Slow Pyrolysis of Vomitoxin-Contaminated Corn in a Batch Reactor

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A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Chemical and Biochemical Engineering

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Abstract

Maize is one of the most important agricultural products in terms of production, consumption, and economic importance. However, its contamination with mycotoxins, particularly deoxynivalenol (DON), frequently occurs around the world due to high humidity. This mycotoxin appears predominantly in grains associated primarily with pathogens such as Fusarium graminearum (Gibberella zeae) or Fusarium culmorum. This phenomenon, threatening both human and animal health, also affects the economy due to the disposal of large amounts of contaminated corn. The overall objectives of this study were to use thermochemical conversions (i.e. pyrolysis) for managing this seasonal waste by converting it into value-added industrial solid (bio-char), liquid (bio-oil) and gaseous products. The pyrolysis of vomitoxin-corn grains was carried out in a bench-scale batch reactor at temperatures between 450 to 650 °C with 15 to 20 °C/min heating rates and without carrier gas.

Pyrolysis resulted in the deterioration of deoxynivalenol (DON) from 5-7 ppm in raw corn grains to zero ppm in the treated biochar, making thermochemical conversion a promising method for industrial applications.

The effect of pyrolysis conditions, including temperature and heating rate, on the conversion of toxic corn grains, was investigated. The results showed the maximum bio-oil yield was achieved at 650 °C (47 wt.%). Bio-char and non-condensable gases were two other products with 28.6 wt.% and 24.5 wt.% yields, respectively.

Further, the chemical composition of the bio-oil was identified using Gas Chromatography-Mass Spectrometry (GC-MS) and quantified by High-Performance Liquid Chromatography (HPLC). The results showed that acetic acid and levoglucosan are the two major components in the bio-oil, which were measured to be 26 g/kg, and 13 g/kg of bio-oil, respectively. Both acetic acid and levoglucosan have potential applications in various industries, such as for the synthesis of polymers, solvents, and pharmaceuticals.
The biochars were analyzed using TGA for proximate analysis, FTIR for identification of significant functional groups, BET for surface area, SEM for measuring the development of the pores, and elemental analysis for CHNS content. Bio-char was upgraded by physical activation using a CO$_2$ at 900 °C. Activation significantly increased the BET surface area of the bio-char from 3 to 419 m$^2$g$^{-1}$. The significant development of the pore structure was verified through SEM images. The performance of activated bio-char has been tested by utilizing three different model molecules, i.e. methylene blue, methyl orange, and ibuprofen. The results showed that adsorption capacity of the activated bio-char was similar to that of commercial activated carbons (CAC).

The gas composition from pyrolysis of corn was analyzed via micro-GC to investigate the potential use of gases as a renewable energy resource for combustion in engines or as for process energy recovery.

In this study, we demonstrated a successful process for eliminating DON from contaminated corn via pyrolysis, while producing value-added products.

**Keywords**

*Deoxynivalenol (DON)*, corn grain, pyrolysis, bio-oil, bio-char, activated bio-char, adsorption
Summary for Lay Audience

Maize (corn) has several applications for human consumption, animal feed, and ethanol production. However, contamination of corn with an ear mould in the areas with high humidity, turns this valuable cereal into a toxic product, which threatens both human and animal health, causing food refusal, vomiting, abdominal pain, and diarrhea. It also affects the economy due to large amounts of contaminated corn disposal. This phenomenon generally occurs in countries with humid climates, such as the United States, Europe, and Canada.

In this study, a thermochemical technology called pyrolysis was used to destroy the toxin and extract value from this wasted crop. Pyrolysis is the thermal decomposition of biomass, which occurs at elevated temperatures (300 to 700 °C) in the absence of oxygen. The products of this process, liquid bio-oil, solid bio-char, and gases, have many potential applications in the chemical, agricultural, and pharmaceutical industries.

The bio-oil is composed of many chemicals, such as acetic acid and levoglucosan. Acetic acid is used for the production of paints, adhesives, and coatings after separation from the bio-oil. Levoglucosan is an organic compound that can be used for the synthesis of polymers. Bio-char is a solid product, which is similar to charcoal and has high mineral contents. This product can be used as a soil amendment, an adsorbent for wastewater treatment and for air pollution control. Finally, the gases can be used for providing the required energy for the pyrolysis process, making it a more sustainable process.
## Co-Authorship Statement

<table>
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<tr>
<th>Article Title</th>
<th>Pyrolytic Conversion of Vomitoxin-Contaminated Corn into Value-Added Products</th>
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Thank you.
Dedication

To my sister, Elham.
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Chapter 1

1 Introduction and Background

1.1 Research motivation

The research project described in this thesis has been motivated by two considerations. The first is the need to explore and develop solutions that would allow the substitution of finite fossil resources, traditionally utilized for the production of fuels and chemicals, with renewable and sustainable ones. The second is the need to eliminate continuously produced wastes, which could contribute to environmental pollution, and convert them into renewable resources which, in turn, can then be converted into value-added chemicals and fuels.

In relation to the first motivation, we need to recognize that the global demand for fossil resources (e.g., crude oil, natural gas, and coal) and petroleum-based chemical and fuel products has increased due to population growth and life style changes, causing severe environmental issues [1]. The most significant problems are the limitation of fossil resources, which will eventually become exhausted and the carbon displacement into atmosphere resulting from their utilization. Such carbon displacement changes the natural carbon cycle and cause climate changes. Consequently, it is necessary to look for alternative and sustainable resources for the production of chemicals and fuels.

Biomass is drawing much attention as an effective renewable resource [2]. The environmental advantages (e.g. low carbon footprint), abundance and continuous renewal, as well as waste reduction potential of biomass make it a sustainable alternative for fossil resources [3]. Although the complete elimination of fossil resources and their total replacement with biomass is impossible, in the near future, multiple approaches are being pursued, many at the research and development level, but several of them have already achieved commercial implementation [4].

There are several pathways for biomass conversion from various feedstocks (i.e. woody products, such as forestry wastes and bark, agricultural products, such as purpose grown
crops, residues and manure, and organic wastes, such as industrial and municipal organic fractions) to chemicals and fuels. These include biological, thermal and mechanical (physical) processes. Pyrolysis is a thermochemical conversion process among other technologies (combustion, gasification, liquefaction, etc.) that has the advantage of being a relatively fast process and does not require intensive feedstock pre-treatments [5]. Besides, this process produces no waste streams, also the pyrolysis products have various applications in agricultural, pharmaceuticals, and chemical industries [1].

During pyrolysis, hundreds of chemical species are produced as a result of cracking and recombination reactions. Pyrolysis products are classified as bio-oil (liquid phase from condensable vapors), bio-char (a carbon rich residual solid phase), and permanent gas (mostly CO, CO₂, CH₄, and H₂) [6, 7].

Two main pyrolysis processes include “slow pyrolysis” and “fast pyrolysis”. Slow pyrolysis is mainly used for the production of bio-char. In slow pyrolysis, the biomass is heated to 300-500 °C with a long particle residence time (minutes to hours) and long vapor residence times (tens of seconds to minutes). In contrast, fast pyrolysis happens at higher temperatures (typically 400 to 600 °C) with shorter vapor residence times (typically < 2s) as high vapour residence times favour gas production, resulting from secondary cracking reactions, which lowers oil yields. The main product of “slow pyrolysis” is bio-char (approximately 50 wt.%), and for “fast pyrolysis” is bio-oil (60-75 wt. % of bio-oil, 15-25 wt. % of bio-char, and 10-20 wt. % of non-condensable gases) [5, 8, 9].

The bio-oil can be used as a fuel or for the production of value-added chemicals. Furthermore, it can be utilized as a combustion fuel in various systems such as boilers, burners, furnaces, diesel engines, and turbines [8]. Bio-char, similarly, has different applications: in soil amendment (fertilizer) and acid gas adsorption. It can also be activated and used for removing pollutants from solids (soil), liquids (wastewater), and gases (air purification) or as catalysts. Using the bio-char as an energy resource is another
rare but possible application [10]. The third and final product of pyrolysis, non-condensable gas, can also be utilized as an energy resource [11].

Related to the second motivation, we have targeted non-edible DON contaminated corn as a potential biomass feedstock. Deoxynivalenol (DON) (also called vomitoxin) is a mycotoxin substance caused by pathogens such as Fusarium graminearum (Gibberella zeae) and Fusarium culmorum that contaminates crops such as maize, wheat, barley, oats, and rye [12, 13]. Low temperature and high humidity are two environmental factors that favors the growth of DON under both fields and storage [12]. Table 1-1 shows DON concentration changes from 2011 to 2020. In 2018, up to half of Ontario corn was infected with DON, due to high humidity of the summer season. Only 33% of corn, produced in 2018, contains DON concentration less than 0.5 ppm. The remaining percentage shows vomitoxin levels as high as 25 ppm, which is 25 times higher than the allowable limit for the pig feed [14].

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<tbody>
<tr>
<td>&lt; 0.5</td>
<td>47</td>
<td>84</td>
<td>83</td>
<td>66</td>
<td>75</td>
<td>48</td>
<td>69</td>
<td>33</td>
<td>84</td>
<td>58</td>
</tr>
<tr>
<td>0.5 to &lt; 2</td>
<td>28</td>
<td>12</td>
<td>15</td>
<td>26</td>
<td>20</td>
<td>26</td>
<td>17</td>
<td>27</td>
<td>12</td>
<td>31</td>
</tr>
<tr>
<td>2 to &lt; 5</td>
<td>17</td>
<td>4</td>
<td>1</td>
<td>6</td>
<td>5</td>
<td>18</td>
<td>8</td>
<td>15</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>5 and greater</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>8</td>
<td>6</td>
<td>25</td>
<td>0</td>
<td>0</td>
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</table>

Ethanol may appear to be a market for toxic corn. However, the dry distiller grains, by-products of this process when toxic maize is used as the feed, would still contain unacceptably high concentrations of the toxin to make it usable as for animal feed [16].

Many studies discussed different procedures for removing DON from maize, wheat, barley, and etc. [12, 17–19]. Konishi et al. [18] studied the effect of high temperatures
(170 to 350 °C) on wheat contaminated with DON in Japan with no reduction of DON occurring. Two more studies discussed solutions such as dissolving DON in water and using additives, which are carried out by Visconti et al. [17] and Vidal et al. [20] for removing DON from wheat in Italy and Spain, respectively. The results showed a 40% reduction when using additives.

The fundamental hypothesis of this work is that pyrolysis could be potentially an efficient method to convert the toxic corn to value-added chemicals and fuels. High temperature of pyrolysis process (450 to 650 °C) is expected to lead to the complete degradation of the DON structure. Although literature is rich in pyrolysis of various feedstock and biomass, no article has been found dealing with the pyrolysis of vomitoxin-contaminated corn grains [21].

Therefore, this study represents an original contribution towards the possible management of a unique seasonal waste, through the utilization of thermal energy for deteriorating, neutralizing, or depolymerizing the *deoxynivalenol* (DON) structure in corn grains while producing value-added products. In this thesis, the batch slow pyrolytic conversion of vomitoxin corn to value-added bio-char, bio-oil, and gas will be discussed. We will elaborate on the effects of reactor temperatures and heating rates on bio-oil and bio-char yields and quality and on the potential valorization of the derived products.

