2008

Pesticides from fast pyrolysis of agricultural and forestry residues

Rohan Bedmutha
Western University

THE UNIVERSITY OF WESTERN ONTARIO
SCHOOL OF GRADUATE AND POSTDOCTORAL STUDIES

CERTIFICATE OF EXAMINATION

Joint-Supervisor	Examiners
Dr. Franco Berruti	Dr. Katherine Albion
Dr. Cedric Briens	Dr. Amir Yazdani
	Dr. Jin Zhang

The thesis by

Rohan Bedmutha

entitled:

Pesticides from fast pyrolysis of agricultural and forestry residues

is accepted in partial fulfillment of the
requirements for the degree of
Master of Engineering Science

Date_____

_____
Chair of the Thesis Examination Board

ABSTRACT

This thesis investigates the production of pesticides through the fast pyrolysis of three biomass feedstocks: tobacco leaves, dried coffee grounds and pinewood killed by beetles. It was observed that a significant fraction of the bio-oil escaped the condensing train as a fine mist; this is a common problem in pyrolysis operations. An electrostatic demister was, therefore, developed to recover this mist.

Tobacco leaves were pyrolyzed to produce bio-oil. Pyrolysis was carried out at six different temperatures from 350°C to 600°C and at three different vapor residence times (5, 10 and 17 s), to study the effect of operating conditions on the bio-oil yield. The trends clearly indicated a strong effect of temperature and vapor residence time on the bio-oil yield. A temperature of 500°C was then selected and the pyrolyzer was operated again at the lowest vapor residence time of 5 s to obtain accurate liquid, gas and char yields. Tobacco bio-oils produced at different temperatures (350-600°C) and at a vapor residence time of 5 s were tested for their bactericidal, fungicidal and insecticidal activities against pests found on plants in Canada that currently require improved control options. A significant finding of the research was that even fractions containing no nicotine had significant activity towards the aforementioned pests.

Dried coffee grounds were pyrolyzed to produce bio-oil. Pyrolysis was carried out at five different temperatures from 400°C to 600°C and at a vapor residence time of 5 s, to study the effect of temperature on the bio-oil yield. The trends clearly indicated a strong effect of temperature on the bio-oil yield. Coffee grounds bio-oils produced at different temperatures (400-600°C) were tested for their bactericidal and insecticidal activities against pests found on plants in Canada that currently require improved control options. While some compounds in the bio-oil, such as phenols, were active against both beetles and bacteria, the coffee bio-oil contained

chemicals that provided additional insecticidal activity but had no bactericidal activity.

Single-stage and two-stage tubular electrostatic precipitators were designed for the recovery of bio-oil mist. Because of concerns regarding bio-oil stability, an inert fogging oil was used for the development of the demisters. A nitrogen stream containing very fine droplets of fogging oil was forced through the electrostatic precipitator chamber. It was found that 98.6 wt% of the oil droplets present in the turbulent jet were mechanically collected on the inner walls of the test chamber. When the electrode was energized at 13 KV, 92.37 wt% of the droplets that had not been mechanically separated were collected in single-stage mode. The collection efficiency was increased to 93.18 wt%, when the electrostatic precipitator was operated in two-stage mode. Voltage-current (V-I) characteristics of the single-stage and two-stage electrostatic precipitators were studied in detail for different test conditions. Nitrogen impurities played a major role in determining the V-I characteristics. They became less relevant with the introduction of mist in the nitrogen stream, presumably due to the presence of water vapor in the gas. The two-stage tubular electrostatic precipitator was scaled up and tested on a fluidized bed pilot plant used for the pyrolysis of biomass. A droplet collection efficiency of 95 wt% was observed. Such demisters will extend, to the product recovery train, the process intensification gains of short residence time processes such as fast pyrolysis.

Keywords: tobacco leaves, coffee grounds, insecticide, fungicide, bactericide, single-stage and two-stage electrostatic precipitator

STATEMENT OF CO-AUTHORSHIP

Chapters 2, 3 and 4 encompass research studies that have been submitted to peer-refereed journals. Individual contributions of the authors for each article are stated.

Chapter 2

Article title	Insecticidal, fungicidal and bactericidal characteristics of the bio-oil from the fast pyrolysis of tobacco leaves
Authors	R. Bedmutha, T. Vogel, A. Gloor, C. Booker, R. Xu, L. Ferrante, F. Berruti, K. K.-C. Yeung, C. Briens, I. Scott, K. Conn
Current status	Submitted to Ind. Eng. Chem.

Pyrolysis of tobacco leaves was carried out by R. Bedmutha, L. Ferrante and R. Xu. Bactericide and fungicide experiments were performed by T. Vogel and C. Booker. Insecticide experiments were done by A. Gloor. R. Bedmutha helped T. Vogel, C. Booker and A. Gloor during their experiments. Consultation regarding experimental work was provided by F. Berruti, C. Briens, K. K.-C. Yeung, I. Scott and K. Conn. The manuscript was written and revised by R. Bedmutha, and reviewed by all the authors.

Chapter 3

Article title	Insecticidal and bactericidal characteristics of the bio-oil from the fast pyrolysis of coffee grounds
Authors	R. Bedmutha, C. Booker, L. Ferrante, C. Briens, F. Berruti, K. K.-C. Yeung, I. Scott, K. Conn
Current status	Submitted to J. Anal. Appl. Pyrol.

Pyrolysis of coffee grounds was carried out by R. Bedmutha. Insecticide and bactericide experiments were carried out by C. Booker and R. Bedmutha. Consultation regarding experimental work was provided by C. Briens, F. Berruti, K. K.-C. Yeung, I. Scott, K. Conn and L. Ferrante. The manuscript was written and revised by Rohan Bedmutha, and reviewed by the rest of the authors.

Chapter 4

Article title	Single and two-stage electrostatic demisters for micron size mist
Authors	R. Bedmutha, L. Ferrante, C. Briens, F. Berruti, I. Inculet
Current status	Submitted to Chem. Eng. Process.

Experiments were designed and conducted by R. Bedmutha. Consultation regarding experimental work was provided by C. Briens, F. Berruti and I. Inculet. The manuscript was written and revised by R. Bedmutha, and reviewed by the rest of the authors

ACKNOWLEDGEMENTS

I wish to express sincere appreciation for my supervisors, Dr. Franco Berruti and Dr. Cedric Briens for their guidance, support and encouragement throughout the course of my master's program. I would also like to thank them for providing me an opportunity to work on this exciting cutting age technology that has the potential to change the way we think. Without their support and help, this dissertation would not have been possible.

I would like to thank Dr. Ken Yeung, Dr. Ian Scott and Dr. Kenneth Conn for their valuable help while conducting experiments with fungi, bacteria and insects. I would also like to thank Dr. Ion Inculet for his valuable advice on electrostatic precipitators and for the direction of research on electrostatic precipitators. I would like to thank Joanna Blom and Marilyn Tudhope for the administrative assistance.

I greatly appreciate the help I received from Dr. Lorenzo Ferrante and Ran Xu while dealing with the production of bio-oils. I would like to thank the members of the Institute for Chemicals and Fuels from Alternative Resources (ICFAR), for their support, friendship and help in dealing with the matters ranging from research to administration. I would also like to thank Christina Booker, Tiffany Vogel and Alex Gloor (Department of Chemistry and Biochemistry) for their help and assistance in dealing with the chemistry of bio-oils.

I would like to thank Natural Sciences and Engineering Research Council of Canada (NSERC), Ontario Centres of Excellence (OCE), Agri-THERM and Canada Foundation for Innovation (CFI) for their financial support.

I would like to thank University Machine Services (UMS), Engineering Stores and Electronics shop for their help from time to time during the course of the two years.

Finally, I wish to express greatest appreciation to my parents, for their moral support and encouragement not only through these two years but during my entire life.

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NOMENCLATURE

η	Electrostatic precipitator efficiency (%)
A	Surface area of the collecting electrodes (m^2/s)
ω	Drift velocity (m/s)
Q	Volumetric gas flow-rate (m^3/s)
T	Time constant (s)
ε_0	Permittivity of free space (F/m)
E	Local electric field (V/m)
I	Discharge current flowing from discharge to collecting electrodes (A)
k	Dielectric constant for droplets
a	Radius of droplets (m)

CHAPTER 1

INTRODUCTION

1.1 Agricultural residues (biomass): An alternative source of energy

With the fast depletion of fossil fuel resources and the threat of global warming looming, alternative sources of energy, that could reduce carbon dioxide emissions and fossil fuel dependency, have gained considerable importance.

Agricultural residues (biomass) are renewable and environmentally friendly, potential source of biofuel and chemicals. It is also a carbon dioxide neutral source of energy, which means that the amount of carbon dioxide emitted on combustion is the same as that captured by the plants during their growth. In addition, it has a very small sulfur content compared to conventional fossil fuel [1].

Definition of biomass: The term "biomass" describes material of recent biological origin that can be used as a source of energy or for its chemical components. It includes trees, crops, algae and other plants, as well as agricultural and forestry residues. It also includes many materials that are considered waste by our society, including food and drink manufacturing effluents, sludges, manures, industrial (organic) by-products and the organic fraction of household waste. Biomass consists of hemi-cellulose, cellulose, lignin and minor amounts of other organics which each pyrolyse or degrades at different rates and by different mechanisms and pathways [2].

Biomass vs bio-oil: Biomass is not an attractive source of energy when used directly because of its high moisture content and low energy density. Biomass combustion results in much higher emissions for the same amount of energy when compared to oil or natural gas [3]. Biomass moisture content varies between 50-60 wt% and passive drying can reduce this to 30 wt%. Active silo drying can reduce the moisture content further to 12-15 wt% [4]. Current technologies to increase biomass bulk density include palletizing, cubing and baling [5]. Biomass, when converted through fast pyrolysis to bio-oil has an energy density five to six times higher than that of raw biomass.

1.2 Fast pyrolysis of agricultural waste (biomass)

Pyrolysis dates back to ancient Egyptian times. Pyrolysis processes have been improved and are now widely used for charcoal and coke production. Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen [6]. It utilizes a very short vapor residence time and a temperature of around $500^{O}C$. It is very important to control the vapor residence time and temperature to freeze the intermediates and thus maximize the liquid bio-oil yield [2]. A rapid cooling of the vapor products is also essential to stop the thermal cracking of the bio-oil into noncondensable gases [7]. Fast pyrolysis process can produce 50-85 wt% of liquid bio-oil, 15-25 wt% of solid bio-char and 10-20 wt% of noncondensable gases, depending upon the feedstock, operating conditions and the reactor configuration. Pyrolysis is a zero waste process. Bio-oil is the desirable product whereas non-condensable gases and char can be as a fuel for endothermic pyrolysis reaction. Char along with ashes can also be used as a fertilizer [6].

1.3 What is bio-oil?

Definition: Bio-oil, also known as pyrolysis oil, pyrolysis liquid etc. is usually a dark brown, free-flowing liquid having a distinctive smoky odor. Bio-oil is a multi-component mixture consisting of different size molecules derived primarily from de-polymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemi-cellulose, and lignin [1].

Chemical composition: Bio-oil contains many reactive species, which contribute to unusual attributes. Chemically, bio-oil is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics [6].

Oxygen content: The elemental composition of bio-oil resembles that of biomass. The oxygen content of the bio-oil is usually 35-40 wt%. Oxygen is present in most

of the compounds identified in bio-oil and it is one of the primary reasons for the differences in the properties and behavior seen between hydrocarbon fuels and biomass pyrolysis oils [1].

Water content: The single most abundant component in bio-oil is water. Water in bio-oil is a result of original moisture content of feedstocks and a product of dehydration reactions occurring during pyrolysis. Water content in bio-oil thus varies over a wide range (15-30%) depending on the feedstocks and process conditions [1].

Viscosity: The viscosity of bio-oil can vary over a wide range (35-1000 cP at 40 °C) depending on the feedstocks and process conditions, and especially on the efficiency of collection of low boiling components. At higher temperatures, the viscosity of bio-oil decreases faster than petroleum-derived oil [1]. However, bio-oil is subjected to ageing when exposed to temperatures at or above room temperatures for a long time. This is manifested by an increase in viscosity over time [1, 6, 8]. This could be due to the various reactions occurring in the bio-oil, leading to the formation of larger molecules [1].

Corrosiveness: Bio-oil contains large amounts of organic acids resulting in a pH value of 2-3, although there have been instances when bio-oil is known to have an alkaline pH. The corrosiveness is especially severe at elevated temperatures and with high water contents [1]. No clear trend has yet been established between the pH values and the pyrolysis temperature. With the pH value of 2-3, bio-oil is especially corrosive to carbon steel and aluminum. Polyolefins are usually acceptable materials of construction for bio-oil contact [1].

1.4 Applications of bio-oil

Fuel Applications: Bio-oil is more attractive than the simple biomass due to its potential to be used as fuel 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 [9].

Chemicals from bio-oil: Several organic compounds with added commercial value can be extracted from the bio-oil for food flavoring and pharmaceutical industries. Additional advantages and benefits of the bio-oil over biomass are that, bio-oil is easy to store and transport. Many commercial products are on their way such as BioLime and bio-oil based fertilizer from Dynamotive Inc [10]. Bio-oil based fertilizer could act as an efficient bio-degradable slow-release nitrogen fertilizer [11]. The only current commercially relevant application of bio-oil chemicals, from the aqueous phase, is that of wood flavours, browning agents and liquid smoke.

Recently, bio-oil has also been proposed as an alternative wood preservative to creosote [12]. Meir et al. [13] did a preliminary study on fungicide and sorption effects of bio-oil used as a wood preservative. No other literature is available on the fungicidal/pesticidal properties of bio-oil.

1.5 Different reactor technologies for bio-oil production from biomass

All over the world researchers have been studying the pyrolysis of agricultural wastes and residues (straw, husks, corncobs, tea wastes, sesame stalks, hazelnuts, sugarcane, sorghum, almond shells, rapeseeds, tobacco stalks and leaves, algae, cotton straw, sunflower bagasse, switchgrass, woods and forestry residues, and many others) by utilizing a variety of different reactor technologies (fixed beds, Heinze-type reactors, retort vessels, wire-mesh reactors and fluidized beds) [14]. The heart of the fast pyrolysis process is indeed the reactor, and considerable research development has focused on different reactor technologies. During the past two decades, several different reactor designs have been studied and some processes have been proposed. 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 [6]. Few of these processes have reached the commercial scale. Bridgewater et al. [15] published an excellent review that classifies the reactors into (1) fluidized beds, (2) circulating fluidized beds, (3) ablative (vortex and rotating blade) reactors, (4) rotating cone and vacuum reactors, and (5) auger reactors.

Scott et al. [16] analyzed several reactors for fast biomass pyrolysis and concluded that none of the reactor concepts fully satisfies all requirements, in their present state of development. They concluded that a biomass conversion process, especially the one producing liquid fuels, would be most useful if it were a simple process, not capital intensive, and that could be operated efficiently on a small scale. Such a plant would not necessarily be suited as a centralized conversion plant, attempting to service a large area. 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. 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 [17]. These considerations inspired the development of a joint venture between our Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at The University and Western Ontario and private investors, leading to the creation of a spin-off company (Agri-Therm). Agri-Therm (http://www.agri-therm.com/) is dedicated to developing, manufacturing and marketing portable (mobile) pyrolysis plants for the production of bio-oils and products from biomass, specifically agricultural residues, wastes and transition crops. The technology is based on an innovative fluid bed reactor technology that addresses the unique issues associated with agricultural products.

1.6 Bio-oil mist separation

Fast pyrolysis of biomass produces condensable vapors, noncondensable gases and solid char. The condensable vapors along with noncondensable gases are then passed through a series of condensers. This process produces liquid bio-oil and is accompanied by the formation of submicron bio-oil mist [2, 3, 15, 18, 19]. Various

gas-liquid separation systems such as cyclones, scrubbers, filters and electrostatic precipitators are operational all over the world. Problems in case of pyrolysis are compounded by submicron size bio-oil droplets in an inert gas at relatively low concentrations. The need for an effective separation of submicron bio-oil droplets has been recognized by researchers all over the world.

1.7 Thesis objectives and outline

A careful review of the vast body of literature available yielded following objectives:

a) In spite of the significant advances in the use of bio-oil as a wood preservative, very limited efforts have been made to actually characterize bio-oil from different feedstocks and to test their pesticidal activities. Three different feedstocks were selected in this study: tobacco leaves, coffee grounds and pinewood based on their natural insecticidal properties.

b) As mentioned above, pyrolysis of biomass produces sub-micron bio-oil droplets dispersed in a gas, which need to be separated. A detailed comparison between various technologies has been presented by several authors [20-22]. Out of the various gas-liquid separation systems available today, electrostatic precipitator is one of the most promising technologies. The most important advantages of electrostatic precipitator over other available technologies are low pressure drop and low energy consumption. Though very extensive literature has been published on electrostatic precipitators, very limited work has been done on the comparison of single-stage and two-stage electrostatic precipitators. The single-stage and two-stage ESPs were thus designed and tested for their droplet collection efficiencies and V-I characteristics. A scaled-up two-stage electrostatic precipitator was designed for fast pyrolysis pilot plant which was tested for its droplet collection efficiency.

Chapter 2 deals with the optimization of tobacco bio-oil yield as a function of pyrolysis temperature and vapor residence time. Pyrolysis was then carried out at a temperature and vapor residence time corresponding to the highest liquid yield to

determine the exact yields of liquid, gas and char. The tobacco bio-oil was tested for its activity against 11 fungi, 4 bacteria and the Colorado potato beetle (CPB). Fractionation of bio-oil was carried out to form nicotine and non-nicotine fractions. Two different fractionation schemes, one for bactericidal and fungicidal assays and one for insecticidal assays were followed. Fractions were tested for their fungicidal, bactericidal and insecticidal inhibition.

Chapter 3 deals with the optimization of pyrolysis product yields as a function of pyrolysis temperature. Liquid, gas and char yields were calculated for all the experimental conditions under consideration. The coffee grounds bio-oil was tested for its activity against 11 fungi, 4 bacteria and Colorado potato beetle (CPB). Bio-oil fractionation was carried out. Fractions were tested for their fungicidal, bactericidal and insecticidal inhibition. Most of the fractions were analyzed using GC-MS.

Chapter 4 deals with the empirical design parameters of single-stage and two-stage electrostatic precipitators. Both single-stage and two-stage electrostatic precipitators were tested under similar conditions for their droplet collection efficiencies. Voltage-current characteristics (V-I) of the single-stage and two-stage electrostatic precipitators were studied in detail for different test conditions. A semi-empirical data fitting exercise was also carried out to see the difference between experimental and predicted droplet collection efficiencies. Malvern-3600 was used to characterize the droplet size distribution. The two-stage electrostatic precipitator was then scaled up and tested on a fast pyrolysis pilot plant. The idea was to test the scaled-up two-stage tubular electrostatic precipitator for the actual industrial application.

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CHAPTER 2

INSECTICIDAL, FUNGICIDAL AND BACTERICIDAL CHARACTERISTICS OF THE BIO-OIL FROM THE FAST PYROLYSIS OF TOBACCO LEAVES

2.1 Introduction

Tobacco leaves and stalk are an important source of plant biomass not only for fuel applications but also for the production of potentially bio-active compounds such as pesticides. Using tobacco waste material could also benefit the grower due to the conversion of low value materials into value-added products.

Synthetic chemical pesticides have provided many solutions for pest control in the past several decades. However, the problems associated with their use include: the need for costly fossil fuels in the manufacturing process; the development of resistance by many pests and the adverse effects to human health and the environment. For example, the Colorado potato beetle has become resistant to most commercial synthetic insecticides [1]. Effective pesticides produced from natural products could offer an alternative solution to help solve these problems as: 1) they are produced from renewable resources, 2) they typically include several active molecules, making resistance development more difficult; and 3) they are usually biodegradable therefore lessening the adverse environmental health effects [2].

Pyrolysis can be used to convert tobacco biomass into a liquid bio-oil, which can be easily transported and stored. Pyrolysis is a thermo-chemical process, which is carried out in the absence of oxygen to convert biomass into liquid bio-oil, char and gases [3]. The bio-oil normally contains a high proportion of oxygenates, reflecting the oxygen content of the original substrates. These products are usually quite reactive and their characteristics may change rapidly during condensation [4].

Tobacco biomass has been characterized [5-7], but very limited work has been published on the pyrolysis of tobacco for the production of bio-oil. One study concentrated on the production of fuel gases but did not perform liquid analysis [8], while another study performed liquid analysis but did not analyze the bio-oil for nicotine [9]. The objective of the current study was the production of bio-oil from tobacco under a wide range of operating conditions and the characterization of its pesticidal properties.

2.2 Materials and methods

2.2.1 Materials

Tobacco leaves were provided by Agriculture and Agri-Food Canada, London, Ontario, Canada. Tobacco leaves were dried at 60°C, they were then ground using a blender/mixing mill and sieved. The Sauter mean diameter of the tobacco particles used for pyrolysis was 60 μm.

2.2.2 Methods

2.2.2.1 Tobacco pyrolysis

2.2.2.1.1 Pilot plant

All pyrolysis experiments were carried out using a fluidized bed pilot plant (Figure 2.1). The heart of the plant was an atmospheric fluid bed reactor, 0.078 m in diameter, with a 0.52 m long cylindrical section, and equipped with an expanded section made up of a 0.065 m long truncated cone with an upper diameter of 0.168 m, topped by a second, 0.124 m long, cylindrical section. The total volume of this configuration is 6.09×10^{-3} m^3. This assembly provided the lowest vapour residence time i.e. 5 s. Two different freeboard extensions were used to increase the vapour residence time to 10 and 17 s. A filter capable of withstanding high temperatures was installed at the gas exit of each of the extensions. Each filter was made up of a perforated pipe connected to the gas exit covered by fibreglass pad and wrapped inside a fine stainless steel mesh cover.

The fluidizing nitrogen was injected at the base of the fluidized bed through a perforated copper distributor plate using a fluidization velocity of around 0.05 m/s. Silica sand obtained from Opta Minerals Inc., having a Sauter mean diameter of 2×10^{-4} m, was used to fill the fluidized bed to a static height of 0.15 m.. The reactor was equipped with seventeen thermowells for temperature measurement and control, using type K thermocouples.

