Hybrid Thermochemical and Biochemical Conversion of Biomass for Value Added Products

by
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ABSTRACT

HYBRID THERMOCHEMICAL AND BIOCHEMICAL CONVERSION OF BIOMASS FOR VALUE ADDED PRODUCTS

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Greenhouse gas emissions can be minimized by reducing the use of fossil fuels and increasing the use of renewable fuel including biofuel. Biofuel feedstock should be economically feasible and consists of a variety of sources, different from the human food chain. Biofuel from lignocellulosic biomass has been recognized as an appropriate substitute to fossil fuels and first generation biofuel such as hydrolysis fermentation. There are a number of studies in progress worldwide to determine a method for the successfully and economically viable production of solid, liquid and gaseous biofuel from lignocellulosic biomass and municipal waste. Gasification-fermentation is one innovative method in the conversion of lignocellulosic biomass to biofuels. Synthesis gas components (CO, H₂, and CO₂) are easily converted to bioethanol by microorganisms such as Clostridium ljungdahlii.

Bioethanol production from lignocellulosic biomass through conventional fermentation process does not utilize the lignin component, resulting in inefficient utilization of raw biomass. In comparison, hybrid thermochemical (gasification) and biochemical (syngas-fermentation) processes utilizes all components of lignocellulosic biomass, including lignin. Major challenges for the commercialization of biofuel include: low gas-liquid mass transfer, low bioethanol yield, impurities, high cost, and limited studies. Presently, most of the work has focused on fermentation; developing microbes for higher gas to energy conversion when the gas supply (mixture of H₂ and CO) is controlled. Additional research is necessary to improve the reactor design such that higher gas-liquid mass transfer can be achieved.

Similarly, the kinetic study of treated biomass-coal is an important factor for the future cascade operation of biomass-coal gasifier and syngas fermentation in the production of bioethanol. The blends of torrefied biomass and coal has potential to lower the net
greenhouse gas emission by reducing carbon dioxide and NOx/Sox from the gasifier including coal fired electrical or thermal power plants by sacrificing heating value and ash content.

This study focuses on the characterization and kinetic analysis of CO2 cogasification of dry torrefied biomass, hydrothermally treated biomass and coal to determine the optimum blend ratio, which has not been previously researched. Bioethanol has then been produced from the simulated syngas through the biochemical (biosynthesis) process in a bioreactor using novel gas-loop-back system. Syngas has been fermented with the microorganism Clostridium ljungdahlii. Different syngas composition and flow rate, media flow, stirrer speed, and reactor design tested to identify the most efficient pathway. This study helps to develop a better understanding of the process, thereby leading to the optimization of the overall system to produce sustainable bioethanol in Ontario. Similarly, mathematical models for thermochemical process (kinetic characterization for the blends) and biochemical process (ethanol extraction models) have been proposed.
Dedicated to:

My loving parents Dr. Shanta Laxmee Acharya and Mr. Ram Kumar Acharya
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Chapter 1  Introduction

1.1 Background
The main rationale behind the study of the technological advancement of biomass energy is to replace fossil fuel in transportation, electrical power generation, heating application, and to optimize biofuel in applications that reduce greenhouse gas emissions (BIOCAP, 2008). Transportation, electricity/heat generation, and commercial/residential heating sectors produced 23.3% (174 Mt CO$_2$e), 17.2% (128 Mt CO$_2$e), and 10.5% (78.8 Mt CO$_2$e), respectively, of greenhouse gas emission in 2005 in Canada. Overall, these three sectors contribute about 51% of the greenhouse gases of Canada (BIOCAP, 2008). This shows that Canada has a sufficient market for sustainable energy products in solid or liquid biofuel. The Ontario government has shut down the last coal operating plant at the Nanticoke generating station to make Ontario a coal free province by 2014, as per the government commitment (MOE, 2014). This commitment has moved Ontario toward being a leader in green energy in North America and is resulting in the minimization of greenhouse gas emissions, cleaner air, and a better atmosphere.

The federal government of Canada has introduced a mandate for gasoline to be composed of 5% of renewable ethanol in 2010 and 2% of renewable fuel in diesel in 2011 [USDA, 2016]. In parallel, provincial government has introduced separate mandate for bioethanol contents like 5% in Ontario, British Columbia, Alberta and Quebec, 7.5% in Saskatchewan, and 8.5% in Manitoba. Ethanol production is expected to increase by 1.5% in 2016 compared to 2015 and reaches to 1.725 billion litters and expected to import additional one billion liters of fuel grade ethanol from USA to meet the blend mandate. Similarly, Canada is also producing only 400 million liters of biodiesel in 2016 [USDA, 2016]. The main crops for the ethanol production are corn and wheat whereas for the biodiesel production is mainly from canola, animal fat, and recycled oils. Even though Canada is a major exporter of wood pellets, it is importing bioethanol and biodiesel from USA. In 2015, Fuel used in Canada was 44698ML of gasoline and 29415ML of diesel and ethanol market percentage blends rate reached to only about 6% [CANSIM].

To maintain a sustainable energy future, renewable energy sources should be increased. Biomass, a renewable energy source, can be used for biofuel production. It can be processed
by thermochemical and/or biochemical pathways to enhance its fuel properties. In the thermochemical pathway, solid and liquid biofuel can be produced. Carbon rich solid biofuel can be prepared thermo-chemically with wet and dry torrefaction and liquid biofuel (bioethanol) can be produced by bio-chemically with fermentation of syngas (generated from gasification of biomass) (Bergman et al., 2005; Richter et al., 2013). Liquid biofuel can be used directly as fuel or mixed with other fossil fuel. Similarly solid biomass, either directly or mixing with coal, can be burned as coal like substance. In order to maximize use of all components of biomass, recent research is focusing on syngas fermentation. In this process, synthesis gas (syngas: CO, H$_2$, and CO$_2$), produced from gasification of biomass, is then fermented through a biochemical pathway using micro-organisms, resulting in bioethanol as an end product.

Bioethanol has been produced from the food grain components of biomass, like corn, for a long time. But, experts are urging not to use food grain components of biomass in the bioethanol production. The “food versus fuel” debate has directed research towards the production of bioethanol from the non-food grain parts of the plants. Current research also focuses on the non-food sources specifically lignocellulosic biomass using second generation technologies to produce solid and liquid biofuel. Agricultural and forest biomass products are the main resources for the lignocellulosic biomass (Uslu et al., 2008).

There are a number of limitations that exist when using raw biomass directly in coal-fired boilers as high moisture contents, hydrophilic properties, biological degradation, low bulk density, high O/C ratio, low energy density, and many others (Svoboda et al., 2009). Thermal treatment is needed to overcome the limitations of raw biomass in order to use it as a replacement of coal in the coal fired power plant. Thermal treatments include drying, torrefaction, hydrothermal carbonization (wet torrefaction), and pyrolysis. These thermal treatments improve the fuel quality by reducing the oxygen-to-carbon ratio in biomass which benefits gasification and enhances the heating value of the feed stock (Acharya et al., 2012; Bergman and Kiel, 2005; Shen et al., 2009; Prins et al., 2006). Torrefaction also improves the energy density of raw biomass by 4-8 folds with the retention of 40-80% of mass and 80-96% of original raw energy and makes the density comparable to coal (Acharya et al, 2012). Torrefaction converts hydrophilic/hydroscopic characteristics of biomass to hydrophobic by breaking down the OH components of the biomass (Tumuluru et
Hydrophobic characteristics help in longer storage without biological degradation and increase the availability of biomass feedstocks all year round (Uslu et al., 2008; Bergman et al., 2005). However, torrefaction degrades the toughness, mechanical strength and abrasion resistance due to the breakdown of the hemicellulose and partial carbonization and depolymerisation of cellulose and lignin (Bergman et al., 2005; Tumuluru et al., 2010).

The key challenges for the successful implementation of syngas fermentation include poor liquid-gas mass transfer properties of syngas specifically CO and H₂, minimum amount of ethanol from biocatalysts, readiness of biomass gasification technology for producing syngas, gas cleaning processes (impurities with Nitric oxide, ammonia, tars, hydrogen cyanide, methane, sulfur dioxide, hydrogen sulfide, carbonyl sulfide), steady production of contaminant free syngas, scale up and commercial fermentation, down-stream processing, and bioreactor design (Richter et al., 2013; Kundiyana et al., 2010; Munasinghe and Khanal, 2010). Types of impurities (tars, nitric oxide, and ammonia) also depend upon the feedstock types, the gasifier type, and gas cleaning conditions so proper knowledge of the merits/demerits of impurities and cleaning techniques are important for commercialization (Richter et al., 2013; Xu et al., 2011).

During ethanol production from syngas fermentation in an anaerobic bioreactor, a variation in bacterial development and concentration of metabolic product are observed. Tar and Nitric oxide have potential to retard cell growth and enzyme activities during syngas production. Tars and H₂S are the inhibitory and stimulatory compounds in syngas. Feedstock development, improvement on the conversion technologies, and system integration could improve the performance of the syngas fermenter with further investigation. Controlling operation of the gasifier to maintain the required syngas quality, controlling temperature and pH in the fermenter, and bioreactor design for enhanced mass transfer are additional challenges during the fermentation process.

Limited research is available on the bioethanol production by syngas fermentation using biomass gasification (Shen et al., 2014; Richter et al., 2013 Munasinghe and Khanal, 2010). Syngas fermentation by using gas-loop-back system has not been reported in the commonly available resources. The aim of the study is to fill the above gaps by producing bioethanol from biomass syngas using Clostridium ljungdahlii in a bioreactor with innovative gas supply system.
Therefore, this study is focused on torrefied (both dry and wet torrefaction) lignocellulosic biomass from energy crops and analyze the different characterizations as well as producing bioethanol from the syngas fermentation (Syngas is produced by the gasification of torrefied products, coal and their blends) by varying different operating conditions including mass transfer (syngas as well as media) with a gas-loop-back system and observe the ethanol yield effect. The optimum condition for producing the maximum bioethanol from the syngas fermentation has been investigated. Different methodologies are used to increase the residence time for improving gas-liquid mass transfer. Exploration of products derived from co-gasification of raw and pretreated biomass with coal and their blends at different ratios has also been carried out during the kinetic characterisations.

1.2 Objectives
The main goal of this study is to explore the possibility of improvement on the ethanol production from the biomass derived syngas fermentation using hybrid thermochemical and biochemical processing technologies. This study focuses on the development of synergistic biomass conversion processes for low grade feedstocks to produce energy and fuels by improving the basic understanding in torrefaction, hydrothermal carbonization (HTC) processing, co-gasification with different blends, and syngas fermentation through following sub-objectives.

1. Investigate the thermochemical pre-processing of wet and dry biomass for biocarbon production and compare fuel characteristics with conventional pre-processing for energy applications (thermochemical).
   - Characterize dry and HTC bio-carbon based on physiochemical properties
   - Kinetic study of co-gasification of blends of coal and pretreated (dry and wet torrefied) biomass using TGA-FTIR to identify the optimum coal-biomass ratio and characterize the product gases and ash.

2. Investigate the means to improve gas-liquid mass transfer to produce bioethanol through fermentation (biochemical).
   - Supply of simulated syngas with a major similar composition as produced by the blends gasification and compare with the results produced with the supply of 100% carbon monoxide.
Investigate the bioethanol production using syngas fermentation technology in a reactor using *Clostridium ljungdahlii* bacteria using loopback gas supply system.

Observe the bioethanol yield by varying syngas flow rate, flow direction, media flow rate, and stirrer speed.

### 1.3 Novelty of the research

A bioethanol extraction method from the syngas that produced from lignocellulosic biomass (different ratio of raw/torrefied) and coal by using novel hybrid thermochemical and biochemical conversion methodology has been proved successfully. Wet and dry torrefaction are used to improve the thermochemical properties of raw biomass using a laboratory scale macro-reactor (QWM reactor). The mass loss and heat flow patterns are analyzed by using micro-reactor (TGA-FTIR). The torrefied biomass is then blended with coal in different ratios and gasified. This produces syngas (mainly carbon monoxide, hydrogen, and carbon dioxide) with minimum impurities. Bioethanol production from syngas fermentation technology using a bioreactor with innovative gas-loop-back system has been conducted successfully and optimized the system. Use of wet and dry torrefied biomass for syngas and extract bioethanol is a new idea of its kind.

The properties of syngas are characterized to develop a kinetic model for the gasification process. Thus, it has opened up a new area of research on co-gasification/cofiring of pretreated biomass with coal at different ratio. This brings new opportunity in the production of renewable bioenergy from pretreated biomass and also explores possibility of co-firing with coal at different ratio. The novelty of the process lies in generation of the syngas obtained by gasification of pretreated biomass-coal mixture which leads towards the development of hybrid thermochemical-biochemical syngas fermentation system in the future.

Mathematical models are developed to represent the kinetic characterization of the co-gasification and ethanol yield during syngas fermentation.

### 1.4 Scope of Research

Global warming is one of the challenges that the world is facing today. The proper management of food is another challenge. Global warming can be minimized by increasing
the use of the renewable fuel including biofuel from non-edible portion of biomass. Present research addresses both of these issues. Liquid biofuel or bioethanol is produced from the lignocellulosic biomass by syngas fermentation. Syngas is produced from the gasification of lignocellulosic biomass. Lignocellulosic biomass is first thermo-chemically treated with the dry or wet torrefaction. These processes improve the fuel properties of biomass and enhance the storability which eventually makes biomass, a solid biofuel available year round for the continuous operation of the electrical or thermal power plant. Gasification utilizes all components of lignocellulosic biomass to produce syngas. The resulted syngas is used for the production of bioethanol in the presence of micro-organism. This research opens up the new scope to reduce environmental pollution and commercial applications of biomass. The generation of bioethanol from the wet and dry biomass including municipal waste, forest, agricultural residue, energy crops in Ontario. This may eventually lead towards the sustainable bioethanol production in Canada.

1.5 Limitations of Research

This study focuses on analyzing two different thermal treatment procedures: wet torrefaction and dry torrefaction using biomass and coal samples collected from Ontario. The processed biomass samples are blended with coal at different ratios and co-gasified in DSC-TGA equipment. However, there may be some variation in the real commercial co-gasification system. Usually, lignocellulosic biomass gasification produces syngas which consists of 60% CO, 35% H₂ and 5% CO₂ so simulated syngas having similar composition has been supplied to the bioreactor to produce bioethanol. In the real gasification, the syngas may contain several impurities which need to be cleaned prior to the feeding to the bioreactor. The optimum torrefaction conditions for miscanthus have been taken from the earlier research of Acharya B. (2013) and Kambo H. (2014). The optimum temperature for the dry and wet torrefaction has been considered as 275°C for 45 minutes residence time and 260°C for 5 minutes respectively.

The main limitation of the syngas fermentation technology is the limitation in the mass transfer between gaseous substrates with liquid. An innovative gas supply system has been incorporated in a laboratory scale bioreactor to improve the liquid-gas mass transfer. In addition, a membrane separation technology has been used to extract the effluent extraction
excluding the microorganism. The developed bioreactor has been tested successfully for the production of ethanol using simulated syngas.

1.6 Structure of Thesis

This thesis has divided into eight chapters, each of which represents a separate information but limited within the objective framework. In the first chapter, basic introduction to research work, objectives, scopes, limitations, and achievements of the research are presented. Chapter 2 presents a review of literature on comparative study on the dry and wet torrefaction of different biomass. It also discusses the available technologies of different torrefiers, economic and environmental impacts in Canada.

Chapter 3 also presents a review of literature on bioethanol production from syngas fermentation techniques. It also discusses the available technologies of different syngas fermentation, economic and environmental impacts in Canada.

Chapter 4 explains the thermochemical process technology specifically dry and wet torrefaction. For the thermogravimetric and product compositions analysis of the one of the most popular thermochemical treatment of miscanthus and wheat straw are respectively carried out in a macro-TGA and DSC-TGA-FTIR equipment. Commercial scale characterization of torrefier is analyzed using macro-TGA, whereas the weight degradation, kinetics, differential scanning and the gaseous products are identified by the latest equipment with micro-TGA-FTIR.

Chapter 5 also explain the thermochemical conversion technology using CO² cogasification. It determines the optimum experimental parameters for the CO² gasification and yields the syngas compositions. The fuel characteristics of hydrothermally torrefied miscanthus show better performance than the dry torrefied miscanthus.

Chapter 6 contains interaction and kinetic behavior of CO² gasification of coal, wet torrefied and dry torrefied miscanthus and their blends at different ratio using TGA-FTIR. Results suggested that CO² gasification could be one option for producing synthesis gas by gasification of coal, torrefied biomass (wet and dry), and their blends.

Chapter 7 represents the biochemical conversion technology. It explains from the fabrication of continuous stirred tank bioreactor to bioethanol production from the syngas fermentation.
Finally, chapter 8 presents the conclusions and recommendations for the future works and chapter 9 contains appendix with reactor fabrication and photographs.

1.7 Contribution of Present Study

Major contributions of present study are summarised on Table 1.3.

Table 1.1 Contribution of Research

<table>
<thead>
<tr>
<th>Research Gap</th>
<th>Thermochemical</th>
<th>Biochemical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• No study performing on identifications of optimum</td>
<td>• Limited study on comparative investigation on CO and syngas</td>
</tr>
<tr>
<td></td>
<td>experimental condition for CO2 gasification</td>
<td>fermentation using <em>Clostridium ljungdahlii</em></td>
</tr>
<tr>
<td></td>
<td>• No study on the CO2 cogasification of blends of</td>
<td>• No study on improvement of</td>
</tr>
<tr>
<td></td>
<td>thermochemically processed (dry and wet torrefaction)</td>
<td>liquid-gas mass transfer using gas-loopback system in a</td>
</tr>
<tr>
<td></td>
<td>biomass and coal.</td>
<td>CSTBR.</td>
</tr>
<tr>
<td>Findings</td>
<td>• The optimum experimental condition are presented</td>
<td>• Developed a continuous stirred tank bioreactor (CSTBR).</td>
</tr>
<tr>
<td></td>
<td>• Observed mass loss rate as linearly proportional</td>
<td>• Concept of syngas fermentation has been proved successfully</td>
</tr>
<tr>
<td></td>
<td>to amount of torrefied biomass in blend.</td>
<td>• Improvement on the ethanol production (5-15%) using loop back</td>
</tr>
<tr>
<td></td>
<td>• Performed kinetic characterization of CO2</td>
<td>system</td>
</tr>
<tr>
<td></td>
<td>cogasification</td>
<td>• Performed Comparative study of CO and syngas fermentation</td>
</tr>
<tr>
<td></td>
<td>• Optimum ratio found at 60:20:20 (coal :dry :wet)</td>
<td></td>
</tr>
<tr>
<td>Proposed Models</td>
<td>• The optimum kinetic characterisation models</td>
<td>• Mass Transfer coefficient</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Ethanol and Acetic Acid production models</td>
</tr>
</tbody>
</table>
1.8 Publications from Present Study

Versions of this thesis have been published in different peer-reviewed journals and two of these chapters (six and seven) are under reviewing process. Publications so far made during the period of this study (2013 to 2016) are listed as follows:


8. **B. Acharya, P. Roy, A. Dutta** Comparative Study of CO and Syngas Fermentation for Ethanol Production using *Clostridium ljungdahlii (Under Finalization process).*

1.9 References


Abstract

Torrefaction is a mild pyrolysis process used to improve the fuel quality of biomass so that it becomes a more appropriate solid fuel for coal fired power plants. The main goal of this study is to review recently published articles on dry and wet (liquid and vapor) torrefaction technologies for biomass and compare the similarities and differences among them. There is a more significant amount of studies on dry torrefaction compared to wet torrefaction, however the number of liquid torrefaction articles has increased significantly in the last year. Torrefied products produced from both methods are hydrophobic, possess lower moisture contents, increased energy density, and increased higher heating values, which improves torrefied biomass to a point, where it is more comparable to the characteristics of coal. Wet or hydrothermal torrefaction produces more energy dense products at lower temperatures and lower residence times compared to dry torrefaction, however design costs due to the presence of high pressure and increased transportation costs of wet biomass, are currently limiting the development of wet torrefaction. Application of dry and wet torrefaction depends on the moisture contents of the biomass; wet torrefaction is preferred for biomass with high moisture contents.

2.1 Introduction

The global interest in renewable and alternative energy resources has increased because of the concern for energy security, energy sustainability, and greenhouse gas emissions. To minimize environmental concern, proper replacement of fossil fuel based products with renewable based products is essential. First generation biomass fuel production, a fully matured technology, is the production of biofuel from edible part of plants. Second

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1 A version of this chapter has already been published as "Acharya, B., Dutta, A., & Minaret, J. (2015). Review on comparative study of dry and wet torrefaction. Sustainable Energy Technologies and Assessments, 12, 26-37.”

12
generation biomass fuel production from non-food components of biomass is the current primary focus of research and development, whereas third generation fuel production from algae is also added recently in research and development [1]. Careful production and management through sustainable harvesting of biomass is important for a sustainable energy future.

Biomass not only provides food to living things and but also acts as a number of other resources, including; renewable fuel, carbon sequestrations, and fertilizers [2]. Biomass is considered a renewable energy source because of its short carbon cycle and reduction of greenhouse gas emissions due to the CO₂ captured during photosynthesis and the decreased amount of NOx and SOx emitted during thermochemical transformations compared to fossil fuels [3]. Ontario, a global leader in renewable energy expansion, shut down all coal fired power plants in 2014, which is a step forward in the plan to reduce carbon dioxide emissions by 30 megatons per year, as well as producing more than 10 thousand megawatts from non-hydro renewable energy sources by 2018 [4]. The North American market has the potential to substitute more than 30 percent of its petroleum consumption with energy derived from biomass [2]. One eighth of the global greenhouse gas emissions from fossil fuel can be captured by carbon sequestering photo-synthetically using biomass [5] and the European Union and United States alone produce about 10 million and 8 million tons of dry based sewage sludge annually [6-7].

Biomass has the potential to completely replace coal for sustainable energy production in the future. However, biomass contains increased heterogeneity, moisture content, alkali content, transportation costs, and grinding energy compared to coal, as well as a decreased energy density, which are all major limitations in every biomass energy production method. These limitations can be minimized by applying a thermochemical pre-treatment method referred to as mild pyrolysis prior to feeding the biomass into coal fired boilers. The two main methods of mild pyrolysis include dry and wet torrefaction. Both processes produce a hydrophobic, homogenized, carbon rich, and energy-dense solid fuel from lignocellulosic biomass, while enhancing the physical properties, durability and hygroscopic characteristics [8-12]. Both wet and dry torrefied products show closer characterization to coal during combustion and gasification processes in comparison to raw biomass [12]. Traditional pyrolysis is the thermal treatment of biomass from 350-550°C in an inert environment [13]. Dry torrefaction (DT) is a
 thermochemical conversion process in the presence of a minimum oxygen environment at a temperature range of 200-300°C for 30-60 minutes [14], at atmospheric pressure. According to Yan et al. (2009) [16], Wet Torrefaction (WT) or Hydrothermal Carbonization (HTC) is defined as the thermochemical conversion process in subcritical water. The exact range of operating conditions for WT varies depending upon the literature source, however, most articles define the process as the thermal treatment of biomass in water at temperatures of 180-260°C, for 5 minutes to several hours at pressures above 1 MPa [7,11,12,17,18]. Hence, wet torrefaction can be redefined as a thermochemical conversion process at temperature range of 180-265°C at subcritical pressure for minimum residence time.

The quality of the solid product produced from both torrefaction techniques can be measured from a variety of parameters that vary in importance depending upon the intended application of the solid product. In terms of producing a solid fuel replacement for coal, the important parameters to consider include; energy yield, equilibrium moisture content (EMC), energy density during compression/pelletisation (GJ/m³), ultimate analysis (C, H, O, N and S content), and proximate analysis (ash, volatile matter and fixed carbon content) [19, 20]. The energy yield is one of the most basic parameters used to assess the solid product of torrefaction, yet it is arguably the most significant in determining the optimum conditions of the torrefaction reaction, in terms of producing a solid fuel. The energy yield involves the combination of the solid yield and energy densification of the torrefied product [19].

The major advantages of the pre-treatment of biomass, either by dry or wet torrefaction, include i) lower transportation cost, ii) low grinding energy, iii) limited size reduction to reduce milling cost, iv) minimum cost of pre-treatment chemicals, v) reduction of waste materials, vi) lower cost of reactor fabrication and scaling up due to fast reactions and non-corrosive chemicals, and vii) the use of facilitates for the production of co-products and its applications [15].

Review papers are available on the cellulosic ethanol production from pre-treated biomass [21-23], on the production of syngas after the torrefaction of biomass prior to gasification and co-firing [24-25], on the improvement of durability of wood from thermal pre-treatment [26-27], and on different torrefaction and densification technologies [14,28]. The previously mentioned review articles involve the DT process, while very few articles to date have reviewed the WT process with liquid and vapor torrefaction processes. The processing
conditions and chemistry behind WT have been reviewed in the literatures [12,18], however, only one review exists that was solely devoted to comparing liquid and dry torrefaction [29]. The review comparing WT and DT focused on the solid products from each process, in terms of their physical structure and possible applications [12,18,29]. Hence, this study attempts to review available literature on both torrefaction technologies and create a comparative study on both types of torrefaction, in order to develop a summary for future research paths. The morphology of the carbonized solid fuels generated by both types of torrefaction procedures is included in the study. Reviewing recent WT research reveals that there is a large discrepancy in the processing conditions of the WT reaction. In some cases the reactor is pre-pressurized to ensure that the water present in the reactor remains in a liquid state for the entire process [8,30], whereas in other cases the reactor is not pre-pressurized and therefore left autogenic, causing water to convert to a vapor during the process [31,32]. Therefore, this study will also review available literature on the WT process in order to identify the two different methods used for the process.

2.2 Fundamental concept on Biomass

Dry and wet torrefaction are capable of processing lignocellulosic and non-lignocellulosic biomass. Lignocellulosic biomass consists of hemicellulose, cellulose, lignin, water extractives, and ash. This type of biomass can be produced from agricultural farms, forest products and municipal biological solid waste [28,33-36]. The composition of each component depends upon the type, maturity, and climatic conditions. Non-lignocellulosic biomass consists of animal manure, animal fat, sewage sludge, etc. Non-lignocellulosic biomass contains fatty acids and protein, as well a significantly less hemicellulose, cellulose and lignin, compared to lignocellulosic biomass [21,37]. Raw biomass derived from the plant family has a low molecular weight with organic and inorganic matter and a macromolecular composition. The product ash from biomass is an inorganic matter, whereas the extractives are the organic matter. Cellulose and hemicellulose are polysaccharides and lignin contains polyoses as shown in Figure 2.1 [37]. The macromolecular composition of biomass derived from the wood family contains, 10-25% lignin, 20-40% hemicellulose and 40-60% cellulose [36], whereas rice straw, an agricultural residue, contains about 14%, 27% and 35% and orchid grass another type of agricultural residue contains 5%, 40% and 32% of lignin, hemicellulose and cellulose respectively [37].
All types of lignocellulosic biomass have similar cell wall structures as shown in Figure 2.2 but there may be variation in the composition and thickness of each type [38]. Most lignocellulosic biomass comprises of about 80% volatile matter and 20% fixed carbon on a dry basis. Composition of the torrefied product depends on the temperature, pressure, residence time and torrefaction environment, which ultimately change the chemical compositions [38]. The thermal treatment of the lignocellulosic biomass breaks down cellulose, hemicellulose and lignin, as shown in Figure 2.2 [13, 38]. The breakdown of lignocellulosic components releases hydro-oxy (OH) compounds, which improves the hydrophobicity of the biomass [13, 38].