### 1.2 Literature review

#### 1.2.1 Vomitoxin corn

Corn is one of the most important cereal grain in terms of quantities produced, consumed, and economic importance. It is not only for human food but also for animal feed and feedstock usage for biofuel production industries [22]. According to the Food and Agriculture Organization (FAO), maize production increased significantly in the United States from 250 million tonnes in 2000 to about 350 million tonnes in 2018 (Figure 1-1).
Mycotoxins appear in corn when certain molds infect the corn. Molds are caused by organisms called fungi that attach themselves on soil or plants such as corn. There are a number of molds, which affect the corn, such as *fusarium* [23]. *Deoxynivalenol* (DON) is produced by a certain *fusarium* that frequently contaminates corn, barley, wheat, oats, and rice. Figure 1-2 illustrates the structure of DON. It is a polar molecule because of its three hydroxyl (-OH-) groups. One of the major characteristics of DON is that it is resistant to high temperatures [13]. Studies show that DON is stable under high temperatures from 170 to 350 °C but since DON is water soluble, its concentration declines after dissolving in water [18, 24]. Table 1-2 shows the major physiochemical properties of DON.
Figure 1-2: Structure of DON molecule (adapted from [13])

<table>
<thead>
<tr>
<th>Property</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{15}H_{20}O_6</td>
</tr>
<tr>
<td>Molar mass</td>
<td>296.319 g.mol$^{-1}$</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>543 ± 50</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>151 to 153</td>
</tr>
<tr>
<td>Polar organic compound</td>
<td>Soluble in water</td>
</tr>
</tbody>
</table>

Deoxynivalenol contamination in corn generally occurs in countries with humid climates, such as the United States, Europe, and Canada, causing *Fusarium* ear rot (pink ear rot) or *Gibberella* ear rot (red ear rot) (Figure 1-3) [25, 26]. *Fusarium* ear rot contamination is favored by warm and dry conditions, while *Gibberella* ear rot is more common in the presence of high levels of moisture [25]. DON affects human and animal health, causing food refusal, vomiting, suppression of immune system, abdominal pain, and diarrhea [22]. Distiller’s dried grains with solubles (DDGS) is a low-cost by-product of the fuel-ethanol industry, which is typically used for animal feed. Currently, maize is the main feedstock used in ethanol production in the United States. If mycotoxin contaminated corn is used for ethanol production, the DDGS by-product remaining after the process would still contain unacceptably high concentrations of DON[27].
1.2.2 Possible outcomes: use or dispose

Many studies discuss the possible solutions for decontamination of the toxic maize. Figure 1-4 illustrates remediation or detoxification of corn grains, which can be categorized as physical, chemical, and biological treatments or combination of these processes. Washing or steeping can be effective for water-soluble toxins such as DON. Table 1-3 provides a summary of studies using different methods and the possible results. Trenholm et al., [28] and Sinha [29] studied the effect of washing on DON concentration changes in contaminated corn and the results shows up to 67% reduction (Table 1-3). Another study by Bullerman and Bianchini shows 19% DON reduction in corn using sorting, trimming, and cleaning [30].

Chemical treatments for mycotoxin corn have been widely studied but there are few implementations due to the complications of treated products for human consumption. Cazzaniga et al., [31] showed how sodium bisulfite is effective at reducing DON concentrations. However, alteration of the corn’s structure makes this product suitable only for animal food. A new study performed in 2021 discussed the effect of ozone as a chemical treatment for removing DON and the results showed 41% reduction after 180
min, indicative of achieving the difficult degradation of DON after long contact times [32]. No chemical or enzymatic treatments have been approved by the European Union for mycotoxin treatments due to the extensive need for safety testing after treatments and possible structural changes in the products [22].

Figure 1-4: Remediation and detoxification methods for DON contaminated corns (adapted from [22])
Table 1-3: Summary of various techniques used for the decontamination of DON from maize

<table>
<thead>
<tr>
<th>Process and physical treatment [33]</th>
<th>Year</th>
<th>Condition</th>
<th>Results</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical and physical treatment</td>
<td>1986</td>
<td>1) Moist ozone (1.1 mol %) in air</td>
<td>1) 90% of DON reduction after an hour</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2) 30% chlorine</td>
<td>2) Total destruction of DON after 0.5 hour</td>
<td></td>
</tr>
<tr>
<td>Washing [28]</td>
<td>1992</td>
<td>Washing three times with DI water, using sodium carbonate solution (1 M)</td>
<td>73 % of DON reduction</td>
<td>Expensive post-treatments such as drying after decontamination</td>
</tr>
<tr>
<td>Cooking [31]</td>
<td>2001</td>
<td>Extrusion process at 180 °C, adding sodium metabisulfite (1%)</td>
<td>95 % of DON reduction</td>
<td>-</td>
</tr>
<tr>
<td>Bt corn [26]</td>
<td>2004</td>
<td>Using Bt corn as a genetically modified crop</td>
<td>Annual loss reduced from $52 to $8 millions</td>
<td>The majority of Bt corn is used for animal feed</td>
</tr>
<tr>
<td>Food processing [30]</td>
<td>2007</td>
<td>Sorting, trimming, and cleaning</td>
<td>DON concentration reduction from 5.5% to 19%</td>
<td>These processes do not fully destroy DON structure</td>
</tr>
<tr>
<td>Ozone [32]</td>
<td>2021</td>
<td>In contact with Ozone for 180 min</td>
<td>42 % of DON reduction</td>
<td>DON appeared to be quite difficult to degrade even at elevated contact times</td>
</tr>
</tbody>
</table>

1.2.3 Thermal remediation

Various processes, including combustion, carbonization/torrefaction, pyrolysis, gasification, and liquefaction, are used for the thermochemical conversion of biomass. Table 1-4 shows the process condition of each process and the type of product extracted [34]. The major differences among these processes are the target product and the process conditions.
Table 1-4: Thermochemical conversion processes of biomass (adapted from [34])

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torrefaction</td>
<td>200-300</td>
<td>0.1</td>
<td>Solid</td>
</tr>
<tr>
<td>Combustion</td>
<td>700-1400</td>
<td>≥ 0.1</td>
<td>Gas</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>300-600</td>
<td>0.1-0.5</td>
<td>Liquid/solid</td>
</tr>
<tr>
<td>Gasification</td>
<td>500-1300</td>
<td>≥ 0.1</td>
<td>Gas</td>
</tr>
<tr>
<td>Liquefaction</td>
<td>250-330</td>
<td>5-20</td>
<td>Liquid fuels</td>
</tr>
</tbody>
</table>

Both carbonization and torrefaction, performed in the absence of oxygen, alter the chemical structure of biomass, which increases its carbon content and lowers its oxygen content. In torrefaction, much of the volatiles are retained in the product to increase energy and mass yields of solid product, while in carbonization most of them are purged to maximize the char yield. Combustion occurs in the presence of added oxygen (air). Two major products, H2O and CO2, are released due to the oxidation of the hydrocarbons. Unlike combustion, pyrolysis takes place in the absence of oxygen and its major products are gas, liquids, and solids. Gasification, performed at temperatures higher than those used for pyrolysis and in the presence of some added oxygen, is done with the objective of producing gases with higher H/C ratios. Hydrothermal liquefaction is the process of producing liquid products from a biomass by bringing it into contact with water at high temperatures and pressures (at either supercritical or near-critical conditions) supercritical and in the presence of a catalyst [9, 34].

1.3 What is pyrolysis

1.3.1 Slow, intermediate, fast pyrolysis and ultra-pyrolysis

In slow pyrolysis, the vapor residence time can be as high as from 5 to 30 min. A longer vapor residence time favours bio-char and non-condensable gases yields. However, fast pyrolysis occurs under short residence times, typically of 0.5 – 3 s, using biomass with less than a 10 % moisture content and with a particle size of less than 3mm. Fast pyrolysis favors higher bio-oil yields [5, 11, 35]. Intermediate pyrolysis occurs at temperatures of 500 to 700 °C with indirect heating and short residence times of vapors.
Ultrafast pyrolysis occurs at high heating rates of 1000 °C/min to 10000 °C/min and vapor residence times of less than 0.5 seconds. Table 1-5 illustrates various types of pyrolysis with their major characteristics.

<table>
<thead>
<tr>
<th>Pyrolysis Process</th>
<th>Vapor residence time (s)</th>
<th>Heating rate (°C/s)</th>
<th>Bio-oil yield (wt.%)</th>
<th>Bio-char yield (wt.%)</th>
<th>Gas yield (wt.%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow (carbonization)</td>
<td>300-1800</td>
<td>0.1-20</td>
<td>30</td>
<td>35</td>
<td>35</td>
<td>300-700</td>
</tr>
<tr>
<td>Intermediate</td>
<td>10-30</td>
<td>20-50</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>500-700</td>
</tr>
<tr>
<td>Fast</td>
<td>0.5-3</td>
<td>50-200</td>
<td>60-70</td>
<td>15-25</td>
<td>10-20</td>
<td>400-800</td>
</tr>
<tr>
<td>Ultra-fast/flash</td>
<td>&lt;0.5</td>
<td>1000-10000</td>
<td>&gt;70</td>
<td>~10</td>
<td>~10</td>
<td>700-1000</td>
</tr>
</tbody>
</table>

1.3.2 Bio-oil and applications

Bio-oil can be used as a fuel (alone or as a blend) for heat generation in boilers/burners/furnaces and power generation in engines/turbines. However, it is also a good source of high value-added chemicals such as resins, flavours, fertilizers, light hydroxylic acids, sugars (e.g. levoglucosan). Bio-oil can also be used in manufacturing processes of pharmaceuticals and polymers [8, 38–40]. Further, the light fraction of bio-oil can be used in fuel cells. The heavy fraction, the phenol-rich fraction is a good candidate for bitumen in asphalt industry and for the manufacturing of adhesives [40].

1.3.3 Bio-char and applications

Bio-char is the pyrolytic charcoal. It is very versatile and has many different applications due to its physical and chemical characteristics that make it inexpensive and
environmentally friendly. Bio-char can be used as fuel, as a soil amendment, as an adsorbent for wastewater treatment and air pollution, and for purification in pharmaceutical industries. Bio-char has significant number of surface functional groups, large specific surface areas, and high mineral contents, leading to a high adsorption capacity [41]. The adsorption characteristics of bio-char depend on various parameters such as type of feedstock [42] and process conditions [41, 43, 44]. Physical and chemical activation of bio-char improves the adsorption capacity as a result of increasing its specific surface area [45–47]. Bio-char improves soil quality and properties by adsorbing pollutants, neutralizing acidic soil, increasing water and oxygen holding capacity [48, 49].

1.3.3.1 Activated bio-char applications for adsorption of chemicals in solutions

Activated carbon products have a well-developed and porous structure. They have high thermal stability, are resistant to acids, have a porous structure, and are hydrophobic [50]. These characteristics enable various applications for activated carbon in water and wastewater treatment, desalination, and air purification. However, such applications are highly dependent on the activated carbon’s pore size and surface functional groups (i.e. presence of heteroatoms such as O-, N-, H-, S-, and P- atoms). Their pore size is categorized into three groups: macropores (> 50 nm), mesopores (2 – 50 nm), and micropores (< 2 nm). Activated carbon surface changes between 500 and 3000 m²/g [51].