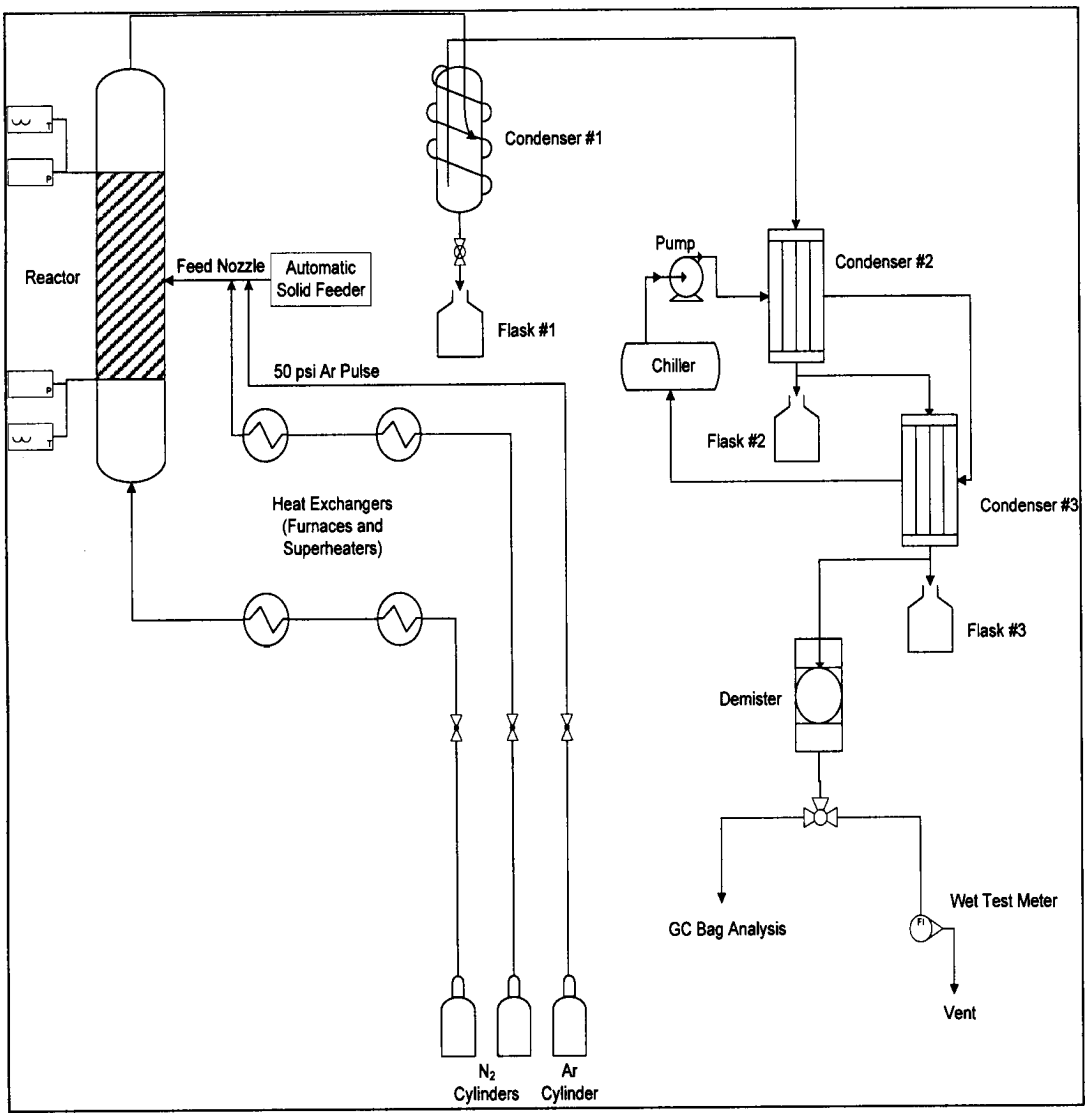

Figure 2.1 - A schematics of the Western Fluidization Group's fluid bed pilot plant

A horizontal pulsating feeder from the distributor plate was used to inject tobacco into the reactor bed at a height of 0.1 m above the distributor plate. A continuous flow of nitrogen was used to convey the tobacco to the reactor. It was supplemented by an intermittent argon pulse that was synchronized with the solids pulses.

Tobacco, when injected into the reactor, produced vapours that exited at the top of the reactor through the hot filter section and flowed into three condensers in series (as shown in Figure 2.1). Persistent aerosols were then separated in a cylindrical demister packed with cotton wool.

2.2.2.1.2 Bio-oil production and its characterization

The exact yield of tobacco bio-oil was obtained from the mass of bio-oil collected in the three condensers and the demister. The demister was weighed before and after the experiment.

Pyrolysis was initially carried out at six different temperatures from 350°C to 600°C and at three different vapor residence times (5, 10 and 17 s). Each test was conducted with 700 g of ground tobacco leaves. Fluidizing and carrier nitrogen volumetric flow rates were controlled using 'Mass Trak' flow-meters from Sierra Instruments Inc., and adjusted to keep the nominal vapor residence time constant at all temperatures. The tobacco bio-oils separated into organic and aqueous phases.

Pyrolysis of tobacco leaves was subsequently carried out at a temperature of 500°C and at a vapor residence time of 5 s, which corresponded to the highest bio-oil yield, to determine the accurate liquid, gas and char yields. All the yields are reported in wt% of biomass fed.

2.2.2.1.3 Characterization of product gases

Gases were sampled in plastic bags at three different time intervals during each experiment. A Hewlett-Packard 5890 Series II Gas Chromatograph (GC) was used to measure the product gas composition. It was equipped with a RESTEK Shin

Carbon ST (micro packed) column (0.001 m ID, 2 m length). A Thermal Conductivity Detector (TCD) detected the composition of the pyrolysis gas mixture, which primarily consisted of N_2, H_2, CO, CO_2 and CH_4. In order to measure product gas yields accurately, N_2 was selected as an internal standard. Argon was selected as the GC carrier gas. A standard gas mixture with a fixed composition of H_2, CO, CO_2 and CH_4 was used to calibrate the GC.

The injector was maintained at 150°C and the TCD was maintained at 275°C. A gas sample of 50 μL was injected with a 100 μL Hamilton syringe. Upon injection, the oven temperature was held at 35°C for 180 s, then increased at 10°C/min to 150°C, and finally increased at 20°C/min to 250°C. The temperature was then held constant at 250°C for 5.5 min.

2.2.2.1.4 Characterization of char

The differential pressure drop across the fluidized bed was measured at minimum fluidization conditions before and after each experiment. Since any solid material produced during the reaction would be retained inside the bed by the hot gas filter, the increase in the bed pressure drop is proportional to the increase in bed mass caused by char accumulation during the run.

2.2.2.2 Fungicidal and bactericidal assays

2.2.2.2.1 Preparation of bio-oil samples

The initial assays performed were aimed to determine if any activity was present in the bio-oil. These tests were not concerned with the accurate quantification of the activity level or determination of the active component(s).

All the tobacco bio-oil samples used for the bactericidal and fungicidal assays were produced at a vapor residence time of 5 s and at different temperatures as specified for each assay. Each bio-oil sample was filtered with a 0.025 m wide, 4.5×10^{-7} m pore size syringe filter.

Tobacco bio-oil naturally separates into an aqueous and an organic phase with suspended solid particles. A mixture was prepared by mixing the organic phases of the tobacco bio-oils produced from 350°C to 600°C. The mixture (0.375 g) was dissolved in 1 mL of acetone. A mixture of the aqueous phases of the tobacco bio-oil was used directly without a solvent. Preliminary samples of both mixtures were tested for inhibition against 11 fungi and 4 bacteria. From these results two bacteria and one fungus were chosen for further characterization.

The organic phases of the tobacco bio-oils produced at 350°C to 550°C were then tested separately for their activity against two bacteria viz. *Streptomyces scabies* and *Clavibacter michiganensis* subsp. *michiganensis* and one fungus, *Pythium ultimum*. The concentration remained at 0.375 g of bio-oil per mL of acetone.

Organic phase of the tobacco bio-oil produced at 450°C was then serially diluted in acetone to 10%, 1% and 0.1%, taking the initial concentration (0.375 g/mL) to be 100%.

Bio-oil fractionation:

It was predicted that the tobacco bio-oil contains large amounts of nicotine. The purpose of bio-oil fractionation was thus to form two fractions, one containing nicotine and the other devoid of nicotine.

The method used for tobacco bio-oil fractionation is illustrated in Figure 2.2.

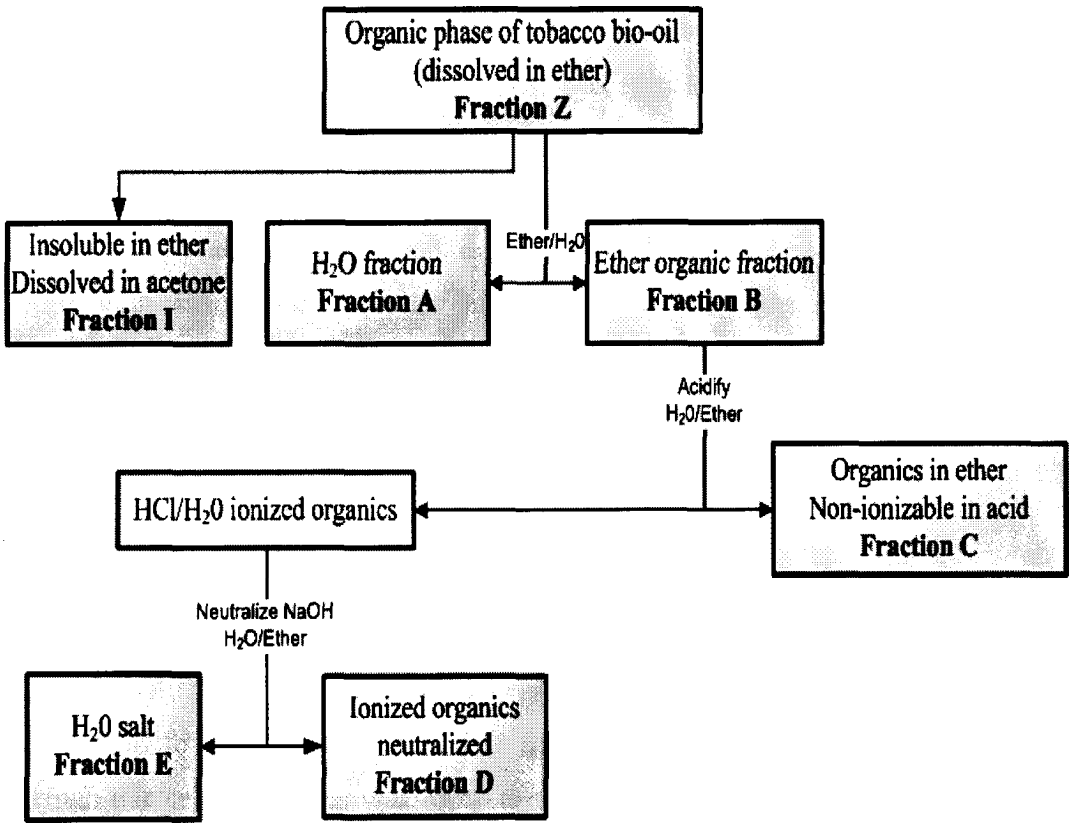

Figure 2.2 - Fractionation scheme of tobacco bio-oil for fungicidal and bactericidal analysis

The organic phase of the tobacco bio-oil produced at 450°C was dissolved in di-ethyl ether at a concentration of 0.375 g/mL (Fraction Z). This fraction was vortexed and sterile filtered with a 0.025 m wide 4.5×10^{-7} m pore size syringe filter with a nylon membrane. Dissolving the bio-oil in di-ethyl ether caused a black precipitate to form on the walls. This precipitate was dissolved in acetone (0.103 g/mL) and was also sterile-filtered (Fraction I). Fraction Z was extracted by adding water in a 1:1 volume ratio with di-ethyl ether. This produced two fractions: an organic di-ethyl ether fraction (Fraction B) and an aqueous fraction (Fraction A). Fraction B was further extracted by adding water in a 1:1 volume ratio with di-ethyl ether and acidifying the water fraction with concentrated HCl to pH 2. This produced two fractions: an organic di-ethyl ether fraction (Fraction C) with compounds that could not be charged under acidic conditions and an acidic aqueous

fraction containing organic compounds that could be charged under acidic conditions. The acidic aqueous fraction was then neutralized with NaOH to drive the charged organic compounds back to their neutral state. This neutralization caused some compounds to return to their neutral state and others to likely polymerize and form a precipitate. Di-ethyl ether was then added in 1:1 volume ratio with water thus separating neutral ionizable organics into the di-ethyl ether fraction (Fraction D), while Fraction E was simply the aqueous salt from the neutralization. Dilution factors were calculated for each fraction and the amount of bio-oil saturated on the disc for biological assays was adjusted so that the concentration on the disc was constant between fractions.

2.2.2.2.2 Disc diffusion agar method

The disc diffusion agar method was used to screen the bio-oil activity on eleven fungi and four bacteria. Petri dishes filled with appropriate media (depending on which bacteria or fungus was to be tested) were inoculated with bacteria or fungi. Media used for different fungi and bacteria included Potato Dextrose Agar (PDA), Tryptic Soy Agar (TSA) and Yeast Media Extract (YME). Bacteria were streaked across the entire media surface, while small agar plugs (1×10^{-4} m^2) of fungi were placed approximately 0.01 m off centre on the media. The bio-oil samples were pipetted onto filter paper discs ($d = 6\times10^{-3}$ m). 5 μL of the sample solution was applied to each disc unless otherwise specified. The saturated disc was allowed to dry and then placed in the centre of the inoculated petri dish. Plates were prepared in triplicate to test for reproducibility. The plates were incubated at 24°C for three days and then evaluated for activity by measuring the diameter of inhibition.

Various negative controls such as water, di-ethyl ether acetone etc. were used depending on the solvent used for dissolving the tobacco bio-oil fraction. Streptomycin sulfate (250 ppm) was used as a positive control for both the bacteria *C. michiganensis* subsp. *michiganensis* and *S. scabies*, while Ridomil (10,000 ppm) was used as positive control for the fungus *P. ultimum.*

2.2.2.3 Insecticidal assays

2.2.2.3.1 Preparation of bio-oil samples

The initial assays performed were aimed to determine if any activity was present in the bio-oil. These tests were not concerned with the accurate quantification of the activity level or determination of the active component(s).

All the tobacco bio-oil samples used for insecticidal assays were produced at a vapor residence time of 5 s and at different temperatures as specified for each assay. Tobacco bio-oil naturally separates into an aqueous and an organic phase with suspended solid particles. A mixture was prepared by mixing the organic phases of the tobacco bio-oils produced from 350°C to 600°C. Similarly, the mixture of the aqueous phases of the tobacco bio-oils was prepared. Preliminary samples of both mixtures were tested against Colorado potato beetle or CPB (*Leptinotarsa decemlineata*).

Tobacco bio-oils produced at 350°C to 550°C were then tested separately against CPB.

Bio-oil fractionation:

It was predicted that the tobacco bio-oil contains large amounts of nicotine. The purpose of bio-oil fractionation was thus to form two fractions, one containing nicotine and the other devoid of nicotine.

The procedure outlined by Oasmaa et al.[10] was deemed appropriate for this task as it closely matched past literature methods of nicotine extraction from tobacco plants [11, 12]. Initial fractionation of the bio-oil was done by liquid-liquid extraction using di-ethyl ether and dichloromethane (DCM) as solvents as shown in Figure 2.3.

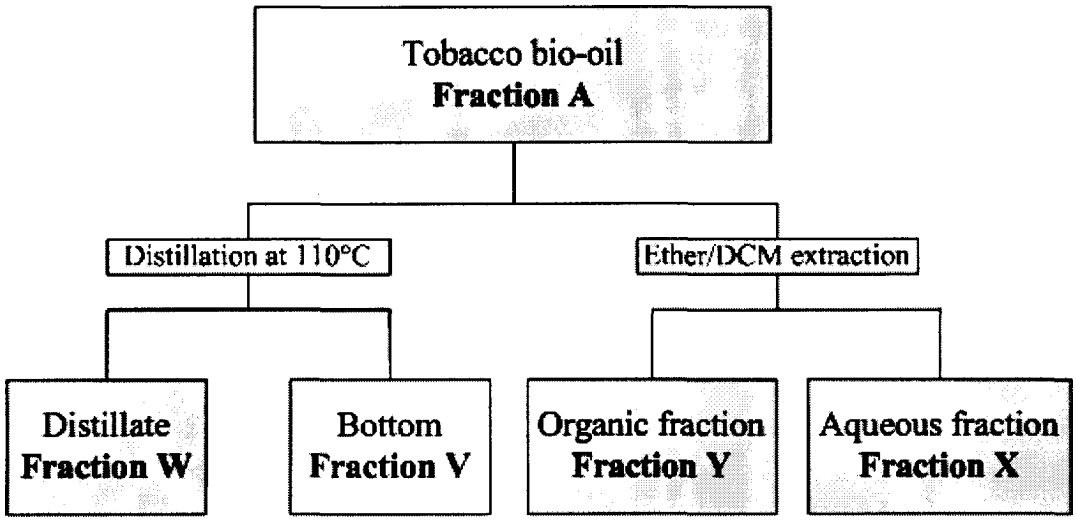

Figure 2.3 - Fractionation scheme of tobacco bio-oil for insecticidal analysis

The procedure involved filtration of 15-20 g of bio-oil through a filter paper to remove the suspended solid particles of the tobacco bio-oil. Suspended solid particles of the tobacco bio-oil were washed with 10 mL di-ethyl ether followed by 10 mL DCM. The filtered bio-oil was then extracted in a 100 mL separator funnel with 20-30 mL of diethyl ether. The extraction was then performed using 20-30 mL of DCM. All organic fractions were combined and the solvent was evaporated using a rotary evaporator (BUCHI R-114). The organic fraction recovered (Fraction Y) was a moderately viscous brown oil, quite similar to the bio-oil itself. The aqueous fraction (Fraction X) was orange and had low viscosity.

Undiluted aqueous and organic fractions (Fractions X and Y respectively) were tested for insecticidal activity. Aqueous and organic fractions were serially diluted to 50%, 10%, 2% and 0.5% concentration and tested for insecticidal activity. Furthermore, Fraction X was analyzed for its nicotine content.

2.2.2.3.2 Leaf disk application

The insecticidal tests were carried out by the leaf disc application, similar to the procedure outlined by Sengonca et al. [13]. The potato plants (var. Cal White) were

grown on site at the Southern Crop Protection and Food Research Centre (SCPFRC), Agriculture and Agri-Food Canada, London, Ontario, with the leaves cut to a diameter of 0.04 m. Fractions were spread on both sides of a potato leaf with a cotton-tipped applicator. The leaves were allowed to dry after sample application. After drying, leaves were transferred to a Gelman® petri dish. Five second instar Colorado potato beetle (*Leptinotarsa decemlineata*) larvae reared at SCPFRC were then transferred to the leaf. Three leaves were tested for each fraction; however most of the tests were repeated on multiple dates to ensure accuracy. Control leaves involved placing the beetles on leaves without any oil present. If a specific test involved dilution of the bio-oil, the control leaves were coated with the solvent used. The mortality rate was recorded at the end of 24 and 48 hr. The mortality rate is defined as the % of beetles dead. The mortality averaged over all tests has been reported in this chapter.

2.2.2.3.3 Distillation

Like the ether extraction, the purpose in distilling the bio-oil was to form one nicotine containing fraction (Fraction V) and one non-nicotine fraction (Fraction W). Distillation is not typically a viable practice in bio-oil fractionation [14] as heating bio-oil causes polymerization to occur, with a solid resin forming upon cooling. However, despite potentially losing a portion of the product, it was worthwhile to investigate the insecticidal properties of the distillate (Fraction W). The distillation was performed using a simple distillation set-up with the sample flask sitting in a heating mantle and the distillate flask in a water bath. The temperature was maintained at 105°C to 110°C for the duration of the distillation, which would take approximately one hr for 30 mL of bio-oil. The distillate was a murky yellow liquid. The remaining mixture in the sample flask is a dark brown liquid at 110°C, although it solidifies into a brown resin when cooled.

Undiluted distillate was tested for insecticidal activity. Distillate was then serially diluted in water to 50%, 10%, 2%, and 0.5% concentration and tested for insecticidal activity. Furthermore, Fraction W was analyzed for its nicotine content..

2.3 Results and Discussions

2.3.1 Pyrolysis

This section deals with the optimization of pyrolysis conditions. Liquid bio-oil yields are reported as a function of pyrolysis temperature and vapor residence time. Pyrolysis temperature and vapor residence time corresponding to the highest liquid yield are selected and the pyrolysis is carried out again to determine the exact liquid, gas and char yields.

The effects of pyrolysis temperature (350°C to 600°C) and residence time (5, 10 and 17 s) on the liquid yield are shown in Figure 2.4. Tobacco bio-oil yields were found to be a strong function of temperature and residence time, peaking at 500°C for all residence times. The bio-oil yield increased sharply as the residence time was decreased, for all temperatures.

As shown in Table 2.1, at a residence time of 5 s and a reaction temperature of 500°C, the bio-oil yield was the highest (43.4%), followed by the char yield (29.4%) and the gas yield (22.4%). The mass balance on the pyrolysis products was close to 95%, a typical margin of error for pyrolysis experiments. Calculations showed that the higher heating value (HHV) of the gases produced was 508 J/g of pyrolyzed biomass. The HHV obtained for pyrolysis of tobacco gases was lower compared to some other feedstocks like coffee grounds and pinewood pyrolyzed in the same pilot plant at the same temperature (1573 J/g and 2694 J/g respectively), as the gases produced from tobacco pyrolysis contained almost 70% CO_2. Gases could be recycled to the pyrolysis reactor to provide the heat required for the endothermic pyrolysis reaction.

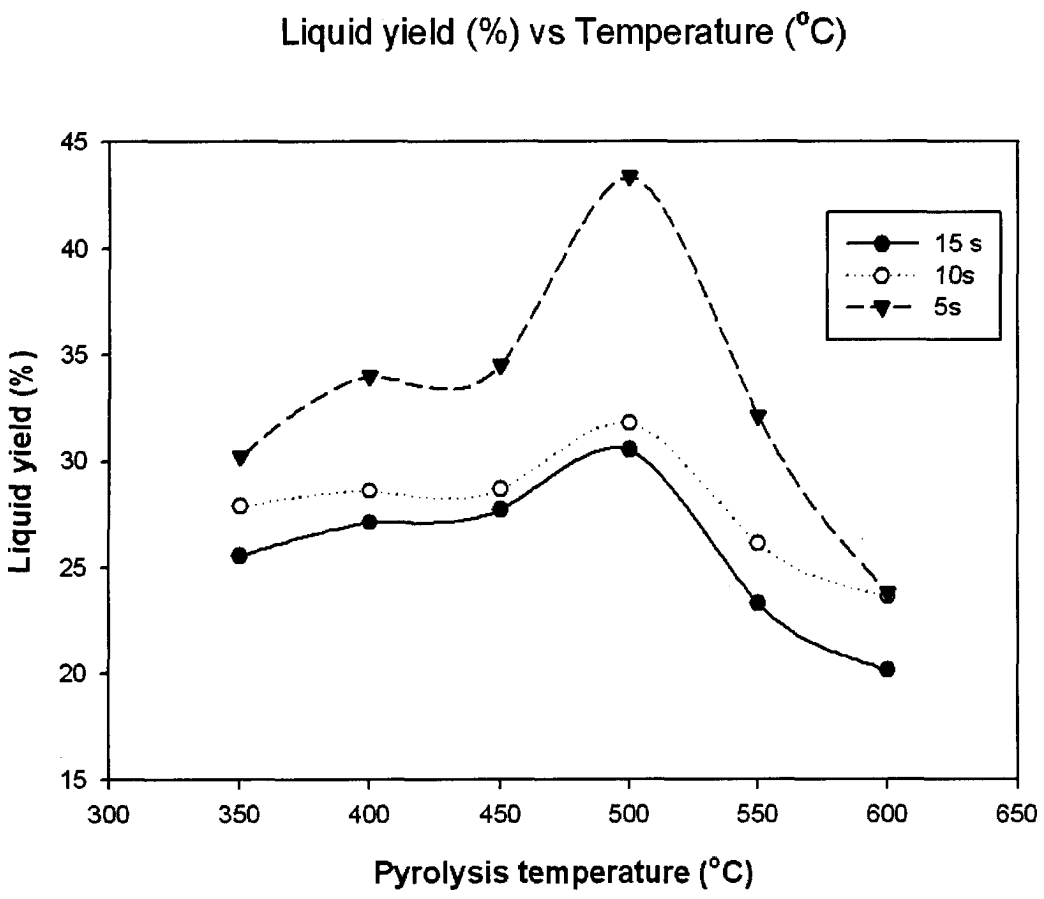

Figure 2.4 - Effect of temperature and residence time on the liquid bio-oil yield

Obtained at fluidization velocity of 0.05 m/s in fluidized bed pilot plant and argon pulse of 50 psi

Table 2.1 - Pyrolysis product yields at a vapor residence time of 5 s

Temperature (°C)	Liquid yield (wt %)	Gas yield (wt %)		Char yield (wt %)
500	43.4	22.4		29.4
		wt% H_2	0.7	
		wt% CO	27	
		wt% CH_4	2.8	
		wt% CO_2	69.5	

The higher liquid yields at lower vapor residence times can be attributed to the fact that secondary reactions such as thermal cracking, repolymerization and recondensation are minimized at lower vapor residence times [15]. It is also known that higher temperature favors gasification (higher gas yields and lower liquid and char yields). Thus the results obtained are consistent with the existing literature on various other biomass feedstocks by Gercel et al., Onay et al. and Bridgewater et al. [4, 16, 17].

