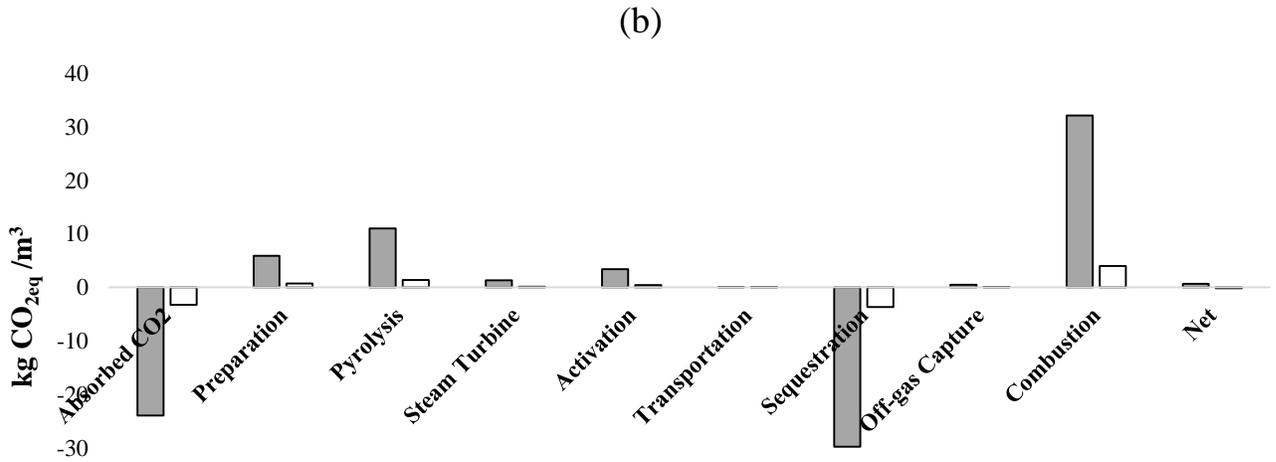
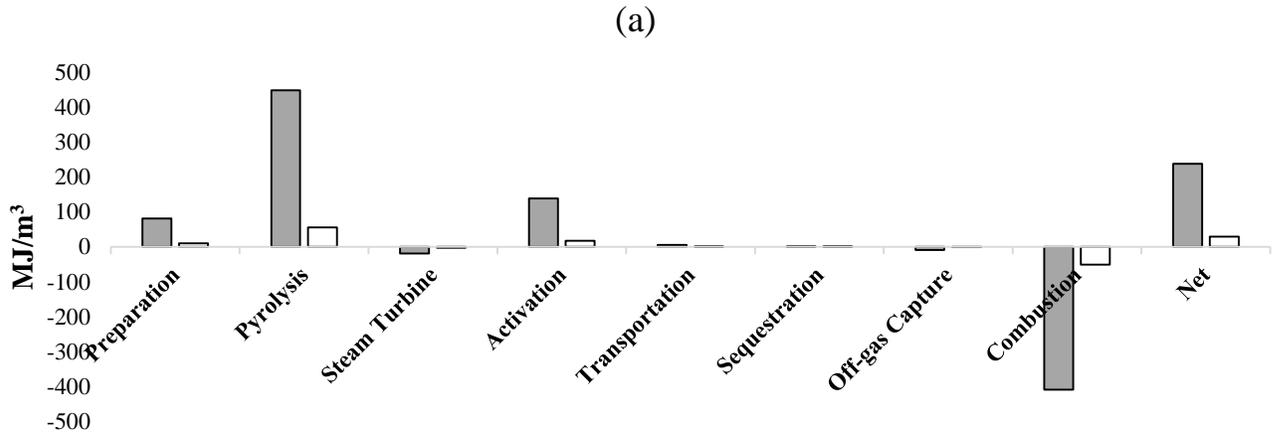


Figure 4-2 (a) Energy requirement of field scenarios for different unit processes. (b) Emissions of field scenarios for different unit processes. (c) Cost of field scenarios for different unit processes. The gray bars show SAGD and white bars show Mining.

As these figures show energy requirement, emissions, and cost of different unit processes for mining is lower than SAGD as the amount of treated water is larger in mining operations compared to SAGD.

According to Figure 4-2(a) pyrolysis consumes the highest amount of energy. The negative value for combustion unit is because of the energy produced by combusting syngas. Thus, reducing the energy requirement of mobile pyrolysis can lead to considerable reduction in total energy requirement of the field scenarios. Based on Figure 4-2(b) combustion is associated with the highest level of GHG emissions and sequestration unit offers significant GHG emissions reduction (more than 200 Mg CO_{2eq} per 1 Mg of biomass). Therefore, sequestration is performing an important role in reduction total GHG emission of the field scenarios (which is the benefit of sequestration). Figure 4-2(c) indicates that labor cost is the main factor determining cost of the field scenario and pyrolysis unit is after in terms of importance. Thus, changing labor cost can considerably influence the total cost of the field scenarios and addition of benefits to salary will have a significant impact so an estimate of benefits is important.

Figures 4-3 (a) to (c) show total energy requirement, GHG emissions, and cost of the factory scenarios for different unit processes per m³ of treated water.

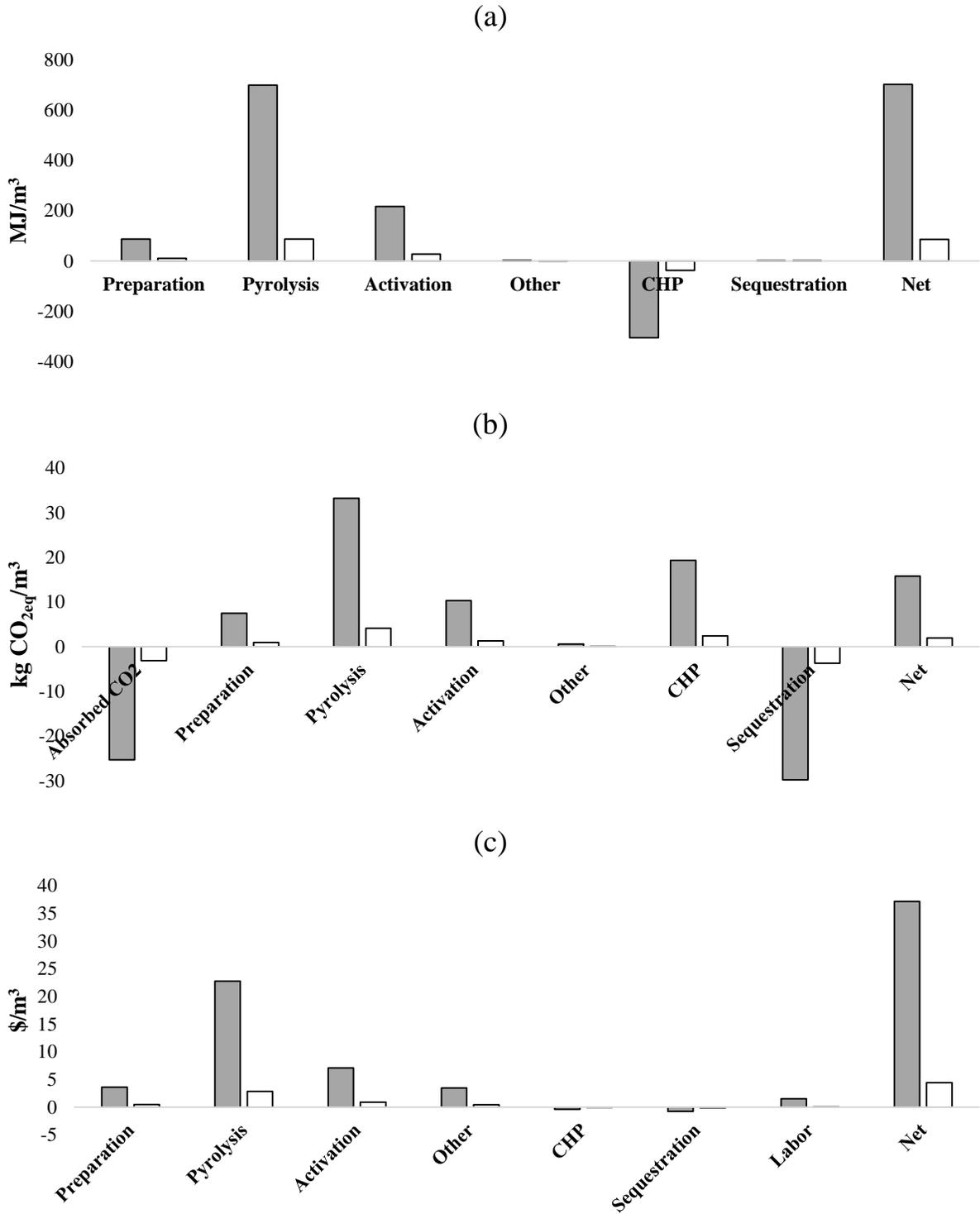


Figure 4-3 (a) Energy requirement of factory scenarios for different unit processes. (b) Emissions of factory scenarios for different unit processes. (c) Cost of factory scenarios for different unit processes. The gray bars show SAGD and white bars show Mining (Other: transportation, off-gas capture and crushing CHP: combined heat and power).

As these figures show similar to the field scenarios in the factory scenarios energy requirement, emissions, and cost of different unit processes for mining is lower than SAGD as the amount of treated water is larger in mining operations compared to SAGD.

With respect to Figure 4-3(a) pyrolysis requires the highest amount of energy and a negative value for energy requirement of combined heat and power unit process is due to energy generation of this unit. Based on Figure 4-3(b) the pyrolysis unit is associated with the highest level of GHG emissions and the sequestration unit offers considerable GHG emissions reduction. Figure 4-3(c) shows that the pyrolysis unit is the main factor determining the cost of the factory scenario and unlike the field scenario, labor income is a small proportion of the total cost of this scenario. In general, Figures 4-3(a) to (c) indicate that the pyrolysis unit is the most important unit process for the factory scenarios and has significant impact on the final results. Therefore, any change in energy requirement, GHG emissions, and cost of this unit process can strongly affect total amounts.

As Figures 4-2(a) to 4-3(c) indicate pyrolysis seems to be one the most important unit processes for all scenarios. Furthermore, in many of the cases energy requirement and emissions seem to be related as when energy requirement of a unit process is high, the emissions of it is high too. Because, burning fuel to satisfy the energy demand of unit processes is associated with emissions and the more fuel is used, the more emissions released.

Since the objective of this project is water treatment in oil sands operations, normalization of net values based on either the amount of treated water, or mass of feedstock can be a beneficial

approach. Net costs, energy requirement, and emissions per 1 Mg of dry biomass and 1 m³ of treated water are provided in the Tables 4-1 and 4-2.

Table 4-1 Daily amount of required energy, released emissions, and cost of each scenario per 1 Mg of dry biomass.

Scenario	Energy (MJ/ Mg dry biomass)	Emissions (kg CO_{2e}/ Mg dry biomass)	Cost (\$/Mg dry biomass)
Field - SAGD	2163±197	85±6	428±22
Factory - SAGD	6366±689	143±14	336±24
Field - Mining	2174±193	86±9	427±21
Factory - Mining	6377±702	144±15	337±24

Table 4-2 Daily amount of required energy, released emissions, and cost of each scenario per 1 m³ treated water.

Scenario	Energy (MJ/ m³ treated water)	Emissions (kg CO_{2e}/ m³ treated water)	Cost (\$/m³ treated water)
Field - SAGD	239±21	4±0.2	47±2.7
Factory - SAGD	703±73	16±1.5	37±2.2
Field - Mining	30±3	0±0.4	6±0.3
Factory - Mining	87±10	2±0.6	5±0.4

As Table 4-1 shows the energy requirement and emissions per Mg dry biomass of the field scenarios are less than factory ones. Whereas, costs of the factory scenarios per Mg dry biomass are less than the field scenarios. The reason is discussed in the next chapter (see Discussions in Chapter 5). Thus, the field scenarios are the best scenarios from a GHG emissions perspective, while, the cheapest ones are the factory scenarios.

According to the Table 4-2, field–mining requires the least energy and releases the lowest level of emissions. Whereas, factory–SAGD needs the biggest amount of energy and is associated with the highest level of emissions and field–SAGD is the most expensive one. As this table

shows the mining scenarios in general require less energy, produce less GHG emissions, and are associated with lower cost. Because concentration of organics in tailings ponds in mining operations is more than 10 times lower than SAGD operations. Both Table 4-1 and 4-2 indicate that energy requirement and emissions of the field scenarios are less than the factory scenarios. While, costs of the factory scenarios are less than the field scenarios. Comparing Table 4-1 with Table 4-2 demonstrates why choosing the different basis has an important effect on the results presented. Therefore, in order to present illustrative results, the basis should be chosen with reference to the aim of study, which is water treatment.

Because, biomass source used in this study (forest residues) is almost free (in most cases forestry industries are even willing to pay for disposing of forest residues [5]) and the purpose of this project is water treatment, the results which are based on volume of treated water are more applicable. Therefore, the final conclusion should be drawn based on Table 4-2. As this Table indicates “factory – mining” is the most economical scenario and “field – mining” is associated with the least GHG emissions and energy requirement, and thus the best scenarios from a GHG emissions perspective.

The uncertainty in the final results is a result of uncertainty in inputs. The uncertainties of the inputs are usually mentioned in the data source used for obtaining the specific input. By considering uncertainty of different inputs such as pyrolysis and activation yields and doing the calculations for different values of inputs the uncertainty of outputs (results) is calculated. When the base value (shown in Tables 4-1 and 4-2) is not exactly at the middle of the range of result values (minimum to maximum values of the results obtained by changing the inputs), the maximum value is reported as uncertainty. For instance, for energy requirement of factory-

SAGD scenario the maximum value is 776 and the minimum value is 635 and the base value is 703 thus, the uncertainty is reported to be ± 73 .

Table 4-3 shows daily and annual amount of produced water in Alberta for SAGD and mining operations. Based on these values, the number of plants required to produce AC and amount of treated water can be calculated.

Table 4-3 Amount of produced water in Alberta for different oil sands technologies [6, 11, 90].

Item	Unit	SAGD	Mining
Oil production	m ³ oil/day	119,250	135,150
Produced water per oil recovered	m ³ water/ m ³ oil	2.7	2.5
Produced water	m ³ water/day	321,975	337,875

Table 4-4 Calculated water treatment capacity and number of required units for different scenarios.

Scenario	Produced water (m³/day)	Calculated treatment capacity (m³/day)	Required units
Factory-SAGD	321,975	3991	80
Factory–Mining	337,875	28,010	12
Field-SAGD	321,975	195	1651
Field-Mining	337,875	1367	247

Based on this table water treatment in mining operations seems more feasible (comparing factory-SAGD with factory-mining and field-SAGD with field-mining) because of lower concentration of organics in tailing water and thus, larger water treatment capacity of the mining scenarios. On the other hand, building 12 units in capacity of 500 Mg/day or 247 units in capacity of 25 Mg/day still seems not feasible (See Discussion in Chapter 5).

Steam turbine unit in the field scenarios and CHP in the factory scenarios produce extra amount of energy by burning syngas. This means that they fulfill the demand for fossil fuel sources (mainly natural gas) for energy generation, which leads to GHG emissions reduction. Another method to estimate this reduction is calculation of the emissions released by using natural gas combined-cycle (NGCC) for producing this amount of energy and subtract this amount from total emissions [91]. Table 4-5 shows GHG emissions per m³ treated water for all the scenarios with and without subtracting NGCC emissions.

Table 4-5 Total GHG emissions per m³ treated water of all the scenarios with and without subtracting NGCC emissions.

Scenario	Without subtracting NGCC (kgCO_{2e}/m³.day)	With subtracting NGCC (kgCO_{2e}/m³.day)
Factory - SAGD	16	3
Factory - Mining	2	0.4
Field - SAGD	4	4
Field - Mining	3	-1

Based on Table 4-5 this subtraction has bigger effect on factory scenarios in comparison with field scenarios. Because, combined heat and power unit in the factory scenarios produces larger amount of energy (more than 300 times) compared to steam turbine in the field scenarios (because of the difference in the mass of produced syngas in the field and factory scenarios).

4.3 Validation of the results

Comparing the obtained results with the results of the published works in this area is an approach to examine the validity of the results. The comparison between the current study and the previous researches [5, 16] indicates that the main difference between these studies is the removal level. Thus, it is important to explore how changing the removal level influences the total emissions of

different scenarios. Figure 4-4 shows the effect of changing removal level on emissions of different scenarios.