The mechanism of the thermal treatment during dry torrefaction follows decarboxylation, dehydration, de-carbonization, de-methoxylation, intermolecular derangement, condensation, and aromatization chemical reactions [18]. However, the mechanism in the wet torrefaction follows hydrolysis process due to the presence of compressed water then results into the cleavage of ether and ester bonds between monomeric sugars due to presence of hydrogen bonds, and thereby decreasing the level of biomass polymer’s activation energy [12]. Therefore, the degradation of hemicellulose during wet torrefaction is comparatively higher than in dry torrefaction process.

Figure 2.1 Composition of Biomass [37]
Cellulose: Cellulose contains a high amount of carbon compared to the other lignocellulosic components and is responsible for a significant proportion of the energy content contained in biomass [23]. The chemical structure of cellulose contains a linear polymer chain with D-glucose connected by β→4 glycosidic bonds and crystalline micro-fibrils circled by amorphous cellulose [35, 40]. Hydrogen bonding among glucose monomers maintains the structural integrity of cellulose. The binding strength of 4 cellulose materials in wood primarily depends on the transformation from cellulose to an amorphous [41]. Ordinary solvents may not dissolve the cellulose easily, so temperature/pressure treatment is good prior to the densification [42].

Hemicellulose: Hemicellulose contains multiple monosaccharides with short branches. The structure of hemicellulose contains β-4 bonded D-xylans the main stream with L-arabinose, D-glucose, D-galactose, 4-0- methyl-D-glucuronic acid, D-mannose, and L-rhamnose in the side stream [9, 43-44]. Hemicellulose may contain some adhesive materials that may act as a bonding element during densification [42, 45], which is why it is difficult to pelletize torrefied biomass without the use of an additive [39].

Figure 2.2 Structures of Biomass & Thermal Treatment [38-39]
**Lignin:** According to Zandersons et al. (2004) [41], lignin is a complex and variable polymer structure with multiple branches of phenyl propane and aromatic rings [37]. The main function of lignin in a lignocellulosic biomass is to work as a binding element for the cellulose and hemicellulose structures [46-47]. Lignin also works as glue in the densification process when heat is applied at temperatures above 125°C and moisture contents between 10-15% [47]. Significant thermal degradation of lignin does not occur until torrefaction temperatures reach above 275 °C, therefore the pelleting of raw biomass requires an additional binder (add extra water or a glue or a binder) at temperatures above 275 °C [39, 48]. Combustion of biomass takes place after 1000°C [49].

### 2.3 Basic Principles of Torrefaction

#### 2.3.1 Dry Torrefaction

As mentioned previously DT is the thermochemical conversion process at temperatures between 200-300°C in the presence of an inert gas for a 30-60 minutes residence time. During this process, biomass is heated at the rate of about 50°C per minute [24]. Torrefaction is also referred as mild pyrolysis [50], low temperature pyrolysis [16], or thermal rectification [51-52]. The mechanism of biomass torrefaction has been studied by different researchers in different part of the world [38, 53-56]. The degradation of hemicellulose during this process causes, the nature of biomass to change from hydrophilic to hydrophobic [39]. Polymerization of cellulose results in the dissipation of moisture and formation of carbonyl and carboxyl groups, as well as the formation of carbon dioxide [57]. The color of the biomass during torrefaction changes to dark brown [58]. However, porosity of biomass does not significantly change for residence times under 15-60 minutes residence time. The torrefied product retains a maximum of 90% of its original energy content, while losing a maximum of 30% of its original mass, which is due to a partial loss of the volatile matter and moisture contained in the biomass [14, 59]. As the temperature increases during the torrefaction process different stages of mass loss occur. The initial mass loss occurs after 100°C due to vaporization of the moisture contained in the biomass. Then, devolatilisation and carbonization of hemicellulose take place once the temperature reaches above 200°C [53]. The degradation of hemicellulose increases the heating value of the torrefied product, however the product also becomes more brittle compared to the raw biomass form. This is
because the effects of devolatilisation and carbonization on cellulose and lignin are not as significant as the effect that the process has on hemicellulose [53]. Therefore the increased ratio of lignin and cellulose in the torrefied product causes the more brittle structure. The mass and energy yield of the torrefied output rely on the torrefaction temperature, residence time, particle size and biomass type [24]. Chen and Kuo (2010) [61] conducted torrefaction experiments for bamboo, willow, coconut shell, and wood at a temperature of 240°C. They observed an almost complete degradation of hemicellulose without any degradation of cellulose or lignin. Kamdem et al. (2002) [62] were able to observe that the degradation of hemicellulose starts at 180°C. During torrefaction, biomass is heated due to convection heat transfer between the surrounding gas and the biomass. Therefore biomass is first chopped or ground into smaller particle sizes to increase the heat transfer rate. DT can be done by using electricity, but alternative power solutions are recommended for commercialization of the process. The energy contained in the gases produced during DT may meet the energy requirements for drying, as well as the torrefaction process itself [59]. However the amount of heat available in the gases depends on the moisture content of the input feedstocks and the degree of torrefaction. Therefore, it is important to minimize the moisture content of the biomass during the drying process, in order to maximize the efficiency of the overall system. One of the options is to combine a combustion/gasification chamber with the torrefaction system, refer to Figure 2.3. This will allow the waste heat of the combustion/gasification system to be utilized as heat in the torrefaction process in order to offset the energy required to dry the biomass. Torrefaction also improves the fungal resistance, dimensional stability, absorption of water vapor and durability [7,62-68].
In order to commercialize the DT process, further research on the technologies available in the present market is required. An overview of the DT technologies can be summarized in a tabular form as stated in Table 2.1(a-b).

Table 2.1a Dry Torrefaction Technologies and their Companies [59]

<table>
<thead>
<tr>
<th>Companies</th>
<th>Reactor Type</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDS-UK;  Torr-Coal-NL; BIO3D-FR; EBES AG-AT; 4Energy Invest-BE; BioEndev/ETPC-SWE; Atmosclear SA-CH; Andritz, EarthCare Products-USA</td>
<td>Rotating Drum</td>
<td>Proven technology continuous reactor, directly or indirectly heated in a rotating drum reactor using superheated steam of flue gas produced from the ignition of volatiles, Process controlled by varying temperature, velocity, length and angle of rotating drum; Particles mixed properly by drum rotation; limited scalability</td>
</tr>
<tr>
<td>BTG-NL;Biolake-NL;FoxCoal-NL; Agri-tech Producers -US</td>
<td>Screw reactor</td>
<td>Proven technology continuous reactor with one or more screws that transport the biomass through the reactor heated directly or indirectly; inexpensive; limited scalability; efficient for improved heat transfer.</td>
</tr>
<tr>
<td>CMI-NESA-BE; Wyssmont-</td>
<td>Multiple</td>
<td>Multiple layers continuous reactor, temperature increases</td>
</tr>
<tr>
<td>USA</td>
<td>Hearth Furnace (MHF)</td>
<td>with increase in layers 220-330°C uniform &amp; gradual mixing of biomass, drying at upper layer and torrefaction at inner layers, heating by internal gas burners &amp; gas injection; scale up to 8 m; handle wider sizes.</td>
</tr>
<tr>
<td>Topell-NL</td>
<td>Torbed reactor</td>
<td>Proven technology for combustion, batch wise &amp; continuously operated Torbed installation with 5-7 m dia; but for the torrefaction only tested for small scale; heat transfer medium blown from bottom with high speed; angled blades; high heat flow needs lower torrefaction residence time (80s); sensitive to variation in particle size.</td>
</tr>
<tr>
<td>Rotawave-UK</td>
<td>Microwave Reactor</td>
<td>Microwave heating for torrefaction; low efficiency due to use of clean energy electricity; High operational cost</td>
</tr>
<tr>
<td>Andritz/ECN-NL; Thermiya-FR; Buhler-D</td>
<td>Compact Moving Bed</td>
<td>Continuous vessel reactor biomass inlet from top and moves down slowly and torrefaction by gaseous medium; No moving parts; torrefied products exit from bottom and cooled; Volatile exit from top; Non uniform product due to channeling;</td>
</tr>
<tr>
<td>Stramproy (NL), Agri-tech producers (USA)</td>
<td>Belt Dryer</td>
<td>Proven technology for biomass drying; torrefied using a moving, porous belt on a hot gaseous medium and produces homogenous products; residence time controlled by belt speed; drawback of clogging/tars formation, difficult to control temp, up scaling challenge; low cost.</td>
</tr>
<tr>
<td>NewEarth Eco Technology (USA)</td>
<td>Fixed Bed</td>
<td>Proven technology for biomass torrefaction on fixed bed part; bed heated using volatile matter of feedstock</td>
</tr>
<tr>
<td>Company</td>
<td>Demo Technology</td>
<td>Supplier</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>3RAgrocarbon, Hungary</td>
<td>Rotary Kiln (3R Pyrolysis Biochar)</td>
<td>Unknown</td>
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<tr>
<td>4Energy Invest. (BE)</td>
<td>Unknown</td>
<td>Stramproy Green Tech. (NL)</td>
</tr>
<tr>
<td>Agri-Tech Producers LLC (US/SC)</td>
<td>Belt Conveyor</td>
<td>Kuster Zima Corporation (US/SC)</td>
</tr>
<tr>
<td>Andritz (Austria)</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Atmosclear (CH)</td>
<td>Rotary Drum</td>
<td>CDS (UK)</td>
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<td>Bioenergy Development (SWE)</td>
<td>Rotary Drum</td>
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<td>Biogreen Energy (FR)</td>
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<td>ETIA (FR)</td>
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<tr>
<td>Biolake BV (NL)</td>
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<td>TurboDryer</td>
<td>Wyssmont</td>
</tr>
<tr>
<td>Company</td>
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<td>Company</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>New Earth Renewable Energy Fuels, Inc. (US/WA)</td>
<td>Fixed Bed/Pyrovac</td>
<td>Pyrovac Group (CA/QU)</td>
</tr>
<tr>
<td>Rotawave Ltd. (UK)</td>
<td>Microwave Heating</td>
<td>Group’s Vikoma</td>
</tr>
<tr>
<td>Stramproy Green Investment B.V. (NL)</td>
<td>Oscillating belt Conveyor</td>
<td>Stramproy Green Tech. (NL)</td>
</tr>
<tr>
<td>Thermya (FR)</td>
<td>Moving Bed</td>
<td>Lantec Group (SP)</td>
</tr>
<tr>
<td>Topell Energy B.V. NL</td>
<td>Torbed</td>
<td>Torftech Inc (UK)</td>
</tr>
<tr>
<td>Torr-Coal B.V.</td>
<td>Rotary Drum</td>
<td>Unknown</td>
</tr>
<tr>
<td>Torrefaction System Inc. (US)</td>
<td>Unknown</td>
<td>Bepex International (US/MN)</td>
</tr>
<tr>
<td>Vattenfall (SWE)</td>
<td>Moving Bed</td>
<td>Unknown</td>
</tr>
<tr>
<td>WPAC (CA)</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Zilkha Biomass Energy (US)</td>
<td>Unknown</td>
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</table>

### 2.3.2 Wet Torrefaction

Wet torrefaction is also a thermochemical conversion process at 180-265°C at subcritical pressure with shorter residence time. Hydrothermal torrefaction uses subcritical water conditions, meaning water remains below its critical point of 374°C temperature and 22.1 MPa pressure. Subcritical water in liquid form contains good solubility characteristics due to its dielectric point and high density compared to its vapor form. With the application of heat, acidic hydronium ions (H$_3$O$^+$) and basic hydroxide ions (OH-) are formed through
dissociation [69]. At the critical point of any substance, its behavior and structure change significantly in the case of water, which shows broken hydrogen on the infinite bonds and separate clusters with a chain structure [69-70].

WT is also referred to as hydrothermal carbonization (HTC) or hydrothermal torrefaction. Wet torrefaction (WT) or hydrothermal carbonization (HTC) is another thermochemical conversion process on which wet lignocellulosic biomass is treated in a subcritical pressurized water vessel from 1-250MPa at 180-265°C in an inert environment for a residence time of 5 minutes to several hours [18, 71-72]. Another torrefaction method exists that uses hot water, which is referred to as the hot water extraction (HWE) method, autohydrolysis [73-75], hydro-thermolysis [76-79], hot compressed water treatment [71,80], water hydrolysis [81], WT (Yan et al., 2010) [82], hydrothermal carbonization [12,18,83], aqueous fractionation, solvolysis or aquasolv [76], aqueous liquefaction [84], or pressure cooking [85-86]. During WT, the hemicellulose contained in biomass is depolymerized through hydrolysis and converted into monomers and oligomers [87-88]. During this process, hydrolysis of hemicellulose and cellulose into oligomers and monomers takes place with minimum impact on lignin, which consequently produces solid biochar with a reduced equilibrium moisture content, compared to raw biomass [13,18]. Funke et al. (2013) [8] conducted a study comparing both types of WT based on energy yield and compared char production from the combination of hydrothermal carbonization (WT) with pyrolysis.

The WT process is considered to be non-toxic, as well as possessing a cheaper chemical reactor media compared to DT, which has resulted in a significant increase in research regarding WT over the last several years. The WT process is non-toxic because the only input streams include biomass, water and an inert gas, however it does require the use of clean distilled water, which creates the environmental issue of using one of the earth’s most valuable finite resources. The liquid output of the WT process is composed of water with traces of alkali compounds, which creates an environmental issue in disposing of the processing water that has not currently been dealt with in WT research studies.

Only a select number of literature articles explain the WT process, therefore a process diagram was developed based on the experimental design of various studies, refer to Figure 2.4 [12, 33, 83]. WT is especially more useful for biomass containing high amounts of moisture, typically above 50% (wet basis) because the samples are mixed with water prior to
the WT reaction. The biomass must be mixed with enough water to fully submerge the solid biomass (Dry Biomass : Water ratio =1:6) prior to the WT reaction [89]. Since biomass is mixed with water the WT process does not require pre-drying of the raw biomass. As previously mentioned, in WT the biomass samples are torrefied in hot compressed water in a reactor at subcritical conditions with normal operating temperature from 180-265°C, with an inert environment filling the remainder of the reactor, as shown in Figure 2.4. During the reaction temperature is controlled and pressure is monitored. The output of the process contains a solid torrefied product, biochar, water, volatile acids, sugar, and gases (mainly in the form of CO₂) [82]. After WT, the biochar is separated from water through a filter and then placed in a desiccator for cooling and drying, after which the dried biochar can be used for pelletisation or for direct applications. The thermal energy required for the WT reaction and the post WT drying can be managed by using waste heat from WT reactor or from combustion exhaust heat. The inert environment is created by supplying inert gases (N₂/He) after the reactor has been filled with the water and biomass mixture.

a) Layout of Reactor [82]
b) Process Diagram with Heat Integration [15]

Figure 2. 4 Reactor Layout & Process Diagram: Wet Torrefaction with Heat Integration

2.3.3 Comparison of Torrefaction Process

WT produces an increased higher heating value product compared to DT, which also contains a decreased amount of inorganic compounds. This is due to the solubility of organic and inorganic components in the pressurized subcritical water, which also decreases the amount of salts and minerals contained in the biomass [20]. Namioka et al. (2011) [90] observed that in the WT of sewage sludge, thermal-odour caused from high sulfur content reduces after the treatment of WT, whereas the amount of aldehydes, light aromatics, and organic acid components increased marginally. During hydrothermal torrefaction with hot compressed water from the 200-265°C disintegration of hemicellulose with water occurs rapidly, whereas lignin is relatively inactive, resulting in good binding properties during pelletisation [91]. The energy content per unit mass is influenced by treatment temperature and water/biomass ratio; however the hydro-carbonization time has an insignificant effect on the solid yield and heating value of the produced hydrochars [92]. The ratio of H/C and O/C decreases with an increase in temperature for all feedstocks [93]. Reza et al. (2013) [11] observed the removal of up to 90% of calcium, magnesium, sulfur, phosphorous, and potassium during WT and reduction of chlorine and silica, as well as slagging and fouling indices were also found. The torrefied process converts municipal waste streams into sterilized, value added products [94],
however valuable components are also lost during WT. Both processes produce a torrefied product in the form of charcoal which is good for improving the soil productivity. In both torrefaction processes, the oxygen content of the solid product decreases with an increase in treatment temperature, which leads to a decrease in the O/C ratio [19]. Research on DT has led to the development of pilot plants and small scale commercial plants. There is still some time left before the commercialization of WT technologies. This can be made possible after resolving the complications that arise from designing high pressure reactors. Product gas management and its contamination, up-scaling, product quality certainty and uniformity, product densification, heat integration and feedstock flexibility are the most significant challenges in the improvement of torrefaction technologies [59].

DT is the more popular for biomass residues with lower moisture contents, whereas WT is more appropriate for municipal waste, sewage slug, animal manures, and direct treatment of the biomass residue from the field. This is because during WT, collected wet samples are submerged in water and heated in a pressurized chamber, which eliminates the need for pre-drying process and in DT the main reactions do not occur until most of the moisture is removed from the biomass. The major characterizations of dry and wet torrefaction are summarized in Table 2.2.

Table 2.2 Process Specifications of Dry and Wet Torrefaction

<table>
<thead>
<tr>
<th>Process Parameters</th>
<th>Dry Torrefaction</th>
<th>Wet Torrefaction</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common Name</td>
<td>Torrefaction</td>
<td>Hydrothermal</td>
<td>Carbonization</td>
</tr>
<tr>
<td>Temperature range (°C)</td>
<td>200-300</td>
<td>185-265</td>
<td>[59, 83]</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>1-200</td>
<td>[29, 39]</td>
</tr>
<tr>
<td>Residence time (min)</td>
<td>10-120</td>
<td>5-240</td>
<td>[29, 39]</td>
</tr>
<tr>
<td>Operating inert condition</td>
<td>Yes</td>
<td>Yes</td>
<td>[29, 39]</td>
</tr>
<tr>
<td>Pre-drying Unit</td>
<td>Yes</td>
<td>No</td>
<td>[16-17]</td>
</tr>
</tbody>
</table>
The carbon content and thermochemical conversion efficiency of different processes are in descending order from hydrothermal torrefaction, followed by a vapor-thermal torrefaction, closed DT and open DT, respectively. This is mainly due to the loss of dissolved organics in the WT [7]. Bach et al. (2014) [95] observed that, yield of solid product is proportional to the sample particle size during hydrothermal torrefaction. The higher heating value of wet torrefied product has more value than that of the dry torrefied product. Wet torrefied biomass has less alkali metal than in dry torrefied products. Both types of torrefied products are well suited for the storage and thermal utilization. Summary of the major differences in DT and both types of WT is listed in Table 2.3.

Table 2.3 General Properties of Dry and Wet Torrefied Biomass

<table>
<thead>
<tr>
<th>Properties of Torrefied Biomass</th>
<th>Dry Torrefaction</th>
<th>Wet Torrefaction</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced Torrefied product</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Moisture contents</td>
<td>Lower</td>
<td>Higher</td>
<td>Higher</td>
</tr>
<tr>
<td>Heating value</td>
<td>Lower</td>
<td>Higher</td>
<td>Higher</td>
</tr>
<tr>
<td>Bulk density</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Storage at open atmosphere</td>
<td>Possible</td>
<td>Possible</td>
</tr>
<tr>
<td>------------------------------</td>
<td>----------------------------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>Purity of the product</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Grinding Energy</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Product</td>
<td>Gas, Tar, Solid</td>
<td>Solid, Gas, Liquid</td>
<td>Solid, Gas, Liquid</td>
</tr>
<tr>
<td>Applications</td>
<td>Fuel and Char</td>
<td>Fuel and Char</td>
<td>Fuel and Char</td>
</tr>
<tr>
<td>Carbon contents</td>
<td>Low</td>
<td>Medium-High</td>
<td>High</td>
</tr>
</tbody>
</table>

**2.4 Applications**

The main application of torrefaction involves co-firing the torrefied biomass with coal in electrical or thermal power plants, combustion facilities used to produce heat, gasification, and furnaces of cement factories, as shown in Figure 2.5. The torrefied product is an attractive source of fuel for combustion and gasification because of its enhanced fuel quality in terms of hydrophobicity, bulk density and heating value, which eventually improves the thermal efficiencies, compared to using raw biomass [96]. Pulverized fuel combustion in coal fired electrical power plants and entrained flow gasification are the most promising applications [49]. In both cases, biomass needs to be crushed into a powder form prior to the feeding to the reactor, which is not only difficult to achieve using traditional coal-mills, but also costly. The use of raw wood pellets in co-firing applications have already been implemented on the commercial scale, however, direct use of wood pellets also creates challenges due to high moisture content, low energy content, high moisture uptake during storage and high transportation costs [97]. In addition, the use of raw wood pellets in coal fired plants requires modifications of the existing infrastructure, which is costly and time consuming. These limitations can be minimized through DT of wood pellets to increase the fuel quality. As previously stated torrefaction increases the energy density and creates a more brittle solid product, which leads to a reduction in energy requirements for transportation and grinding. Therefore, the potential exists for co-firing torrefied biomass with coal or using it directly in combustion and gasification systems [96]. However, torrefaction integrated with
combustion and gasification system have yet to reach the commercial scale. Bioethanol is also produced from the exhaust of the system. Syngas is synthesised from flue gas treatment then fermented to produce bioethanol. Potential market segments include large scale power production using co-firing in coal-fired boilers, industrial heating, and residential/district heating using combustion at blast furnaces/stoves/boilers. Other household applications include space heating, barbeque, cooking stoves, etc.

Figure 2.5 Application of Torrefied Biomass for Co-firing with coal [98]

The possibility of co-firing with coal can be better understood by comparing the characteristics of torrefied biomass with coal as shown in Table 2.4.

Table 2.4 Comparison of coal properties with torrefied biomass

<table>
<thead>
<tr>
<th>Properties</th>
<th>Coal</th>
<th>Dry Torrefaction</th>
<th>Wet Torrefaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (wt%)</td>
<td>8.8</td>
<td>7.1</td>
<td>High</td>
<td>[39, 89]</td>
</tr>
<tr>
<td>Ultimate analysis (wt% dry)</td>
<td></td>
<td></td>
<td></td>
<td>[71, 99]</td>
</tr>
<tr>
<td>C</td>
<td>71.8</td>
<td>53.2</td>
<td>71.4</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>4.8</td>
<td>5.8</td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>
### Proximate Analysis (%db)

<table>
<thead>
<tr>
<th></th>
<th>Volatiles</th>
<th>Char</th>
<th>Fuel Ratio</th>
<th>Heating Value (MJ/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>35.7</td>
<td>52.6</td>
<td>1.5</td>
<td>29.5</td>
</tr>
<tr>
<td>N</td>
<td>82.5</td>
<td>17.1</td>
<td>0.2</td>
<td>23.5</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
<td>28.6</td>
</tr>
<tr>
<td>Ash and others</td>
<td>0.4</td>
<td>0.4</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

[71, 99]

### Snap shots of Dry and Wet Torrefaction Literature Articles

Numerous studies have been conducted on the application of dry and wet thermochemical treatments of different types of biomass and petroleum based products for the production of biomaterials. Examples of these studies are listed in Table 2.5.

### Table 2.5 Application of Dry and Wet Torrefaction

<table>
<thead>
<tr>
<th>Sample Biomass</th>
<th>Wet Torrefaction</th>
<th>Ref.</th>
<th>Operation/Results</th>
<th>Sample Biomass</th>
<th>Dry Torrefaction</th>
<th>Operation/Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood chips+</td>
<td>Polypropylene</td>
<td>[100]</td>
<td>160°C/90min</td>
<td>Spruce + Polypropylene</td>
<td>[104]</td>
<td>210°C/30min</td>
</tr>
<tr>
<td>Yellow Pine + Polypropylene</td>
<td>[101]</td>
<td>170°C/60min</td>
<td>Wood Composites</td>
<td>P. Taeda L.+</td>
<td>[106]</td>
<td>200/240°C/30min</td>
</tr>
<tr>
<td>Maple + resin Polypropylene</td>
<td>[102]</td>
<td>160°C/30-45min</td>
<td>Wood Composites</td>
<td>Scots pine + Polylactic acid</td>
<td>[107]</td>
<td>212°C with N2</td>
</tr>
</tbody>
</table>
### 2.6 Advantages of Torrefaction

The major advantage of torrefaction is the improvement of the biomass fuel quality, which during combustion demonstrates behaviors that are similar to the coal [39]. In general, the fuel qualities of coal include: a moisture content of 10-15%, a heating value of 23-28MJ/kg, a fixed carbon content of 50-55% (dry basis), and a bulk energy density of 18-24 GJ/m³ [38, 59]. The fuel qualities of torrefied biomass pellets include: a moisture content of 1-5%, a heating value of 20-24 MJ/kg, a fixed carbon content of 28-35% (dry basis), and a bulk energy density of 15-19 GJ/m³ [27, 38, 59, 60]. Acharya & Dutta (2013) [14] observed in the experiment of DT of oat pellets that the increase in higher heating value was about 42%.

Both types of torrefaction can be carried out for any type of lignocellulosic biomass, even though hydrothermal is preferred for the feed stocks with higher moisture contents. WT torrefaction also has the ability to combine multiple types of biomass in the same reactor, while still creating a nearly homogeneous solid product. CEATI International Inc. is leading a project involving the manufacturing of solid sustainable energy carriers by means of torrefaction (SECTOR), as well as a torrefaction research program using agricultural biomass to study the potential applications of using torrefied biomass [59].

Pelletizing is a densification process, where torrefied biomass is ground and compressed into a cylindrical pellet form. The pellets provide advantages for transportation, handling, and storage because the pelletizing process increases the energy density (GJ/m³) of the solid fuel
by up to 8 times its original value [55, 97]. The hydrophobic nature of torrefied pellets allows them to be stored in areas open to natural environmental conditions, similar to coal. Torrefied pellets typically require a binder or additional moisture to hold the form of the pellet, due to the low moisture content of torrefied biomass. However, the addition of a binder will increase the mechanical strength of the torrefied pellet compared to raw biomass pellets and reduces the amount of dust produced from broken pellets during handling applications [16].

Torrefaction reduces weight but not volume, therefore the torrefied biomass must be densified in order to increase the energy density (GJ/m$^3$) and therefore save on transportation and storage space costs [15]. Densification also reduces the possibility of self-ignition during storage, and transportation of torrefied biomass, due to the decrease of dust produced from torrefied pellets compared to traditional pellets. Transportation distance is one of the major barriers for the commercialization of torrefied products. Therefore, it is more economical to build torrefaction and thermal power plant facilities in close proximity to the biomass source, as thermal power plants are capable of handling torrefied biomass without the need for densification, thus eliminating densification and transportation costs [97].

The increase in hydrophobic characteristics of biomass is another advantage of torrefaction, which leads to easier handling and storage of the solid fuel. The hydrophobic nature of the torrefied biomass is due to the replacement of OH groups from the non-polar groups during torrefaction [96]. This enables the torrefied product to become less susceptible to biodegradation, self-ignition, and moisture uptake during storage, even in damp conditions. The increase in handling is due to the brittle nature of torrefied biomass caused by the decomposition of hemicelluloses and softening of lignin and cellulose. At torrefaction temperatures above 275°C, the strong fibers contained in raw biomass become almost completely destroyed, which decreases the energy required to grind the biomass by about 50-85% and raises the throughput by nearly 2-6.5% [55, 59, 109-111].