As mentioned before, tobacco bio-oil consisted of aqueous and organic phases. The aqueous phase comprised 40-50% of the bio-oil produced. Low bio-oil yields compared to other feedstocks like coffee grounds, distiller's grain or sawdust processed in the same pilot plant, accompanied by high water concentration in bio-oils produced from tobacco, made the overall process slightly unattractive from the point of view of fuel production.

2.3.2 Bio-oil as fungicide and bactericide

2.3.2.1 Organic and aqueous phases of tobacco bio-oil

The purpose of these assays was to see if the different phases of the tobacco bio-oil were active or not.

Organic and aqueous phase bio-oil mixtures were tested for inhibition against 11 fungi and 4 bacteria. Aqueous phase of the tobacco bio-oil was inactive whereas the organic phase of the tobacco bio-oil showed considerable activity against two bacteria, *S. scabies* and *C. michiganensis* subsp. *michiganensis* and one fungus, *P. ultimum*.

It was particularly important to find activity against aforementioned species because: *Pythium ultimum* is a fungus that affects plants through a seedling damping-off disease [18]. Plants affected include eggplant, pepper, lettuce, tomato and cucumber. *Clavibacter michiganensis* subsp. *michiganensis* kills young plants and deforms fruits, primarily tomatoes [19]. *Streptomyces scabies* is a common

potato scab disease that infects potatoes and makes them unmarketable [20]. There is currently no safe pesticide in the market that can control this widespread disease.

2.3.2.2 Optimizing pyrolysis temperature for fungicidal and bactericidal activity

The purpose of these assays was to optimize the pyrolysis temperature responsible for the fungicidal and bactericidal activity. All the assays were performed with the organic phases of the tobacco bio-oils produced at various temperatures.

As shown in Figure 2.5, bio-oil produced at 450°C was the most effective against fungus *P. ultimum*; whereas bio-oils produced at 350°C and 450°C were the most effective against *C. michiganensis* subsp. *michiganensis* and *S. scabies*.

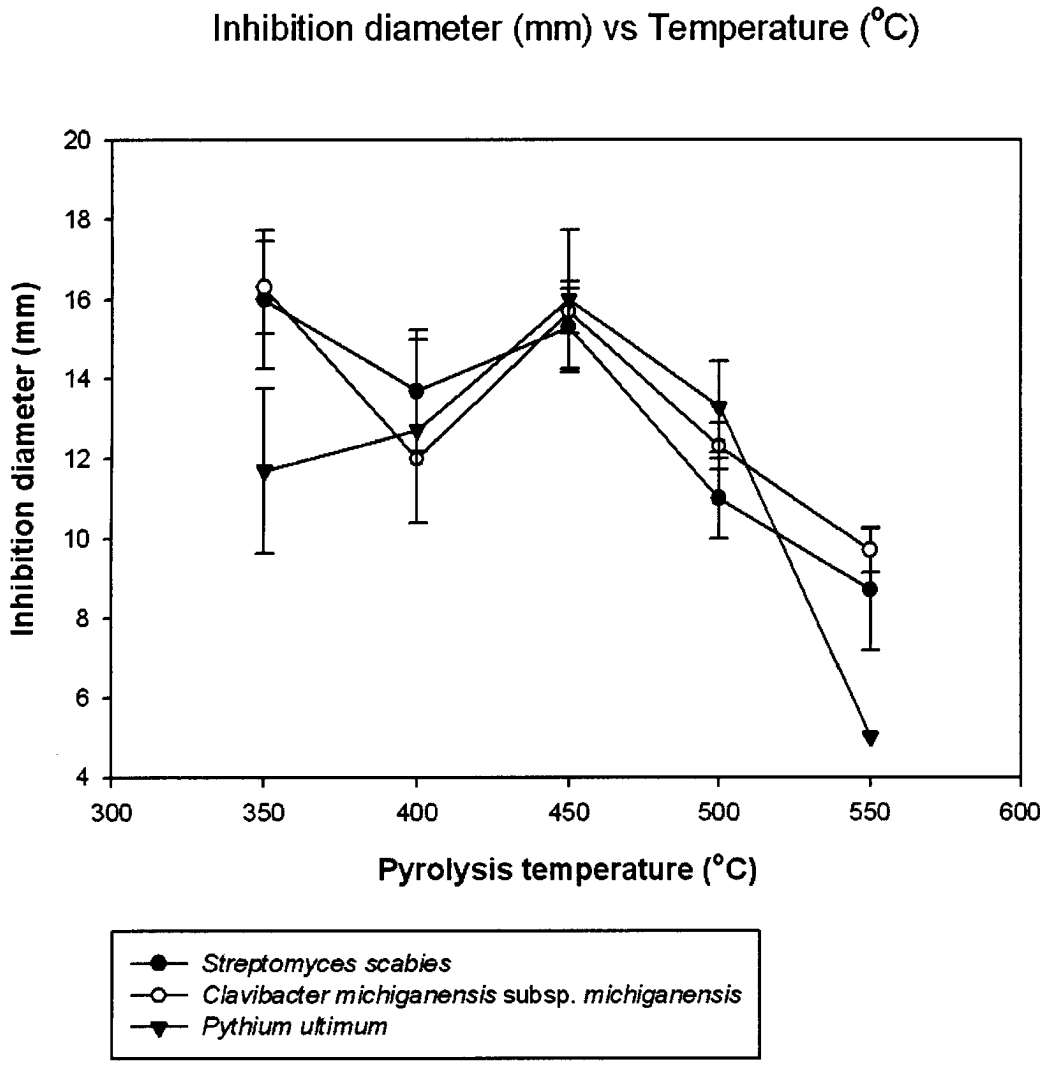

Figure 2.5 - Effects of reactor temperature on inhibition activity of fungus and two bacteria

These results indicated that: Two different components might be active against bacteria and fungus, explaining why the 350°C bio-oil was not active against the fungus but was active against the bacteria. An alternate explanation is that the concentration of active component required might be different for the bacteria and the fungus.

Bio-oil produced at 450°C showed significant bactericidal and fungicidal activities as mentioned above. Thus bio-oil produced at 450°C was chosen for further analysis.

2.3.2.3 Potency of tobacco bio-oil by dilution assays

The purpose of these assays was to determine the potency of the bio-oil through dilution assays. All the assays are performed with the organic phase of the tobacco bio-oil produced at 450°C.

As 450°C was found to be the optimal pyrolysis temperature for fungicidal and bactericidal activity, it was important to assess the potency via dilution assays. As shown in Figure 2.6, the bio-oil was active against *C. michiganensis* subsp. *michiganensis* at 1% concentration, while it was hardly active against *S. scabies* at this concentration. It was only active at 100% concentration against *P. ultimum.*

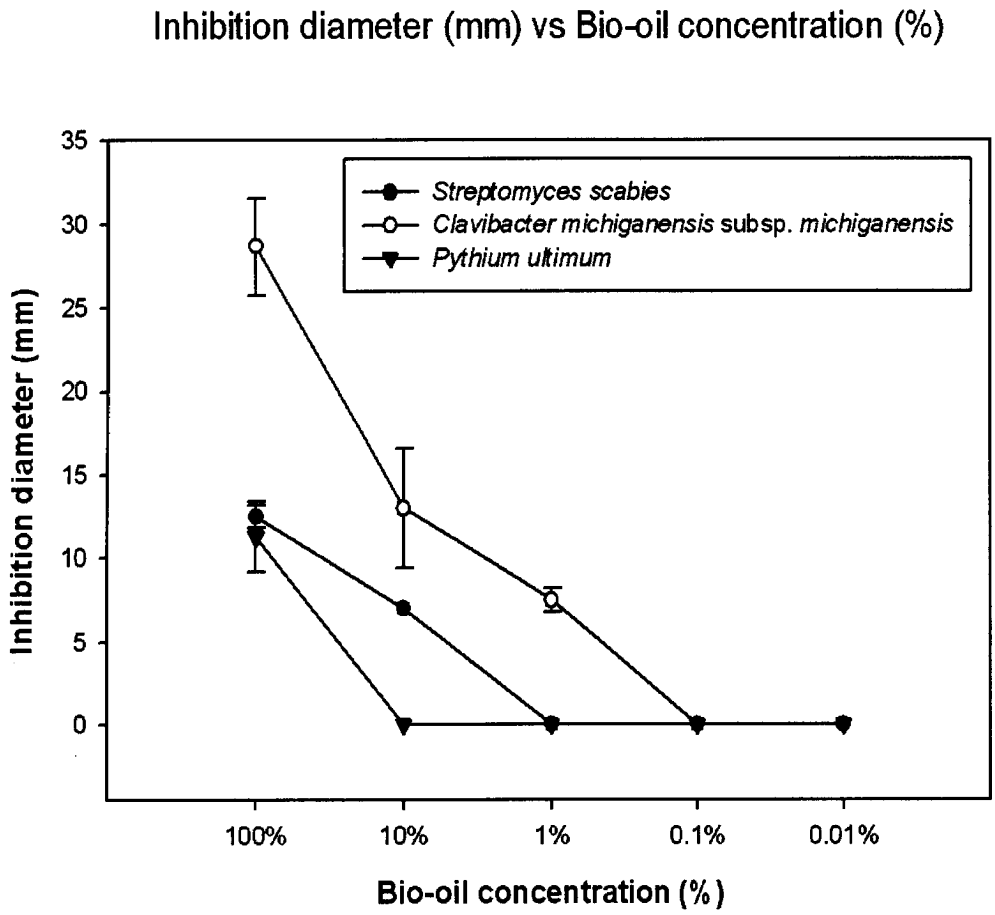

Figure 2.6 - Effect of dilution on inhibition of a fungus and two bacteria

Results clearly indicated that the bio-oil was not very potent, and that isolation and concentration of the active component(s) might be very important to realize the potential inhibitory activity of the bio-oil.

2.3.2.4 Bio-oil fractionation and GC-MS analysis

The purpose of these assays was to determine if nicotine is solely responsible for the activity against two bacteria and a fungus using bio-oil fractionation and GC-MS analysis.

As shown in Table 2.2, Fractions Z and C were found to be active whereas Fractions I, A, D and E were inactive against the two bacteria and one fungus under consideration. The GC-MS analysis revealed that, Fraction Z and D contained high concentration of nicotine whereas Fraction C was devoid of nicotine.

Table 2.2 - Fungicidal and bactericidal inhibition for different fractions

Fractions	**Average diameter of inhibition in mm (n=3) (Standard Deviation in mm)**		
	Pythium ultimum	***Streptomyces scabies***	***Clavibacter mich.* subsp. *michiganensis***
I	0 (0)	0(0)	0(0)
Z	10.7 (2.3)	7.3(6.4)	5(4.4)
A	0 (0)	0(0)	0(0)
C	11.3(1.2)	10(2)	0(0)
D	0(0)	0(0)	0(0)
E	0(0)	0(0)	0(0)
Water control	0(0)	0(0)	0(0)
Acetone control	0(0)	0(0)	0(0)
Ether control	0(0)	0(0)	0(0)
Ridomil positive control	positive	n/a	n/a
Streptomycin sulfate positive control	n/a	positive	positive

This clearly reveals that nicotine is not the chemical responsible for the activity of the bio-oil against the bacteria and the fungus.

2.3.3 Bio-oil as insecticide

2.3.3.1 Organic and aqueous phases of tobacco bio-oil

The purpose of these assays was to see if the different phases of the tobacco bio-oil were active or not.

Organic and aqueous phase bio-oil mixtures were tested against CPB. Both organic and aqueous phases of the tobacco bio-oil mixture showed very high 24 hr mortality of beetles.

2.3.3.2 Optimizing pyrolysis temperature for insecticidal activity

The purpose of these assays was to optimize the pyrolysis temperature responsible for the insecticidal activity. All the assays were performed with the tobacco bio-oils produced at various temperatures (A representative tobacco bio-oil sample was used by taking into consideration the amount of aqueous and organic phases produced).

Tobacco bio-oils obtained at different pyrolysis temperatures were tested by the leaf disc assay, with the results summarized in Table 2.3.

Table 2.3 - Mortality of Colorado potato beetles using raw tobacco bio-oil

Pyrolysis Temperature (°C)	24 hr mortality (% dead)	48 hr mortality (% dead)
350	87	100
400	87	100
450	93	100
500	92	100
550	93	100
Negative control	0	0

It was concluded that there was no correlation between pyrolysis temperature and beetle mortality for tobacco bio-oil. The potency of the bio-oil was quite strong given the high mortality levels seen. This is especially true because the sample matrix in bio-oil is so complex that the majority of compounds present are in low concentrations [21].

The insecticide activity might have been caused solely by high concentration of nicotine in the bio-oil. Nicotine is a moderately effective insecticide against the CPB with an LD_{50} (the median lethal dose) of 61 μg per CPB [22]. This was not especially low given that many neonicitinoids, synthetic compounds with a similar chemical structure and that target the same receptor as nicotine, have LD_{50} values of less than 0.05 μg per CPB [22]. Given the moderate activity of the nicotine, if it was the sole active analyte then it has to be in sufficient amounts.

2.3.3.3 Bio-oil fractionation and HPLC analysis

The purpose of these assays was to determine if nicotine is solely responsible for the activity against beetles using bio-oil fractionation and HPLC analysis.

As shown in Table 2.4, both organic and aqueous fractions were active. Table 2.5 summarized dilution assays for organic fraction. Organic fraction at as low as 2% concentration showed significant 48 hr beetle mortality. The significant increase in mortality of beetles from 24 hr to 48 hr for the three highest aqueous fraction concentrations (Table 2.6) indicated that the compounds present in the aqueous fraction affect CPB more slowly.

Table 2.4 - Mortality of Colorado potato beetles using the organic fraction after ether/DCM extraction

Sample	24 hr mortality (% dead)	48 hr mortality (% dead)
Organic fraction	100	100
Aqueous fraction	53	87
Control	2	4

Table 2.5 - Mortality of Colorado potato beetles using the organic fraction diluted with ether

% Organic fraction (v/v)	24 hr mortality (% dead)	48 hr mortality (% dead)
100	100	100
50	100	100
10	77	97
2	10	23
0.5	0	13
Negative control	3	3
Positive control	100	100

Table 2.6 - Mortality of Colorado potato beetles using the aqueous fraction diluted with water

% Aqueous fraction (v/v)	24 hr mortality (% dead)	48 hr mortality (% dead)
100	53	87
50	45	85
10	5	45
2	0	5
0.5	0	0
Negative control	0	5
Positive control	53	87

It was also worth noting that application of these fractions resulted in a greatly reduced appetite for the beetles. Studies have shown that 24 hr starvation of the CPB does not prove fatal; however starvation may cause increased susceptibility or may interact in a negative way with other applied insecticides. Whether or not the compounds that caused mortality were the same as the compounds that acted as an antifeedant or a repellant was not known, but it would be worthwhile to investigate the synergistic effect of these fractions with other insecticides.

HPLC analysis of organic fraction (Fraction Y) showed a huge nicotine peak, likely responsible for the toxicity observed whereas HPLC analysis of aqueous fraction (Fraction X) showed no nicotine peak. Furthermore, it was predicted that nicotine should be captured fully by the organic fraction [11], while the aqueous fraction should be mainly composed of water, high molecular weight compounds, carbohydrates and acids. This confirmed that there were indeed multiple components responsible for the bio-oil activity against CPB.

2.3.3.4 Distillation and HPLC analysis

The purpose of these assays was to confirm if nicotine is solely responsible for the activity against beetles using bio-oil distillation and HPLC analysis.

As shown in Table 2.7, the distillate (Fraction W) showed very high 24 hr mortality of beetles. Furthermore, distillate in 50% concentration showed significant 48 hr beetle mortality (Table 2.8). Distillate at concentrations lower than 50% showed negligible 48 hr beetle mortality (Table 2.8).

Table 2.7 - Mortality of Colorado potato beetles using undiluted distillate

Sample	24 hr mortality (% dead)	48 hr mortality (% dead)
Distillate	92	98
Control	0	0

Table 2.8 - Mortality of Colorado potato beetles using distillate diluted with water

% Distillate (v/v)	24 hr mortality (% dead)	48 hr mortality (% dead)
100	84	98
50	22	53
10	4	20
2	2	4
0.5	0	2
Negative control (water)	0	0
Positive control	92	98

2.4 Conclusions

The bio-oil yield for tobacco pyrolysis was found to be a strong function of pyrolysis temperature and vapor residence time. To maximize tobacco bio-oil yield, one should operate at a temperature of 500°C with a low vapor residence time.

This is the first study to ever report a novel pesticidal use for tobacco bio-oil, focusing on its inhibitory activity on plant pathogenic bacteria, fungi and Colorado potato beetles. Tobacco bio-oil produced at 450°C was the most effective for a fungus and two bacteria, whereas pyrolysis temperature had no significant impact on the beetle mortality, indicating that there might be different chemicals responsible for the activity against bacteria, fungi and beetles. Dilution studies for the bacteria, the fungus and the beetles clearly indicated that the bio-oil had to be at a high concentration to exhibit any acute toxicity. Though the nicotine fraction showed no activity against the bacteria and the fungus, it was very active against beetles. Furthermore, fractionation studies confirmed that the non-nicotine fractions were active against the bacteria, the fungus and the beetles.

The findings thus indicate that, future applications of tobacco bio-oil may lie not only as an alternative fuel source but as a natural pesticide.

2.5 References

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CHAPTER 3

INSECTICIDAL AND BACTERICIDAL CHARACTERISTICS OF THE BIO-OIL FROM THE FAST PYROLYSIS OF COFFEE GROUNDS

3.1 Introduction

Coffee (*Coffea arabica* or *C. robusta*) is a widely consumed stimulant beverage prepared from roasted coffee beans. With over 500 billion coffee cups consumed every year, considerable waste is generated as coffee grounds. Currently, coffee grounds have no significant market and are considered a waste. Converting coffee grounds to natural pesticides via pyrolysis would help reduce this waste, provide additional income and reduce the consumption of synthetic pesticides.

Synthetic chemical pesticides have provided many solutions for pest control in the past several decades. However, the problems associated with their use include: the need for costly fossil fuels in the manufacturing process; the development of resistance by many pests and the adverse effects to human health and the environment. For example, the Colorado potato beetle has become resistant to most commercial synthetic insecticides [1]. Pesticides produced from natural products offer major advantages over synthetic pesticides: 1) they are produced from renewable resources, 2) they typically include several active molecules, making resistance development more difficult; and 3) they are usually biodegradable therefore lessening the adverse environmental health effects [2].

Pyrolysis can be used to convert coffee grounds into a liquid bio-oil, which can be easily transported and stored. Pyrolysis is a thermo-chemical process, which is carried out in the absence of oxygen to convert biomass into liquid bio-oil, char and gases [3]. The bio-oil normally contains a high proportion of oxygenates, reflecting the oxygen content of the original substrates. These products are usually quite reactive and their characteristics may change rapidly during condensation [4].

Masek et al. [5] carried out pyrolytic gasification of coffee grounds in a drop tube reactor (DTR). A brief primary pyrolysis study was performed using wire-mesh reactor (WMR) but no liquid analysis was performed. This chapter looks into pyrolysis of coffee grounds and the analysis of the coffee grounds bio-oil for bactericidal and insecticidal properties.

3.2 Materials and methods

3.2.1 Materials

Wet coffee grounds were collected after brewing from Tim Hortons and Souheil Afara at The University of Western Ontario (UWO), London, Ontario, Canada. They were dried overnight in an oven at 60°C. The Sauter mean diameter of coffee grounds used was 300 μm.

3.2.2 Methods

3.2.2.1 Coffee grounds pyrolysis

3.2.2.1.1 Pilot plant

The procedure described below has already been described in Chapter-2. Reader can safely skip this section.

All pyrolysis experiments were carried out using a fluidized bed pilot plant (Figure 3.1). The heart of the plant was an atmospheric fluid bed reactor, 0.078 m in diameter, with a 0.52 m long cylindrical section, and equipped with an expanded section made up of a 0.065 m long truncated cone with an upper diameter of 0.168 m, topped by a second, 0.124 m long, cylindrical section. The total volume of this configuration is 6.09×10^{-3} m^3. This assembly provided a nominal vapor residence time of 5 s. A nominal vapor residence time is calculated by dividing the volume of the reactor by the total nitrogen flow-rate. A filter capable of withstanding high temperatures was installed at the gas exit. A filter was made up of a perforated pipe connected to the gas exit covered by fiber glass pad and wrapped inside a fine stainless steel mesh cover.

The fluidizing nitrogen was injected at the base of the fluidized bed, having a static sand bed of 0.15 m, through a perforated copper distributor plate. Silica sand obtained from Opta Minerals Inc., having a Sauter mean diameter of 2×10^{-4} m was used to form the fluidized bed. The reactor was equipped with seventeen thermowells for temperature measurements and control, using type K thermocouples.

