Commercial Application of Pyrolysis Technology in Agriculture



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Preface

n 2010, the Ontario Federation of Agriculture (OFA) received Agriculture and Agri-Food Canada (AAFC) funding through the Canadian Agricultural Adaptation Council (CAAP) to conduct producer level research and value chain determination in support of commercializing agricultural biomass to energy and co-products.

In earlier studies, the OFA examined the opportunities to use biomass as a substitution for coal and natural gas, including a business case for purpose-grown biomass as a combustion fuel and the sustainable harvest of crop residues. As follow-up, a worldwide search of emerging commercial technologies resulted in more than 20 different technologies being evaluated by a technical panel and summarized in the report "Alternative Technologies to Transform Biomass into Energy". This report along with other biomass studies is available on the OFA website. Please visit www.ofa.on.ca/issues/overview/ biomass to access these previous studies including this report.

In this report, pyrolysis technology was identified as one of the emerging technologies with a significant potential for producing energy, bio-oil and bio-char from agricultural biomass. Building off of work done through ICFAR, Western University, potential uses were investigated for bio-oil and bio-char produced from pyrolysis of agricultural biomass. ICFAR is developing a commercial scale mobile pyrolysis unit that could offer the advantage of lower logistics costs and energy / co-products to producers. Under this value chain scenario, biomass is simply processed at the farm offering flexibility with harvesting and reducing costs. Particular focus was given to review ICFAR technology.

The ultimate goal of this study was to identify paths for commercializing pyrolysis technology in the agricultural sector in Ontario, developing the value chain from farm field to bio-products and linking proponents to produce a network capable of moving this potential opportunity forward.

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AAFC is committed to working with industry partners. The opinions expressed in this document are those of the OFA and not necessarily those of AAFC.

he objective of this report is to identify paths for commercializing pyrolysis technology in the agricultural sector in Ontario, developing the value chain from farm field to bio-products and linking proponents to produce a network capable of moving this potential opportunity forward. This objective was met by assessing the current state of pyrolysis technology with a particular focus on commercial applications for bio-oil and bio-char, by understanding the availability, cost and special characteristics of pyrolysis products from agricultural biomass, by testing the commercial readiness of the most promising pyrolysis technologies in agricultural applications and finally, by identifying key participants in this area of technology development within Canada.

There are numerous pyrolysis technologies developed. For agricultural applications, auger and fluidized bed (BFB and CFB) technologies are the most commercially relevant today. There have been a number of attempts to commercialize these technologies with the failures outnumbering the successes to date. Auger technology shows great promise for agricultural biomass conversion where bio-char production for agricultural applications is the priority. Both technologies can be effectively used for bio-oil production for CHP generation when low cost biomass sources can be made readily available.

Extracting maximum value from all of the product streams of pyrolysis is essential to commercialize this technology on a broad scale. NCG is best used for its energy content. Bio-oil is a very challenging mixture of biochemicals and water. Finding pathways to maximize its value has been and continues to be a priority. Today, bio-oil use is limited to energy generation despite all the claims of significant value-add potential. There is more innovation and development work required to extract this potential but a number of applications are emerging that could become commercial within the next two to three years. Canada must remain engaged in these initiatives to ensure that Canada can be an early adopter of any advances in technology. Bio-char is a low quality carbon source which has significant commercial potential in agricultural and environmental applications. Further application development is required to bring bio-char to market. Continued focus is needed during the next couple of years to accomplish commercial success.

Agricultural biomass is readily available from many sources. The major challenge is finding a source of biomass which is sufficiently low cost and low moisture content to allow conversion to pyrolysis products economically. Agricultural biomass can be generally categorized into two groups:

- Dry biomass (< 20 wt% moisture) which generally has a minimum price above \$60 per dry tonne (eg. Corn stover, wheat straw, energy crops etc.)
- Wet biomass (50-65 wt% moisture) which is currently considered waste and is a cost to producers for disposal (eg. Mushroom growing media, vegetable greenhouse residue, etc.)

The pyrolysis products produced vary greatly depending on the conversion technology and the biomass source used. Development is needed to understand these differences in order to identify commercial opportunities. An integrated system utilizing auger pyrolysis technology to convert mushroom growing media residue appears economical and should be demonstrated at commercial scale. The analysis shows that a positive business case can be generated with an integrated commercial unit of 10,000 wet tonnes per year capacity. Auger systems have been scaled to this capacity. However, further development of a fully integrated system and bio-char applications is required

Mobile fast pyrolysis using BFB technology as demonstrated by ICFAR shows promise but cannot be commercialized until dry agricultural biomass sources with lower cost are available. The analysis shows that the technology has significant promise but will require a source of dry biomass (< 20 wt% moisture) with a cost below \$60 per dry tonne. Through this study, no such agricultural biomass sources were identified. Further work is required to identify ways to reduce the cost of biomass. Removal of corn stover from agricultural land is in a nascent stage. The quantities of corn stover that can be sustainably removed and the economic benefits from its removal need to be determined based on the local conditions of soil, weather and farming practices. In the meantime, this technology needs to be advanced through its demonstration phase so that full proof of commercialization potential is available for exploitation.

Bio-char, when used for soil amendment or other agricultural applications, provides the opportunity for carbon to be sequestered for long periods of time. Half of the carbon in the biomass can be concentrated in the bio-char and sequestered. Bio-char is not a structured homogeneous material, but rather it possesses a range of chemical structures and a heterogeneous elemental composition. The scientific understanding between the bio-char chemical and structural characteristics and its longevity/stability (recalcitrance) in the natural soil environment remains poorly characterized. The ability of bio-char to resist abiotic and biotic degradation is crucial to its successful deployment as a carbon sequestration media. More work is required to better understand the ability of bio-char to sequester carbon in soil for the longer term.

Ontario needs to develop its R&D capabilities to understand the relevance of bio-char within this region. Currently, the Alberta Bio-char Initiative is making great strides in developing understanding in Alberta. Once Ontario establishes its R&D capability, a strong national collaboration can be developed to share relevant knowledge and implement solutions within the regions of Canada. The use of bio-char in agricultural applications is not fully understood. Addition of bio-char as a soil amendment could have benefits but this is greatly affected by land type, weather and farming practices. Unfortunately, these parameters vary greatly across Canada and there needs to be R&D conducted taking into account the local conditions. The University of Guelph Simcoe Research Station could be an ideal location to research bio-char impacts on agricultural and horticultural crops, due to the diversity of crops it can research.

1 - Overview of Pyrolysis and Chemical Conversion Technologies

everal parts of this Section were composed by Federico M. Berruti as the sole author and have been extracted from Federico M. Berruti's PhD thesis with his permission.

1.1 Introduction & Background

The declining reserves of fossil fuels and fossilfuel-related environmental issues, especially greenhouse gas (carbon dioxide, methane) emissions, have posed a great threat and challenge to the sustainability of the world economy, the global environment and hence the quality of life of human beings. The depleting resources and fluctuating prices of petroleum have intensified the search for alternative resources for both energy and chemical production. Forest and agricultural resources have traditionally been viewed as the source for only timber/pulp/paper, combustion and food, whereas the emerging "green" bio-economy of Canada targets new processes to convert them into not only traditional products but also renewable fuels and other value-added products. This can be accomplished by developing advanced bio-refining technologies fractionating biomass into various valuable products, including bio-energy, bio-fuels, and bio-based chemicals and materials, as outlined in the "Roadmap for Canadian Forest Biorefineries".

It is estimated that the share of global power generation from biomass power has reached about 10% in 2011. Fig. 1.1 illustrates the contribution of biomass and renewables to the world primary energy demand. Although this percentage is in the same order of magnitude as the other conventional sources such as oil, nuclear and natural gas, its application and use is relatively limited to biomass combustion for personal use in rural and underdeveloped areas. However, as a result of increasing awareness of environmental impacts of conventional energy technologies and new environmental legislation being passed in many industrialized countries, researchers now project that the overall percentage of global energy demand derived from biomass renewable sources worldwide could increase to nearly 16% by 2035.





1.2 Introduction to Biomass Pyrolysis

Biomass is a composite material made up of oxygen-containing organic components (cellulose, hemicellulose, lignin, organic extractives) and of inorganic minerals. It is a renewable and carbon dioxide neutral source of energy, essentially a form of stored solar energy captured through the process of photosynthesis by green plants. The green plants obtain their carbon by fixing the atmospheric carbon dioxide during photosynthesis. Traditionally, the term "biomass" also includes animal materials and source separated organic waste. Typically, the moisture content of the biomass varies between 50 and 60% and passive drying can reduce this to 30%. Active silo drying can reduce the moisture content further. The high moisture content and the low energy density of the raw biomass (one tenth of that of conventional liquid fuels) make it an uneconomical source of energy. Nevertheless, biomass can be converted through pyrolysis into a transportable liquid known as biooil with an energy density five times higher than that of the biomass. Originally the term pyrolysis implied the slow carbonization of carbon containing materials, like wood, for the production of charcoal. Today, however, pyrolysis is being applied as the thermochemical decomposition of organic matter in the absence of oxygen to produce liquid (biooil), solid (bio-char) and non-condensable gas (NCG) products. The aim of these products is to create added commercial value, including chemicals, petrochemicals and fuels, by controlling the reactor heating rate, reaction temperature residence times. Fig. 1.2 illustrates the process of pyrolysis and some potential product utilization.



Figure 1-2 Pyrolysis Chart (Berruti F.M., 2013).

1.3 Environmental Benefits of Pyrolysis

The conversion of agricultural, food, biofuel and forestry residues into value-added products via pyrolysis has many advantages:

- 1. It prevents these types of materials from being landfilled with potential environmental hazards such as surface and groundwater pollution, biohazards, foul odours and other noxious gases, and degrading under conditions that result in release of methane, which is a highly damaging greenhouse gas.
- It prevents direct combustion in open-air of the materials by users with no pollution or particulate controls.
- It produces renewable and sustainable alternatives to depleting fossil fuel reserves that produce lower emissions than fossil fuels when combusted:
 - a. Biomass fuels produce virtually no sulphur emissions, and help mitigate acid rain.
 Emissions of NO_x are typically much lower as well. Additionally, the utilization of biomass is carbon-neutral (or even carbonnegative with the carbon sequestration within the Bio-char produced, if it is returned to the earth for soil amendment purposes). The plants or crops from which biomass fuels are derived feed on carbon dioxide as they grow. As such, their use as a fuel does not add to the existing levels of carbon in the atmosphere.

1.4 Types of Pyrolysis

Conventional pyrolysis (also known as slow pyrolysis) is defined as the thermal cracking of organic-based materials in the absence of oxygen at slow heating rates (0.1-10°C/s). Slow pyrolysis chars are primarily used for soil based applications (ameliorant, slow release fertilizers, etc.) and can be used for energy applications.

Fast pyrolysis is a high-temperature process (400-550°C) in which biomass is rapidly heated (10-200°C/s) and decomposed to form vapours, aerosols, gases and char. Bio-oil is collected by rapid quench and condensation of the vapours and by coalescence of aerosols. Fast pyrolysis processes can produce 50-85% of liquid bio-oil, 15-25% of solid char and 10-20% of noncondensable gases, depending upon the feedstock used and the operating conditions. No residue is produced: bio-oil contains a wide range of chemical compounds and water which has potential uses beyond fuel while char can be handled and has properties that could be attractive for soil amendment (high surface area, water retention, greenhouse gas absorption), and the gases can be recycled back into the process as fuel (Mohan et al, 2006). As per discussions with Don Harfield (Alberta Innovate-AITF), fast pyrolysis bio-char contains higher concentrations of volatiles which limit its value for soil applications.

Flash pyrolysis is the term used to characterize a thermal-cracking process at a very high heating rate (>1000°C/s) and a very short vapour residence time to minimize secondary cracking and keep the liquid yields high. In flash pyrolysis, particle size must be small to mitigate internal heat transfer limitations. This type of pyrolysis can typically only be achieved in fluidized beds or circulating fluidized beds, which are also technologies.

Table 1.1 summarizes the types of pyrolysis andtypical reactor configurations used for theprocesses.

Auger type pyrolysis units are currently being tested in conventional pyrolysis for bio-char production at demonstration scale by AITF

Table 1-1	Characteristics of Various	Types o	f
Pyrolysis			

	Conventional Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
Operating Conditions Heating Rate (°C/s) Particle Size (mm) Vapour Residence Time (s)	0.1-10 5-50 450-550	10-200 <1 0.5-10	>1000 <0.2 <0.5
Product Yield (wt% wet basis) Liquid Char Gas	~30 ~35 ~35	60-75 15-25 15	~80 ~15 ~5
Reactor Configurations	Fixed Bed, Vacuum Reactors	Ablative, Auger, Fluidized Bed, Circulating Fluidized Bed Reactors	Fluidized Bed, Circulating Fluidized Bed, Downer Reactors

through funding from Western Economic Diversification.

1.5 Pyrolysis Reactor Technologies

All over the world researchers have been studying the pyrolysis of agricultural residues (straw, husks, corncobs, tea residues, sesame stalks, hazelnuts, sugarcane, sorghum, almond shells, rapeseeds, tobacco stalks and leaves, algae, cotton straw, sunflower bagasse, switch grass, woods and forestry residues, and many others) by utilizing a variety of different fluidized beds.

The heart of the fast pyrolysis process is the reactor, and considerable research and development has focused on different reactor technologies. During the past two decades, several different reactor designs have been studied and some processes have been tested. Examples include the Tech-Air process, the

Ensyn circulating fluidized bed; the Waterloo Fast Pyrolysis fluid bed, from which the RTI and the Dynamotive processes have been derived; the BTG rotating cone; the Karlsruhe BTL2; the Georgia Tech entrained flow reactor; the NREL vortex ablative system; and the Pyrovac vacuum process (Mohan et al, 2006). Few of these processes have reached the commercial scale, and none of them is fully operational on a continuous basis. The only current commercially relevant application of bio-oil chemicals, from the aqueous phase, is that of wood flavours, browning agents and liquid smoke. Bridgwater published an excellent review that classifies the reactors into (1) bubbling fluidized beds, (2) circulating fluidized beds, (3) ablative (vortex and rotating blade) reactors, (4) rotating cone and vacuum reactors, and (5) auger reactors.

1.5.1 Fluidized Bed Reactor

These types of reactors utilize vessels containing a mass of heated particles, such as inert sand or catalyst particles, that are "fluidized" by passing inert gas or recycled product gas through the particle bed. Biomass residue particles are injected into or above the hot sand bed by a solids feeder, such as a screw feeder or intermittent solid slug feeder.

1.5.1.1 Bubbling Fluidized Bed (BFB) Reactor

Bubbling fluidized bed reactors utilize fluidized bed reactors with gas passing through the reactor so that the solids fluidization is in the "bubbling" regime, i.e. the bed has fully expanded and is bubbling aggressively, but without reaching the turbulent flow regime. A schematic of a bubbling fluidized bed reactor process can be seen in Fig. 1.3. Industrially, this type of reactor has been used for pyrolysis by Dynamotive Inc. (400 kg/h) and RTI (20 kg/h) for stationary plants and by Agri-Therm Inc.