Torrefied biomass shows similar characteristics to coal during combustion, while producing less ash and containing lower moisture contents. Torrefied biomass contains a higher reactivity compared to coal, due to the presence of increased volatile matter contents, results in a higher boiler exit temperature [98]. Improved characteristics of biomass have increased the possibility of commercial co-firing with coal in the near future.
2.7 Current Market and economic status

Commercialization of DT technologies is presently in the early stage, however, several companies are moving towards the developing industrial scale systems [15]. In North America, the development of commercialized WT systems has yet to be achieved, due to the difficulty in developing high pressure continuously flowing reactors. Numerous academic institutions and research agencies are working towards the improvement of both torrefaction technologies. For DT, Topell B.V. has developed a full scale demonstration plant with 60,000 ton/year in 2010, using forest biomass located in Netherland. Green Investments (SGI), a Belgian company, has finalized the construction of an integrated wood and biomass DT demonstration plant based on a modified belt dryer with a capacity of 45,000 tons/year in Steenwijik, the Netherland. In Belgium, Torr-Coal B.V has built a wood based DT plant with a capacity of 35,000 ton/year. A pilot plant based on a rotating screw reactor feeding straw at 1 ton/hour has been built by Dutch-BioLake B.V. Airex Energy is currently operating a DT facility with a biomass input of 250Kg/hour in Quebec, Canada since March, 2011. This company has also planned to scale up the process to 2 tons/hour, sometime in the near future. Similarly, Andritz/ECN has planned to run a combined torrefying and pelletizing facility using wood chips with a capacity of 700,000 tons/year. A USA based company; New Biomass Energy Company has been producing torrefied biomass materials since early 2011 targeting to produce 22 tons/hour capacity by the end of 2015. Another USA based company: Earth Care Products Inc. has constructed a facility that is producing 20,000 tons/year and they are currently targeting to enhance the capacity to 19 tons/hour.

The present use of torrefied wood in the European market can be increased by three folds if 5% of coal utilization is replaced by torrefied wood [99]. Large scale market applications using torrefied wood have the potential to replace 50% of the current usage in Europe. Wilen et al.(2013) [99] estimated that the utilization of the torrefied wood will increase from 12 million tons in 2010 to 25 million tons in 2020, in Western Europe alone. The future increase in the utilization of biomass pellets will require torrefied wood imports from Eastern Europe, Russia, and North America to meet the demand. In 2012 alone, more than 3 million tons of biomass pellets were transported from North America to Europe [99]. In global distribution of woody biomass availability, EU alone has the potential to produce 1.3 billion m$^3$, whereas;
Eastern Europe, South America, North America, Asia, and Australia have the potential to supply biomass to the global market as well [99].

In order for the production and utilization of torrefied pellets to reach a global scale, a set of standards and regulations must be developed to ensure all produced torrefied pellets meet a certain level of fuel quality. Several technology developers from the EU and the United States have invested significantly in DT technologies. Canada has approximately 979.1 million hectares of land, which consists of 397.2 million hectares of forests. In 2004, Canadian sawmills produced 83.5 million cubic meters of lumber, 47% of which were from British Columbia, followed by 24% from Quebec, and 10% from Ontario. Although Lumber production has slowed down in recent years due to the US-led recession [113], wood-based products still remain one of the main sources of bioenergy feedstocks in Canada, along with agricultural residues. Wood waste from mills, residual biomass remaining after harvesting, and crops grown specifically for biomass production are all sources for forest and agricultural type biomass [114]. The wood waste from mills is the most widely used among the three categories for pellet production and other biofuel applications.

BIOCAP Canada published results on the analysis of major agricultural and forestry based resources to evaluate the availability of bio-resources obtainable in Canada [114]. They concluded that 245 million hectares of timber forests in Canada have a biomass carbon stock of about 15.8 billion tons of carbon, totaling 566 Exajoules of energy, which is 69 times Canada’s current annual energy demand met by fossil fuel. On the basis of annual harvesting the annual energy content of the biomass crops in Canada amount to 5.1 Exajoules, which is 62% of the energy recovered from fossil fuel ignition. On the basis of biomass residues, about 60 million tons of carbon streams may be considered “available” feedstock for a bio-based economy, this is conservatively expected to be between 1.5-2.2 Exajoules of energy per year, which is 18 – 27% of the energy that Canada received from fossil fuels in 2000 [114]. BIOCAP is considering wood and straw pellets as a potential solid biofuel for replacing coal and it was estimated that a government subsidy of $4 per gigajoule is necessary to compete with coal in the present market. In 2005/06, British Columbia alone sold 500,000 tonnes of wood pellets at a “Freight on Board” cost of $6-7/GJ(thermal energy). The feedstock cost in Ontario is approximately $7.5-9.0 per Gigajoule and the cost of coal is $3.0-4.0/GJ (thermal energy) resulting in a gap of about $4.0-5.0 per Gigajoule [115]. This indicates that a subsidy
of $4GJ is required for the Ontario farmers to compete with coal. Hence, the replacement of coal by solid biofuel significantly helps to minimize the greenhouse gas emissions in Ontario. Biomass can compete with coal if a government subsidy is used. Canada retains substantial benefits in bioenergy from its arable land and forested areas. About 1,866 megawatts of biomass power capacity is currently available in Canada [116]. In 2007, 11.9 million tons of Municipal solid waste (MSW) amounting to about 211-187 MW of electricity generating capacity was available in Canada without considering the thousands of MWs of potential energy lost in sewage. Biomass feedstock extends from forest and agricultural residues to poultry litters and MSW. So, an effective implementation of commercially operable torrefaction plants can revolutionize the green energy business potential, leading the economy towards sustainable energy systems, while helping in minimizing the utilization of fossil fuels.

Topell [112] estimated that the total investment cost, including costs of collecting wood, drying equipment, grinding mills, pellet mills, storage, civil workers, and a reactor for DT was approximately 19.5 million USD for a wood pellet plant and 29 million USD for a torrefied pellet plant, which is more than estimated by Bergman (2005) [117-118]. Detailed cost structure is given in Table 2.6, which shows marginally higher costs for torrefied pellets with an 18% ROE for investors. However, in regional and global marketing of pellets, torrefied pellets are slightly cheaper after accounting for the transportation and handling costs of the product (IEA, 2012). The present market price of coal is about US$ 140 per ton or US$ 5 per GJ, when it is used in coal fired power plants, which is less expensive compared to torrefied pellets. However including the cost of carbon credits, significantly increases the cost of using coal and therefore the replacement of coal with torrefied pellets could become an economic alternative to producing energy, while at the same time, minimizing the amount of greenhouse gas emissions [59].
Table 2.6 Cost Analysis of one GJ torrefied and raw wood pellets [59]

<table>
<thead>
<tr>
<th>Components</th>
<th>Wood Pellets WP in US$</th>
<th>Torrefied Pellets TP in US$</th>
<th>Cost Difference (TP-WP) US$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>4.28</td>
<td>4.28</td>
<td>0.00</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.60</td>
<td>0.74</td>
<td>0.14</td>
</tr>
<tr>
<td>Labor</td>
<td>0.48</td>
<td>0.47</td>
<td>-0.01</td>
</tr>
<tr>
<td>Financial costs</td>
<td>1.01</td>
<td>1.49</td>
<td>0.49</td>
</tr>
<tr>
<td>Other costs</td>
<td>0.40</td>
<td>0.43</td>
<td>-0.03</td>
</tr>
<tr>
<td>Cost Price at Production site</td>
<td>6.76</td>
<td>7.41</td>
<td>0.65</td>
</tr>
<tr>
<td>Land logistic plant-Port</td>
<td>1.12</td>
<td>0.57</td>
<td>0.65</td>
</tr>
<tr>
<td>Deep sea shipment</td>
<td>2.04</td>
<td>1.28</td>
<td>-0.76</td>
</tr>
<tr>
<td>Land logistics from port to utility</td>
<td>0.94</td>
<td>0.55</td>
<td>-0.39</td>
</tr>
<tr>
<td>Cost Price Delivered at Utility</td>
<td>10.87</td>
<td>9.81</td>
<td>-1.06</td>
</tr>
<tr>
<td>Extra cost at power plant</td>
<td>1.93</td>
<td>0.00</td>
<td>-1.93</td>
</tr>
<tr>
<td>Total cost of coal replacement</td>
<td>12.80</td>
<td>9.81</td>
<td>-2.99</td>
</tr>
</tbody>
</table>

Detailed economic studies of using wet torrefied biomass are not available in the open access journals and libraries so could not be included in the analysis.

2.8 Conclusions and Recommendations

DT is the thermochemical conversion process at 200-300°C at atmospheric pressure, with a minimum to no oxygen (near to inert) environment. DT requires feedstocks with moisture contents below 15% (dry basis) so prior drying before torrefaction is essential for the treatment of wet biomass. WT, commonly known as hydrothermal torrefaction, is another
thermochemical conversion process, that utilizes pressurized subcritical water at 180-265°C in an inert environment. The wet biomass, a major issue for the DT, can be treated through liquid or vapor torrefaction (WT) without initially drying the biomass. The wet torrefied products have a higher heating value compared to dry torrefied products and the treatment temperature and residence time for lignocellulosic biomass are less in WT than in DT, while achieving similar fuel characteristics of the torrefied products. Both processes produce energy dense products, which are more suitable compared to raw biomass for co-firing with coal. The torrefied products are also hydrophobic, possess a higher bulk density, and require less energy to grind.

Currently, wood pellets are commonly used in the coal-fired power plants. Torrefied biomass can be used in pulverized co-firing boilers with coal. The composition of torrefied biomass can be up to 50% during co-firing, however, there are still technical limitations in using torrefied biomass alone in a coal-fired boiler, which require slight modifications at the feeding stage of a boiler. These products can also be used in industrial and domestic heating. Similarly, torrefied biomass can be used for the improvement of soil fertility in the form of char.

Commercial operation of a DT plant has yet to be realized due to technical problems observed during the operation of pilot plants. WT is still under the research and development phase, and in order to commercialize the process, further research on the designing of reactors to handle the high pressure associated with subcritical water at temperatures above 189°C is required.

Major recommendations to move forward are i) Development of product standards, ii) Increase in studies associated with the transition of pilot scale torrefaction plants to commercial scale facilities, iii) Exploration of the attractiveness of waste derived from co-firing torrefied biomass, iv) Development of a WT pilot scale plant, v) Study on the characterizations of biomass porosity change due to the structural changes undergone in the thermal treatment of biomass and its impact on the manufacturing of biomass composites vi) Storage of torrefied biomass in different open environments to test its durability vii) Design of continuous commercial DT reactors viii) In-depth research for the commercialization of WT ix) Design of continuous WT reactors.
2.9 References


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Chapter 3  Review of syngas fermentation processes for bioethanol

Abstract

Bioethanol is recognized as an important renewable and sustainable transportation fuel. Although synthesis gas (syngas: CO, H₂, CO₂) produced from lignocellulosic biomass (forest or agricultural biomass) is being used in the production of bioethanol by both chemical catalytic and biosynthesis processes, latter noted to have more advantages. In the biosynthesis process, bioethanol is produced along with acetate, hydrogen, butanol, butyrate, methane, peptone, and formaldehyde. Although progress has been made on research and development for the utilization of syngas on fermentation technology, the major barriers for the commercialization still include low yield, expensive biological catalyst, slow kinetics, low gas-liquid mass transfer, and challenges with catalytic separation and recycling. This chapter presents a review on fermentation product impurities, microorganisms, chemical reactions, separation techniques, bioreactor types, fermentation conditions, gas-liquid mass transfer, current status of the technology and economics. It seems selection of the appropriate microorganism, nutrient medium, and appropriate hollow fiber membrane biofilm reactor might lead toward achieving increased mass transfer efficiency for commercialization of the bioethanol.

3.1 Introduction

The global debate on the use of the food grain portion of biomass for producing biofuels (bioethanol or biodiesel), rather than nourishment for the human population has sparked an interest in producing biofuels from the non-food grain part of plants [1]. Both biochemical and thermochemical conversions methods are used to produce bioethanol. First generation biofuels are produced from food crops, especially, from corn and sugar cane. United States, one of the leaders in first generation biofuel production, produces 127,000 m³ of biofuel per

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day followed by South America, EU and Asia [2]. Due to the “food versus fuel” debate, the second generation of biofuels are produced from the non-food part of the lignocellulosic biomass such as herbaceous/woody plants, agricultural and forest residues, municipal and biobased industrial solid waste, organic waste, etc [3-5].

In recent development, ethanol has been produced by fermenting synthesis gas produced from the gasification of biomass or municipal biological waste was fermented into ethanol by using microorganisms [1-2]. Research is being conducted to identify the most effective microorganism for this process [4-5]. Anaerobic bacteria, acetogens like Clostridium families, are used to grow hemolithotrophically on syngas components of CO, H₂ and CO₂ through the Wood-Ljungdahl method to volatile fatty acids and alcohols like ethanol, acetate, and butyrate at a temperature of 37°C and atmospheric pressure [4, 6-9]. Ethanol production using the biomass/ fossil fuel gasification is gaining popularity [10-11]. The production of ethanol not only depends on the type of organism used but also depends on the types of fermenting reactors like hollow fiber membrane stirred tank reactor and continuous stirred tank reactor [12-14]

Even though, global companies Lanzatech, Coskata and IneosBio are suggesting the possibilities of expanding syngas fermentation technology in the commercial markets, there are still techno-economic challenges such as low ethanol concentration (2%), toxic contaminants cleaning process, high cost media ingredients, and high operational cost [14-16]. For the commercialization of the bioreactor; high cell concentrations, homogeneous mixing, and high volumetric mass transfer are essential. The dual Rushton type impeller showed the highest volumetric mass transfer rates and lowest mass transfer performance [17].

There are different methods to produce ethanol from coal, natural gas, petcoke, biomass, and municipal waste. The ethanol production routes from biomass and fossil fuel are presented in Figure 3.1.
The key challenges for the successful fermentation of syngas are poor mass transfer properties of syngas specifically CO and H\textsubscript{2}, low ethanol yield, readiness of biomass gasification technology for producing syngas and gas clean-up processes (impurities with Nitric oxide, ammonia, tars, hydrogen cyanide, methane, sulfur dioxide, hydrogen sulfide, carbonyl sulfide). Additional challenges include steady production of syngas, scale up and commercial fermentation, downstream processing, and bioreactor design [7,14,18]. Therefore proper knowledge of the merits/demerits of impurities and cleaning techniques are important for the commercialization of the process [15]. Feedstock development and improvement, as well as system integration could improve the performance of the syngas fermenter. Improvement in the cleaning of the impurities on the syngas could also enhance the productivity of the biofuel reactor [19-20]

Several researcher have reviewed the syngas fermentation into ethanol and discussed its pros and cons [2,5,10,19], especially, gasification, fermentation, microorganism, bioreactors and gas-liquid mass transfer, some of the recent development in syngas fermentation are yet to be reported. Therefore, this chapter attempts to compile studies on syngas fermentation by incorporating some of the recent and robust development in syngas fermentation and focused on syngas impurities and cleaning, microorganism, bioreactor design and configuration, gas-liquid mass transfer. The economics of syngas fermentation and challenges in the commercialization of syngas fermentation are also discussed to identify the challenges for further improvement.
3.2 Syngas Impurities and Cleaning

Synthesis gas generally comprises of carbon monoxide, hydrogen, and carbon dioxide but during the process of gasification, numerous products can be expected along with the syngas including some solid and liquid products, as well as other gaseous compounds. Usually, the solid product is mainly composed of ash, the liquid products consist of water and tars, and the gaseous products consists of ethane, benzene, hydrogen sulfide, sulfur dioxide, ammonia, nitrogen, hydrogen cyanide, NOx, methane, acetylene, and ethylene, as well as the syngas components mentioned previously[20-25]. Table 2.1 presents a list of impurities reported during gasification of biomass, coal, and their mixture. Impurities may have an effect on the performance of the gasifier, cleaning methodology, and syngas production, as well as operation and maintenance [21-22]. Impurities affect microbial activities and pH of the fermenting broth, could lead towards cell toxicity, enzyme inhibition and osmolarity [23-25].

Table 3.1 Biomass, Coal and Mixture Gasification Impurities

<table>
<thead>
<tr>
<th>References</th>
<th>Components</th>
<th>Level of Impurities (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Biomass</td>
</tr>
<tr>
<td>[21,26]</td>
<td>Methane</td>
<td>15.00%</td>
</tr>
<tr>
<td>[22]</td>
<td>Acetylene</td>
<td>0.69%</td>
</tr>
<tr>
<td>[21,26]</td>
<td>Ethylene</td>
<td>5.30%</td>
</tr>
<tr>
<td>[26,27]</td>
<td>Ethane</td>
<td>0.80%</td>
</tr>
<tr>
<td>[28]</td>
<td>Benzene</td>
<td>0.30%</td>
</tr>
<tr>
<td>[27]</td>
<td>Naphthalene</td>
<td>0.30%</td>
</tr>
<tr>
<td>[28]</td>
<td>Sulfur dioxide</td>
<td>0.06%</td>
</tr>
<tr>
<td>[28]</td>
<td>Mono nitrogen oxides</td>
<td>0.12%</td>
</tr>
<tr>
<td>[26,27]</td>
<td>Ammonia and hydrogen cyanide</td>
<td>0.28%</td>
</tr>
<tr>
<td>[26,27]</td>
<td>Hydrogen sulfide and Carbonyl</td>
<td>~0</td>
</tr>
</tbody>
</table>

The major challenge during the ethanol production from the fermentation of syngas is the cleaning of the impurities in an environmentally and economically manner. Cyclones clean up the particulate during the gasifying process, however the most recent and commonly used method is the hot gas cleaning method applied after gasification, which involves physical and chemical treatments. In such treatments, cyclones, filters, rotating particle separators,
electrostatic filters and scrubbers, as well as downstream cracking techniques are used [29]. In recent research, tar cracking for cracking the hydrocarbons; water quench scrubbers for removing ammonia; amine treatment for sulfur and carbon dioxide; Zinc oxide/Zinc titanates treatment for sulfur removal are also used for syngas cleaning purpose [30,31]. Ammonia decomposition in parallel to the absorption of hydrogen sulfide is possible by mixing cobalt and nickel into a zinc-titanate solvent, in addition tar can be minimized by using calcined dolomites with a nickel catalytic [31].

Types of impurities (tars, nitric oxide, and ammonia) also depend upon the feedstock types, the gasifier type, and cleanup conditions. The common syngas purification methods used to minimize tar, char, particulate matter and other contaminants include; cyclones, adsorption columns, water or oil scrubbers and filters [8,18]. There are a number of literature articles available in the analysis of the impacts of impurities in the production or bioethanol from fermentation of syngas [19-20]. Ethanol production decreases with an increase in oxygen concentration [19]. In anaerobic fermentation of syngas, a variation in bacterial development and the concentration of metabolic products also effect the production of bioethanol [19]. Tar and Nitric oxide have potential to retard cell growth and enzyme activities during fermentation of syngas. Tars and H₂S are the inhibitory and stimulatory compounds in the syngas [20].

During the fermentation process, impurities may play a negative role due to cell toxicity, enzyme inhibition, redistribution of product, and changing of the pH level/redox potential [31]. There are many enzyme inhibitor species in the syngas itself. Common enzymes inhibitors in acetogens and wood-Ljungdahl are listed in the Table 2.2. Tar may cause cell dormancy and product redistribution; nitrous oxide acts as an inhibitor of hydrogenase leading towards cell growth and product distributions [1]. Nitrous oxide (NO) with a concentration of more than 0.004 mol%, may also increase the ratio of ethanol to acetic acid, which retards cell growth [15]. Another impurity, ammonia may cause toxic effects if the concentration is above 215mol/m³. Hence, a cleanup system that is appropriate for the particular syngas fermentation is required, in order to maintain maximal bacterial activity and minimized char/tar accumulation in the delivery line that would otherwise result in clogging, line breaking, and unstable gas flow. Absence of syngas impurities may bias the experimental results required for the commercialization of syngas fermentation technology. Therefore, careful clean up the impurities should be a target research area for further exploration.
### Table 3.2 Syngas Impurities and its effect

<table>
<thead>
<tr>
<th>References</th>
<th>Impurities</th>
<th>Enzymes</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>[15]</td>
<td>Ammonia (NH3)</td>
<td>Alcohol Dehydrogenase (ADH), Amidase</td>
<td>Inhibition of ADH at very high concentration</td>
</tr>
<tr>
<td>[1]</td>
<td>Nitric Oxide (NO)</td>
<td>Hydrogenase, ADH</td>
<td>0.015 mol % (100% inhibition Hydrogenase (No effect at 0.004 mol %))</td>
</tr>
<tr>
<td>[32]</td>
<td>Nitrogen Dioxide (NO2)</td>
<td>Formate Dehydrogenase (FDH), Nitrate reductase</td>
<td>1 mol/m3 (5% inhibition for FDH and 20% inhibition of nitrate reductase)</td>
</tr>
<tr>
<td>[33]</td>
<td>(Hydrogen Sulfide) H2S</td>
<td>Thiosulfate Sulfurtransferase (TS), L-ascorbate oxidase (LAO)</td>
<td>&gt;30mol/m3 for TS and 1mol/m3 for 97% inhibition for LAO.</td>
</tr>
<tr>
<td>[15]</td>
<td>Sulfur dioxide (SO2)</td>
<td>Ascorbic Acid Oxidase (AAO)</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3 Microorganisms Involved in Biofuel Production

There are number of mesophilic and thermophilic microorganisms available for the fermentation of syngas. The alcohol production was doubled in the fermentation of syngas using *Alkalibaculum bacchi strain CP15* and propionic acid producer *Clostridium propionicum* together [4]. Higher amounts of ethanol can be produced using a specific type of acetogone *Clostridium ljungdahlii* [5]. The microbial catalysts mostly used in fermentation of syngas are *C. acetobutylicum*, *Clostridium beijerinckii*, *M. thermoacetica*, *B. methylotrophicum*, *A. woodii*, *Clostridium ljungdahlii*, *Clostridium autoethanogenum*, *Acetobacterium woodii*, *Clostridium carboxidivorans* and *Peptostreptococcus*[8,9]. Heiskanen et al.(2007) pointed out that the production of bioethanol from syngas using biological catalysts such as *Acetobacterium woodii*, *Clostridium carboxidivorans*, and *Peptostreptococcus* ferments more efficiently compared to chemical catalysts like copper, cobalt or iron [9].
This method offers advantages on the feedstock flexibility, high rate of energy, carbon capture and manufacturing cost in comparison with conventional fermentation and thermochemical approaches [7]. In addition to these advantages, this technique provides system robustness, catalyst flexibility, selectivity, and high development potential [7].

The optimum temperature range of the mesophilic bacteria is from 37°C - 40°C, whereas for the thermophilic bacteria the range is 55°C-80°C [34]. The commonly used microorganisms and their optimum operating temperature, pH level, etc. for the fermentation of syngas are listed in Table 3.3.

**Table 3.3 Commonly Used Microorganisms**

<table>
<thead>
<tr>
<th>References</th>
<th>Microorganism</th>
<th>Syngas Composition (%)</th>
<th>Product</th>
<th>Temp (°C)</th>
<th>pH level</th>
</tr>
</thead>
<tbody>
<tr>
<td>[8]</td>
<td>Acetobacterium woodii</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Acetate</td>
<td>30</td>
<td>6.8</td>
</tr>
<tr>
<td>[35]</td>
<td>Acetogenium Kivui</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt; (13:14:5:68)</td>
<td>Acetate</td>
<td>N/A</td>
<td>6.6</td>
</tr>
<tr>
<td>[8]</td>
<td>Butyribacterium methylotrophicum</td>
<td>CO 100%</td>
<td>Acetate, ethanol, butyrate, butanol</td>
<td>37</td>
<td>6.0</td>
</tr>
<tr>
<td>[36]</td>
<td>Butyribacterium methylotrophicum</td>
<td>CO 100%</td>
<td>Acetate, lactate, butyrate, pyruvate</td>
<td>37</td>
<td>6.8/6.0</td>
</tr>
<tr>
<td>[9]</td>
<td>Butyribacterium, methylotrophicum</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Acetic acid</td>
<td>37</td>
<td>6.9</td>
</tr>
<tr>
<td>[37]</td>
<td>Clostridium acetici</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/Ar (78:4:18)</td>
<td>Acetate</td>
<td>30</td>
<td>8.5</td>
</tr>
<tr>
<td>[38]</td>
<td>Clostridium autoethanogenum</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Acetate, ethanol</td>
<td>37</td>
<td>5.8-6.0</td>
</tr>
<tr>
<td>[39]</td>
<td>Clostridium autoethanogenum</td>
<td>CO/CO&lt;sub&gt;2&lt;/sub&gt; (95:5)</td>
<td>Acetate, ethanol</td>
<td>37</td>
<td>4.74</td>
</tr>
<tr>
<td>[38]</td>
<td>Clostridium autoethanogenum</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt; (20:10:20:50)</td>
<td>Ethanol</td>
<td>37</td>
<td>6.0</td>
</tr>
<tr>
<td>[8]</td>
<td>Clostridium carboxidivorans</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Acetate, ethanol, butyrate, butanol</td>
<td>38</td>
<td>6.2</td>
</tr>
<tr>
<td>[40]</td>
<td>Clostridium carboxidivorans</td>
<td>CO/CO&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt; (25:15:60)</td>
<td>Ethanol, butanol</td>
<td>37</td>
<td>5.2</td>
</tr>
<tr>
<td>[41]</td>
<td>Clostridium carboxidivorans</td>
<td>CO/H&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Acetate, ethanol, butyrate, butanol</td>
<td>37</td>
<td>5.8-5.9</td>
</tr>
<tr>
<td>P7</td>
<td>butanol</td>
<td>References</td>
<td></td>
<td></td>
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<td>---------------------------</td>
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<td></td>
</tr>
<tr>
<td>Clostridium leatocellum SG6</td>
<td>CO/H₂/CO₂</td>
<td>[42]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate, lactate, ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium ljungdahlii</td>
<td>CO/H₂/CO₂</td>
<td>[43]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate, ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium ljungdahlii</td>
<td>H₂/CO₂ (75:25) /CO/CO₂(70:30)</td>
<td>[44]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium ljungdahlii ERI2</td>
<td>CO/H₂/CO₂/N₂ (14:17:4:65)</td>
<td>[35]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium ljungdahlii</td>
<td>CO/H₂/CO₂/Ar (55:18:10:15)</td>
<td>[14]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium ljungdahlii</td>
<td>CO/H₂/CO₂/N₂ (20:10:20:50)</td>
<td>[45]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium ragsdalet</td>
<td>CO/H₂/CO₂/N₂ (20:5:15:60)</td>
<td>[8]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate, ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium strain P11</td>
<td>CO/H₂/CO₂/N₂ (20:5:15:60)</td>
<td>[45]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eubacterium limosum</td>
<td>CO/H₂/CO₂</td>
<td>[8]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eubacterium limosum</td>
<td>100%CO and CO/CO₂(80:20)</td>
<td>[46]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate, butyrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moorella sp. HUC22-1</td>
<td>H₂/CO₂ (80:20)</td>
<td>[47]</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesophilic bacterium P7</td>
<td>CO/CO₂/N₂ (25:15:60)</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate, ethanol, butyrate, butanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxabactor pfennigii</td>
<td>CO/H₂/CO₂</td>
<td>[48]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate, n-butyrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peptostreptococcus productus</td>
<td>CO/H₂/CO₂</td>
<td>[49]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thermophilic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxydocella sporoproducens</td>
<td>CO/H₂/CO₂</td>
<td>[50]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen</td>
<td></td>
<td></td>
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<tr>
<td>Clostridium thermocellum</td>
<td>CO/H₂/CO₂</td>
<td>[51]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desulfotomaculum thermobenzoicum subsp.</td>
<td>CO/H₂/CO₂</td>
<td>[52]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate, H₂S</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moorella thermoacetica (Clostridium thermoacetica)</td>
<td>CO/H₂/CO₂</td>
<td>[53]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moorella sp. HUC22-1</td>
<td>H₂/CO₂ (80:20)</td>
<td>[54]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moorella thermoautotrophica</td>
<td>CO/H₂/CO₂</td>
<td>[55]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4 Chemical Reactions

The most common syngas fermentation reactions in the presence of a fermenting microorganism can be expressed in the following chemical equations.

\[
4\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{CO}_2
\]

\[
6\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} + 4\text{CO}_2
\]

\[
6\text{H}_2 + 2\text{CO}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}
\]

Bioethanol production from the process of syngas fermentation is a complete conversion process with irreversible products without producing thermodynamic equilibrium. The process involves mixing together carbon monoxide, hydrogen and carbon dioxide, which are converted into acetate, followed by ethanol. There are numerous reaction pathways to get alcohol and ethanol; several of them are presented in Table 3.4.