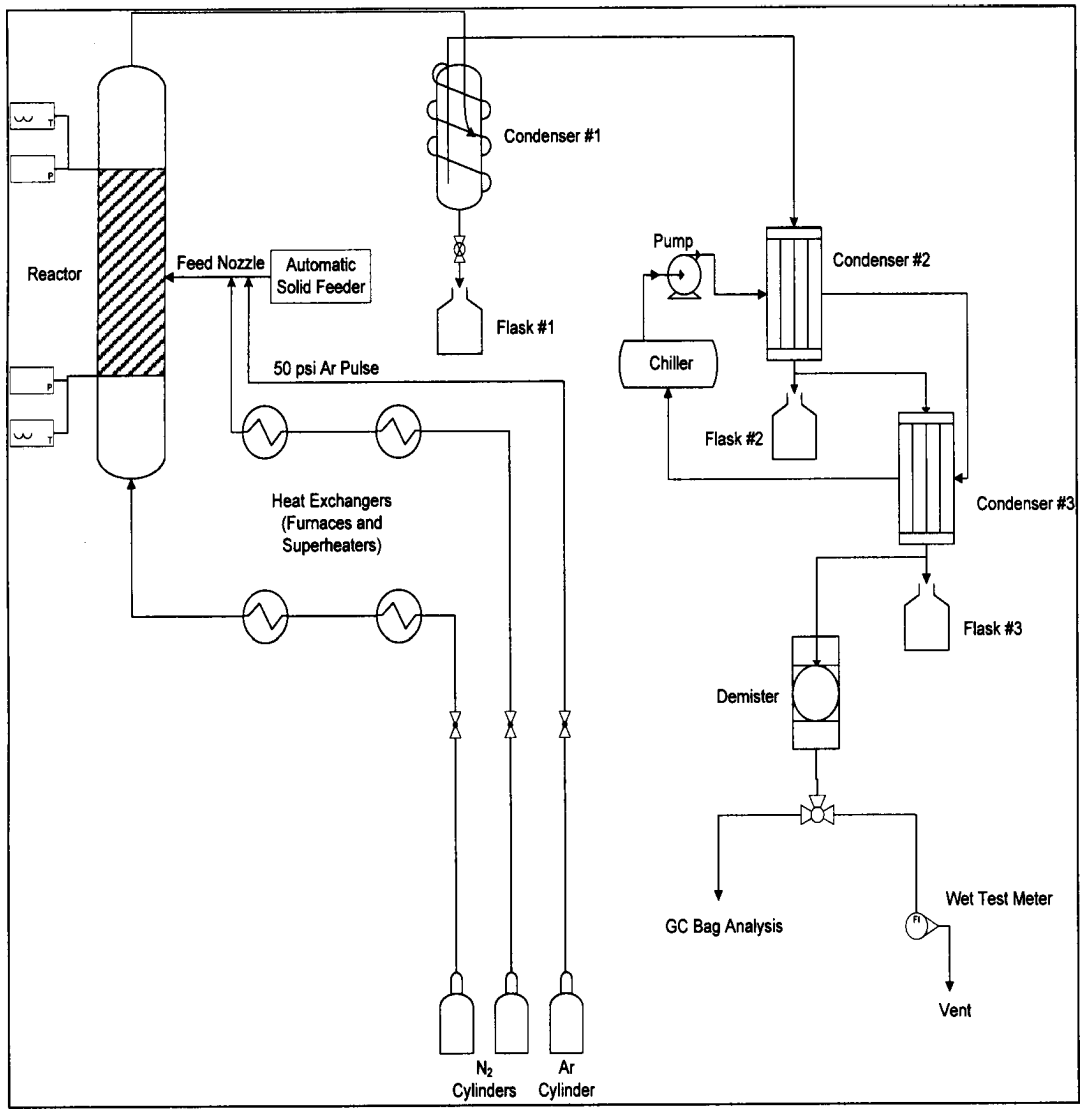

Figure 3.1 - A schematics of the Western Fluidization Group's fluid bed pilot plant

A horizontal pulsating feeder was used to inject coffee grounds into the reactor at a height of 0.1 m above the distributor plate. A continuous flow of nitrogen was used to convey the coffee grounds to the reactor. It was supplemented by an intermittent argon pulse that was synchronized with the solids pulses.

Coffee grounds, when injected into the reactor, produced vapors that exited at the top of the reactor through the hot filter section and flowed into three condensers in series (as shown in Figure 3.1). Persistent aerosols were then separated in a cylindrical demister packed with cotton wool.

3.2.2.1.2 Bio-oil production and its characterization

The exact yield of coffee grounds bio-oil was obtained from the mass of bio-oil collected in the three condensers and the demister. The demister was weighed before and after the experiment.

Pyrolysis was carried out at five different temperatures from 400°C to 600°C and with a vapor residence time of 5 s. Each test was conducted with 300 g of coffee grounds. Fluidizing and carrier nitrogen volumetric flow rates were controlled using 'Mass Trak' flow-meters from Sierra Instruments Inc., and adjusted to keep the nominal vapor residence time constant at all temperatures. In contrast to most bio-oils, bio-oils produced in these experiments from coffee grounds were homogeneous and did not split into aqueous and organic phases. The bio-oil was stored in a flame-proof refrigerator at -4°C.

3.2.2.1.3 Characterization of product gases

The procedure described below has already been described in Chapter-2. Reader can safely skip this section.

Gases were sampled in plastic bags at three different time intervals during each experiment. A Hewlett-Packard 5890 series II Gas Chromatograph (GC) was used to measure the product gas composition. It was equipped with a RESTEK Shin

Carbon ST (micro packed) column (0.001 m ID, 2 m length). A thermal conductive detector (TCD) detected the composition of the pyrolysis gas mixture, which primarily consisted of N_2, H_2, CO, CO_2 and CH_4. In order to measure product gas yields accurately, N_2 was selected as an internal standard. Argon was selected as the GC carrier gas. A standard gas mixture with a fixed composition of H_2, CO, CO_2 and CH_4 was used to calibrate the GC.

The injector was maintained at 150°C and the TCD was maintained at 275°C. A gas sample of 50 μL (5×10^{-8} m^3) was injected with a 100 μL (1×10^{-7} m^3) Hamilton syringe. Upon injection, the oven temperature was held at 35°C for 180 s, then increased at 10°C/min to 150°C, and finally increased at 20°C/min to 250°C. The temperature was then held constant at 250°C for 330 s.

3.2.2.1.4 Characterization of char

The procedure described below has already been described in Chapter-2. Reader can safely skip this section.

The differential pressure drop across the fluidized bed was measured at minimum fluidization conditions before and after each experiment. Since any solid material produced during the reaction would be retained inside the bed by the hot gas filter, the increase in the bed pressure drop is proportional to the increase in bed mass caused by char accumulation during the run.

3.2.2.2 Bactericidal and insecticidal assays

3.2.2.2.1 Preparation of bio-oil samples

A mixture was prepared by mixing the coffee grounds bio-oils produced at 400°C to 600°C. Each bio-oil sample was filtered with a 0.025 m wide, 4.5×10^{-7} m pore size syringe filter. Mixture was tested for inhibition against 11 fungi and 4 bacteria. From these results, two bacteria were chosen for further characterization. Mixture was then tested for mortality of Colorado potato beetle or CPB (*Leptinotarsa*

decemlineata). The mixture was serially diluted in water to 50%, 10% and 1% concentration for insecticide assays.

The coffee grounds bio-oils produced at 400°C to 600°C were then tested separately for their activity against two bacteria viz. *Streptomyces scabies* and *Clavibacter michiganensis* subsp. *michiganensis*. Insecticide assays were also performed. Coffee grounds bio-oils produced at 400°C to 600°C were serially diluted in water to 50% and 10% concentration for insecticide assays.

Bio-oil fractionation:

The method used for coffee grounds bio-oil fractionation is illustrated in Figure 3.2.

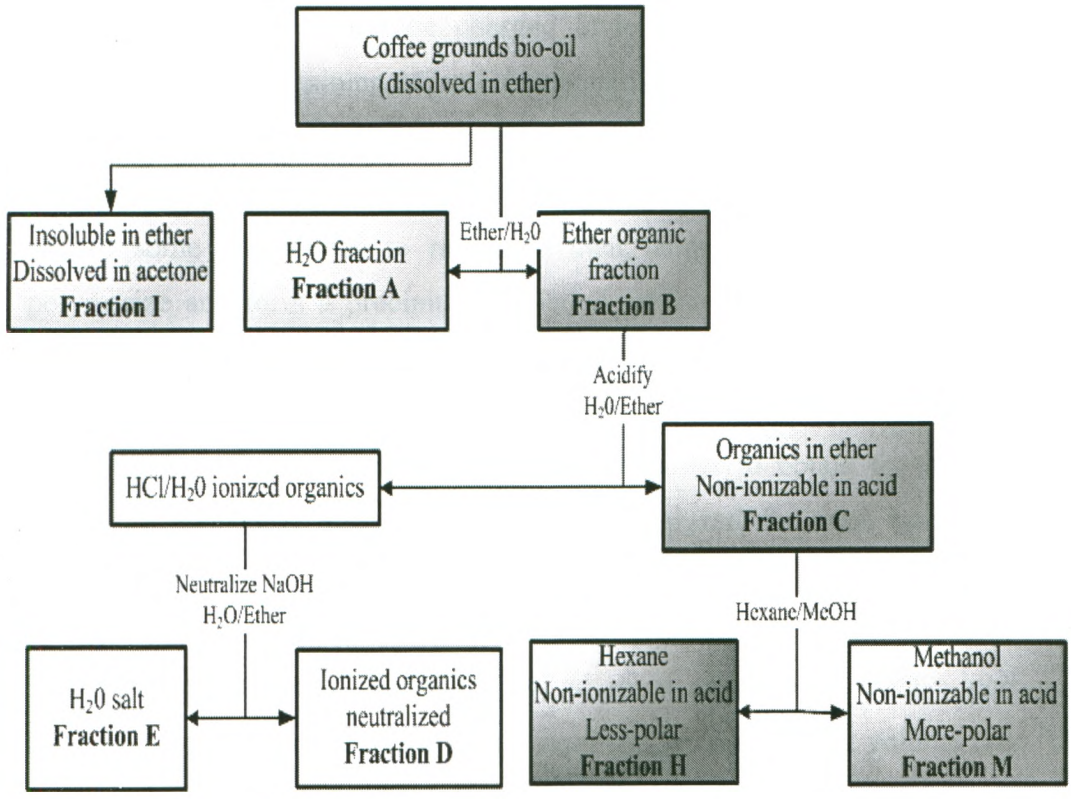

Figure 3.2 - Fractionation scheme of coffee grounds bio-oil for bactericidal and insecticidal analysis

The coffee grounds bio-oil produced at 550°C was dissolved in di-ethyl ether at a concentration 0.375 g/mL (375 kg/m^3). A portion of the bio-oil did not solvate in di-ethyl ether, so water was added in a 1:1 volume ratio to the di-ethyl ether and the fractions were separated and filtered with a 0.025 m wide, 4.5×10^{-7} m pore size syringe filter with a nylon membrane. This gave an aqueous fraction, Fraction A, and an organic fraction, Fraction B. Dissolving the bio-oil in di-ethyl ether and water caused a black precipitate to form on the walls. This precipitate was dissolved in a portion of acetone (equal to that of di-ethyl ether added initially) and was sterile-filtered (Fraction I).

Fraction B was further extracted by adding water in a 1:1 volume ratio with di-ethyl ether and acidifying the water fraction with concentrated HCl to pH 2. This produced two fractions: an organic di-ethyl ether fraction (Fraction C) with compounds that could not be charged under acidic conditions, and an acidic aqueous fraction containing organic compounds that could be charged under acidic conditions. The acidified water fraction was then neutralized with NaOH to drive the charged organic compounds back to their neutral state. This neutralization caused some compounds to return to their neutral state and others to likely polymerize and form a precipitate. Di-ethyl ether was then added in 1:1 volume ratio with water thus separating neutral ionizable organics into the di-ethyl ether fraction (Fraction D), while Fraction E was simply the aqueous salt from the neutralization. The salt precipitation made it harder to obtain the representative sample. Fractions D and E were thus not analyzed for their bactericidal and insecticidal activity.

The di-ethyl ether was evaporated off at room temperature from a portion of Fraction C and then re-solvated in methanol and hexane in a 1:2 volume ratio. This formed a methanol fraction (Fraction M) and hexane fraction (Fraction H). Dilution factors were calculated for each fraction and the amount of bio-oil saturated on the disc for biological assays was adjusted so that the concentration on the disc was constant between fractions.

Fractions I, A and B were analyzed for their bactericidal and insecticidal activity whereas fractions C, M and H were analyzed only for their bactericidal activity. Fractions D and E were not analyzed for their bactericidal and insecticidal activity as mentioned above. Fractions I, B, C, M and H were analyzed using GC-MS. Fractions D and E were not analyzed using GC-MS for the inability to obtain the representative sample.

3.2.2.2.2 Disc diffusion agar method for bactericidal assays

The procedure described below has already been described in Chapter-2. Reader can safely skip this section.

The disc diffusion agar method was used to screen the bio-oil activity on eleven fungi and four bacteria. Petri dishes filled with appropriate media (depending on which bacteria or fungus was to be tested) were inoculated with bacteria or fungi. Media used for different fungi and bacteria included Potato Dextrose Agar (PDA), Tryptic Soy Agar (TSA) and Yeast Media Extract (YME). Bacteria were streaked across the entire media surface, while small agar plugs (1×10^{-4} m^2) of fungi were placed approximately 0.01 m off centre on the media. The bio-oil samples were pipetted onto filter paper discs of 0.006 m diameter. 5 μL (5×10^{-9} m^3) of the sample solution was applied to each disc unless otherwise specified. The saturated disc was allowed to dry and then placed in the centre of the inoculated petri dish. Plates were prepared in triplicates to test for reproducibility. The plates were incubated at 24°C for three days and then evaluated for activity by measuring the diameter of inhibition.

Various negative controls such as water, di-ethyl ether, acetone etc. were used depending on the solvent used for dissolving the coffee grounds bio-oil fraction. Streptomycin sulfate (250 ppm) was used as a positive control for both the bacteria *C. michiganensis* subsp. *michiganensis* and *S. scabies*.

3.2.2.2.2 Leaf disc application for insecticidal assays

The procedure described below has already been described in Chapter-2. Reader can safely skip this section.

The insecticidal tests were carried out by the leaf disc application, similar to the procedure outlined by Sengonca et al. [6]. The potato plants (var. Cal White) were grown on site at the Southern Crop Protection and Food Research Centre (SCPFRC), Agriculture and Agri-Food Canada, London, Ontario, with the leaves cut to a diameter of 0.04 m. Fractions were spread on both sides of a potato leaf with a cotton-tipped applicator. The leaves were allowed to dry after sample application. After drying, leaves were transferred to a Gelman® petri dish. Five second instar Colorado potato beetle (*Leptinotarsa decemlineata*) larvae reared at SCPFRC were then transferred to the leaf. Two leaves were tested for each fraction; however most of the tests were repeated on multiple dates to ensure accuracy. Control leaves involved placing the beetles on leaves coated with water. If a specific test involved dilution of the bio-oil with a solvent other than water, the control leaves were coated with the solvent used. The mortality rate was recorded at the end of 24 and 48 hr. The mortality rate is defined as the % of beetles dead. The mortality averaged over all tests has been reported in this chapter.

3.3 Results and discussions

3.3.1 Pyrolysis

This section deals with the optimization of pyrolysis conditions. Liquid, gas and char yields are reported as a function of pyrolysis temperature. Gases are analyzed using GC-MS for the exact composition. Heating value of the gases is also reported. Gases could be recycled to the pyrolysis reactor to provide the heat required for the endothermic pyrolysis reaction.

The effect of pyrolysis temperature (400°C to 600°C) on the liquid, gas and char yields is as shown in Figure 3.3. The bio-oil yields were a strong function of

temperature, peaking at 500°C. Char yields decreased from around 35.2% at 400°C to 19.6% at 600°C. Char yields were in accordance with the published literature [7-9]. Gas yields increased from 17.6% at 400°C to 32.1% at 600°C. Heat of combustion of gases is tabulated in Table 3.1. Figure 3.4 shows mol% of H_2, CO, CH_4 and CO_2 produced at different pyrolysis temperatures. Calculations showed that the higher heating value (HHV) of the gases produced increased from 575.5 J/g of pyrolyzed biomass at 400°C to 3445.8 J/g of pyrolyzed biomass at 600°C. Gases could be recycled to the pyrolysis reactor to produce the heat required for the endothermic pyrolysis reaction.

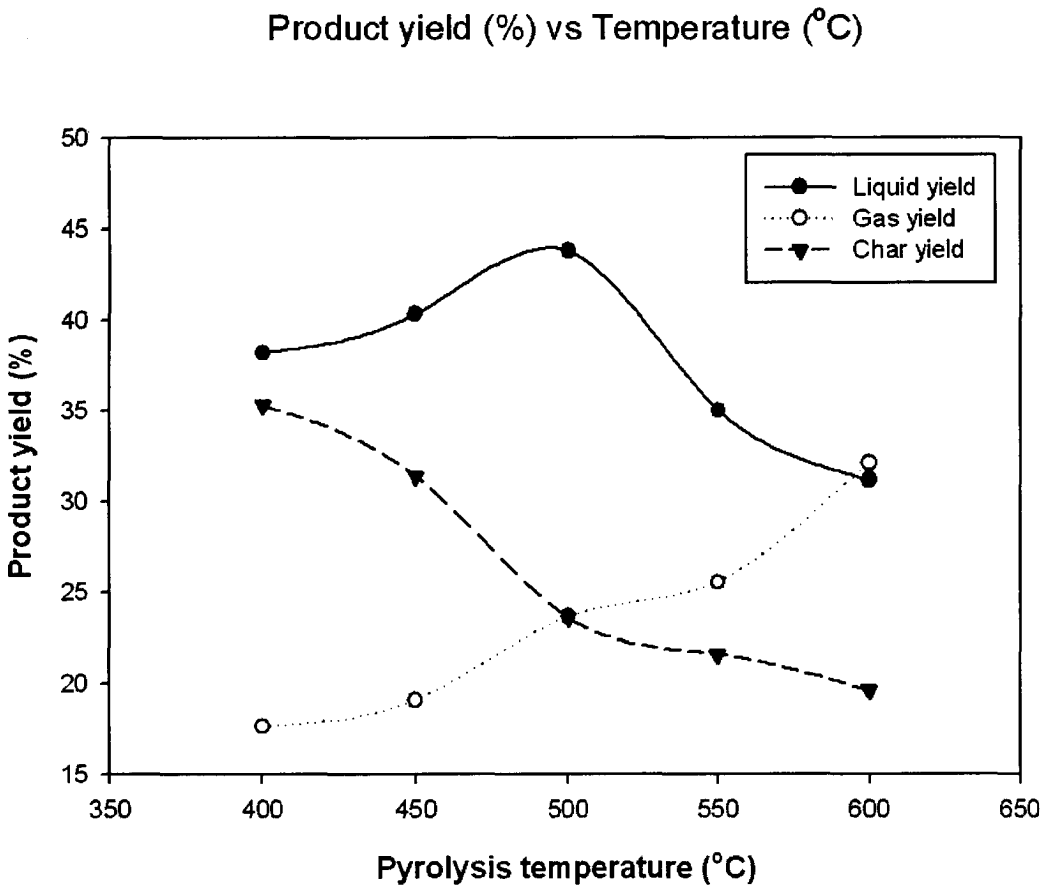

Figure 3.3 - Effect of temperature on liquid, gas and char yields

Obtained at fluidization velocity of 0.05 m/s in fluidized bed pilot plant and argon pulse of 50 psi

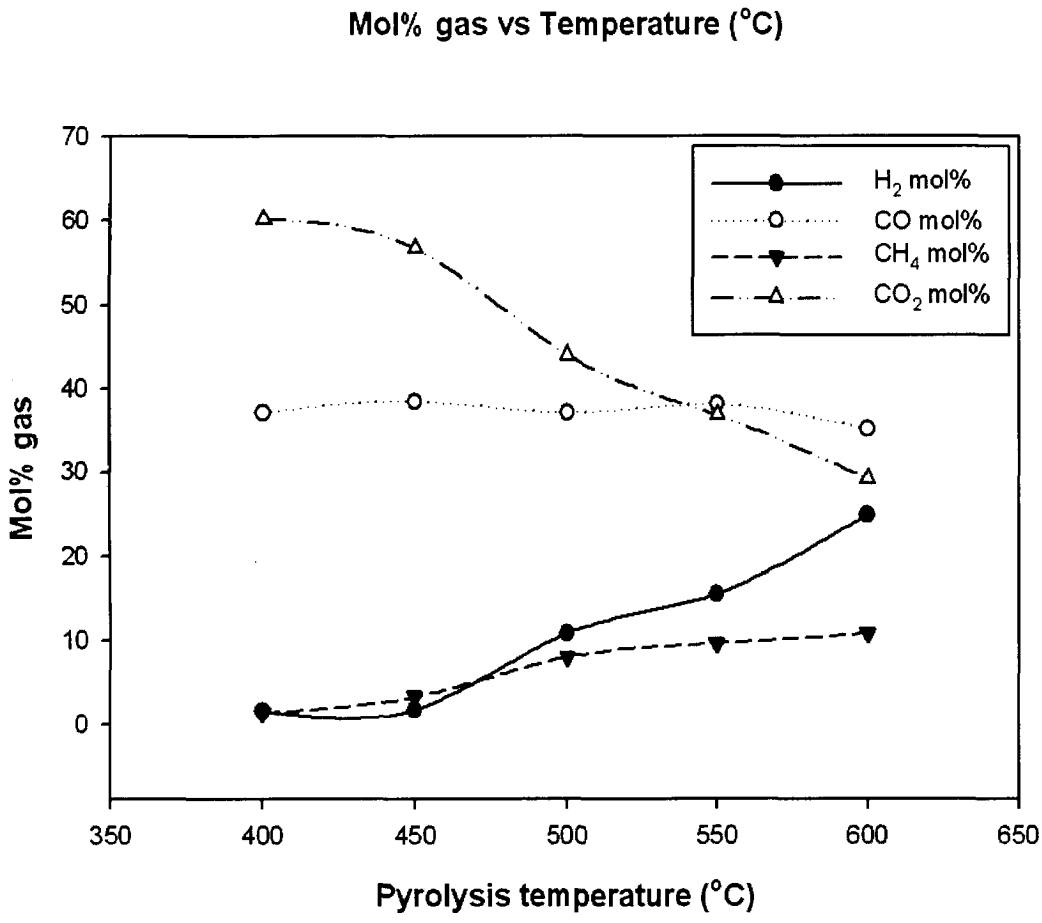

Figure 3.4 - Effect of pyrolysis temperature on the gas yields

Obtained at fluidization velocity of 0.05 m/s in fluidized bed pilot plant and argon pulse of 50 psi

Table 3.1 - HHV of gases as a function of temperature

Temperature (°C)	Heat of combustion (HHV) (J/g of biomass fed)
400	575.5
450	751.7
500	1573.1
550	2116.1
600	3445.8

Although coffee grounds bio-oil was homogeneous, it was comprised of almost 40-50% water. Low bio-oil yields compared to some other feedstocks such as distiller's grain and saw dust processed in the same pilot plant, accompanied by a very high percentage of water produced, made the overall process slightly unattractive from the fuel production point of view.