Figure 1-3 BFB Reactor Technology.

(200 kg/h) as a modified bubbling fluidized bed for a mobile pyrolysis system. After the shredded biomass enters the bed, it interacts with the hot and abrasive bubbling sand environment while reacting. Once the particles become small enough, they are blown out of the fluidized bed and captured in specially designed cyclones. For larger particle sizes, specially designed char segregation zones can be created in the reactor to segregate the char produced from the bed material and continuously remove it from the reactor with high purity. In laboratory-scale reactors, hot filters can be used to retain the char particles in the bed until the end of the experiments. Typically, vapour residence times in bubbling fluidized bed reactors are between 0.2-5s, depending on the reactor size.

Bubbling fluidized bed reactor capacities are dependent on surface heat transfer limitations (depending on reactor size) and also on the heat supply. Heat can be provided by preheating the recycled product gas used for fluidization or direct heating of the sand through the reactor wall in small scales or using heat exchangers. Table 1.2 illustrates the advantages andchallenges of the BFB reactor technology.

1.5.1.2 Circulating Fluidized Bed (CFB) Reactor

Like BFB reactors, CFB reactors also have high heat transfer rates and short vapour residence times (0.5-1 s). In these reactors, the heat transfer medium is the bed of particles (sand, catalyst, etc.) which is circulated, using high flowrates of gas, from the reactor vessel into a burner. In the burner, the particles are exposed to oxygen and recycled product gas or solid reaction products are burned to heat the particles and then they are circulated back into the reactor vessel (Fig. 1.4). As a result, the solid residence time is approximately the same as the vapour residence time, and the reactor operates at high superficial gas velocities (in transport conditions). As a result of these high flowrates, solids separation and bio-oil vapour condensation can become more challenging. CFB reactors can be either upflow (more traditionally) or downflow (used for plug flow control of short residence times).

Table 1.3 illustrates the advantages andchallenges of the CFB reactor technology.

Table 1-2 Advantages and Drawbacks of the BFB

Advantages	Drawbacks
Good temperature control and mixing	Product dilution from fluidization gas
Easy to scale up	Condensation train & separation challenges
Well-established technology	Particle size restricted
Intense heat and mass transfer	Char traps some sand



Recycled Gas Pre-heat

Figure 1-4 Circulating Fluidized Bed Reactor Technology.



Figure 1-5 Ablative Reactor Technology.

1.5.2 Ablative Reactor

Ablative pyrolysis processes involve the contact between the biomass residue and a hot reaction surface, which also performs mechanical ablation of the biomass surface removing the char layers formed. Heat transfer limitations do not exist within the particle in these processes as a result of the ablation, and therefore relatively large particles can be used (< 20 mm), however heat transfer limitations are often present in delivering the heat required to the reaction surface. Fig. 1.5 illustrates the Ablative reactor process and Table 1.4 summarizes the advantages and drawbacks of this system.

Table 1-3 Advantages and Drawbacks of the CFB

Advantages	Drawbacks
Well-established technology	Challenging to operate/condensation/ separation
Very large processing capacity	Smaller biomass particles required
Controllable residence time	High gas flow and product dilution
High heating rate	Char attrition, Char contains some sand
Good heat and mass transfer	High separation and quenching requirements

Table 1-4Advantages and Drawbacks of theAblative Reactor

Advantages	Drawbacks
Large particle sizes can be used	Reaction rates limited by heat transfer to the reactor
Inert gas is not required	Process is surface area controlled, high cost to scale up
Controllable residence time	High gas flow and product dilution
System is more intensive	
Good heat transfer	

Overview of Pyrolysis and Chemical Conversion Technologies



Figure 1-6 Rotating Cone Reactor Technology (Wagenaar et al, 1994).

1.5.3 Rotating Cone Reactor

Developed by a joint collaboration between the University of Twente and BTG, the rotating cone reactor involves the introduction of biomass residue particles at 120 kg/h and heat carrier particles (sand or catalyst) at the bottom of a rotating cone where the solids are mixed and

Table 1-5Advantages and Drawbacks of theRotating Cone Reactor

Advantages	Drawbacks
Centrifugal forces moves heated sand and biomass	Complex process
No carrier gas needed	Difficult to scale up
Easy quenching	High capital costs
	Small particle size needed

forced against the hot rotating surface for reaction. The solids are then forced upwards and out by the rotating cone (residence time can be controlled by rotation speed). Upon exiting the cone, the vapours are diverted to a condensation train while the solids are combusted in a fluidized bed (generating the heat for the process). Fig. 1.6 illustrates the rotating cone reactor technology and Table 1.5 summarizes the advantages and drawbacks of this system.

1.5.4 Vacuum Reactor

As the name suggests, vacuum pyrolysis is performed at a total pressure of about 15 kPa, with the biomass material moving in a hot (~450°C) agitation device. The biomass particles are exposed to a long residence time to fully react (due to the low heat transfer rate); while the organic vapour residence time is very short due to being under vacuum. Fig. 1.7 illustrates the Vacuum pyrolysis technology and Table 1.6 summarizes the advantages and drawbacks of this system. This technology was developed at the Université Laval and commercialized by Pyrovac (Xu, 2010). Pyrovac has completed the construction of one commercial facility which operated for a short period of time (Meier et al, 2013).

Table 1-6 Advantages and Drawbacks of theVacuum Reactor

Advantages	Drawbacks
Feed particle size flexibility	Low Bio-oil yield, Increased pyrolytic water generation
Fewer aerosols formed (easier quenching)	Low heating efficiency
Bio-oil free of char	Absorption of liquid effluents in the liquid ring compressor pump
No additional carrier gas/product dilution	High capital cost, maintenance cost and high sealing/gasket requirements



1.5.5 Auger Reactor

Auger pyrolysis reactors (Fig. 1.8) were developed and commercialized by Renewable Oil International (ROI, 200 kg/h), and ABRI-TECH Inc. (1 dry tonne/day). ABRI-Tech has sold a number of units at the 1 dry tonne per day scale and is presently manufacturing pyrolysis systems from 20 kg/day to 50 dry tonnes per day to address industry requirements (www.advbiorefineryinc.ca). Biomass is mixed with a dense heat carrier in the auger reactor. By using high thermal conductivity heat carriers, the energy required for fast pyrolysis is rapidly transferred to the biomass. The vapours generated are guickly diverted to a condensation train to minimize reaction time and the char produced is separated from the heat carrier independent of the pyrolysis reactions and into a char storage system. Table 1.7 summarizes the advantages and drawbacks of this system.

1.6 Pyrolysis Reactor Selection Criteria

Scott and others analyzed several reactors for fast biomass pyrolysis and concluded that none of the reactor concepts fully satisfy all requirements, in their present state of development (Scott et al, 1999). Based on their analysis, they indicated that the bio-oil quenching



Figure 1-8 Auger Reactor Technology (www.abritechinc.com, 2013).

Table 1-7 Advantages and Drawbacks of the Auger Reactor

Advantages	Drawbacks
Low pyrolysis temperature (400°C)	Plugging risk
Compact, flexible design	Lower bio-oil yield
No carrier gas/dilution	Moving parts in the hot zone
Quality bio-char produced	Heat transfer limitations at large scale

requirements should be minimized using the smallest possible gas to biomass feed ratio, and that the pyrolysis reactor should operate at the minimum possible temperature. They also concluded that a biomass conversion process, especially one producing liquid fuels, would be most useful if it were a simple process, not capital intensive, and that it could be operated efficiently on a small scale, while being scalable to larger sizes as well. Such a plant would not necessarily be suited as a centralized conversion plant, attempting to service a large area, as raw material shipping costs would make the economics prohibitive. On the contrary, an economical plant would have to be sited where the raw material could be easily supplied at a

reasonable or at no cost – with minimum transportation requirements and raw materials that have a "negative" value. The liquid product could then be used or modified on site, or more readily and economically transported to a central upgrading facility than the raw biomass (Scott & Piskorz, 1984).

Table 1.8 illustrates the valuation of the different reactor technologies, given these considerations. The BFB reactor and auger reactor technologies are shown to be the most promising overall.

The BFB Reactor technology was selected at ICFAR as the reactor of choice for laboratoryscale testing of different biomass feedstock, as it could also be scaled and give representative results of a potentially large-scale economic process. In addition, these considerations inspired the development of a joint venture between ICFAR and private investors, leading to the creation of a spin-off company. Agri-Therm is dedicated to developing, manufacturing and marketing portable (mobile) pyrolysis plants for the production of bio-oil and bio-products from biomass, with a focus on agricultural residues, forestry residues and transition crops. Berruti and Liu published a business case study (and teaching note) based on a mobile pyrolysis company called Agri-Therm Inc.. The case

Reactor Type	Simple	Capital Expense	Low Temperature	Low Gas/Solid Ratio	Operating Expense	Easy Scale-up
BFB	Very Good	Excellent	Very Good	Good	Very Good	Excellent
CFB	Fair	Good	Very Good	Poor	Fair	Very Good
Ablative	Fair	Very Good	Very Good	Excellent	Good	Very Poor
Rotating Cone	Fair	Good	Very Good	Very Good	Fair	Poor
Vacuum	Fair	Excellent	Excellent	Excellent	Poor	Good
Auger	Very Good	Excellent	Very Good	Excellent	Good	Poor

Table 1-8 Reactor Selection Criteria (Scott & Piskorz, 1984).

outlines the technical and business challenges and potential solutions for operating a smallbusiness enterprise within the renewable energy industry.

Dynamotive (OTCBB: DYTMF), a high-profile Canadian company in the bio-oil market also focused on the commercialization of bubbling fluidized bed technology. In 2005, Dynamotive completed its first demonstration scale plan in West Lorne, Ontario to produce up to 100 dry tonnes per day from wood waste biomass with moisture content less than 10%. The project was scheduled to deliver up to 2.5 MWe to the grid from the Orenda turbine. In 2006, Dynamotive broke ground for the MegaCity Recycling, 200 tonnes per day bio-oil plant in Guelph, Ontario (Meieret al, 2013). In 2010, due to plant performance setbacks and the lack of a large, stable and continuous supply of woody biomass feedstock to be shipped to its centralized facilities, Dynamotive's operations in Canada ceased and the plants were put into receivership.

Auger reactor technology is currently being deployed by ABRI-Tech. This technology can also be deployed in a pseudo-mobile (modular parts on skids). As of March 2012, ABRI-Tech has sold a number of 1 tonne per day pyrolysis demonstration units to Bioterre in Quebec, Alberta Innovates/Lakeland College in Alberta and USDOE Battelle Memorial laboratory in Ohio USA (Meier et al, 2013). Auger pyrolysis systems have generally been limited in size on account of the limited heat transfer through the auger shell wall. ABRI-Tech solved that problem by mixing the biomass with a dense heat carrier in the reactor auger. The biomass and the heat carrier are in intimate contact and therefore the transfer of energy from the heat carrier is guick and efficient. By using high thermal conductivity heat carriers, the energy required for fast pyrolysis is rapidly transferred to the biomass without the need for a fluidizing gas. The distance between

the reactor gas outlet and the first quench is short and hence residence times are similar to those reported for fluid and transport bed systems. A blower downstream of the condensers improves the removal of the hot vapours and maintains a reactor pressure close to atmospheric. Since a fluidizing gas is not required, then the condensers are required to cool and condense only the pyrolysis vapours and not the recirculating gas used in fluid and transport bed reactors. Condensers are therefore smaller and more efficient. The char is separated from the steel heat carrier using a simple gas recycle loop independent of the main pyrolysis reactions. Given the density difference between the char and the shot, only limited gas velocity is needed to strip the char from the shot. ABRI-Tech is presently manufacturing pyrolysis systems from 20 kg/day – a laboratory scale apparatus for research and development to 50 dry tonnes per day (15,000 dry tonnes per year). All units are skid mounted for easy rapid assembly and disassembly for moving (www.advbiorefineryinc.ca).

Pyrovac, in 1998 completed its vacuum-assisted pyrolysis plant (84 dry tonnes per day feed) in Jonquiere, Quebec and operated it for approximately 2000 hours before being mothballed. Recently, it has been announced that the plant has been sold to the USA-based company Three Dimensional Timberlands (TDT). The plant will be moved to the city of Gold Beach, Oregon where its initial focus will be to produce biochar (Meier, et al., 2013).

An updated **list of global companies and research groups,** with descriptions of their respective technologies for fast pyrolysis and upgrading, can be found in "Review of fast pyrolysis of biomass and product upgrading" (Bridgwater A., 2012).

1.7 State of Thermochemical Conversion Technologies

Significant research and development is ongoing on thermochemical conversion technologies. The US Department of Energy through its Energy Efficiency and Renewable Energy's multi-year program is providing significant financial and technical resources to this area of study. Research and development of bio-oil pathways focuses on numerous technologies. Two pathways are of particular interest:

- Liquefaction technology which thermally or chemically decomposes biomass to bio-oil intermediate such as fast pyrolysis. Catalytic fast pyrolysis employs a catalyst to produce a bio-oil with lower oxygen content than conventional fast pyrolysis. Other liquefaction technologies include hydrothermal liquefaction, solvent liquefaction, and hydropyrolysis. Each technology produced bio-oils with varying characteristics and properties for oxygen content, water content, or viscosity that depend on the processing conditions.
- 2. Bio-oil stabilization and upgrading technology which mitigates reactive compounds to improve storage and handling properties. This encompasses the removal of water, char, and ash particulates, and destabilizing components such as metals and oxygenated species. Hydroprocessing and similar thermal-catalytic processing techniques reduce the total oxygen and acid content, thereby increasing stability. This processing is required before a bio-oil intermediate can be processed under conventional hydroprocessing conditions in a stand-alone biorefinery or before it can become a suitable feedstock for a petroleum refinery.

The Bio-Oil Pathways R&D has prioritized its efforts in overcoming technical barriers based on techno-economic analysis. The design case



Figure 1-9 Conversion of Woody Feedstocks to Renewable Gasoline and Diesel Blend Stocks via Fast Pyrolysis.

results for a bio-oil pathway utilizing fast pyrolysis of woody biomass followed by hydroprocessing are illustrated below in the Figure 1.9. This analysis was completed using a 2,000 dry tonnes per day pyrolysis system with biomass costs at approximately \$80 US per dry tonne. Current state of technology shows fuel prices in excess of \$4 US per gallon with significant technological breakthroughs are required in order to achieve competitive fuel prices.

Current performance milestones under investigation would see fully integrated, pilot scale conversion processes for a "high impact" biomass feedstock to renewable gasoline or diesel via a direct liquefaction conversion process with bio-oil processing to a finished fuel by the end of 2017.