Table 3.4 Reactions for Ethanol and Higher Alcohol Synthesis (HAS) [10]

<table>
<thead>
<tr>
<th>Name of Reaction</th>
<th>Chemical Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol synthesis</td>
<td>(\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{COH} + 2\text{CO}_2)</td>
</tr>
<tr>
<td>Water–gas shift</td>
<td>(\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2)</td>
</tr>
<tr>
<td>CO beta addition</td>
<td>(\text{CH}_3\text{OH} + \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>Methanol homologation</td>
<td>(\text{CH}_3\text{OH} + \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>HA homologation</td>
<td>(\text{C}<em>n\text{H}</em>{2n+1}\text{OH} + \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3(\text{CH}_2)_n\text{OH} + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>Condensation/coupling</td>
<td>(2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>Dehydration/DME formation</td>
<td>(2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{O} + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>Branched iso-alcohols formation</td>
<td>((\text{CH}_3)_2\text{CO} + \text{H}_2 \rightarrow (\text{CH}_3)_2\text{CHOH})</td>
</tr>
<tr>
<td>Methyl ester formation</td>
<td>(2\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3)</td>
</tr>
</tbody>
</table>

3.5 Biomass Gasification

Gasification, a thermochemical conversion technique, where the feedstock is converted to carbon monoxide and hydrogen-rich synthesis gas by utilizing reagents such as air, oxygen, or steam. In the gasification of biomass, clinkering/slagging issues in the pipe lines are most common, along with cell dormancy, which can procedure inhibitions due to excessive production of
ash and volatile matter [62]. One of a key functioning consideration for the syngas fermentation is the type of gasification technology used, which primarily includes fixed bed (up draft, downdraft or cross-flow) and fluidized bed gasifiers. Out of these two gasifiers, fixed bed gasifiers offer the more simple design and a decreased amount of output particulate but produce a lower calorific value syngas compared to fluidized bed gasifiers. The typical conversion efficiency of gasifying reactors is up to 80% [25].

However, these reactors require certain modification for the gasification of biomass and coal blends. Further investigations are still necessary for the proper selection of a gasifier for the gasification of biomass or coal-biomass blends. Controlling operation of the gasifier to maintain the required syngas quality, controlling temperature and pH in the fermenting bioreactor, and fermenting bioreactor design (for enhancing syngas-liquid mass transfer) can be other areas of investigation.

In industry, traditional moving bed, fluidized bed, and entrained flow gasifiers are commonly used [15]. Moving bed gasifiers can operate in co-current, counter-current, or cross current arrangements, with the co-current arrangement releasing the minimum amount of tar. The entrained flow gasifier operates only in co-current mode can obtain the most enhanced carbon conversion process [25]. In the fluidized bed gasifier, sand, ash, or char improves the heat transfer by providing a uniform temperature and a higher feed rate. To achieve better performance of all types of gasifiers, they should be operated at higher temperatures and a smaller input feedstock particle size [15]. Most of the gasifiers are capable of accepting a different variability of input feed stock, from biomass to fossil fuels. However, more than 55% of commercially produced syngas is still produced from coal. Major limitations of biomass include higher moisture contents, biodegradability, larger in physical size, impurities, large variation in inorganic compounds, low bulk density, lower heating value in comparison with coal, which results in higher costs for biomass gasification compared to coal [56]. Similarly, coal gasification produces increased amounts of sulfur components, tar and ash compared to the gasification of woody biomass [3,21]. These limitations can be minimized by gasifying a mixture of coal and biomass, which ultimately helps in reducing CO₂ and NOₓ emissions [57]. Damirbas, (2003)[3] observed that the gas production increases with a reduction in tar and char; the CO₂ portion of syngas increases and the H₂ portion decreases with an increase in the proportion of biomass in the biomass-coal ratio. It was also
observed that the composition of carbon monoxide and hydrocarbons remained unchanged with an increase in the biomass proportion of the biomass-coal ratio.

Biomass use is increasing, more specifically herbaceous and woody biomass with minimum moisture contents, in the production of liquid biofuel [58]. Hence, further research is essential for improving the current gasification technology, in order to increase the use of biomass in the co-gasification process.

3.6 Distillation and Separation of Biofuel

The standard process of distillation and dehydration is being used to separate bioethanol from the mixture of water and other syngas fermentation byproducts. However, this process requires high energy costs. The basic operation principle of multistage, nonstop, counter-current, liquid-gaseous mixing distillation is the use of different boiling temperatures for the different substances.

Some of the other alternates currently under investigations include; vapor reuse and vacuum distillation, vapor recompression, ultrasonic atomization, and selective adsorption of water [8]. During the fermentation of syngas, ethanol, acetic acid, 2-3 butanediol, butyric acid, and butanol etc. are formed by the activities of certain anaerobic microorganisms like acetogens. These microorganisms convert the syngas energy source (mainly the mixture of carbon monoxide, hydrogen, and carbon dioxide) to the liquid biofuel, along with other unwanted liquid mixtures [59]. The unwanted liquid portion of the mixture needs to be removed in order to extract the desired biofuel.

The development of this technology could lead towards global energy sustainability by utilizing non-food and lignocellulosic materials such as; forest residues, agricultural residues, energy crops, and municipal/biobased industrial wastes [59, 60]. Bioconversion of syngas using biological catalysts is more promising due to the high tolerant behavior of catalysts with sulfur contaminants, compared to inorganic catalysts. During the biochemical conversion process of lignocellulosic biomass, polysaccharides are hydrolyzed by cellulose enzymes into simple sugars and fermented into ethanol by microorganisms, where polyccharides are cross linked in the plant cell walls with the hydrophobic structure of lignin, which impedes enzymatic deconstruction [60].
3.7 Reactor Technology

The product output from the fermentation of syngas depends up on the pre-treatment of the feedstock (drying, chopping, fractionation and filtering with water to minimize nitrogen and alkali), characterization of biomass, gasifier used, gas cleaning process, types of microorganism used, environment, and fuel synthesis [24]. The efficiency of the syngas fermentation process can be increased by state-of-the-art reactor designs, which allow for greater mass transmission rates, choice of biocatalysts with more yields and efficient recovery methods using nanotechnology and membrane separation [62]. Richter et al. (2013) has conducted a two stage continuous fermentation experiment with a 1 liter continuously stirred tank reactor used as a growth stage and a 4 liter bubble column equipped with a cell recycle module as an ethanol production stage. The bubbling column produces ethanol from syngas (60% CO+ 35% H₂+ 5% CO₂) using Clostridium ljungadhlii, where up to 0.37 g/L-h of ethanol has been produced resulting in a recovery of 28% of C and 74% of H₂ from the original syngas composition [12]. Gaddy et al. (2003) reported that a continuously stirred tank reactor produced 1.6g/L-h and 15g/L-h of ethanol using a Clostridium ljungadhlii strain at 1 and 6 atmospheric pressure, respectively [13]. Kundiyana et al.(2010) demonstrated successfully the installation, operation, and commissioning of 100 liter pilot scale fermenter using Clostridium strain P11 and achieved six fold improvement in ethanol concentration (25.26g/L of ethanol in 59 days) in comparison to serum bottle fermentation [14].

Shen et al. (2014) [61] studied syngas fermentation using Clostridium carboxidivoran P7 in a hollow fiber membrane biofuel reactor experiment with 3.44 g/L-day ethanol productivity and 23.93g/L ethanol concentration. It was observed that the effectiveness of syngas fermentation depends up on the mass transfer/biological characteristics of the strain, and physical properties of membranes such as bio-fouling and abrading of biofilm.

The research and development on bioethanol derived from syngas fermentation has reached the pilot scale level but has not been yet fully commercialized because of lower yield and higher catalytic/operational cost [8-10]. Bioethanol produced from syngas fermentation using biomass still has benefits compared to the biochemical process due to acceptance of low quality biomass feedstocks; avoidance of costly enzymes and complex pretreatment; non reliance on H₂:CO ratio for transformation; high biocatalysts specificity; syngas aseptic
operation at higher temperatures; no concern of Nobel metal poisoning; and reactor operation at room temperature and atmospheric pressure [9-11].

The development of commercial fermentation reactors depend upon the inputs, outputs and catalytic elements. One of the major limitations of biofuel production from syngas fermentation is the low rate of gas-liquid mass transfer. This is due to the low aqueous solubility of syngas components: mainly carbon monoxide and hydrogen. Such engineering challenge can be addressed with further investigation on proper designing of a commercial fermentation reactor to generate sufficient gas-liquid mass transfer, in an energy efficient method. Stirred tank reactors are commonly used to increase power to volume ratio by increasing the gas-liquid mass transfer ratio. However, this method consumes more power for large scale reactors and is not economically viable. Hence, investigations of alternate reactors are required, which are proposed in this chapter. Different types of batch and continuous flow bioreactors are summarized in Table 3.5.

**Table 3.5 Different Types of Syngas Fermentation Reactors**

<table>
<thead>
<tr>
<th>References</th>
<th>Type of Reactor</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[8,18]</td>
<td>Continuous Stirred</td>
<td>-Most commonly used</td>
</tr>
<tr>
<td></td>
<td>Tank Reactor (CSTR)</td>
<td>-Continuous injection of gaseous substrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Flow of a liquid nutrient into a bioreactor to feed nutrients for microbial activities</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Same product flow rate output</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Mixed properly by agitation by baffled impellers to improve mass transfer between substrate and microbes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Gaseous substrate more accessible to microbes by breaking down the bubbles into finer particles by increasing rotational speeds of impellers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Higher mass transfer rates due to longer retention in the aqueous medium by slow increase in speed of finer bubbles</td>
</tr>
<tr>
<td>[19]</td>
<td>Bubble Column Reactor</td>
<td>-Developed primarily for industrial uses with large working volume</td>
</tr>
<tr>
<td></td>
<td>(BCR)</td>
<td>-Greater mass transfer rates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Lower operating and maintaining cost</td>
</tr>
<tr>
<td>Reference</td>
<td>Reactor Type</td>
<td>Advantages</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------</td>
<td>------------</td>
</tr>
</tbody>
</table>
| [8,18] | Monolithic Biofilm Reactors (MBR) | - Gaseous substrate passes through a bed of carrier media  
- Microbes culture on a media as biofilm  
- Ethanol, acetic acid etc. produced by using gaseous substrate by attached microorganisms in a biofilm  
- Operates under atmospheric pressure making it economical |
| [63] | Trickle Bed Reactor (TBR) | - Packed bed, continuous reactor  
- Liquid cultures flows down over packing media  
- Syngas movement by co-current or counter-current direction  
- No need of mechanical agitation  
- Power consumption is less than CDTR |
| [63] | Microbubble Dispersion Stirred-tank Reactor (MDSR) | - Stirred tank connected with a micro-bubble sparger  
- Increase in mass transfer due to increase in driving force/ internal pressure by reducing size of bubble and due to the increase in the flux by reducing diameter of the bubble. |
| [64] | Membrane-based System Reactor (MSR) | - Mass transfer by composite hollow fiber membrane (HFM)  
- Not yet commercially used in syngas fermentation but used in H2/O2 transfer water treatment  
- Syngas diffused on the wall of the membranes without bubble  
- Ethanol and acetic acid formed from CO and H2 by growing microbial elements on the surface of membrane wall  
- Higher yield, higher reaction rate, higher tolerance to toxic elements |

3.8 Syngas Fermentation Conditions

Nutrient components and concentrations, pressure, temperature, medium pH, inoculums level, liquid/gas flow rate, speed of agitation for stirred tank reactors, and gas/product concentration are the main contributing factors in fermentation process. These factors need to be optimized in such a way that maximize biofuel yield.

a) Nutrient components and concentration (Media composition): Syngas fermentation utilizes microorganism to produce bioethanol. These microorganisms use syngas as
carbon and energy sources. For the maximum growth of microorganisms, it requires carbon, nitrogen, sulfur, phosphorous, minerals and vitamins [65]. Hence, necessary action should be taken to retard the unnecessary components of the production process and a favourable environment need be created. Philips et al. (1993) [16] optimized the fermentation medium of *C. ljungdahlii* to enhance the ethanol extraction over acetate by decreasing concentration of vitamin B, while stopping yeast collection from media. Similarly, Gaddy and Clausen (1992) [66] observed a molar ethanol to acetate ratio of 0.11 with 0.005/0.01/0.05% yeast extraction and a 0.05 ratio with 0.1/0.2% of yeast extraction in a batch fermentation of *C. ljungdahlii*. The cost of the fermentation media is an obstacle for large scale commercialization. Kundiyana et al. (2010b) [67] performed experiments using cotton seed extract as a medium for the *Clostridium* strain P11 to produce ethanol, which succeeded in producing 2.66 g/L of ethanol in a batch medium containing 0.5g/L of extract in 15 days.

b) Effect of Organic Source: Even though carbon monoxide is toxic, it is easily metabolized by the use of microorganisms such as; aerobic carboxydotrophs, anaerobic acetogens, phototrophs, sulfate-reducers and methanogens [20]. Anaerobic conditions are generally preferred due to minimization on the production of unnecessary chemical by-products [68]. Syngas components CO and CO₂ are used as a substrate for energy source for the bacteria during fermentation and also metabolize the extraction of by-products like organic acids, alcohols and hydrogen [63]. Ethanol concentration from fructose was higher compared to syngas during the testing of growth of *C. ljungdahlii* on syngas (N₂=50%, CO=20%, CO₂=20%, H₂=10%) and fructose [39]. Gaseous components (55% CO, 20% CO₂, 10% H₂ and 15% Ar), carbohydrates (glucose, fructose, and sucrose) and organic acids (formate, acetate, and malate) are used for the growth of *Rhodospirillum rubrum* bacteria [69]. Acetate is found to be a good carbon source for the hydrogen production via acetate to acetyl CoA, which converts to tricarboxylic acid with *R. rubrum* bacteria [70].

c) The pH level of medium: The productivity of biofuel from syngas also depends upon the pH level of a fermenting media, which regulates the substrate metabolism and changing of the physiological components (pH, membrane and proton motive force). Biological activities accelerate for a small range of pH levels but deviation from the range may cause
death of microorganisms or no production of any desired products. Acetogenic bacteria, commonly used in syngas fermentation, produce more ethanol at lower pH levels, where the product spectrum shifts from acidogenic to solventogenic state [65]. The optimum pH level for the production of acetate is from 5-7 (growth level), whereas the optimum level for the extraction of ethanol is from 4-4.5 (non-growth level) using C. ljungdahlii bacteria, which consequently results in the development of a two stage continuous stirred tank bioreactor for efficient ethanol production [66].

d) Reducing Agent: The production of biofuel from syngas fermentation also depends on the level of oxygen concentration in the medium, which needs to be optimized so that maximum growth of the microorganisms can take place. Increase in the oxygen concentration certainly retards the growth of anaerobic bacteria that is why Redox (Reduction +Oxidation) needs to be maintained properly, in order to create an optimum environment for bacteria growth. Hence, lowering the redox potential of the medium is an important parameter for the growth of anaerobic bacteria. Commonly available redox lowering chemicals are cysteine, sodium sulfide, dithiothreitol, sodium thioglycolate, ascorbic acid, tinanium (III)-citrate, potassium ferricyanide, methyl viologena and benzyl viologen [71]. Sulfur compounds present in the biomass derived syngas, aids in reducing redox potential of the medium and results in creating favorable growth conditions for anaerobic bacteria.

e) Trace Metals: Metallic components of the syngas in the form of impurities may play an important role on enhancing the bacteria growth resulting in cell growth and ethanol formation by the metalloenzymes effect. During the testing of iron, molybdenum, cobalt, nickels and copper in syngas fermentation using C. ragsdalei, it was observed that the presence of all metals without molybdenum improves solvent to acid ratio [72]. The ethanol production was doubled with an increase in iron concentration of ten times compared to the standard medium used in the fermentation culture of Clostridium carboxidivorans, whereas the production of acetic acid and butyric acid has diminished. During the testing of lignocellulosic biomass, doubling the amount of metal trace components almost doubles the cell concentration [40].

f) Fermentation medium: The biological activities may be slowed or stopped by the reactants, products or contaminants, as a result of a variation in pH levels due to
formation of carbonic acid or carbonate derivatives. The formation of carbonic acid and carbonate derivatives are from carbon dioxide and high acetate concentrations, which have the potential to retard microbiological activities in the batch media. Biomass generated syngas has the potential to stop hydrogen production and to alter the product distribution between acetate and ethanol, as well as the potential to keep microbial cell growth in dormant stages, during the process of bioethanol formation from biomass syngas fermentation using c. carboxidivorans P7 [62,72,73]. Similarly, tar in the syngas may cause cell dormancy and product redistribution; however 0.025mm filters provide a possible solution to remove tar from the syngas. Similarly, during the production of syngas, hydrogen production may be stopped due to blockage of hydrogenase enzymes produced from oxygen or carbon monoxide, acetylene and nitric oxide products [19]. Nitric oxide with more than 40 ppm concentration may have potential to inhibit hydrogenase [19]. Therefore it was concluded that C. carboxidivorans bacteria is capable of tolerating biomass syngas containing NO with less than 40 ppm without any impacts occurring on the hydrogenase enzyme performance, microbial cell growth and production dissemination.

g) Mass transfer: One of the limiting factors for the syngas fermentation is the limitation on the mass transfer rate of gas to liquid. The effectiveness of the mass transfer rate among different reactor setups is generally compared using the gas-liquid volumetric mass transfer coefficient (Kla), which indicates the hydrodynamic condition of the reactor [18]. Hence, stirred tank reactors are the most commonly used reactors, where interfacial surface area is increased by breaking up larger bubbles into a smaller size, to improve the mass transfer coefficient [63,74]. The speed of the stirrer should be controlled such that it will not increase the shear level to a point that the shear-sensitive microorganisms are affected. The bioreactor should have capability of operating with high cell concentrations and enhanced mass transfer rates.

h) Substrate pressure: Growth and metabolic activities of microorganisms are sensitive to the substrate exposure, therefore the partial pressure of gas components should be maintained at an optimum level so that there is minimum impact on the microbial growth and product distribution [75,76]. During a batch culture of C. ljungdahlii with syngas pressure of 0.8-1.8 atm., cell concentration and acetate concentration became almost
equal for all of the syngas total pressures without inhibiting cell population, even at high syngas pressures and increased production of ethanol [69,77].

Table 2.6 shows the impact of syngas composition, microorganism and reactor designs in the production of bioethanol from the syngas fermentation. *Clostridium ljungdahlii* with a single/ two stage CSTR bioreactor with a syngas composition of CO, H2, CO2 and small amount of methane (65%/20%/10%/5%) d increased bioethanol yield The variation of CO, H2, CO2 in the syngas composition could be in the range of 50-100%, 15-81%, and 3-60% respectively. However, the microorganism *Clostridium ragsdalei P11* and *Clostridium carboxidivorans P7* showed their candidacy in the syngas fermentation, therefore further study is required for selecting the microorganism that will maximize bioethanol yield. There is still room for further investigation to increase ethanol production by using a CSTR hollow fiber membrane reactor by maintaining large cell density and acidic pH levels, increasing the number of stages of reactors, selection of proper micro-organism, mass transfer characteristics, and physical properties of the membrane [62,88,90]. Shen et al (2014) [62] claimed that HFM-BR is better than suspended-growth bioreactors using *C. carboxidivorans P7* for the continuous syngas fermentation process. Klasson et al. (1991) [88] had also claimed that ethanol concentration reached up to 48g/L by *C. ljungdahlii* by the restriction of pH and media for syngas fermentation. For improving the gas-liquid mass transfer, it is very important to select a proper membrane, which optimally mixes the gas components with the liquid media so that the microorganism will use the optimum syngas to produce maximum bioethanol.

**Table 3.6 Major Impact Parameters on Bioethanol Yield during Syngas Fermentation**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reactor / Syngas</th>
<th>Composition approx.(%)</th>
<th>Bioethanol Yield g/L</th>
<th>Use CO% / H2%</th>
<th>pH</th>
<th>Microorganism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow Fiber Membrane Reactor (HFMR)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[61]</td>
<td>CO/H2/CO2/N2</td>
<td>20/5/15/60</td>
<td>24.0</td>
<td>54/68</td>
<td>4.5-6.0</td>
<td>C. carboxidivorans P7</td>
</tr>
<tr>
<td>[87]</td>
<td>CO/H2/CO2</td>
<td>40/30/30</td>
<td>15.0</td>
<td>-</td>
<td>4.5</td>
<td>C. ragsdalei P11</td>
</tr>
<tr>
<td>Reference</td>
<td>Reactant</td>
<td>Temperature</td>
<td>Pressure</td>
<td>Specific Activity</td>
<td>Species</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>----------</td>
<td>-------------</td>
<td>----------</td>
<td>------------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>[76]</td>
<td>CO/H₂/CO₂/Ar</td>
<td>56/19/10/15</td>
<td>2.0</td>
<td>98/92 4.0</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
<tr>
<td>[88]</td>
<td>CO/H₂/CO₂/Ar</td>
<td>55/20/10/15</td>
<td>-</td>
<td>90/70 4.5</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
<tr>
<td>[36]</td>
<td>CO/H₂/CH₄</td>
<td>45/50/5</td>
<td>21.0</td>
<td>85/50 5.1</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
<tr>
<td>[89]</td>
<td>CO/H₂/CO₂/Ar</td>
<td>55/20/10/15</td>
<td>4.5</td>
<td>96/10 4.0</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
<tr>
<td>[78]</td>
<td>CO/H₂/CO₂/Ar</td>
<td>55/20/10/15</td>
<td>0.6</td>
<td>- 4.6</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
<tr>
<td>[90]</td>
<td>CO/H₂/CH₄</td>
<td>16/81/3</td>
<td>26.0</td>
<td>92/43 4.5</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
<tr>
<td>[89]</td>
<td>CO</td>
<td>100</td>
<td>7.5</td>
<td>83 4.0</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
<tr>
<td>[5]</td>
<td>CO/H₂/CO₂/Ar</td>
<td>55/20/10/15</td>
<td>6.5</td>
<td>98/10 4.0</td>
<td>C. ljungadhlii</td>
<td></td>
</tr>
</tbody>
</table>

**Two Stage CSTR**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reactant</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Specific Activity</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>[90]</td>
<td>CO/H₂/CO₂/CH₄</td>
<td>65/20/10/5</td>
<td>30</td>
<td>96/60 5.0</td>
<td>C. ljungadhlii</td>
</tr>
<tr>
<td>[12]</td>
<td>CO/H₂/CO₂</td>
<td>60/35/5</td>
<td>20.7</td>
<td>80/77 4.5-5.5</td>
<td>C. ljungadhlii</td>
</tr>
</tbody>
</table>

**Stirred Tank Reactor (STR)**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reactant</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Specific Activity</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>[14]</td>
<td>CO/H₂/CO₂/N₂</td>
<td>20/5/15/60</td>
<td>25.3</td>
<td>- 4.7-5.9</td>
<td>C. ragsdalei P11</td>
</tr>
<tr>
<td>[14]</td>
<td>CO/H₂/CO₂/N₂</td>
<td>20/5/15/60</td>
<td>9.6</td>
<td>15/05 4.7-6.0</td>
<td>C. ragsdalei P11</td>
</tr>
</tbody>
</table>

**Bubble Column Reactor (BCR)**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reactant</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Specific Activity</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>[42]</td>
<td>CO/CO₂/N₂</td>
<td>25/15/60</td>
<td>1.6</td>
<td>- 5.3</td>
<td>C.carboxidivoran s P7</td>
</tr>
<tr>
<td>[20]</td>
<td>CO/H₂/CO₂/CH₄/N₂</td>
<td>15/5/18/5/57</td>
<td>1.6</td>
<td>22/21 5.4</td>
<td>C.carboxidivoran s P7</td>
</tr>
</tbody>
</table>
3.9 Current Status

The possibilities of converting syngas into valuable biofuels and biochemicals with the inherent merits and activities of microbial catalyst have been confirmed. However, significant effort needs to be continued to advance the technology in terms of cost effectiveness, efficiency, and reliability for the large scale commercialization. There are already 144 plants operating in the production of the syngas from 412 gasifiers worldwide, from which a total of 71 gigawatts of thermal (GWth) power was produced in 2010. The total targeted production of syngas will be increased to 72% by 2016 i.e. 122 GWth [78]. Previously, syngas production was from 51% coal, 22% natural gas, 1% petcoke, and 0.5% biomass and waste. Typical composition of unpurified syngas derived from fossil fuel contains 25-30% hydrogen, 30-60% carbon monoxide, 5-15% carbon dioxide, and 2-3% water [79]. Syngas technology needs further improvement to reach large scale commercialization.

Coskata, INEOS Bio, and LanzTech are three leading companies on their way towards the commercialization stage through the construction of pilot and demonstration plants. Coskata built a pilot scale microbial ethanol production plant that utilizes syngas produced from wood and municipal solid waste in 2009 and currently a commercial plant is in the planning phase, which will use *C. carboxidivorans*, *C. ragsdalei*, and *C. coskattii* acetogenic bacteria [80]. INEOS Bio has started commercialization of renewable energy at Indian River Bioenergy Center, Florida, USA and has targeted to produce an ultimate annual capacity of 30.3 million liters of ethanol and 6 MW of power from vegetative waste material and municipal waste by using *C. ljungdahlii* acetogenic bacteria [82]. LanzaTech has built a demonstration plant in China and pilot plant in New Zealand for the production of ethanol from steel mill off-gases and it has also produced 2-3 butanediol, butadiene, and butanol from carbon monoxide using *C. autoethanogenum* acetogenic bacteria [7]. Coskata has successfully operated for two years and produced advanced biofuels (cellulosic ethanol) and biochemicals derived from biomass and waste, through the semi-commercial facility at Madison, Pennsylvania and have now targeted to produce 100 gallons of ethanol from wood biomass and municipal waste.