3.3.2 Bio-oil as bactericide and insecticide

3.3.2.1 Mixture of coffee grounds bio-oil

The initial assays performed with the bio-oil mixture were aimed to determine if any activity was present in the bio-oil, and were not concerned with the accurate quantification of the activity level or determination of the active component(s).

The bio-oil mixture was tested for its activity against 11 fungi, 4 bacteria and CPB. The mixture showed activity for two bacteria viz. *S. scabies* and *C. michiganensis* subsp. *michiganensis* and beetles. Figure 3.5 summarizes the insecticide assays for mixture (100%, 50%, 10% and 1% concentration tests). Though mixture was

considerably active at 100% and 50% concentration, activity decreased sharply at 10% concentration.

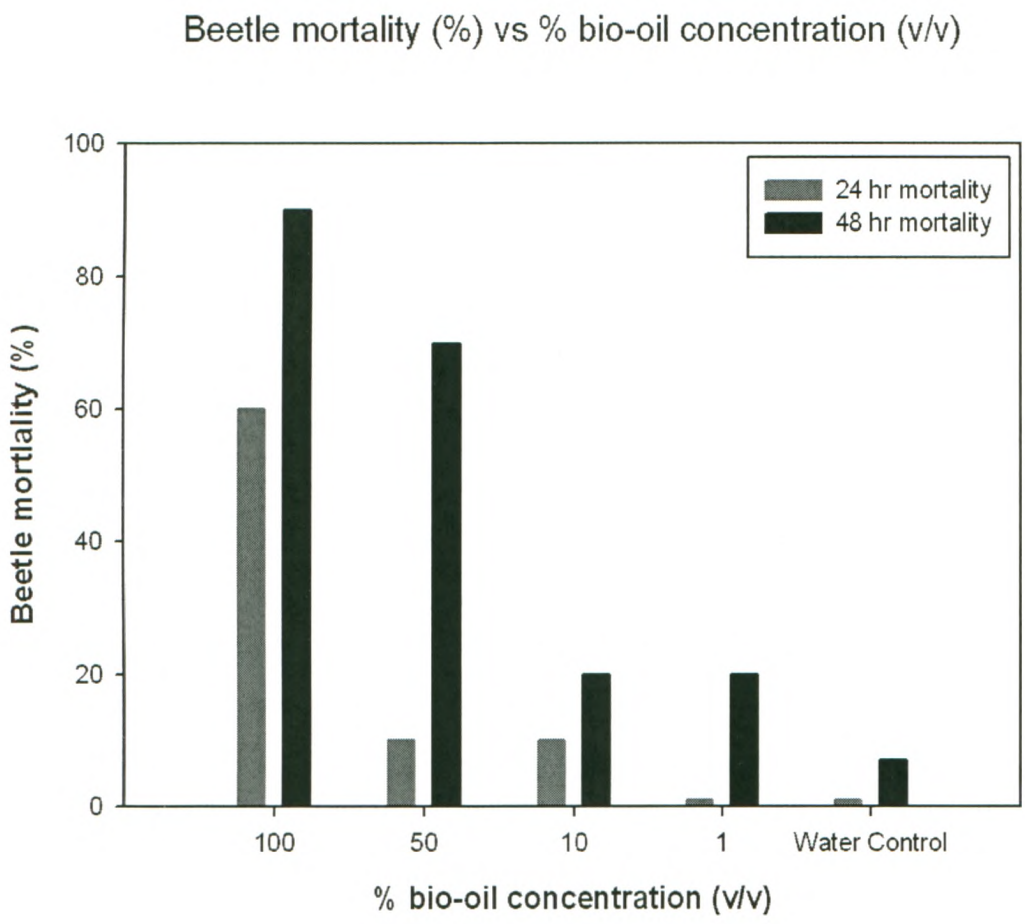

Figure 3.5 - Mortality of Colorado potato beetle using mixture of bio-oil diluted using water

It was particularly important to find activity against aforementioned species because: *Clavibacter michiganensis* subsp. *michiganensis* kills young plants and deforms fruits, primarily tomatoes [10]. *Streptomyces scabies* is a common potato scab disease that infects potatoes and makes them unmarketable [11]. There is currently no safe pesticide in the market that can control this widespread disease. The Colorado potato beetle (CPB) is a common pest of potatoes. In North America

and Europe, the CPB is the most serious pest for potatoes and can defoliate an entire crop.

3.3.2.2 Optimizing pyrolysis temperature for bactericidal and insecticidal activity

The purpose of these assays was to optimize the pyrolysis temperature responsible for the bactericidal and insecticidal activity.

As shown in Figure 3.6, bio-oil activity increased sharply from 400°C to 500°C for *S. scabies* and then decreased gradually from 500°C to 600°C. On the other hand, bio-oil activity increased sharply from 400°C to 450°C for *C. michiganensis* subsp. *michiganensis* but fluctuated from 450°C to 600°C. The bio-oil activity for both *S. scabies* and *C. michiganensis* subsp. *michiganensis* was considerably higher at pyrolysis temperatures from 450°C to 600°C than 400°C. The results clearly indicated that the bio-oils produced at 500°C and 550°C were the most effective against two bacteria (Figure 3.6).

As shown in Table 3.2, bio-oils produced at 400°C-600°C, at 100% concentration, showed 100% beetle mortality at the end of 24 hr. Bio-oil samples at 450°C, 500°C and 600°C, at 50% concentration, showed considerably lower beetle mortality at the end of 24 hr than the bio-oils at 100% concentration. Interestingly, bio-oils produced at 400°C-600°C, at 50% concentration, showed 100% beetle mortality at the end of 48 hr. All bio-oil samples at 10% concentration showed considerably reduced activity even at the end of 48 hr, 400°C and 550°C being an exception to certain extent. An interesting observation was that, at concentrations as low as 10%, CPB ate little or none of the leaf. Studies have shown that 24 hr starvation of the CPB does not prove fatal; however starvation may cause increased susceptibility or may interact in a negative way with other applied insecticides. Furthermore, as shown in Table 3.2, 7% mortality for water control could be due to the mishandling of the beetles (while transferring them from plants to petri dishes). The results

clearly indicated that 400°C bio-oil was the most effective against beetles followed closely by the bio-oil produced at 550°C (Table 3.2).

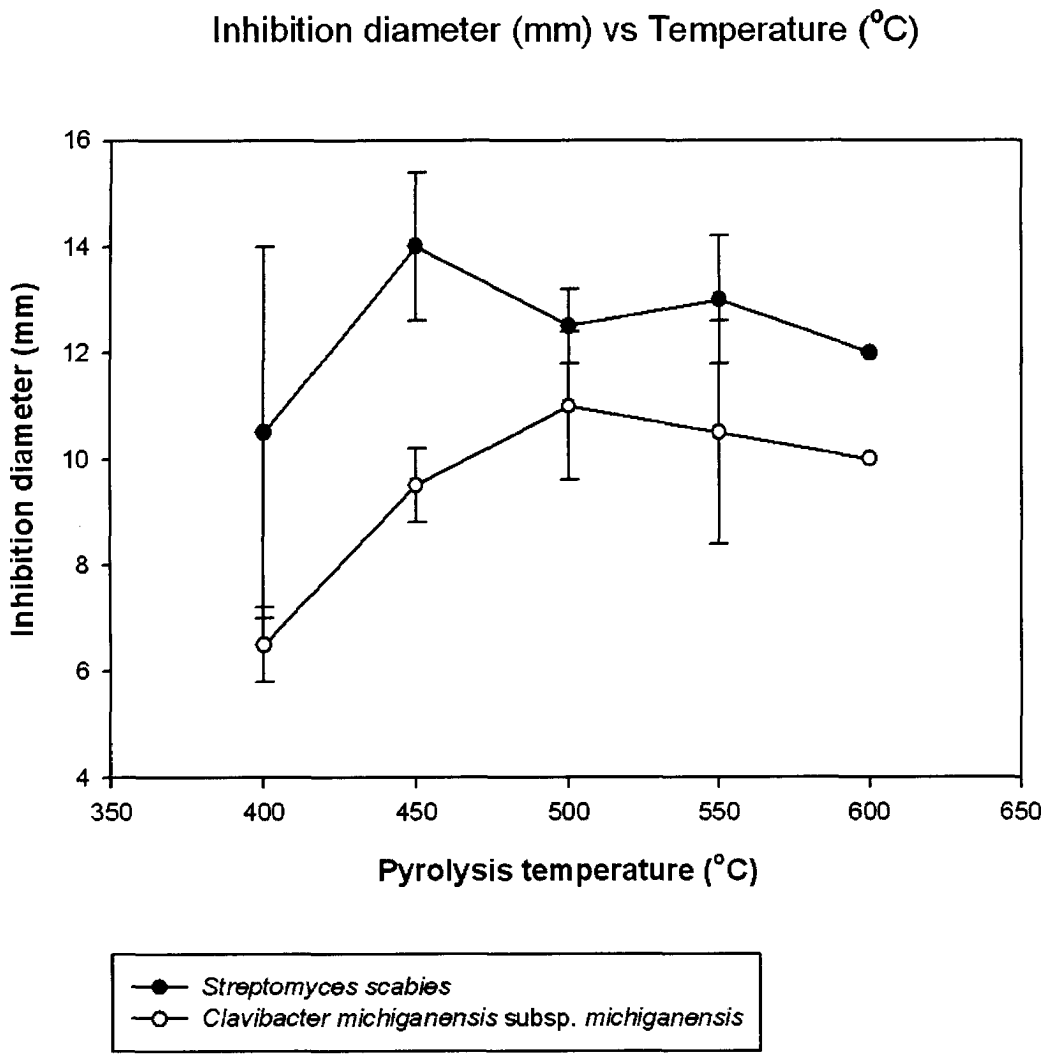

Figure 3.6 - Effects of pyrolysis temperature on inhibition activity of two bacteria

Table 3.2 - Effect of pyrolysis temperature and dilution (in water) on mortality of Colorado potato beetles

Pyrolysis temperature (°C)	% bio-oil concentration (v/v)	24 hr mortality (% dead)	48 hr mortality (% dead)
400	100	100	-
	50	90	100
	10	30	70
450	100	100	-
	50	40	90
	10	0	20
500	100	100	-
	50	60	100
	10	10	20
550	100	100	-
	50	80	100
	10	30	30
600	100	100	-
	50	60	100
	10	0	10
Water control		0	7

As discussed above, 500°C and 550°C bio-oil samples were the most active against bacteria whereas 400°C and 550°C bio-oil samples were the most active against beetles. Different chemical/s might thus be responsible for the activity of the bio-oil against bacteria and beetles.

Bio-oil produced at 550°C showed significant bactericidal and insecticidal activities as mentioned above. Thus bio-oil produced at 550°C was chosen for further analysis.

3.3.2.3 Bio-oil fractionation and GC-MS analysis

The purpose of these assays was to determine the chemical/s responsible for the activity against two bacteria and beetles using bio-oil fractionation and GC-MS analysis.

As mentioned before, Fractions I, A and B were analyzed for their bactericidal and insecticidal activity whereas fractions C, M and H were analyzed only for their bactericidal activity. Fractions D and E were analyzed for neither bactericidal nor insecticidal activity for the inability to obtain the representative sample. Fractions I, B, C, M and H were analyzed using GC-MS. Fractions D and E were not analyzed using GC-MS for the inability to obtain the representative sample.

3.3.2.3.1 Bactericidal characteristics of different bio-oil fractions

As shown in Table 3.3, fractions B, C and M were found to be active against two bacteria whereas fractions A, I and H showed no activity for the two bacteria.

As shown in Figure 3.2, Fraction C was derived from Fraction B and Fraction M from Fraction C. As mentioned, fractions B, C and M were active against two bacteria and they were analyzed using GC-MS. Fraction M being the most refined fraction of these three, it was chosen for the detailed analysis. Figure 3.7 shows the GC-MS analysis of Fraction M whereas Table 3.4 shows the tentative compounds assigned and the percentage area for selected peaks. It indicated that the majority of the compounds present in Fraction M were phenols (known to have bactericidal activity) and related low molecular weight aromatic compounds. It has not been yet established fully whether phenols are the only chemicals responsible for the activity shown by these fractions and thus the bio-oil. A detailed study has been undertaken to accurately quantify the activity and the chemicals responsible for the activity.

Table 3.3 - Bactericidal inhibitions for different fractions

Fractions	Average diameter (mm) (Standard Deviation in mm)	
	S. scabies	***C. michiganensis* subsp. *michiganensis***
I	0(0)	0(0)
A	0(0)	0(0)
B	10.6(1.5)	7.5(0.5)
C	10 (1.2)	6(0)
M	10.3(1.8)	6.5(0.5)
H	0(0)	0(0)
Water control	0(0)	0(0)
Acetone control	0(0)	0(0)
Di-ethyl ether control	0(0)	0(0)
Hexane	0(0)	0(0)
Methanol	0(0)	0(0)
Streptomycin sulfate positive control	positive	positive

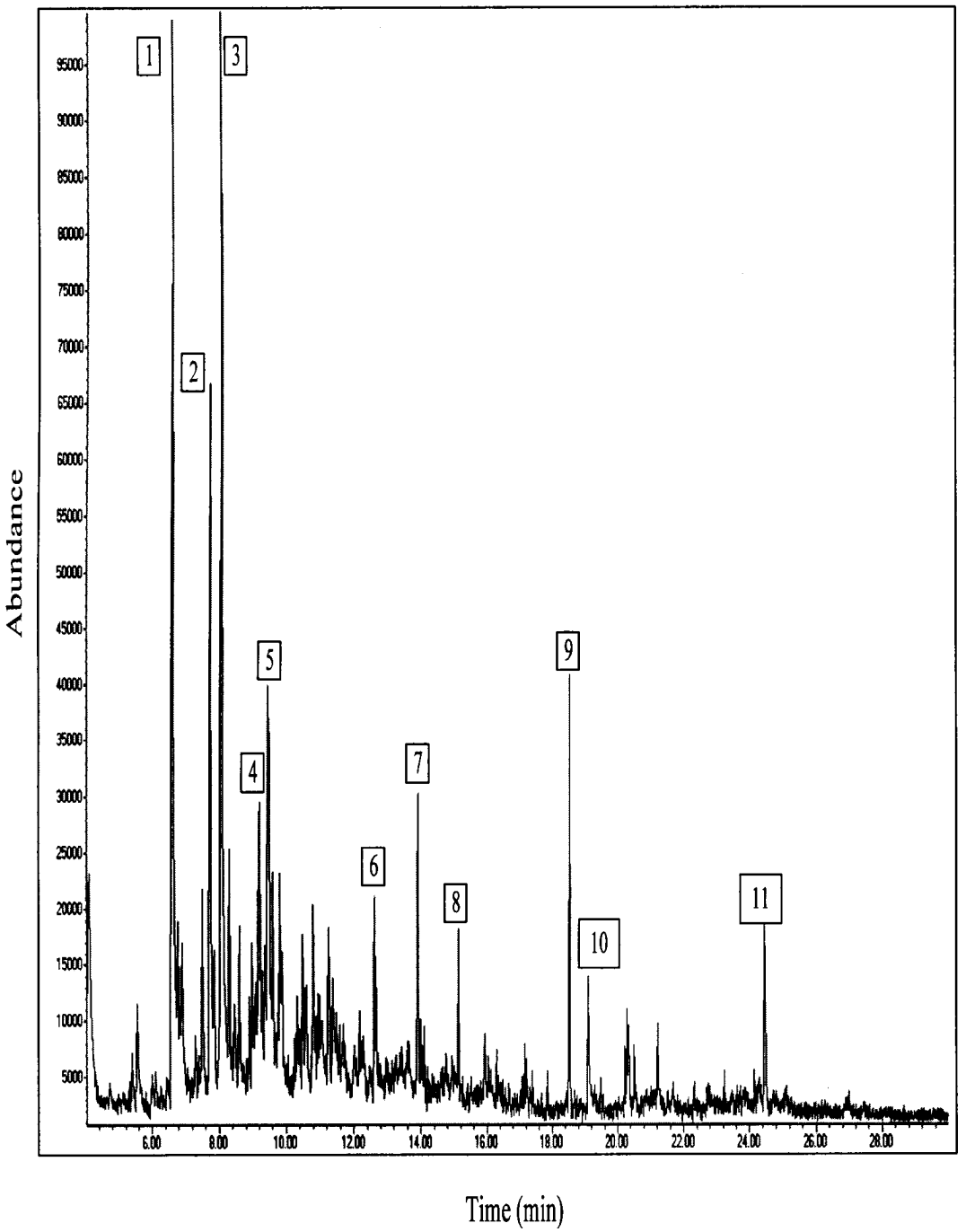

Figure 3.7 - GC-MS analysis of Fraction M

Table 3.4 - GC-MS characterization of fraction M

Peak number	Residence time (min)	% Area	Tentative assignment
1	6.57	15.78	Phenol
2	7.71	8.12	Methyl substituted phenol
3	8.042	16.48	Methyl substituted phenol
4	9.192	5.03	Phenol, 2,3-dimethyl
5	9.469	4.47	Ethyl substituted phenol
6	12.61	1.19	5-Octadecene
7	13.90	2.02	1-Hexadecanol
8	15.13	1.43	Trifluoroacetic acid, n-heptadecyl ester
9	18.53	3.04	2-Nonadecanone
10	19.09	1.62	Dodecanoic acid
11	24.46	2.2	exo-7-(trans-1-Propenyl)bicyclooct-1(2)-ene

3.3.2.3.2 Insecticidal characteristics of different bio-oil fractions

As shown in Table 3.5, all the tested fraction i.e. fractions A, I and B were found to be active against CPB. Fractions C, M and H were not tested for their insecticidal activity as it would not yield any useful information in terms of the chemical/s responsible for the insecticidal activity. The significant increase in mortality of beetles from 24 hr to 48 hr for the fractions A and I indicated that the compounds present in these fractions affect CPB more slowly.

Table 3.5 - Mortality of Colorado potato beetle with different fractions

Fractions	24 hr mortality (% dead)	48 hr mortality (% dead)
I	40	70
A	20	60
B	70	100
Water control	0	7
Acetone control	0	7
Di-ethyl ether control	0	0

It was also worth noting that application of these fractions resulted in a greatly reduced appetite for the beetles. Studies have shown that 24 hr starvation of the CPB does not prove fatal; however starvation may cause increased susceptibility or may interact in a negative way with other applied insecticides. Whether or not the compounds that caused mortality were the same as the compounds that acted as an antifeedant or a repellant was not known, but it would be worthwhile to investigate the synergistic effect of these fractions with other insecticides.

GC-MS analysis of Fraction B revealed a considerable presence of phenols (known to have insecticidal activity). Furthermore, although it could be assumed that Fraction A contained traces of phenols, phenols being highly soluble in di-ethyl ether and sparingly soluble in water, repeated extractions ensured that the concentration of phenols in Fraction A would be very small. A GC-MS comparison of Fractions I and B is shown in Figure 3.8. It clearly showed that, Fraction I contained a range of chemicals in a very low concentration.

These results indicated that while some compounds in the bio-oil, such as phenols, were active against beetles and bacteria, bio-oil contains chemicals that provide additional insecticidal activity but may not have bactericidal activity.

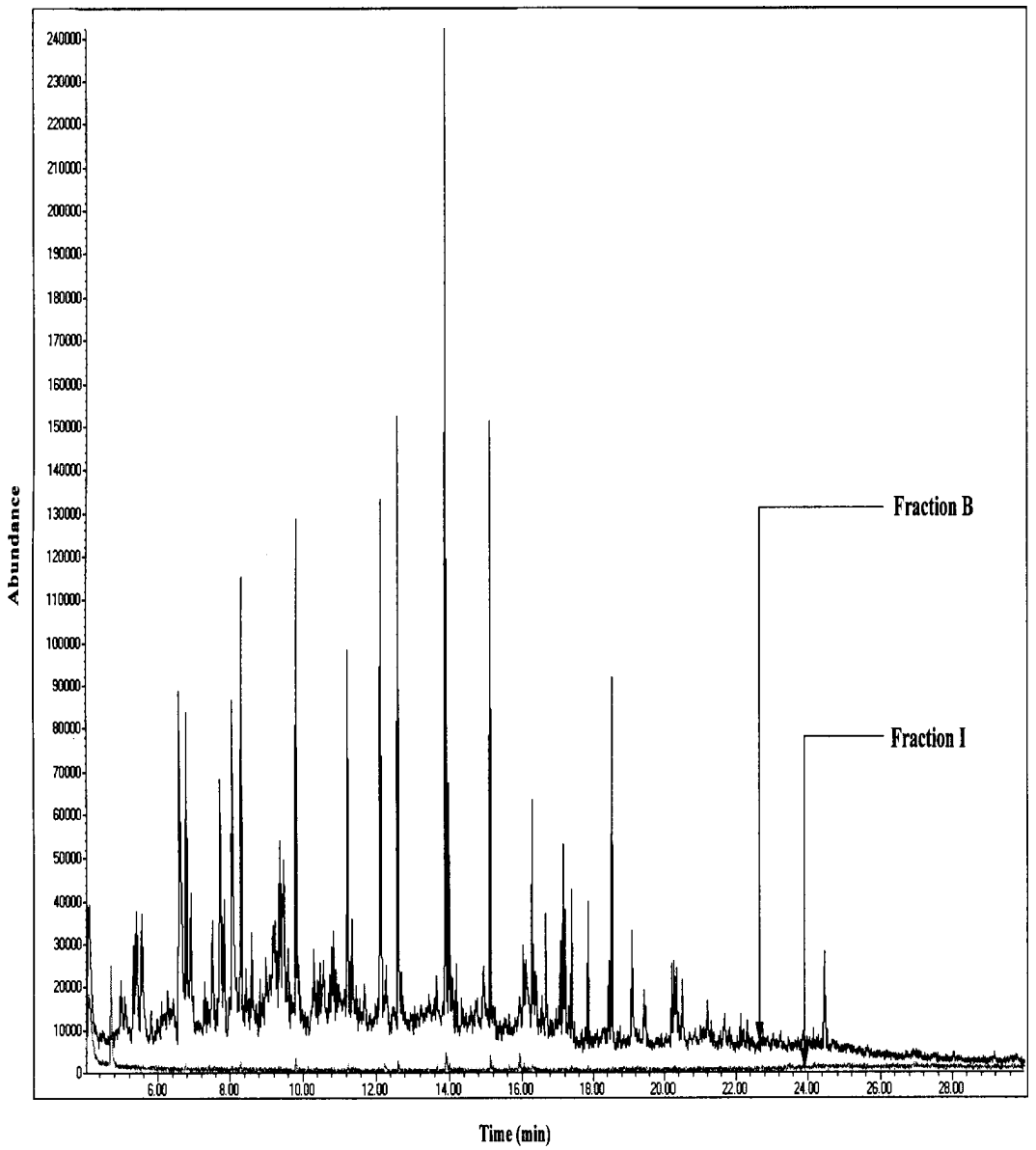

Figure 3.8 - GC-MS analysis of Fractions B and I

3.4 Conclusion

The liquid, gas and char yields for coffee grounds pyrolysis were a strong function of pyrolysis temperature. To maximize the coffee grounds bio-oil yield, one should operate at a temperature of 500°C.