UOP LLC has taken a leading role in this area through their partnership with Ensyn that has formed the joint venture company, Envergent. UOP LLC was recently granted US Patent No: 8,519,203 B2 which makes a number of claims for LOW OXYGEN BIOMASS-DERIVED PYROLYSIS OILS AND METHODS FOR PRODUCING THE SAME. There were no specific ranges of oxygen content levels specified in the patent and it made no claims for full oxygen removal. Envergent is directly commercializing biomass fast pyrolysis for energy production with four plants in design around the world (Meier, et al., 2013).

The "Status of fast pyrolysis bio-oil technologies" was presented at the 21st European Biomass Conference and Exhibition in June 2013 which further supports the current view that bio-oil for combined heat and power (CHP) applications are commercially viable (Solantausta, et al., 2013). It further points to pilot/demonstration

plant construction sponsored by the US Department of Energy in the United States by Envergent in Hawaii and KiOR to produce transportation fuels (diesel and gasoline) through thermochemical transformation using fast pyrolysis.

CanmetENERGY has also carried out research on catalytic hydroprocessing of bio-oils to liquid biofuels. They have identified promising formulations for a relatively inexpensive welldispersed catalyst coupled with use of a liquid medium in which the bio-oil can react. Oxygen removal rates exceeding 90% were consistently obtained. This work has the potential to develop technology in Canada that can support the cost effective upgrading of bio-oil for integration into traditional petrochemical operations.



S everal parts of this Section were composed by Federico M. Berruti as the sole author and have been extracted from M. Berruti's PhD thesis with his permission.

2.1 Description & Properties

Bio-oil is a dark brown complex homogeneous mixture containing hundreds of polar organic compounds (including oxygenated organic compounds) and water (20-25 wt%). Bio-oils are more attractive than the simple biomass due to their potential to be used as fuels in internal combustion engines, furnaces, boilers and turbines as substitutes for fuel oil or diesel, either alone or as a suspension with other liquid fuels (Pütün, 2002). Several organic compounds with added commercial value can potentially be extracted from the bio-oil for food flavouring and pharmaceuticals. Additional advantages and benefits of the bio-oil over the biomass is that it is more easily stored and transported. In power generation systems, like turbines and engines, the gasification of bio-oil gives higher efficiencies as compared to those processes where direct gasification of the solid biomass is done.

Bio-oil can be made from a wide variety of forestry and agricultural residue materials, including wood, sugar cane bagasse, rice hulls and straw, peanuts hulls, switchgrass, wheat straw, corn, tobacco stalks, coconut fibres, and many others. Other organic byproducts of the poultry industry (chicken litter), of the pulp and paper industry (sludge), and of the ethanol manufacturing (dry distillers' grains) are also excellent feedstock. The physical properties and composition of the bio-oil depend on the type of feedstock and the operating conditions at which the pyrolysis reaction is carried out. Short vapour residence times and long solid residence times have been reported to give high yields of liquid bio-oil (75-80 wt % on a dry feed basis). The particle size of the feedstock fed to the pyrolysis reactors also influences the yield of bio-oil. Small biomass particle sizes (< 2 mm) render higher yields of liquid bio-oil than large particle sizes (if they are not early elutriated out of the reactor) as they have higher surface area per unit mass. The rapid cooling of the vapour products is essential to stop the thermal cracking of the bio-oil into non-condensable gases thus reducing the liquid yield. Bio-oil contains 45-50% oxygen, which is the primary difference between bio-oil and hydrocarbon fuels. Among the many species found within bio-oil, the most important are hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids and phenolics. With water, bio-oil forms microemulsions with a continuous aqueous phase and a discontinuous phase largely made from pyrolytic lignin. The lower heating value (LHV) of bio-oil is typically 17 to 30 MJ/kg, or approximately 50-75% of that of hydrocarbon oils, due to the oxygen and water content and the higher density (bio-oil specific gravity of 1.2 as compared to hydrocarbon oil 0.94). Addition of water causes the separation of the bio-oil into two fractions; a viscous lignincontaining phenolic fraction that settles and a water-soluble fraction, rich in carbohydratederived compounds, that floats. Bio-oil typically has a viscosity between 35-1000 cP at room temperature and therefore they can require some mild heating to pump easily.

In addition to transforming a low-value residue into a potentially high-value energy source; the

manufacture and use of bio-oil has the following properties:

- It is CO₂ neutral, contains no sulphur and less than 50 percent of the NO_x found in fossil fuels.
- It is combustible (with lower particulate emissions and fouling than direct biomass combustion).
- It contains 50-75% of the energy value of fossil fuels.
- It can rely exclusively on residues, eliminating impacts on food supply and pricing.
- It can be transported and potentially refined using existing petroleum shipping and refinement infrastructure.
- It is completely biodegradable (in the event of a spill or accident).
- It reduces the negative environmental impacts of burning biomass and agricultural residues.
- It mitigates the impact of directing these residues to existing landfills.

However, bio-oil is subject to aging when exposed to temperatures at or above room temperature for long periods of time. This deterioration is manifested in an increase in viscosity, typically reaching a plateau after 2-3 months. The addition of ethanol or methanol improves the bio-oil properties and the stability of the product. In addition, bio-oil can have a wide range of pH, depending on the feedstock, and can be corrosive on common construction materials such as aluminum and copper (Darmstadt H., et al., 2004). Bio-oil can also contain ash depending on the condensation and filtration system, which can cause corrosion and fouling of combustion equipment (Zhang, et al., 2007).

Table 2.1 illustrates the physical property differences between typical bio-oil and heavy fuel oil. Most of the refining challenges for the pyrolysis bio-oil are the result of the high water and oxygen content (leading to diluted hydrogen/carbon ratios) and the low pH, which can result in corrosion. In addition, pyrolysis biooil has higher content of sodium, calcium, potassium and (sometimes) chlorides, resulting in higher fouling rates. Pyrolysis bio-oil however has significantly lower sulphur content. Finally, a key difference is the lower heating value of the pyrolysis bio-oil relative to the heavy fuel oil,

Table 2-1 Physical Properties of Typical Bio-oil and Heavy Fuel Oil

Analysis	Pyrolysis Bio-oil	Heavy Fuel Oil
Water, wt%	20-30	0.1
Solids, wt%	<0.5	0.2-1.0
Ash, wt%	<0.1	0.03
Carbon, wt%	35-50	85.6
Hydrogen, wt%	8.5	10.3
Nitrogen, wt%	<0.4	0.6
Oxygen, wt%	44-50	0.6
Sulphur, wt%	<0.05	2.5
Vanadium, ppm	0.5	100
Sodium, ppm	38	20
Calcium, ppm	100	1
Potassium, ppm	220	1
Chloride, ppm	80	3
Stability/Aging	Can be unstable/age	Stable
Viscosity	15-35 at 40°C	351 at 50°C
Density (15°C), kg/dm ³	1.1-1.3	0.95
Flash Point, °C	40-110	100
Pour Point, °C	-10 to -35	+21
LHV, MJ/kg	15-30	40.7
рН	1.8-9	N/A

which typically is 50-75% of the heavy fuel oil value.

2.2 Bio-oil Applications and Upgrading

Crude bio-oil has the potential for multiple applications ranging from a variety of combined heat and power generation options to the extraction of specialty chemicals and flavours.

2.2.1 Applications for Heat and Power Generation

Liquid bio-oil has a significantly higher energy density than biomass and can be easily transported and stored with existing infrastructure and technology. Significant work has been carried out on research and development of bio-oil for heat and power generation, including the design and study of specialized bio-oil burners at CanmetENERGY and the Combustion Research Laboratory, at the University of Toronto (Tzanetakis T., et al., 2010). However, as discussed earlier, several bio-oil properties including the oxygen content, water content, oil stability/phases and aging, and ash content can make the conversion into heat and power significantly more challenging and ultimately limit the range of its applications.

Water content in the bio-oil has an impact on the heating value of the bio-oil. Water is present from two sources:

- 1. Water liberated during the pyrolysis process from the breakdown of the biomass
- 2. Water content of the biomass feed source.

Maintaining the moisture content of the biomass feed source below 10% provides a bio-oil with

moisture content generally between 15 to 30 percent by weight (Mullen, et al., 2010).

During recent industrial scale bio-oil combustion tests in Europe, bio-oil has been found to be technically suitable for replacing heavy fuel oil in district heating applications. This kind of replacement needs some modifications to be made to the existing units, which need to be engineered carefully. For example, all the parts in contact with bio-oil should be replaced with parts made of stainless steel or better, and the suitability of all gaskets and instruments needs to be checked. Special care has to be taken due to the instability of bio-oil. Heating should be carried out indirectly with a low temperature surface (e.g. warm water heat exchanger, jacketed tanks). Temperatures between 40-80°C are recommended for pumping in order to keep the viscosity low and reduce the rate of decomposition. Prolonged recycling of liquids with thermal cycling leads to a significant deterioration in quality and increase in viscosity.

In summary, when the unusual properties of bio-oil are taken into account, their combustion without a pilot flame or support fuel is feasible on an industrial scale.

2.2.2 Applications in Transportation Fuels

Currently there is extensive research underway in the areas of emulsification and blending (Boucher, et al., 2000; Boucher, Chaala, & Roy, 2000; Ikura, Stanciulescu, & Hogan, 2003), deoxygenation by catalytic vapour cracking and hydrotreating (Czernik, Evans, & French, 2007), and aqueous phase fermentation and steam reforming (Czernik, et al., 2002). This research is being performed to facilitate the economic use of bio-oil in conventional fuel products.

A number of technical reports provide in-depth reviews of the challenges associated with bio-oil

upgrading, technologies, products, and blending with biodiesel (Bridgwater, 2011 & 2012; Alcala & Bridgwater, 2013; Jacobson, Maheria, & Dalai, 2013; Karimi, et al., 2010).

As noted earlier in this report, conversion of biomass to transportation fuels using thermochemical processes is still in early stages of development. There are limited examples of pilot and demonstration plants currently under construction in the US. These projects are sponsored by funding from the US Department of Energy (USDOE). Current projections from the USDOE are that these technologies will take until at least 2017 before becoming economically viable. Commercialization of these technologies can then follow.

Recent discussions with Corporate Development at Suncor Energy have confirmed that the use of bio-oil in refining operations could be of long term strategic interest. However, the state of the technology today does not support imminent commercialization. The commercial potential of this technology is being assessed against other potential technologies in the renewable energy area. Resources will only be committed towards those technologies with the highest probability of commercial success within a reasonable investment window. Suncor Energy is not yet at a stage to make such a commitment.

2.2.3 Chemicals & Materials

Bio-oil contains hundreds of components, some of which are attractive due to their higher value

compared to fuels and energy products. As a result, the most economically sound approach to developing products from bio-oil may be to extract valuable chemicals and material building blocks from the oil first, and then to utilize the remaining bio-oil as a crude fuel. This residual bio-oil could be upgraded and fractionated into conventional fuels as required. Currently, there is a significant amount of research and development focused on the extraction and production of the chemicals and products from bio-oil. A list of potential bio-oil products and applications is shown in Table 2.2.

Food flavouring agents are commercially produced from wood pyrolysis products in many countries (Radlein & Piskorz, 1997), with the key components being guaiacols (Simon, et al., 2005). One such product (liquid smoke) is produced from the pyrolysis of specified blends of woody biomass and sold directly as a finished product without significant post-processing.

Chemical markets require sufficient quantities to be produced to allow for sufficient market penetration. Corn stover is the largest single source of agricultural residues. To better appreciate this potential, a number of individual chemical compounds found in the bio-oil produced from the fast pyrolysis of corn cobs and corn stover are quantified and shown in Table 2-3.

The chemical compounds most abundant in the bio-oil are small water soluble oxygenated molecules derived from the cellulose and

Products	Acetic Acid	Sugars	Hydrogen	Levoglucosan	Flavouring Agents/Guaiacols
Applications	Pharmaceuticals	Adhesives /Resins	Pesticides	Preservatives	Fire-Resistant Foams

Table 2-2 Potential Bio-oil Products and Applications (Bridgewater, et al., 2001 & Xu, 2010)

Table 2-3 Quantification of Bio-oil Compounds Produced from Corn Residues (Mullen, et al., 2010)

		Corn cob bio-oil			Corn stover bio-oil		
Method	Compound	Condensers 1–4	ESP	Whole oil ^b	Condensers 1-4	ESP	Whole oil ^b
K-F ^c	Water (wt% of bio-oil)	37.68	11.27	24.83	15.54	5.94	9.15
Cellulose/her	micellulose derived compounds (wt% of	bio-oil)					
HPLC	Levoglucosan	6.91	3.63	5.31	14.75	11.33	12.36
HPLC	Hydroxyacetaldehyde	0.86	2.05	1.44	4.03	3.99	4.00
HPLC	Acetic acid	6.44	6.42	6.43	7.56	6.20	6.26
HPLC	Acetol	10.38	9.89	10.14	8.58	6.40	7.08
GC	Furfural	0.89	1.53	1.20	0.60	0.79	0.71
GC	Furfuryl alcohol	0.24	0.36	0.30	0.14	-	0.04
GC	3-Methyl-2-cyclopenten-1-one	0.26	0.51	0.38	0.08	0.09	0.09
GC	4-Hydroxy-4-methyl-2-pentanone	0.08	0.17	0.12	0.07	0.13	0.11
Lignin-derive	ed compounds (wt% of bio-oil)						
GC	Phenol	0.64	0.96	0.79	0.13	0.33	0.30
GC	o-Cresol	0.15	0.22	0.17	0.08	0.12	0.10
GC	p-Cresol	0.15	0.22	0.19	0.05	0.13	0.12
GC	m-Cresol	0.13	0.15	0.17	0.03	0.03	0.03
GC	2,4-Dimethyl phenol	0.05	0.04	0.05	-	-	-
GC	3,5-Dimethylphenol	0.03	0.38	0.02	-	-	-
GC	4-Ethyl phenol	0.37	0.33	0.54	0.17	0.25	0.22
GC	3-Ethylphenol	0.03	-	0.02	-	-	-
GC	2-Ethylphenol	0.02	-	0.01	-	-	-
GC	Guaiacol	0.44	0.78	0.61	0.19	0.29	0.25
GC	2-Methoxy-4-methyl phenol	0.37	0.25	0.31	0.22	0.15	0.17
GC	Isoeugenol	0.22	0.35	0.28	0.14	1.26	0.82
GC	2,6-Dimethoxyphenol	0.41	0.84	0.63	0.24	0.46	0.38

a Average from two pyrolysis runs for each feedstock.

b Whole bio-oil percentages based on a weighted sum of the condenser and ESP bio-oils.

c K-F: Karl-Fischer Titration.

hemicellulose in the corn crop residues. The most abundant compounds in this class are levoglucosan, hydroxyacetaldehyde, acetol and acetic acid.