Activated carbon is produced from various feedstocks. Many agricultural residues, such as corn, bagasse, fruit stones, fruit pulp, coffee beans, corn stalks, almond shells, rice straw, and pistachio shells, are suitable sources for producing activated carbon. On the other hand, bitumen charcoal, lignite, wood, peat shells, anthracite, and coconut shells are the most common sources used for producing commercially activated carbon on an industrial scale. The reason that these residues are common for producing activated char is that they are cost-effective and in abundance [52].

Around 100,000 tonnes of activated carbon are produced annually around the world [53].
In 2002, the global consumption of activated carbon reached 750,000 tonnes [54]. According to “Activated Carbon Market Size and Forecast”, the global activated carbon market was valued at 6.99 billion USD in 2019 and is projected to reach USD 13.36 billion USD by 2027 [55].

1.3.3.2 Dye removal

Dyes are among the major groups of pollutants in wastewater, contributing to environmental problems. Therefore, many researchers have discussed the application of activated carbons to adsorb synthetic dyes [56]. In particular, several researchers have studied the adsorption of methylene blue on activated carbon by chemical activation. They have identified initial concentration as the most significant variable in dye adsorption. Ashour et al. [57] studied the adsorption of methylene blue on activated carbon by physical activation with steam. Parameters such as initial concentration, temperature, and pH affect the adsorption results, and after 2 hours, 55 mg/g of MB was adsorbed on activated carbon at 27 °C and a pH of 3.

1.3.3.3 Pharmaceuticals removal

The presence and propagation of pharmaceutical substances in the environment have had severe negative effects on ecosystems, including the spread of toxins and antibiotics that are resistant to adsorption. Studies demonstrate that activated carbon is practical for pharmaceutical removals, including ibuprofen, acetaminophen, glyphosate, sulfamethazine, and atrazine [58].

1.3.3.4 Heavy metals removal

Several researchers have studied the adsorption of heavy metals, including Cd, As, Hg, Cu, and pb [59]. The adsorption mechanisms of heavy metals on activated bio-char mainly involve ion-exchange, electrostatic attraction, and physical adsorption. Activating the bio-char increases the oxygen-containing functional groups, pore-volume, and surface area. Studies show that among all the parameters affecting the adsorption capacity of activated bio-char, the inclusion of the functional groups such as hydroxyl (-OH),
carboxyl (-COOH), and amino groups (-NH2) have the most significant effect on heavy metals adsorption through electrostatic attraction and cation exchange [60].

1.3.4 Gas applications

Non-condensable gas produced from biomass pyrolysis are mainly composed of H2 and CO and contain smaller percentages of CO2, C2H4, and CH4 based on the type of feedstock and pyrolysis conditions. The gases product can be used for contributing to the required energy of the pyrolysis process, making it a more sustainable process. Further, H2 and CO, called syngas, are the major Fischer-Tropsch feedstock for liquid fuel production. Gas has also been used as a renewable source of fuel (power generation) for combustion in engines or as energy carriers [37]. Although the heating value of syngas is ~ 6 MJ kg⁻¹, which is low compared to natural gas (~ 54 MJ kg⁻¹), various applications has been found on small scales. For instance, syngas can be burned and used as a source of energy for feedstock drying process or for electricity generation [6].

1.4 Previous studies on corn pyrolysis

1.4.1 Comparison of corn pyrolysis with other feedstocks

Corn kernels composed of 70% starch, 10% protein, and 5% hemicellulose, which is different from the composition of the most common pyrolysis feedstocks such as forestry waste, municipal solid wastes, food waste, digestate, and distillers grains, which is cellulose, hemicellulose, and lignin [61]. Since corn grains are important food sources around the world, very limited studies discussed the pyrolysis of these valuable cereals. In the study performed with Oana et al. [62] the pyrolysis of corn grains in a fixed bed reactor under carbon dioxide flow was carried out. The decomposition of corn endosperms was studied during this pyrolysis (Figure 1-5). The first starch decomposition happened between 140 and 190 °C in the floury endosperm, and the second one in the horny endosperm between 240 to 300 °C, which was more significant. The effects of different parameters, including carbon dioxide superficial velocity, grain size, and heat flux, were investigated and among them only the heat flux had a significant impact on the
pyrolysis products. In other words, by increasing the heat flux, the bio-char yield decreased, whereas the bio-oil yield increased.

Figure 1-5: Corn kernel composition (adapted from [63])

Yingyun et al. [64] studied the thermal decomposition of corn starch, castor oil, and soy protein during fast pyrolysis. Table 1-6 shows the results of the proximate and ultimate analyses of these feedstocks. Since the C-C energy content is higher than C-O or C-H, if the feedstock has lower ratios of H/C or O/C, its heating value is higher. For instance, castor oil has the lowest O/C content; therefore, its HHV is the highest compared to the remaining feedstocks and is close to the petroleum’s heating value.

Figure 1-6 shows the TG and DTG analysis for corn at different heating rates (100, 300, 500 °C/min). For corn starch, the pyrolysis temperature zones at three heating rates are quite close with an average of 320-354 °C, which is not a wide range compared to other feedstocks. The DTG curves for castor oil and corn starch exhibit only one peak, meaning that, a high mass loss occurs at a specified peak for these two feedstocks. However, soy protein has two peaks. The highest mass loss rate occurred for the corn starch over all the heating rates. Yang et al. [65] studied the thermal decomposition of corn starch and argued that it could be considered as taking place within two first-order reactions. The high heating rate plays the role of promoter. Therefore, due to the fact that the decomposition mechanism of corn starch is simple, the high mass loss is evident in the curves [65].
Table 1-6: Elemental analysis of corn starch (adapted from [64])

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corn starch</th>
<th>Soy protein</th>
<th>Castor oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>0.41</td>
<td>3.91</td>
<td>0</td>
</tr>
<tr>
<td>VM</td>
<td>90.92</td>
<td>81.11</td>
<td>100</td>
</tr>
<tr>
<td>FC</td>
<td>8.67</td>
<td>14.98</td>
<td>0</td>
</tr>
</tbody>
</table>

Proximate analysis (wt.%)

<table>
<thead>
<tr>
<th>Ultimate analysis (wt.%)</th>
<th>Corn starch</th>
<th>Soy protein</th>
<th>Castor oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>43.74</td>
<td>50.17</td>
<td>71.88</td>
</tr>
<tr>
<td>H</td>
<td>7.09</td>
<td>7.33</td>
<td>11.67</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>14.68</td>
<td>0.18</td>
</tr>
<tr>
<td>S</td>
<td>0.34</td>
<td>0.85</td>
<td>0.30</td>
</tr>
<tr>
<td>O</td>
<td>48.83</td>
<td>26.97</td>
<td>9.97</td>
</tr>
</tbody>
</table>

High heating value

<table>
<thead>
<tr>
<th>High heating value (MJ/kg)</th>
<th>Corn starch</th>
<th>Soy protein</th>
<th>Castor oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV</td>
<td>17.31</td>
<td>22.30</td>
<td>39.21</td>
</tr>
</tbody>
</table>

O/C and H/C ratios

<table>
<thead>
<tr>
<th>O/C</th>
<th>Corn starch</th>
<th>Soy protein</th>
<th>Castor oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/C</td>
<td>1.12</td>
<td>0.54</td>
<td>0.14</td>
</tr>
<tr>
<td>H/C</td>
<td>0.16</td>
<td>0.15</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Yang et al. [65] studied the pyrolysis of corn starch for the purpose of levoglucosan (LG) production. The effects of furnace temperature (360-420 °C) and vacuum condition were evaluated during this study.

Figure 1-7 illustrates the yield of LG under the two conditions of vacuum and atmospheric pressure. LG yield was higher under vacuum than atmospheric pressure. The reason for this could be due to the fact that vacuum conditions reduce the residence time of LG during the process and therefore the LG yield increased significantly from 17 % at atmospheric pressure to 56% under vacuum condition.
Figure 1-7: The effect of temperature on the pyrolysis product yields produced from corn starch (left: vacuum condition, right: atmospheric pressure) (adapted from [65])

1.5 Research objectives

Based on the research motivation and on the current state-of-the-art, the main objectives of this study are summarized as follows:

1. Investigating the feasibility of using thermochemical processes (pyrolysis) for deteriorating DON in corn grains, which has not been performed before as a solution for managing this seasonal waste.

2. Pyrolytic conversion of unusable corn waste to value-added products such as bio-char, bio-oil, and non-condensable gases, which may have various industrial applications.
   - Optimizing reaction temperature and heating rate for increasing bio-oil and bio-char yield and quality
   - Characterizing bio-oil, bio-char and identification of potential uses for industrial applications
   - Increasing adsorption capacity of bio-char by its physical activation and evaluate the possible applications of this adsorbent
Chapter 2

2 Materials and Methods

2.1 Feedstock characterization

2.1.1 DON concentration in feedstock

Field corn grains samples were obtained from the Grain Farmers of Ontario, Guelph, London, Ontario and used as a feedstock. According to the reports, the corn was contaminated with a toxic component called deoxynivalenol (also known vomitoxin due to the strong vomiting effect after consumption [13]) with concentration of 5-7 ppm.

2.1.2 Proximate and ultimate analysis

Before the proximate analysis, corn grain was ground and sieved to a particle size of 1-mm, then dried in the muffle oven at 105 °C for 2 hours to remove the moisture. The proximate analysis indicates the amount of volatile matter (VM), fixed carbon (FC), and ash content based on ASTM D1762. Ultimate analysis was conducted to determine carbon, hydrogen, nitrogen, and oxygen content, using Thermo Flash EA 1112 elemental analyzer (CHNSO). The system was calibrated using the first four samples, 0.5, 1, 2, and 2.5 mg of BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene) (CE Elantech, NJ, US). Each of the tin capsules contained 1-2 mg of bio-char (biomass) and 8-10 mg of vanadium pentoxide in order to achieve complete conversion of sulphur. Samples were combusted at 900°C in a stream of helium with a known volume of oxygen. This technique produces N2, CO2, H2O, and SO2, which were then subjected to separation and quantification using gas chromatography, which comprises of a steel column 2 m long and 5 mm in diameter, and helium as a carrier gas (flow rate of 140 mL min⁻¹). Finally, the elements were detected using a Propack model thermal conductivity detector (TCD).
2.2 Pyrolysis reactor

2.2.1 Experimental setup

The slow pyrolysis experiments were performed in a batch mechanically mixed flow reactor (MFR) illustrated in Figure 2-1 and Figure 2-2. The reactor consists of a 316 stainless steel horizontal cylinder 33 cm long, and 20 cm in internal diameter, with a capacity of 8.5 L. The reactor used an internal paddle to achieve high mixing performance and allowing for back-mixing between char and fresh feedstock [66].