3.10 Economic Analysis

The global energy demand will reach to 702 quadrillion Btu by 2030 which results in an increase on demand of oil to 118 million barrels per day and will be mainly supplied by fossil fuels, more specifically coal and oil [10]. Petroleum production is depleting day by day
and excessive use of it increases the global warming. Therefore alternative means for supplying energy is an essential requirement for sustainable future. This shows that sustainable bioethanol from biomass and municipal waste will have huge market and demand in the future. Bioethanol production using syngas not only helps on green energy production but will also capture the carbon components from the gasifier and minimizes the greenhouse gas emissions.

The US Department of Energy estimated that cellulosic ethanol can reduce up to 87% of greenhouse gas emissions compared to gasoline and US forest and agricultural products can contribute 1.3 billion dry tons of lignocellulosic biomass [6.7]. Life cycle assessment with environmental, financial and technical analysis is required for the attraction of investors and policy makers to any business, including syngas fermentation. In the comparison of biochemical and thermochemical pathways using detailed modeling, process optimization, heat and power generation, and financial analysis including cost comparisons in producing bioethanol, the biochemical (fermentation) process is the more favorable of the two [82]. Another study compared three different pathways; acid hydrolysis-fermentation, biocatalyst syngas fermentation, and gasification chemical synthesis using mass and energy balances [83]. The highest single day processing rate with the lowest water consumption in the third pathway, the highest energy and water consumption and a modest processing rate with five days on the first pathway, and the highest mass and energy conversion rate with the lowest processing rate of 28 days in second pathway were observed [83].

Research in syngas fermentation has been carried out for an extended amount of time, however commercialization of the technology is yet to be realized. Choi et al (2010) [84] concluded with the possibility of the production of polyhydroxialkanoate (PHA) from the fermentation of syngas using *R. rubrum* at $1.65 per kg, which shows PHA production from syngas to be cheaper than the PHA production from sugar fermentation at $2-4/kg.

### 3.11 Conclusions and Recommendations

Biofuel from syngas may substitute fossil fuels and contribute to greenhouse gas mitigation policies, as well as offer a sustainable solution for future energy demand. So far, the *Clostridium* family provided the highest bioethanol yield from syngas in the CSTR (continuous stirred tank reactor), along with the proper selection of a gas-liquid mass transfer
membrane. Though, bioethanol production from syngas fermentation using the gasification of biomass is possible, yet it still requires improvement in: efficiency of bioethanol production, gas cleaning technology, and economically viable production. The syngas is produced along with different impurities such as tar, char, nitrogen and sulfur through the gasification of biomass. The production of biofuel from syngas fermentation is in an early stage of development; therefore, a number of successful pilot and demonstration scale plants need to be constructed and tested, prior to successful commercialization.

From the review of recent literature articles on bioethanol production from syngas fermentation, the following conclusions were extracted: (i) Syngas fermentation technology is a feasible technique to produce bioethanol from non-food based biomass for a sustainable future, (ii) Production of ethanol has a long history but the commercialization of bioethanol from syngas fermentation has yet to be realized. The commercialization will be possible after successful completion and testing of current pilot and demonstration small scale plants, (iii) The process of bioethanol production from syngas fermentation is kinetically controlled and is thermodynamically justifiable, (iv) There are a number of technical challenges to produce syngas from non-food based biomass at a lower cost compared to food based biomass and fossil fuel, (v) Any type of biomass and biobased product can be converted into bioethanol from syngas fermentation, (vi) Syngas fermentation technology not only helps to create a new market but also minimizes the greenhouse gas emission to the atmosphere.

Main concerns about syngas fermentation are the cleaning of the syngas impurities, separation of biofuel and water, efficiency, high yield microbial selection, limitations of gas/liquid mass transfer, product recovery, and reactor design. In order to commercialize the syngas fermentation technology, more attention to the issues above is required to identify possible solutions through research and development.

Areas of further research could be on: integration of gasification, syngas cleanup, and syngas conversion units to make cost effective bioethanol production; improvement of the ethanol yield and selectivity during syngas fermentation by enhancing the kinetics with proper selection of catalyst; selection of reactors with an optimum environment for fermenting conditions (temperature, pressure, pH level, reactivity, and selectivity of ethanol); optimization of H₂/CO ratio for the maximum bioethanol production; maximization of gas to
liquid mass transfer ratio by measuring the volumetric mass transfer coefficient through the enhancement of impeller design, fluid flow patterns, and aerated power efficiency.

Similarly further area of investigation could be on: enhancement on the syngas quality by using proper cleaning technologies; selection of microbial catalysts; identification and improvement of bioethanol separation techniques from the mixture of other components, including water and biofuels; redirection of metabolic pathways by blocking the acid production pathway, in order to optimize pH levels. Further study is recommended on: system integration and entire life cycle assessment from the collection of biomass to production of bioethanol and its transportation, delivery, distribution and marketing; lignin utilization on the syngas fermentation techniques; technology development on ethanol separation and purification of mixtures.

3.12 References


[58]. Tillman DA. Biomass cofiring: the technology, the experience, the combustion consequences. *Biomass Bioenergy* 19,365-384 (2000).


Chapter 4    Qualitative and Kinetic Analysis of Torrefaction of Lignocellulosic Biomass using DSC-TGA-FTIR

Abstract

Torrefaction is a thermochemical conversion technique to improve the fuel properties of lignocellulosic biomass treated at temperature 200\(^\circ\)C-300\(^\circ\)C in the minimum oxygen environment for a reasonable residence time. In this study, thermal decomposition and thermal activities of miscanthus and wheat straw during the torrefaction at 200\(^\circ\)C, 275\(^\circ\)C, and 300\(^\circ\)C in a nitrogen environment for 45 minutes of residence time are analyzed in a simultaneous thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) and in a micro-TGA and macro-TGA. The output of the TGA is fed into the Fourier transform infrared spectrometry (FTIR) and qualitative analysis of the gaseous product is carried out. The composition of different gas products during the torrefaction of biomass are compared critically and kinetic analysis is also analyzed. The degradation of weight of initial biomass in second stage (torrefaction process) is a much faster conversion process than the weight loss process in the first stage (drying process). The weight loss of biomass increases with increase in the residence time and torrefaction treatment temperatures. The resulted torrefied products are the solid bio-coal. The torrefied product has nearly 25\% more heating value than the raw biomass. Raw biomass is more reactive than the torrefied one. Torrefied miscanthus is more stable fuel than the torrefied wheat straw. The major gaseous components observed during torrefaction are water, carbon dioxide, carbon monoxide, 1,2-Dibromethylene.

4.1 Introduction

Canada, one of the largest forest and agricultural biomass resource center with 998 million hectares of land, produces about 143 million tons of carbon per year, which is equivalent to

the carbon emissions from the use of fossil fuel locally to the atmosphere [1]. Canada has an ample opportunity to become a biofuel production leader in North America. Use of biomass not only benefits the environment, energy security, waste management but also increases the new market, employment, economic opportunities for the local farmers. The technological development in the production of biofuel from biomass has reached from first generation to the third generation. Direct feeding of biomass feedstock in a coal fired boiler to produce heat and electricity has a number of limitations such as high moisture contents, huge investment on the transportation, and storage problem due to biological degradation, poor grindability, low energy/bulk density, and lower heating value. To minimize these limitations, a pretreatment method by thermochemical conversion, called torrefaction is used. Torrefaction is a mild pyrolysis at temperature from 200°C-300°C with the minimum oxygen environment at a reasonable residence time and atmospheric pressure with heating rate less than 50°C/min [2-5]. Main processes of torrefaction are drying, heating/mild pyrolysis and cooling processes. Lignocellulosic biomass consists of hemicellulose, lignin, and cellulose out of which mostly devolatilisation and carbonization of hemicellulose takes place, whereas lignin and cellulose experiences very little impact [5-6]. After the torrefaction, the product yield would have lower moisture contents, hydrophobic, non-biodegradable, higher heating value, higher energy density, improvement on grindability [7-8].

There are a number of works on torrefaction to explore the characterizations, pelletisation, grindability, gasification etc., which depends upon the torrefaction temperature, residence time, particle size, and biomass constituents [3,5,8,9]. For the establishment of the torrefaction facility at any area, local feedstocks need to be examined. Hence, this study explores the different properties of Miscanthus from energy crop family and wheat straw from an agricultural family from Ontario. There are very few studies available on the comparison of different biomass available [9] but this study fulfills the gap of the deficiency on the different characterizations available on the torrefaction of energy crop and agricultural residue from Ontario using DSC-TGA-FTIR. So far no literature available in the open access claimed about the use of DSC-TGA-FTIR for the torrefaction of biomass. For the mass loss kinetics, temperature lag, heat flow, heat/mass transfer limitations and the product gas yield can be better and precisely monitored by DSC-TGA-FTIR than a laboratory scale torrefier. DSC-TGA-FTIR is a precise tool for analyzing the heat flow, weight loss, derivatives of
weight loss, and monitoring output gaseous composition by FTIR.

4.2 Materials and Methods

4.2.1 Materials and Methods

Samples of energy crop-miscanthus and agricultural residue-wheat straw are collected from the Ontario farm near University of Guelph, Willington County. The collected samples are dried in a thermo fisher muffle furnace then chopped and ground in a Retsch PM 100 grinder and are sieved in a sieve AS 200 to prepare sample size of up to 500 microns.

Torrefaction is carried out in macro-TGA as well as micro-TGA with FTIR for the analysis of thermogravimetric analysis, differential scanning and gas composition identification.

4.2.2 Characterizations

Characterization: ASTM standards ASTM E871, ASTM E872, and ASTM D1102 are used for the identification of moisture contents, volatile matter, and ash contents respectively. The proximate analyses of torrefied biomass are identified using ASTM 1762-84 standard methods. For raw and torrefied biomass, the fixed carbon contents is determined by the difference with 100%, i.e. Carbon contents% = 100 - (ash + VM + MC). The carbon, hydrogen, nitrogen, sulfur contents are determined by using Flash 2000 Organic Elemental Analyzer/ CHNS-O Analyzer, Thermo Scientific, the Netherland. The oxygen sample is determined from the difference and verified using the same analyzer. The heating value is determined using IKA C-200 bomb calorimeter. Fiber analysis is performed according to the method explained by Harper and Lynch (1981) and Sule (2012) where ASTM standard for ash analysis; hot water treatment for the hot water extraction; acid, acetic acid and sodium chloride treatment for lignin; and 24% KOH for hemicellulose is used for the treatment during raw and wet biomass. Another method used by Aravantinos-Zafiris et al (1994) had used ethanol for sugar contents, NaOH for hemicellulose identification, sulfuric acid for cellulose.

4.2.3 Macro-TGA

A novel macro-TGA reactor (Figure 4.1), similar to Quartz Wool matrix (QWM) reactor [7],
was designed, developed and fabricated in the machine lab at University of Guelph for the purpose of continuous torrefaction to produce a torrefied product. The reactor consists of a Stainless Steel (SS) tube heated by four electric heaters of 1.25KW capacity in close contact with the reactor wall and separately controlled by two PID controllers. The SS tube has an inner diameter of 75 mm and height of 600 mm. The percentages of different composition of gaseous particles inside the reactor were observed using a gas analyzer (Testo-350). Experiments are conducted for different samples (10-20 mm size) at different temperature 200°C, 250°C, 275°C and 300°C and in 40 minutes. The residence time is measured from the point at which desired torrefaction temperature is reached. This reactor allows to observe simulation of any gas-solid relative velocity; to monitor gas compositions and gas temperature in a reactor while a precision electronic balance continuously measures the mass change (weight) of a reaction. Such reactor could thus accurately simulate the conditions that would expect in a real fixed, moving or entrained flow reactor. Before starting an experiment, the reactor was heated until an equilibrium temperature or steady state was attained. A stream of inter gas (N2) of flow rate of 1-16 liters per minutes was flushed through a flow meter (FMA 5400/5500, Mass Flow Controller, Omega, USA) to maintain an inert environment inside the reactor. Temperatures are measured at two different locations, one from an upper mid portion of the reactor and another from a lower mid portion of the reactor by two separate thermocouples through the temperature controller (CNi16D, Temperature and Process Controller, Omega, USA). Then the sample of biomass of known mass and moisture content was placed into the reactor. The residence time was recorded from that instant. During torrefaction, temperatures of the gas passing through the biomass are continuously recorded. The electronic balance (Model: MS204S, Mettler Toledo, Switzerland) continuously measures the mass of the biomass. The gas composition is determined by collecting gas in a gas-bag, then the quantity of gas is determined with the help of the gas chromatographic analyzer (GC).

Percentage of Mass Yield (MY), Percentage of Energy Yield (EY) and Energy Density Radio (EDR) are determined by using the following formula:

\[ MY = \frac{M_{tb}}{M_{rb}} \]  

(1)
\[
EY = \frac{M_{tb} \times HHV_{tb}}{M_{rb} \times HHV_{rb}} - (2)
\]

\[
EDR = \frac{HHV_{tb}}{HHV_{rb}} - (3)
\]

Where,

\(M_{tb}\) = Mass (daf) of torrefied biomass
\(M_{rb}\) = Mass (daf) of raw biomass
\(HHV_{tb}\) = Higher Heating Value of torrefied biomass
\(HHV_{rb}\) = Higher Heating Value of raw biomass

Figure 4.1 Experimental Setup for Macro-TGA [7]

4.2.4 Micro-TGA

Torrefaction was carried out in a micro-TGA SDT Q 600 TA Instruments in order to compare the differences between the macro-TGA and micro-TGA. A sample of up to 500 microns in a powder form of raw lignocellulosic biomass are dried and kept in a desiccator then used for thermal treatment in micro-TGA. Micro-TGA was heated up at the rate of 5°C/min to the
desired torrefaction temperature (200˚C, 250˚C, 275˚C and 300˚C). The sample weight of about 10-12 mg was placed in a crucible heated for duration of 40 minutes. Nitrogen is supplied inside the reactor at the rate of 30 mL/minutes to create a minimum oxygen environment. The weight loss and heat flow characteristics were monitored and analyzed by using DSC-TGA plots and the gas compositions are identified by FTIR (Figure 4.2).

![Experimental Setup Layouts for DSC-TGA](image)

**Figure 4.2 Experimental Setup Layouts for DSC-TGA**

### 4.2.5 Torrefaction Weight Loss Kinetics

The pyrolysis of lignocellulosic biomass and cellulose above 300˚C was generally expressed by the Broido-Shafizadeh model [11] based on which Di-Blasi and Lanzetta (1997) [12] developed a kinetic model expressed in two kinetic reactions for the isothermal degradation of xylan in torrefaction. A similar model was used for torrefaction weight loss kinetics for willow, and wheat straw that are studied by Prins et al.(2006) [13], Nocquet et al.(2011) [14] and Shang et al. (2013) [15] respectively. In their research, lignocellulosic biomass is torrefied, where A is broken down in V1 volatiles with reaction rate of kv1 with the solid yield of B with reaction rate of k1. In process of thermal treatment, the intermediate solid product breakdown into volatile V2 with reaction rate of kv2 and a solid product C with reaction rate of k2 as shown in the process diagram Figure 4.3.
Figure 4.3 Two Step Torrefaction Kinetic Model [12]

Two step torrefaction kinetic parameters are expressed in the differential equations 4-9 [12].

\[
\frac{dA}{dt} = -(k_1 + k_{v1})A 
\]  \hspace{1cm} (4)

\[
\frac{dB}{dt} = k_1A - (k_2 + k_{v2})B 
\]  \hspace{1cm} (5)

\[
\frac{dC}{dt} = k_2B 
\]  \hspace{1cm} (6)

\[
\frac{dV_1}{dt} = k_{v1}A 
\]  \hspace{1cm} (7)

\[
\frac{dV_2}{dt} = k_{v2}B 
\]  \hspace{1cm} (8)

\[
k_i = k_0e^{\frac{E_A}{RT}} 
\]  \hspace{1cm} (9)

Where, \( k_i \) is the reaction rate in the form of Arrhenious equations.

Hence, the torrefied net solid residue yield will be the addition of A, B and C as expressed by Prins et al. (2006) [13].

\[
M(t) = A + B + C 
\]  \hspace{1cm} (7)

\[
\frac{M(t)}{M_0} = 1 + \left[\frac{k_1K_2 - k_1K_2}{K_1(K_2 - K_1)}e^{-K_1t} + \left[\frac{-k_1K_1 + k_1K_2}{K_2(K_2 - K_1)}e^{-K_2t} + \frac{k_1K_2}{K_1K_2}\right\right] \hspace{1cm} (8)
\]
4.3 Results and Discussions

4.3.1 Characteristics

The proximate analysis and ultimate analysis are carried out as per the ASTM standard in a macro-TGA only and Flash 2000 Organic Elemental Analyzer, CHNS-O Analyzer, Thermo Scientific respectively and found the following results as shown in Table 4.1 and Table 4.2. Percentage of mass and energy yield decreases with the treatment temperatures, whereas energy density increases with the increase in the torrefaction treatment temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C) for 45 minutes</th>
<th>Biomass</th>
<th>Heating Rate °C/min</th>
<th>Environment</th>
<th>Mass Yield (%)</th>
<th>Energy Yield (%)</th>
<th>Energy Density (ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscanthus Raw</td>
<td>200 Torrefied 10</td>
<td>Nitrogen</td>
<td>84.13±2.0</td>
<td>93.12±1.8</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 Torrefied 10</td>
<td>Nitrogen</td>
<td>73.35±0.8</td>
<td>88.45±1.4</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>275 Torrefied 10</td>
<td>Nitrogen</td>
<td>67.92±1.3</td>
<td>74.36±1.5</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 Torrefied 10</td>
<td>Nitrogen</td>
<td>58.44±0.7</td>
<td>68.93±1.3</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>Wheat Straw Raw</td>
<td>200 Torrefied 10</td>
<td>Nitrogen</td>
<td>82.56±1.8</td>
<td>98.56±1.6</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 Torrefied 10</td>
<td>Nitrogen</td>
<td>70.25±1.2</td>
<td>87.48±1.5</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>275 Torrefied 10</td>
<td>Nitrogen</td>
<td>64.56±1.0</td>
<td>72.25±1.4</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 Torrefied 10</td>
<td>Nitrogen</td>
<td>54.83±0.9</td>
<td>67.59±1.7</td>
<td>1.39</td>
<td></td>
</tr>
</tbody>
</table>

The volatile matter (VM), mass contents (MC), ash contents, and higher heating value (HHV)

88
are in the range of ±2%, ±1%, and ±0.8% respectively. Experiments were discarded if the variations were out of the above range. Each experiment was repeated a minimum of three times per sample. Averages of them are listed in the Table 2. The heating value of the energy crop (miscanthus) is higher than the heating value of agricultural residue (wheat straw). In both biomass samples, heating value increases with increase in the torrefaction treatment temperatures. Similarly, ash contents of both samples also increase with the temperatures.

Carbon contents increase with the increase in the torrefaction temperature, whereas the oxygen concentration decreases with the increase in the treatment temperatures. This shows, the torrefaction improves the fuel quality of biomass by improving C/O ratio.

Table 4.2 Proximate and Ultimate Analysis of Biomass

<table>
<thead>
<tr>
<th>Treatment Temperature (°C) 45 min</th>
<th>Biomass Type</th>
<th>Proximate Analysis (%)</th>
<th>Ultimate analyzer (%)</th>
<th>HHV MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>VM</td>
<td>MC</td>
<td>Ash</td>
</tr>
<tr>
<td>Miscanthus Raw</td>
<td></td>
<td>83.96</td>
<td>5.47</td>
<td>1.79</td>
</tr>
<tr>
<td>200°C Torrefied</td>
<td></td>
<td>82.21</td>
<td>2.01</td>
<td>2.01</td>
</tr>
<tr>
<td>250°C Torrefied</td>
<td></td>
<td>80.84</td>
<td>1.20</td>
<td>3.24</td>
</tr>
<tr>
<td>275°C Torrefied</td>
<td></td>
<td>78.82</td>
<td>0.95</td>
<td>3.99</td>
</tr>
<tr>
<td>300°C Torrefied</td>
<td></td>
<td>74.17</td>
<td>0.73</td>
<td>4.58</td>
</tr>
<tr>
<td>Wheat Straw Raw</td>
<td></td>
<td>77.55</td>
<td>5.83</td>
<td>5.16</td>
</tr>
<tr>
<td>200°C Torrefied</td>
<td></td>
<td>77.25</td>
<td>1.03</td>
<td>6.68</td>
</tr>
<tr>
<td>250°C Torrefied</td>
<td></td>
<td>75.29</td>
<td>0.82</td>
<td>7.84</td>
</tr>
<tr>
<td>275°C Torrefied</td>
<td></td>
<td>64.88</td>
<td>0.65</td>
<td>8.71</td>
</tr>
<tr>
<td>300°C Torrefied</td>
<td></td>
<td>52.54</td>
<td>0.33</td>
<td>9.77</td>
</tr>
</tbody>
</table>
4.3.2 Fiber Analysis (Lignocellulosic Composition and Surface Area)

Lignocellulosic composition (Lignin, Hemicellulosic, and Cellulose) has been analysed by using the methodology as explained by Sule (2012) and Harper and Lynch (1981) [17, 18]. Similarly, the Brunauer-Emmett-Teller (BET) surface area of a moisture free sample (degassed for 9 hours at 50°C) has been determined using a Quantachrome 4200e Surface Area and Pore Analyzer with the adsorptive liquid nitrogen at 77.35K temperature (boiling temperature of N₂) having a density of 0.808 g/cm³. The results of fiber analysis of the raw, torrefied biomass are presented in Table 4.3. The hot water extractive in the raw miscanthus is higher than the wheat straw. The major extractives of such herbaceous biomass are monomeric sugars like fructose and glucose, oligomeric sugars, and phenolic glycosides. alditols, aliphatic acids [10]. The miscanthus contains 36.3% hemicellulose, 11.5% lignin, and 49.1% cellulose, whereas wheat straw has 26.8% hemicellulose, 10.7% lignin, and 38.8% cellulose, which shows all lignocellulose components are higher in miscanthus than in wheat straw. This could be due to the presence of higher amount of a polysaccharide of glucose with β-(1-4) glucosidic bonds (Funkr and Ziegler, 2010). The thermal treatment decreases the hemicellulose in the biomass more so than the cellulose and lignin, which is due to devolatilisation of hemicellulose at lower temperature. Association of analytical community (AOAC) official method 973.18 (2014) for acid detergent fiber and detergent lignin, AOAC official method 942.05(2015) for ash, and ANKOM technology method 13 (2015) are also used by Zarrinbakhsh et al.(2016) for the characterization of wastes and coproducts from the coffee industry [20]. Another method used by Yan et al (2009) for determining the contents of hemicellulose, cellulose, lignin and solubles was Van Soest method using ANKOM A200 Filter Bag Technique (FBT) were determined from the deference of neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent liquid (ADL) [21].
Table 4.3 Fiber Analysis and Surface Area of Lignocellulosic Biomass

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Lignocellulosic Biomass Composition (%)</th>
<th>Hot Water Extraction</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hemicellulose</td>
<td>Cellulose</td>
<td>Lignin</td>
</tr>
<tr>
<td>Miscanthus</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>36.3</td>
<td>38.8</td>
<td>11.5</td>
</tr>
<tr>
<td>Torrefied at 275°C 45min</td>
<td>14.2</td>
<td>35.5</td>
<td>41.7</td>
</tr>
<tr>
<td>Wheat Straw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>26.8</td>
<td>49.1</td>
<td>10.7</td>
</tr>
<tr>
<td>Torrefied at 275°C 45min</td>
<td>17.7</td>
<td>36.6</td>
<td>38.2</td>
</tr>
</tbody>
</table>

4.3.3 DSC-TGA and Kinetics

Differential scanning calorimetry is a method to study thermal transitions of a biomass/polymer, when they are under thermal treatment. The heat absorbed by the biomass or difference in heat output of two heaters against temperature is plotted in DSC. Once the glass transition temperature reached, the biomass needs more heat because the heat capacity of the biomass is increased. This helps to identify the glass transition temperature by DSC. After the glass transition temperature, biomass polymers are free to move and finally attained a systematic arrangement which is called as crystallization temperature. At this temperature, biomass give off heat due to exothermic transition, i.e. heater 1 needs less heat to catch up the reference heater 2 heating rate, which consequently gives bid dip in the plot of heat flow and temperature. The temperature at the lowest dip is the crystallization temperature and the area under dip gives the latent energy of crystallization for the biomass. Once more heat is added above the crystallization temperature, biomass reaches towards melting temperature at which biomass absorbs more heat from heater 1 due to an endothermic transition on melting to keep the same rate as reference pan heating. This gives large peak on the DSC plot.
The % weight loss increases with an increase in the treatment residence time as shown in Figure 4(a-d). The first loss is due to the loss in the moisture contents of biomass below 150°C and 15 minutes of residence time. Another sharp weight loss of biomass starts after 150°C and above 15 minutes of residence time. This may be due to the rapid devolatilisation of hemicellulose of biomass. Derivative of weight loss shows the rate of change of weight loss is much faster during devolatilisation of biomass. Micro-TGA shows more precise weight loss (%) and derivative weight (%/min) than the macro-TGA. However, the sampling handling capacity of the micro-TGA (5-10 mg) is too small in comparison to the Macro-TGA (1-5g). Macro-TGA shows a closer pattern with the practical boiler.

The weight % verses residence time of torrefaction process at three various temperatures (200°C, 250°C, and 275°C) captured from the TGA data for miscanthus and wheat straw are presented in Figure 1(c-d). Trends of both plots show that weight % increases with the increase either in temperature or residence time. The slope of TGA curves increases with the increase in temperature from 200°C to 250/275°C. This slope signifies the effect of residence time on weight % change. Overall, the effect of temperature and residence time on the thermal degradation of wheat straw is higher than on the miscanthus in a similar thermal treatment environment. This may be due to higher contents of volatile matters and hemicellulose in miscanthus than in the wheat straw as shown in Table 2 and 3. This shows wheat straw is more reactive than the miscanthus as a solid fuel.
4.4a. Macro-TGA Weight-% & Derivative Wt-%/min for Torrefaction of Miscanthus

4.4b. Micro-TGA Weight-% & Derivative Wt-%/min for Torrefaction of Miscanthus
Figure 4.4 TGA: Impact of Temperature & Residence Time during Torrefaction

Table 4 shows the kinetic parameter of miscanthus during torrefaction. The kinetic energy for
the miscanthus is higher than the wheat straw, which implies that the Miscanthus torrefaction process needs more energy than the torrefaction process for wheat straw. Similarly, higher activation energy \((E)\) implies the smooth reaction, whereas lower activation energy implies the quick reaction. Raw biomass is more reactive than the torrefied biomass [15].