Isolating chemical compounds from complex mixture such as bio-oil is very difficult and will prove to be uneconomical in most circumstances. For example, levoglucosan is the most concentrated compound in the bio-oil from corn stover at 12% by weight. A process has been patented that claims the "Isolation of levoglucosan from pyrolysis oil derived from cellulose" (US Patent No: 5,371,212). This patent describes how high purity levoglucosan can be prepared using a five step process described simply here as:

- 1. Diluting and adjusting pH above 12 with a basic metal hydroxide, oxide or salt
- 2. Drying azeotropically with methyl isobutyl ketone solvent and further drying by evaporation
- 3. Reducing the levoglucosan residue into a powder
- 4. Continuously extracting said powder with ethyl acetate, and
- 5. Concentrating the levoglucosan-rich extract by removing the ethyl acetate

Producing high purity levoglucosan economically with this multi-step process which requires two different solvents would be very challenging due to anticipated capital/operating costs and yield losses. A very high price for levoglucosan would be required to justify the expense of such a complex process.

Decomposition of the lignin found in the corn crop residues results in the production of numerous water insoluble phenolic compounds both monomeric derivatives (phenol, ethyl phenol, cresol, guaiacol, isoeugenol) and higher molecular weight lignin oligomers.

Phenolic compounds contained in the bio-oil can also be used to replace fossil-fuel based phenols in the production of resins, adhesives and fireresistant foams (Athanassiadou, Tsiantzi, & Nakos, 2008). This study concluded the following:

- Bio-oil can be used in the manufacture of phenolic resins for various wood pane types with positive results.
- 2. Up to 50% phenol substitution can be realized, and
- 3. The price of the bio-oil phenolic fraction could be maximum 50% of the hydrocarbon-based phenol price in order to provide incentive to the resin manufacturer.

The recent contract settle price for phenol in North America is ca. 84¢US per pound (\$1850 US/tonne). If this application could be commercialized, then this would translate into a price for the bio-oil phenolic fraction of 42¢ US per pound (\$925 US/tonne). The potential to use bio-oils from the pyrolysis of lignin isolated from agricultural residues may be an interesting area for further study (Gosselink, et al., 2011).

2.2.4 Pharmaceuticals and Bioactive Compounds

Plants produce a wide variety of chemicals that can be used as active ingredients in drugs and pharmaceuticals. Unfortunately, plants often contain only minor amounts of these chemicals.

Extraction and concentration of active ingredients at industrial scale are particularly difficult and mostly uneconomical. Fast pyrolysis has shown promise as a method for extracting and concentrating some valuable chemicals, including alkaloids, even when they have low volatility and limited thermal stability. Nicotine is an alkaloid present in tobacco that may offer alternative applications such as the manufacturing of nicotine patches for pharmaceutical use. Nicotine concentrations of 1.5 – 4.0 mg/mL in the tobacco bio-oil have been produced (Berruti, et al., 2007). Further work should be done to compare the cost competitiveness of nicotine production through the pyrolysis route versus the traditional extraction process from raw tobacco.

Due to its typical insecticidal, fungicidal and bactericidal characteristics, bio-oil can be used as a wood preservative (Freel, 2009) or for its pesticidal activity (Bedmutha, 2008). Cresol and phenolic compounds formed from the pyrolysis of the lignin portion of agricultural residues are known for their wood preservative properties.

Tomato, potato and tobacco are members of the solanaceae family which produce solanesol which is known for its pesticidal properties. Bio-oil from the pyrolysis of tobacco residues has shown pesticide characteristics toward three problematic microorganisms (C. michiganensis, S. scabies, or P. ultimum) as well as the Colorado Potato Beetle (CPB), a major agricultural pest. Nicotine was found to be active against the CPB. However, the nicotine-free fractions of tobacco bio-oil were also found to be active (Booker, et al., 2010; Booker, Conn, & Briens, 2010). Work conducted at the AAFC Research Centre in London has shown that tomato plant residue biooil also has, albeit weaker, pesticide properties toward CPB than tobacco residue bio-oil.

Work continues to isolate the specific chemical species which are primarily responsible for the pesticide properties of the bio-oil. It will be necessary to separate these species from the bio-oil in order to gain regulatory approval for their commercial use. Researchers at the AAFC Research Centre in London Ontario believe that this work is a long term initiative worthy of continued study due to its significant potential benefits.

2.3 Bio-oil Pricing

The market for bio-oil is still developing, and it is currently not a traded commodity. There may be value as a result of the special chemicals and products contained within the bio-oil. However, this value potential of the bio-oil cannot be realized at this time as the technology required to extract this value is not commercially available. The value of bio-oil can be quantified by comparing its heating value to heavy fuel oil as combustion of bio-oil in CHP is the most probable commercial use. As an initial approximation, the price of bio-oil can be prorated to the price of fuel oil based on the relative heating value. A price of 15Ø/litre for bio-oil was used based on having 40% of fuel oil energy content. A second, more practical way to value bio-oil in CHP systems is its value based on the price of electricity generated and the cost of the local fuel source that it displaces to generate the steam and power. In Ontario, the price of electricity from biomass at FIT rate is \$0.13/kWh. In most cases, the fuel source displaced will be natural gas or heavy fuel oil. It is important to consider the full delivered cost of the fuel source to the boiler burner tip and the CHP conversion efficiency. This may be unique to each system.



he term "bio-char" is commonly used to describe anything that is black, powdery or granular, and made from organics or biomass. Bio-char is more accurately defined as the solid carbon-rich product that is produced when biomass, such as wood, agricultural residues and wastes are heated in an oxygen deficit system. Bio-char is created during pyrolysis and to a minor extent from gasification and imperfect combustion processes. Bio-char can be applied to soil as a means to improve soil health, to filter and retain nutrients from percolating soil water. It is claimed to provide a means to sequester and remove carbon from the atmosphere when applied as a soil amendment that stores carbon and reduces emission from soils of strong greenhouse gases such as nitrous oxide and methane (NERC, 2013 & Barrow, 2012).

Bio-char's chemical and physical characteristics can vary widely depending on the converted feedstock and the operating conditions of the pyrolysis process. As a result, bio-char should be characterized and defined by its production process in addition to its specific chemical composition and solid structure (Lehmann, 2009).

Bio-char can be modified through subsequent processing to increase its surface area thereby improving its ability to perform as an activated carbon which can remove heavy metals, pollutants and other contaminants from waste water and flue gas (Cruz-Cabllos, 2013).

3.1 Bio-char Description & Properties

Bio-char is generally characterized by its physical properties (eg. particle size, particle size distribution, surface area, moisture content, volatile matter content and pH) and its chemical composition (eg. elemental analysis, heating value). Considering all the various sources of feedstock and pyrolysis operating conditions, it is not surprising that bio-char behaviour is not easily predicted.

3.1.1 Bio-char Surface Area

Bio-char from pyrolysis processes can have surface area values ranging from $0.5 - 450 \text{ m}^2/\text{g}$, which is significantly lower than commercial activated carbons produced from petroleum sources (500-1200 m²/g). As a result, thermal, physical or chemical activation of bio-char is required in order to increase its adsorption characteristics for metals, pollutants and other contaminants. Bio-char produced from corn stover and cobs through fast pyrolysis was shown to have surface area values $< 5 \text{ m}^2/\text{g}$. Because of these relatively low surface areas, this bio-char may not be ideal for soil quality enhancement (Mullen, 2010). Generally, bio-char produced through slower pyrolysis processes have higher surface area properties.

3.1.2 Bio-char Elemental Analysis

Bio-char is the solid carbon-rich portion from the pyrolysis process. Typically carbon content is greater than 50% and can be as high as 80% depending upon the elemental breakdown of the biomass feedstock coupled with the pyrolysis process used. A typical elemental analysis of corn biomass components (corn cobs and corn stover) is shown in Table 3.1.

The carbon: oxygen and the carbon: hydrogen ratios are significantly higher in the bio-char relative to the biomass feedstock as the oxygen and hydrogen partition themselves during pyrolysis toward the non-condensable gases and water (CO, CO_2 and H_2O).

Table 3-1 Elemental Analysis (Dry Basis) of Bio-char from Fast Pyrolysis of Corn Cobs and Corn Stover (Mullen, 2010).

Element Content (wt %)	Bio-char from Cobs	Bio-char from Stover
Carbon	77.6%	57.29%
Hydrogen	3.05%	2.86%
Nitrogen	0.85%	1.47%
Sulphur	0.02%	0.15%
Oxygen	5.11%	5.45%
Ash	13.34%	32.78%

The nitrogen content is split between the bio-oil and the bio-char. The plant mineral nutrients such as potassium (K), phosphorous (P), calcium (Ca) and magnesium (Mg) are concentrated in the bio-char as ash. The bio-char ash content can generally be predicted from the mineral content in the raw biomass and the bio-char yield.

3.1.3 Bio-char Heating Value

Because of the high carbon content and the relatively low moisture content, bio-char has heating values comparable to some coals. Biochar from corn biomass had LHV values between 21 and 30 MJ/kg (Mullen, 2010). Nitrogen and sulphur levels in the bio-char are relatively low. This is important information for predicting NOx and SOx emissions from the combustion of biochar.

3.1.4 Bio-char Soil Application Properties

On April 11, 2013, the International Bio-char Initiative (IBI, non-profit organization) released the Bio-char Standardization report, which is the result of a multi-year project with international input from various stakeholders on how to sell and use bio-char safely for soil applications. This has led to a significant improvement in defining bio-char characteristics and contains useful references (IBI, 2013). The report specifies the annual testing (or after a material change in feedstock or production process) procedures that are necessary and optional for bio-char to be sold on the market as follows:

- Test Category A Basic Utility Properties (required for all bio-char).
 - Particle size, moisture, chemical properties (full elemental analysis), ash %, electrical conductivity (EC), and pH/liming. The ratio of hydrogen to organic carbon is an indicator of the carbon stability, and allows the bio-char to be classified.
- 2. Test Category B Soil Toxicant Report (required for all Bio-chars).
 - A maximum allowable threshold (MAT) table is given for various compounds and tests and must be followed (including polycyclic aromatics, dioxin, PCBs, arsenic, lead, mercury, etc.). Some compound MATs are jurisdictional.
- 3. Test Category C Advanced Analysis and Soil Enhancement Properties (optional).
 - Extra tests and evidence of soil enhancement properties can be attached by the producer/supplier to the reports, summarized in a specific table with typical fertilizer (mineral nitrogen, available phoshorous, potassium, surface area, etc.) and performance measures.

Introduction of these bio-char soil application properties will allow for a consistent assessment of bio-char for soil applications. This will aid in separating the wide array of bio-char claims made for the various feedstock and with the various pyrolysis processes.

3.2 Bio-char Applications

3.2.1 Agricultural Applications

Potential agricultural applications include soil amendment, greenhouse growth media, mushroom growth media, nutrient-enriched soil supplement (fertilizer) and carbon sequestration.

Bio-char volatile matter has been identified as key property for its suitability in soil amendment applications (Don Harfield, Alberta Innovate-AITF, Personal Communications). Volatile matter content has been specifically measured and is being correlated to the existence of toxic polycyclic aromatics (PAHs). According to Don, three quality grades of bio-char exist based on differences in the volatile matter and PAH contents:

- Premium quality bio-char with volatiles content less than 8 wt% dry basis. This biochar has been used to partially displace coconut coir in greenhouse applications
- Mid-grade quality bio-char with volatiles content between 12-15 wt% dry basis. This bio-char could potentially be used in horticultural blends with compost
- Regular quality bio-char with volatiles content between 20-25 wt% dry basis which could be used on land applications with green manure

Bio-char has also been produced from mushroom farm residue and has been used to partially displace fresh peat in mushroom media.

Bio-char in soil releases mineral nutrients to help plant development and may be able to decontaminate soils through pollutant adsorption, thus increasing plant yields through increased soil quality (NERC, 2013; Barrow, 2012; Lehmann, 2009).

3.2.2 Activated Carbon Applications

Bio-adsorbents can be used for land reclamation, water remediation or air emission control. This is accomplished through adsorption of heavy metals, pollutants and other contaminants.

Bio-adsorbents can be created from bio-char, either by treating the bio-char itself as an adsorbing agent, or by using the bio-char as a precursor for activated carbon. Thermal or chemical activation with steam or CO2 following pyrolysis is known to increase the surface area of the bio-char. Literature, process, research and specific applications can be found in the Chapter 1, pages 11-19 from the book, "Biochar: Potential for countering land degradation and for improving agriculture" (Cruz-Cabllos, 2013).

Commercially relevant activated carbon is a crude form of graphite (100% carbon) containing less than 10 wt% ash/impurities and free of volatile matter. Commercial activated carbon has a porous carbon structure that is created through thermal activation at 750°C. Chemical activation with CO2 or steam further increases the surface area (Dr. M. Greenbank, Sr. Surface Scientist Calgon Carbon Corporation, Personal Communications).

Dr. Greenbank confirms that activated carbon can be produced from bio-char but with a significant yield loss. The carbon content of carbohydrates (major component in biomass) is 45% and as such establishes the theoretical maximum yield of activated carbon. Experience has shown that typical activated carbon yields are 10 wt% of the biomass used. These yield losses occur through the pyrolysis process and any subsequent thermal and chemical activation steps that are done to eliminate volatile matter and increase the surface area towards 1000 m2/g. With these low activated carbon yields, ash content of the activated carbon is too high and requires acid and water washing to reduce the ash content below 10 wt%.

Currently charred coconut shells are used to produce activated carbon. These charred coconut shells are produced by farmers in Southeast Asia and India. According to Dr. Greenbank, prices of 5-10¢ US per pound (\$110-\$220 US/tonne) have been published in conference papers.

Based on the required processing and the typical market price of 50¢ US per pound (\$1100 US/tonne), it will not be economical to produce activated carbon from agricultural biomass with current price structures.

Bio-char could potentially be used directly in one of the least challenging applications for activated carbon such as soil remediation. In this application, lower quality activated carbon is added to soil to trap and hold volatiles. This application is controlled by the environmental authorities and there are strict requirements for volatile leaching rates. More bio-char would be required than activated carbon due to the lower surface area and adsorption capacity. This would require the bio-char to be priced lower than activated carbon to allow substitution into this application. Furthermore, any bio-char used in this application must have a very low volatile content.

3.2.3 Heat Source for Heat and Power Generation (Bio-coal)

Bio-char can be used directly for clean heat and power generation. Bio-coal can be created via torrefaction (a mild pyrolysis in the 200-300°C range) to mitigate problems with direct biomass combustion, such as non-homogenous combustion, low bulk density, high water affinity, low energy content, and rotting characteristics, to then be used for clean heat and power generation (Cruz-Cabllos, 2013).

3.2.4 Other Applications

Other potential applications include metallurgical (redefined as bio-coke) and advanced materials manufacturing (nanotubes, fibers, composites, etc.). These applications are not well developed at this time and there has been no further consideration of these applications in this study.

3.3 Bio-char Pricing

Bio-char can be used to generate steam and power. In this application, bio-char has a value equivalent to the relative heat content of the heating media displaced from the heating system.

Currently, there are initiatives in the precommercial stage which can provide some indication of the potential value of bio-char in agricultural applications.