After loading the biomass, the lid was closed using a gasket to have a proper sealing. The reactor was heated up using an induction unit (5-100 KW, Superior Induction Company, California, US) with an on-off controller. The pressure inside the reactor was measured using a pressure gauge (15 psi) acting as a pressure relief valve (McMaster-Carr, Cleveland, OH, USA). A stainless-steel shell and tube condenser kept in a water bath (filled by tap water) was used to collect condensable vapours. Non-condensable gases exiting the condenser would then pass through a cotton filter and eventually directed to the exhaust line.
Figure 2-1: Schematics of mechanically mixed flow reactor (MFR) used for pyrolysis of corn grains.

Figure 2-2: Process Flow Diagram (PFD) of mechanically mixed flow reactor.
2.2.2 Experimental methods

In each batch slow pyrolysis test, 500 grams of biomass were loaded into the reactor. The mixer speed rate was at 30 to 40 rpm for all experiments. The reactor was heated up to the final desired temperatures of 450 to 650 ºC at a heating rate of 10 to 20 ºC/min. Once the reactor reached the final temperature, it was held for further 30 minutes to make sure all the feedstock inside the reactor was completely pyrolyzed. The bio-char and bio-oil were collected from the reactor and condenser respectively after cooling down the entire set up overnight. The bio-oil yield was determined by weighing the condenser and cotton filter before and after each experiment (equation 2-1). The bio-char yield was determined directly by weight of the residual material collected from the reactor (equation 2-2). The non-condensable gas yield was determined by difference (2-3).

\[
\text{Biooil Yield (wt. %)} = \frac{\text{Weight of full condenser} - \text{weight of empty condenser} + \text{difference weight of cotton filter (g)}}{\text{Weight of biomass (g)}} \times 100 \tag{2-1}
\]

\[
\text{Bio – char Yield (wt. %)} = \frac{\text{Weight of produced bio – char (g)}}{\text{Weight of biomass (g)}} \times 100 \tag{2-2}
\]

\[
\text{Non condensable gases (wt. %)} = 100 - \text{weight of biooil} - \text{weight of bio – char} \tag{2-3}
\]

2.3 Bio-oil characterization

2.3.1 Gas Chromatography – Mass Spectrometry (GC-MS)

2-Propanol was used as solvent for GC-MS analysis throughout the experiments. A solution of 50 mg/ml concentration was obtained by mixing 50 mg of sample with 1 ml of 2-Propanol. This was followed by filtering each sample through a 0.2-micrometer filter. The GC–MS system comprises of a gas chromatograph coupled to a quadrupole mass spectrometer (GC–MS QP 2010, Shimadzu) using a capillary column (DB- 5MS, 30 m × 0.25 mm i.d.; film thickness, 0.25 μm). The ion source temperature and interface
temperature of the Electron ionization (EI) was maintained at 200 °C and 250 °C, respectively. While using EI, the instrument was initially used in SCAN mode to acquire the identity of the compounds. The GC system was equipped with a split/spitless inlet. AOC-20S autosampler with a 10 μl syringe was employed to inject 1 μl of sample at a rate of 10 μl s⁻¹. Helium (UHP) was the carrier gas entering the system at a constant flow of 1.5 mL min⁻¹. The oven temperature program had an initial temperature of 40 °C, which was held for 10 min and then rose by 10 °C/min to 200 °C. It was held for 10 min and increased with the same heating rate of 10 °C/min to reach 300°C. The sample was held for another 30 min, with a total run time of 75 min. This temperature was selected to provide an effective separation of the compounds of interest.

2.3.2 High Performance Liquid Chromatography (HPLC)

The concentration of the main components, i.e. sugars, organic acids, furfural, 5-HMF, alcohols, and acetol, were determined by a Shimadzu high performance liquid chromatography (HPLC), using external standards for identification and quantification of peak areas. These components were quantified using an Agilent Hi-plex H (7.7 × 300 mm) column (Agilent USA, Santa Clara) at 50°C using 10 μL of injection volume, with H₂SO₄ 0.005 mol/L as the mobile phase at 0.5 mL/min, 50 °C, and RID-10A detector. Before injection, samples were diluted to the appropriate concentration with H₂SO₄ 0.005 mol/L and filtered through a 0.2 μm membrane filter.

2.3.3 Higher Heating Value (HHV)

Higher heating value of the bio-oil and bio-char was measured using a IKA C200 Oxygen Bomb Calorimeter (Wilmingon, USA) following ASTM D 240-92 [67]. For each sample, 0.3 to 0.4 g of bio-oil was weighed in a plastic bag and placed inside a quartz crucible. Then the column, which contained 5 ml DI water was filled with 30 bar oxygen and placed inside the Bomb Calorimeter. The HHV is the amount of heat released due to the combustion and increases the temperature of water inside the column. The instrument subtracts the heating value of the plastic bag from the heating value of the sample and shows the HHV by unit mass of the sample.
2.3.4 Water content

The water content of bio-oil was determined using Karl Fischer titration (Mettler Toledo V20) following ASTM E203-16 [68].

2.4 Bio-char characterization

2.4.1 Surface Area (BET)

Surface area measurements for bio-char and activated carbon samples were obtained using the Brunauer-Emmett-Teller B.E.T. method. This was carried out using a Nova 1200e Surface Area & Pore Size Analyzer (Quantachrome Instrument, Florida, US). 0.3 g of each samples were subjected to tests by nitrogen gas sorption at 77.35 K. Samples were then degassed at 105°C for 1 hour to remove any moisture content. This was followed by subjecting the samples to elevated temperatures (300°C) and maintaining them for at least 3 hours, prior to analysis.

2.4.2 Scanning Electron Microscopy (SEM) analysis

SEM-EDX analysis of the biomass and bio-char samples was performed using the Hitachi SU3500 Scanning Electron Microscope (SEM) combined with an Oxford AZtec X-Max50 SDD energy dispersive X-ray (EDX) detector available at Surface Science Western. Backscatter Electron (BSE) imaging was used to provide a superior analysis of the particles, with variations in greyscale based on the average atomic number of the material. EDX is a semi-quantitative technique capable of detecting all elements with a minimum detection limit of approximately 0.5 wt%. An accelerating voltage of 10-kV was used for these analyses. The samples surfaces were coated with a thin layer of gold to minimize any charging effects.

2.4.3 Thermogravimetric Analysis (TGA)

TGA tests were performed using the Pyris I TGA Thermogravimetric Analyzer (PerkinElmer, Massachusetts, United States) also available at Surface Science Western. In each experiment, approximately 8–10 mg of each sample were heated from 30 °C to
750 °C with a heating rate of 15 °C min⁻¹, and nitrogen flow rate of 50 mL min⁻¹, under atmospheric pressure. The gas was then changed to air with the flow rate of 50 mL min⁻¹ and maintained in this condition for 15 minutes. Since the previous method shows wrong results for raw corn, another method was developed. 5 mg of the sample was heated from 30 °C to 300 °C with a heating rate of 10 °C min⁻¹ nitrogen flow rate of 50 mL min⁻¹, sample was held at 300 °C for 30 minutes, and the temperature was then raised to 700 °C. The sample was held at 700 °C for 5 minutes. The last step was to reduce the temperature from 700 °C to 50 °C with 10 °C min⁻¹.

2.4.4 Thermogravimetry – Infrared Spectroscopy (TG-FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is an optical spectroscopy technique that allows to determine the bonding present in a material. It is sensitive to components that are present in concentrations greater than approximately 3 – 5 wt.% of the total. Small portions of the samples were analyzed by FTIR spectroscopy using the Platinum® attenuated total reflectance (Pt-ATR) attachment equipped with a diamond crystal in the main box of a Bruker Tensor II spectrometer, Coventry, England. This experimental setup allows one to analyse an area of approximately 2mm x 2mm to a depth of 0.6 – 5 microns. The spectra were collected from 4000 – 400 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans. The spectra were corrected for the contribution from water vapour and carbon dioxide. Some of the spectra were baseline corrected.

2.4.5 pH

The pH of bio-char samples produced at different temperatures (450 to 650 °C). The pH was measured based on the Rajkovich et al [69] procedure. One gram of each sample of bio-char was suspended in 20 ml of deionized water. All the samples were put in the BNIS-100 Bionexus Thermo Incubator Shaker (Oakland, CA, USA) for 1.5 hours. The slurry was filtered with Whatman, Grade 1 filter paper and the pH was measured by the Orion 2 STAR pH meter (Thermo Fisher Scientific, Massachusetts, United States).
2.4.6 Micro Gas Chromatography (Micro-GC)

A Varian mobile Micro-GC (CP-4900) equipped with M5Å (Molecular Sieve 5 Å, 10 m), PPU (PolarPlot U, 10 m), and 5 CB (CP-Sil 5 CB, 8 meter) column modules was used to analyze the concentration of H2, CH4, CO, CO2, C2H4, C2H6, C3H6, C3H8, and C4H10. Helium and Argon (99.999%) were used as carrier gases for the thermal conductivity detector (TCD) at a pressure of 80 psi. Prior to their entry into the Micro-GC, the carrier gases were passed through an external gas clean moisture and oxygen filter to eliminate any suspended moisture and traces of oxygen associated with the carrier gas. The gas components from each sample were detected over a period of 3.0 min and automatically integrated using the Galaxie software. Due to the high utilization frequency, the micro-GC was conditioned every week. The conditioning time was extended overnight to remove any water present inside the column as a result of the gas samples or the carrier gas. The conditioning was carried out by maximizing the oven temperature. Each gas sample was analyzed a minimum of three times, and the average was calculated to determine the gas concentration.

2.5 Bio-char upgrading by activation

2.5.1 Experimental setup

Samples of bio-char obtained from the pyrolysis of corn grains at different temperatures were physically activated using a SS316 tubular reactor with 5 cm O.D and 100 cm long. A 240 volts electric tube furnace (Lindberg/Blue M, Ashville, USA) was used for heating up the activation reactor, which consists of built-in temperature control system (Figure 2-3).
2.5.2 Experimental methods

The bio-char activation experiments were performed in the tube furnace reactor at 900 °C using CO2 flowrate of 0.5 L/min and different holding times (0.5 to 3 hours) [71]. In each experiment, 50 g of bio-char was loaded into the furnace. Once the furnace reached 900 °C, it was maintained at that temperature for 0.5, 1, 2, or 3 hours.

2.6 Adsorption experiments

Adsorption studies were performed using solutions of methylene blue, methyl orange, and ibuprofen model compounds. The concentration of methyl orange and methylene blue solutions was 250 mg/L containing 1 g of bio-char, activated bio-char, or commercial activated carbon (CAC). CAC samples (Norit® SX2, CAC number 7440-44-0) were purchased from Sigma Aldrich, Canada. They were produced from peat, activated with steam and acid washed. However, the ibuprofen concentration was 120 mg/L adding 100 mg of adsorbents [72, 73].

All the adsorption experiments were done at room temperature (25°C) in a stirrer (INTLLAB) with constant agitation rate for 3 hours. The concentration of samples was measured using UV-VIS spectrophotometer (Thermo Scientific Evolution 220). The amount of MB, MO, and ibuprofen components adsorbed was calculated using equation (2-4):

\[
Q = \frac{(C_0 - C_t)V}{m}
\]  

(2-4)
Where \( C_0 \) (mg/L) is the initial concentration of solution, \( C_t \) is the solution concentration after adsorption. \( V \) (mL) is the dye volume and \( m \) (g) is the amount of adsorbent [74].