Table 4.4 (a-c) Torrefaction Kinetic Characteristics

a) Descriptive Statistics for Variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Minimum Value</th>
<th>Maximum Value</th>
<th>Mean Value</th>
<th>Standard Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T ) (K)</td>
<td>448.15</td>
<td>548.15</td>
<td>498.15</td>
<td>31.02</td>
</tr>
<tr>
<td>(Y = \ln(\text{derivative wt%/min/ 100}))</td>
<td>-6.69</td>
<td>-3.79</td>
<td>-5.48</td>
<td>0.93</td>
</tr>
<tr>
<td>(X=\text{Weight%/100})</td>
<td>0.93</td>
<td>0.96</td>
<td>0.95</td>
<td>0.01</td>
</tr>
</tbody>
</table>

b) Calculated Parameter Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Miscanthus</th>
<th>Wheat Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A ) (min(^{-1}))</td>
<td>(8.8 \times 10^3)</td>
<td>(1.2 \times 10^4)</td>
</tr>
<tr>
<td>(N)</td>
<td>0.88</td>
<td>0.91</td>
</tr>
<tr>
<td>(E) (kJ/mol)</td>
<td>59.95</td>
<td>51.72</td>
</tr>
</tbody>
</table>

c) Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F-value</th>
<th>Prob (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2</td>
<td>16.25750</td>
<td>8.12875</td>
<td>161.51</td>
<td>0.00001</td>
</tr>
<tr>
<td>Error</td>
<td>18</td>
<td>0.90594</td>
<td>0.05033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>20</td>
<td>17.16344</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Arrhenius plots for the study of the kinetics of the torrefied miscanthus and wheat straw are presented in Figure 5. It seems that the kinetic rate of thermochemical reaction for torrefied miscanthus is lower than that of torrefied wheat straw. Torrefaction kinetics take two steps: drying of biomass and devolatilisation of hemicellulose.

Figure 4.5 Arrhenius Plot of Torrefaction Process for Biomass: Ln(dw/dt) vs. 1/T(K-1)

4.3.4 FTIR

TGA is one of a very reliable method for studying the thermo-chemical analysis of a wide varieties of biomass samples. When FTIR is cascaded as a complementary method with TGA, it can give valuable information on the constituents of gaseous products as they are released by the thermal treatment of biomass samples. Hence, in this study, TGA is cascaded with FTIR to identify the torrefaction behavior of different biomass samples and measure the main gaseous constituents of the products released during the thermal treatment. The exhaust gas composition during the torrefaction process is monitored by FTIR by directly coupling with TGA. The majority of the exhaust gas contains carbon dioxide, carbon monoxide and water.
vapor. Traces of methane are also observed from the FTIR. The maximum exhaust released can be observed during the maximum weight loss period, which was also observed by Eseltine et al. (2013) [16]. The output of the torrefaction process captured by the FTIR has been presented in the Figure 6. The major gaseous components observed during torrefaction were water, carbon dioxide, carbon monoxide, 1,2-Dibromethylene, and many other components. Figure 6 (b) shows the gaseous components identified by TGA–FTIR analysis are CO at 2100 cm$^{-1}$, CO2 at 2350 & 700 cm$^{-1}$, and H2O at 3500-3700 and 750-1000 cm$^{-1}$. TGA–FTIR study shows that the emission of gaseous products increases with the increase in the treatment temperature.

![Figure 6](image_url)

**a) Output of FTIR**
4.4 Conclusions and Recommendations

For the thermogravimetric and product compositions analysis of the one of the most popular, purposely grown energy crop and one of the most popular agricultural product residue of Canada, thermochemical treatment of miscanthus and wheat straw respectively are carried out in a macro-TGA and DSC-TGA-FTIR equipment. Commercial scale characterization of torrefier is analyzed using macro-TGA, whereas the weight degradation, kinetics, differential scanning and the gaseous products are identified by the latest equipment with micro-TGA-FTIR. Both torrefied samples show better solid fuel performance than the raw biomass in terms of moisture contents, energy contents, density, hydrophobicity, ignitibility etc. The torrefied biomass performs similar to coal. However, biomass has many limitations. The torrefaction temperature has more impact on the torrefaction process than the residence time. The higher torrefaction temperature results on the higher hydrophobicity. The gaseous product yields are mainly carbon dioxide and water. The drying process starts at a lower temperature at around 100°C, whereas the devolatilisation of hemicellulose takes place from 200°C. From the study of the characterization of torrefied lignocellulosic biomass, it can be concluded that torrefied energy crops and agricultural residue are a good candidate to be used in thermal or electrical power plants. The longer durability of the torrefied material also increases the probability for pelletization and exporting local and global markets for the domestic use for longer time. The raw biomass shows more reactive than the torrefied one.
during the kinetic study, which shows torrefied biomass are more stable in a boiler. The kinetic rate of the thermochemical reaction for torrefied miscanthus is lower than that of torrefied wheat straw. Heating value is increased by 25% after torrefaction.

4.5 References


Chapter 5  
Optimum Experimental Conditions of CO2  
Cogasification of Coal-Torrefied-Miscanthus in a TGA-FTIR

Abstract

Gasification is a thermochemical conversion method that transforms carboneous constituents into synthesis gas (syngas: CO, H2, CO2) at high temperatures, generally at more than 700 °C, in a control amount of oxygen, carbon dioxide, steam environment so that there will be no combustion. Syngas is a good fuel for producing ethanol or diesel. Gasification in a CO2 environment is an interest of this research. This study finds the optimum experimental condition parameters for the carbon dioxide (CO2) cogasification of Ontario coal and torrefied biomass blends for the equal ratio of each sample using TGA-FTIR. The operating conditions for the heating rate, CO2 flow rate, maximum gasification target temperature, Nitrogen and CO2 flow combinations are observed with the 10mg of coal-biomass mixture. The higher the amount of coal, the higher is the gasification period, whereas, an increase in the torrefied miscanthus shortens the gasification period, i.e. gasification is faster as the ratio of torrefied miscanthus increases in the blends. The optimum CO2 flow rate is found at 50 ml/min; the optimum heating rate could be 10°C/min; the optimum condition to run N2 is up to 800°C followed by CO2 up to the final temperature 1300°C.

5.1 Introduction

Global warming caused by the excessive use of fossil fuel can be taken care by the cautious consumption of renewable green-energy resources for the energy applications. Biomass has many limitations for the direct combustion/gasification in a boiler/gasifier (Acharya et al., 2012). Thermo-chemical treatment called torrefaction is one of the methods for minimizing these limitations. The torrefied product has higher process efficiency (Vincent et al., 2014). There are number of different treatment methods used in the processing of biomass.

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4 A version of this chapter has been published as B Acharya, A Dutta, Optimum Experimental Conditions of CO2 Co-gasification of Coal-Torrefied-Miscanthus in a TGA-FTIR, International Journal of Materials Chemistry and Physics 2 (2), 75-83
However, in this study, torrefaction and hydrothermal carbonization are used for the treatment of biomass. Dry torrefaction is a process of mild pyrolysis with the treatment temperature of 200-300°C with reasonably longer residence time in a nearly an inert environment at atmospheric pressure, whereas the hydrothermal carbonization or wet torrefaction is a treatment of biomass in a subcritical water temperature from 180-265°C for a shorter residence time in an enclosed pressurized hydrothermal reactor operated at high pressure (Acharya, 2013; Funke et al., 2013; Tumuluru et al., 2011). These torrefied products are good candidates for gasification in production of syngas.

Torrefied biomass is a better candidate for the gasification than raw biomass due to lower O/C ratio. The optimum temperature of gasification can be lowered by minimizing moisture contents and O/C ratio and tar production can be reduced by the cogasification of coal with torrefied biomass (Prins et al., 2006). Even though dry torrefaction retains alkali contains in the torrefied products by releasing moisture and carbon dioxide, these alkali inorganic matters sodium, potassium act as a catalyst during the cogasification process (Deng et al., 2009). The torrefied biomass shows near to coal characteristics, so the blending ratio of raw biomass-coal can be significantly improved by blending torrefied biomass-coal ratio, which ultimately lead to insignificant reductions in energy efficiency and variations in boiler load (Li et al., 2012).

Gasification is a thermochemical conversion method that transforms carboneous constituents into synthesis gas (syngas: CO, H₂, CO₂) at high temperatures, generally at high temperature with the help of some reacting element, such as air, steam, or carbon dioxide (Xu et al., 2014). There will be no combustion during this process. Syngas is a good fuel for producing ethanol or diesel. Gasification in a CO₂ environment is an interest of this research. Efficient way of converting carbon components even from the fossil fuel into the syngas, a storable and transportable gas, reduces the environmental pollution (Fermoso et al., 2010; Matsumoto et al., 2009). It is very important to know the optimum experimental conditions for the CO₂ gasification for the kinetic analysis. Different literatures are using different conditions for the CO₂ gasification (Xu et al., 2014; Idris et al., 2010).

Researchers: Xu et al., 2014; Goldfarb & Liu, 2013; Fermoso et al., 2010; Idris et al., 2010; have studied on thermochemical treatment, including gasification but there are not any accessible literatures available in the open platform in finding optimum experimental
conditions of CO$_2$ gasification of Ontario-bitumen-coal and torrefied miscanthus using TGA-FTIR for the analysis of product gases. Hence, this study fills this gap to observe the optimum condition for characterization of kinetic interaction in a coal-WT-DT blend by conducting CO$_2$ gasification in TGA and resulting products are also observed using FTIR directly connected with TGA.

5.2 Materials

Energy crop miscanthus samples are collected from a field and bituminous coal is collected from the Hamilton, Ontario. The collected raw biomass samples are chopped into smaller pieces, and then milled in a ball mill (PM100, Retsch Inc., Newtown, PA, USA). The raw miscanthus is dried in a muffle furnace then torrefied in a macro-TGA at 275°C for 45 minutes. Similarly, raw miscanthus is mixed with water in 1:6 ratios then hydrothermally carbonized in a wet torrefier as explained in Acharya and Dutta, 2013 and Kambo and Dutta, 2014.

5.3 Methods

CO$_2$ gasification is carried out in a differential scanning calorimetric / thermogravimetric analyser (DSC-TGA). A biomass / biomass-coal mixture sample of about 10mg is placed in a crucible, then heated up to desired temperature from 700 to 1300°C for gasification at a heating rate of 5 to 50°C in the carbon dioxide environment. Nitrogen is also supplied to observe the pyrolysis and charring state prior to the gasification. Hence, Nitrogen is supplied to find the optimum charring temperature, where Nitrogen needs to be switched by carbon dioxide for the gasification. Nitrogen is supplied from 0°C - 700°C at the beginning, then switched to carbon dioxide during gasification. Carbon dioxide is supplied at the desired rate from 10-100mL/min as per the requirement of cogasification to test the optimum flow rate required. The outputs of the product gas are passed through the Fourier transform infrared (FTIR) to monitor the spectrum of the gases continuously. Schematic diagram for the TGA-FTIR is shown in Figure 5.1. Heat flow, thermal degradation, stability, and weight loss are monitored by DSC-TGA. The degradation pattern is identified by the derivative thermogram (DTG) plot.
5.4 Results and Discussion

From the TGA results, the reactivity of the coal is slower than the raw biomass and similar patterns are observed on the wet torrefied biomass than dry torrefied biomass. Miscanthus contains 36.3% of hemicellulose, 38.8% of cellulose, 11.5% of lignin, 12.6% of hot water extractives, and 0.8% of ash (Kambo & Dutta, 2014). This could be due to more availability of volatiles and hemicellulosic components in the raw and wet torrefied biomass. Dry torrefied fuel gasification needs more time for the complete gasification than the gasification of wet torrefied biomass. This could be due to removal of alkali components in the wet torrefied biomass.

5.4.1 Proximate, Ultimate Analysis, and Heating Value

Proximate and Ultimate analysis of the raw miscanthus and the hydrothermally carbonized (HTC) or wet torrefied (WT) and dry torrefied (DT) miscanthus at different treatment temperatures and the residence time are presented in Figure 2. The result shows that O/C ratio decreases with the rise in treatment temperatures due to increase in carbon contents and decrease in oxygen contents with the increase in the treatment temperature. However, variation in the residence time during the wet torrefaction does not show the significant improvement on the fuel quality of miscanthus. Hence, for the gasification, wet torrefied biomass treated as 260°C with 5
minutes of residence time (Kambo & Dutta, 2014) is considered, whereas the optimum dry torrefaction temperature of 275°C for 45 minutes residence time found by Acharya (2013) is considered optimum for the samples for treatment in this experiment.

5.4.2 Mass Yield and Energy Yield

The percentage of mass yield, energy yield, and higher heating values (HHV) with its varying factors of torrefied miscanthus treated at different temperatures and residence times are presented in Figure 5.2 to 5.4. The percentage mass yield and energy yield decreases with the increases in the torrefaction temperature and residence time. However, the heating values rise with the increase in the treatment parameters. During the wet torrefaction, miscanthus and water are mixed at a ratio of 1:6 throughout the experiment. Even though mass yield goes down to about 45% from 85%, energy yield stands in the range of about 70-90%. This shows heavy weight loss is primarily due to devolatilisation of hemicellulosic components of the biomass. Hence, the overall thermal treatment from drying to torrefaction processes ultimately reduces the transportation cost in the total supply chain of the system.

![Figure 5.2 Proximate and Ultimate Parameters w.r.t. Torrefaction Treatment Temperature](image-url)
Figure 5.3 Mass Yield, Energy Yield, and HHV of Miscanthus at Different Conditions

Figure 5.4a. Comparative Study of Weight % of Wet Torrefied Miscanthus with Variable Flow Rate of CO₂
5.4.3 Optimum Experimental Conditions for CO₂ Gasification

5.4.3.1. CO₂ Flow Rate

For identifying the required optimum flow rate of carbon dioxide, three different flow rates are run keeping all parameters as constant. The weight % pattern is observed with respect to temperature at a fixed heating rate of 10°C/min by varying the CO₂ flow rate on raw and wet torrefied miscanthus, which shows reactivity of the raw miscanthus is higher than the treated biomass. Char CO₂ gasification with the flow of 100mL/min is nearly matching with the flow of 50mL/min (Figure 5.4a). Even though 25mL/min closely resembles with the other higher CO₂ flow rate with little deviation on the weight % pattern, 50°C/min CO₂ gasification could be a recommended optimum value for the CO₂ coal-char gasification process. The residue on the crucible of cogasification with 50mL/min is less than the 25mL/min. From the observation, the flow of 50mL/min of carbondioxide is supplied on the remaining experiments, considering this as a recommended flow rate required for the gasification process.

5.4.3.2. Variation with N₂ and CO₂

The weight % is observed with respect to temperature by varying the gasification media N₂, CO₂, and the combination of N₂ and CO₂ (N₂ is supplied up to the 850°C then switched to CO₂ till 1300°C) at heating rate of 10°C/min and gas flow rate of 50mL/min as shown in Figure 4b. The gasification of wet torrefied miscanthus shows similar characteristics during the gasification either by using CO₂ only or combination of N₂ and CO₂. However, the charring process has been observed in the N₂ treatment of which about 40% of char is produced in treatment temperature of 1300°C. The rate of change of weight loss is higher in the raw biomass than in the thermo-chemically treated biomass. This may be due to loss of moisture and the devolatilisation of hemicellullosic components of the biomass during the thermochemical treatments. Experiment result show that gasification with Nitrogen does not work. However, gasification using carbon dioxide throughout the gasification process and gasification using Nitrogen up to 850°C then replaced with carbon dioxide from 850°C to 1300°C shows similar results. Hence, Nitrogen at the beginning for torrefaction and charring process is recommended then followed by the carbon dioxide for the gasification stage for commercial applications. Price and availability of nitrogen is cheaper and easier than carbon dioxide. In the other side, for the greenhouse gas emissions
mitigation, use of carbon dioxide for the gasification process is recommended.

**Figure 4b.** Weight % of Wet Torrefied Miscanthus by Varying N₂, CO₂, & their mixture Flow.

**Figure 4c.** Weight % of Wet Torrefied Miscanthus by Varying Heating Rates.
5.4.3.3. Heating Rate Variation

Effect of different heating rate of 5°C/min, 10°C/min, 20°C/min, and 50°C/min on the CO₂ gasification at 50mL/min of raw and hydrothermally torrefied miscanthus has been observed as shown in Figure 4c. The result shows that increase in the heating rate does not have a significant impact on the drying and carbonization process but there is an impact on gasification state. Low heating rate produces a higher rate of change on weight % and lowers the maximum temperature, which consequently improves the reactivity. This may be due to the uniform transfer of heat into the biomass polymer structure due to slow and steady flow of heat at the lower heating rate. Higher heating rate increases the maximum gasification temperature and lowers the reactivity, while low heating rate increases the energy cost for the gasification so 10-20°C could be an option for the CO₂ gasification process. Heating rate of 50°C/min does not complete the gasification process so it is not viable for the experiment. Heating rate of 5°C/min consumes lots of energy and time for the gasification process so it needs to discard. Hence, for the reliability, 10°C/min has been considered throughout this experiment.

5.4.4 Gasification of Mixtures

The mixture of raw and hydrothermally torrefied miscanthus, raw and dry torrefied, and hydrothermally torrefied and dry torrefied miscanthus in the ratio of 1:1 is gasified with the 50mL/min of carbon dioxide at a heating rate of 10°C/min and observed the kinetic behavior of miscanthus as shown in Figure 5. This process undergoes the four stages: drying up to 150°C, devolatilisation from 150-450°C, chars production from 450-850°C, and finally chars gasification from 850-1200°C. The rate of weight loss is higher as the treatment process moves from coal-torrefied mixture towards the raw mixture. This may be due to fast devolatilisation of moisture and hemicellulose present in the raw biomass. The reactivity of the raw mixture is higher than the mixture of the torrefied biomass-coal mixture. The torrefied-coal mixture shows better fuel characteristics during the gasification than the raw mixture. The reactivity of the dry torrefied biomass shows faster charring process than the wet torrefied miscanthus, which may be due to presence of alkali metals components in the dry torrefied biomass. Wet torrefied biomass is nearly free from the alkali metals by washing in high temperature and pressure treatments. Hence, mixture of wet and dry torrefied biomass with coal may be an optimum solution for the environmental friendly gasification process.
Figure 5.6 Weight % of Blends of DT/Torr, HTC/WT, and Coal (equal % ratio)

5.4.5 DSC-TGA

DSC-TGA plot on the blends of dry torrefied biomass and the raw miscanthus improves the reactivity of the blends than the dry and wet torrefied biomass as shown in Figure 5.6. In both curves, the first stage peak is weight loss due to the evaporation of moisture contents of the samples and hydroxyl groups on the pores of the samples. The large peak of the derivative weight (%/min) shows the fast weight loss due to extensive devolatilisation of volatile matters and hemicellulosic components. The final peak is due to the char gasification. The char gasification of the blends of raw and dry torrefied miscanthus completes at a lower temperature than blends of the two torrefied samples. Char gasification completes at around 1000°C.

Due to the compact molecular structure of coal, more energy is required for the disintegration of its structure, whereas the thermal reactivity of the raw miscanthus is higher than the torrefied one due to removal of the volatiles during torrefaction. The presence of the torrefied miscanthus improves the overall reactivity of the co-gasification process. The treatment temperature for the
co-gasification is lower than the coal gasification alone. The mass loss is the fastest when the raw miscanthus is blended with coal, as the torrefied is added, the mass loss rate decreases slowly. This is due the contents of high moisture, and volatiles on the raw biomass, whereas the moisture and volatiles are removed in the torrefied biomass during the thermal treatment. BET analysis of miscanthus is presented on Table 5.1 which signifies that wet torrefied has less surface area than the raw and dry torrefied miscanthus. The % of hemicellulose has reduced significantly whereas the % of lignin has increased significantly during the wet torrefaction of miscanthus.

**Table 5.1 BET Analysis of Miscanthus at Different Conditions**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Residence Time (Minutes)</th>
<th>Hemicellulose (%)</th>
<th>Cellulose (%)</th>
<th>Lignin (%)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>-</td>
<td>36.30</td>
<td>38.80</td>
<td>11.50</td>
<td>11.44</td>
</tr>
<tr>
<td>WT-260</td>
<td>5</td>
<td>0.97</td>
<td>27.50</td>
<td>30.57</td>
<td>4.50</td>
</tr>
<tr>
<td>DT-275</td>
<td>45</td>
<td>21.46</td>
<td>36.21</td>
<td>41.81</td>
<td>14.19</td>
</tr>
</tbody>
</table>

![Figure 5.6 TGA Plot for CO₂ Gasification of Miscanthus Coal:DT:WT (1:1:1)](image)
a) Raw

b) Wet Torrefied at 260°C, 5min
5.4.6 SEM (Scanning Electron Microscopy) Analysis

Information on the structure of polymers, during the wet and dry torrefaction, can be observed by
using Scanning Electron Microscopy (SEM) analysis. Raw, wet torrefied miscanthus at 260°C, 5 minutes, and dry torrefied miscanthus at 275°C for 45 minutes are presented in Figures 7(a-d). In both dry and wet torrefaction process, the fibrous structures of the miscanthus broken down due to breaching of chemical bonding of the biomass structure as the treatment temperature increases. The breaking of the bonding structure increases the porosity of the product, which eventually increases the opportunity to flow air components leading towards the increase in the reactivity. Pores in the dry torrefied miscanthus are higher than the wet torrefied miscanthus. This may be due to the devolatilisation of hemicellulose and partial devolatilisation of cellulose and lignin in the dry torrefaction process, whereas higher subcritical pressure makes more compaction in the wet torrefaction process. Brunauer-Emmett-Teller (BET) surface areas are illustrated in Table 1, which also shows dry torrefied miscanthus has a higher surface area than wet torrefaction. The reactivity of the gasification process depends upon the surface area, particle size and pores (Vincent et al., 2014). This also shows raw biomass is most reactive then followed by dry torrefied, wet torrefied, and bitumen coal in chronological order.

5.4.7 Product Composition from FTIR

The FTIR showed the presence of synthesis gas mainly carbon monoxide, hydrogen and H₂O including a minor portion of CH₄ shown in Figure 5.8.

Figure 5.8 FTIR Output during CO2 gasification 3-D View
5.5 Conclusions and Recommendations

Gasification is a thermochemical conversion method that transforms carboneous constituents into synthesis gas (syngas: CO, H₂, CO₂) at high temperatures, generally at more than 700 °C, in a control amount of oxygen, carbon dioxide, steam environment so that there will be no combustion. Syngas is a good fuel for producing ethanol or diesel. Gasification in a CO₂ environment is an interest of this research. The fuel characteristics of hydrothermally torrefied miscanthus show better performance than the dry torrefied miscanthus. SEM shows more porosity in the dry torrefied miscanthus than wet torrefied miscanthus and bitumen coal, which shows dry torrefied miscanthus are more reactive than the wet torrefied miscanthus. The operating conditions for the heating rate, CO₂ flow rate, maximum gasification target temperature, and Nitrogen and CO₂ flow combinations are observed with the 10mg of coal-torrefied miscanthus blends. Experiment shows that duration of gasification increases with the increase in the amount of the coal portion in the blends. Similarly, the duration of gasification decreases with the increase in the biomass portion in the blends i.e. gasification is faster as the ratio of torrefied miscanthus increases in the blends. The optimum CO₂ flow rate is found at 50 mL/min; the optimum heating rate could be 10°C/min; the optimum condition to run N₂ is up to 800°C followed by CO₂ up to the final temperature 1300°C. The FTIR showed the presence of primarily of carbon monoxide, hydrogen, and H₂O including a minor portion of CH₄.

5.6 References


Abstract

The main goal of this study is to investigate the kinetic characteristics and interaction of the carbon dioxide cogasification of blends of coal and thermochemically processed miscanthus (Miscanthus spp.) using thermogravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR). Thermochemically processed miscanthus are prepared by wet torrefaction (WT), or hydrothermal carbonization (HTC) at 533K with residence time of 5 minutes at 5.5MPa pressure with 1:6 biomass-water mass ratio and dry torrefaction (DT) at 548K with residence time of 45 minutes at atmospheric pressure and blended with different ratios of coal. The kinetic characteristics show that the activation energy of the gasification of the processed biomass blends decreases with the increase in the biomass portion in the blends. Out of the blends tested, Coal-WT-DT at 60%:20%:20% shows the most synergistic interaction after analysis of TGA data. Hence, this ratio shows the most potential for replacing solid-fossil-fuel. A mathematical equation for kinetics characterization has been proposed to represent the best fit model.

6.1 Introduction

Biomass products are considered as a potential solid biofuel for replacing coal from thermal power plants and efficient way of converting carbon components to the safer gaseous fuel [1]. Raw biomass has high moisture content, low energy value, is hygroscopic in nature, undergoes biological degradation, and has many other limitations. These factors limit the raw biomass to be used only as direct fuel in industrial applications [2]. Torrefied products have high energy density and bulk density resulting in lower storage and transportation cost. The torrefied product has a higher process efficiency of about 94% compared with 84% efficiency of pelletized product, followed by pyrolyzed product of about 64% efficiency [3]. Tar is formed during gasification of biomass, which is also a major limitation for commercial application due to

5 A version of this chapter has been submitted to Biomass and Bioenergy for publication.
associated high energy and capital required for removing tar from the product gases. These limitations can be minimized by thermochemical treatment using torrefaction, hydrothermal carbonization, pyrolysis, and then followed by gasification. However, in this study, dry torrefaction and wet torrefaction (or hydrothermal carbonizations) are used for the treatment of biomass. Dry torrefaction is a process of mild pyrolysis with treatment temperature of 473-573K with reasonably long residence time in an inert environment at atmospheric pressure, whereas the hydrothermal carbonization is a treatment of biomass in subcritical water temperature from 458-538K for a reasonable length of residence time in an enclosed pressurized hydrothermal reactor operated at high pressure [4-6]. Thermochemically treated products can be used for solid fuel in the form of char, liquid fuel in the form of bioethanol or biodiesel, and gaseous fuel in the form of synthesis gas or methane. Synthesis gas (syngas) can be produced by a gasification process. Combustion of fossil fuel increases environmental pollution, so utilization of any portion of carbon neutral biomass is environmentally friendly. The torrefied biomass has always shown superior quality than the raw biomass for the gasification. It is even more important for cogasification with coal because most of the thermochemical characteristics of torrefied biomass are closer to that of coal. This is due to the lowering of the oxygen to carbon (O/C) ratio of biomass after torrefaction, which prevents over-oxidation of biomass during cogasification leading to thermodynamic losses [7] for raw wood gasification. The optimum temperature for gasification can be lowered by increasing moisture content and O/C ratio, which improves the thermochemical processing of biomass. Furthermore, tar production can be reduced by cogasification using torrefied biomass [7]. Torrefied biomass releases most of the tar forming matter during thermal treatment. The dry torrefaction of biomass retains alkali contents in the torrefied products. These alkali inorganic matters in the form of sodium and potassium act as a catalyst during the cogasification process for improving the char gasification process [8]. Due to the major removal of tar-forming condensable volatiles during dry torrefaction, the tar formation can be reduced during cogasification. During the wet torrefaction, washing of wet biomass in a high temperature pressurized reactor removes most of the alkali metals [5]. Hence, cogasification of coal, wet and dry torrefied biomass improves the gasification process due to the presence of alkalis in the dry torrefied biomass.

Agricultural biomass has negligible amounts of sulfur, which has potential to reduce the greenhouse gas emissions CO2 and SOx [9]. Blending of biomass-coal could be a striking option
for using environmentally friendly solid fuel, even though it lowers the heating value of the overall fuel and degrades O/C and O/H ratios. The lower heating value of biomass may be due to lower energy released from the weak bonding of C-H and C-O than the strong C-C bonding of coal. On the other hand, higher content of oxygen in the biomass indicates the higher reactivity than coal leading towards the lower requirements of activation energy for devolatilisation and oxidation [10]. Ash decomposition, slagging and fouling on the heating surfaces of the boilers has been often major issues due to the heterogeneous nature of biomass. Low bulk density, higher moisture contents, high hygroscopicity, present infrastructure for coal, and grinding issues are other limiting issues for the direct use of biomass in the coal fired boilers [6]. These issues can be minimized by using blends of coal-torrefied biomass [11]. The torrefied biomass shows near-to-coal characteristics, so the fuel characteristics of raw biomass-coal blend can be significantly improved by blending torrefied biomass-coal in the right ratio, which ultimately lead to insignificant reductions in energy efficiency and variations in boiler load [12].