Bio-char has been produced with sufficient quality that it can partially replace existing growing media used in the greenhouse and mushroom industries. The successful displacement of these existing materials could allow bio-char to be priced in the range of \$250-\$1000 per tonne. As per discussions with Don Harfield, most bio-char currently produced in larger quantities would be valued at the lower end of this range.

Without a full assessment of the life cycle impacts of bio-char in agricultural applications, it is not possible to predict any potential value from carbon sequestration. Any value placed here would be speculative as it would require a carbon pricing structure to be put in place.

To move bio-char towards commercialization, there is a need to broaden the scope of bio-char

research to include perspectives such as the use of bio-char for adaptation of Canadian agricultural practices to climate change, improvement of marginal soils in order to increase the area of land suitable for food production, filtration of agricultural runoff from farms to reduce fertilizer-associated water pollution, removal of heavy metal contaminants from soils and improved nutrient management which could help insulate crop producers against volatility in nitrogen prices and delay the time of peak phosphorus extraction.

Lakeland College and AITF with assistance from WD and industry support have developed the Alberta Bio-char Initiative (ABI). ABI is spearheading the bio-char related research in Canada covering the full spectrum from production, characterization, application development, registration, protocol/guideline development, to life cycle analysis (LCA) and carbon sequestration quantification of bio-char. The Alberta Biochar Initiative (http://albertabiochar.ca) has been developed around six themes that address the business and technology gaps identified above. These six themes are:

- 1. Bio-char production
- 2. Growth media for greenhouse crops
- 3. Bio-char for land reclamation/remediation and waste water treatment
- 4. Demonstrating bio-char as a soil amendment to boost crop yield
- 5. Alberta bio-char partner engagement
- 6. Quantification of the carbon sequestration potential of bio-char

Further work needs to be coordinated across Canada to understand local agricultural issues and advance this technology. ABI offers a conducive platform for such Canada-wide consultation and collaboration.



here are wide array of agricultural biomass that can be considered as potential feedstock for commercial pyrolysis applications. Each source has its own set of issues and opportunities which need to be considered when assessing its potential for commercial use with pyrolysis technology. This section of the report will review the current availability and state of knowledge regarding the most prominent sources of agricultural biomass.

4.1 Corn Stover and Wheat Straw

4.1.1 Availability and Pricing

Corn stover can be sustainably removed from farmland in Ontario. Based on Oo and Lalonde's work within the four county area of Lambton, Huron, Middlesex and Chatham-Kent, the average sustainable corn stover harvest rate is approximately 1.2 tonnes per acre. On a 100% dry matter basis, this equates to approximately 1.0 tonne per acre. This is based on the assumptions that conservation tillage is used and that corn is grown in a rotation with soybeans and wheat. This is a typical rotation for many farms in this region. From 2003 to 2012, the average amount of corn stover that could be harvested sustainably in this region was over 500,000 dry tonnes per year.

Wheat straw is also available southwestern Ontario in large amounts. Wheat straw can be sustainably harvested at 1.2 tonnes per acre (15% moisture). The amount of wheat straw that could be harvested sustainably in this region was over 350,000 dry tonnes per year.

Both biomass sources are produced once annually (summer for straw and fall for corn stover) which must be considered in the logistics of the pyrolysis processing. Either of these biomass sources would need to be stored to spread out their processing throughout the year or they would need to be processed on a campaign basis following harvest. These considerations will have an impact on the size and mobility of any pyrolysis processing plant.

Bale handling and biomass feed preparation (e.g. grinding) would need to be considered as part of the pyrolysis processing of these biomass sources.

Harvest costs for corn stover were recently studied and summarized as part of a larger corn stover to bioproducts study (Duffy & Marchand, 2013). From this work, stover costs based on harvest costs (discbine, raking and baling, stacking) averaged \$66 per dry tonne over the last ten years. Nutrient value in the corn stover would add, on average over the same period, \$9 per dry tonne to the cost of the stover. This value would be minimized if the bio-char from the pyrolysis was returned to the farm land for soil amendment.

There continues to be much discussion about the potential detrimental effects of excess corn stover on the subsequent year's crop yields as corn yields continue to climb higher. At some point in time, corn stover may need to be removed from the fields to minimize this impact. Currently, the corn stover would require processing in some fashion and pyrolysis could be a solution.

Wheat straw has alternative uses in livestock feed rations and as bedding. Based on the annual fair market value from 2003 to 2012 reported by Agricorp, the value of straw ranged from \$89 to \$149 per tonne with an average of \$108 per tonne (Duffy & Marchand, 2013).

4.1.2 Pyrolysis Products

As noted above, there is an abundant supply of corn stover that can be sustainably removed from agricultural lands in Ontario. Corn stover is made up of cellulose, hemicellulose and lignin. It is a typical agricultural biomass and has a composition which is representative of other agricultural biomass such as wheat straw and purpose grown crops such as miscanthus and switchgrass. Pyrolysis products from wheat straw biomass sources are similar to those from corn stover (Demirbas, 2004 & Pütün, 2002). Fast pyrolysis of corn cobs and corn stover has also been studied in detail (Mullen, 2010). For these reasons, fast pyrolysis of corn stover was used as the basis for much of the discussion regarding bio-oil and bio-char properties summarized above in Section 3.

Bio-oil from corn stover does not contain significant quantities of known chemicals with unique bioactive or pharmaceutical properties. As such, bio-oil from corn stover will be limited to use as a fuel source in commercial energy applications.

A mobile fast pyrolysis unit could be used in this application as energy densification is needed to minimize logistics costs. Collection and transportation of the bio-oil to a centralized power generation facility could be envisioned. Bio-char produced remotely could be used as soil amendment thereby ensuring that the minerals contained in the biomass are returned to the farm. However, bio-char from corn stover residues has not yet been sufficiently studied to determine its quality and establish a value as a soil amendment above an accepted baseline value of \$250 per tonne (Section 3.3). A business case has been produced for this application and is outlined in more detail in Section 6.

4.2 Purpose Grown Crops

4.2.1 Energy Crops

Crops such as miscanthus, energy sorghum, tall prairie grass and switchgrass have the potential to be used as biomass feedstock for pyrolysis. As noted above, these energy crops consist of the cellulose, hemicellulose and lignin and will produce similar bio-oil and bio-char as corn stover and wheat straw (Palma, Richardson, & Roberson, 2011).

A study conducted for the Ontario Federation of Agriculture looked at the price for purpose-grown crops that would be needed to provide a net return to the farmer of \$100 per acre. The acceptable price of purpose-grown biomass at the farm gate in Ontario ranges from \$104 per dry tonne to \$148 per dry tonne, based upon industry-based inputs, average production and cost estimates outlined in the study. Of the purpose-grown crops identified, miscanthus offers the lowest production cost due to its comparatively high yield. Based on the analysis presented in this study, the acceptable price of miscanthus bales at the farm gate would be \$104 per dry tonne to provide a comparable margin with conventional cash crops. The establishment cost of miscanthus including the fixed costs is \$1179 per acre, but can vary widely from farm to farm as producers are just learning how to grow the crop. There has been a significant reduction in this establishment cost since it was developed. Today, if the establishment cost is \$300 per acre lower, the acceptable price of miscanthus bales at farm gate would be reduced by \$7 per dry

tonne. The acceptable price of switchgrass bales at the farm gate would be \$135 per dry tonne. The acceptable price of biomass bales at the farm gate for Tall Grass Prairie (TGP) and sorghum are \$148 per dry tonne and \$103 per dry tonne, respectively. Although TGP offers the maximum environmental benefits, information on fuel quality of the mixed biomass is limited. The higher establishment cost and the relatively lower yield could be issues. The higher moisture content of current sorghum species at harvest is also an issue in using this feedstock for pyrolysis.

4.2.2 Jerusalem Artichoke (JART)

Jerusalem artichoke has been investigated for its potential as a biomass source for pyrolysis to produce biofuels and biochemicals that can be used for food additives, flavours, and pharmaceuticals (Encinar, et al., 2009 & Scachetto, 2012). The study concluded that the Jerusalem artichoke plant can be pyrolysed to produce bio-oil containing chemicals such as acetic acid, furfural, acetone and carbonyl derivatives in reasonably high concentrations. Other interesting biochemicals were found in lesser concentrations. In particular, flavouring potential was found in these bio-oils. As noted in Section 2.2 above, isolation of these chemicals from the bio-oil is not economically viable at this time.

Energy recovery is possible from the bio-char and the non-condensable gas where there is a high carbon and hydrogen concentration. The bio-oil generally had lower heating values due to the higher concentration of water.

Extraction of the soluble carbohydrates such as glucose, fructose and inulin from the Jerusalem artichoke roots prior to pyrolysis, enhances the pyrolytic yields and should improve the business case for JART. Novagreen (www.Novagreen.ca) is using their proposed technology to extract xylitol, XOS and inulin from JART. AITF is currently growing JART on 10-12 acre field plots with an expected harvest of 60-80 tonnes. The cultivation will be doubled next year in anticipation of Novagreen commercialization plans.

4.3 Dried Distillers Grains (DDG)

4.3.1 Availability and Pricing

Dried distillers grains are produced from the production of grain ethanol using corn. There are a number of plants in Ontario such as Greenfield Ethanol, Suncor Ethanol and IGPC. Potential production of DDG is estimated at 180,000 tonnes per year based on the combined capacities of the ethanol production facilities operating in the province of Ontario.

Dried distillers grains are normally sold as animal feed and the price is set in the market based on supply and demand. With the significant growth in ethanol production over the last decade, the market for DDG has been oversupplied resulting in lower prices for this material.

A wholesale price of by-product DDG of \$180 per tonne has been used in previous economic assessments of alternative technologies.

DDG is produced continuously throughout the year in the ethanol production facilities and is free-flowing as a dried material minimizing the feed preparation for the pyrolysis process.

4.3.2 Pyrolysis Products

Products produced from the pyrolysis of DDG have been characterized (Xu, 2010; Wang, et al., 2012; Lei, et al., 2012). The products of DDG pyrolysis products are similar in composition and heat content to those from other agricultural sources such as corn stover and wheat straw.

4.4 Mushroom Residues

4.4.1 Availability and Pricing

There are 300 million tonnes of wet mushroom biomass residue (65% moisture content) produced in Canada each year of which approximately 60% is produced in Ontario. The biomass is the residual growing media after the mushroom harvest. The growing media is initially a blend primarily made of various peat materials, straw and chicken litter. This material creates significant issues for the mushroom industry due to the sheer volume produced. This volume of wet biomass is concentrated on approximately 36 farms in Ontario, most of which are geographically located within Middlesex County and the Niagara region. The quantity available on a mushroom farm in Ontario varies significantly from 3,000 to over 30,000 wet tonnes per year.

Due to the significant volume and inability to reuse the material for further mushroom production, the biomass represents a disposal cost to the farmers. Currently, the disposal costs are estimated at \$10 per wet tonne of biomass.

4.4.2 Pyrolysis Products

Whitecrest Mushrooms Ltd has been working with Canadian Carbon Solutions (CCS) to develop a process for the pyrolysis of mushroom biomass. In this process, the biomass must first be dried to 10% residual moisture content before being processed in CCS's unique auger-style pyrolysis unit to produce a bio-char with good surface properties. The bio-char has been used for soil amendment in agricultural applications and has a projected commercial value of \$430 per tonne.

CCS's unique process of sequestering carbon in bio-char is different from all other technologies. The process raises feedstock temperature up to the thermochemical equilibrium point, converting the calorific value of the feedstock to a bio-char with high carbon purity. The pilot unit is capable of producing a bio-char of consistent quality. CCS has proven that bio-char properties can be controlled in the pilot unit through process adjustments. This allows CCS to operate with various feedstocks and meet diverse customer requirements.

A stationary pyrolysis plant can be envisioned for this application. The pyrolysis plant would include the following:

- biomass and bio-char handling equipment
- a steam heated rotary dryer
- a CCS auger-style pyrolysis unit for production of bio-char
- a low pressure steam boiler for combustion of the bio-gas and bio-oil
- an integrated energy management system to minimize energy consumption

A business case has been built for this application and is outlined in detail in Section 6.

The CCS technology has been piloted and now needs to be built to demonstration scale (4.5 dry tonnes per day biomass capacity) and integrated with the other unit operations described above. Once this scale has been successfully demonstrated and the economics validated, then a full commercial unit can be built.

4.5 Other Plant Residues

4.5.1 Greenhouse Vegetable Growers

Vegetable greenhouse operations produce primarily tomatoes, peppers and cucumbers in Ontario. According to the Greenhouse Growers of Ontario, there are 2,270 acres of greenhouses where vegetables are grown in Ontario. These operations are concentrated in the Essex region where over 75% of the acreage is grown with most of the remaining acreage grown in Huron, Kent, Lambton and Niagara Counties.

The organic biomass from vegetable greenhouses consists of vines and culls from the plants. There are lesser amounts of growing media in the biomass which is made up primarily of rockwool (silica) and washed coconut husks. The greenhouses are cleared once per year with between 20 to 30 tonnes of wet biomass removed per acre of greenhouse. Total biomass available from this source is approximately 50,000 tonnes per year. The moisture content of the biomass is unknown but is expected to be in the range of 50-60 wt%.

Currently, the biomass is removed from the greenhouse sites by a third party waste handling contractor. One of the contractors is centrally located in Essex County and removes the biomass from the sites, then separates the plastic for recycling prior to processing the biomass. The contractor charges a tipping fee in the range of \$36 - \$40 per wet tonne.

As stated above, the majority of the biomass is produced once per year. This agricultural residue would need to be processed on a campaign basis within a short period of time due to its high moisture content. It is likely that the material would need to be removed to a central processing location as is currently done by the third party contractor unless there was a financial incentive for the greenhouse operator to accept the inconvenience of on-site processing.

4.5.2 Greenhouse Flower Growers

According to Flowers (Canada) Ontario, there are very little organic biomass residues from their industry. Most growers in Ontario are producing potted plants for the spring season and very little biomass remains after the sale of the potted plants. Cut flowers are not grown in Ontario to any extent.

4.5.3 Tobacco Residues

Availability of tobacco residues is currently unknown.

4.5.4 Pyrolysis Products

As summarized in Section 2.2.4, bio-oil from tomato and tobacco residues has shown bioactive properties. Unfortunately, the bioactive chemical species are not yet clearly identified so that work can be done to isolate them from the bio-oil.

As noted in 4.5.1, the greenhouse biomass contains significant quantities of rockwool. The impact on the rockwool on the bio-char properties is not understood and further study is required.

Due to the high moisture content of the biomass, drying down to approximately 10% residual moisture would be required prior to any processing in a pyrolysis unit. The only foreseeable potential for commercialization would come through collection of this biomass and processing it through a centralized unit similar to the unit described in Section 4.4.2. This would only be commercially feasible if a high quality bio-char could be developed that would garner a market price competitive with bio-char produced from mushroom biomass residues.

Further study is required to understand the properties of bio-char from vegetable plant residues using auger-type pyrolysis units. Understanding properties such as surface area and volatile matter content will be critical to assessing any advantages of using this bio-char for soil substrate or other higher value soil amendment applications.