2.6.1 UV-VIS spectrophotometer

The initial and final concentration of solution during the adsorption experiments was measured using UV-vis spectrophotometer. Plastic cuvettes were used for methyl orange and methylene blue and quartz cuvettes for ibuprofen. The maximum wavelength for MB, MO, and ibuprofen was assumed 668, 464, and 220 nm, respectively. Each cuvette was filled with a specific ratio of solution and DI water to reach 3 ml and put the cuvette inside the instrument.
Chapter 3

3 Results and Discussion

3.1 Feedstock characterization

The proximate analysis of raw corn shows the high percentage of volatile content. The nitrogen percentage (1.34 %) is higher than typical forestry wastes (0.5-1.3 %) [61], which is promising for producing biochar with high quality for fertilizer applications (Table 3-1). Maximum DON levels according to the US Food and Drug Administration (FDA) for human and animals consumption are shown in Table 3-2 [14]. The concentration of DON in the feedstock was measured using an Enzyme-Linked Immunoassay (ELISA), Diagnostix, EZ-TOX DON (detection limit 0.5 ppm) by SGS Canada Inc., Hensall, Ontario was found to be 0.7 ppm, in contrast to the reported information from the providers at the time of sample collection.

<table>
<thead>
<tr>
<th>Proximate analysis (wt.%)</th>
<th>Raw corn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>8.21</td>
</tr>
<tr>
<td>Volatiles</td>
<td>79.87</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>10.95</td>
</tr>
<tr>
<td>Ash</td>
<td>0.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate analysis (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>O</td>
</tr>
</tbody>
</table>

\[ \text{High heating value (MJ kg}^{-1}) \] 15.98

---

1 By difference

2 By difference
Table 3-2: Standard DON levels in human and animal food according to FDA (ppm)

<table>
<thead>
<tr>
<th></th>
<th>Ruminating beef, feedlot cattle and chickens</th>
<th>Swine</th>
<th>All other animals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human</td>
<td>1</td>
<td>5, not to exceed 50 % of the diet</td>
<td>5, not to exceed 40 % of the diet</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Production yields

3.2.1 Effect of temperature

Figure 3-1 illustrates the effect of temperature on the product yields from slow pyrolysis of contaminated corn. The bio-oil yield increases (30% to 46%) as the pyrolysis temperature increases from 450 °C to 650 °C, while the bio-char yield decreases (42% to 24%). Duplicate experiments confirmed the accuracy of the results as shown in the figures of section 3.2. The gas yield remained almost constant over all different experiments. Three primary competitive reactions (corn to bio-oil, corn to bio-char, and corn to gas) convert biomass to bio-products and higher pyrolysis temperatures typically accelerate the reactions that produce bio-oil, resulting in lower char production. This trend is aligned with previous studies on corn starch [62, 65].
3.2.2 Effect of heating rate

Figure 3-2 depicts the effect of heating rate on the pyrolysis yield of corn grains. The heating rates tested ranged from 5 °C min\(^{-1}\) to 35 °C min\(^{-1}\). The effect of heating rate was similar to the effect of temperature on the yield of products. Bio-oil production increases at higher heating rates, while char production decreases.
3.3 Bio-oil product

3.3.1 GC-MS analysis

GC-MS analysis was performed on bio-oils produced at temperatures between 450 °C to 650 °C. The bio-oil mainly consisted of an aqueous phase and only a thin organic layer on top (Figure 3-3). As it is evident from Table 3-3, the peak areas were highest for acetic acid, followed by levoglucosan. The acetic acid peak area percentage was 51% at 450 °C and 54% at 500 °C. However, at higher temperatures it relatively decreased and stayed constant at 47%. The highest peak area percentage of levoglucosan was 20% at 650 °C. The peak percentages provided with GC-MS are only a rough indication of the relative concentrations of the different components identified, which quantified by HPLC in the next section.

Figure 3-2: Effect of heating rate on the yields of products (reaction time: 30 minutes, target temperature: 500 °C)
Figure 3-3: Schematic of bio-oil composed of two phases (organic phase and aqueous phase)
### Table 3-3: Chemical constituents of bio-oil identified by GC-MS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Peak area (%)</th>
<th>Temperature (°C)</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td></td>
<td></td>
<td>50.72</td>
<td>54.23</td>
<td>47.28</td>
<td>47.09</td>
<td>47.34</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>1.62</td>
<td>ND(^3)</td>
<td>1.27</td>
<td>1.45</td>
<td>1.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furfural</td>
<td>7.40</td>
<td>10.40</td>
<td>4.05</td>
<td>ND</td>
<td>ND</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-methyl-2-Furancarboxaldehyde</td>
<td>4.48</td>
<td>4.13</td>
<td>2.20</td>
<td>1.34</td>
<td>1.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,3-dimethyl-2-Butanone</td>
<td>2.21</td>
<td>1.85</td>
<td>2.20</td>
<td>1.15</td>
<td>1.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-(acetyloxy)-2-Butanone</td>
<td>1.85</td>
<td>1.56</td>
<td>1.25</td>
<td>0.87</td>
<td>0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-hydroxy-3-methyl-2-cyclopenten-1-one</td>
<td>2.82</td>
<td>3.06</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maltol</td>
<td>1.62</td>
<td>1.71</td>
<td>1.52</td>
<td>0.50</td>
<td>0.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4:3,6-Dianhydro-.alpha.-d-glucopyranose</td>
<td>4.07</td>
<td>3.18</td>
<td>5.90</td>
<td>4.60</td>
<td>3.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>levoglucosan</td>
<td>6.69</td>
<td>4.32</td>
<td>4.87</td>
<td>15.94</td>
<td>20.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>1.38</td>
<td>1.14</td>
<td>2.31</td>
<td>2.90</td>
<td>1.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Furanmethanol</td>
<td>1.49</td>
<td>ND</td>
<td>1.38</td>
<td>1.53</td>
<td>1.87</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-4: GC-MS result for the bio-oil at 450 °C

\(^3\) Not detected
Figure 3-5: GC-MS result for the bio-oil at 500 °C

Figure 3-6: GC-MS result for the bio-oil at 550 °C

Figure 3-7: GC-MS result for the bio-oil at 600 °C
3.3.2 HPLC

The main bio-oil components in the samples were quantified by HPLC. Table 3-9 reports the production of five main components in the bio-oil at different pyrolysis temperatures. The highest yield of acetic acid occurred at 600 °C, which was 26 g/kg of bio-oil. Levoglucosan is the second components that shows higher yield at 650 °C, around 13 g/kg of bio-oil.
3.3.3 Water content and HHV

The bio-oil water content is dependent on both the initial moisture content of the feedstock and dehydration reactions during pyrolysis [8]. Figure 3-10 shows that the water content of bio-oil decreased by increasing the final target temperature, while the high heating value of samples increased. The maximum water content (85%) and HHV (1.8 MJ/kg) of bio-oil were observed at 450 °C and 650 °C, respectively. The key products of thermal degradation of starch are levoglucosan and condensable fraction, which includes water [65]. Since corn grains are mainly composed of starch (70%), one reason for high-water content percentages may be the water released during starch thermal degradation. The HHV of bio-char increased from 23 to 29 MJ/kg (Figure 3-11), which is significant compared to raw corn HHV (16.6 MJ/kg). As the HHV increases, C–C bonds, which have a high energy content, make up more of the bonds, while C–H and C–O bonds are broken down [64]. Water is the main liquid product from the primary
reactions of the solid material. The organic phase or heavier components are generated from the secondary reactions of the condensable organic compounds [62, 65].

**Figure 3-10**: Water content and HHV of bio-oil samples at temperatures between 450 to 650 °C

**Figure 3-11**: HHV of bio-char samples produced at temperatures between 450 to 650 °C
3.3.4 DON concentration in bio-oil

DON concentration in the samples, including bio-oil at 450 °C, 550 °C, 650 °C, and activated bio-chars, were measured using ELISA, Diagnostix, EZ-TOX DON (detection limit 0.5 ppm) as discussed in Chapter 2. The results illustrate that the DON concentration is less than 0.5 ppm in all samples, which is negligible. Even though the primary exposure risk of DON for human is through consumption [13], it is good to know that DON was completely destroyed during the pyrolysis process.

3.4 Bio-char product

3.4.1 Physical and chemical characteristics

Table 3-4 illustrates that the hydrogen and oxygen content of bio-chars decreased by increasing the pyrolysis temperature, while the carbon and ash content increased. The highest amount of fixed carbon was observed at 650 °C, which is about 82%. A decrease in oxygen and hydrogen content is due to the easy cracking of weak bonds at higher temperatures, producing H₂O, CO, and CO₂ [75]. Compared to woody and grassy feedstocks, which have less than 1% nitrogen content [3, 21], corn biomass has a higher nitrogen content of 2%, which makes it more attractive as a potential fertilizer for soil amendment applications (Figure 3-12).

![Figure 3-12: Bio-char produced at 550 °C from toxic corn grains](image-url)
Table 3-4: The effect of pyrolysis temperature on the yield of products and characteristics of bio-char

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bio-char yield (wt.%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>41.05</td>
<td>36.85</td>
<td>31.45</td>
<td>27.65</td>
<td>23.65</td>
</tr>
<tr>
<td><strong>Bio-oil yield (wt.%)</strong></td>
<td></td>
<td>29.6</td>
<td>34.3</td>
<td>39.4</td>
<td>43.55</td>
<td>46</td>
</tr>
<tr>
<td><strong>Non-condensable gases (wt.%)</strong></td>
<td></td>
<td>29.35</td>
<td>28.85</td>
<td>29.15</td>
<td>28.8</td>
<td>30.4</td>
</tr>
</tbody>
</table>

**Proximate analysis (wt.%)**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td></td>
<td>1.95</td>
<td>1.89</td>
<td>1.88</td>
<td>2.8</td>
<td>2.54</td>
</tr>
<tr>
<td>Volatiles</td>
<td></td>
<td>49.87</td>
<td>32.55</td>
<td>24.9</td>
<td>15.38</td>
<td>7.33</td>
</tr>
<tr>
<td>Fixed Carbon⁵</td>
<td></td>
<td>44.09</td>
<td>60.94</td>
<td>67.5</td>
<td>74.13</td>
<td>81.77</td>
</tr>
<tr>
<td>Ash</td>
<td></td>
<td>4.09</td>
<td>4.62</td>
<td>5.72</td>
<td>7.69</td>
<td>8.36</td>
</tr>
</tbody>
</table>

**Ultimate analysis (wt.%)**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td></td>
<td>72.56</td>
<td>73.16</td>
<td>75.66</td>
<td>79.12</td>
<td>82.65</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>3.94</td>
<td>4.19</td>
<td>3.34</td>
<td>2.47</td>
<td>1.49</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td>2.2</td>
<td>1.75</td>
<td>2.14</td>
<td>2.3</td>
<td>2.44</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H/C</td>
<td></td>
<td>0.054</td>
<td>0.057</td>
<td>0.044</td>
<td>0.031</td>
<td>0.018</td>
</tr>
<tr>
<td>O/C</td>
<td></td>
<td>0.29</td>
<td>0.30</td>
<td>0.25</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>6.19</td>
<td>6.26</td>
<td>6.69</td>
<td>7.28</td>
<td>7.45</td>
</tr>
<tr>
<td>High heating value (MJ kg⁻¹)</td>
<td></td>
<td>23.67</td>
<td>27.75</td>
<td>28.48</td>
<td>30.44</td>
<td>29.55</td>
</tr>
</tbody>
</table>

⁴ By difference
⁵ By difference
⁶ By difference
3.4.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on biomass (raw corn), bio-char produced at 450 to 650 °C, and ACB-3h to investigate the thermal degradation behaviour. The DTG curve in Figure 3-13 shows that degradation started around 80°C due to moisture loss, followed by another major weight loss at 300 °C (45 % reduction) caused primarily by starch decomposition reactions. This 45 % weight reduction was observed after 30 minutes holding time at 300 °C during the TG analysis.