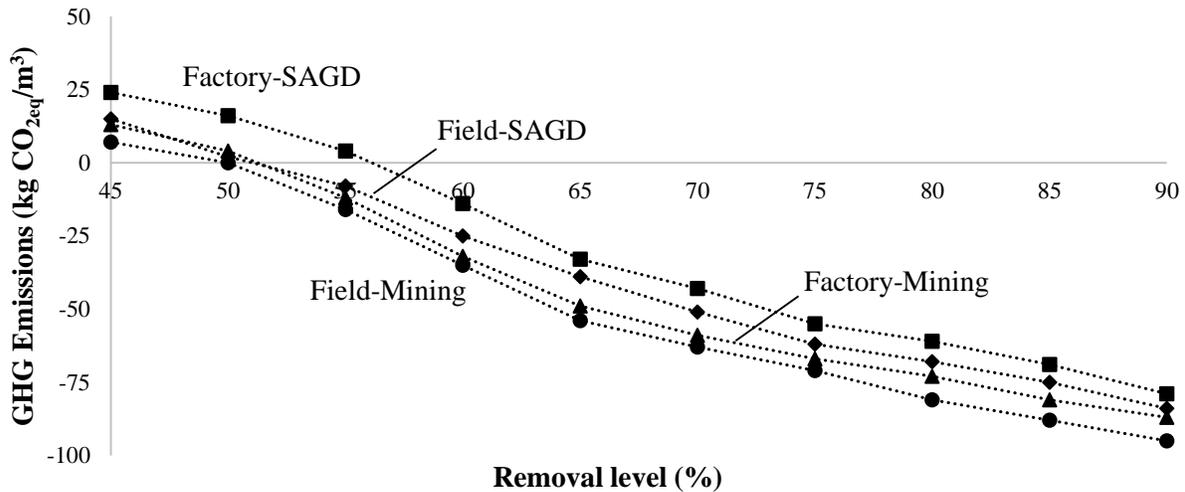


Figure 4-4 Effect of changing removal on GHG emissions of different scenarios.

Based on the Figure 4-4 at 60% removal all the scenarios have negative net emissions. Between 50% to 60% removal, some of the scenarios show negative emissions and before 50% all the scenarios have positive emissions. This figure also indicates by increasing removal the emissions of all the scenarios decreases. Because removing more organics results in the larger GHG emissions reduction in the sequestration unit process (see Chapter 5).

The removal for SAGD water treatment is reported to be up to 75% [5]. For the SAGD scenarios the emissions become negative for removal $\geq 55\%$. Based on the lab results, at 70% removal, the burn-off is approximately 54% and at 75% removal the burn-off is 65%. Because, burn-off can change from 30% to 70% [10], up to 75% removal for SAGD is feasible. Figure 4-4 also shows that at higher removal levels ($\geq 85\%$) the total emissions of all the scenarios are almost the same

(less than 5% difference), which means that at higher removal levels all the scenarios are equally promising from a GHG emissions perspective and provide almost the same amount of reduction in emissions. Therefore, currently the maximum achievable GHG reduction by using these systems is at 75% removal and range between -55 to -60 kg CO_{2eq}/m³ for SAGD scenarios and -73 to -76 kg CO_{2eq}/m³ for mining scenarios.

Table 4-6 shows comparison of estimated net emissions of different studies in this area. The base points show the results obtained by different studies in this area with different conditions and assumptions.

Table 4-6. Comparison of estimated net emissions of different studies in kg CO_{2eq}/m³ of treated water.

	SAGD			Mining	
	This study	Kimetu et al.	Bess-Ouko	This study	Kimetu et al.
Base Points	16 to -60	-64	-8 to -66	2 to -76	-7
Bess-Ouko Conditions [16]	-5 to -84	-	-8 to -66	-	-
Kimetu et al. Conditions [5]	-12 to -91	-64	-	-29 to -97	-7

The study conducted in 2013 by Claudia Bess-Ouko [16], developed an LCA model to estimate the environmental and economic impacts of using different sources of biomass for water treatment in SAGD operations. Comparing the obtained results with the results of Bess-Ouko's study shows although the emissions are higher at the base points, by using conditions that Bess-Ouko has used, the calculated net emissions are almost in the same range reported in Bess-Ouko's study. In addition, the maximum emissions reduction estimated in this study is approximately 22% lower than the maximum amount reported in Bess-Ouko's study (-66 kg

$\text{CO}_{2\text{eq}}/\text{m}^3$). In Bess-Ouko's study it is assumed that biochar system is located close to the oil sands operations, which avoids the necessity of transporting activated carbon to oil sands operations and thus, reduces the emissions. However, as it will be discussed in Chapter 5, transportation has minor impact on emissions of different scenarios and thus, the effect of omitting activated carbon transportation is not considerable.

In addition, Bess-Ouko reported that the input significantly affects the final results is removal and transportation has minor effect on final results, which is in line with the results of this study as activation yield is directly related to removal and transportation also reported to have minor effect on final results. Bess-Ouko's work also showed that moisture content significantly influences the energy requirement of biochar system, which is the same conclusion drawn for the field scenarios.

Table 4-6 indicates that the net emissions reduction estimated in Kimetu et al.'s study [5] for SAGD produced water treatment is within range calculated in this study. For mining water treatment this amount is much higher (-7 compared to -29 to -97 $\text{kg CO}_{2\text{eq}}/\text{m}^3$). The reason of the difference between Kimetu et al.'s results and the obtained results seems to be that Kimetu's work assumed the emissions of biochar production systems to be -40 to -100 $\text{kg CO}_{2\text{eq}}/\text{Mg}$ biomass (reported in [17]) and used these values for doing calculations. By looking at the source [17], this amount is a rough amount obtained from using switchgrass and stover as feed. But, source of biomass in this study is aspen wood. Moreover, this paper has considered biochar system (biomass pyrolysis with biochar returned to soil) which is not the purpose of my study (using biomass to produce activated carbon for water treatment). It means that in this paper only pyrolysis of biochar is considered and after producing biochar, it is applied to soil for increasing

the fertility of soil. Therefore, their study is conducted for agricultural purposes, while, the purpose of this study is water treatment.

Because the main difference between the current study and the previous studies conducted in this area is the amount of removal level and the removal level has considerable effect on emissions of different scenarios (see Figure 4-4), it is important to discuss why 50% removal level is assumed in this study, notwithstanding the higher removals assumed in the previous studies.

A laboratory study conducted by my colleagues, Andrei Veksha and Waheed Zaman, in Laboratory for Environmental Catalytic Applications (LECA) research group has found a relationship between total yield and removal level for the AC prepared from biomass in our laboratory (see Figure 4-5). Figure 4-5 shows effect of changing total yield on removal level of organics on activated carbon at room temperature.

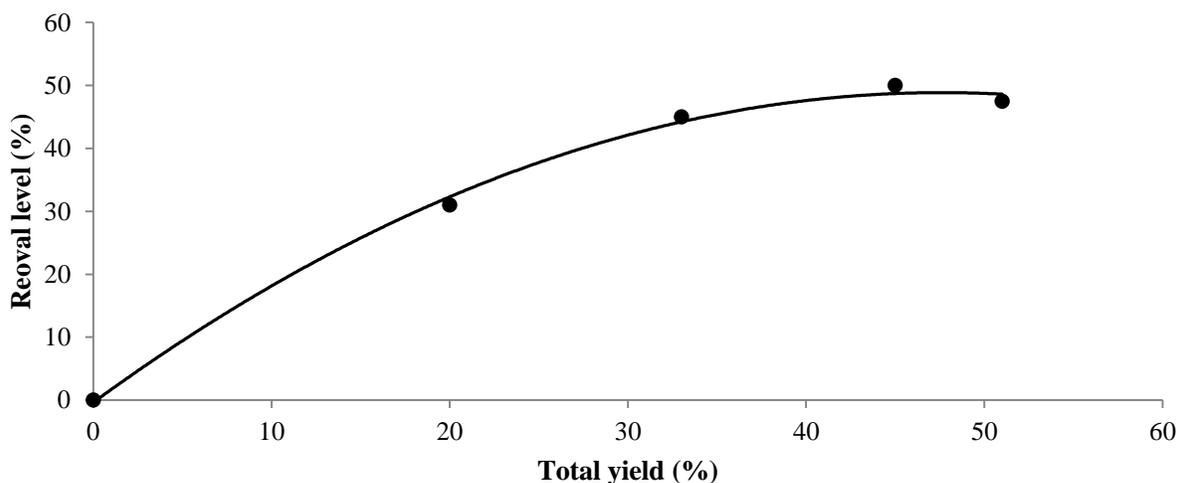


Figure 4-5 Effect of changing total yield on removal level of organics on activated carbon at room temperature.

In this figure markers are data and line is the polynomial fit. As Figure 4-5 shows before obtaining 50% removal, by increasing the total yield the removal level increases, while, after obtaining this amount the removal level decreases by increasing the total yield. Thus, 50% is the maximum removal level achieved in the lab for the system used in this study. However, the previous lab study was not comprehensive enough to define if higher values for the removal level are practically possible to achieve in the lab because as this figure shows there is only one data point after 50% removal. Furthermore, as this method is scaled up and/or other methods developed, the relationship between burn-off and adsorption capacity may change. Thus this relationship is given just to show what is currently possible. In this regard, 50% removal level is the maximum removal level we are certain that is achievable, however, comprehensive lab studies are required to ensure whether this value is the maximum removal level can be obtained by this method and if any improvement in one or a number of the unit processes can result in achieving higher removal levels.

The removal level assumed in this study is based on the laboratory study conducted in the Laboratory for Environmental Catalytic Applications (LECA) and is related to the different method, recycling bio-oil to increase the yield of pyrolysis process. This means that one of the reasons that the removal level assumed in this study differs from the previous studies in this area is different methods for pyrolysis the forest residues. Different methods for pyrolysis produce different biochars, which results in different activated carbons and thus, different removals. Therefore, in this study instead of assuming a value for the removal level and doing the calculations based on the assumed value the removal level is chosen with reference to the

previous lab study which makes the obtained results more realistic. Therefore, 50% removal is the maximum removal level has been achieved in the lab for the system used in this study.

Furthermore, in Bess-Ouko's study [16] the removal level is arbitrarily assumed as it is mentioned in [16]: "*A 60% organic carbon removal from the SAGD produced water stream was arbitrarily assigned as there was no data available to inform a removal rate which might be acceptable to meet standards for managing the maintenance of boiler tubes*". Higher removal levels in Kimetu et al.'s study [5] are based on the experiments that are different from what was done in our laboratory in terms of experimental method and procedure, biomass source (aspen wood versus lignite coal and commercial hardwood) and the adsorption conditions (e.g. temperature and time). Different systems, experimental procedures, biomass sources, and adsorption conditions leads to the different removal levels.

4.4 Summary

In this chapter outputs of the LCA model and energy requirement, GHG emissions, and cost of each unit process as well as total amounts were discussed. Based on the results the pyrolysis unit seems to be one of the most important unit processes for all the scenarios as it mostly accounts for more than 60% of the final results (energy requirement, emissions, and cost). Moreover, the field scenarios are more environmentally friendly, while, the cheapest ones are the factory scenarios. The emissions of the systems were calculated to be between 2 to 16 kgCO_{2e}/m³ for the factory scenarios and 0 to 4 kgCO_{2e}/m³ for the field scenarios. In addition, this study indicated that by increasing the removal amount up to 60% or more (at approximately 56% removal all the scenarios show negative emissions- see Figure 4-4), which is theoretically feasible (up to 75% is possible), the net GHG emissions of all the scenarios become negative. Therefore, at 75%

removal, the maximum feasible amount for the systems, the net emissions range between -55 to -76 kgCO_{2e}/m³.

Chapter Five: Sensitivity Analysis

The effect of changing inputs of the LCA model (e.g. pyrolysis yield, activation yield, biomass moisture content) on energy requirement, GHG emissions, and cost of each scenario is explored in this chapter and the results of the model will be discussed.

Each unit process has a main stream and a number of secondary streams. The main stream contains the main products of the unit process and the secondary streams contain the by-products. In this study the main stream of all unit processes is the stream which directly defines the amount of activated carbon (e.g. biochar in pyrolysis unit) as activated carbon plays the role of removing organics from water, which is the purpose of the project. Any change in the input that changes the amount of main stream of any unit process results in changing the amount of other streams in all other following unit processes because each unit process uses the main product of the previous unit process as feedstock. However, changing an input that changes the secondary streams, only results in changing the amount of streams in that specific unit process and does not have any effect on other unit processes. For instance, in this study biochar is the main stream in pyrolysis unit, which is used as feedstock of activation unit, and activated carbon is the main stream in activation unit process. But, bio-oil is a secondary stream and changing the amount of bio-oil only influences the pyrolysis unit.

The mass of produced activated carbon plays a key role in calculation of final results. Because mass of activated carbon defines the amount of organics removed from produced water and thus, the amount of treated water. Moreover, the amount of produced activated carbon is directly related to the capacity of both pyrolysis and activation (see how pyrolysis and activation yields

are calculated in Chapter 3). Therefore, how a change in an input changes the mass of activated carbon will be important to be considered in sensitivity analysis.

Since, changing activation burn-off (and thus activation yield) changes the removal capacity of organics (see Equation 4-1) by changing activation yield, removal capacity changes too and therefore, the effect of changing removal capacity is not considered in this study.

5.1 Energy

Figures 5-1 (a) to (c) represent effect of biomass moisture content (before drying) and pyrolysis and activation yields on total energy requirement of each scenario. These figures show the daily energy requirement of each scenario per m^3 of water that can be treated versus various inputs. The maximum values for moisture content in the following figures is assumed to be 40% as in both scenarios forest residues are stored before drying and typically biomass storage reduces the moisture content to at least 40% [82].

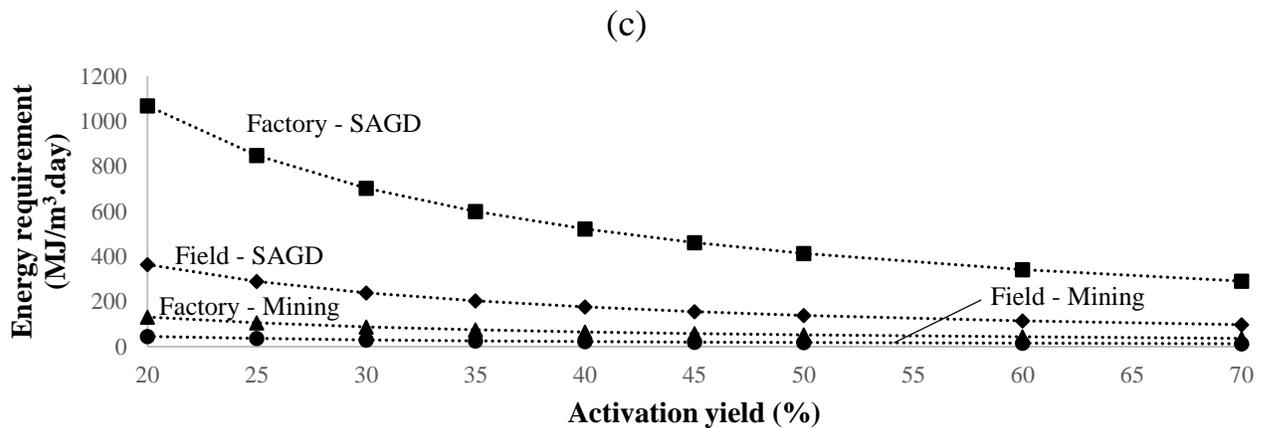
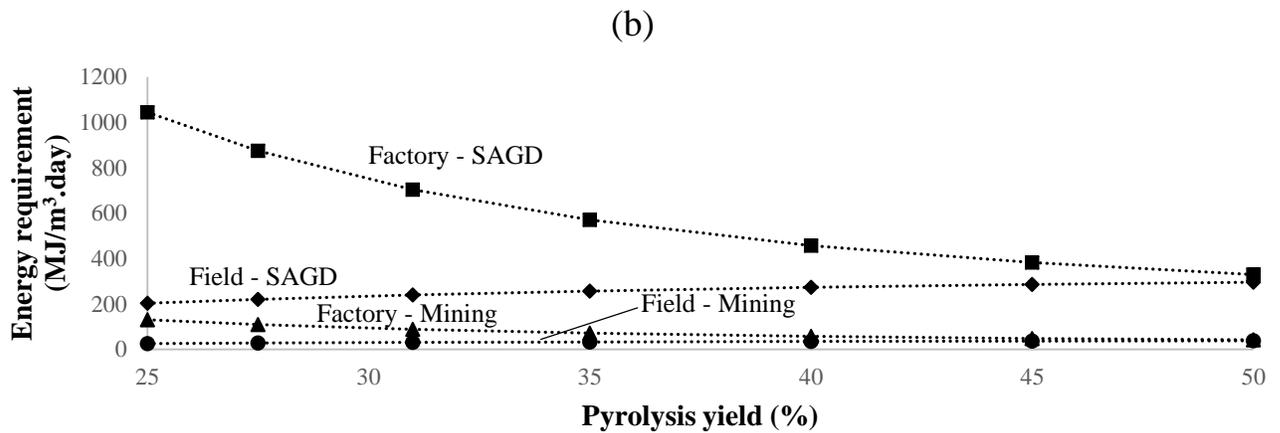
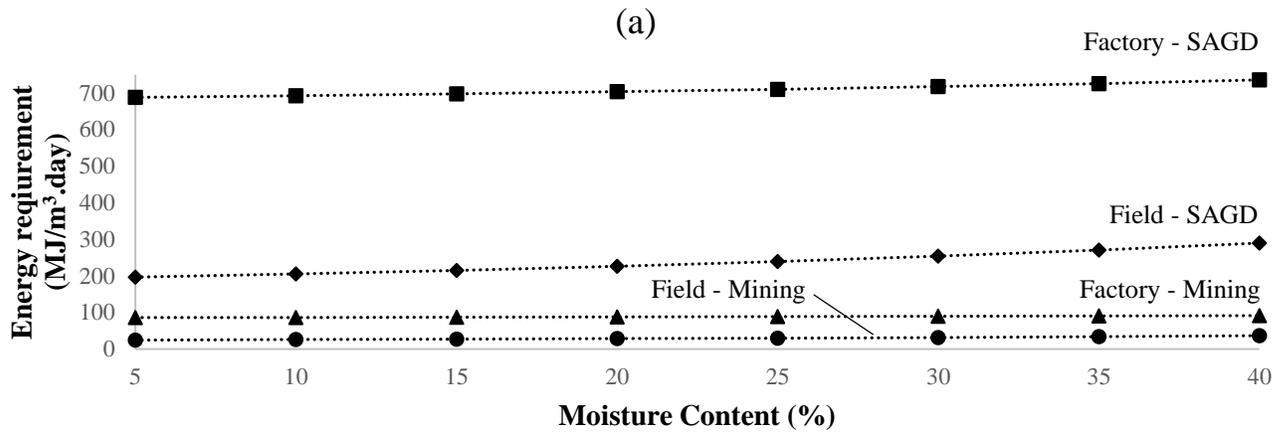


Figure 5-1(a) Effect of changing biomass moisture content on energy requirement of different scenarios. (b) Effect of changing pyrolysis yield on energy requirement of different scenarios. (c) Effect of changing activation yield on energy requirement of different scenarios.