Gasification is an efficient technique for converting any type of carbon rich material, including coal and biomass into the fuel enriched gaseous product called syngas with the help of some reacting element, such as air, steam, or carbon dioxide [13]. The use of torrefied biomass-coal blends is an efficient way of converting carbon components even from fossil fuels into the syngas, which is storable and transportable and reduces environmental pollution [14]. Gasification stages start from drying of the feedstock, followed by devolatilisation of hemicellulosic and cellulosic components of biomass, slow decomposition of lignin then ends with char reaction. Char reaction process is very fast; energetic demand is very high and uses high temperature. The biomass contains more volatiles, so the time and temperature required for the full gasification of biomass is less than the coal [13]. The reactivity of the gasification process depends upon the surface area, particle size and pores [3]. However, the thermochemically processed biomass needs more time for the gasification than the raw biomass due to the presence of lower moisture and volatiles content than raw biomass. Full gasification of coal may be expected at higher rate by blending the coal with biomass due to synergistic interactions [13-14].

There are a number of research conducted in the area of co-pyrolysis, co-combustion, or co-gasification of coal and biomass [13-18]. However, there are no literatures available (to the knowledge of current researchers) on the kinetic analysis and interaction among a Ontario-
bituminous-coal, a hydrothermally carbonized biomass and a torrefied biomass along with the raw biomass blends in a carbon dioxide environment using TGA-FTIR for the analysis of product gases. Hence, this study fills this gap to observe the kinetic characteristics and interaction among coal-WT-DT, raw-WT, raw-DT, WT-DT blends, and torrefied biomass-coal by conducting CO2 gasification in TGA and resulting products are also observed using FTIR directly connected with TGA. The main aim of this research is to explore the theoretical possibility of cogasification of thermochemically treated dry-biomass and wet-biomass, so that exploration of co-gasification of the treated municipal waste (sludge) and dry agricultural-forest biomass could be possible in future. This may also lead towards exploring the possibility of using these blends in co-firing with coal in coal-fired boilers in the future.

### 6.2 Kinetics of CO2 Gasification

Kinetic reaction during the CO2 gasification process can be explained by the Arrhenius equation. The constant gasification reaction rate \( k \) depends upon the activation energy \( E \) in kJmol\(^{-1}\) and the variation in temperature \( T \) in Kelvin. The rate of degradation depends upon a temperature dependent rate constant \( k \), reaction order \( n \), and a temperature-independent function of conversion \( f(x) \).

\[
k = Ae^{-\frac{E}{RT}} \quad (1)
\]

\[
\frac{dx}{dt} = kf(x) = k(1 - x)^n \quad (2)
\]

\[
x = \frac{w_i - w_f}{w_i - w_t} \quad (3)
\]

Where,

R = gas constant (8.314 JK\(^{-1}\).mol\(^{-1}\))

\[
\frac{dx}{dt} = \text{rate of reaction}
\]

\( x \) = conversion rate of char gasification

\( f(x) \) = function model for reaction mechanism

\( n \) = reaction order

\( \frac{w_i}{w_f} / w_t = \text{Initial/at time t/final mass of the sample} \)

The complex nature and structure of the biomass and coal gasification is hard to express simply by a simple solution. Schnial et al. (1982)[19] had used a mixed model of pyrolysis and
gasification to express the gasification kinetics of biomass and coal. However, this model itself has a number of limitations like reaction environments and fuel composition, which consequently have an impact on the reaction order n. Xu et al. believed that the combined model of homogeneous reaction model (HRM) and shrinking core model (SCM) are more effective in the analysis of carbon conversion rate with time, but an alternate model known as the random pore model is better for having more factors other than carbon and time [13]. As this study focuses on the gasification kinetics of biomass, processed biomass, coal, and their blends, the HRM and SCM model are used for the kinetic analysis as expressed in equation 4 and 5, using the heating rate as $\alpha$, by transforming the Arrhenius equation (1) [1].

\[ X = 1 - \exp \left( -\frac{RT^2}{\alpha E} A e^{\frac{E}{RT}} \right) \]  

(4)

\[ X = 1 - \left[ 1 - \frac{RT^2}{3\alpha E} A e^{\frac{E}{RT}} \right]^3 \]  

(5)

6.3 Material and Methods

Samples of energy crop, naturally dried miscanthus, are collected from the field of University of Guelph, Guelph, Ontario and kept in an open plastic bag inside the room of research lab for one year. The collected raw biomass samples are chopped into smaller pieces, dried in a muffle furnace, and then milled in a ball mill (PM100, Retsch Inc., Newtown, PA, USA). The powder form of biomass from the ball mill is then sieved in a sieving-vibrating machine (AS 200, Retsch Inc., Newtown, PA, USA) to prepare uniform size of 200mm-3. The torrefied samples are prepared by using macro-TGA or QWM reactor, according to the procedure explained in Acharya & Dutta (2013)[20] and hydrothermal (wet torrefaction) reactor (Figure 1a & 1b). These WT and DT samples are then ground and sieved to produce uniform size of 200mm-3. Blending of raw-WT miscanthus, raw-DT miscanthus, and WT-DT samples is carried out in a blending machine. Similarly, Bitumen coal in powder form is collected from the Hamilton, ON and kept in a desiccator after drying in a muffle furnace.

6.3.1 Biomass Characterization

Drying process of all biomass samples is conducted at 378K according to ASTM standard D1762-84 procedure [21]. Muffle furnace is used to determine the moisture content of the
biomass. Different samples of biomass weighing from 1-2 gram are placed in the muffle furnace for two hours at 378K and then allowed to cool in a desiccator and weights are taken. The experiments are repeated till a constant weight is reached. The change in weight of biomass is considered as the total moisture present in biomass and its percentage determined [4].

6.3.2 Proximate and Ultimate Analysis

Proximate analysis is conducted to determine the moisture, volatile matter, ash, and fixed carbon contents according to the procedure as specified on a modified ASTM D 5142-04 method on a muffle furnace of Thermo Scientific [21]. Ultimate analysis of the samples is carried out according to ASTM D 5373-08 method using Flash 2000, CHNS-O analyzer, Fisher scientific to determine the CHNS of biomass. The oxygen content was determined after subtracting CHNS and ash from 100%. The oven temperature was set to 1223K. Samples of uniform size of 500mm-3 are prepared by conducting drying, milling, and sieving processes prior to the experiment. During the experiment, the combustion is carried out at 1223K under Helium atmosphere while the reduction was carried out at 923K.

6.3.3 Heating Value

The samples are ground in a grinder, then sieved in a sieve-vibrating machine to prepare samples of a uniform size of 500mm-3 for a Bomb Calorimeter (Model IKA C-200). The calculation of the calorific value is based on ASTM D 240 and ASTM D 5865. Combustion is carried out in a calorimeter in the presence of oxygen. The decomposition vessel is filled with a fuel sample with weight of less than 1 gram and pure oxygen at a maximum of 3MPa, the fuel sample is ignited and the temperature increase in the calorimeter system measured. The heat quantity required to raise the temperature of the calorimeter system by one Kelvin is used to determine the C-Value of the system. The specific calorific values for higher heating value (HHV) of the sample are calculated as follows:

\[
H_0 = \frac{C \times DT - Q_{Ext1} - Q_{Ext2}}{m}
\]  

(6)

Where

m = weight of fuel of the sample

C = Heat capacity (C-value) of the calorimeter system.

DT = Calculated temperature increase of water in the inner vessel of measuring cell
\( Q_{\text{Ext1}} \) = The correction value of the heat energy generated by the cotton thread as ignition aid (supplied by manufacturer)

\( Q_{\text{Ext2}} \) = The correction value of the heat energy generated from other burning aid (if applicable)

### 6.3.4 Dry Torrefaction

A reactor (Fig. 6.1a) is designed, developed and fabricated in a workshop of the University of Guelph for the purpose of continuous torrefaction, which is similar to the Quartz Wool matrix (QWM) reactor [22].

![Figure 6.1a. Experimental Setup for Torrefaction and Weight Loss [22]](image)

### 6.3.5 Wet Torrefaction

Wet Torrefaction (WT) or Hydrothermal Carbonization (HTC) is carried out in a locally modified version of Parr reactor called Subcritical High Pressure Reactor (SHPR) as shown in Figure 6.1b. Biomass sample is mixed with deionized water in 1:6 mass ratios and kept in a glass tubular container, which is then placed in stainless steel metal tubular reactor. With the help of double air sealed jackets, the reactor is sealed and tightened. The air tight reactor is placed in an
electrical tubular furnace. The electrical power is supplied using temperature controller and power supply. Once the reactor is heated up to the desired temperature 458-538K and pressure up to 5.5MPa, the biomass is kept for a desired residence time 5-60 minutes. The temperature and pressure are continuously monitored using a thermocouple with a digital multi-meter and a pressure gauge respectively. The electrical supply is disconnected after the residence time and the reactor is allowed to cool down to room temperature and atmospheric pressure. Then, the reactor is opened in a fume hood place to limit the smell around the lab. The torrefied biomass is filtered by 20 mm-3 filter, and then kept in an open air for 24 hours to dry. The nitrogen is used to flush the air inside the reactor at the beginning of the experiment to make it an inert environment.

![Diagram of experiment setup](image)

**Figure 6.1b Experiment Setup for HTC: Subcritical High Pressure Reactor (SHPR)**

### 6.3.6 CO₂ Gasification

Samples of miscanthus and coal are collected from Ontario and thermochemically processed for enhancing the fuel characteristics of biomass. Thermochemical processes used here are the dry torrefaction (DT) and wet torrefaction (hydrothermally carbonized or WT). These torrefied Miscanthus samples are blended with coal in different ratios. The percentage values of the blend components are varied from 0 to 100. The samples of blended mixture are gasified up to 1573K
in presence of carbon dioxide as shown in Figure 6.1c. The product gases are captured using FTIR.

![Figure 6.1c. Schematic Diagram of CO₂ Gasification](image)

**Figure 6.1 (a-c) Experiment Setups and Schematic Diagram**

### 3.5 Thermogravimetric Analysis–Fourier Transform Infrared Analysis (DSC-TGA-FTIR)

Differential scanning calorimetric and thermogravimetric experiment is carried out in a thermogravimetric analyzer (DSC-TGA). FTIR was also heated up to 498 K on line side to avoid condensation during the transfer from DSC to FTIR. A biomass / biomass-coal mixture sample of about 10mg is placed in a crucible, then heated up to desired temperature (548 K, 45 minutes for dry torrefaction and 1573 K for gasification) at heating rate of 10 Kmin⁻¹. Nitrogen/Carbon dioxide is supplied at the desired rate from 10 cm⁻³min⁻¹ to 100cm⁻³min⁻¹ as per the requirement of torrefaction and cogasification to test the optimum flow rate required. The outputs of the product gas are passed through the Fourier transform infrared (FTIR) for 130 minutes to monitor the spectrum of the gases continuously. The temperature of FTIR was set to 523 K. Heat flow, thermal degradation, stability, and weight loss are monitored by DSC-TGA. The degradation pattern is identified by the derivative thermogram (DTG) plot. The range of FTIR spectra was set to 400-4000 cm⁻¹. Similarly, the spectra were observed at a resolution of 4 cm⁻¹ and samples were observed by scanning at 32 times per minutes using double-sided two-
way acquisition mode and at a scanner rate of 20 kHz. FTIR library was used to identify the gas composition.

6.4 Results and Discussion

6.4.1 Biomass Characterization

6.4.1.1 Proximate and Ultimate Analysis

Proximate and Ultimate analysis of the raw miscanthus and the wet torrefied (WT) and dry torrefied (DT) miscanthus at different treatment temperatures and the residence time are presented in Table 6.1 after repeating three experiments for a sample. The result shows that the carbon contents of the treated samples are increasing with rise in treatment temperature, whereas the oxygen contents are in decreasing order with the similar treatments. There is not a significant improvement on the fuel quality of miscanthus by increasing the residence time from 5 minutes to 30 minutes in the wet torrefaction. Hence, for the gasification, wet torrefied biomass treated as 533 K with 5 minutes of residence time [21] is considered, whereas the optimum dry torrefaction temperature of 548 K for 45 minutes residence time found by Acharya (2013)[4] is considered.
Table 6.1 Proximate and Ultimate Analysis of Miscanthus

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Res. Time</th>
<th>Proximate Analysis (%)</th>
<th>Ultimate Analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mins</td>
<td>MC</td>
<td>VM</td>
</tr>
<tr>
<td>Raw</td>
<td>-</td>
<td>3.78</td>
<td>84.21</td>
</tr>
<tr>
<td>WT-463 K</td>
<td>5</td>
<td>-</td>
<td>82.55</td>
</tr>
<tr>
<td>WT-498 K</td>
<td>5</td>
<td>-</td>
<td>79.23</td>
</tr>
<tr>
<td>WT-533 K</td>
<td>5</td>
<td>-</td>
<td>69.87</td>
</tr>
<tr>
<td>WT-533 K</td>
<td>30</td>
<td>-</td>
<td>68.31</td>
</tr>
<tr>
<td>DT-548 K</td>
<td>45</td>
<td>0.01</td>
<td>79.66</td>
</tr>
<tr>
<td>Coal</td>
<td>-</td>
<td>-</td>
<td>76.54</td>
</tr>
</tbody>
</table>

MC=Moisture Contents, VM=Volatile Matter, FC=Fixed Carbon

### 6.4.1.2 Dry and Wet Torrefaction (Mass Yield, Energy Yield, and Heating Value)

The percentage of mass yield, energy yield, and higher heating values with its varying factors of torrefied miscanthus treated at different temperatures and residence times are presented in the Table 6.2. The percentage mass yield and energy yield decreases with the increase in the torrefaction temperature and residence time. However, the heating value rises with the increase in the treatment temperature and residence time. During the wet torrefaction, miscanthus and water are mixed at a mass ratio of 1:6 throughout the experiment.
### Table 6.2 Mass Yield, Energy Yield, and Heating value of miscanthus

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Mass Yield (%)</th>
<th>Energy Yield (%)</th>
<th>HHV (MJ.kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torrefaction-Temp (K) Residence time (mins)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WT-463 5</td>
<td>83.5±0.5</td>
<td>89.4±0.4</td>
<td>19.1±0.2</td>
</tr>
<tr>
<td>15</td>
<td>77.8±0.6</td>
<td>86.6±0.6</td>
<td>20.4±0.1</td>
</tr>
<tr>
<td>30</td>
<td>72.5±0.7</td>
<td>83.5±0.4</td>
<td>20.9±0.4</td>
</tr>
<tr>
<td>5</td>
<td>66.8±0.9</td>
<td>76.9±0.8</td>
<td>21.1±0.3</td>
</tr>
<tr>
<td>15</td>
<td>63.9±0.7</td>
<td>80.1±0.3</td>
<td>22.9±0.4</td>
</tr>
<tr>
<td>30</td>
<td>62.4±1.2</td>
<td>79.9±0.6</td>
<td>23.3±0.6</td>
</tr>
<tr>
<td>WT-533 5</td>
<td>47.8±0.8</td>
<td>67.3±0.9</td>
<td>25.4±0.2</td>
</tr>
<tr>
<td>15</td>
<td>45.9±1.0</td>
<td>73.1±0.6</td>
<td>28.5±0.4</td>
</tr>
<tr>
<td>30</td>
<td>44.9±0.8</td>
<td>72.8±0.7</td>
<td>29.9±0.1</td>
</tr>
<tr>
<td>DT-548 45</td>
<td>67.5±1.2</td>
<td>79.1±0.9</td>
<td>24.6±0.5</td>
</tr>
</tbody>
</table>

### 6.4.2 CO2 Gasification and DSC-TGA-FTIR

Figure 6.2a-b shows the TGA mass loss in percentage and derivative mass loss (% min⁻¹) of raw, dry and wet torrefied miscanthus, and coal by varying CO2 flow rate, heating rate, and their blends in the different percentage ratios of Coal:WT:DT (100:0:0; 0:100:0; 0:0:100; 50:50:0; 40:30:30; 33.3:33.3:33.3; 20:40:40; 80:10:10 etc.). Weight (%) decreases with increase in the treatment temperature. At the beginning up to 393 K, the weight loss is mainly due to the loss of the hydrate (H₂O) components present in the biomass sample. From temperature range 473-723 K, the major loss of weight (%) may be due to extensive devolatilisation and carbonization of the hemicellulose, cellulose and lignin. The hydroxyl components are broken down into smaller
molecules, which make the sample more hydrophobic in nature. At the third stage, the extensive breakdown of cellulose/ carbon components takes place and releases the syngas.

The reactivity depends upon the temperature variation and the rate of weight-loss of the system during the gasification process. With the increase in the temperature, the reactivity decreases, whereas the reactivity increases with the increase in the rate of weight loss of the sample. The temperature is inversely proportional and the rate of change of mass is directly proportional to the reactivity of the sample.

From the TGA results, the reactivity of the coal is slower than the raw biomass and similar patterns are observed on the wet torrefied biomass than dry torrefied biomass. Miscanthus contains 36.3% of hemicellulose, 38.8% of cellulose, 11.5% of lignin, 12.6% of hot water extractives, and 0.8% of ash [21]. This could be due to more availability of volatiles and hemicellulosic components in the raw and wet torrefied biomass. Dry torrefied fuel gasification needs less time than the wet torrefied biomass. This could be due to removal of alkali components in the wet torrefied biomass [7].

The overall characteristic parameters of the DSC-TGA are summarized in a Table 6.3.

Table 6.3 Description of the activities during the CO2 gasification of Miscanthus

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Stage I</th>
<th>Stage II</th>
<th>Stage III</th>
<th>Stage IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>Up to 473</td>
<td>473-723</td>
<td>723-1123</td>
<td>1123-1423</td>
</tr>
<tr>
<td>Processes</td>
<td>Drying</td>
<td>Pyrolysis</td>
<td>Heating/Charing</td>
<td>Gasification of char with carbon, cellulose and lignin</td>
</tr>
<tr>
<td>Gaseous/vapor products released</td>
<td>H2O</td>
<td>H2O + CO2</td>
<td>CO2+CO</td>
<td>CO2+CO+CH4+Others</td>
</tr>
<tr>
<td>Heat Flow Pattern</td>
<td>-</td>
<td>Endothermic</td>
<td>-</td>
<td>Endothermic</td>
</tr>
</tbody>
</table>
Equations

| Heating of C-H polymers releases water vapor | C-H + CO₂ + O₂ → CO₂ + H₂O | - | C + CO₂ → 2CO
| C + 3H₂ → CH₄ + H₂O |

Activities

| Releasing of water components | Breaking down of OH components, emission of volatiles, fast weight loss, violent decomposition reaction | Heating | Breakdown of C components, CO₂ char gasification, mass loss rate less than 1%/min (lower than stage III) |

Properties changes

| Weight to dry | Hydrophilic to Hydrophobic | Extensive charring | Gaseous fuel |

6.4.2.1 CO₂ Gasification of Torrefied Miscanthus

The miscanthus is torrefied using hydrothermal carbonization and dry torrefaction method. After conducting extensive experiments, the optimum CO₂ flow rate and the optimum heating rate for the gasification of miscanthus samples are identified. The resulted torrefied products are treated under the CO₂ environment with the CO₂ flow rate of 50mL/min at a heating rate of 10 K/min-1. The weight loss undergoes four stages of the raw and hydrothermally carbonized miscanthus, but the dry torrefied miscanthus shows the three stages as shown in Figure 6.2a. This may be due to complete drying and devolatilisation of hemicellulose during torrefaction at 548 K with the residence time of 45 minutes, whereas the raw and hydrothermally carbonized products still contains some moisture and lignocellulosic components. The rate of weight-loss of dry torrefied biomass is very high at 1123-1273 K, whereas the hydrothermally carbonized biomass shows higher weight loss at 1223-1423 K. This may be due to the fewer amounts of alkali metals (43%) in the hydrothermally carbonized biomass than the dry torrefied biomass (88%) [21]. During the
subcritical water temperature treatment of biomass in hydrothermal carbonization, most of the alkali metals are dissolved in the water and washed away from the carbonized products [7].

**Figure 6.2a. Weight % of Wet Torrefied and Dry Torrefied Miscanthus**

### 6.4.2.2 CO₂ Gasification of Blends

The mixture of raw and hydrothermally torrefied miscanthus, raw and dry torrefied, and hydrothermally torrefied and dry torrefied miscanthus in the ratio of 1:1 is gasified with the 50 mLmin⁻¹ of carbon dioxide at a heating rate of 10Kmin⁻¹ and the kinetic behavior of miscanthus is observed as shown in Figure 6.2b. Each process undergoes the four stages: drying up to 423 K, devolatilisation from 423-723 K, char production from 723-1123 K, and finally char gasification from 1123-1473 K. The rate of weight loss is higher as we move from torrefied mixture towards the raw mixture which signifies the movement of reactivity. This may be due to fast devolatilisation of moisture and hemicellulose present in the raw biomass. The reactivity of the
The blends of dry torrefied biomass and the raw miscanthus improves the reactivity of the blends than the dry and wet torrefied biomass blends as shown in DSC-TGA plot in Figure 6.3 (a-i and a-ii). In both curves, the first stage peak is weight loss due to the evaporation of moisture contents of the samples and hydroxyl groups available in the pores of the biomass samples. The
large peak of the derivative weight (%min-1) shows the fast weight loss due to extensive devolatilisation of volatile matters and hemicellulosic components. The final peak is due to the char gasification. The char gasification of the blends of raw and dry torrefied miscanthus completes at a lower temperature than blends of the two torrefied samples. Char gasification completes at around 1273 K.

Fig. 6.3a-i. TGA Plot for CO2 Gasification of Miscanthus Raw:DT (1:1)
The CO2 gasification of blends of wet and dry torrefied miscanthus shows (Figure 3b-f) four major peaks on the derivative weight (% min-1) in the DSC-TGA curve, which signifies that first peak is the sign of drying process with the loss of a small portion of weight % that last up to 423 K. A second peak in the temperature range of 473-723 K is the devolatilisation and carbonization of hemicellulosic components present in the blends. The sign of small peaks may be due to the variation of devolatilizing components of blends i.e. reactivity of devolatilizing components of wet torrefied biomass may be different than the devolatilizing components of dry torrefied miscanthus. Similarly, in the final stage of CO2 char gasification from the temperature range of 1073-1423 K, the reactivity of char from the wet torrefied miscanthus and dry torrefied miscanthus activated at two different temperatures. The first, fast rate of derivative weight loss peak may be due to the weight loss of wet torrefied biomass and a second could be the dry torrefied miscanthus. During the gasification of blends of wet and dry torrefied miscanthus, it shows continuous heat generation with the continuous weight % loss from the thermo-chemical activities of biomass and needs less heat flow than the normal furnace of the boiler. The CO2
gasification of the blends of two torrefied samples last longer than the blends of raw and torrefied products. Two torrefied blends lasts up to the 1423 K for the CO2 gasification. Due to the compact molecular structure of coal, more energy is required for the disintegration of its strong C=C bonding structure, whereas the thermal reactivity of the raw miscanthus is higher than the torrefied one due to removal of the volatiles during torrefaction. The presence of the torrefied miscanthus improves the overall reactivity of the co-gasification process. The treatment temperature for the co-gasification is lower than the coal gasification alone. The mass loss is the fastest when the raw miscanthus is blended with coal. However, the mass loss slows down with the addition of the torrefied miscanthus in the coal-biomass blends. This could be due to the contents of high moisture, and volatiles on the raw biomass, whereas the moisture and volatiles are mostly removed during the thermal treatments of the torrefied biomass.

Fig. 6.3b. TGA Plot for CO2 Gasification of Miscanthus Coal:DT:WT (0:1:1)
Fig. 6.3c. TGA Plot for CO2 Gasification of Miscanthus Coal:DT:WT (1:1:1)

Fig. 6.3d. TGA Plot for CO2 Gasification of Miscanthus Coal:DT:WT (0:0:1)
Figure 6.3 [a.i-a.ii, b-f] TGA Plot for CO$_2$ Gasification of Miscanthus Coal:DT:WT (Different Ratios)
**6.4.2.4 FTIR**

DSC-TGA-FTIR combined system not only generates the results of heat flow pattern, mass loss, % derivative of weight per minute during charring and gasification process, but also displays the gaseous components produced during the treatment process. Different gaseous products are displayed on the FTIR screen at different times and temperatures during the process. During the co-gasification of equal ratios of blends of coal, wet torrefied, and dry torrefied biomass, FTIR results show that the gasification products observed are mainly carbon dioxide, carbon monoxide, water vapor, 1-2-Dibromoethylene, Phosgene, carbonyl dichloride, etc. as shown in Figure 6.4. The amount of hydrogen could not be detected out of the eight main gases (FTIR setting). However, some of the reference analysis data used in FTIR shows the presence of trace amount of hydrogen. This shows that the major reaction could be the reaction of carbon contents of blends and carbondioxide to produce carbon monoxide. The major possible reactions may be as follows:

1) \( \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \)
2) \( \text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \)
3) \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)
4) \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \) (Partial combustion)

Fu et al. (2011)[23] stated that methane is produced below 773K due to the cracking of methoxyl; carbon monoxide is produced above 773K by breaking of the aromatic rings and decomposition of volatiles and carbon components of the residues. During the cogasification process, Boudouard reaction, char forming reaction, and free radical combination reactions leads the kinetics or chemical activities of the gas forming activities [24]. The fuel constituents play a big role in gasification just like in combustion reaction. For example, elements other than C, H, and O are undesired since they cause pollutants and deposit formation, corrosion (S), and ash (K, Fe, Na, Mg). Another important parameter in gasification and combustion is the fuel to air ratio because it plays a significant role in the extent of the combustion reaction, the constituent of the flue gas and finally, the useful energy released. Reaction-1 is used to determine the stoichiometric amount of air required for a given fuel of known composition (Nussbaumer, 2003). Generally, 25% of oxygen required for the combustion
is required for the gasification of the same fuel when oxygen is used as a gasifying agent. However, CO₂ as a gasifying agent is not as reactive as oxygen so reactivity is low and hydrogen production during CO₂ gasification is excessively low. Hence, when hydrogen is the desired product, then the gasifying agent should be oxygen or steam instead of CO₂ environment.

\[ C_t H_x O_y N_z + m(O_2 + 3.76N_2) = aC0_2 + bH_2 O + cN_2 + dO_2 \] \( \text{(R1)} \)

Where,
- \( t, x, y, z \) = the number of atoms of carbon, hydrogen, oxygen and nitrogen.
- \( m \) = the theoretical amount of air required for complete combustion of the fuel
- \( a, b, c, d \) = the number of moles of CO₂, H₂O, N₂, and O₂ respectively.