Qiao et al., 2019 [64] studied the pyrolysis of corn starch and the results showed the major decomposition during corn starch pyrolysis takes place between 320-354 °C, which is not a wide range compared to other feedstocks (Figure 1-6 (a)). This is due to the difference in the structure of the feedstocks. Table 3-5 shows that corn is mainly composed of starch (70%) and protein (10%) [76]. However, most of the other feedstocks are composed of hemicellulose, cellulose, and lignin [21]. The TGA results match the work conducted by Yang et al. on maize [65] (section 1.4.1). According to these studies [64, 65] the main decomposition of corn starch happens between 300 °C to 400 °C, which is the temperature of starch decomposition.

Figure 3-14 illustrates that activated bio-char and BC-650 have a small weight loss, which seems to be a slight downward trend (~5%), due to devolatilization and almost complete removal of components during the pyrolysis at 650 °C and activation at 900 °C. However, BC-450 and BC-550 show 35% and 15% weight loss, respectively. Since during pyrolysis at temperatures above 600 °C, the majority of the volatiles and starch are already gone from the biochar structure, the weigh loss percentage seen through TGA is not significant.
Table 3-5: Composition of corn grains (adapted from [76])

<table>
<thead>
<tr>
<th>Material</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>71.7</td>
</tr>
<tr>
<td>Cellulose</td>
<td>2.4</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>5.5</td>
</tr>
<tr>
<td>Protein</td>
<td>10.3</td>
</tr>
<tr>
<td>Oil</td>
<td>4.3</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.2</td>
</tr>
<tr>
<td>Ash</td>
<td>1.4</td>
</tr>
<tr>
<td>Other</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Figure 3-13: TGA and DTG of raw corn biomass
3.4.3 pH

The pH of bio-char suspension in water increases with temperature due to the increase in ash content of bio-char [48]. Table 3-4 shows that the bio-char is alkaline, which pH ranging from 6.19 to 7.45 at temperatures rising from 450 °C to 650 °C. The alkalinity of bio-char makes it a good fertilizer for soil amendment in order to decrease soil acidity [3]. Table 3-4 shows the average pH of the bio-char dispersion in water at different temperatures.

Figure 3-14: TGA and DTG results for bio-char produced at 450, 550, and 650 °C (holding time: 30 min), and activated bio-char with activation holding time of 3 hours.
3.4.4 FTIR

FTIR is utilized for both structural determination of organic compounds and for bio-char bond description [3]. Figure 3-15 shows the FTIR patterns for raw corn and bio-char products. Four main regions are identified: single bond (alcohol and hydroxyl components), triple bond, double bond, and fingerprint. Fingerprint region consists of complex components with different bonds, overlapping with each other [77–79].

Table 3-6 shows the wavenumber corresponding to the main peaks and the functional groups attributed to each region. In the corn starch spectrum, O–H, CH$_2$, and –C–C– stretching vibrations are attributed to 3200-3400, 2850-2900, and 1600-1700 wavenumber (cm$^{-1}$), respectively. For raw corn, the peaks with 1300-1450 cm$^{-1}$ and 850-900 cm$^{-1}$ wavenumber represents O–H and –C–C–bending vibration [80]. Raw corn has the highest number of peaks at single bond and fingerprint region. The changes show that by increasing the temperature, the intensity of light components (3252 band) with hydroxyl (–OH) and carboxyl (–COOH) groups decreased for bio-char at 450 °C and disappeared at higher temperatures. Raw corn has two peaks with high absorbance intensity of 3252, and 1014, showing the presence of great number of alcohols, hydroxyls, and aliphatic compounds in its structure, compared to other samples. As the temperature increases, only complex compounds within the fingerprint region remained. For instance, two peaks of 1581 and 868 show the aromatic rings, and 1155 shows the amine compounds with CN stretch. This finding is aligned with the ratio of H/C and O/C from the elemental analysis illustrated in Table 3-4. These two ratios decreased by increasing the temperature [81], which confirms the disappearance of light components.

Figure 3-15 illustrates that complex compounds such as aromatics and aliphatic can be seen even at high temperatures (900 °C). The results are in accordance with another studies by A. R. Oromiehie et al. [80] and Kizil et al. [77].

When the hydroxyl (–OH) and carboxyl (–COOH) groups disappear from the surface of the bio-char, the negative charge of the bio-char decreases, which affects the adsorption characteristics and the bio-char is then more basic. Table 3-4 indicates that the pH of bio-
char suspension in water increased by increasing the target processing temperature, which is consistent with FTIR results [78].

Table 3-6: FTIR peaks analysis (adapted from [78])

<table>
<thead>
<tr>
<th>Spectrum Region</th>
<th>Region wavenumber range (cm(^{-1}))</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Functional group/assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single bond (O-H, N-H, C-H)</td>
<td>4000-2500</td>
<td>3252</td>
<td>3400-3200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2919</td>
<td>2935-2915</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2847</td>
<td>2865-2845</td>
</tr>
<tr>
<td></td>
<td>3300-3030</td>
<td>Ammonium ion, NH(_4^+)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2500-2000</td>
<td>No peak was observed</td>
<td>-</td>
</tr>
<tr>
<td>Triple bond (C≡C, C≡N)</td>
<td>2500-2000</td>
<td>No peak was observed</td>
<td>-</td>
</tr>
<tr>
<td>Double bond (C=C, C=O, C=N)</td>
<td>2000-1500</td>
<td>1581</td>
<td>1615-1580</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1328</td>
<td>1410-1310</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1630-1575</td>
<td>(-N=N-)</td>
</tr>
<tr>
<td></td>
<td>1075 and 1014</td>
<td>1150-1000</td>
<td>Aliphatic fluoro compounds. C-F stretch</td>
</tr>
<tr>
<td></td>
<td>868</td>
<td>800-860</td>
<td>Aromatic ring (para)</td>
</tr>
<tr>
<td></td>
<td>770</td>
<td>770-735</td>
<td>Aromatic ring (ortho)</td>
</tr>
<tr>
<td>Fingerprint</td>
<td>1500-500</td>
<td>1155</td>
<td>1190-1130</td>
</tr>
<tr>
<td></td>
<td>1075 and 1014</td>
<td>1150-1000</td>
<td>Aliphatic fluoro compounds. C-F stretch</td>
</tr>
<tr>
<td></td>
<td>868</td>
<td>800-860</td>
<td>Aromatic ring (para)</td>
</tr>
<tr>
<td></td>
<td>770</td>
<td>770-735</td>
<td>Aromatic ring (ortho)</td>
</tr>
</tbody>
</table>
Figure 3-15: FTIR spectra of raw corn, bio-char produced at 450, 550, and 650 °C (holding time: 30 min), and activated bio-char produced at 900 °C with activation holding time of 3 hours

3.4.5 BET surface area and porosity analysis

Measuring different parameters such as surface area, pore volume, and porosity of the bio-char helps to develop a thorough understanding of its adsorption capacities. Table 3-7 indicates that the porosity and BET surface area of the bio-char before activation is low. However, activating the bio-char increases its specific surface area as shown in Figure 3-16. The surface area of the ACB increased significantly from 63 m²g⁻¹ to 419 m²g⁻¹ by increasing the activation time from 0.5 h to 3 h. The maximum BET surface area achieved during the experiments is almost similar to that of CAC (595 m²g⁻¹).
Increasing the activation time increases the evolution of volatiles from bio-char, leading to the development of the pores structures (Table 3-7). Continuous activation improves pore formation and also creates new pores, increasing the BET specific surface area and the total pore volume.

**Table 3-7: BET surface area and pore volume results for bio-char produced at 450, 550, 650 °C and activated bio-char produced at 900 °C with activation times of 0.5 to 3 hours**

<table>
<thead>
<tr>
<th>Sample name-</th>
<th>BET surface area (m²g⁻¹)</th>
<th>Pore volume (cm³g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrolysis temperature (°C)-activation time (hour)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC-450-0</td>
<td>0</td>
<td>0.003</td>
</tr>
<tr>
<td>BC-550-0</td>
<td>0.13</td>
<td>0.013</td>
</tr>
<tr>
<td>BC-650-0</td>
<td>2.84</td>
<td>0.01</td>
</tr>
<tr>
<td>ACB-500-0.5</td>
<td>63</td>
<td>0.04</td>
</tr>
<tr>
<td>ACB-500-1</td>
<td>151</td>
<td>0.094</td>
</tr>
<tr>
<td>ACB-500-2</td>
<td>253</td>
<td>0.149</td>
</tr>
<tr>
<td>ACB-500-3</td>
<td>419</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Figure 3-16: Effect of activation holding time on the surface area of activated bio-char samples produced at 900 °C with activation holding times of 0.5, 1, 2, and 3 hours, also comparing their BET surface areas with that of CAC.

3.4.6 SEM analysis

The surface morphology of corn, bio-chars, and activated bio-chars are shown in the SEM images of Figure 3-17 and Figure 3-18 with two different magnitudes of ×100 and ×500, respectively. Figure 3-18 illustrates that the raw corn surface is smooth and homogenous with no pores. SEM images show that the structure of corn changed from non-porous to a porous structure after pyrolysis. At 500 °C, some pores are detected, however, the presence of volatiles does not allow for the formation of more pores (Figure 3-18 b). The results shows that the size and quantity of pores developed by increasing the pyrolysis temperature (Figure 3-18, c and d) attributed to further removing volatiles or organic matters from the whole char structure [75]. This finding is in agreement with the literature [82, 83]. Activation affects the number of pores and also the appearance of the cracks (channel structure), increasing externally available surface area of the activated bio-char [84]. Figure 3-18 shows by increasing the activation time from 1 hour to 3 hours, an obvious increase of pores and surface heterogeneity was observed in correspondence with the increase in the BET surface area from 63 to 419 m²g⁻¹ and in the
pore volume from 0.04 to 0.23 cm³g⁻¹ (section 3.4.5), which confirms the SEM images results.
Figure 3-17: SEM images (100 magnitude) of (a) raw biomass, (b) bio-char at 500 °C, (c) bio-char at 600 °C, (d) bio-char at 650 °C, and activated bio-chars produced at 900 °C with activation times of (e) 0.5, (f) 1, (g) 2, and (h) 3 hours
Figure 3-18: SEM images (500 magnitude) of (a) raw biomass, (b) bio-char at 500 °C, (c) bio-char at 600 °C, (d) bio-char at 650 °C, and activated bio-chars produced at 900 °C with activation times of (e) 0.5, (f) 1, (g) 2, and (h) 3 hours.
3.4.7 DON concentration in bio-char

The DON concentration in the samples including bio-chars at 450 °C, 550 °C, 650 °C, and activated bio-chars were measured using ELISA, Diagnostix, EZ-TOX DON (detection limit 0.5 ppm) by SGS Canada Inc., Hensall, Ontario. The results illustrate that the DON concentration was less than 0.5 ppm in all samples, which is considered negligible.