4.6 Processed Vegetable Residues

Field tomatoes, corns, peas and beans are grown in Ontario for the processed vegetable industry. The majority of this production is concentrated in the southern Ontario region between Strathroy and Leamington.

Information was not readily available for quantities and cost of corn, peas and bean residues. However, the majority of processing plant residues from these crops would be corn cobs and husks. These residues would have high moisture content (50-60 wt %) and would require pre-drying before pyrolysis. The products from pyrolysis of the dried biomass would be similar to the products from field corn stover and cobs.

The majority of field tomatoes are processed by three companies in Ontario: Heinz, ConAgra Foods and Sunbrite Canning Ltd. Collectively, 500,000 tonnes of fruit are processed per year. In discussions with Don Roberts from ConAgra Foods, 5,000-7,000 wet tonnes (60% residual moisture) of tomato pomace are produced per year in Ontario. The pomace is made up of skins and seeds and is produced during the 5 week harvest period each fall. It is sold currently for \$10-\$20 per wet tonne and is used in cat and dog food as a source of soluble fibre. Until such time as there are opportunities to extract high value chemicals, pharmaceuticals or pesticides, tomato pomace will continue to be used in cat and dog food.

4.7 Grape Skins and Grape Seed Residues

Grape skin and grape seed residues (6% moisture content) have been pyrolyzed at the pilot scale to produce bio-oil and bio-char (Xu, et al., 2009; Demiral & Ayan, 2011). Under fast pyrolysis, the yield of bio-oil is lower than that seen from other agricultural biomass such as

corn stover. Bio-char yields were higher as a result of the lower bio-oil yields. It was also noted that bio-char yields continued to increase as the residence time increased to 20 seconds and the pyrolysis temperature increased to 500°C (Xu, et al., 2009).

The heat of pyrolysis was also measured and compared with the available energy in the noncondensable gas (NCG) stream. It was determined that there was insufficient energy in the NCG to fully sustain the pyrolysis reaction and that a secondary energy sources such as bio-oil or natural gas would be required for a commercial application.

An approximate quantitative analysis of the biooil product components was done and the study indicated that the concentration of valuable chemicals is not high enough to justify their extraction.

Due to the tendency for higher bio-char yields, the use of grape skins and grape seeds for specialty bio-char applications could be of interest.

4.8 Animal Products

4.8.1 Meat and Bone Meal (MBM)

Experiments have proven that it is possible to feed dried meat waste and MBM (5 – 6 wt% moisture content) continuously in a pilot scale fluidized bed pyrolysis unit under typical conditions (Cascarosa, et al., 2011; Cascarosa, Becker & others, 2011; Burruti, et al., 2012).

The bio-oils produced in the MBM pyrolysis process have a dark brown and homogeneous colour and a strong pungent odour. The average heating value of the bio-oil obtained was significantly higher than that of the bio-oil obtained from cellulosic biomass. However due to their high nitrogen content (7% - 9%), these bio-oils could not have a direct use as a fuel (Cascarosa, et al., 2011). The bio-oils contain mainly fatty acids, fatty nitriles and some fatty acid esters.

The bio-char yields from the pyrolysis of meat waste and MBM range between 20–30 wt%. Not surprisingly, the ash content of the bio-char was very high and in the range of 63–77 wt%. The ash contains a high proportion of calcium in the form of carbonates and phosphates (Cascarosa, et al., 2011).

As noted here, the properties and composition of the bio-oil and bio-char from the pyrolysis of MBM are significantly different that those from other biomass sources. Further study is warranted to understand the commercial impact of these differences.

Currently, there are two types of MBM:

- 1. MBM which is suitable for animal consumption and is used in high protein animal feed. This product has a high market value
- MBM which cannot be used for animal feed since it may be contaminated with disease such as BSE. This material is gasified at temperatures above 750°C in order to meet the regulatory requirements for destroying reinfectivity of disease. Pyrolysis does not meet the threshold temperatures required for this application.

Consequently, the pyrolysis of MBM is not seen as providing commercial value.

4.8.2 Chicken Litter

Chicken litter is a high nitrogen content (6 wt% nitrogen) biomass material which is rich in cellulose as sawdust is a major component used as bedding material (Schnitzer, et al., 2007). Dried chicken litter has been processed in a pilot scale fast pyrolysis auger-style unit. Approximate yields of 10% non-condensable gases, 63% bio-oil and 27% bio-char were obtained from this process (Monreal & Schnizer, 2011; Schnitzer, et al., 2007; Kazi, et al., 2011).

In a first study, the raw bio-oil contained 6.3% nitrogen and 23.3% oxygen (Monreal & Schnizer, 2011). Later work obtained bio-oil with nitrogen contents of 7.4 and 12% (Schnitzer, et al., 2007). As noted with the bio-oil from MBM, due to the high nitrogen content, this bio-oil does not have a direct use as a fuel. However, through further chemical processing, the authors were able to produce a refined bio-oil with less than 2% residual oxygen content and 0.2% nitrogen content. Unfortunately, the yield was only 10 wt% based on the bio-oil processed. Although this approach is interesting, the status of this work is still experimental and not yet of commercial significance.

An analysis of the bio-char resembled that of the initial chicken litter except that the concentration of carbohydrates was lower (Schnitzer, et al., 2007).

4.9 Other Raw Material Sources

The breadth of work conducted on pyrolysis of carbon sources is endless. For the sake of completeness, references for various other raw material sources are list here:

- Sawdust (Demirbas, 2004; Bridgwater, et al., 2001; Xu, 2010; Czernik & Bridgwater, 2004; Bridgwater, 2012; Radlein & Piskorz, 1997; Meier, et al., 2013; Elliott, et al., 2012; Grigiante, et al., 2010).
- Lignin (Palmisano, et al., 2011; Pielhop, et al., 2011; Zhang, et al., 2011; Ingram, et al., 2008; Tapin-lingua, et al., 2011; Gosselink, et al., 2011).
- Coffee Grounds (Bedmutha, et al., 2011 & Bok, et al., 2012).
- Wastewater Treatment Sludge (Grigiante, et al., 2010; Manara & Zabaniotou, 2012).
- Polymer and Tires (Grigiante, et al., 2010; Quek & Balasubramanian, 2013)



5.1 Overview of Company and Product Development

Agri-Therm Inc., a spin-off company from Western University Institute for Chemicals and Fuels from Alternative Resources, has developed the first mobile pyrolysis system (MPS) for rapidly converting low value bio-residue at the source into higher-value bio-oil and bio-char for use in meeting renewable fuel content requirements and making special chemicals, pharmaceuticals, and materials. Mobile pyrolysis takes the pyrolysis plant directly into the agricultural and forestry operation, reducing transportation costs and converting low value stalks, leaves, straws, bagasse, chips, sawdust and branches, into higher value and high-energy density bio-oil and bio-char.

5.2 First Generation Demonstration Unit (MPS100)

5.2.1 Overview of Technology

Agri-Therm built the first bubbling fluidized bed mobile pyrolysis unit on the market, the MPS100 (original prototype), which was ready for complete testing starting in 2008. The MPS100 was the first demonstration unit and numerous challenges were identified that are being resolved before commercial deployment. These operational challenges are outlined in this section, and have been addressed in the MPS200 design. Fig. 5.1 is a photograph of the MPS100.

5.2.2 Product Advantages and Demonstrated Capabilities

The MPS100 was designed to be an efficient, 10 dry tonnes per day, mobile pyrolysis unit engineered to address four major issues:

- Mobility bring the processor to the biomass to reduce collection, handling and shipping expenses.
- Simplicity operator-friendly, easy-to-learn, easy-to-use, mitigate operational labour costs.
- Adaptability designed for multiple market uses and feedstocks.
- Affordability one of the least expensive technologies on the market.

The MPS units were engineered to exceed the market need for each of these key attributes:

 It is mounted on a heavy-duty, standard-size pull trailer for easy transport and setup. The unit is made using heavy grade galvanized steel to mitigate wear and protect the unit from the elements. The unit is also collapsible,



Figure 5-1 MPS100 Being Prepared for Operation (Berruti, F.M., 2013)

making it safe and energy efficient to transport over existing roads.

- It is operated from a standard operating control panel with push-button controls that are easy to understand and simple to use. More importantly, the MPS generates its own self-sustaining thermal power (by combustion of the pyrolysis non-condensable gas in the central furnace), mitigating the need for access to the power grid and/or fuel depots (except for start-up propane requirements, and electrically powering the control systems/fans/blowers, which requires roughly 20 kW at peak operation).
- The feeder system can be adapted to meet most feedstock needs (size and type flexibility, only mild chipping to about 1 cm3 required). This allows the product to be flexibly and quickly modified to fit market requirements.

5.2.3 Conversion and Product Yields

Fifteen to 20 trials were successfully conducted with the MPS100. These trials included both cold commissioning and hot operation with feeding and pyrolysis. The longest hot operation was 5 hours of continuous operation. Trials were stopped due to operational challenges that are further described and addressed in the following section. Two types of feedstock were used during the trials. These were birch sawdust/bark and dried distillers' grain (DDG).

During the testing, conventional farm diesel was used in the bio-oil tank as the quenching fluid in the cooling tank. Diesel was used in order to avoid putting the bio-oil through too many temperature cycles. As a result, exact bio-oil properties could not be determined from the main bio-oil tank. As an alternative, condensed aerosol bio-oil samples were analyzed from the demister. The bio-char was collected and its physical characteristics were determined. Full elemental analysis was not conducted. Good size and handling properties were observed and dusting was not a significant issue.

The bio-oil produced from the feedstock was consistent with bio-oil characterized in literature. The bio-oil yield from pyrolysis of birch sawdust/bark (~60 wt% on average) was higher than the bio-oil yield from pyrolysis of DDG (~50 wt%). The water content was in the typical range of 20 wt% in all cases. The water-free higher heating value (HHV) was ~30 MJ/kg for bio-oil produced from wood. The heating value was ~26 MJ/kg for bio-oil produced from DDG.

As Xu described in 2010, treating the bio-oil organic phase with CaO increased the LHV of the DDG bio-oil to nearly 25 MJ/kg. This was achieved by capturing and precipitating the water out of the bio-oil with the CaO. The demister bio-oil had undetectable amounts of solids or ash. It is anticipated that the bio-oil from the storage tank would require further cleaning and filtration prior to upgrading.

5.3 Second Generation Unit (MPS200)

5.3.1 Improvements from MPS100

The second generation MPS unit (MPS200) has been partially constructed and is currently undergoing cold and hot testing from 2013. The MPS200 has been professionally designed and engineered. Full documentation, with AutoCAD modeling and construction drawings are available. This will better facilitate identifying further improvements and making changes for future MPS units. Figures 5.2-5.4 illustrate the new MPS200. The unit has design improvements that will increase reliability and output and will put Agri-Therm one step closer to a commercially proven mobile pyrolysis solution. The design improvements include:

- The reactor unit has been re-designed completely with safety, maintenance (many extra ports available for cleaning and access) and thermal expansion issues properly taken into consideration.
- The MPS200 has been designed to operate at 10 dry tonnes per day for extended production trials. The heat transfer was examined closely and over-designed to mitigate any limitations. In addition, commercial burners with full safety

control have been purchased for the MPS200 units. The constructor will participate in the R&D efforts with Agri-Therm in order to successfully combust the pyrolysis product gas with the new burners.

3. The MPS200 has been designed with a novel continuous char segregation zone, cooling and removal system to continuously remove and store the bio-char in barrels. This can be seen in Fig. 5.3 as the "jacket" around the reactor system. This avoids the "batch" problem identified in the MPS100 unit. The bio-char segregation design was thoroughly studied at ICFAR in the lab and at smaller scales, but will now be optimized on the MPS200 unit.



- 4. A much improved condensation system has been designed but not yet implemented on the MPS200 unit. The final design parameters will be obtained during cold testing of the reactor unit. Further testing will be required to optimize this system and ensure economic energy efficiency before commercialization.
- The next generation MPS200 has a gas distributor re-design utilizing a 4-hole "Tuyere" system. The new design has not yet been fully tested for long-term stability in the field.
 Special testing will be required to ensure that

sand shifting during relocation of the unit does not lead to plugging of the new system.

6. The MPS200 has been designed to fit on the footprint of a commercial custom trailer mount (not shown in these figures).

It is projected that the capital cost of a commercial mobile pyrolysis unit with be in the order of \$1.5 million.



Figure 5-3 MPS200 Reactor Cut-Away (Side View) (Berruti, 2013)



Figure 5-4 MPS200 Undergoing Cold Testing (Berruti, 2013)

wo business cases have been developed to provide an indication of the state of commercialization of pyrolysis technology in agriculture. The cases are described as follows:

- 1. Mobile fast pyrolysis of biomass (20 wt% moisture) without pre-drying. The bio-oil is collected and transported to a centralized combined heat and power (CHP) generating facility. The mobile unit is energy selfsustained by using the non-condensable gases from pyrolysis. The CHP unit generates steam for the production of renewable power (FIT price 13 cents/kWh). The residual steam is used to displace natural gas as a heat source for a secondary purpose. Natural gas is priced at 30 cents/m³. The bio-char produced is of lower technical quality and is valued at the lower end of the price range (\$250 per tonne). Corn stover will be used as the biomass source for this business case.
- 2. Integrated auger-style slow pyrolysis of biomass (10 wt% moisture content) with predrying in a steam heated rotary dryer. The non-condensable gases and bio-oil vapours are directly burned in a steam boiler which provides the heat source to dry the wet biomass prior to pyrolysis. To close the energy balance, natural gas is used to direct heat the auger-style pyrolysis unit and to supplement steam production in the boiler. Natural gas is priced at 30 cents/m³. The bio-char produced is of higher technical quality and is valued in the middle of the price range (\$430 per dry tonne). Mushroom residue (65 wt% moisture content) will be used as the biomass source for this business case.