This is the first study to ever report a novel pesticidal use for coffee grounds bio-oil, focusing on its inhibitory activity on plant pathogenic bacteria and Colorado potato beetles. Bio-oils produced at 500°C and 550°C were the most active against bacteria whereas bio-oils produced at 400°C and 550°C were the most active against beetles. It might thus be possible that different chemical/s is/are responsible for bactericidal and insecticidal activity. Dilution studies for insecticide assays clearly indicated that bio-oil had to be at a high concentration (at least 10%) to exhibit any acute toxicity (< 48 hr), although some insecticidal activity may be present at lower concentrations, where antifeedant or repellant actions may predominate. The bio-oil fractions rich in phenols were very active against bacteria and beetles. On the other hand, bio-oil fractions that contained no phenols still showed high 48 hr mortality for beetles, indicating that phenols were not the only insecticide chemicals in the coffee bio-oil. Further analytical investigations will be conducted to identify these compounds.

3.5 References

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CHAPTER 4

SINGLE AND TWO-STAGE ELECTROSTATIC DEMISTERS FOR MICRON SIZE MIST

4.1 Introduction

Many processes produce very fine droplets that must be separated from a gas stream. An example is pyrolysis process that converts biomass into bio-oil: very fine and persistent bio-oil aerosols are formed in the condensers and must be recovered before the non-condensable gases are collected or burned to generate energy for the process [1].

The removal of submicron droplets using cyclones and scrubbers is a difficult task [2-4]. Cyclones are not very effective with sub-micron droplets, whereas scrubbers require very high volumes of sprayed liquids and high velocities in the active zone of the apparatus [5]. Electrostatic precipitators (ESP) can remove suspended droplets from gas by charging the droplets in a corona discharge and separating them from the gas by means of an electric field. In a single-stage ESP, the electric field generates a corona discharge to charge the droplets and to attract them to the grounded wall, where they are collected. In a two-stage ESP, charging and removal of the droplets occurs in two separate electric fields [5].

In the past, an ESP has been used for the removal of submicron droplets by Bologa et al., Riahi-Nezhad et al. and Boichot et al [5-7]. The only study to quantitatively compare single-stage and two-stage tubular ESPs was by Surati et al. [8].

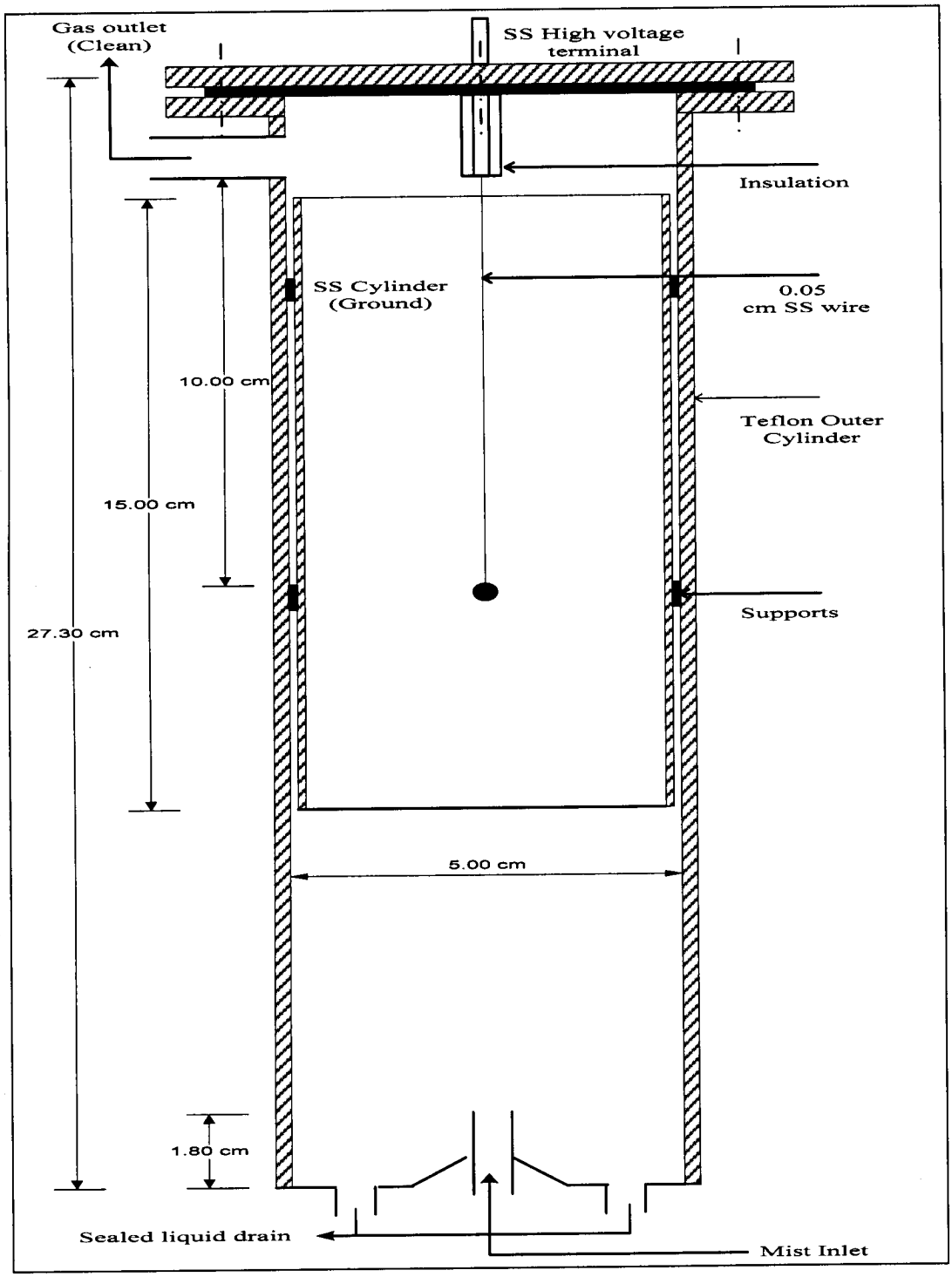
This chapter reviews basic design criteria for electrostatic precipitators used for the recovery of micron-sized droplets. It uses a completely new method for the accurate measurement of the collection efficiency of droplets [9] and the droplet size distribution is characterized using a Malvern 3600. Moreover, it compares single-stage and two-stage ESPs based on their droplet collection efficiencies and voltage-current (V-I) characteristics. The two-stage ESP was then scaled up and tested on a fast pyrolysis pilot plant. The idea was to test the scaled-up two-stage tubular ESP for the actual industrial application.

4.2 Design Characteristics of experimental and scaled-up equipment

As shown in Figures 4.1 and 4.2, the outer cylinder of the tubular ESP consisted of Teflon, selected because of its resistance to corrosion and its exceptional di-electric properties. Teflon has a high dielectric strength over a wide range of frequencies, a low dissipation factor and a high surface resistivity. Dielectric strength is the high voltage that the insulating material can withstand before it breaks down. A dissipation factor is the percentage of electrical energy absorbed and lost when current is applied to an insulating material. A low dissipation factor means that the absorbed energy dissipated as heat is low. The surface resistivity refers to the electrical resistance between opposite edges of a unit square on the surface of an insulating material [10].

The inner cylinder consisted of stainless steel and was electrically grounded. It was 0.05 m in diameter and 0.15 m long. The assembly of inner and outer cylinder used for both single-stage and two-stage ESPs was identical.

As shown in Figure 4.1, the single-stage ESP used a 5×10^{-4} m diameter, 0.10 m long, high potential wire called the discharge electrode, co-axial with the inner cylinder. As shown in Figure 4.2, the two-stage ESP used a central, high-potential electrode made of two sections: a short, 0.04 m long ionizing section with a diameter of 5×10^{-4} m, and a 0.06 m long collecting section with a diameter of 6.3×10^{-3} m. In a two-stage ESP, the corona is only generated in the ionizing section.



Scale- 1:1

Figure 4.1 - A schematics of single-stage ESP

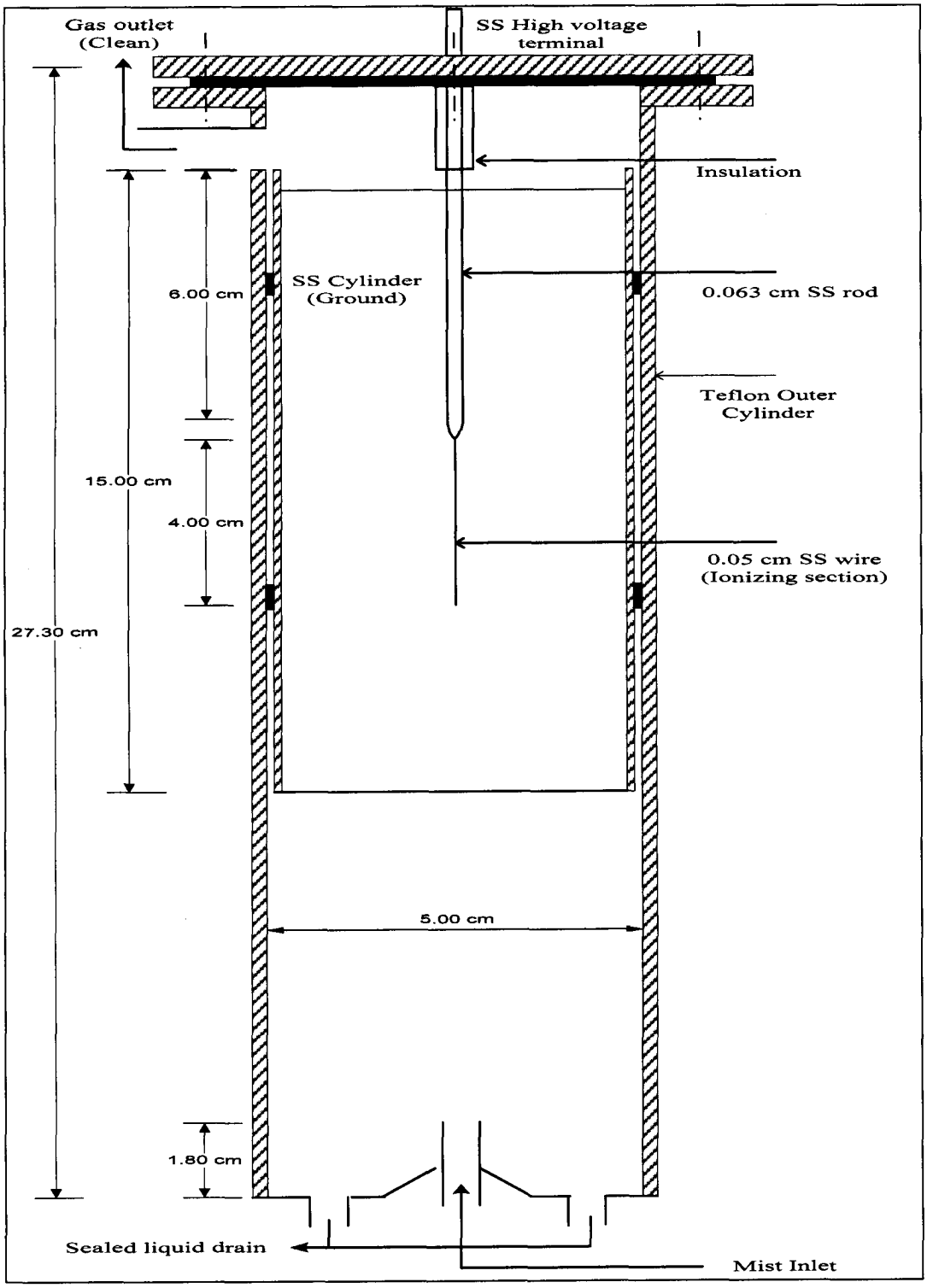


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Figure 4.2 - A schematics of two-stage ESP

The main design parameters were selected as follows:

1] The gas velocity in the ESP column was chosen to be 0.30 m/s as a compromise between drift velocity and entrainment. For the required gas flowrate, the calculated column diameter was 0.046 m. The column diameter was chosen as 0.05 m (based on the closest available standard tube size).

2] A drift velocity of 0.27 m/s was estimated by linear interpolation for the droplets generated in these experiments [11], which had a Sauter mean diameter of 8.95×10^{-6} m.

3] The Deutsch-Anderson equation was then used to calculate the surface area required for the collection of 99% of the droplets, which, for this calculation, were assumed to be monosize with a diameter of 8.95×10^{-6} m, equal to the Sauter mean diameter of droplets measured using Malvern-3600.

$$\eta = 1 - e^{\frac{-A.\omega}{Q}} \tag{1}$$

where:

η= ESP efficiency = 0.99

A= surface area of the collecting electrode (m^2)

ω= drift velocity = 0.27 m/s

Q= volumetric gas flow-rate = 5.15×10^{-4} m^3/s (Refer section 4.3.1.1)

Calculations showed that the height of the column required to separate 99% of the droplets was 0.056 m. The precision of estimates from the Deutsch-Anderson equation is usually ± 50%. So, 0.15 m was selected as the actual height of the column (based on the closest available size).

4] Field charging is the most common process by which particles/droplets in an ESP are charged [12]. Diffusion charging is negligible for particles with a diameter greater than 1×10^{-6} m. To get an idea of the magnitude of the charging times involved, a time constant T was calculated using the following equation [12]:

$$T = \frac{4\varepsilon_o EA}{I} \tag{2}$$

where:

T = time constant (s)

ε_o = permittivity of free space = 8.85×10^{-12} F/m

E = local electric field (V/m)

A = surface area of the collecting electrode = 0.024 m^2

I = discharge current flowing from discharge to collecting electrode (A)

Values of E and I were not known at this point in time. Therefore, typical literature values were used: $I = 7.5\times10^{-6}$ A and $E = 5\times10^{4}$ V/m.

The value of the time constant (T) was found to be 5.6×10^{-3} s. A particle/droplet is substantially charged in ten time constants [12]. The droplets would therefore take 5.6×10^{-2} s to charge completely. The gas velocity in the chamber was 0.26 m/s. Therefore, all the droplets would ideally be charged by the time they travel 0.015 m. This was used as a reference while designing the ionizing section of the two-stage ESP. The 0.04 m long ionizing section of two-stage ESP would thus ensure that the droplets were completely charged.

Furthermore, the idea was to develop a demister for fast pyrolysis pilot plant where nitrogen or inert gas is used as the fluidizing gas. Nitrogen and hydrogen (one of the main pyrolysis product gases), do not form negative ions by electron attachment and the generation of a negative corona is practically impossible. A positive corona was, therefore, generated instead by using a positive potential for the central, ionizing electrode.

A scaled-up two-stage ESP designed for the fast pyrolysis pilot plant consisted of a tubular stainless steel cylinder (SS), 0.064 m in diameter and 0.45 m long (Figure 4.3). The scaled-up two-stage ESP used a central, high-potential electrode made of two sections: a short, 0.1 m long ionizing section with a diameter of 5×10^{-4} m, and 0.3 m long collecting section with a diameter of 6.3×10^{-3} m. The dimensions for the scaled-up two-stage ESP were selected using the information generated in this study.

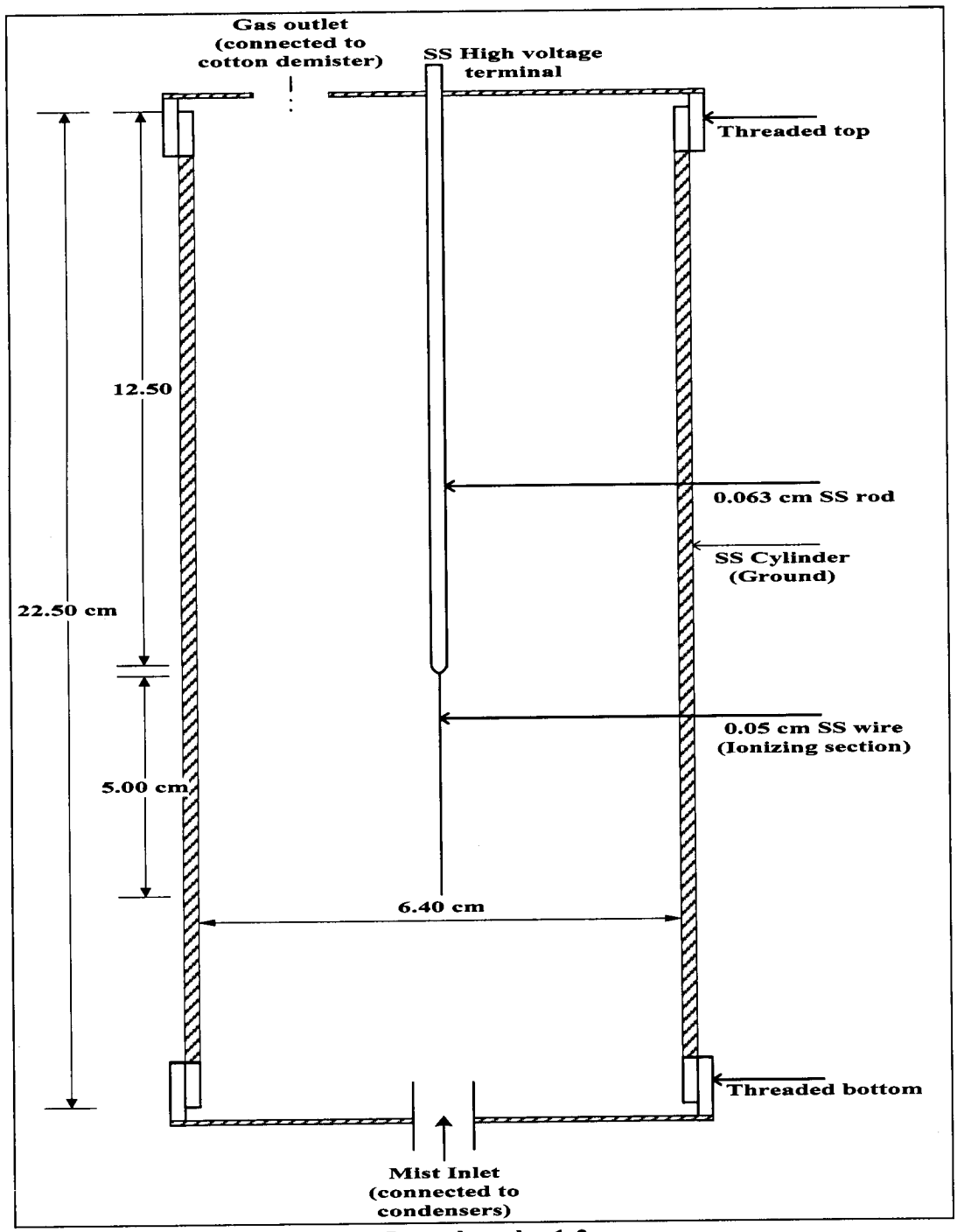


Figure 4.3 Scaled-up two-stage ESP for pilot plant

4.3 Materials and methods

4.3.1 Experimental single and two-stage ESPs

4.3.1.1 Operating conditions

A practical objective of this study was to develop an effective ESP that could be applied to the fast pyrolysis pilot plant illustrated in Figure 4.4. Detailed description of the process was published elsewhere [1]. This pilot plant operates at a maximum nitrogen volumetric flow-rate of 4.8×10^{-4} m^3/s at normal temperature and pressure and can handle a biomass feedrate of around 2.7×10^{-4} kg/s.

A typical pyrolysis operation would produce 60-85 wt% bio-oil, 15-25 wt% char and 10-20 wt% gas [1]. For calculation purposes, the following yields were selected: 70 wt% bio-oil, 20 wt% char and 15 wt% gas. Using gas density of 1.17 kg/m^3 at NTP, calculated using the ideal gas law [13], the pyrolysis process would produce 3.46×10^{-5} m^3/s of gases at NTP. Thus, the actual volumetric flow rate of gases would be 5.15×10^{-4} m^3/s. Practical experience has shown that around 2% of bio-oil is lost as fine droplets exiting the condenser with the gas. These conditions were replicated using a liquid injector (containing misting oil), calibrated nitrogen flow and a misting nozzle PJ10 from BETE generating 90° hollow cone mist.