3.5 Non-condensable gases

3.5.1 Gas characterization

The gas composition of four gas bag samples produced during pyrolysis at temperatures of 300, 400, 500, and 550 °C was analyzed using a Micro-GC (Figure 3-19). Duplicate experiments confirmed the accuracy of the results in section 3.5. CO and CO₂ were present in the highest concentrations, followed by lower percentages of CH₄, H₂, and C₂H₄. The amount of H₂ increased with increasing temperatures, because more volatiles leave the structure of the biomass at higher temperatures.

Figure 3-19: Gas composition of samples produced during pyrolysis at temperatures of 300, 400, 500, and 550 °C
3.5.2 Gas flow rates measurements

The gas flow rates produced during the pyrolysis were measured using a 100 ml bubble flow meter, purchased from Sigma-Aldrich, Canada, when the reactor had reached the pyrolysis temperatures of 300, 400, 500, and the final target temperature of 550 °C. The flow meter was connected to the gas exit line (Figure 3-20) and the produced gas temperatures at the measuring location were measured using a thermocouple. The gas flow rates increased from 2 to 6 L min\(^{-1}\) between 300 and 500 °C and started decreasing after reaching 500 °C until no further gas was detectable after 1 hour (Figure 3-21). The gas temperature of the produced gas increased from 29 to 40 °C during the reaction time. No significant gas production was noticeable before 280 °C and the first was at 300 °C. Also, the results show that most of the cracking products were generated between 300 and 500 °C, similarly to the previously reported studies involving the cracking of starchy feedstocks [64, 85].

![Image of bubble flow meter](image)

Figure 3-20: Schematic of bubble flow meter during gas flow meter measurements
3.6 Activated bio-char

3.6.1 Physical and chemical characteristics

Yields of activated bio-chars were calculated by loading the same amount of bio-chars (50 g) produced at various temperatures of 450, 500, 600, and 650 °C and then subtracting the remained weight of biochar after the activation divided by the original weight. The holding time for all four samples was 3 hours during which the activation conditions were held constant. Since, BC-650 samples contain less volatiles (7 %, Table 3-4), no significant weigh loss occurred after activation. Therefore, higher yields were observed for ACB-650 and ACB-600 compared to ACB-500 and ACB-450 (Figure 3-22). Although the yield of activated bio-char per gram of raw bio-char increased from 48% to 85%, the yield of activated bio-char per gram of biomass as shown in Figure 3-22 remained constant (20%) over the experiments at different temperatures.
Figure 3-22: Yield of activated carbon produced by using bio-char samples generated at 450, 500, 600, and 650 °C with the same activation time of 3h based on the gram of bio-char and biomass.

Table 3-8 illustrates the elemental analysis for the four activated bio-chars produced at different holding times of 0.5, 1, 2, and 3 hours. The carbon content of activated bio-chars is 84%, which is ~10% higher compared to its original bio-char (73.2%). Activated carbons with high carbon contents have a potential use in catalytic applications. Also, activated bio-char with high nitrogen percentages is practical as a fertilizer in soil [86]. Adding activated bio-char to the soil has been proven to be beneficial. The high number of pores and increased surface area of the activated bio-char are two parameters that make it valuable as a soil amendment by increasing its porosity (storing the minerals), pH, and water retention capabilities [87].

Table 3-8: Elemental analysis results for four activated bio-chars produced with different activation holding time of 0.5, 1, 2, 3 hours

<table>
<thead>
<tr>
<th>Sample name-activation time (h)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACB-0.5h</td>
<td>84.73</td>
<td>0.6</td>
<td>2.19</td>
<td>0</td>
<td>12.48</td>
</tr>
<tr>
<td>ACB-1h</td>
<td>84.79</td>
<td>0.7</td>
<td>2.39</td>
<td>0</td>
<td>12.11</td>
</tr>
<tr>
<td>ACB-2h</td>
<td>84.41</td>
<td>0.64</td>
<td>1.56</td>
<td>0</td>
<td>13.38</td>
</tr>
<tr>
<td>ACB-3h</td>
<td>84.0</td>
<td>1.49</td>
<td>1.53</td>
<td>0</td>
<td>12.98</td>
</tr>
</tbody>
</table>
3.7 Application of bio-char and activated bio-char to adsorption

3.7.1 Methylene blue (MB)

The adsorption performance of original bio-chars and of the activated bio-chars produced from the pyrolysis of corn grains was measured using dyes (MB and MO) as model molecules and ibuprofen as a real molecule representing a typical pharmaceutical. The results were also compared with commercial activated carbon for further investigation. Two main reasons for choosing methylene blue (MB), methyl orange (MO), and ibuprofen for adsorption experiments are: being UV active and their different molecular sizes (MB = 2 nm, MO = 1.2 nm, IBU = 1 nm). Methylene blue is a cationic molecule and its structure consists of 6 carbon aromatic rings, nitrogen, and sulphur [88]. The molecular size of this dye is ~2 nm [89] and its adsorption on the surface of the bio-char reveals the presence of mesopores in the structure of adsorbents [90]. The activated bio-char samples are represented as ACB at different activation holding times.

Adsorption of methylene blue molecules were performed using a constant bio-char sample mass (1 g). Figure 3-23 and Figure 3-24 illustrate the comparison between the performance of bio-char produced at 500 °C (BC-500) and of four activated bio-chars with holding times of 0.5 (ACB-0.5h), 1 (ACB-1h), 2 (ACB-2h), and 3 (ACB-3h) hours. CO₂ penetration into the internal structure of bio-char during activation leads to widening of the pores obtained from the pyrolysis step [91]. Figure 3-23 illustrates that the ACB-2h sample adsorbed about 11.5 mg of MB after 3 hours of contact time, which was higher compared to the other two samples in that group. Among all activated bio-char samples by activation duration time of 0.5, 1, 2, and 3 hours, ACB-3h showed the highest adsorption capacity, with a total adsorption (25 mg) of MB after 5 minutes (Figure 3-24 and Figure 3-25). This result is in agreement with Section 3.6.5’s results, which show that the BET surface area of activated bio-char (3 h) was higher (419 m²g⁻¹) compared to other activated carbons (63, 151, and 253 m²g⁻¹). The performance of ACB-3h was also compared to that of commercial activated carbon (CAC). Figure 3-24 shows CAC and
ACB-3h exhibit almost the same adsorption behaviour with only 3 minutes time difference, which could be due to the higher surface area of CAC (595 m$^2$ g$^{-1}$) compared to ACB-3h (419 m$^2$g$^{-1}$).

Figure 3-23: Methylene blue adsorption profiles for four samples of biochar generated at 500 °C and activated bio-chars produced at 900 °C with activation holding times of 0.5, 1, and 2 hours.
Figure 3-24: Comparison of MB adsorption profile using ACB-3h sample and commercial activated carbon (CAC)

Figure 3-25: Transformation of MB adsorption using 1 gram of ACB-3h adsorbent sample in 250 mg L\(^{-1}\) of MB solution

There are many parameters that can affect adsorption such as initial dye concentration, solution pH, amount of adsorbent, and temperature. In this study, the focus was the effect of pH. The effect of pH is different depending on the type of adsorbent [92]. Kannan et al. [73] discussed the pH effect on methylene blue (MB) adsorption and the results showed increased adsorption rates after increasing the pH for various adsorbents suspensions in water such as activated carbons from bamboo dust, coconut shells, rice
husks, and straw. According to the pK_a value of MB, MO, and IBU, which is 3.8, 3.5, and 4.9, respectively, their molecular charges are different at pH > pK_a. The MB molecule is positively charged at pH > 3.8, MO and IBU molecule are both negatively charged at pH > 3.5, and pH > 4.9, respectively [94–96].

Table 3-9 indicates how the pH of activated bio-char dispersion in water samples increased after increasing the activation time from 1 hour to 3 hours, which increased the adsorption rate. The activated carbon characteristics, such as surface area, porosity, pore volume, pore distribution, and functional groups, significantly affect the adsorption process [52]. In Section 3.6.5, the BET surface area, pore volumes, and comparison of activated bio-chars are discussed in detail.

Studies show that, apart from the parameters discussed above, the presence of functional groups such as aromatic rings –C=O, –C=N, –C–O–C–, –OH, –NH₂, –C=S, and –S=O on the surface of the adsorbent (activated bio-char) play a significant role in MB adsorption [89, 97]. In Section 3.4.4, FTIR results of ACB-3h illustrate the presence of –C=O, –C=N functional groups, which improved the MB adsorption mechanism.

**Table 3-9: Comparing the pH of bio-char suspension in water produced at 500 °C, activated bio-chars produced at 900 °C (different activation times changing from 0.5 to 5 hours), and CAC**

<table>
<thead>
<tr>
<th>Sample-activation time (hour)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC - 500 °C</td>
<td>6.26</td>
</tr>
<tr>
<td>ACB - 0.5</td>
<td>7.15</td>
</tr>
<tr>
<td>ACB - 1</td>
<td>7.75</td>
</tr>
<tr>
<td>ACB - 2</td>
<td>8.22</td>
</tr>
<tr>
<td>ACB - 3</td>
<td>8.98</td>
</tr>
<tr>
<td>ACB - 5</td>
<td>10.12</td>
</tr>
<tr>
<td>CAC - NA&lt;sup&gt;7&lt;/sup&gt;</td>
<td>6.59</td>
</tr>
</tbody>
</table>

<sup>7</sup> Not available
3.7.2 Methyl orange (MO)

Figure 3-26 shows the adsorption of methyl orange using original samples of the same type of bio-char and of the activated bio-chars used for the experiments described in section 3.7.1. The initial concentration of stock solution was 250 mg/L, which is similar to the MB experiments. The results show that almost 10 mg of MO out of 25 mg was adsorbed using 1 g of AC-2 h. Comparing the MB adsorption graphs in Figure 3-23 with Figure 3-26, the rate of MB adsorption in the first 30 minutes of the experiments was higher for the same experiment and activated samples.