A relationship between two variables is *direct* when both variables either increase, or decrease together. Similarly, two variables are *indirectly proportional* (also known as *inversely proportional*) when by increasing one of the variables another one decreases, and vice versa [92]. Based on Figure 5-1(a) relationship between biomass moisture content and energy requirement for all the scenarios is direct, because by increasing biomass moisture content more energy is required to decrease this amount to the satisfactory amount (3-5%), therefore, more fuel would be used to provide this energy (see Equations 5-1 and 5-2). Burning more fuel leads to an increase in GHG emissions and total cost of each scenario (see Figures 5-2(a) and 5-3(a)). According to Figure 5-1(a), the slope of field-SAGD curve is larger than factory-SAGD because the total energy requirement in the field scenarios is smaller, thus an increase in the required energy for drying is more considerable in the field scenarios. Furthermore, smaller numbers suggest that effect of moisture content on energy requirement of the factory scenarios are not significant (this will be discussed in the following sections).

As Figure 5-1(b) shows the energy requirement decreases with increasing pyrolysis yield for the factory scenario, while the opposite occurs for the field scenarios. For the factory scenarios this relationship is because of the amount of energy produced in the off-gas capture stage (negative energy requirement). Although, by increasing yield, mass of produced biochar increases, which requires more energy for operation and transportation, the activation unit produces bigger amount of activated carbon. The more activated carbon, the higher level of organics that can be removed, which leads to an increase in energy generation in off-gas capture stage. Similarly, for the field scenarios increasing yield of pyrolysis improves energy generation in off-gas capture stage, however, this amount is not enough to compensate for the increase in energy requirement

of operation and transportation as the capacity of the field scenarios is smaller compared to the factory scenarios. Thus, by increasing yield, net energy requirement of the field scenarios increases.

The slope of graphs indicates that changing pyrolysis yield has bigger impact on the SAGD scenarios compared to mining ones. In addition, by increasing yield, energy requirement of scenarios become closer and factory-SAGD scenario crosses field-SAGD scenario near 50% yield and factory – mining crosses field – mining at 50%. Thus, at higher pyrolysis yields the SAGD scenarios become more beneficial compared to lower yields and impact of biomass preparation method (factory vs. field) on energy requirement becomes minor. This figure also shows energy requirement of field – mining and factory – mining are the same for any pyrolysis yield bigger than 50%. However, achieving 50% pyrolysis yield or more is usually impossible as the carbon content of biomass sources are mostly less than 50% [23]. Moreover, Figure 5-1(b) offers increasing pyrolysis yield as a technical way to make the factory scenarios less energy-intensive and more economical.

The descending trend of the factory scenarios curves in Figure 5-1(b) suggests that by increasing pyrolysis yield the factory scenarios become more economical as by increasing yield energy requirement of the factory scenarios decreases. Thus, pyrolysis yield seems to be an important factor affecting energy requirement of different scenarios.

Figure 5-1(c) indicates that increasing activation yield leads to reduction in energy requirement in all the scenarios. The reason is that increasing activation yield produces larger amount of activated carbon and as it was discussed above improves energy production in off-gas capture

stage. Based on this Figure, by increasing activation yield, the difference between energy requirements of different scenarios decreases. Therefore, it is concluded that at higher activation yield (>50%) the difference between energy requirement of different scenarios becomes small compared to this difference at lower activation yield values especially for the mining scenarios. In addition, slopes represent that activation yield has the biggest influence on energy requirement of factory–SAGD scenario. Therefore, at higher activation yields the SAGD scenarios become more beneficial compared to lower yields. At any activation yield greater than 50%, the mining scenarios are the same in terms of energy requirement. The maximum activation yield depends on many factors (e.g. biochar composition, temperature), but theoretically it cannot be more than 70% as carbon content of biochar is usually around this amount [93].

The descending trend of curves indicates that by increasing activation yield all the scenarios become more economical as by increasing activation yield energy requirement of all the scenarios decreases. Thus, activation yield as well as pyrolysis yield are an important factor affecting energy requirement of different scenarios.

5.2 Emissions

In general, by increasing energy requirement of a unit process, more fuel is required to satisfy the demand, which leads to an increase in emissions of the unit process. Figures 5-2(a) to 5-2(c) show the effect of biomass moisture content and pyrolysis and activation yields on total emissions of each scenario. These figures show daily emissions of each scenario per m³ of water that can be treated versus various inputs.

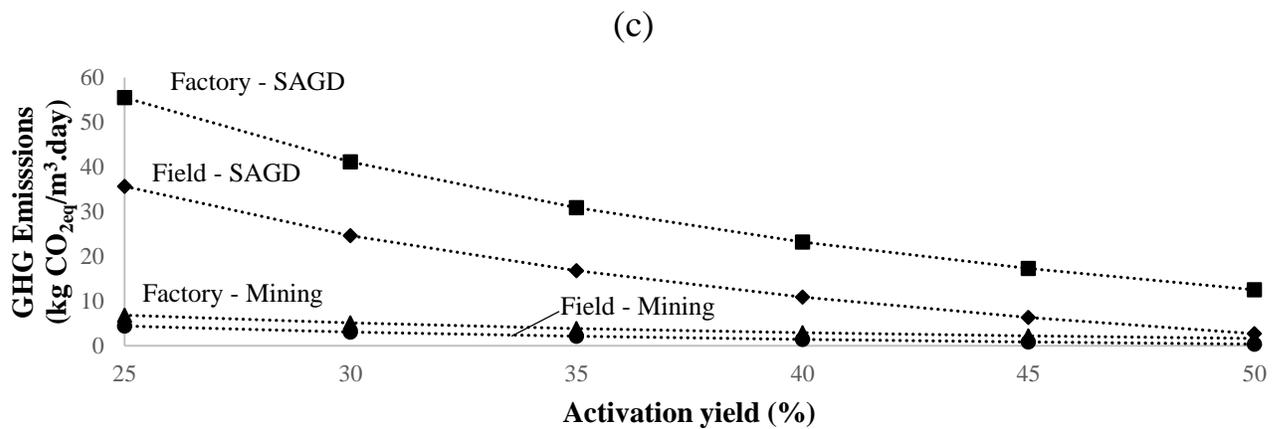
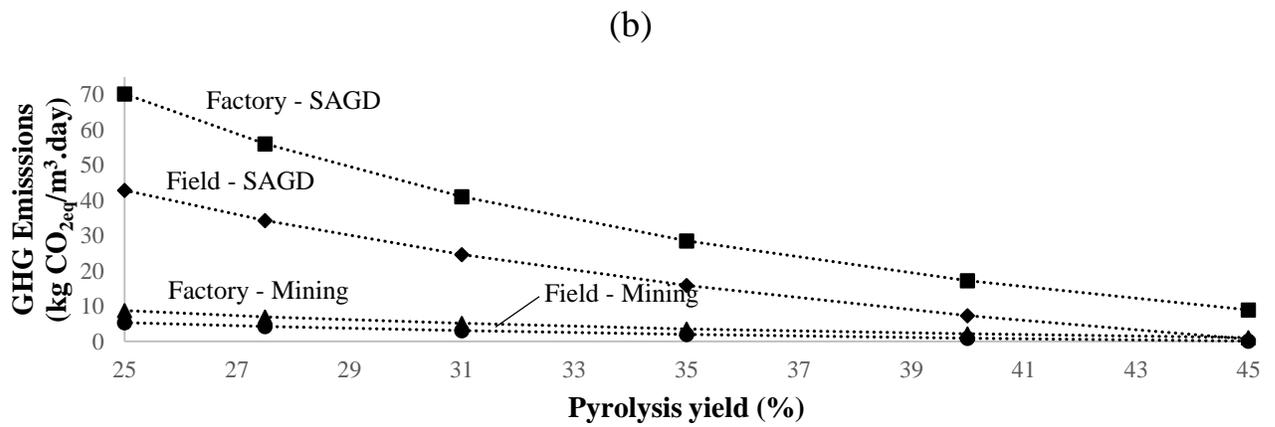
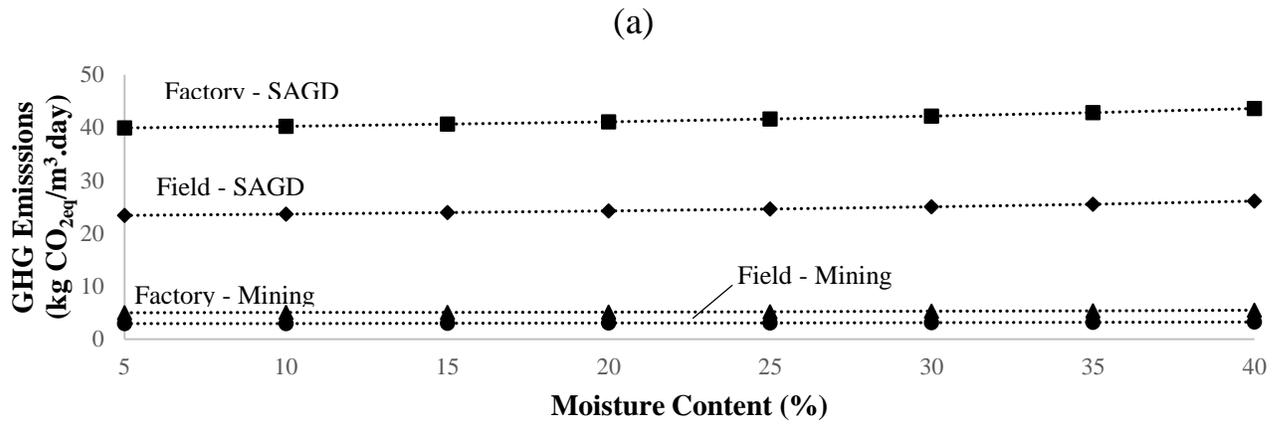


Figure 5-2 (a) Effect of changing biomass moisture content on emissions of different scenarios. (b) Effect of changing pyrolysis yield on emissions of different scenarios. (c) Effect of changing activation yield on emissions of different scenarios.

As it was discussed previously (Figure 5-1(a)), the biomass moisture content and emissions of all the scenarios are directly proportional, because by increasing moisture content in biomass more fuel would be used. According to Figure 5-2(a), small slopes indicate that effect of moisture content on emissions of different scenarios should not be considerably significant (see Section 3-4).

Descending trend of curves in Figure 5-2(b) and (c) indicates total emissions of all the scenarios are indirectly proportional to both pyrolysis and activation yield and slopes show that these two variables have the biggest impact on emissions of factory-SAGD scenario. This behavior is because of the GHG reduction in sequestration stage. The higher pyrolysis or activation yield, the bigger amount of activated carbon and the higher GHG reduction in sequestration stage. According to Figure 5-2(c), field-SAGD crosses both factory – mining and field – mining at 45% yield. This means that total GHG emissions of these three scenarios are almost the same at 45% yield, thus by increasing the yield of pyrolysis process the SAGD scenarios become more beneficial compared to lower yields. The same trend is observed for activation yield (at 50% yield). The higher activation yield is the closer curves of different scenarios are.

Based on Figures 5-2(b) and 5-2(c) increasing either pyrolysis, or activation yield leads to reduction in total GHG emissions. Therefore, increasing these two variables not only decreases energy requirement, but also reduces GHG emissions of all the scenarios. Moreover, at higher pyrolysis or activation yields field-SAGD, field-mining, and factory-SAGD are associated with almost the same amount of emissions and energy requirement, which means increasing yields makes the SAGD scenarios more environmentally friendly and economical compared to lower yields.

5.3 Cost

In general, by increasing energy requirement of a unit process, more fuel is required to satisfy the demand, which leads to an increase in both emissions and cost of the unit process. Figures 5-3(a) to 5-4(c) indicate the effect of diesel price, pyrolysis and activation yields, natural gas price, annual income, and carbon offset. These figures show daily cost of each scenario per m³ of water that can be treated versus various inputs.

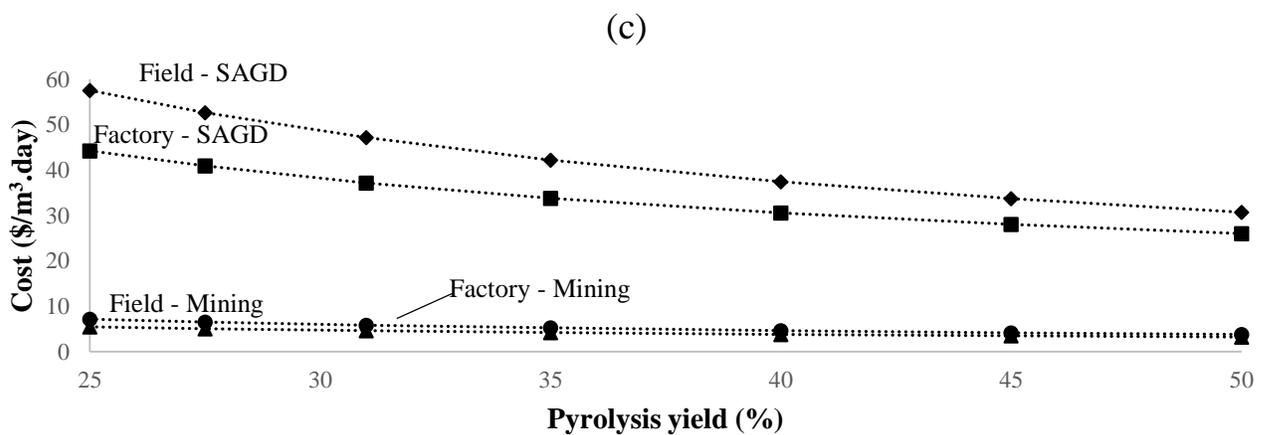
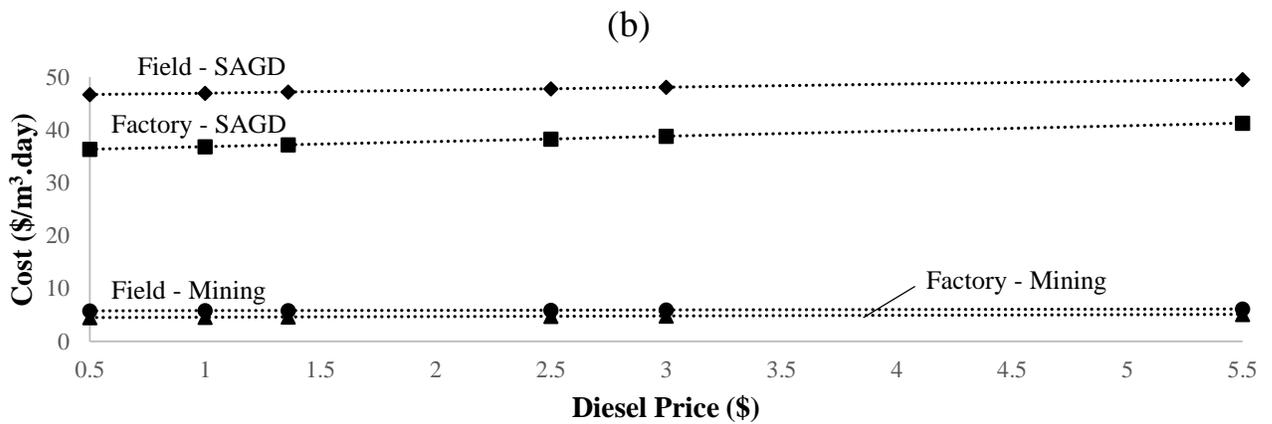
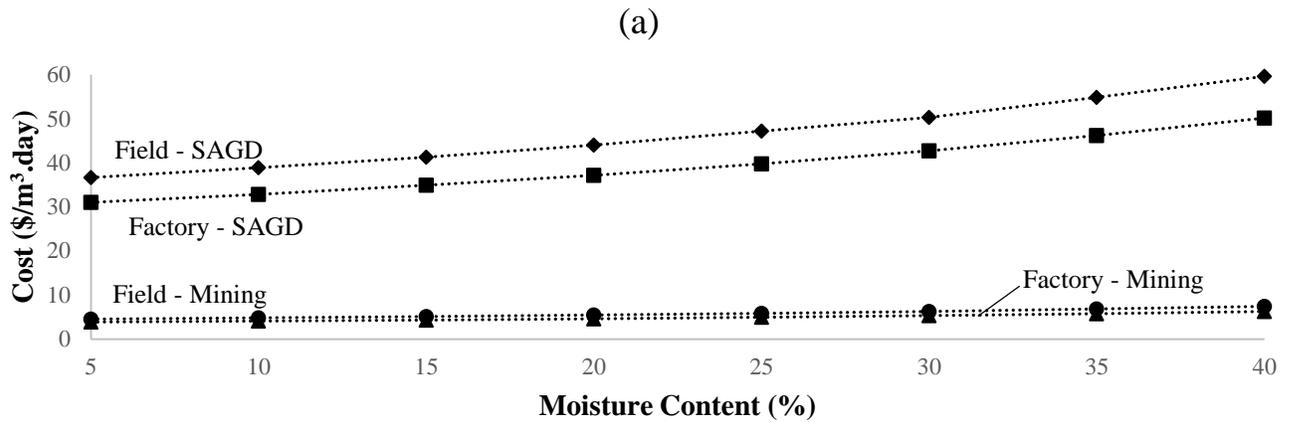


Figure 5-3 (a) Effect of changing biomass moisture content on cost of different scenarios. (b) Effect of diesel price fluctuation on cost of different scenarios. (c) Effect of changing pyrolysis yield on cost of different scenarios.