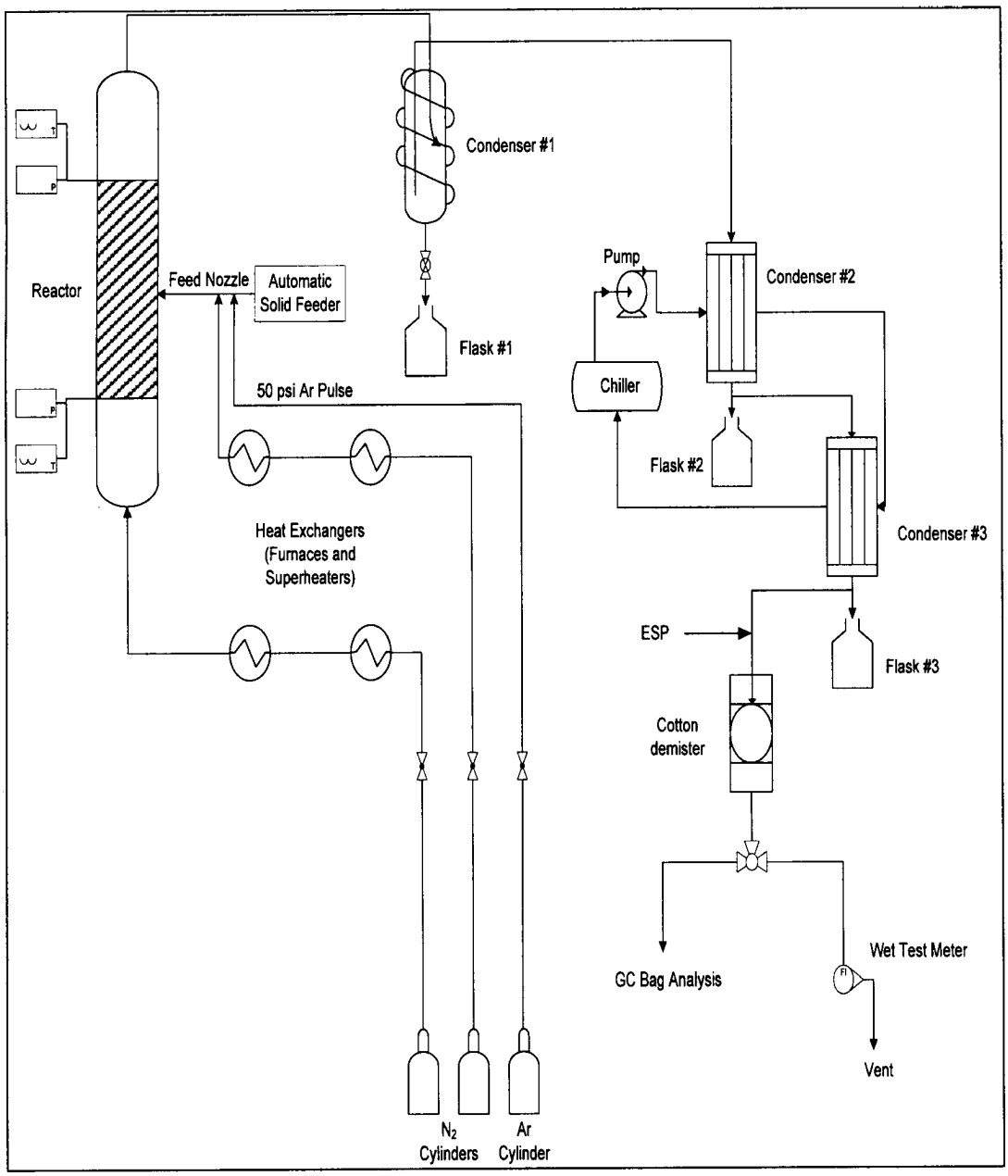


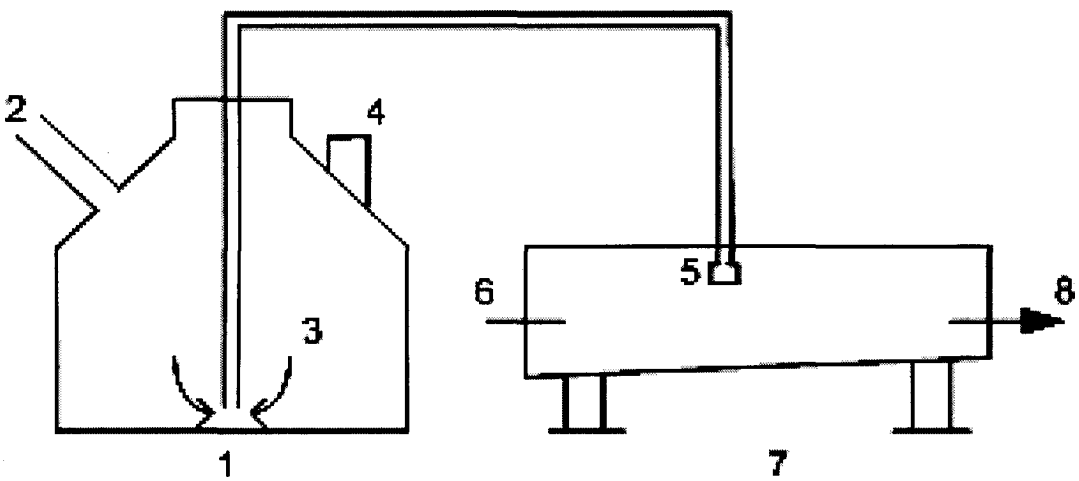
Figure 4.4 - A schematics of the Western Fluidization Group's fluid bed pilot plant

4.3.1.2 Fog fluid

Fluid "100A" purchased from Corona Integrated Technologies Inc. was used as a misting fluid. Ingredients of fluid 100A were glycerin and de-ionized water. Fluid "100A" was then colored using methylene blue in 0.1% concentration. Mythelene blue was used as a tracer. Henceforth, fluid 100A with methylene blue in 0.1% concentration is referred to as colored oil.

4.3.1.3 Mist generator and carrier assembly

The mist generator and carrier gas assembly are illustrated in Figure 4.5.



1. Liquid Injector
2. Pressurized air
3. Liquid pumped to PJ10
4. Safety valve
5. PJ 10 misting nozzle
6. N_2 through sonic nozzle
7. Mist carrier chamber
8. Mist towards ESP

Figure 4.5 - Mist generator and carrier assembly

The colored oil in the liquid injector was pressurized to 8.27×10^5 Pa. It was then sprayed into the mist carrier chamber using a PJ10 nozzle from BETE, which

generated a 90° hollow cone. The bigger droplets were collected on the walls of the mist carrier chamber, whereas the finer droplets were carried to the ESP by the nitrogen entering the mist carrier chamber through a 7×10^{-4} m diameter sonic nozzle. The nitrogen pressure upstream of the sonic nozzle was maintained at 7.58×10^{5} Pa to replicate the flowrate of nitrogen in the pyrolysis unit. Compressed nitrogen (99.9% purity) was used for all the experiments unless otherwise specified.

4.3.1.4 Droplet characterization using Malvern-3600

The mist coming out of the mist carrier chamber was analyzed using a Malvern-3600 apparatus for complete droplet characterization. The Malvern-3600 uses the principle of diffraction from the droplets as a means to measure the droplet size. The incident light is diffracted by the droplets, which are illuminated to give a stationary diffraction pattern. The diffraction pattern evolves, always reflecting the instantaneous size distribution. Thus, by integration over a suitable period, a representative bulk sample contributes to the final measured diffraction pattern. A Fourier transform lens then focuses the diffraction pattern onto a multi-element photo-electric detector, which produces an analog signal proportional to the received light intensity. This detector is interfaced directly to a computer, allowing it to read the diffraction pattern and perform the necessary integration digitally.

The size distribution of the droplets entering the ESP is shown in Figure 4.6. It clearly shows that the mist consisted of droplets smaller than 16.7×10^{-6} m with a Sauter-mean diameter of 8.95×10^{-6} m.

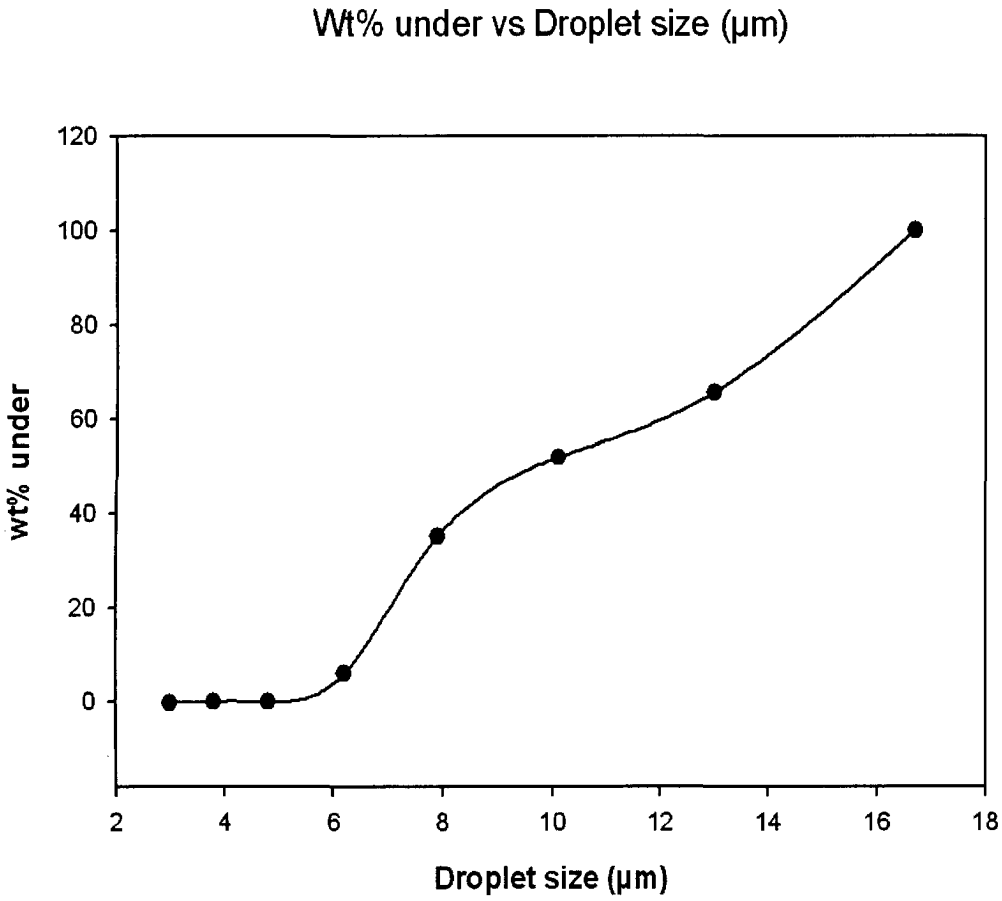


Figure 4.6 - Droplet size distribution

4.3.1.5 Experimental procedure

Both, single-stage and two-stage ESPs, were operated by setting the central electrode at a positive potential ranging from 9 kV to 13 kV. Each experiment was conducted for 30 min (1800 s). A cylindrical demister packed with the cotton wool and the porous polyethylene plate at one end of the demister was attached to the exhaust of the ESP. This demister could capture droplets as small as 1×10^{-7} m in diameter. Therefore, it can be assumed that all the droplets escaping the ESP were captured by the demister.

The total mist flow-rate entering the ESP was measured with a similar method. During this test, the cotton-packed demister was directly attached to the exhaust of the mist carrier chamber.

4.3.1.6 Droplet collection efficiency

The efficiency was measured by using a non-vaporizable and high UV absorbance tracer that was mixed with the fluid 100A. After each run, the cotton demister was washed with ethanol, so that the entire tracer was recovered from the demister. The relative absorbance of the tracer in the washed ethanol was then measured by UV spectrophotometry. This provided the amount of tracer collected by the filter. A mass balance then gave the amount of colored oil escaping the ESP for a particular run. Methylene blue was used as tracer. This method has been developed and validated by Xu et al. for measuring the efficiency of high-efficiency demisters [9].

This method of measuring efficiency offers several advantages over conventional methods. In particular, it is not affected by the partial vaporization of the liquid collected by the cotton demister. It can accurately measure efficiencies of the order of 99.99% due to the high sensitivity of UV spectrophotometry.

A 30 minute test at 0 kV determined the collection due to inertial impaction and brownian diffusion. This inertial efficiency was then assumed to be independent of the electrode voltage.

The electrostatic efficiency was calculated from the difference between the overall measured collection efficiency and the inertial efficiency. All efficiencies are reported as wt% of droplets separated from gas stream.

4.3.2 Scaled-up two-stage ESP for fast pyrolysis pilot plant

Sawdust was pyrolyzed at 550°C in the fast pyrolysis pilot plant. Detailed processing and operating conditions for the pyrolysis are available elsewhere [14, 15].

As shown in Figure 4.4, the scaled-up two-stage ESP was installed downstream of the condenser train and upstream of a cotton demister. The droplets exiting the ESP were captured by a cotton demister, which was 0.3 m long and 0.07 m in diameter. The mist collection efficiency of the combined ESP and cotton demister was assumed to be 100%. The ESP was operated at 16 kV.

The gases entering ESP were primarily nitrogen with significant concentrations of carbon dioxide, carbon monoxide, hydrogen and methane (pyrolysis gases). The concentration of pyrolysis gases in nitrogen could range anywhere from 15-25%. The gases were saturated with water vapor at 15°C and an absolute pressure of 1.013×10^5 Pa. The gas flowrate was about 4×10^{-4} m^3/s.

4.4 Results and discussions

4.4.1 Experimental single and two-stage ESPs

4.4.1.1 V-I characteristics

The V-I characteristics for single-stage and two-stage ESPs are shown in Figures 4.7 and 4.8 respectively.

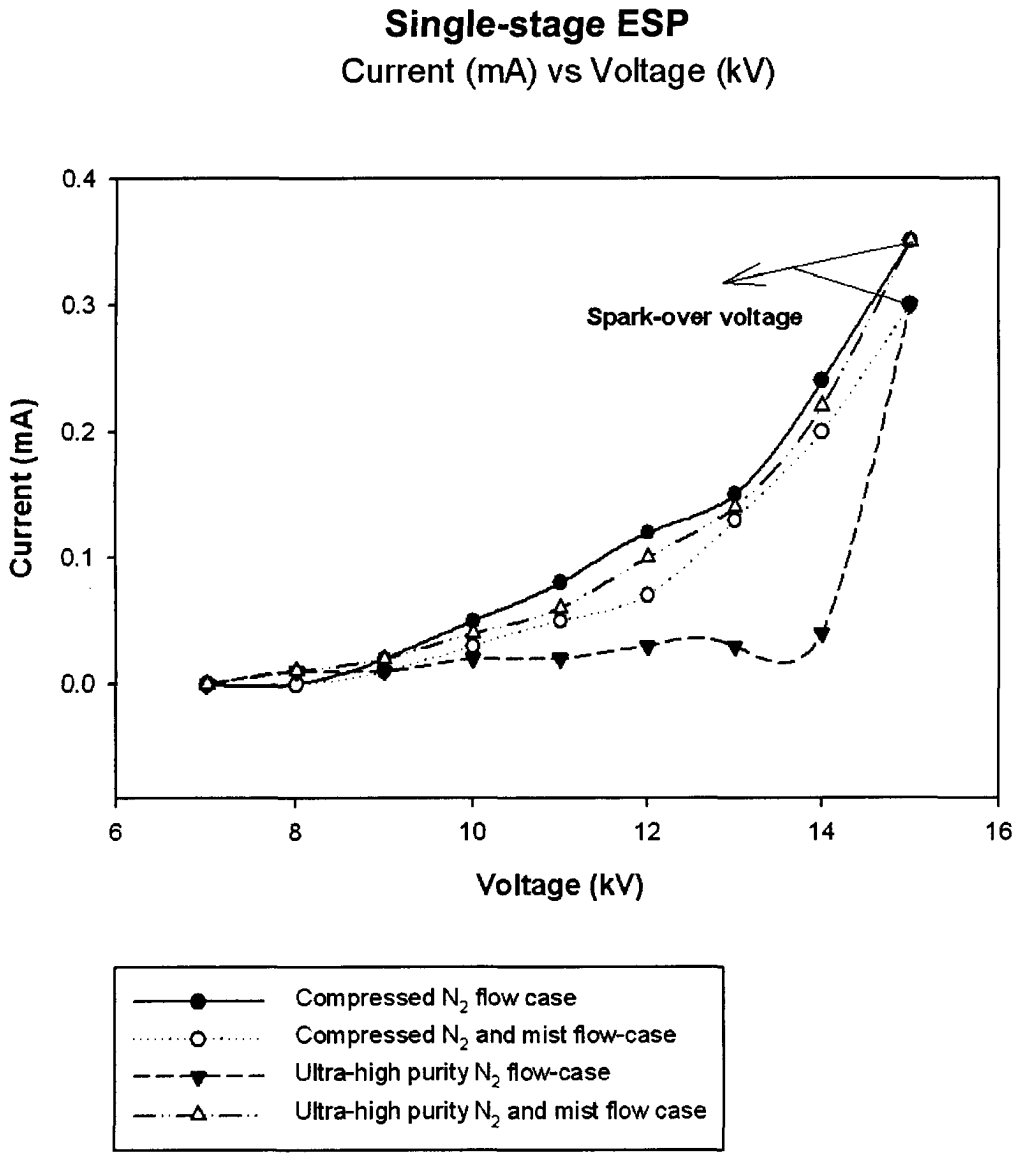


Figure 4.7 - Current vs Voltage characteristics for single-stage ESP

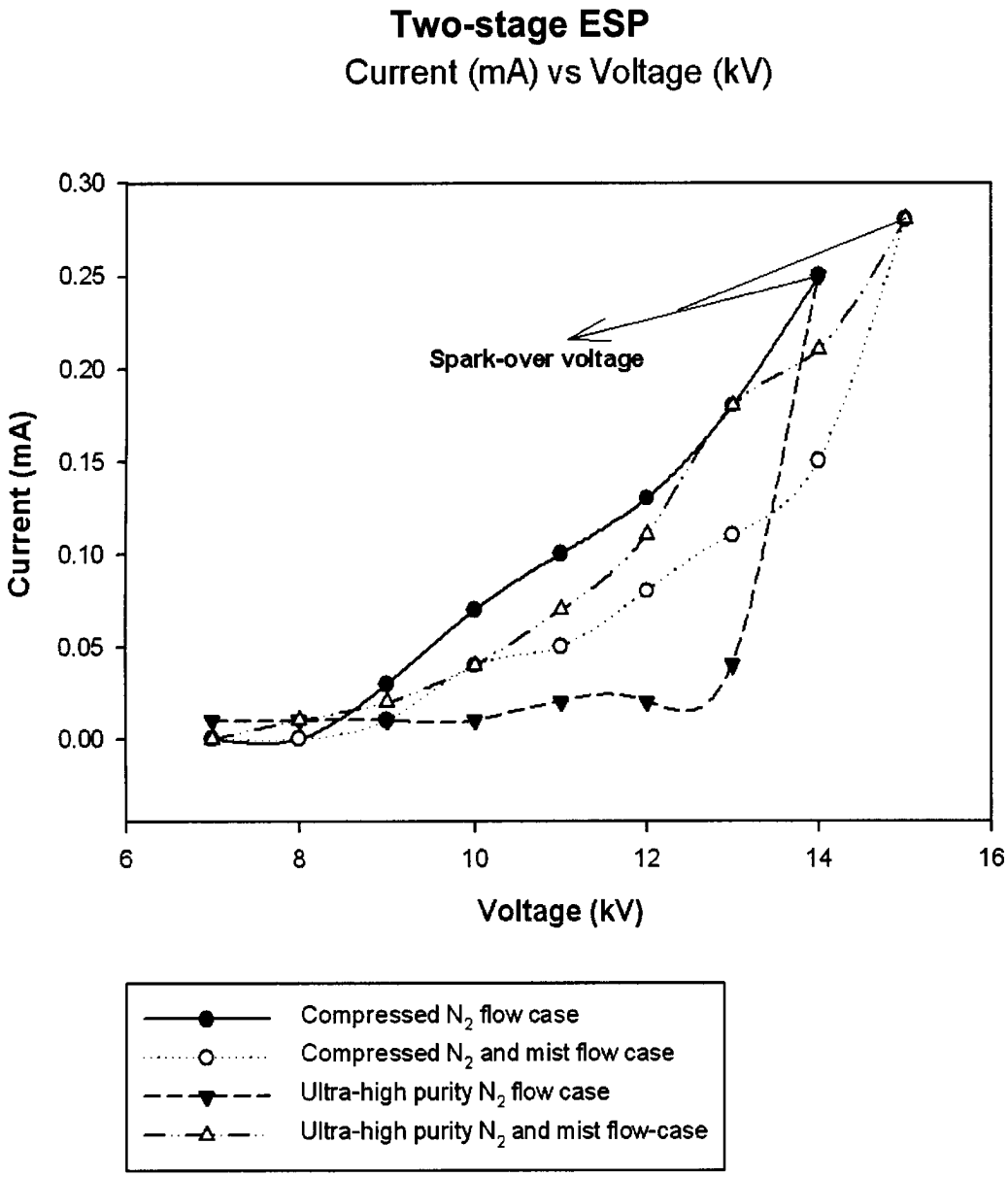


Figure 4.8 - Current vs Voltage characteristics for two-stage ESP

For both single-stage and two-stage ESPs, V-I characteristics differed significantly for compressed nitrogen and ultra-high purity nitrogen, indicating that impurities could play a major role in V-I characteristics. With ultra-high purity nitrogen, the current increased very slowly with the voltage indicating poor conductivity. These results are in accordance with the results published by Kucerovsky et al. [16, 17].

Because the collection efficiency of an electrostatic precipitator is affected by the V-I characteristics, there was a question of which type of nitrogen should be used for the rest of the experiments.

Additional tests, however, showed that the type of nitrogen that was used became much less relevant in the presence of mist. According to Figure 4.7, switching from compressed nitrogen to ultra-high purity nitrogen had no significant impact on the V-I characteristics in the presence of mist, for the single-stage ESP. For the two-stage ESP, the presence of mist greatly reduced the difference between the two types of nitrogen (Figure 4.8). Compressed nitrogen was, therefore, used in the rest of this study.

The spark-over voltage is important since ESPs must be operated below this voltage. For the single-stage ESP, the spark-over voltage was 15 kV in all cases. For the two-stage ESP, the spark-over voltage was 14 kV for compressed nitrogen and ultra-high purity nitrogen. In the presence of mist, the spark-over voltage increased to 15 kV with the two-stage ESP.

To operate safely below the spark-over voltage, the voltage was kept at or below 13 kV.

4.4.1.2 Single-stage and two-stage ESP efficiency

The inertial efficiency was found to be 98.59% and was constant for all the experiments under consideration.

The measured electrostatic efficiency is plotted in Figure 4.9 as a function of the voltage for single-stage and two-stage ESPs. The electrostatic efficiency increased from 76.48% at 9 kV to 92.37% at 13 kV for the single-stage ESP and from 78.73% at 9 kV to 93.18% at 13 kV for the two-stage ESP.

Total efficiency, which is a result of the combination of inertial and electrostatic collections, is plotted in Figure 4.10 as a function of voltage for single-stage and two-stage ESPs. The total efficiency increased from 99.67% at 9 kV to 99.89% at 13 kV for single-stage ESP and 99.70% at 9 kV to 99.90% at 13 kV for the two-stage ESP.