6.1 Case 1: Mobile Fast Pyrolysis of Corn Stover

6.1.1 Operating Conditions for Conversion of 3,600 Dry Tonnes per Year of Biomass

Operating conditions were developed for the mobile pyrolysis unit scenario using the following assumptions:

- Pyrolysis unit has a capacity of 10 dry tonnes per day corn stover. The corn stover processed has a moisture content of 20 wt%.
- Pyrolysis unit is operated on a continuous basis, 24 hours per day. Unit utilization rate is 95% (350 operating days per year). Corn stover processed is 3,600 dry tonnes per year (4,500 wet tonnes per year).
- 3. The product slate from the fast pyrolysis of corn stover is described in Fig. 6-1:



Figure 6-1 Product Slate from Fast Pyrolysis of Corn Stover (Mullen, 2010)

- a. 21.9 wt% non-condensable gases (higher heat content (HHV): 6 MJ/kg)
- b. 61.6 wt% bio-oil (higher heat content (HHV): 22.1 MJ/kg "as is")
- c. 17.0 wt% bio-char (market value: \$250 per dry tonne)

6.1.2 Operating Costs

Operating costs were developed using the following assumptions:

- Corn stover is delivered to the processing location at a price of \$60 per dry tonne (20 wt% moisture content). Raw material costs have been determined at \$337,500 per year
- Two persons are required to operate the unit at all times. These employees will receive an hourly wage of \$20 with overhead costs of 20%. Personnel costs have been determined at \$403,000 per year
- Bio-oil produced is collected, transferred and stored in a quad-axle semi-trailer. The trailer holds 40 m3 of bio-oil but is restricted to 34 tonnes for transport. It will be transported at its weight limit to a central CHP unit within 100 km. The trailer rental costs are included in the variable cost of transportation. The cost of transport is \$966 per load of bio-oil (34 tonnes per load). Cost of transportation has been determined at \$73,000 per year
- Maintenance costs are set at 2% of capital costs. The costs of the mobile unit is estimated to be \$1.5 million and the cost has been determined at \$30,000 per year
- Energy costs are minimal as the noncondensable gases and entrained bio-oil from the pyrolysis are used to provide an energy self-sustaining operation.

 Other costs were determined at \$20,000 per year. This category covers miscellaneous costs such as environmental, safety and logistics costs.

6.1.3 Energy Balance of Mobile Pyrolysis Unit and CHP Plant

The energy balance around the mobile pyrolysis unit will define the quantity of bio-oil that is available for shipment to a CHP generation plant for conversion into steam and power. The following assumptions have been used to determine the volume and energy value of the bio-oil produced by the mobile pyrolysis unit:

- 1. The quantities and the higher heat value (HHV) of the non-condensable gases and the bio-oil are summarized above in Section 6.1.1.3
- The heat of pyrolysis describes the energy required to pyrolyze the biomass within the pyrolysis unit. This quantity of energy is process and biomass specific. A value of 1.75 MJ/kg is used and based on input from a study (Berruti, et al., 2013).
- Based on the pyrolysis system mass balance, HHVs (NCG and bio-oil) and the heat of pyrolysis, 2,150 tonnes per year of bio-oil will be transported to the CHP plant

6.1.4 Revenue Streams from Conversion of 3,600 Dry Tonnes per Year of Biomass

Revenue generated from this mobile pyrolysis unit was determined using the following assumptions:

1. Boiler/steam turbine CHP system performance data were used to determine the quantities of

steam and electricity that would be produced from the bio-oil provided from US EPA. A 500 kW back pressure CHP system was used to process the bio-oil. Based on the reference used, this unit has a CHP electric efficiency of 6.4% and a total CHP efficiency of 79.6%. From the energy balance, 98 kW of electricity would be produced in the CHP unit. Using an electricity price of 13¢/kWh (FIT), the value of this electricity is \$118,000 per year. Similarly, 89,000 MJ/day of steam would also be generated from the bio-oil. The value of displacing natural gas to produce this quantity of steam is \$272,000 using a natural gas price of 30¢/m³).

 Bio-char will be collected continuously, quenched to avoid spontaneous combustion and stored in drums. Bio-char is valued at \$250 per dry tonne (\$153,000 per year) based on the details described in Section 3.3.

6.1.5 Outcome of Business Case Analysis

The business case for a mobile pyrolysis unit processing 10 dry tonnes per day (3,600 dry tonnes per year) of corn stover is summarized in Table 6.1.

Table 6-1 Business Case for Mobile PyrolysisUnits converting Corn Stover (Estimation)

	Biomass Through	put Rate (dry tonnes)
Operating Costs	10 Tonne/day	23 Tonne/day
Raw Materials	\$337,500	\$750,000
Personnel	\$403,000	\$403,000
Logistics	\$73,000	\$137,000
Maintenance	\$30,000	\$30,000
Energy	-	-
Other	\$20,000	\$20,000
TOTAL COST	\$863,500	\$1,340,000
Revenue		
Electricity	\$118,000	\$263,000
Steam	\$272,000	\$604,000
Bio-char	\$153,000	\$340,000
TOTAL REVENUE	\$543,000	\$1,207,000
CASH FLOW	(\$320,500)	(\$133,000)

A second business case was developed using the same assumptions and a throughput rate of 23 dry tonnes per day (8,000 dry tonnes per year). The result from this business case is also summarized in Table 6.1.

Cash flow is negative in both of these two cases and the 10 tonnes per day (4,000 tonne/year) case cannot become cash flow positive using any reasonable assumptions.

A sensitivity analysis on cash flow was conducted on the 23 tonnes per day (10,000 tonnes per year) capacity case using the following variables:

- Price of corn stover per dry tonne. When keeping the bio-char and renewable energy prices constant, the price of corn stover (20 wt% moisture content) would need to be reduced from \$60 per dry tonne to \$50 to reach a breakeven cash flow excluding the cost of capital
- Price of bio-char per dry tonne. Keeping corn stover and renewable energy prices constant, the price of bio-char would need to increase to \$350 per dry tonne to reach a breakeven cash flow excluding the cost of capital
- Price for renewable electricity under the FIT program (cents/kWh). Keeping corn stover and bio-char prices constant, the price for renewable energy would need to increase to 20 cents/kWh to reach a breakeven cash flow excluding the cost of capital

Since manpower costs constitute the most significant part of the operating costs, increasing the throughput of the pyrolysis process with constant manpower improves the business case. Consequently, a third scenario was created with a 30,000 tonne per year pyrolysis unit keeping the manpower requirements constant. Under these circumstances, a positive cash flow of \$480,000 could be generated. It may be possible to generate a project payback at this scale. A number of impacts could fundamentally change which would alter the conclusions made here. Access to agricultural biomass at a lower cost would accomplish this. For example, if a dry biomass source became available at a lower cost (eg. if excess corn stover residue on the field became an issue, then removal would be required to ensure crop yield), then the economics of a large scale mobile pyrolysis unit would become more economical.

6.1.6 Outcomes from Similar Case Study

Palma outlined an interesting approach (Monte Carlo simulation) to predicting the potential for positive net present value (NPV) of investments and operations in mobile pyrolysis units in 2011 economic conditions using corn stover or energy sorghum in three locations in the USA (Texas, Illinois, Nebraska). The results of the simulation confirm a high sensitivity to yields, oil prices and the energy efficiency of the pyrolysis systems (Palma, et al., 2011)

The study uses a feedstock cost range of \$60-\$75US per dry tonne. There may be opportunities to obtain dry biomass at prices below these price points. However, most dry agricultural biomass identified in Ontario has a projected value equal to or higher than the costs used in this study.

The study assumed that the major incomegenerating product is a bio-oil equivalent to crude oil, which is transported to the nearest refinery, and sold at a 5% discount from the price of crude. The cost to upgrade the raw bio-oil to high quality bio-oil usable in an oil refinery was within the range of 20–40 cents per gallon and a subsidy of \$1.00 per gallon of refined bio-oil was provided.

The bio-char value was determined based on the soil amendment value as a soil additive. According to this study, bio-char produced in 2011 can be sold for \$24 per dry tonne and its value varies by feedstock. This value is significantly lower than that used in this study.

The results showed a low probability of economic success for all scenarios. Although this analysis was done using different assumptions, the general outcome from this assessment is consistent with those found in this study.

6.2 Case 2: Fixed Auger-style Pyrolysis of Mushroom Residue

6.2.1 Operating Conditions for Conversion of 3,200 Wet Tonnes per Year of Biomass

Operating conditions were developed for the integrated fixed auger-type pyrolysis unit. The auger-type pyrolysis unit is integrated into a plant with a steam heated rotary dryer, steam generation boiler and feeding systems using the following assumptions:

- Pyrolysis unit has a capacity of 10 dry tonnes per day (3,500 dry tonnes per year) mushroom media residue. The mushroom residue processed has 65 wt% moisture content.
- A steam heated rotary drier is used to reduce the moisture content of the mushroom media residue to 10 wt% moisture
- The non-condensable gases and bio-oil vapours are combusted in a low pressure steam boiler and the steam is used to heat the rotary drier
- 4. The auger-style pyrolysis unit is operated on a campaign basis, 24 hours per day for extended periods. Unit utilization rate is 95%. The mushroom residue processed in this case is 3,200 wet tonnes per year (1,120 dry tonnes per year). Based on the capacity of the pyrolysis unit, there will only be sufficient feedstock to operate the unit for approximately 109 days per year.

- 5. The product slate from the slow pyrolysis of mushroom residue as described as follows
 - a. 10 wt% non-condensable gases (higher heat content (HHV): 1.8 MJ/kg)
 - b. 40 wt% bio-oil (higher heat content (LHV): 13.6 MJ/kg)
 - c. 50 wt% bio-char (market value: \$430 per dry tonne)

6.2.2 Operating Costs

Operating costs were developed using the following assumptions:

- Mushroom media residue will be available at the processing location and will avoid a tipping fee of \$10 per wet tonne (65 wt% moisture content). Raw material cost credit has been determined at \$32,000 per year
- 2. Two persons are required to operate the unit at all times. These employees will only be required when the unit is in operation. These employees will receive an hourly wage of \$20 with overhead costs of 20%. Personnel costs have been determined at \$126,000 per year
- 3. Bio-oil vapour and non-condensable gases are injected directly into a low pressure steam boiler as fuel. Natural gas is used in the boiler to supplement the energy content of the pyrolysis products to close the energy balance. Natural gas is also used for direct heating of the pyrolysis auger-style unit. The boiler energy efficiency is 85%. The rotary drier efficiency was determined from "Energy Manager Training" to be 69%. A natural gas price of 30⊠/m3 was used for this analysis. From this energy balance, the cost of natural gas has been determined to be \$31,000 per year.

- Maintenance costs are set at 2% of capital costs. The costs of the integrated pyrolysis unit is estimated to be \$1.5 million and cost has been determined at \$30,000 per year
- Other costs were determined at \$20,000 per year. This category covers miscellaneous costs such as environmental, safety and logistics costs.

6.2.3 Energy Balance of the Integrated Pyrolysis Unit

The energy balance around the integrated fixed auger-type pyrolysis unit determines the quantity of natural gas required. The following assumptions were used to determine the energy content of the non-condensable gases and the bio-oil produced by the auger-style pyrolysis unit:

- The quantities and the higher heat value (HHV) of the non-condensable gases and the bio-oil are summarized above in Section 6.2.1.3
- The heat of pyrolysis describes the energy required to pyrolyze the biomass within the pyrolysis unit. This quantity of energy is process and biomass specific. A value of 2.6 MJ/kg is used (Palmisano, et al., 2011). Revenue Streams for Conversion of 3,200 wet tonnes per year of Biomass.

The only revenue generated from the integrated pyrolysis unit is bio-char which is collected continuously, quenched to avoid spontaneous combustion. Bio-char is valued at \$430 per dry tonne (\$257,000 per year).

6.2.4 Outcome of Business Case Analysis

The business case for the integrated fixed augertype pyrolysis unit processing 10 dry tonnes per day (3,200 wet tonnes per year) of mushroom media residue is summarized in Table 6.2. Two additional business cases were developed using the same assumptions with the following changes:

- Operate the integrated unit at full capacity of 10,000 wet tonnes per year (340 days operation per year)
- Operate a larger integrated unit with a capacity of 30,000 wet tonnes per year

The results from these business cases are also summarized in Table 6.2.

Cash flow was positive in all three scenarios.

Cash flow was marginally positive for the 3,200 wet tonnes per year case and can be seen as the breakeven throughput case.

Cash flow was sufficient from the 10,000 wet tonnes per year case to generate a simple payback period approaching 4 years. A sensitivity analysis on cash flow was conducted on the 10,000 tonnes capacity case using the following variables:

- Removal of the tipping fee. For the 10,000 tonnes per year plant and keeping all other parameters constant, removal of the tipping fee would extend the simple payback period by almost 2 years
- Price of bio-char per dry tonne. For the 10,000 tonnes per year plant and keeping all other parameters constant, the price of bio-char could be reduced to \$250 per dry tonne before reaching the breakeven cash flow point excluding the cost of capital

Since manpower costs constitute the most significant proportion of the operating costs, increasing the throughput of the integrated pyrolysis plant with constant manpower will improve the business case. Consequently, the third business case was created with 30,000 wet tonnes per year capacity and constant manpower requirements. A positive cash flow of nearly \$2 million per year was generated. If sufficient feedstock could be gathered and the auger-style pyrolysis unit could be scaled to this capacity, a very interesting business case could be generated.

Table 6-2 Business Case for Pyrolysis ofMushroom Residue (Estimation)

Bior	mass Throug	hput Rate (wet t	onnes per year)
Operating Costs	3,200 T	10,000 T	30,000 T
Raw Materials	(\$32,000)	(\$100,000)	(\$300,000)
Personnel	\$126,000	\$392,000	\$392,000
Energy	\$31,000	\$98,000	\$293,000
Maintenance	\$30,000	\$30,000	\$30,000
Other	\$20,000	\$20,000	\$20,000
TOTAL COST	\$175,000	\$440,000	\$435,000
Revenue			
Bio-char	\$257,000	\$802,000	\$2,405,000
TOTAL REVENUE	\$257,000	\$802,000	\$2,405,000
CASH FLOW	\$82,000	\$362,000	\$1,970,000

7.1 Sustainability Impacts of Bio-char

Biomass is produced by photosynthesis and captures atmospheric CO₂. This carbon is sequestered into the biomass but is normally released back into the environment by breakdown of the biomass through normal aerobic and anaerobic processes such as combustion, composting, rotting and fermentation. Generally CO_2 is the primary gas generated through these processes. However in anaerobic processes, methane is also generated and has a greenhouse gas impact over 100 years which is 25 times higher than that of CO_2 . Pyrolysis is a process in which the carbon content of the biomass is segregated into three components: non-condensable gases, bio-oil and bio-char. In most cases, NCG and bio-oil are used as energy sources and this portion of the carbon is released again back into the environment primarily as CO₂. Bio-char, when used for soil amendment or other agricultural applications, provides the opportunity for the carbon to be sequestered for long periods of time. According to the Alberta Biochar initiative, 50 wt% of the carbon in the biomass can be concentrated in the bio-char and can be sequestered. This life cycle is shown in Figure 7.1. Bio-char is not a structured homogeneous material, but rather it possesses a range of chemical structures and a heterogeneous elemental composition. This variability is based on the conditioning of pyrolysis and the biomass parent material. The scientific understanding between the bio-char chemical and structural characteristics and its longevity/stability (recalcitrance) in the natural soil environment remains poorly characterized. The ability of bio-char to resist abiotic and biotic degradation is crucial to its successful

deployment as a potential carbon sequestration media. More work is required to better understand the ability of bio-char to sequester carbon in soil for the longer term.

Companies such as Walmart are driving sustainability through their procurement strategy. There is a great potential to place bio-char into consumer applications such as organic fertilizers, compost blends and other horticultural applications. Recent work from IBI as outlined in Section 3.1.4 establishes standards for bio-char in soil applications. Further study is required to assess bio-char against these standards in order to assess their value in these applications.