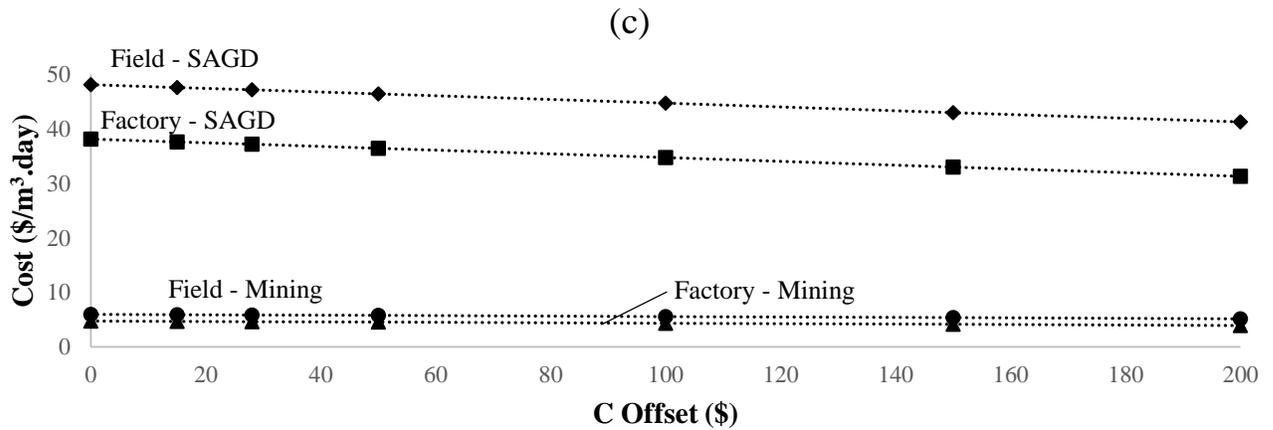
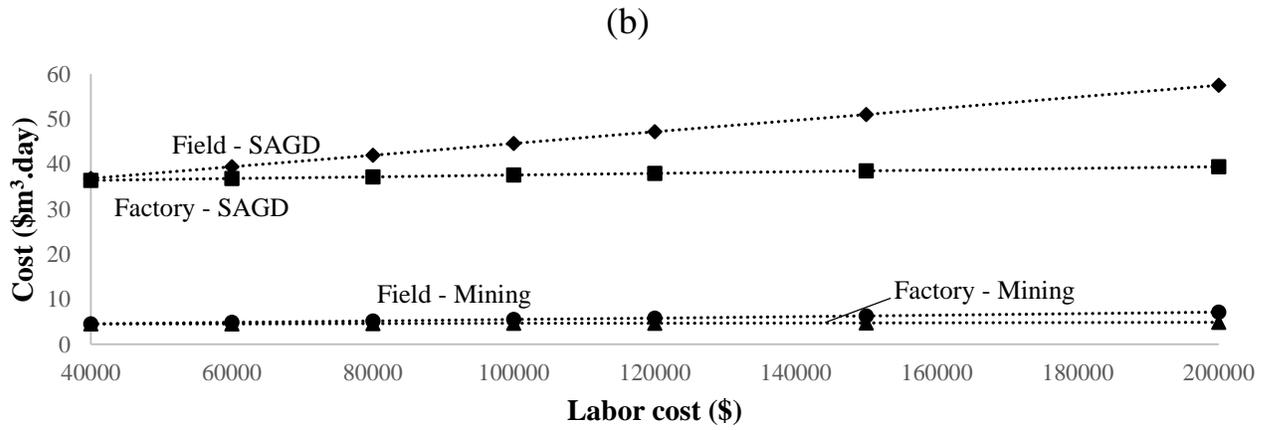
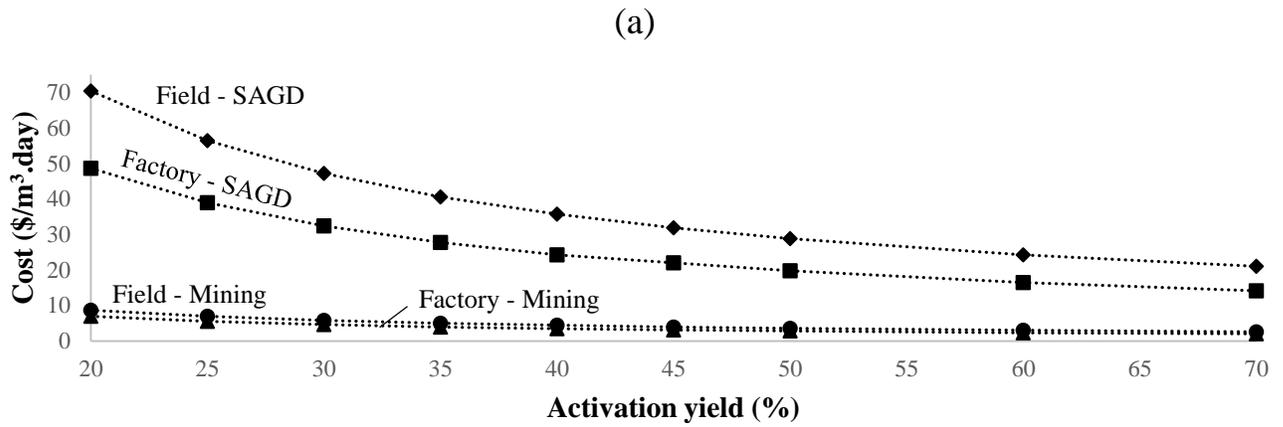


Figure 5-4 (a) Effect of changing activation yield on cost of different scenarios. (b) Effect of changing labor cost on cost of different scenarios. (c) Effect of changing C offset on cost of different scenarios.

As it was discussed previously (Figure 5-1(a)), biomass moisture content and cost of all the scenarios are directly proportional, because by increasing moisture content in biomass more fuel would be used. Burning more fuel leads to an increase in GHG emissions and total cost of each scenario (see Figure 5-2(a) and 5-3(a)). According to Figure 5-3(a), slopes of curves for the SAGD scenarios are larger, which means moisture content has bigger effects on cost of the SAGD scenarios in comparison with mining scenarios. The reason is that costs of the field scenarios are larger than factory ones per m^3 of treated water (see Section 5-5). However, small slopes suggest that effect of moisture content on cost of different scenarios should not be considerably significant (see Section 5-4).

Figure 5-3(b) shows how an increase in diesel price, increases total cost of each scenario. Since, slope of curves are almost the same, it can be concluded that changing diesel price has almost the same effect on total cost of different scenarios. Although, this effect seems to be more significant for factory–SAGD scenario, the effect of diesel price on total cost of different scenarios should not be significant, as slopes of all curves are small. This conclusion means that changing diesel price does not considerably influence the total cost of all the scenarios.

Based on Figure 5-3(c) by increasing yield of pyrolysis process, total cost of all the scenarios decreases and curves of the SAGD scenarios become closer. This behavior is a results of both C offset and energy offset (negative values for cost). With reference to what was discussed in the previous sections, increasing pyrolysis yield not only improves energy generation in off-gas capture stage, but also causes bigger GHG reduction in sequestration process. Producing more energy and reducing GHG emissions both decrease total cost of each scenario. Figure 5-3 (c) also shows that at 50% or more yield field – mining has almost the same cost as factory – mining

scenario, which means by increasing pyrolysis yield, the field scenarios become more economically beneficial compared to lower yields. Moreover, at higher yields the differences between different scenarios become smaller thus, increasing yield is one approach to make the field scenarios more economical.

According to Figure 5-4(a) by increasing activation yield total cost of all the scenarios decreases and curves of the SAGD scenarios become closer. In addition, the differences between the factory and field scenarios become smaller. This behavior is due to an increase in energy production and GHG reduction. Figure 5-4(a) also shows the SAGD scenarios are more dependent on activation yield values than the mining scenarios and for any activation yield bigger than 50% costs of the mining scenarios are almost the same. Since, at higher activation yields the differences between different scenarios become smaller, increasing activation yield is one approach to make the field scenarios more economical.

Figure 5-4(b) indicates the dependence of different scenarios upon labor cost of labors. This dependence is more significant for the SAGD scenarios. This figure also shows that at lower annual incomes scenarios are closer and at the same annual income total costs of the mining scenarios are almost the same. Therefore, effect of changing annual income for the mining scenarios is not significant enough but, changing annual income has considerable impact on the SAGD scenarios especially field-SAGD, which is the most expensive scenario.

As Figure 5-4(c) represents, by increasing C offset values total cost of all the scenarios decreases as all the scenarios benefit from sequestration, which leads to reduction in greenhouse gas emissions. Based on this figure, C offset value has almost the same effect on all the scenarios

and by increasing C offset values, the field scenarios become more economical in comparison with lower C offset values. However, small slopes of curves suggest that effect of changing C offset value on cost of different scenarios should not be considerably significant (see Section 5-4).

In summary, based on Figures 5-1(a) to 5-4(c) pyrolysis and activation yields seem to have significant effect on energy requirement, GHG emissions, and cost of all the scenarios per m³ and other factors (moisture content and labor cost) in the field scenarios considerably influence the energy requirement and cost. In the next section the validity of these findings will be examined.

Finally, based on Figures 3-2 and 3-3 in biomass the field scenarios steam is produced for activation and the remaining amount is used for electricity generation in a steam turbine. Since, composition of biomass is prone to change it needs to be ensured for different biomass compositions extra steam is available to be used in a steam turbine. As Equation 3-1 shows, required amount of steam depends on C content of biomass. Figure 5-5 indicates effect of biochar carbon content on amount of available steam for steam turbine. Based on this figure by increasing C content of biomass the mass of available steam decreases because when this percentage is high, higher amount of steam is required to produce activated carbon, which means less steam is available to be used in steam turbine (assuming total amount of steam produced in boiler is constant). As Figure 5-5 indicates even if the carbon content of biochar is 100% (which is not feasible), still the extra amount of steam exits to be used in the steam turbine. Therefore, regardless of biochar C content, always extra steam is available for electricity generation. However, because this amount varies, amount of generated electricity is prone to fluctuations.

Based on Figure 5-5 and Table 3-1 minimum size of the steam turbine would be around 50 KWe. Equations 5-1 to 5-3 show how the mass of available steam for electricity generation is calculated (the initial temperature of water is assumed to be 25 °C):

$$\text{Mass of required steam (Mg)} = \frac{\text{mass of biochar (Mg)} \times \text{biochar C content (\%)} \times (\text{Excess steam (\%)} + 100)}{10000} \quad 5-1$$

Mass of produced steam (Mg) =

$$\frac{\text{mass of syngas (Mg)} \times (\text{syngas enthalpy of combustion} (\frac{\text{MJ}}{\text{Mg}}) + \text{Specific heat capacity of water} (\frac{\text{MJ}}{\text{K.Mg}}) \times 75\text{K})}{\text{enthalpy of vaporization of water} (\frac{\text{MJ}}{\text{Mg}})} \quad 5-2$$

$$\text{Mass of available steam (Mg)} = \text{mass of produced steam (Mg)} - \text{mass of required steam (Mg)} \quad 5-3$$

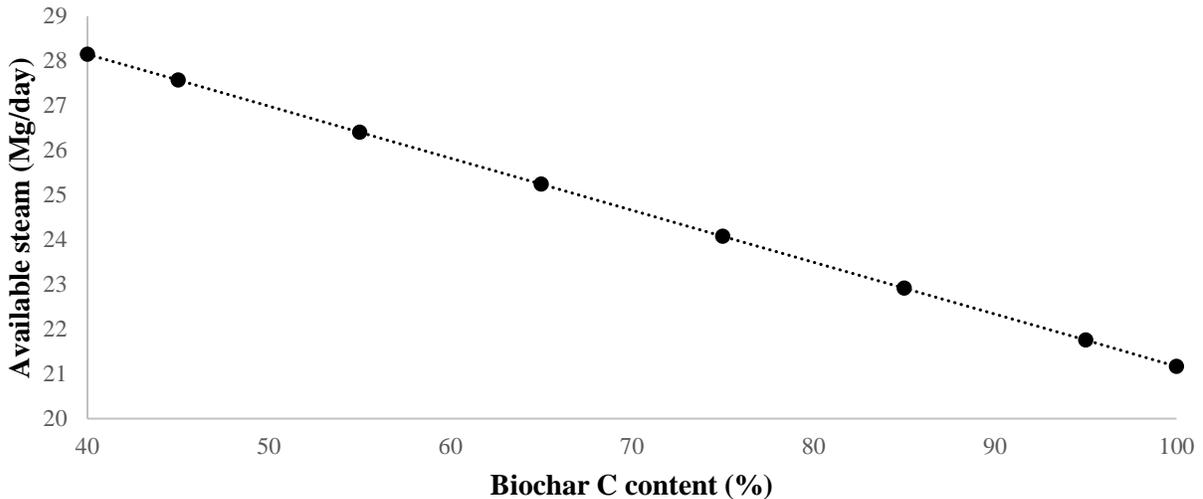


Figure 5-5. Effect of biochar carbon content on amount of available steam for electricity generation.

The inputs considered for sensitivity analysis in this study were pyrolysis yield, activation yield, moisture content, labor cost, diesel price, natural gas price, transportation distance, C offset, and the percentage of C retained in storage in the landfill. However, the effect of changing

transportation distance and percentage of C retained in storage was observed to be minor on energy requirement, emissions, and cost of all the scenarios. Furthermore, as the results of Section 5-3 showed, diesel price and the price of natural gas have minimal effect on cost of all the scenarios, thus they are not considered in Section 5-4.

5.4 Important inputs

To explore which inputs have the most significant impacts on energy requirement, GHG emissions, and cost of different scenarios one practical approach is calculating the change needs to be made in different inputs to see certain amount of change in energy requirement, emissions, or cost (e.g. 10%). Because dependence of energy requirement, GHG emissions, and cost on some inputs (e.g. pyrolysis or activation yields) is not linear (to compare the effect of changing different inputs on final results by changing slopes of lines) the best approach could be plotting percentage of change in energy requirement, GHG emissions, and cost of different scenarios versus percentage of change in different inputs. The approach is used in the following sections to explore which inputs have the most significant impacts on energy requirement, GHG emissions, and cost of different scenarios. By applying this method it is observed that the field scenarios (field-SAGD and field-mining) have similar results. The factory scenarios (factory-SAGD and factory-mining) also show the same trend. Because most of the unit processes for the field scenarios (field-SAGD and field – mining) are the same and only the adsorption unit is different (the same reason for the factory scenarios). Therefore, in next section one graph is used to show the effect of changing different inputs on energy requirement, GHG emissions, and cost of the field scenarios (the same as the factory scenarios). Showing the effect of changing different

inputs (inputs) on final results (outputs) in percentage helps to understand these effects more easily. The base points for different inputs are listed in Table 5-1:

Table 5-1 Base points of different inputs of the LCA model.