![Graph showing adsorption profile](image)

**Figure 3-26: Methyl orange adsorption profile for four samples: biochar produced at 500 °C and activated bio-chars produced at 900 °C with activation holding times of 0.5, 1, and 2 hours**

One reason for observing different results, while using dye for both experiments could be related to the size of the molecules (MO: 1.2 nm, MB: 2 nm). Also, the adsorption of MB and MO occurs via electrostatic interactions, electron donor-acceptor relationships, or π-π
interactions. These forces develop between the functional groups on the surface of the carbon and of the dye molecules and any of them could be responsible for the different dye adsorption behaviour between two dyes [88].

Figure 3-27 shows the comparison between the adsorption performance of the ACB-3h sample and of the CAC sample. Total adsorption of MO (25 mg) occurred after 2 minutes using the CAC. However, the contact time required for the total adsorption increased to 8 minutes while using ACB-3h sample.

![Graph Comparison of MO adsorption profile using ACB-3h sample and commercial activated carbon (CAC)](image_url)

**Figure 3-27: Comparison of MO adsorption profile using ACB-3h sample and commercial activated carbon (CAC)**

### 3.7.3 A sample pharmaceutical: Ibuprofen

Ibuprofen with the molecular formula of $C_{13}H_{18}O_2$ is an anti-inflammatory drug with widespread global consumption. However, due to its chemical structure, it also spreads and accumulates widely in the aquatic environments, which is a serious concern for both humans and the environment [98, 99]. There are various chemical, physical, and biochemical processes for removing ibuprofen. The existing processes have two downsides: they are expensive processes and secondly, they are not sufficiently effective
Bio-chars and activated carbons acquired from agricultural by-products have high adsorption capacities and low costs. Therefore, these products offer good alternatives for drinking water treatments because of their strong interactions with organic contaminants in the aqueous phase [101].

Similar experiments were performed for ibuprofen starting with ACB-3h sample and exploring the adsorption profile of this pharmaceutical. Unlike MB and MO, ACB-3h did not demonstrate sufficient performance for removing ibuprofen from water since the contact time of 3 hours was required to remove the total amount of ibuprofen, which was 12 mg (Figure 3-28). Therefore, a bio-char sample was activated with a holding time of 5 hours to examine if this would improve the ibuprofen adsorption profile. After increasing the activation time to 5 hours (Figure 3-29), the adsorption contact time decreased from 3 hours to 15 minutes. The BET surface area of ACB-5h is 551 m²g⁻¹, which is similar to CAC (595 m²g⁻¹).

Figure 3-28: Ibuprofen adsorption profile using ACB-3h sample in an ibuprofen solution with the concentration of 120 mg L⁻¹.
3.8 Applications of bio-oil

3.8.1 Acetic acid

Acetic acid is the major organic acid in the bio-oil produced via pyrolysis. The market size of this valuable acid is expected to be USD 17.9 billion by 2024 [102]. Acetic acid has many applications including in the derivation of vinyl acetate monomer (VAM), which has been used for the production of paints, adhesives, and coatings. Acetic acid is also used by the food and medical industries [103]. There are several techniques for the separation of acetic acid, like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis membranes (RO). Compared to traditional separations, such as adsorption, solvent extractions, and distillation, membrane separations are more energy efficient and simple to operate [104, 105].

3.8.2 Levoglucosan

The main motivation for the pyrolysis of carbohydrates (starch, glucose, and cellulose) is the production of levoglucosan. Levoglucosan is an organic compound that can be used for the synthesis of polymers. Other applications of levoglucosan are as a carbon source...
for fermentation in order to produce bioethanol and itaconic acid [106]. Levoglucosan is expensive because its production generally results in low yields, yet it cannot be efficiently separated from a mixture. Many studies [106–108] report yields of levoglucosan between 30-70% using pure cellulose or starch. However, these processes have been carried out only at the lab-scale. Accordingly, efficient larger scale productions are required for commercial applications [65].

Separation of levoglucosan from other bio-oil components is challenging due to its compositional complexity. Choi et al. [106] discussed the effect of metal salt impregnation and microwave-assisted solvent pre-treatment for increasing the levoglucosan selectivity in Ashe juniper waste. Levoglucosenone (LGO) selectivity increased from 22 % to 25 % with a four-fold increase in the presence of CuSO₄ concentrations, and the microwave solvent treatment increased O/C and H/C ratios of Ashe juniper waste. Rover et al. [108] studied the purification of levoglucosan produced from red oak with bio-oil fractionation, liquid-liquid extraction, and resin filtration. The results showed a solution with 81 wt.% total sugars, which contains 45% wt.% levoglucosan.

Despite the identification of several value-added chemicals (levoglucosan, acetic acid) and the potential of the biochar as adsorbent, the commercial implementation of a process needs to be based on the economics derived from the products in relation to the energy requirements to sustain the process itself and all the costs associated with the downstream processing also pre-processing and post-processing to make the products marketable.

### 3.9 Applications of non-condensable gases

As mentioned in 1.3.4, the gas product is mainly used to provide heat to drive various processes, such as the pyrolysis process itself. The pyrolysis process was carried out at temperatures between 300 to 550 °C. The Higher Heating Value (HHV) of the gas mixtures was calculated using equation 3-1.
\[(\text{HHV}_v)_{T_r, P_r} = \Sigma (\text{HHV}_v)_{i, T_r, P_r} \times V_i\]  

3-1

Where:
- \(\text{HHV}_v\) is the higher heating value of the mixture on volumetric (mole) basis
- \((\text{HHV}_v)_{i, T_r, P_r}\) is the higher heating value of each component of the mixture at standard condition \((P_r = 1 \text{ atm and } T_r = 0 \text{ °C (273.15 K)})\) (Table 3-10)
- \(V_i\) is the mole (volumetric) fraction of the component

The standard calorific values for the gas components were evaluated based on National Renewable Energy Laboratory (NREL), USA standard values (Table 3-10).

<table>
<thead>
<tr>
<th>Component</th>
<th>Standard HHV (MJ/Nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>12.77</td>
</tr>
<tr>
<td>CO</td>
<td>12.62</td>
</tr>
<tr>
<td>CH₄</td>
<td>39.78</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>63.00</td>
</tr>
</tbody>
</table>

The molar percentages of each gas components was calculated from the Micro-GC analyses and shown in Table 3-11.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO</th>
<th>C₂H₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.1</td>
<td>8.9</td>
<td>52.7</td>
<td>1.8</td>
</tr>
<tr>
<td>400</td>
<td>11.0</td>
<td>19.0</td>
<td>51.1</td>
<td>2.3</td>
</tr>
<tr>
<td>500</td>
<td>13.6</td>
<td>20.1</td>
<td>50.2</td>
<td>1.8</td>
</tr>
<tr>
<td>550</td>
<td>16.1</td>
<td>20.0</td>
<td>42.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

By using these gas compositions in combination with the standard calorific values reported in Table 3-10 in equation 3-1, the HHV values of gas mixture was calculated at standard condition and reported in Table 3-12.
Table 3-12: HHV of gas stream at $T_r = 0$ °C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>HHV (MJ/Nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>11.63</td>
</tr>
<tr>
<td>400</td>
<td>16.87</td>
</tr>
<tr>
<td>500</td>
<td>17.24</td>
</tr>
<tr>
<td>550</td>
<td>16.46</td>
</tr>
</tbody>
</table>

Comparing the HHV of the gas produced at the highest temperature (16.5 MJ/m$^3$) with that of town gas, which is 18 MJ/m$^3$, confirms the possible future applications of this product for energy production.
4 Conclusions and Recommendations

4.1 Conclusions

In this study, contaminated corn was converted into value-added (e.g. bio-char and bio-oil) products, using slow pyrolysis in a batch reactor. The effect of pyrolysis on the deterioration of deoxynivalenol (DON) was a prominent decrease, from 5-7 ppm in the raw corn grains to zero ppm, making the thermochemical conversion a promising method for industrial applications.

The pyrolysis experiments were performed reaching final target temperatures between 450 and 650 °C, with typical heating rates of 15 to 20 °C/min. The results showed that bio-oil yields increased from 29 to 47 wt.%, while bio-char yields decreased from 41 to 25 wt.%. Gas yields remained approximately constant (30 %) over different experiments. The results showed that the maximum bio-oil yield was achieved at 650 °C (47 wt.%).

The effect of heating rate was investigated by extending the range of heating rates between 5 and 35 °C min⁻¹, and the result showed maximum bio-oil yield of 46 wt.% achieved at the highest heating rates of 35 °C/min.

Acetic acid and levoglucosan were the most significant components in the bio-oil, representing the highest GC-MS peaks, with yields of 26 and 13 per kg of bio-oil. The HHV of the bio-oil produced from the pyrolysis of corn is 2 MJ/kg at 650 °C, which is excessively low for its application as a fuel. The reason is that 65 % of the bio-oil is comprised of water at this temperature. However, compared to raw corn biomass (16.6 MJ/kg), the HHV of bio-char increased to 23-28 MJ/kg.

Bio-char, produced at 500 °C was physically activated at 900 °C using CO₂. The BET surface area of the activated bio-char increased significantly from 63 to 551 m² g⁻¹ when increasing the activation time from 0.5 to 3 hours also compared that of the original bio-char (0 to 2.8 m² g⁻¹). The high adsorption capacity of activated bio-char depends on the large pores, which were confirmed through SEM analysis. This activated bio-char showed a significantly improved adsorption potential compared to untreated bio-char.
Methylene Blue and Ibuprofen were completely adsorbed by activated corn bio-char after 5 and 15 minutes, respectively, showing a similar performance to that of Commercial Activated Carbon (CAC). The high adsorption rate of these two molecules is due to high pH (6 to 9) of the activated bio-char dispersion in water, and the presence of functional groups on the surface of the adsorbent, which was confirmed by FTIR analysis.

The gas product is comprised mainly of H2, CO, CO2, CH4, and C2H4 based on the Mic-GC analysis, and the HHV of this stream was calculated to be 16.46 MJ/Nm³, which shows the potential application of this product as an energy recovery source.

The results show the potential industrial applications of bio-oil, activated bio-char, and non-condensable gases as chemicals, adsorbents, and energy resources, respectively.

### 4.2 Recommendations

Since the adsorption results were promising, one recommendation for future study is to perform further adsorption experiments using real molecules that are present in the wastewater treatment industries such as acetaminophen, glyphosate, sulfamethazine, atrazine, and cannabinoids. It is also recommended to investigate other parameters affecting the adsorption process such as the solution concentration, and the amount of adsorbent.

In this study, only the effect of activation time on the improvement of BET surface area and pore volume of bio-char was discussed. Other parameters such as heating rate, the type of activation agent and its flow rate should be investigated. Consideration should be given to post-treatment processes, such as acid washing of the bio-char for improving its quality by strategically affecting its mineral composition and the surface functionalities.

Fast pyrolysis experiments and continuous operation should be carried out by upgrading the induction unit used for heating the reactor and incorporating a continuous biomass
feeding and a bio-char extraction system. The reason for this suggestion is to increase bio-oil yields and also improve the biochar quality.

Since acetic acid and levoglucosan are two valuable components with higher yields, fractional condensation is recommended for separating these components and any other valuable components produced during pyrolysis.

Furthermore, modeling of the batch reactor is recommended as well as of a continuous system to scale up the reactor for industrial applications.
References


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# Curriculum Vitae

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