7.2 Sustainability of the Mobile Pyrolysis Units

Westerhof outlines the effects of feedstock water content on the pyrolysis and condensation conditions (Westerhof, et al., 2007). Above



Figure 7-1 The Bio-char Cycle of Carbon Sequestration courtesy of Biochar Solutions Inc.

20 wt%, excess water in the feedstock simply vaporizes in the reactor and then creates challenges and product loss in the condensation system due to the sweeping water vapour pressure. Therefore, if excess water is present, one would have to operate the reactor in a manner that could generate more heat. In order to accomplish this, the pyrolysis reactor must be operated at higher reactor temperatures to create more thermal cracking leading to the production of extra pyrolysis product gas. This gas can be recycled and combusted to generate the extra heat to compensate for the higher water content. As a result of operating at a higher temperature, bio-oil and bio-char yields are reduced and CO₂ emissions increase.

If sacrificing bio-oil and bio-char yields is not preferred, then excess heat for water vaporization can be provided by fossil fuels such as propane or natural gas to the reactor furnace. Unfortunately, this will result in increased emissions. It is estimated that for every 1% increase in feedstock moisture content (above 20 wt%), the MPS units (processing dry tonnes of biomass per day) would emit an extra 18-20 kg of CO_2 per day.

As a result, ideal organic feedstock for pyrolysis units should contain < 20 wt% moisture content. If a given feedstock contains more moisture, it is recommended that the material be dried.



yrolysis has yet to break through into business success and, in fact, has had its fair share of failures. Many companies have come and gone, and there are always articles about the next greatest pyrolysis breakthrough, often not to be heard about as a commercial reality. The fact of the matter is that technical development is challenging; it took the oil industry over 100 years to be standardized and a fully successful enterprise world-wide. Pyrolysis is attempting to develop in a shorter time-frame while competing with fossil-based raw materials. Bio-oil is not low quality raw crude. It has typically high water and oxygen content making it challenging to upgrade to conventional fuels. It is unstable, can separate and age with time, and tends to be highly corrosive, viscous containing heavy tars. Suffice it to say, there are still many significant technical challenges in this "blue-ocean" new market.

In order to maximize current market opportunities and to optimize pyrolysis technology for the most promising of markets, pyrolysis companies should focus product development and testing programs around the two largest biomass sources of wood and corn residue. The International Energy Agency (IEA) estimates the annual worldwide biomass contribution from wood to be 1.4 billion dry tonnes, over two times the next closest contributor, corn.

Heat and electric power generation and the manufacturing of renewable fertilizers and soil amendments will be a first step toward renewable bio-oil and bio-char markets, respectively. As the market for both bio-oil and bio-char become more established, higher-value uses will emerge for these products. Value added uses may include specialty chemical and material production from bio-oil, upgraded and refined bio-oil into conventional fuels and upgraded biochar for adsorption and expanded soil amendment applications.

However, in order to implement technologies to harness this, one must consider that labour and transportation are the dominant operating costs and find an optimum operating model to minimize these costs (Brown, et al., 2011). Moreover, steady biomass availability is a challenge, being seasonal and geographically distributed. Stationary or centralized pyrolysis units require that the entire raw material biomass residue be readily available near the plant site. Transportation costs limit the economic transportation radius to less than 200 km from the plant location (Badger & Fransham, 2006). In contrast, centrally located plants can take advantage of economies of scale and can support several energy users in distributed locations, while also reducing downside risk and increasing net returns (Palma, et al., 2011).

Mobile pyrolysis plants may successfully reduce raw material and product transportation costs by a factor of 2 (Badger & Fransham, 2006), but are subject to increased labour and set-up costs, depending on how often and how far the unit are moved (Palma, et al., 2011).

Ultimately, the probability of success of both mobile and stationary pyrolysis business models will heavily depend on the steady availability of feedstock and on mitigating raw material costs. Improvements in pyrolysis technologies can further increase yields and process energy efficiency increasing the probability of a strong business model.

¹Berruti, "DEVELOPMENT AND APPLICATIONS OF A NOVEL INTERMITTENT SOLIDS FEEDER FOR PYROLYSIS," 2013 & Berruti, "Biomass Residue Fast Pyrolysis: the Future Outlook," 2013

9 - Conclusions

S ociety is searching for economical renewable energy sources as one of the ways to mitigate climate change. Pyrolysis technology has shown promise and continues to garner significant attention. The USDOE Energy Efficiency and Renewable Energy program is an example of the effort that is being put forth to find commercial solutions.

Extracting maximum value from all of the product streams of pyrolysis is essential to commercialize this technology on a broad scale.

- The NCG stream has limited potential beyond use as an energy source. Most pyrolysis technologies today use NCG for this purpose effectively.
- Bio-oil is a very challenging mixture of biochemicals and water. Finding pathways to maximize its value has been and continues to be a priority. Today, bio-oil use is limited to energy generation despite all the claims of significant value-add potential. There is more innovation and development work required to extract this potential but a number of applications are emerging that could become commercial within the next two to three years.
- Bio-char is a low quality carbon source which has significant commercial potential in agricultural and environmental applications.
 Further application development is required to bring bio-char to market. Continued focus is needed over the next couple of years to accomplish commercial success.

Business cases were developed for two pyrolysis applications:

- Mobile fast pyrolysis using BFB technology to produce bio-oil for commercial applications. The biomass source used was corn stover. The analysis shows that the technology shows significant promise but will require a source of dry biomass (< 20 wt% moisture) with a cost below \$60 per dry tonne. Through this study, no such agricultural biomass sources were identified. Further work is required to identify ways to reduce the cost of biomass sources and to find applications with higher value for bio-oil. In the meantime, this technology needs to be advanced through its demonstration phase so that full proof of commercialization potential is available for exploitation.
- 2. Slow pyrolysis using auger technology to produce bio-char for agricultural applications. The biomass source used was mushroom growing media (65wt% moisture content). The analysis shows that a positive business case can be generated with an integrated commercial unit of 10,000 dry tonnes per year capacity. Some auger systems have been scaled to this capacity. However, further development of a fully integrated system and the bio-char quality produced is required

10 - Recommendations

he following initiatives should be supported to ensure that pyrolysis technology continues to progress in Canada to commercial application.

10.1 Create a Bio-char Development Centre in Ontario

The use of bio-char in agricultural applications is not fully understood. Addition of bio-char as a soil amendment could have benefits but this is greatly affected by land type, weather and farming practices. Unfortunately, these parameters vary greatly across Canada and there needs to be R&D conducted taking into account the local conditions. Bio-char is also showing promise in vegetable greenhouse and mushroom farming applications. Further study is required to understand the relationships between bio-char properties and its agricultural applications. The University of Guelph Simcoe Research Station could be an ideal location to research bio-char impacts on agricultural and horticultural crops, due to the diversity of crops it can research.

Ontario needs to develop its R&D capabilities to understand the relevance of bio-char within the region. Currently, the Alberta Bio-char Initiative is making great strides in developing understanding in this area. Once Ontario establishes its R&D capability, a strong national collaboration can be developed to share relevant knowledge and implement solutions within the regions of Canada. This work should take into account the multitude of local issues such as land type and biomass type and availability. The work should be broad based looking across both agriculture and forestry biomass sources and applications. Finally, a critical recommendation for the pyrolysis industry is to team-up. With government support and commitments from industry, a national consortium should be created that maximizes the "know-how" of every aspect of the production chain and connects the forestry and agricultural operators, pyrolysis experts (academic and business), market uptake, and business world. The epistemology of pyrolysis exists for all of these areas, but is fragmented – in order to push through and become a commercial success and reality, these connections are absolutely necessary. Individuals or organizations with the following areas of expertise should be part of a consortium:

- Biomass residue preparation, drying and transportation.
- Pyrolysis technology: reactor design and operation (both small and large scale; mobile and stationary).
- Bio-char characterization, handling, pelletization, transportation and utilization for energy applications.
- Bio-oil characterization, stabilization, handling, upgrading, transportation and utilization (oil & petrochemical companies).
- Bio-char characterization, handling, upgrading and utilization in applications with a focus on agricultural applications
- Bio-char utilization in environmental treatment applications such as reclamation and remediation applications, oil sand tailings water treatment and lake restoration (de-eutrophication)
- Business: management, financing, securing preliminary contracts and upgrading partnerships, and connecting the dots.

10.2 Construct an Integrated Augerstyle Pyrolysis Demonstration Unit

Support the construction of a 10,000 wet tonnes per year integrated auger-style pyrolysis demonstration plant for the conversion of mushroom residues to high quality bio-char for agricultural applications as outlined in the business case shown in Section 6.2.

Currently, the auger-style pyrolysis technology has been proven at the pilot scale with mushroom residue feedstock. Development of the demonstration plant will address four technology risks:

- scale-up of the auger-style pyrolysis technology to 10,000 wet tonnes per year (3,500 dry tonnes per year) mushroom media feedstock
- demonstrate that NCG and bio-oil vapours can be fed directly to a steam boiler and combusted efficiently to generate low pressure steam at commercial scale
- demonstrate that mushroom media residue can be effectively dried to less than 10 wt% moisture content in a steam heated rotary drier, and
- demonstrate that the complete system of auger-style pyrolysis unit, steam boiler, rotary drier and solid transporting systems can be integrated into an energy efficient process unit

Once demonstrated on mushroom media residue, this integrated pyrolysis process unit can be used to test the ability to convert other agricultural residue with high moisture content such as vegetable greenhouse residue at large scale for further application testing.

Financial support for the construction of an integrated auger-style demonstration plant could

come in the form of grants and low-interest loans from the SDTC Technology Fund and other Federal and Provincial funding sources.

10.3 Support Development of Mobile Pyrolysis Technology

Support the construction of a MPS200 Agri-Therm demonstration unit to prove its capability. Agri-Therm is currently actively seeking client/partners for the MPS200 client-field project phase of the unit development to demonstrate and operate the unit on their site with their feedstock. The initial focus should be on forestry residue as the price point for all known dry agricultural residues are too high to be pyrolyzed economically as outlined in the business case shown in Section 6.1.

The MPS200 units can be thoroughly tested in different environments with various forestry residue for extended periods of time. The data generated can be used to complete the final design iteration leading to a fully proven MPS300 unit.

Based on the financial considerations shown in the business case, one should assess the capability to design a mobile pyrolysis plant that can operate at a larger-scale (minimum 10,000 t/year wet biomass). Achieving this scale would still minimize transportation costs, but allow for the more cost-effective operation. This processing plant would be large enough to realize economies of scale but small enough to be realistic about how much process-worthy biomass could be in one location. It is important to be able to operate continuously for a period of time without shutdown, relocation and start-up costs. Financial support for the construction of mobile pyrolysis demonstration plant could come in the form of grants and low-interest loans from the SDTC Technology Fund and other Federal and Provincial funding sources.

10.4 Conduct a Full Economic Impact Assessment for the Sustainable Removal of Corn Stover

Removal of corn stover from agricultural land is in a nascent stage. Numerous studies have been conducted around North America to assess the sustainable removal of corn stover. Unfortunately, gaps of knowledge remain. The quantities of corn stover that can be sustainably removed and the economic benefits from its removal need to be determined based on the local conditions or soil, weather and farming practices. Through this understanding, there may be the opportunity to make more stover available and impact the economics of corn stover as a feedstock for further processing. Mobile pyrolysis technology such as from Agri-Therm will only become economic if the unit cost for agricultural biomass decreases.

10.5 Contribute to Development Work to Extract Higher Value from Bio-oil

Currently, there is significant work ongoing around the world to establish routes to higher value products from bio-oil. R&D has been ongoing in Canada and is contributing to this knowledge pool. This work has not yet created opportunities ready for commercialization. However, progress continues and Canada must remain engaged in these initiatives to ensure that Canada can be an early adopter of any advances in technology. Canada should continue to contribute to development work to upgrade bio-oil to higher value-added products in areas such as:

- Economic conversion of bio-oil to a refined bio-oil for integration into existing oil refineries or as feedstock for biochemical extraction. The CanmetENERGY Centre is focused in this area for their R&D. They also provide a very valuable link to the work done in the United States through the Energy Efficiency & Renewable Energy initiative of the US Department of Energy.
- Identification, isolation and registration of bioactive chemicals and pharmaceuticals from bio-oil which have social and economic value. Currently, the Agriculture and Agri-Food Canada Centre in London Ontario plays a key role in these research activities in Canada. Their R&D work is a long term initiative worthy of continued study due to its significant potential benefits
- Economic extraction of biochemicals from the bio-oil. Work is ongoing in many Canadian Universities and Colleges. This work is still early stage and needs time and effort to develop.

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12 - List of Acronyms and Units of Measure

AAFC	Agriculture and Agri-Food Canada
ABI	Alberta Bio-char Initiative
AITF	Alberta Innovate – Technology Futures
BFB	pyrolysis reactor type using a bubbling fluidized bed
BIC	Bio-Industrial Innovation Canada
BSE	bovine spongiform encephalopathy – mad cow disease
BTG	British Thermal Group at Swansea University in England
CAAP	Canadian Agricultural Adaptation Council
°C	unit of measure of temperature – degrees Celsius
CaO	calcium oxide – a solid chemical compound
CFB	pyrolysis reactor type using a circulating fluidized bed
CHP	combined heat and power generation system
CO	carbon monoxide, a gaseous product from incomplete combustion
CO ₂	carbon dioxide, a gaseous product from the combustion of fossil fuels
ср	unit of measure of viscosity - centipoise
СРВ	Colorado Potato Beetle
DDG	dried distillers grain – the solid residual product from ethanol production
ESP	electrostatic precipitator
GC	gas chromatography
HPLC	high performance liquid chromatography
ICFAR	Institute for Chemicals and Fuels from Alternative Resources, Western University, London, Ontario
IEA	International Energy Agency

- IGPC Integrated Grain Processors Cooperative Aylmer, Ontario
- kPa unit of measure of pressure kilopascals
- kWh unit of measure of electrical energy kilowatt-hour
- LCA Life cycle analysis
- LHV measure of heat content lower heating value
- MAT maximum allowable threshold
- MBM meat and bone meal
- mg/ml unit of measure of concentration milligrams per milliliter
- MJ/kg unit of measure of heat content megajoules per kilogram
- m²/g unit of measure of surface area square meters per gram of solid
- MPS mobile pyrolysis system
- MWe unit of measure of electrical energy megawatt electricity
- NCG non-condensable gases generated during pyrolysis
- NO_x gases containing nitrogen and oxygen known for impacts on air quality
- NREL National Renewable Energy Laboratory
- OFA Ontario Federation of Agriculture
- pH unit of measure of acidity and basicity logarithmic scale
- ppm unit of measure of concentration part per million on a mass basis
- SO_x gases containing sulphur and oxygen known for impacts on air quality
- TPG tall prairie grass
- USDOE United States Department of Energy
- WD Western Economic Diversification

Notes



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