Input	Base point
Moisture content (%) – Factory scenarios	20
Moisture content (%) – Field scenarios	25
Pyrolysis yield (%)	31
Activation yield (%)	30
C offset (\$/(kg CO _{2eq}))	28
Labor cost (\$/year)	80,000

5.4.1 Energy

Figures 5-6 and 5-7 show effect of changing inputs (pyrolysis yield, moisture content, and activation yield) on energy requirement per m³ of treated water in different scenarios. In these figures x-axis shows input change (%) and y-axis shows energy requirement change (%).

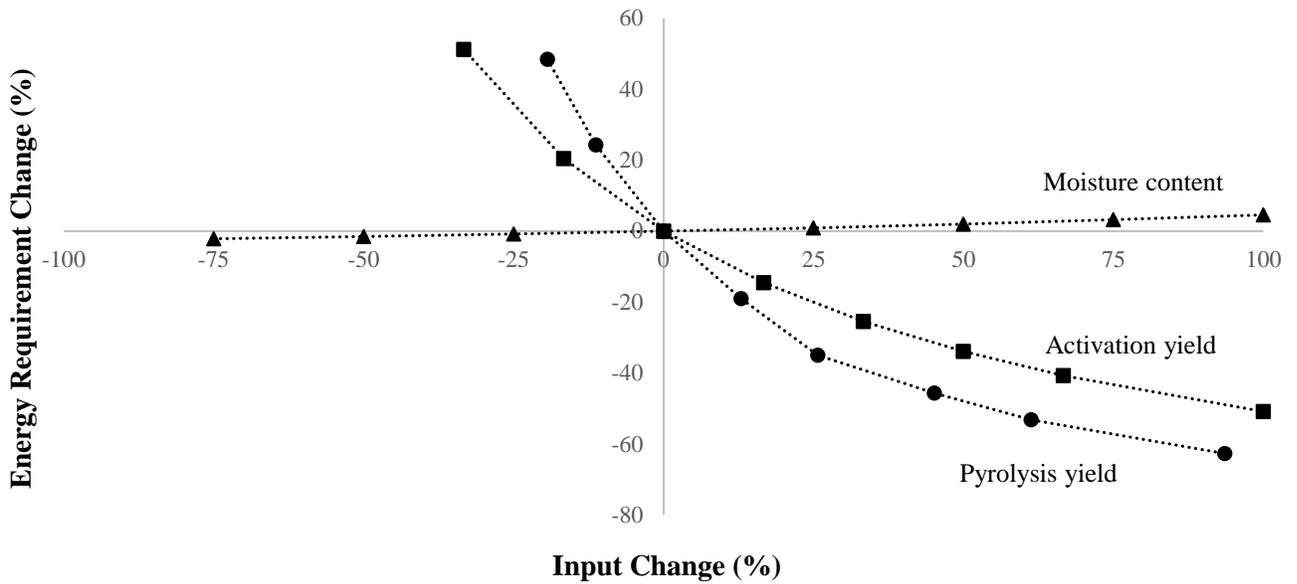


Figure 5-6 Effect of changing different inputs on energy requirement of factory scenarios.

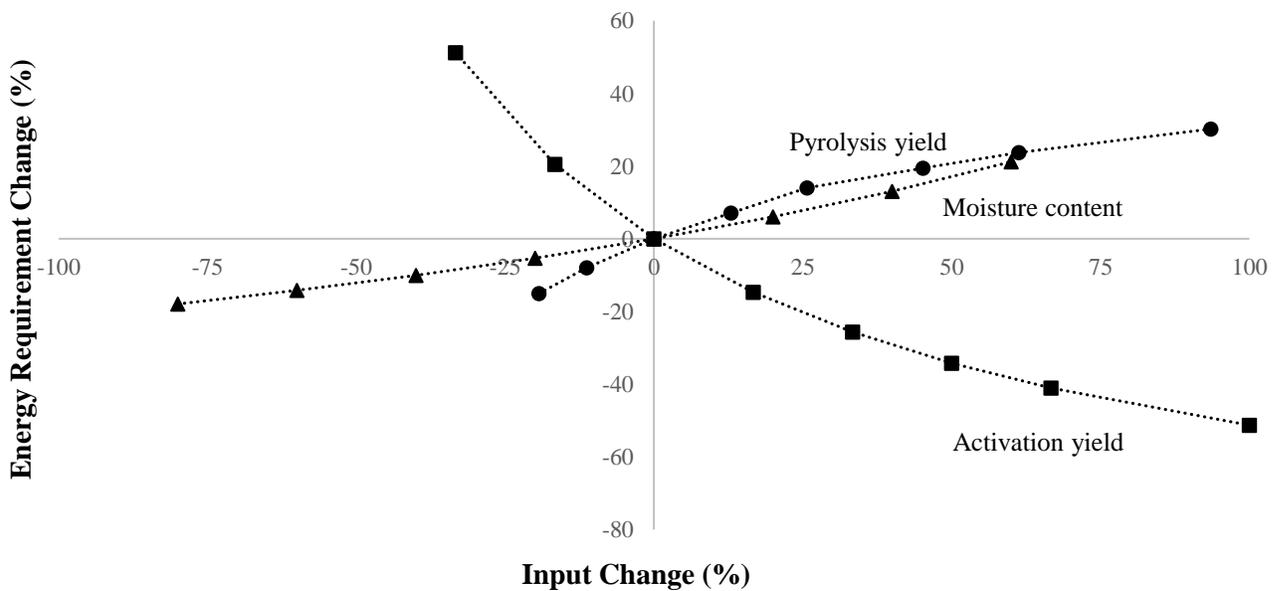


Figure 5-7 Effect of changing different inputs on energy requirement of the field scenarios.

As Figure 5-6 represents pyrolysis yield and activation yield have significant effect on energy requirement of the factory scenarios, while, moisture content shows negligible effect on energy

requirement of the factory scenarios. Because the objective of sensitivity analysis is to find out which inputs need to be considered to reduce total energy requirement of different scenarios, the negative energy requirement changes section, below the x-axis, is applicable (0% change in both input and output shows the current status or base point). Based on Figure 5-6 lower moisture content has minor effect on energy requirement. However, by increasing pyrolysis and activation yields a significant reduction in energy requirement of the factory scenarios can be observed.

By comparing Figure 5-7 to Figure 5-6 two points are worth to be noted. First, unlike the factory scenarios in the field scenarios moisture content shows considerable effect on energy requirement. Second, unlike the factory scenarios by increasing pyrolysis yield energy requirement of the field scenarios decreases thus, for reducing energy requirement in the field scenarios yield of pyrolysis needs to be reduces. As it was discussed previously, the reason is that although, increasing yield of pyrolysis improves energy generation in off-gas capture stage, this amount is not enough to compensate for the increase in energy requirement of operation and transportation as the capacity of the field scenarios is smaller compared to the factory scenarios.

Based on Figure 5-7 lower moisture content has still smaller effect on energy requirement of the field scenarios in comparison with higher activation yield or lower pyrolysis yield. This figure also indicates that in the same amount of change in different inputs, activation yield causes larger reduction in energy requirement of the field scenarios. Therefore, unlike the factory scenarios activation yield is the input showing the biggest impact on energy requirement of the field scenarios.

The negligible effect of moisture content on energy requirement of the factory scenarios seems confusing at first, because by increasing biomass moisture content more energy is required to decrease this amount to the required amount (3-5%). An example helps to clarify the reason. By assuming enthalpy of vaporization of water to be 2257 MJ/Mg [94], the additional energy required to dry biomass from 20 to 5 % for the factory and field scenarios are:

$$\text{Field scenarios: } 25 \frac{\text{Mg biomass}}{\text{day}} \times \frac{(20-5)\text{Mg water}}{100 \text{ Mg biomass}} \times 2257 \frac{\text{MJ}}{\text{Mg water}} = 8,464 \text{ MJ} \quad 5-4$$

$$\text{Factory scenarios: } 500 \frac{\text{Mg biomass}}{\text{day}} \times \frac{(20-5)\text{Mg water}}{100 \text{ Mg biomass}} \times 2257 \frac{\text{MJ}}{\text{Mg water}} = 169,275 \text{ MJ} \quad 5-5$$

This amount for the field scenario is approximately 21% of total energy requirement, while, only 7% of the factory scenarios. The numbers reported in all figures are per m³ of treated water. Thus, in all figures the effect of changing different inputs on energy requirement, GHG emissions, and cost of different scenarios per m³ of treated water (not the absolute amounts), are explored.

In general, as Figures 5-6 and 5-7 indicate pyrolysis yield and activation yield are main factors, which need to be considered for reducing energy requirement of different scenarios.

5.4.2 Emissions

In general, by increasing energy requirement of a unit process, more fuel is required to satisfy the demand, which leads to an increase in emissions of the unit process. Figures 5-8 and 5-9 show effect of changing inputs (pyrolysis yield, moisture content, and activation yield) on GHG emissions per m³ of treated water in different scenarios. In these figures x-axis shows input change (%) and y-axis shows GHG emissions change (%).

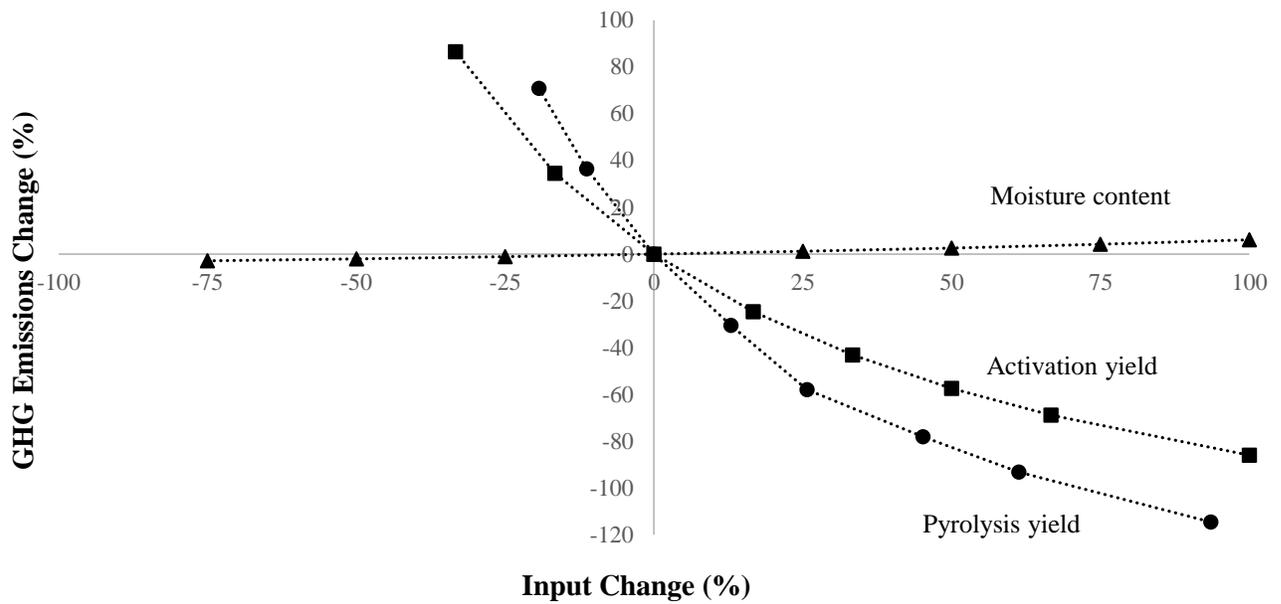


Figure 5-8 Effect of changing different inputs on GHG emissions of factory scenarios.

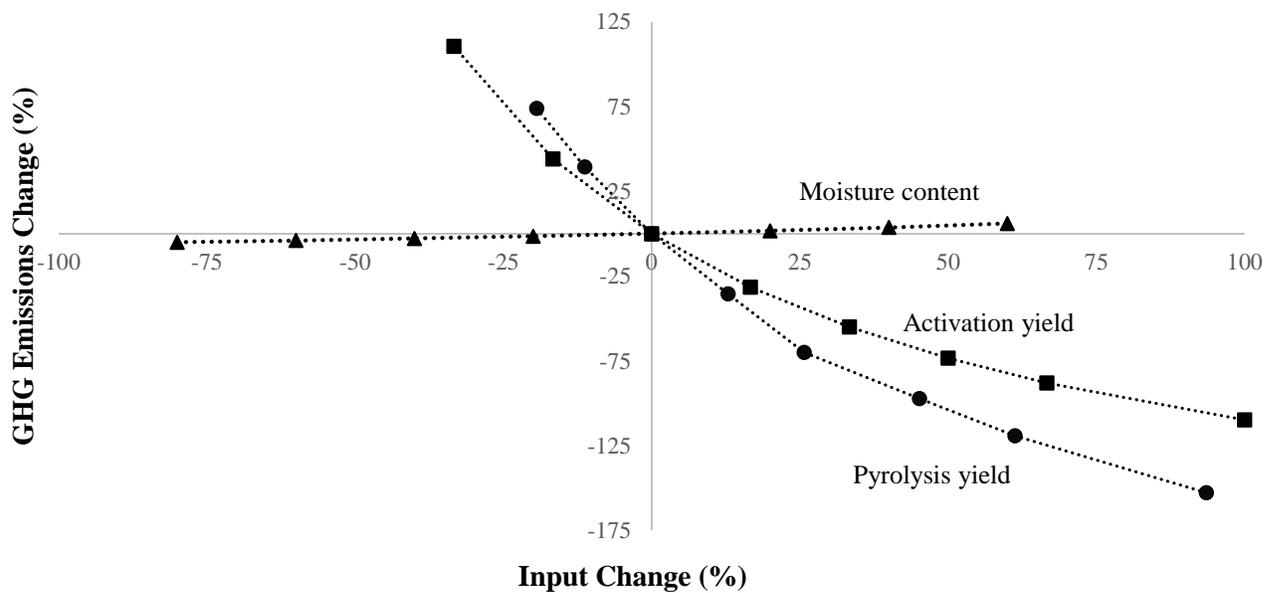


Figure 5-9 Effect of changing different inputs on GHG emissions of field scenarios.

As Figure 5-8 represents pyrolysis yield and activation yield have significant effect on emissions of the factory scenarios, while, moisture content shows negligible effect on emissions of the

factory scenarios. Because, the objective of sensitivity analysis is to find out which inputs need to be considered to reduce total GHG emissions of different scenarios, the negative energy requirement changes section, below the x-axis, is applicable (0% change in both input and output shows the current status or base point). Based on Figure 5-8 lower moisture content has minor effect on emissions, however, by increasing pyrolysis and activation yields a significant reduction in emissions of the factory scenarios can be observed.

Curves in Figure 5-9 show similar trend in the field scenarios. Again, pyrolysis and activation yields have significant effect on total emissions and effect of moisture content is negligible. Moreover, in the same amount of change in pyrolysis and activation yields, pyrolysis yield causes larger reduction in emissions of the field scenarios. Based on Figures 5-8 and 5-9 moisture content has negligible effect on GHG emissions of all the scenarios and inputs that have considerable impact on this amount with respect to their importance are pyrolysis and activation yields. Moreover, by comparing Figures 5-8 and 5-9 it is concluded that pyrolysis and activation yields and moisture content have similar effect on emissions of both field and factory scenarios.

5.4.3 Cost

In general, by increasing energy requirement of a unit process, more fuel is required to satisfy the demand, which leads to an increase in both emissions and cost of the unit process. Figures 5-10 and 5-11 show effect of changing inputs (pyrolysis and activation yields, moisture content, C offset, and labor cost) on cost per m³ of treated water in different scenarios. In these figures x-axis shows input change (%) and y-axis shows cost change (%).