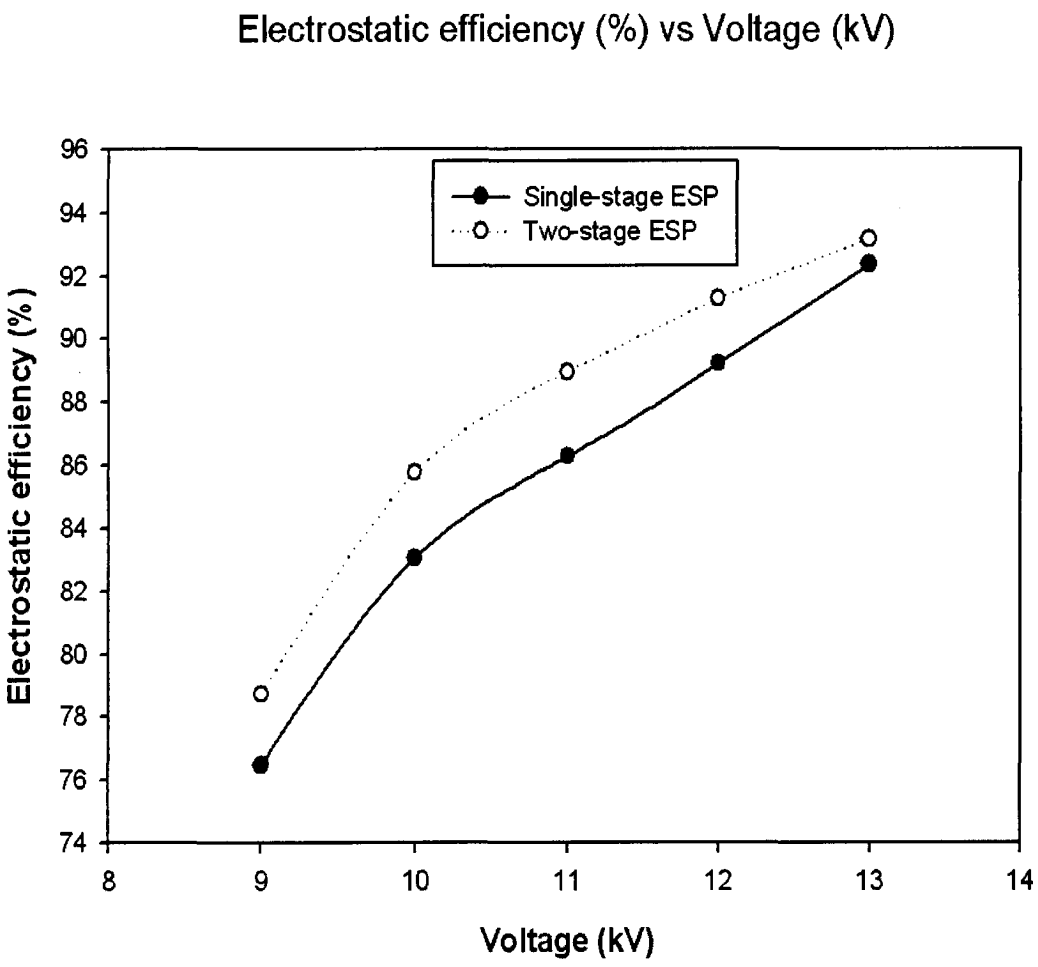


Figure 4.9 - Electrostatic efficiency as a function of voltage for single-stage and two-stage ESP

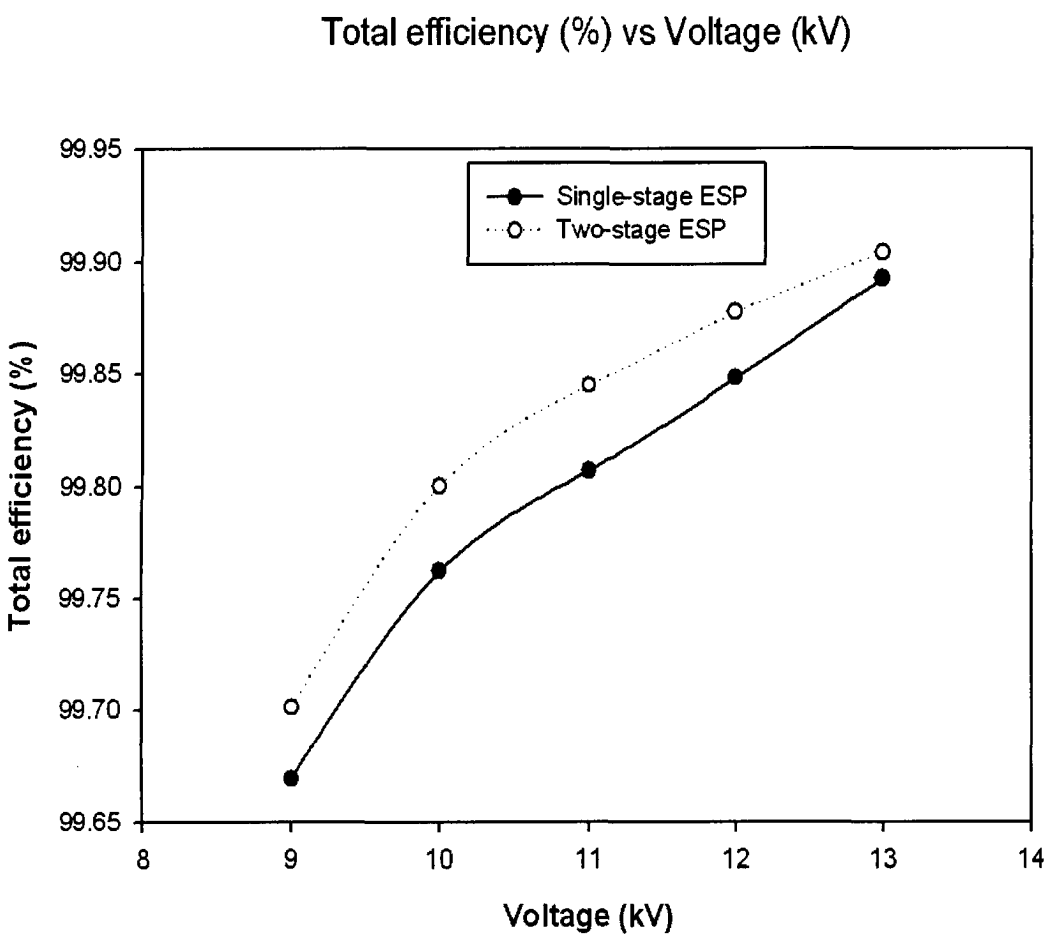


Figure 4.10 - Total efficiency as a function of voltage for single-stage and two-stage ESPs

The higher droplet collection efficiency of the two-stage ESP may be attributed to the lack of ionic space charge in the second-stage where the space charge comes only from the charged droplets. It may also be attributed to the fact that, in a two-stage ESP, a non uniform field exists in the ionizing section, whereas a uniformly high electrostatic field exists in the collecting section [11]. Surati et al. [8] also mentioned that saturation charging can be achieved in 0.01 s for most industrial applications encountered, thus confirming that the droplets could be charged in the short ionizing section of a two-stage ESP.

An attempt has been made to predict the measured efficiencies with the existing equations in the literature for tubular ESPs.

A drift velocity is calculated using following formula [12]:

$$\omega = \frac{6 k \varepsilon_o}{\eta (k + 2)} E^2 a \qquad (3)$$

where,

ω= drift velocity (m/s)

k = dielectric constant of droplets

ε_o = permittivity of free space (F/m)

η= viscosity of the gas (Pa.s)

E = local electric field (V/m)

a = radius of droplets (m)

Both single-stage and two-stage ESPs were operated from 9 kV to 13 kV,

- ✓ $E = 4.2 \times 10^5$ V/m (for 13 kV at the wire surface)
- ✓ a = radius of droplets in each fraction (m)
- ✓ $\eta = 1.75 \times 10^{-5}$ Pa.s
- ✓ k = 80.4 (the dielectric constant of water at 20^{O}C is 80.4. Fluid "100A" consists of de-ionized water and glycerin).
- ✓ $\varepsilon_o = 8.85 \times 10^{-12}$ F/m

The droplet size distribution is as shown in Figure 4.6. As mentioned above, the inertial efficiency was found to be 98.59%. The remaining 1.41% droplets were separated by the electrostatic precipitator. It was assumed that the 98.59 wt% of the droplets that were collected by inertial impaction were the largest droplets. The drift velocity and droplet collection efficiency were separately calculated for each fraction cut to yield the drift velocity and collection efficiency associated with each fraction cut.

An average electrostatic collection efficiency of 99.99% was obtained. The discrepancy between the measured and calculated electrostatic efficiencies could be due to the fact that the Deutsch-Anderson theory assumes that the turbulence inside the precipitator is so large that the droplet concentration remains constant across the precipitator, despite the movement of droplets towards the collecting electrode. A fuller description of the process should take into account the effect of gas turbulence on the transport of the droplets. This is particularly necessary to take into account, to calculate the precise time required for the droplets to travel to the collecting electrodes (Drift velocity) [12]. Furthermore, re-entrainment of collected droplets could be one of the major reasons responsible for the lower experimental collection efficiencies when compared to the theoretical efficiencies, which do not account for re-entrainment.

4.4.2 Scaled-up two-stage ESP for fast pyrolysis pilot plant

The ESP performed flawlessly. Its droplet collection efficiency was found to be 95% at an applied voltage of 16 kV. The spark-over voltage was 20 kV and varied slightly with operating conditions.

It would have serious implications on how the pilot plant would be operated in the future: Though a cotton demister can capture submicron bio-oil droplets with a very high efficiency, it quickly becomes saturated and must be replaced frequently to avoid an excessive pressure drop. It is also nearly impossible to recover the bio-oil from the cotton demister, preventing a representative measurement of the properties of the overall bio-oil product. All these problems were easily resolved with the installation of a simple ESP with a low pressure drop, from which most of the bio-oil can be easily recovered.

Using ESP for the recovery of mist emissions from fast pyrolysis pilot plant has many advantages. They make it possible to extend to the product recovery train, the process intensification gains of short residence time fast pyrolysis process.

ESP is very compact, safe, and energy-efficient and can be operated for long periods without maintenance.

4.5 Conclusions

Nitrogen impurities had a large impact on the V-I characteristics of both single-stage and two-stage ESPs. However, they became less relevant when mist was introduced in the nitrogen stream thus minimizing the significance of a carrier or pyrolysis gas. Spark-over voltage remained relatively unchanged for the various cases under consideration.

A two-stage tubular ESP was more efficient than a single-stage ESP of the same basic geometry. Although this may be attributed to the lack of ionic space charge in the second-stage, where the space charge consists of only charged droplets, further investigation needs to be done to establish a clear relation between the efficiencies of tubular single-stage and two-stage ESPs.

An ESP was successfully demonstrated for the recovery of fine bio-oil mist from the gas stream of a fast pyrolysis pilot plant. Such demisters will extend, to the product recovery train, the process intensification gains of short residence time processes such as fast pyrolysis.

4.6 References

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Three different feedstocks, tobacco leaves, coffee grounds and pinewood (Chapter 2, Chapter 3 and Appendix I) were fast pyrolyzed to yield liquid bio-oil, non-condensable gases and solid char. Accurate measurements of liquid, gas and char yields were carried out in order to optimize the pyrolysis conditions. Liquid bio-oils produced from tobacco leaves, coffee grounds and pinewood were fractionated and tested for their pesticidal (fungicidal, bactericidal and insecticidal) properties. It was observed that a significant fraction of the bio-oil escaped the condensing train as a fine mist; this is a common problem in pyrolysis operations. An electrostatic demister was, therefore, developed to recover this mist.

Chapter 2 dealt with the pyrolysis of tobacco leaves at three different vapor residence times; 5 s, 10 s and 17 s and at six different pyrolysis temperatures from 350°C to 600°C. Liquid bio-oil yields were a strong function of temperature and residence time. The highest liquid bio-oil yield was found to be 43.4% at 500°C and at the lowest vapor residence time of 5 s. This is the first study to ever report a novel pesticidal use for tobacco bio-oil, focusing on its inhibitory activity on plant pathogenic bacteria, fungi and Colorado potato beetles. Fractionation of bio-oil was carried out and various bio-oil fractions were tested against Colorado potato beetle (CPB), the fungus *Pythium ultimum* and the two bacteria viz. *Streptomyces scabies* and *Clavibacter michiganensis* subsp. *michiganensis*. It was found that the non-nicotine fraction was active against all the tested species. Though the nicotine-rich fraction showed no activity against fungi and bacteria, it was active against beetles. This confirmed that there were multiple chemicals active against fungi, bacteria and beetles.

Chapter 3 dealt with the pyrolysis of coffee grounds at a vapor residence time of 5 s and at 5 different pyrolysis temperatures from 400°C to 600°C. Liquid, gas and char yields were a strong function of temperature. Gas yields increased from 400°C to 600°C, whereas, char yields decreased from 400°C to 600°C. Liquid bio-oil yields peaked at 500°C. This is the first study to ever report a novel pesticidal use for

coffee grounds bio-oil, focusing on its inhibitory activity on plant pathogenic bacteria and Colorado potato beetles. Bio-oils produced at 500°C and 550°C were the most active against bacteria whereas bio-oils produced at 400°C and 550°C were the most active against beetles. It might thus be possible that different chemicals are responsible for bactericidal and insecticidal activity. Dilution studies for insecticide assays clearly indicated that bio-oil had to be at a high concentration (at least 10%) to exhibit any acute toxicity (< 48 hr), although some insecticidal activity may be present at lower concentrations, where antifeedant or repellant actions may predominate. The bio-oil fractions rich in phenols were very active against bacteria and beetles. On the other hand, bio-oil fractions that contained no phenols still showed high 48 hr mortality for beetles, indicating that phenols were not the only insecticide chemicals in the coffee bio-oil.

Chapter 4 dealt with the development of single-stage and two-stage electrostatic precipitators and testing them under different conditions. Nitrogen impurities had a large impact on the V-I characteristics of both single-stage and two-stage ESPs. However, they became less relevant when mist was introduced in the nitrogen stream thus minimizing the significance of carrier or pyrolysis gases. Spark-over voltage remained relatively unchanged for the various cases under consideration. A two-stage tubular ESP was more efficient than a single-stage ESP of the same basic geometry. Although this may be attributed to the lack of ionic space charge in the second-stage, where the space charge consists of only charged droplets, further investigation needs to be done to establish a clear relation between the efficiencies of tubular single-stage and two-stage ESPs. An ESP was successfully demonstrated for the recovery of fine bio-oil mist from the gas stream of a fast pyrolysis pilot plant. Such demisters will extend, to the product recovery train, the process intensification gains of short residence time processes such as fast pyrolysis.

Appendix I dealt with the pyrolysis of pinewood at a vapor residence time of 5 s and at 7 different temperatures from 300°C to 600°C. Liquid, gas and char yields were a strong function of temperature. Gas yields increased from 300°C to 600°C,

whereas, char yields decreased from 300°C to 600°C. Liquid bio-oil yields peaked at 550°C. The raw pinewood bio-oil was then tested against 11 fungi, 4 bacteria and Colorado potato beetle (CPB). It showed moderate to no activity against these species and further testing was aborted.

Recommendations

It was observed that the liquid bio-oil yield was a strong function of temperature and residence time. The minimum vapor residence time that can be reached in ICFAR fast pyrolysis pilot plant is 2 s. A downer having a vapor residence time of a fraction of a second should be tested and optimized for liquid bio-oil yield.

All the pyrolysis experiments were carried out with the cotton demister downstream of condenser train, which significantly affected the time for which the fast pyrolysis unit can be operated continuously. A novel two-stage electrostatic precipitator designed for the fast pyrolysis pilot plant should be used henceforth for all pyrolysis experiments.

A detailed fractionation study followed by detailed analytical study should be undertaken to identify the individual chemicals responsible for pesticidal activity of the tobacco and coffee grounds bio-oil. Once the individual chemicals are identified, concentration profiling should be undertaken, which would involve, testing various concentrations of the identified chemicals for their pesticidal activity. GC-MS could then be calibrated to test the exact concentration of chemicals in the bio-oil fractions tested for their pesticidal activity.

Biomass feedstocks such as neem, tomato plants which are known to have natural pesticidal properties should be pyrolyzed and tested for their fuel and pesticidal properties.

APPENDIX I

INSECTICIDAL, FUNGICIDAL AND BACTERICIDAL CHARACTERISTICS OF THE BIO-OIL FROM THE FAST PYROLYSIS OF PINE WOOD

I.2.2 Methods

I.2.2.1 Coffee ground pyrolysis

I.2.2.1.1 Pilot plant

Detailed description could be found in Chapters 2 and 3.

I.2.2.1.2 Bio-oil production and its characterization

The exact yield of pinewood bio-oil was obtained from the mass of oil collected in the three condensers and the demister. The demister was weighed before and after the experiment.

Pyrolysis was carried out at seven different temperatures from 300°C to 600°C and with a vapor residence time of 5 s. Each test was conducted with 150 g of pinewood. Fluidizing and carrier nitrogen volumetric flow rates were controlled using 'Mass Trak' flow-meters from Sierra Instruments Inc., and adjusted to keep the nominal vapor residence time constant at all temperatures. All the pinewood bio-oils produced in these experiments separated into organic and aqueous phases.

I.2.2.1.3 Characterization of product gases

Detailed description could be found in Chapters 2 and 3.

I.2.2.1.4 Characterization of char

Detailed description could be found in Chapters 2 and 3.

I.2.2.2 Bactericidal, fungicidal and insecticidal assays

Raw bio-oil (both organic and aqueous phases) was used for primary characterization of bactericidal, fungicidal and insecticidal activity. Raw bio-oil was tested against 11 fungi, 4 bacteria and Colorado potato beetle (CPB).

I.2.2.2.1 Disc diffusion agar method for bactericidal and fungicidal assays

Detailed description could be found in Chapters 2 and 3.

I.2.2.2.2 Leaf disc application method for insecticidal assays

Detailed description could be found in Chapters 2 and 3.

I.3 Results and discussions

I.3.1 Pyrolysis

The effect of pyrolysis temperature (300°C to 600°C) on the liquid, gas and char yields is as shown in Fig. I.1. The bio-oil yields were a strong function of temperature, peaking at 550°C. Char yields decreased from around 54.6% at 300°C to 3.9% at 600°C [5-7]. Gas yields increased from 12% at 300°C to 43.6% at 600°C. Heat of combustion of gases is tabulated in Table I.1. Fig. I.2 shows mol% of H_2, CO, CH_4 and CO_2 produced at different pyrolysis temperatures. Calculations showed that the higher heating value (HHV) of the gases produced increased from 524.7 J/g of pyrolyzed biomass at 300°C to 3443.2 J/g of pyrolyzed biomass at 600°C. Gases could be recycled to the pyrolysis reactor to produce the heat required for the endothermic pyrolysis reaction.

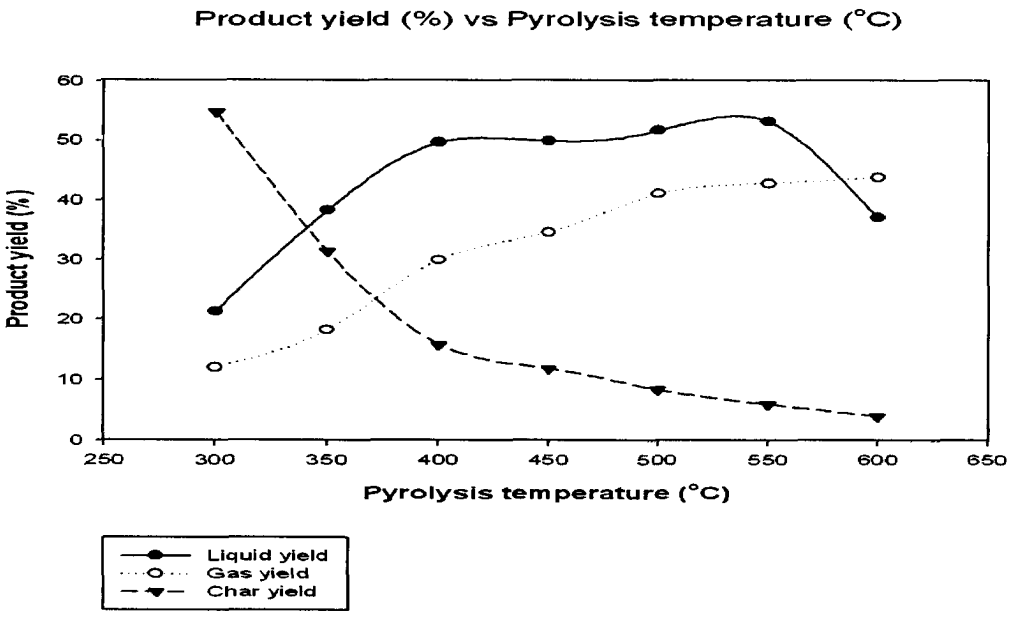

Figure I.1 – Effect of temperature on liquid, gas and char yields

Obtained at fluidization velocity of 0.05 m/s in fluidized bed pilot plant and argon pulse of 50 psi

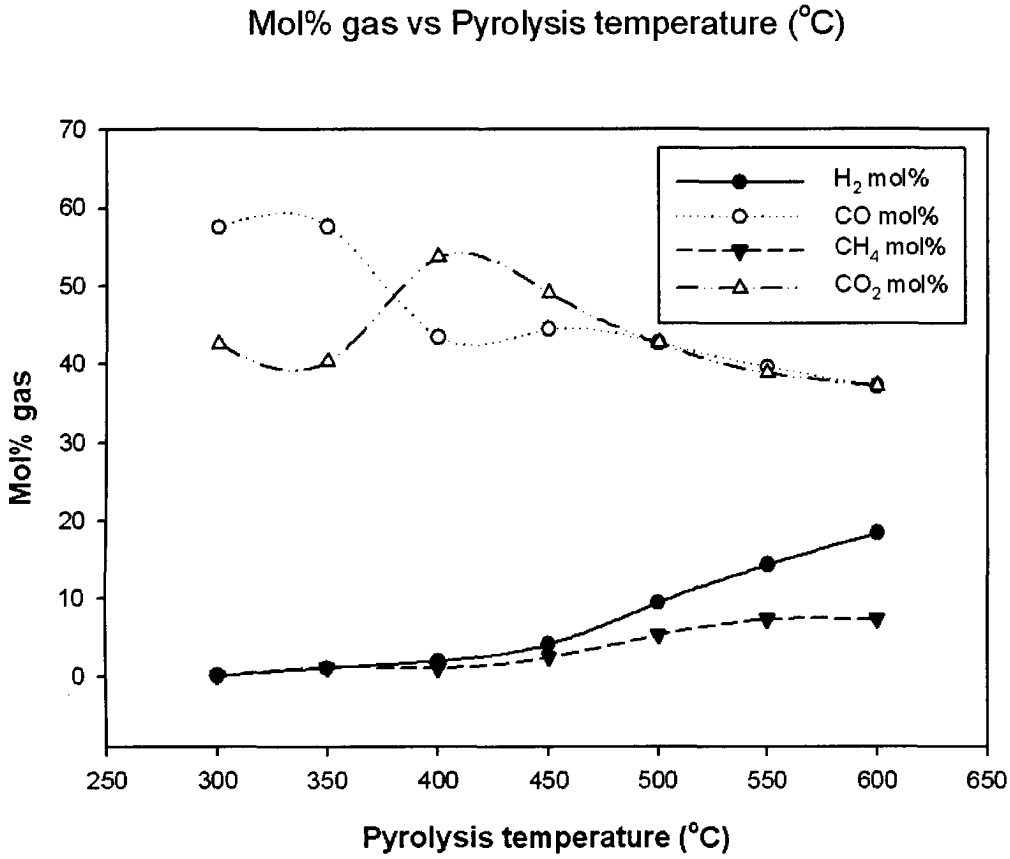

Figure I.2 – Effect of pyrolysis temperature on the gas yields

Obtained at fluidization velocity of 0.05 m/s in fluidized bed pilot plant and argon pulse of 50 psi

Table I.1 - HHV of gases as a function of temperature

Temperature (°C)	Heat of combustion (HHV) (J/g of biomass fed)
300	524.7
350	935.1
400	1142.6
450	1593.9
500	2514.4
550	3146.8
600	3443.1

As mentioned before, pinewood bio-oil consisted of aqueous and organic phases. The aqueous phase comprised 50-60% of the bio-oil produced. Low bio-oil yields compared to other feedstocks like distiller's grain or sawdust processed in the same pilot plant, accompanied by high water concentration in bio-oils produced from pinewood, made the overall process unattractive from the point of view of fuel production.

I.3.2 Bio-oil as bactericide, fungicide and pesticide

Pinewood aqueous phase showed no inhibition for 11 fungi and 4 bacteria under consideration. Pinewood organic phase showed mild inhibition for two bacteria viz. *Streptomyces scabies* and *Clavibacter michiganensis* subsp. *michiganensis*. Both pinewood aqueous and pinewood organic phases showed very low 48 hour mortality for Colorado potato beetle (CPB).

I.4 Conclusion

The liquid, gas and char yields for pinewood pyrolysis were a strong function of pyrolysis temperature. To maximize the liquid yield, one should operate at a temperature of 550°C.

This is the first ever study to report the testing of pinewood bio-oil as a pesticide. From the results obtained, it could be easily concluded that, pinewood bio-oil showed moderate to no inhibitory activity for various fungi, bacteria and beetles under consideration.

I.5 References

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