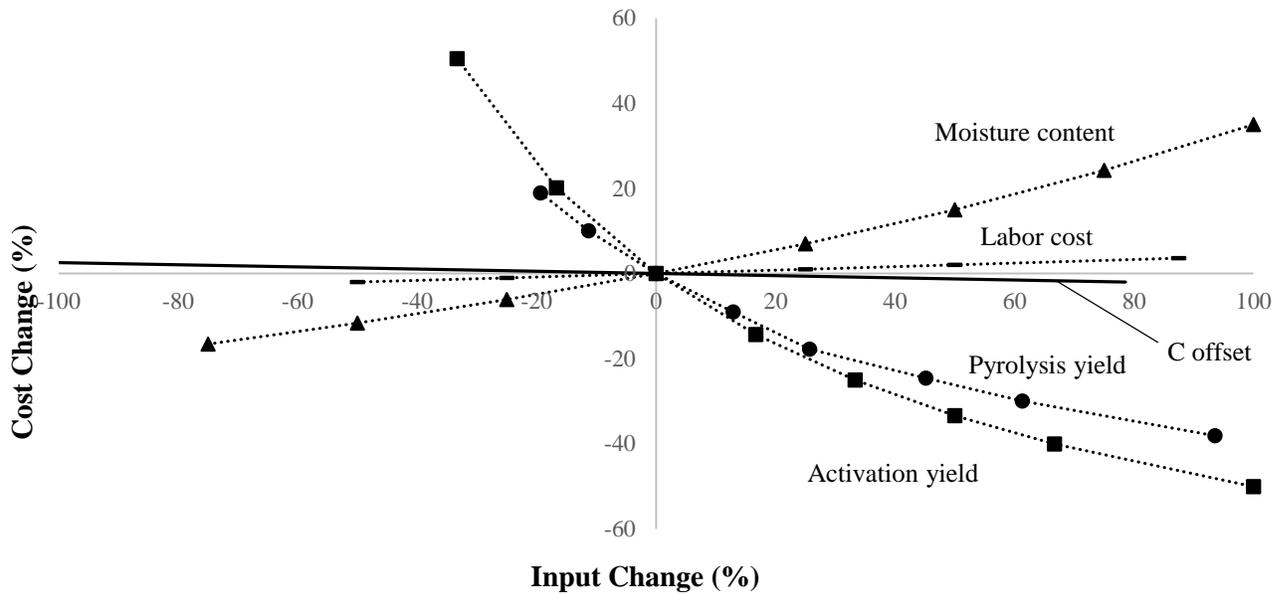


Figure 5-10. Effect of changing different inputs on cost of factory scenarios.

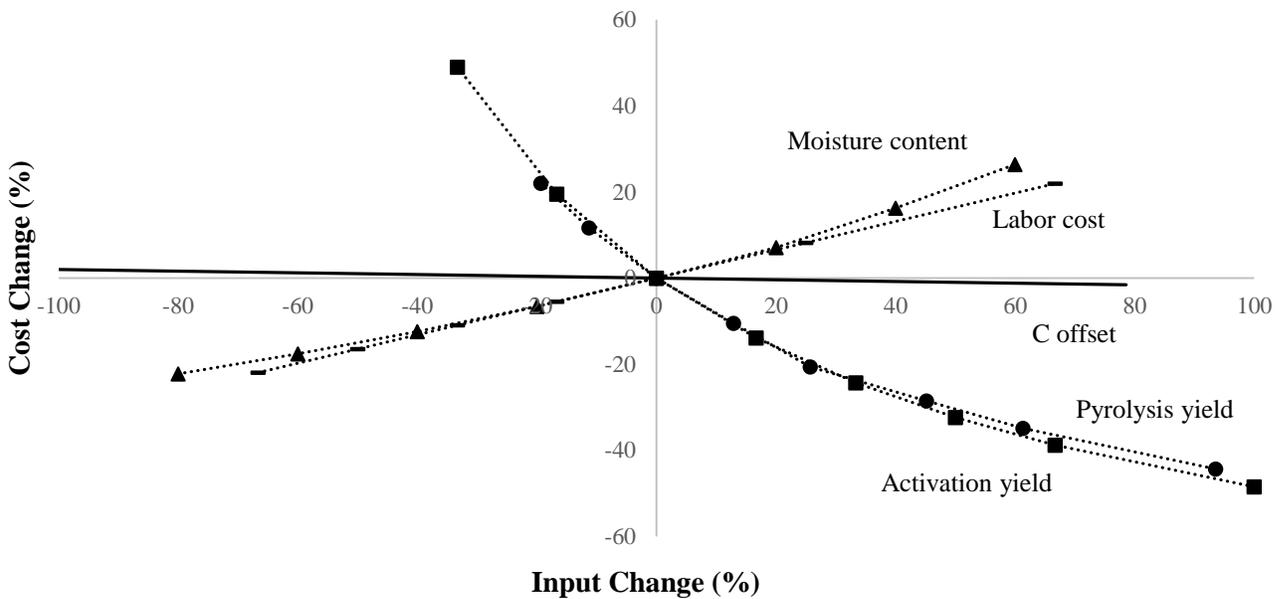


Figure 5-11. Effect of changing different inputs on cost of field scenarios.

As Figure 5-10 represents pyrolysis and activation yields and moisture content have significant effect on cost of the factory scenarios, while, C offset, and labor cost show negligible effect on

cost of the factory scenarios. Based on Figure 5-10 increasing pyrolysis and activation yields as well as decreasing moisture content leads to significant reduction in cost of the factory scenarios. This figure also indicates that in the same amount of change in different input, activation yield causes larger reduction in emissions of the factory scenarios in comparison with pyrolysis yield and moisture content. Because the difference between pyrolysis yield and activation yield curves in a certain input change is negligible it can be concluded that both pyrolysis and activation yields have the largest influences on cost of the factory scenarios. This finding was expected as the slopes of curves in Figures 5-3(c) and 5-4(a) are larger than slopes of the curves in Figures 5-3(a), 5-3(b), 5-4(b), and 5-4(c).

By comparing Figure 5-11 to Figure 5-10 two points are of interest. First, unlike the factory scenarios in the field scenarios labor cost has a considerable effect on cost. Second, pyrolysis and activation yields have almost the same effect on cost of the field scenarios and labor cost curve is close to moisture content. In Figure 5-11, the effect of moisture content and labor cost are more significant and close to effect of pyrolysis and activation yields. In addition, unlike energy requirement and GHG emissions, moisture content has considerable effect on cost of the factory scenarios. According to Figures 5-10 and 5-11, C offset is still inputs with minor effect on cost.

In general, C offset shows negligible effect on cost of all the scenarios and pyrolysis and activation yields strongly influence the cost of all the scenarios, which is in line with results of previous sections.

Conclusively, based on Figures 5-6 to 5-11, pyrolysis and activation yields are the most important factors with having significant impact on energy requirement, GHG emissions, and

cost of all the scenarios and in order to reduce value of final results (energy requirement, GHG emissions, and cost) these two factors need to be considered for achieving more satisfactory results.

5.5 Discussion

By considering Table 4-1 it is observed that amount of required energy, emissions, and cost of the field scenarios are close. The same situation exists for the factory scenarios. This fact indicates that preparation method (field vs. factory) has higher impact on results in comparison with oil sands technologies (SAGD vs. mining) as unit processes are the same for the two scenarios and the difference is the amount of water brought to the adsorption unit and its concentration. Since, the amount of treated water in mining is significantly larger than this amount for SAGD due to the concentration of organics in produced water (1020 mg/ L in SAGD vs. 75 mg/ L in mining), larger amount of produced water can be treated in the mining scenarios. This reason makes values of the mining scenarios significantly smaller in Table 4-2 compared to the corresponding values for SAGD.

Table 4-2 indicates that energy requirement of field–SAGD scenario is 33% of energy requirement of factory–SAGD scenario and energy requirement of field–mining scenario is 35% of this amount for factory–mining. Therefore, in terms of energy requirement the field scenarios are preferable as the energy requirements of the field scenarios are almost one-third (33%) of energy requirements of the factory scenarios per m³ of treated water. Based on Table 4-2 GHG emissions of field–SAGD scenario is 25% of this amount for factory–SAGD scenario and emissions of field–mining scenario is 100% lower than this amount for factory–mining scenario. Therefore, in terms of GHG emissions, the field scenarios are preferable as the emissions of the

field scenarios are less than 25% of the emissions of the factory scenarios per m³ of treated water.

Comparing the field and factory scenarios in terms of cost is not as straightforward as energy requirement and emissions. As Table 4-2 shows the cost of factory - mining scenario is close to cost of field–mining scenario (83% of cost of field-mining). This difference can be due to error in calculation (but the calculation shows it is not see Table 4-2). However, comparing cost of factory–SAGD scenario and field– mining shows that cost of the factory scenarios are smaller than field one (79% cost of factory-mining). The reason that cost of field–mining and factory–mining are close is the amount of treated water in mining processes. Because, the amount of treated water in the mining scenarios is large the difference between absolute costs of these two scenarios is significant enough to make cost per m³ treated water of one scenario considerably larger than another one. Comparing cost of field – SAGD and factory – SAGD scenario validates this claim. Because, the amount of treated water is less in SAGD processes the difference between cost of the factory and field scenarios is more considerable. Thus, in terms of cost, the factory scenarios are preferable as the costs of the factory scenarios are almost 80% of costs of the field scenarios per m³ of treated water.

In summary, comparing different scenarios in terms of energy requirement, emissions, and cost per m³ of treated water indicates that the difference between the field and factory scenarios in energy requirement, emissions, and cost are around 65%, more than 75%, and 20%, respectively. Therefore, the field scenarios have lower emissions in comparison with the factory scenarios. In addition, Table 4-2 indicates that the field scenarios are more environmentally friendly and require lower level of energy in comparison with the factory scenarios. On the other hand, the

factory scenarios are more economical. Thus, the best scenario from a GHG emissions perspective is not the most economical one.

As Table 4-2 shows the field scenarios is more environmentally friendly and less energy-intensive compared to the factory scenarios. Comparing field-SAGD scenario with factory-SAGD helps to figure out the reason. As Figures 4-2(b) to 4-3(c) show, pyrolysis is the unit process associated with the highest energy requirement in both field and factory scenarios and GHG emissions in the factory scenarios. In field scenario the syngas combustion produces the highest energy, while, in factory scenarios the combined heat and power units plays this role. Furthermore, in both scenarios sequestration is in charge of providing GHG reduction. The interesting point is that in the field scenario energy requirement of pyrolysis is 1.1 times larger than generated energy by syngas combustion and emissions of pyrolysis unit is 0.4 of total emissions reduction of sequestration. On the other hand, in the factory scenario energy requirement of pyrolysis is 2.3 times larger than total generated energy by CHP unit and emissions of pyrolysis unit is 1.1 of total emissions reduction of sequestration. These numbers indicate that pyrolysis unit as major source of demand for energy and releasing emissions in the factory scenario is one of the main factors making the factory scenario less environmental friendly and more energy-intensive compared to the field ones.

Comparing Figure 4-3(a) to (c) indicates that the major source of cost in the field scenario seems to be labor cost. The larger effect of labor cost on total cost of the field scenarios compared to the factory scenarios also can be realized by comparing Figure 5-10 with 5-11. Table 3-1 shows that larger labor cost in the field scenarios compared to the factory scenarios is due to their working hours (12 vs. 8 h/day). The reason is that in the field scenarios pyrolysis and activation occur at

roadsides (in field), which are far from cities. Therefore, using labor for fewer hours is not feasible. Furthermore, being far from cities raises another issue, the number of people for each shift. As Table 3-1 represents, although capacities of the factory scenarios are 20 times larger than the field scenarios, the number of people it requires is only 2 times larger. The reason is that at a centralized unit fewer people are required compared to pyrolyzing and activating at roadside (field) [81].

Based on Table 4-1 the total emissions of all the scenarios are positive, which means using forest residues for producing activated carbon to be used for organics removal from water in oil sands operations does not reduce the total emissions throughout its life cycle. However, this study showed that by increasing organics removal level the total GHG emissions of all the scenarios decreases and at $\geq 55\%$ removal level the total emissions of all the scenarios become negative (see Figure 4-4). It was also indicated that at higher removal levels ($\geq 80\%$) the total emissions of all the scenarios are almost the same (less than 5% difference), which means that at higher removal levels all the scenarios are equally promising from a GHG emissions perspective and lead to almost the same amount of reduction in emissions.

Moreover, it cannot be concluded that the current alternative, replacing equipment in SAGD operations or leaving tailing ponds without removing the organics, is more environmental friendly. Because producing new equipment and transporting it to the oil sands operation is not only associated with emissions, but also requires cost and energy. Furthermore, tailings ponds are also associated with negative environmental impacts. Water in the Athabasca River is expected to decline due to climate change while oil sands development expands in the future especially during the winter when flows are naturally lower [9]. Water withdrawal during this

time can affect fish habitats and decrease the amount of dissolved oxygen available to fish in the winter [9]. Therefore, a life cycle analysis as required to estimate the energy requirement, emissions, and cost of the current alternative in oil sands operations to compare with this method and make a comprehensive conclusion to indicate which method is more economical and environmental friendly.

Figure 5-7 shows that by increasing pyrolysis yield energy requirement of the field scenarios increases. However, according to Figure 5-11 by increasing yield the cost of the field scenarios decreases. In addition, Table 4-1 and 4-2 show the scenario with the biggest energy requirement is not necessarily the most expensive one. This conclusion seems confusing at the first, because cost of any process is predominantly determined by amount of energy it uses. However, labor income is another important factor. Labor cost makes factory preparation more economical than field preparation. Table 5-1 also shows the same point. This table shows total labor cost per dry biomass for factory and field preparation.

Table 5-2 Total labor cost, capacity, and labor cost – capacity ratio for biomass field and factory preparation.

Scenario	Labor Cost (\$/day)	Capacity (Mg/day)	Labor Cost/Capacity (\$/Mg)
Field scenario	2630	25	105
Factory scenario	5260	500	11

As Table 5-2 indicates the labor cost–capacity ratio of field preparation is almost 10 times bigger than factory preparation. The reason is that although capacity of factory preparation is 20 times bigger than field preparation, its labor cost is only two times bigger. This means that preparing biomass at roadside requires additional number of labors, which increases total cost. In addition,

it is worth mentioning that for the field scenarios labor cost accounts for approximately 33% of the total cost, while, this amount is only 6% for factory ones.

In the Chapter 4 it was mentioned that labor cost in this study is assumed to be only labor income and their benefit or any other type of cost is not considered as it usually depends on the employer and the company they are working for. However, it is important to know whether addition of benefits on top of the salary will make a significant change in the results. Because the benefits offered by companies usually vary it is difficult to specify a certain amount as an average for benefits but, in general the benefits range from 15% to 55% of the labor income [86]. Assuming benefits to be 35% of the labor income (average amount) for all the scenarios makes the field scenarios even more expensive, but does not change the total cost of the factory scenarios significantly (see Figure 5-10, 5-11, and 5-4(b)). As Figures 5-10 and 5-11 show increasing the labor cost by 35% leads to 17% increase in total cost of the field scenarios, while, only 5% in total cost of the factory scenarios.

Table 4-2 also indicates that energy requirement, GHG emissions, and cost of the mining scenarios are between 10 to 20% of the corresponding values of the SAGD scenarios. As it was mentioned before the reason is that amount of treated water in the mining scenarios is considerably larger (more than 8 times). This means that for removing organics from 1 m³ of water less energy and investment are required and lower amount of GHG emissions releases to the air. On the other hand, whether using surface mining or in-situ technology depends on the type of reservoir. Therefore, comparing the mining scenarios with the SAGD scenarios is meaningless.

With respect to Figures 4-2(b) to 4-3(c), it can be concluded that the pyrolysis and sequestration unit processes play key roles in total energy requirement, GHG emissions, and cost of all the scenarios. The pyrolysis unit consumes high level of energy and is associated with high level of emissions and cost. On the other hand, sequestration unit offers high level of GHG emissions reduction, which leads to significant energy and cost reduction (see Chapter 4). Therefore, any approach that can reduce the amount of energy the pyrolysis unit requires and emissions this unit releases as well as any method for enhancing performance of sequestration unit would lead to considerable reduction in energy requirement, emissions and as a result cost of all the scenarios (with respect to carbon and energy offset values). Pyrolysis yield is the important factor can enhance the performance of the pyrolysis and consequently increasing GHG emissions reduction in the sequestration unit. Because by increasing yield, pyrolysis produces larger amount of activated carbon. The more activated carbon, the higher level GHG reduction in sequestration unit. Other methods for reducing energy requirement of the pyrolysis process by reducing amount of lost energy can be also helpful.

Since, the pyrolysis unit plays a key role in energy requirement and emissions of different scenarios it is necessary to examine the validity of data used for this unit process. By considering the paper it can be found that the biomass source used in the pyrolysis plant is wood (kind of wood is not specified) [72, 95]. Table 5-3 shows the characteristics of the biomass used in this study and the feed used in the source.

Table 5-3 Carbon content and heating value of aspen and wood source used in the literature.

Biomass	Carbon content (%)	HHV (MJ/Mg)
Aspen	45	16200
Wood	49	17310

As table shows, the heating value and carbon content of the feedstock (wood) of this power plant are close to the corresponding values of the forest residues (aspen wood) used in this study (less than 10% difference). Therefore, the feed of this plant is similar to the forest residues used in this study. A number of researchers reported that among different factors influencing the yield of biomass pyrolysis and thus, its energy requirement and emissions (e.g. temperature, pressure, flow rate, heating rate, biomass particle size) temperature has the largest impact on yield of pyrolysis [96-98]. They reported the temperature should be chosen between 600°C to 750°C to optimize the amount of resulting biochar (the temperature assumed in this study is 650°C, which is with respect to the experiment has been conducted and thus, the reported amount for biochar and syngas yield). Because pyrolysis yield has significant impact on final results (see previous sections of this chapter), it is concluded that the temperature of pyrolysis unit is an important factor and can significantly affect the energy requirement, emissions, and cost of different scenarios.

As Figures 3-2 to 3-5 show the off-gas capture unit is in charge of capturing off-gas to prevent the gradual emission of methane and convert it to carbon dioxide. Because, the off-gas consists of methane and carbon dioxide (67% and 33%, respectively), which is similar to the composition of landfill gas captured in landfills (typically have 60 to 75% methane and 15 to 30% carbon dioxide [85]) the produced off-gas is feasible to be captured in the same way. Since, off-gas capture and combustion converts methane to carbon dioxide it reduces the amount of emissions in kg CO_{2eq}/m³ (GWP of methane is 25 times larger than GWP of carbon dioxide 1). Based on the calculations capturing and combusting the produced off-gas reduces the amount of GHG

emissions of this unit process by approximately 90% (considering the amount of GHG emissions resulted from using fuel to satisfy the energy requirement of this unit process).

As it was discussed in the Chapter 3, in this study it is assumed that 85% of carbon is retained in soil and 90% of activated carbon is carbon (the remaining 10% chiefly consists of H and N - see Sections 2.5 and 2.7) [68]. The organics removed by activated carbon along with a 15% of activated carbon converts to methane and carbon dioxide due to anaerobic metabolism. Thus, landfilled spent AC leads to emissions of greenhouse gases (chiefly CH₄ and CO₂) [5].

Although there are a number of studies addressing the portion of stable carbon (retained in soil) in the biochar [16-18], this portion for activated carbon is not defined yet and should be studied in the future work in this area. In this study, the portion of stable carbon in the activated carbon is assumed to be 85% but, this value varies up to 90% [17], which means that the chosen value for stable carbon in activated carbon is associated with uncertainty and the impact of changing this value on the final results should be explored. Changing the portion of stable carbon from 70% to 100% ($\sim \pm 15\%$) changes the net GHG emissions of system only by 3 to 7% for different scenarios, which means that the portion of stable carbon in the spent activated carbon does not significantly change the net GHG emissions of the systems and still resulting in C sequestration and negative GHG emissions. This finding is in line with the sensitivity analysis conducted in previous studies to show the effect of changing stable carbon in biochar [17]. Therefore, even assuming 100% stable carbon in activated carbon does not significantly change the net GHG emissions.

The obtained results in Chapter 4 show the sequestration unit process plays a key role in GHG emissions reduction and without this stage the net GHG emissions of all the scenarios increases by 40 to 50%. On the other hand, off-gas capture accounts for less than 10% of the net emissions of all the scenarios. This statement means that sequestration has bigger impact on total GHG emissions of all the scenarios compared to the off-gas capture unit process and this unit is the most important factor influencing the net GHG emissions; thus, any improvement in performance of this unit process leads to considerable reduction in the net GHG emissions of the systems and the future studies should focus on this unit process to reach even lower net emissions.

Based on Table 4-2 water treatment in mining operations seems more feasible because of lower concentration of organics in tailings water and thus, larger water treatment capacity of the mining scenarios. However, building 12 units in capacity of 500 Mg/day or 247 units in capacity of 25 Mg/day still seems not feasible. Therefore, instead of removing organics from entire amount of produced water in oil sands operation by using activated carbon from forest residues, implementation of a policy for removing organics from a proportion of produced water in oil sands operation can be an achievable objective. It means that even removing organics from a proportion of produced water in oil sands operation is still attractive enough to be funded as it provides many benefits (such as increasing lifetime and efficiency of the entire process) for oil and gas industry and environment.

Another worthwhile point is that by considering Figures 5-1(a) to 5-4(c) it can be observed that changing different inputs mostly has more significant impact on the SAGD scenarios compared to mining ones and the factory scenarios in comparison with the field ones. The reason of

dramatic change in the SAGD scenarios is that amount of treated water in the SAGD scenarios is considerably less than this amount in the mining scenarios. As a result any change in total energy requirement, GHG emissions, or cost has a larger effect on the SAGD scenarios. Since, the capacity of the factory scenario is larger, there is a major difference between energy requirement, cost, and GHG emissions of this scenario and the field scenario. Therefore, any change in different inputs has relatively larger impact on the factory scenarios.

Sensitivity analysis indicates that yields of pyrolysis and activation processes are main factors, which strongly impact energy requirement, GHG emissions, and total cost of each scenario. Moreover, at higher pyrolysis and activation yields the difference between different scenarios become negligible and all the scenarios are almost the same either from environmental, or economic perspective. Since, increasing pyrolysis and activation yields leads to lower level of energy requirement, emissions, and cost for all the scenarios the main focus of research and development (R&D) should be on finding new approaches to increase these factors. Higher pyrolysis and activation yields makes all the scenarios more beneficial in terms of both emissions and cost.

In conclusion, based on the obtained results, this study supports the idea of adding value to a low value biomass, forest residues, by using it for removing organics from water in oil sands operation, which is in line with the findings of the previous studies in this area [6, 10, 16]. Moreover, with reference to the results in Chapter 4 and as it was discussed in previous sections of this chapter, this study showed applying carbon to the soil (carbon sequestration or landfilling) as a practical method for waste management scenario, which results in GHG reduction. This finding proves the results of the previous studies [6,17, 99]. This study showed the lower price

for treating water in mining operations makes this method more economical than produced water treatment in SAGD operations. The study conducted by Kimetu et al. drew the same conclusion [5]. The emissions of the systems were calculated to be between 2 to 16 kgCO_{2e}/m³ for the factory scenarios and 0 to 4 kgCO_{2e}/m³ for the field scenarios. In addition, this study indicated that although under the conditions used in this study the net GHG emissions is positive (0 to 16 kgCO_{2e}/m³) by increasing the removal amount up to 60% or more (at approximately 56% removal all the scenarios show negative emissions- see Figure 4-4), which is theoretically feasible (up to 75% is possible), the net GHG emissions of all the scenarios become negative. Therefore, at 75% removal, the maximum feasible amount for the systems, the net emissions range between -55 to -72 kgCO_{2e}/m³. This finding means that using forest residues for producing activated carbon to be used for organics removal from produced water in oil sands operations in lower removal values not only does not reduce the total emissions throughout its life cycle but also releases emissions to the atmosphere, whereas, by increasing the removal level the net emissions becomes negative.

5.6 Summary

In this chapter, sensitivity analysis of the study was presented and important factors influencing energy requirement, GHG emissions, and cost of the field and factory scenarios were indicated. Moreover, the result of chapter 4 and 5 were discussed and preliminary conclusions were drawn. Sensitivity analysis showed that pyrolysis and activation yields are the main factors affecting energy requirement, GHG emissions, and total cost of each scenario. In addition, at higher pyrolysis and activation yields (>50%) the difference between different scenarios become

negligible and all the scenarios are almost the same either from environmental, or economic perspective.

Chapter Six: Conclusions and recommendations

6.1 Conclusions

The main purpose of this study was making a comparison between two biomass preparation scenarios, field and factory, for water treatment in two types of oil sands operations, SAGD and mining, i.e. four scenarios: field-SAGD, field-mining, factory-SAGD, and factory-mining, in terms of energy requirement, GHG emissions, and cost. Furthermore, this study aimed to address the main economic and environmental issues of different scenarios as well as their major sources of cost.

The results of calculations conducted throughout the study indicated that the two field scenarios are more environmentally friendly (approximately 75% lower GHG emissions) and require lower amount of energy (approximately 65% lower energy requirement) in comparison with the two factory scenarios. On the other hand, the factory scenarios are more economical (approximately 20% lower cost). Thus, the best scenario from a GHG emissions perspective is not the most economical one. Based on the obtained results, labor cost is the main factor making the field scenarios more expensive and the pyrolysis unit is the main source of energy demand and releases the highest emissions in the factory scenarios. Thus, pyrolysis is the main factor making the factory scenarios less environmental friendly and more energy-intensive compared to the field scenarios.

The main demerit of the field scenarios is labor cost, whereas, the biggest issue associated with the factory scenarios is the high level of energy requirement and GHG emissions of pyrolysis unit process. Furthermore, pyrolysis and sequestration unit processes play the key roles in total energy requirement, GHG emissions, and cost of all the scenarios. The pyrolysis unit consumes

high amount of energy and is associated with high level of emissions and cost. On the other hand, the sequestration unit provides high level of GHG emissions reduction, which significantly reduces the total energy requirement and cost. Therefore, any approach reducing the amount of energy the pyrolysis unit requires and the emissions this unit releases as well as any method enhancing performance of the sequestration unit leads to considerable reduction in energy requirement, emissions, and consequently, cost of all the scenarios.

In this study, the net emissions of the systems were calculated to be between 2 to 16 kgCO_{2e}/m³ for the factory scenarios and 0 to 4 kgCO_{2e}/m³ for the field scenarios. The results of calculations indicated that although the emissions of all the scenarios at 50% removal level, the maximum removal level achieved in the lab for the system used in this study, are positive, by increasing the removal the net GHG emissions of all the scenarios decreases. Moreover, at $\geq 55\%$ removal the total emissions of all the scenarios become negative and at 75% removal, the maximum feasible removal for the systems used in this study, the net emissions of different scenarios range between -55 to -76 kgCO_{2e}/m³. In addition, at higher removal levels ($\geq 80\%$) the total emissions of all the scenarios are almost the same, that is at higher removal levels all the scenarios are equally promising from a GHG emissions perspective and release almost the same amount of GHG emissions.

A practical solution making the field scenarios more economical and the factory scenarios more environmentally friendly and less energy-intensive is increasing pyrolysis and activation yields, which also indirectly results in higher removal levels. By increasing pyrolysis and activation yields, or even one of them, larger amount of activated carbon is produced leading to lower amount of energy requirement, emissions, and cost in all the scenarios. Therefore, pyrolysis and

activation yields are the two important factors future studies should focus on to decrease the energy requirement, emissions, and cost of all scenarios.

6.2 Recommendations for future research

The results of this study helps research and development to investigate feasible methods to deal with high concentrations of organics in water in oil sands operation. The results of this study also is interesting for the oil sands industry as removing organics from water not only increases lifetime of equipment and efficiency of the oil sands recovery process, but also mitigates harmful environmental impacts of organics in water, such as gradual emission of methane. Moreover, this study provides a new market for forestry industry and helps government agencies to know how to allocate funding and directs the research towards achieving desirable results.

Comparing the previous studies conducted in this area with the current study indicates that the major difference between these studies is the assumed value for removal level. One of the reasons that the removal level assumed in this study differs from the previous studies is using different methods for pyrolysis the forest residues. Therefore, in this study instead of assuming a value for removal level and doing the calculations based on the assumed value the removal level is chosen with reference to the previous lab study which makes the obtained results more realistic. Although, the previous lab study was not comprehensive enough to define whether higher values for removal level is practically possible, it was a good starting point for future studies in this area and provides a basis for the removal level which can be obtained by this method. However, comprehensive lab studies are required to ensure whether this value is the maximum removal level can be obtained and if any improvement in one or a number of the unit processes can result in achieving higher removal levels. In this regard, the focus of the future

studies in this area should be finding ways to improve this method and obtaining higher removal levels as increasing the removal results in considerable reduction in the net GHG emissions of all the scenarios.

Because under the conditions used in this study the net GHG emissions is positive (0 to 16 kgCO_{2e}/m³), this method cannot be commercialized at this point (for example removing organics from tailings ponds in mining operations in Alberta by this method results in emission of 136 to 676 tonnes CO_{2eq}/m³ per day). Therefore, to make this method promising from a GHG emissions perspective enough to be commercialized, finding possible ways to increase the performance of the system and thus, the removal level is crucial.

However, it cannot be concluded that the current alternative, replacing equipment in SAGD operations or not removing organics from tailings ponds without removing organics, is more environmental friendly than this method. Because producing new equipment and transporting it to the oil sands operation is not only associated with emissions and cost, but also requires energy. Furthermore, mining operations also lead to negative environmental impacts such as gradual emissions of methane and decline in amount of available dissolved oxygen due to oil sands development and water withdrawal during mining operations (see Chapter one). Therefore, a life cycle analysis is required to estimate the energy requirement, emissions, and cost of the current alternative in oil sands operations to compare with this method to make a comprehensive conclusion and offer a practical solution for the problems associated with high concentration of organics in produced water of oil sands operation.

For instance, the cost of replacing equipment and decreasing efficiency of operations need to be compared with the cost of using activated carbon for water treatment to know which method is more economical and feasible. Because, estimating these sources of costs is difficult and due to a lack of valid documents reporting this cost, comparing the proposed method in this study with other alternatives is not possible yet. However, regarding the harmful environmental impacts of organics in produced water the proposed method should be more environmental friendly than the alternatives such as not removing organics from tailings ponds or replacing equipment. Thus, the biggest issue associated with using of activated carbon for water treatment in oil sands operations seems to be economic ones.

Using on site data for a study requires receiving data from industry. However, companies are usually not willing to provide detailed data of different unit processes. Moreover, because these sets of processes (Figures 3-2 to 3-5) either for the field, or factory scenarios are new and these methods have not been employed so far, it is not possible to have access to on-site source of data. Because on-site or primary source of data provided by industry was not available for this study, the generic sources including previous LCA studies, LCA databases, official reports, published papers, and theses were used. Using generic data sources instead of on-site data increases uncertainty of the inputs and thus, decreases the reliability of the results as the collected data are not completely consistent with the different unit processes. Moreover, because a reliable source of data for energy requirement, cost and the amount of released emissions for activation unit was not found, it is assumed that the activation unit is the same as mobile pyrolysis unit with the same capacity for all the scenarios. Using generic data sources and the lack of reliable data for the activation unit process for this study emphasizes the necessity of conducting a study by using

on-site data sources to ensure the accuracy of the obtained results. Although, these sets of unit processes considered in this study (Figures 3-2 to 3-5) are novel and these methods have not been employed yet, the data for energy requirement, GHG emissions, and cost of each unit process separately are available and can be used for the future studies.

The sets of unit processes in Figures 3-2 to 3-5 are proposed methods for activating forest residues to produce activated carbon and using activated carbon for water treatment in oil sands operations. Although, for designing these sets of unit processes the adaptability of each unit process to its next and previous units is considered, technical feasibility of these methods has not been studied yet, which means the combination of unit processes shown in Figures 3-2 to 3-5 might not be technically feasible. Furthermore, some of the products can be used in different ways. For instance, syngas can be either combusted in a combustor, or used as a fuel in a combined heat and power generation unit, or any unit process producing electricity. Therefore, a technical feasibility study is required to ensure whether these unit processes can work together effectively. This study also can suggest new sets of unit processes by replacing some of the unit processes or changing the combinations of units to improve the performance of the proposed systems.

In summary, to offer a practical solution for the problems associated with high concentration of organics in water of oil sands operation, comprehensive life cycle analyses considering possible alternatives to the proposed method, using forest residues for activated carbon production to be used for removal of organics, are required. These studies must compare the energy requirement, emissions, and cost of replacing equipment with using activated carbon for water treatment to know which method is more economical and environmental friendly. To conduct these analyses

using on-site data available for each unit process and a technical feasibility study of the proposed sets of unit processes will be helpful. Furthermore, comprehensive lab studies are required to define the maximum removal level can be obtained and whether any improvement in one or a number of the unit processes can result in achieving higher removal levels. Thus, the focus of the future studies in this area should be finding ways to improve this method and obtaining higher removal levels as increasing the removal level results in considerable reduction in the net GHG emissions of all the scenarios.

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APPENDIX A: SAMPLE OF CALCULATIONS

Calculating energy requirement, emissions, and cost for different unit processes in the factory scenarios:

A.1. Biomass transportation

A.1.1. Energy requirement

$$\text{Energy requirement(MJ)} = \text{Truck energy requirement} \left(\frac{\text{MJ}}{\text{Mg} \times \text{km}} \right) \times \text{Distance(km)} \times$$

$$\text{Mass of biomass(Mg)} \quad \text{A.1-1}$$

A.1.2. GHG Emissions

$$\text{Emissions(kg CO}_{2\text{eq}}) = \text{Transportation emissions} \left(\frac{\text{kg CO}_{2\text{eq}}}{\text{Mg} \times \text{km}} \right) \times \text{Distance(km)} \times$$

$$\text{Mass of biomass(Mg)} \quad \text{A.1-2}$$

A.1.3. Cost

$$\text{Cost(\$)} = \text{Transportation cost} \left(\frac{\$}{\text{Mg}} \right) \times \text{Mass of biomass(Mg)} = (5.7 + 0.1367 * 100) \times$$

$$500 \times 1.301 \left(\frac{\text{CAD 2004}}{\text{USD 2004}} \right) \times 1.19 \left(\frac{\text{CAD 2014}}{\text{CAD 2004}} \right) = 14994\$ \quad \text{A.1-3}$$

A.2. Pyrolysis

A.2.1. Energy requirement

$$\text{Conversion factor} = \frac{\text{Capacity of power plant (MW}_e\text{)} \times \text{Capacity factor (\%)} \times 365 \frac{\text{day}}{\text{year}} \times 24 \frac{\text{h}}{\text{day}} \times 3600 \frac{\text{MJ}}{\text{MWh}}}{\text{Biomass heating value} \left(\frac{\text{MJ}}{\text{Mg}} \right) \times 500 \text{Mg} \times \frac{1}{\text{efficiency (\%)}} \times 10000} \quad \text{A.2-1}$$

$$\text{Energy requirement (MJ)} = \left(\text{Construction energy requirement} \left(\frac{\text{MJ}}{\text{Mg}} \right) + \right.$$

$$\left. \text{Plant energy requirement} \left(\frac{\text{MJ}}{\text{Mg}} \right) \right) \times \frac{\text{Mass of biomass (Mg)}}{\text{Conversion factor}}$$

A.2-2

A.2.2. GHG Emissions

$$\text{Emissions (MJ)} = \left(\text{Construction emissions} \left(\frac{\text{kg CO}_{2\text{eq}}}{\text{Mg}} \right) + \text{Plant emissions} \left(\frac{\text{kg CO}_{2\text{eq}}}{\text{Mg}} \right) \right) \times$$

$$\text{Mass of biomass (Mg)} \quad \text{A.2-3}$$

A.2.3. Cost

$$\text{Cost (\$)} = \text{Capital cost (\$)} + \text{Operating cost (\$)} \quad \text{A.2-4}$$

A.3. Combined heat and power

A.3.1. Energy requirement

In this study, energy requirement is the amount of energy provided by external sources of energy such as fuels and if a unit process satisfies the energy demand of another unit process (e.g. the combined heat and power unit uses the syngas produced by pyrolysis unit as a source of energy)

this amount is not considered as energy requirement of the unit process. Therefore, the input energy of the combined heat and power unit is zero ($\text{Energy}_{\text{input}} = 0$).

$$\text{Energy requirement} = \text{Energy}_{\text{input}} - \text{Energy}_{\text{output}} = -\text{Produced heat} - \text{Produced electricity} \quad \text{A.3-1}$$

$$\begin{aligned} \text{Produced electricity (MJ)} &= \Delta H_{\text{combustion Syngas}} \left(\frac{\text{MJ}}{\text{Mg}} \right) \times \text{Mass of Syngas (Mg)} \times \text{Efficiency} = \\ 13160 \times 115.248 \times 0.35 &= 530832 \text{ MJ} \end{aligned} \quad \text{A.3-2}$$

$$\begin{aligned} \text{Produced heat (MJ)} &= \text{Produced electricity} \times \text{Heat – power ratio} = 530832 \times 1 = \\ 530832 \text{ MJ} \end{aligned} \quad \text{A.3-3}$$

A.3.2. GHG emissions

$$\text{Emissions (kg CO}_{2\text{eq}}) = \sum_i (M_i \times \text{GWP}_i) = M_{\text{CO}_2} \times \text{GWP}_{\text{CO}_2} + M_{\text{N}_2\text{O}} \times \text{GWP}_{\text{N}_2\text{O}} \quad \text{A.3-4}$$

$$M_{\text{CO}_2} = \text{Energy – emission factor CO}_2 \left(\frac{\text{Mg CO}_2}{\text{MJ}_e} \right) \times \text{Produced electricity (MJ}_e) \quad \text{A.3-5}$$

$$M_{\text{CO}_2} = \text{Energy – emission factor N}_2\text{O} \left(\frac{\text{Mg N}_2\text{O}}{\text{MJ}_e} \right) \times \text{Produced electricity (MJ}_e) \quad \text{A.3-6}$$

A.3.3. Cost

$$\text{Cost} = \text{Capital cost} + \text{Operating and Maintenance cost} - \text{Energy offset} \quad \text{A.3-7}$$

$$\text{Energy offset} = (\text{Produced heat (MJ)} + \text{Produced electricity (MJ)}) \times \text{Price of Natural gas} \left(\frac{\text{CAD 2014}}{\text{MJ}} \right) \quad \text{A.3-2}$$

Because capital and operating cost are reported in USD 2007, these values need to be converted to CAD 2014. According to website of Bank of Canada (<http://www.bankofcanada.ca>):

$$\text{CAD 2007} = 1.075 \times \text{USD 2007} \quad \text{A.3-8}$$

$$\frac{\text{CPI}_{2014}}{\text{CPI}_{2007}} = \frac{\text{Price}_{2014}}{\text{Price}_{2007}} \rightarrow \frac{\text{CAD 2014}}{\text{CAD 2007}} = \frac{123.1}{109.4} = 1.125 \quad \text{A.3-9}$$

A.4. Activation

Because a reliable source of data for energy requirement, cost and the amount of released greenhouse emissions for activation unit was not found, it is assumed that the activation unit is the same as mobile pyrolysis unit with the same capacity (mass of biochar instead of mass of dried biomass).

A.5. Activated carbon transportation

All calculations is the same as section A.1 (biomass transportation). The distance is assumed to be 200 km.

A.6. Landfill (Sequestration)

A.6.1. Energy requirement

Because the mass of spent AC is different in SAGD and the mining scenarios, in the following equation the mass of spent AC is showed as M_{SAC} .

$$\text{Energy requirement(MJ)} = (\text{Fuel consumption} \left(\frac{\text{MJ}}{\text{ha}} \right) + \text{Operation energy requirement} \left(\frac{\text{MJ}}{\text{ha}} \right)) \times$$

$$\frac{\text{Mass of Spent AC (Mg)}}{\text{Carbon application rate} \left(\frac{\text{Mg}}{\text{ha}} \right)} \quad \text{A.6-1}$$

A.6.2. GHG emissions

$$\begin{aligned} \text{Emissions (kg CO}_{2\text{eq}}) &= \text{Operation (kg CO}_{2\text{eq}}) - \text{Avoided N}_2\text{O (kg CO}_{2\text{eq}}) - \\ &\text{Benefit of landfilling (kg CO}_{2\text{eq}}) \end{aligned} \quad \text{A.6-2}$$

$$\begin{aligned} \text{Avoided N}_2\text{O (kg CO}_{2\text{eq}}) &= \text{Mass of Spent AC (Mg)} \times \text{Avoided N}_2\text{O (kg N}_2\text{O/Mg)} \times \\ \text{GWP}_{\text{N}_2\text{O}} &= M_{\text{SAC}} \times 0.394 \times 298 \end{aligned} \quad \text{A.6-3}$$

$$\begin{aligned} \text{Benefit of landfilling (kg CO}_{2\text{eq}}) &= \text{Mass of Spent AC (Mg)} \times \text{C retained in storage} \times \\ \text{C content of AC} \times \frac{\text{Molar mass of CO}_2}{\text{Molar mass of C}} &= M_{\text{SAC}} \times 0.85 \times 0.85 \times \frac{44}{12} \end{aligned} \quad \text{A.6-4}$$

$$\text{Operation (kg CO}_{2\text{eq}}) = \text{Energy requirement (MJ)} \times \text{Diesel emissions} \left(\frac{\text{kg CO}_{2\text{eq}}}{\text{MJ}} \right) \quad \text{A.6-5}$$

A.6.3. Cost

$$\begin{aligned} \text{Cost} &= \text{Diesel price} \left(\frac{\$}{\text{MJ}} \right) \times \text{Energy requirement (MJ)} - \text{C offset} \left(\frac{\$}{\text{kg CO}_{2\text{eq}}} \right) \times \\ &(\text{Avoided N}_2\text{O (kg CO}_{2\text{eq}}) + \text{Benefit of landfilling (kg CO}_{2\text{eq}})) \end{aligned} \quad \text{A.6-6}$$

A.7. Off-gas capture and combustion

A.7.1. Energy requirement

$$\begin{aligned} \text{Energy requirement(MJ)} &= \text{Energy}_{\text{input}} - \text{Energy}_{\text{output}} = \text{Operation energy requirement} \left(\frac{\text{MJ}}{\text{Mg}} \right) \times \\ &\text{Mass of removed organics(Mg)} - \left(\text{Mass of removed organics(Mg)} \times \right. \\ &\left. \text{Composition of methane in off - gas} \times \left(1 - \frac{\text{Percentage of methane converting to CO}_2(\%)}{100} \right) \right) \times \\ &\Delta H_{\text{combustion CH}_4} \left(\frac{\text{MJ}}{\text{Mg}} \right) \end{aligned} \quad \text{A.7-1}$$

A.7.2. GHG emissions

$$\begin{aligned} \text{Emissions (kg CO}_{2\text{eq}}) &= \text{Released emissions(kg CO}_{2\text{eq}}) + \\ &\text{Operation emissions(kg CO}_{2\text{eq}}) - \text{Avoided emissions(kg CO}_{2\text{eq}}) \end{aligned} \quad \text{A.7-2}$$

$$\text{Released emissions(kg CO}_{2\text{eq}}) = M_{\text{CO}_2} \times \text{GWP}_{\text{CO}_2} + M_{\text{CH}_4} \times \text{GWP}_{\text{CH}_4} \quad \text{A.7-3}$$

$$\begin{aligned} M_{\text{CO}_2} &= \text{Mass of removed organics(Mg)} \times \text{Composition of methane in off - gas} \times \\ &\frac{\text{Percentage of methane converting to CO}_2(\%)}{100} \end{aligned} \quad \text{A.7-4}$$

$$\begin{aligned} M_{\text{CH}_4} &= \text{Mass of removed organics(Mg)} \times \text{Composition of methane in off - gas} \times \\ &\left(1 - \frac{\text{Percentage of methane converting to CO}_2(\%)}{100} \right) \end{aligned} \quad \text{A.7-5}$$

$$\text{Operation emissions(kg CO}_{2\text{eq}}) = \text{Operation energy requirement} \left(\frac{\text{MJ}}{\text{Mg}} \right) \times$$

$$\text{Mass of removed organics(Mg)} \times \text{Diesel emissions} \left(\frac{\text{kg CO}_{2\text{eq}}}{\text{MJ}} \right) \quad \text{A.7-6}$$

$$\text{Avoided emissions (kg CO}_{2\text{eq})} = M_{\text{CO}_2} \times \text{GWP}_{\text{CH}_4} \quad \text{A.7-7}$$

A.7.3. Cost

$$\begin{aligned} \text{Cost(\$)} &= \text{Capital cost (\$)} + \text{Operating cost(\$)} - \text{C offset(\$)} - \text{Energy offset(\$)} = \\ &\text{Capital cost (\$)} + \text{Diesel price } \left(\frac{\$}{\text{MJ}} \right) \times \text{Energy requirement (MJ)} - \text{C offset} \left(\frac{\$}{\text{kg CO}_{2\text{eq}}} \right) \times \\ &\text{Avoided emissions (kg CO}_{2\text{eq})} - \text{Energy}_{\text{output}} \text{ (MJ)} \times \text{Price of Natural gas} \left(\frac{\text{CAD 2014}}{\text{MJ}} \right) \quad \text{A.7-8} \end{aligned}$$

APPENDIX B: ASSUMPTIONS

B.1. Field scenarios:

Assumption	Value	Source
Biomass preparation		
Diesel price (\$/L) - March 2014	1.36	[100]
Diesel emissions (kg CO ₂ eq/MJ)	0.07	[101]
Distance (km) – round trip	6	
Chipping cost (\$/Mg) – at landing	7.14	[81]
Chipping fuel consumption rate (L/h)	15.82	[71]
Transportation emissions (kg CO ₂ eq/Mg)	0.338	[82]
Drying		
Enthalpy of vaporization of water (MJ/Mg)	2257	[94]
Moisture content before (%)	25	
Moisture content after (%)	5	
Dryer fuel cost (\$/Mg) - wood shaving 10% moisture	40	[82]
Carbon content of wood shaving (%) assumed Bark	52.8	[77]
Energy content of wood shaving (MJ/kg) - Bark	19.2	[77]
Mobile pyrolysis		
Temperature (°C)	650	[10]
Biochar yield (%)	31	[10]
Syngas yield (%)	30	[10]
Distillate yield (%)	34	[10]
Energy requirement (MJ/kg dry feed)	4.07	[63]
Syngas enthalpy of combustion (MJ/Mg)	13160	[94]
Enthalpy of vaporization of water (MJ/Mg)	2257	[94]
Annualized fixed costs (\$)	120519	[66]
Annual variable costs (\$)	571640	[66]
Steam turbine		
Steam-power ratio (kg steam/ h.kWe)	17.65	[83]
Efficiency (%)	35	[67]
Capacity Factor (%)	75	[67]
Diesel Emissions (kg CO ₂ eq/MJ)	0.07	[101]
Estimated capacity (kWe)	50	
Lifetime (year)	5	
Replaced fuel (Natural gas) price (\$/MJ) - March 2014	0.0056	[84]
Combustion		
Capital cost (\$)	1215000	[87]
Lifetime (yr)	5	
Activation		
Excess steam (%)	100	
Burn-off (%)	30	
AC Transportation		
Distance (km) – round trip	400	

Adsorption		
SAGD		
Produced water organics concentration (mg/L)	1020	Experiment
Removal (%)	50	Experiment
Boiler Feed Concentration (mg/L)	497	
Removal Amount (g org/kg AC)	50	Experiment
Mining		
Tailings ponds organics concentration (mg/L)	75	[5]
Removal (%)	50	[5]
Treated water organics concentration (mg/L)	18.75	[5]
Removal Amount (g org/kg AC)	50	[5]
Sequestration		
Carbon Application Rate (Mg C/ha)	5	[17]
C retained in Storage (%)	85	[17]
C offset (\$/Mg CO _{2e}) - average amount	28	[5]
C content of AC (%)	85	[68]
Avoided N ₂ O (kg N ₂ O/Mg AC)	0.394	[17]
Fuel consumption (MJ/ha)	506	[17]
Operation energy requirement (MJ/ha)	60	[17]
Off-gas capture		
Capture efficiency (%)	75	[85]
CH ₄ in off-gas (%)	67.2	[5]
CO ₂ in biogas (%)	32.8	[5]
CH ₄ conversion to CO ₂ (%)	50	[5]
Methane enthalpy of combustion (MJ/kg)	50	[94]
Collection system cost (\$/ha)	40000	[102]
Gas pump system cost (\$/m ³ gas.hr)	137.5	[102]
Investment cost (\$) - Direct use	783	[102]
Operating and Maintenance Cost (\$)	47	[102]
Density of CH ₄ (Mg/m ³) - gas	0.00066	
Density of CO ₂ (Mg/m ³) - gas	0.002	
Density of off-gas (Mg/m ³)	0.00153	

B.2. Factory scenarios:

Assumption	Value	Source
Biomass transportation		
Moisture content before	25	
Moisture content after	20	
Distance (km) – round trip	100	
Transportation emissions (kg CO ₂ eq/Mg)	0.338	[82]
Biomass preparation		
Enthalpy of vaporization of water (MJ/Mg)	2257	[94]
Moisture content before drying (%)	20	
Moisture content after drying (%)	3	
Dryer Energy requirement (MJ/Mg)	350	[82]
Baling energy requirement (MJ/Mg)	199.6	[103]
Forwarding bales energy requirement (MJ/Mg)	46.67	[103]
Storage energy requirement (MJ/Mg)	26	[82]
Storage cost (\$/Mg)	0.08	[82]
Drying cost (\$/Mg)	10.3	[82]
Pyrolysis		
Temperature (°C)	650	[10]
Biochar yield (%)	31	[10]
Syngas yield (%)	30	[10]
Distillate yield (%)	34	[10]
Biomass HHV (MJ/Mg)	16200	[16]
Syngas enthalpy of combustion (MJ/Mg)	13160	[94]
Enthalpy of vaporization of water (MJ/Mg)	2257	[94]
Combined heat and power		
Heat-power ratio (kWth/kWe)	0.5	[73]
Power efficiency (%)	35	[74]
Syngas enthalpy of combustion (MJ/Mg)	13160	[94]
Lifetime (year)	25	
Replaced fuel (Natural gas) price (\$/MJ) - March 2014	0.0056	[84]
Activation		
Excess steam (%)	100	
Burn-off (%)	30	
AC Transportation		
Distance (km) – round trip	200	
Adsorption		
SAGD		
Produced water organics concentration (mg/L)	1020	Experiment
Removal (%)	50	Experiment
Boiler Feed Concentration (mg/L)	497	
Removal Amount (g org/kg AC)	50	Experiment
Mining		
Tailings ponds organics concentration (mg/L)	75	[5]

Removal (%)	50	[5]
Treated water organics concentration (mg/L)	18.75	[5]
Removal Amount (g org/kg AC)	50	[5]
Sequestration		
Carbon Application Rate (Mg C/ha)	5	[17]
C retained in Storage (%)	85	[17]
C offset (\$/Mg CO _{2e}) - average amount	28	[5]
C content of AC (%)	85	[68]
Avoided N ₂ O (kg N ₂ O/Mg AC)	0.394	[17]
Fuel consumption (MJ/ha)	506	[17]
Operation energy requirement (MJ/ha)	60	[17]
Off-gas capture		
Capture efficiency (%)	75	[85]
CH ₄ in off-gas (%)	67.2	[5]
CO ₂ in biogas (%)	32.8	[5]
CH ₄ conversion to CO ₂ (%)	50	[5]
Methane enthalpy of combustion (MJ/kg)	50	[94]
Collection system cost (\$/ha)	40000	[102]
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