In the experiment, different gaseous products are observed during the gasification of equal mixture of coal, wet torrefied (WT), and dry torrefied (DT) miscanthus. The product gases vary with respect to the time and temperature. Carbon monoxide is observed only in the last stage of gasification above 773K, whereas the rest of the other gases like water vapor (H₂O), methane (CH₄), acetic acid (CH₃COOH), formic acid (HCOOH), phenol or carbolic acid (C₆H₅OH) is observed during/prior to the second stage i.e. prior to 723K. This may be due to the presence of higher carbon components at high temperature and less carbon and more volatiles in the lower treatment temperature. Higher amount of HCOOH, CH₃OOH, and CH₄ is observed if more raw biomass portion is blended with coal due to availability of Na₂O, K₂O and CaO in biomass [13].

Experimental wave numbers are 750-1550 cm⁻¹ for water vapor, 1100-1200 cm⁻¹ for formic acid, 1200-1400 cm⁻¹ for phenol or carbolic acid, 1600-1900 cm⁻¹ for acetic acid, 2000-2300 cm⁻¹ for carbon monoxide, and 2800-3500 cm⁻¹ for methane. In most of the blends co-gasification, carbon monoxide has been observed from the second to last stages. As the portion of raw miscanthus increases, the CO release starts at a lower temperature in the second stage below the dry torrefaction maximum temperature during charging process, whereas more CO is also released at higher temperature above 773K during the cogasification process.
6.4.3 Kinetics Characterization

Coal and torrefied biomass are blended in the different ratios in different compositions and observe the kinetic characteristics of the co-gasification process. Kinetic characteristics of co-gasification of coal, torrefied, and raw miscanthus are studied by CO$_2$ gasification of blending of different ratio (weight/weight basis) of coal, wet torrefied and dry torrefied miscanthus. Kinetic study is characterized by observing activation energy (E), pre-exponential factor (A), and reaction order (n) as shown in Table 6.4. From the result, higher activation energy is required when blended with coal rather than the blended with raw and torrefied miscanthus. Miscanthus, as a lignocellulosic biomass, contains hemicellulose, cellulose and lignin. Hemicellulose is the weakest, very chemically unstable, the least thermally stable polymer with branched chain molecules which undergoes decomposition prior to 573K temperature. In the second order, cellulose is a longer and stronger polymer with more thermally stable crystals, which starts breaking from 300-673K. The most thermally stable part is the lignin from 473-773K with long chains of the polymer [2, 6]. Observation of multiple peaks in the DSC-TGA is due to variation in the thermal stability of different components of biomass and coal. Coal is less reactive than
biomass due to strong bonding of carbon polymers. On the other hand, raw biomass is found to be the most reactive among tested samples, which may be due to the presence of high volatiles and higher O/C ratio. The higher O/C ratio is due to higher oxygen present, and lower carbon content in the sample pores. As the portion of raw or processed biomass increases in the sample blends, the required activation energy decreases. The activation energy of coal and torrefied miscanthus mixture needs 85.81 kJmol-1 of activation energy, whereas the torrefied miscanthus mixed with raw biomass has the least activation energy of 56.5 kJmol-1 during the charring process. Similarly, during the gasification process, 182.22kJmol-1 is found for the coal, torrefied miscanthus blends, whereas 116.26 kJmol-1 is found in the blends of wet torrefied and raw miscanthus. The required activation energy for the gasification process is higher than the charring process, which may be due to the absence of any kind of volatiles or unstable compounds in the blends. This proves that thermal conversion completes at the gasification stage rather than the curing stage. This also indicates that charring process converts the unstable raw biomass into the stable fuel. The optimum kinetic parameters extracted from the experimental data are best represented by equations (7-8).

\[
X_1 = 1 - \exp \left( -\frac{RT^2}{198.33\alpha} \cdot 9.4 \times 10^6 e^{-\frac{198.33}{RT}} \right) \quad (7)
\]

\[
X_2 = 1 - \left[ 1 - \frac{RT^2}{594.99\alpha} \cdot 9.4 \times 10^6 e^{-\frac{198.33}{RT}} \right]^3 \quad (8)
\]

Thermal characteristics of co-gasification shows that any kinds of biomass can be processed for the curing process then converted in the gasification process. Presence of raw or torrefied biomass increases the reactivity of the coal blends and required less activation energy for the overall system. This gives the possibility of the co-gasification of processed biomass with coal in the commercial reactor for the energy generation.
Table 6.4 Kinetic Parameters of Gasification of Coal-Miscanthus Blends

<table>
<thead>
<tr>
<th>Sample Ratio</th>
<th>Stage II &amp; III</th>
<th>Stage III &amp; IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal:WT:DT</td>
<td>Temp Range (K)</td>
<td>E (KJ.Mol⁻¹)</td>
</tr>
<tr>
<td>100:00:00</td>
<td>630-726</td>
<td>100.13</td>
</tr>
<tr>
<td>80:10:10</td>
<td>601-724</td>
<td>94.55</td>
</tr>
<tr>
<td>60:20:20</td>
<td>580-721</td>
<td>81.55</td>
</tr>
<tr>
<td>50:50:00</td>
<td>571-717</td>
<td>91.55</td>
</tr>
<tr>
<td>50:00:50</td>
<td>547-716</td>
<td>89.92</td>
</tr>
<tr>
<td>40:40:20</td>
<td>579-927</td>
<td>87.64</td>
</tr>
<tr>
<td>33.3:33.3:33.3</td>
<td>621-686</td>
<td>85.81</td>
</tr>
<tr>
<td>30:30:40</td>
<td>594-929</td>
<td>78.63</td>
</tr>
<tr>
<td>20:20:60</td>
<td>609-869</td>
<td>73.59</td>
</tr>
<tr>
<td>10:10:80</td>
<td>618-907</td>
<td>71.88</td>
</tr>
<tr>
<td>00:50:50</td>
<td>571-651</td>
<td>71.34</td>
</tr>
<tr>
<td>00:100:00</td>
<td>515-745</td>
<td>70.79</td>
</tr>
<tr>
<td>00:00:100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Raw Miscanthus</td>
<td>479-630</td>
<td>49.73</td>
</tr>
</tbody>
</table>

Blending with Raw Miscanthus

<table>
<thead>
<tr>
<th>Coal:Raw:DT</th>
<th>Stage II &amp; III</th>
<th>Stage III &amp; IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>496-664</td>
<td>56.82</td>
<td>7.1x10⁵</td>
</tr>
<tr>
<td>00:50:50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

143
The characteristic parameters of cogasification of coal-biomass blends are presented in the Table 6.5. The higher treatment temperature is required as the ratio of the coal portion increases in the mixture. Gasification of coal alone occurs in the temperature range of 1220-1399 K whereas the raw miscanthus needs only 1102-1184 K. There are multiple peaks at different stages of the treatment temperatures, which is due to the presence of different characteristic samples. The weight loss is the highest in raw miscanthus and the lowest in the bituminous coal during and prior to the charring stage, whereas the converse is true during the co-gasification. This might indicate that cogasification makes a more reactive product and lowers required kinetic energy during the gasification process. This shows the synergistic effect of CO2 gasification of coal-torrefied miscanthus blends.

Table 6.5 Characteristic Parameters of Gasification of Coal and Biomass Blends

<table>
<thead>
<tr>
<th>Sample Ratio</th>
<th>Stage II &amp; III</th>
<th>Stage III &amp; IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal:WT:DT</td>
<td>Temp Range</td>
</tr>
<tr>
<td></td>
<td>(%:%:%)</td>
<td>(K)</td>
</tr>
<tr>
<td>100:00:00</td>
<td>630-726</td>
<td>1.94</td>
</tr>
<tr>
<td>80:10:10</td>
<td>601-724</td>
<td>1.31</td>
</tr>
<tr>
<td>60:20:20</td>
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<td>571-717</td>
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<tr>
<td>Percentage</td>
<td>Temperature</td>
<td>Pressure</td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>----------</td>
</tr>
<tr>
<td>30:30:40</td>
<td>594-929</td>
<td>1.24</td>
</tr>
<tr>
<td>20:20:60</td>
<td>609-869</td>
<td>1.26</td>
</tr>
<tr>
<td>10:10:80</td>
<td>618-907</td>
<td>1.27</td>
</tr>
<tr>
<td>00:50:50</td>
<td>571-651</td>
<td>1.35</td>
</tr>
<tr>
<td>00:100:00</td>
<td>515-745</td>
<td>1.34</td>
</tr>
<tr>
<td>00:00:100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Raw miscanthus</td>
<td>479-630</td>
<td>5.6</td>
</tr>
</tbody>
</table>

**Blending with Raw Miscanthus**

<table>
<thead>
<tr>
<th>Blending Type</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Mass Loss</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal:Raw:DT</td>
<td>496-664</td>
<td>6.41</td>
<td>629</td>
<td>44.75</td>
<td>1059-1367</td>
<td>1.69</td>
</tr>
<tr>
<td>00:50:50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal:WT:Raw</td>
<td>500-656</td>
<td>6.34</td>
<td>633</td>
<td>44.35</td>
<td>1046-1371</td>
<td>1.68</td>
</tr>
<tr>
<td>00:50:50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 6.5 Conclusions

Interaction and kinetic behavior of CO₂ gasification of coal, wet torrefied and dry torrefied miscanthus and their blends at different ratio were observed by using TGA-FTIR. Results suggested that CO₂ gasification could be one option for producing synthesis gas by gasification of coal, torrefied biomass (wet and dry), and their blends. The blends of up to 40% addition of torrefied biomass with coal (coal: WT:DT=60:20:20) shows optimum performance in the cogasification. The activation energy required decreases with the increase in the percentage of processed biomass in the coal-biomass mixture during cogasification due to increase in the reactive components of mixture by adding processed biomass. The mixture of dry and wet torrefied biomass feedstock shows improved performance over raw biomass during the cogasification with coal. The best fit mathematical model for kinetics characterization has been proposed.
6.6 References


New York, 92-6, 2010.


Chapter 7   Ethanol Production by Syngas Fermentation in a Continuous Stirred Tank Bioreactor using Clostridium ljungdahlii

Abstract

Ontario Biomass could be thermochemically processed by dry and wet torrefaction to produce high quality solid biofuel. These solid fuels could also be gasified to produce syngas. This study analyzes and demonstrates the successful and efficient way of production of bioethanol from syngas fermentation using Clostridium ljungdahlii in a laboratory scale continuous stirred tank bioreactor (CSTBR) having an innovative gas supply and effluent extraction structures. At the beginning, a batch process is conducted to grow microorganisms and allow it to reach to the maximum cell density in a reactor without supplying gas. Ethanol production is observed by supplying two different gas compositions which includes 100% CO and simulated syngas blend, mimicking the composition of syngas extracted from lignocellulosic biomass having 60% CO, 35%H2, and 5% CO2. CO and Syngas are fermented with different gas (5-15mL/min), effluent flow (0.25-0.75mL/min), and media flow rates and stirrer speed (300-500 rpm) at atmospheric pressure and 37°C. The gas flow rate, media and effluent flow rate, pH level, and stirrer speed are also controlled. The exhaust gas is reused for the improvement of residence time and thus the improvement on the gas-liquid mass transfer. Excessive foam has been observed during the fermentation process, which is controlled by using diluted antifoam-204. The maximum optical cell density reached up to 2.4 g/L. More bioethanol production was observed by syngas fermentation rather than the Carbon monoxide fermentation. CO fermentation produces 0.17-1.33 g/L-effluent ethanol and 8.92-23.67 g/L-effluent acetic acid whereas syngas fermentation produces 0.85-3.75 g/L-effluent ethanol and 8.89-14.97g/L-effluent acetic acid.

A version of this chapter has been published in Biofuel: B. Acharya, A. Dutta, P. Basu, (2017) Ethanol Production by Syngas Fermentation in a Continuous Stirred Tank Bioreactor using Clostridium ljungdahlii, Biofuels (Accepted on Feb 17, 2017)
7.1 Introduction

Biofuels, produced from the lignocellulosic biomass, are good options for the replacement of the fossil fuels in the future. Bio-ethanol and biodiesel are produced from the lignocellulosic biomass through the biochemical and thermochemical transformation processes. Both processes have merits and demerits but the biochemical process is more matured and dominating process than the thermochemical process in the bioethanol production [Subramani and Gangwal, 2008]. Jian et al. (2015) claimed that ethanol produced from the syngas fermentation using industrial off-gas or natural gas or syngas extracted from biomass could be a cheaper feedstock. There are two paths to produce bioethanol from syngas using metallic catalyst or biological catalyst. Metallic catalysts, either metal based or modified methanol catalysts, are expensive, higher operating temperature, and pressure [Datta et al., 2011; Subramani and Gangwal, 2008]. Bioethanol produced from syngas using the biological catalysts are economical and operates at ambient temperature and atmospheric pressure with low grade feedstocks including lignocellulosic biomass and municipal wastes [Acharya et al., 2015; Munasinghe and Khanal et al., 2010]. Thermochemical conversion, syngas fermentation process has many advantages over the biochemical conversion process like: possibility of using 100% of lignocellulosic biomass including lignin; independence of feedstock compositions; elimination of complex pre-treatment and high enzyme cost; and independence of H₂:CO:CO₂ ratio in syngas fermentation [Munasinghe and Khanal et al., 2010]. However, main constraints of syngas fermentation using biocatalysts are lower gas-liquid mass transfer, production of inhibitory products during fermentation, low productivity associated with cell density [Roy et al., 2016]. Another likely limiting factor for the ethanol production is its high concentration of un-dissociated acetic acid in the bioreactor [Richter et al., 2013].

Syngas; a mixture of carbon monoxide, hydrogen and carbon dioxide; used in a biochemical conversion process in a presence of biocatalyst or micro-organism is called syngas fermentation to convert syngas into various chemical products like ethanol, alcohols and organic acids. Commonly used biological catalysts or micro-organisms in the syngas fermentation are Clostridium ljungdahlii, Clostridium ragsdalei, Clostridium carboxidivorans, Clostridium autoethanogenum, Alkalibaculum bacchi [Devarapalli et al. 2016; Abubacckar et al., 2015; Liu et al., 2012]. These biocatalysts play an important role to metabolize syngas into bioethanol and acetic acid through the Wood-ljungdahl pathway. The major constraints during the production of
ethanol by syngas fermentation are low gas-liquid mass transfer due to low solubility of the carbon monoxide and hydrogen gases into the media and generation of inhibitory products [Acharya et al., 2014; Huhnke, 2013; Munasinghe and Khanal, 2010]. There are number of challenges to operate economically the biomass extracted syngas for continuous fermentation which are necessary of complex distillation for low ethanol concentration; requirement of advanced cleaning of toxic contaminants in biomass extracted syngas; obligatory finding of cheaper sources of growth medium or media ingredients [Saxena and Tanner, 2012; Phillips et al., 2012; Xu et al., 2011; Vane et al., 2010].

The continuous fermentation process is better than the batch process because continuous flow of nutrition never allow to decrease the nutrition level on the reactor for the microorganism. This favors the continuous growth of the biocatalyst once they are at the highest concentration level. However, a batch culture requires more time to re-grow the fermenting organism after each fermentation cycle. For the commercial ethanol production, batch culture may be non-realistic. Similarly, two stage continuous cultures could be better option than the single stage continuous fermentation processes because separate treatments can be made for acetogenesis and solventogenesis stages like separate pH level, temperature, working volume level, dilution rate, nutrition level, growth rate, cell density, reactor productivity etc. [7].

The mass transfer in substrate and microbes depends on the amount of dissolution of syngas process in the fermentation media. This process brings more gas-liquid interfacial area and retention time in the fermentation media. The mass transfer rates and microbe accessibility to syngas can also be improved by creating finer bubbles or decreased rising velocity in the fermentation media with increased in agitation speed [5]. To improve the mass transfer of gasses into the liquid medium, different bioreactor designs such as bubble columns, packed columns, trickle beds, hollow fiber reactors, and continuously stirred tank reactors with micro-spargers are utilized and studied by different researchers [6-8,11,16-18]. Richter et al.(2013) concluded that the continuous culture has more advantages than the batch culture in a syngas fermentation technology[7]. Even though, there is improvement in the mass transfer by increasing the agitation speed or gas flow rate, the overall process may not be commercially viable due to high energy consumption or high power to volume ratio and stress to the biocatalysts [19-20]. If the amount of cells in the bioreactor is not sufficient to consume the gas provided then the increase in syngas flow rate means eventually increase in the loss of syngas at the exhaust system i.e.
lower in gas conversion efficiency and the productivity of the biocatalysts decreases with the increase in the stress on them either by mechanical or increase in the cell density [18, 21]. In the orthodox syngas fermentation technology, single orifice or multiple orifices are used to release the gas into the fermentation broth in both batch and continuous fermentation process [18, 22]. Shen et al. (2014) and Richter et al. (2013) have used the hollow fiber membrane for the gas supply system [7, 16]. Tricle bed reactors (TBR) are used in syngas fermentation to produce hydrogen using photosynthetic bacterium e.g Rhodospirillum rubrum and Rubrivivax gelatinosus; CH₄ using tri-cultures of R. rubrum; acetate using Peptostreptococcus productus; and alcohol using Clostridium ragsdalei [8]. To the knowledge of the authors, there are no accessible literatures on the study of fermentation using continuous feed-back-loop gas supply system with locally fabricated simple bioreactor. Hence, this study tries to utilize a simplified continuous stirred tank bioreactor employing a novel gas flow with feedback gas supply system and effluent abstraction schemes to improve gas-liquid mass transfer, ease inhibitory stress, and increase bioethanol production and compare the productivity of bioethanol by using carbon monoxide and syngas. Further, the influence of gas and liquid flow rates on gas conversion efficiency, bioethanol yield, acetic acid yield, pH level, and mass transfer are analysed.

### 7.2 Mass Transfer and Product Yield

One of the major limitations of the syngas fermentation technology is the low mass transfer between substrate and microbes. Numbers of studies are conducted to enhance the mass transfer [5, 7-8, 11, 16]. They observed the improvement on mass transfer rates by improving residence time of syngas with bacteria, gas supply system, gas flow rate, reactor design, gas supply system design etc. Increasing the agitation speed of stirrer up to the optimum limit improves the accessibility of syngas to biocatalysts by forming finer bubbles by reducing rising velocity in fermentation media. The mass transfer coefficients, k,CO/V_L and k,L,H₂/V_L are the major parameter for determining the mass transfer rate which can be calculated by using following equations 1 (general) and 2 (boundary layer theory) [23].

\[
k_{L,i} \cdot a \frac{V_L}{V_L} = \left[ -\frac{1}{V_L} \frac{dn_i}{dt} \right] \left[ \frac{C_{out,i} - C_{in,i}}{\ln\left(\frac{C_{out,i}}{C_{in,i}}\right)} \right]
\]
Similarly, overall mass transfer coefficient value can also be determined for hollow fiber membrane by equation (3) [24]. The slope of \(\ln\left(\frac{C_{\text{out},i}}{C_{\text{out},i} - C_{\text{in},i}}\right)\) vs time can be used to determine the mass transfer coefficient.

\[
\ln\left(\frac{C_{\text{out},i}}{C_{\text{out},i} - C_{\text{in},i}}\right) = \frac{Q}{V_L}\exp\left(-k_{L,i}a \frac{L}{V_L}\right) t
\]

(3)

Where,

\(\frac{dn_i}{dt} = \text{Instantaneous molar rate of gas components } i \text{ transferred into the medium, mmol/h}\)

\(V_L = \text{Dynamic liquid holdup volume in the Bioreactor, L}\)

\(k_{L,i} \text{ or } j \cdot a V_L = \text{Volumetric mass transfer coefficient of supplied gas, } \frac{1}{h}\)

\(i = \text{Components of composition of gas like CO, H}_2, \text{CO}_2, \text{CH}_4 \text{ etc.}\)

\(C_{\text{in},i} = \text{Liquid phase concentration of gas reactant } i \text{ in equilibrium by Henry's Law with the gas at the inlet of bioreactor, mmol/h}\)

\(C_{\text{out},i} = \text{Liquid phase concentration of gas reactant } i \text{ in equilibrium by Henry's Law With the gas at the outlet of bioreactor, mmol/h}\)

\(D_i, D_j = \text{Diffusivities for } i \text{ and } j \text{ gases e.g. at } 37^\circ C, \text{ CO } (3.26x10^{-9}) \text{ and } \text{H}_2 (6.48 \times 10^{-9}) \text{ m}^2/\text{s}\)

\(Q = \text{Liquid recirculation rate}\)

\(L = \text{Length of gas supply pipe line in meter}\)

\(t = \text{Sampling time, seconds}\)

\(a = \text{Specific surface area of gas supply system, m}^2\)

Even though equation (1) indicates that increase in the inlet syngas increases the volumetric mass transfer coefficient. However, Devarapalli et al.(2016) observed that \(k_{L,\text{CO}} a/V_L\)
increased by 24% when the syngas flow rate was doubled while $k_{L, H2} a/V_L$ decreased by 46% which may be due to limitations of concentration of hydrogen by large concentration of liquid phase carbon monoxide. Origill et al. (2013) concluded that decrease in the mass transfer coefficient $k_{L,i} a/V_L$, for both carbon monoxide and hydrogen is due to high liquid holdup volume, $V_L$ which was resulted by the increased liquid recirculation rate [17]. The hydrogenase activity of CO limits the mixing ability of hydrogen gas in to the media [25]. Similarly, the mass transfer coefficient declines with the rise in the media flow rate in pure CO environment [17].

Klasson et al. (1992) used equation (4) for determining the mass transfer coefficient ($k_L$) for a slightly soluble gaseous substrate [26].

$$\frac{1}{V_L} \frac{dN_s^G}{dt} = \frac{k_L a}{H} (P_s^G - P_s^L)$$

(4)

Where,

$N_s^G = \text{Molar substrate transferred from gas phase (mol)}$

$V_L = \text{Volume of the bioreactor (L)}$

$P_s^G$ and $P_s^L = \text{Partial pressure of the gaseous substrate in gas and liquid phase (atm)}$

$H = \text{Henry’s laws constant (L.atm/mol)}$

During CO and syngas fermentation, the product yield can also be expressed by using different statistical formula equation (3-5) as outline by Liu et al.(2011) [10]:

$$\text{Ethanol Yield} = \frac{\text{total moles of ethanol produced}}{\text{total moles of CO consumed}} \times 100\%$$

(3)

$$\text{Cell Mass Yield} = \frac{\text{Maximum cell mass} - \text{Initial cell mass}}{\text{moles of CO consumed}}$$

(4)

$$\text{[Gas]}_i \text{ utilization} \% = \frac{\text{Total moles of [Gas]}_i \text{ consumed}}{\text{Total moles of [Gas]}_i \text{ supplied}} \times 100\%$$

(5)
7.3 Methodology

7.3.1 CSTBR Fabrication
Continuous Stirred Tank Bioreactor has been designed and fabricated at Bio-renewable Innovative Lab (BRIL), University of Guelph, ON. The fabricated 3L laboratory scale low cost reactor (made by transparent PVC pipe type PVC-9002-86-20 for tank and Plexiglass sheet type VH-100 Acrylic resin for base and lid) with working volume of 2L broth media is very handy, simple, robust, and easy for maintenance, data reading, cleaning. Locally available low cost innovative gas diffuser has been positioned at 1cm and on the fringe, and an in situ cell retention filter at 15cm height of the reactor. For monitoring the data, the reactor is connected with a temperature and pH meter (PHE-1411, Omega Environmental Inc., Laval, QC, Canada); and digital pressure gauge (PHH-222, Omega Environmental Inc., Laval, QC, Canada). Gas flow meter (PMR1-0106018, Cole Parmer Inc., USA) and a micro-pump (GE-F155001, Gilson Inc, USA) with desired rate by using F117938 tubes are connected with the reactor to monitor the gas flow amount and insertion/extraction of the media/product. Membrane support has been positioned at 2/3rd level of the bioreactor to install the membrane on the higher level of fermentation broth. For the continuous supply of media and extraction of effluent, modified 2L anaerobic glass jars are used.

7.3.2 Microorganism and Media Preparation
An anaerobic bacterium biocatalyst, *Clostridium ljungdahlii*, an American Type Culture Collection (ATCC#55380) is collected from Cedarlane, Burlington, Ontario. Cedarlane has also supplied the broth media agents with broth media preparation manual. About one litre of broth media is prepared by adding 10g of peptone, 10g of beef extract, 3g of yeast extract, 5g of salt, 1g of soluble starch, 3g of sodium acetate and 4ml of 0.0025% resazurim as an oxygen indicator and 1000ml of deionized water. Dissolve all ingredients and boil the medium for 10 minutes to drive off oxygen. Cool down medium with bubbling with oxygen free gas. Add 0.5g of L-cysteine HCl as a reducing agent and adjust pH to 6.8 then dispense under oxygen free environment and autoclave at 121°C. The freeze dried 0.5ml of biocatalyst has been transferred aseptically into the broth media in test tubes, cultured for 72 hours and disseminated anaerobically in the broth media jar at 37°C. Benson burner is used for creating aseptical and incubator is used for maintaining constant temperature environment. Finally, cultured
microorganism is transferred anaerobically into the CSTBR for syngas fermentation process. Schematic design diagram of continuous stirred tank bioreactor is presented in Figure 7.1.

7.3.3 Experimental Setup and Procedure

The schematic diagram of the experimental setup for syngas fermentation is presented in Figure 1. All apparatus for the experiment including CSTBR and accessories are sterilized in an autoclave at 121°C for 20 minutes. The nitrogen gas has been supplied inside the reactor for 2 hours to create an anaerobic environment. Initially, the prepared and sterilized 1.9L fresh broth media has been transferred to the 3L CSTBR in a nitrogen environment. An inoculum of 100mL is added in the medium in the same environment. Medium with inoculum is kept air tight with proper sealing. To drive off the oxygen, nitrogen is continuously purged into the reactor with medium for 2 hours to create complete anaerobic environment by using a closed chamber and a vacuum pump. The reactor is placed in a temperature controlled environment for 48 hours to allow it for propagation of microorganism in the reactor. Now, the batch is ready to run the reactor with different fermenting gases, Carbon monoxide and Syngas in a continuous fermentation process. Carbon monoxide has been run in the first batch at the beginning then switched to syngas in the second batch fermentation processes. After the 48 hours of each batch, reactor is operated in continuously for 90 days.

Pure Carbon monoxide has been supplied in a reactor in the first cycle and then switched to the syngas with 60% CO, 35%H₂, and 5% CO₂ at different rates of 5-15 mL/min, then compared the results on the bioethanol production. Throughout the experiment, anaerobic environment has been created at atmospheric pressure. The pH level has been set to 4.5±0.5 by using base-NaOH or acid-HCl whenever necessary and the stirrer speed is also adjusted from 300-500 rpm [7, 18]. The medium and effluent extraction flow rates are set at 0.5±0.25 mL/min. Pressure is controlled by using back pressure regulator in the reactor. To capture the exhaust unwanted product in vapor form, a bubbler has been used. The main aim of syngas fermentation here is to extract bioethanol from the gasification of biomass product. The composition of syngas released from the gasification of all types of biomass consists of CO, H₂, CO₂, CH₄ and few other gases with tar and ashes [18]. Similar composition of the syngas from the local gas supplier is used during
the experiment. For the investigation of products, gas and liquid samples are collected intermittently. The nutrient level and activities of microorganism is maintained by continuous supplying of the broth media using micro-pump. The cell mass, excluding suspended cells in bioreactor could be captured in a droplet, form a biofilm or suspended in the medium. The gas flow rates of 5, 10, and 15 mL/min; the media flow rates of 0.25, 0.5, and 0.75mL/min; and the stirrer speed of 300 and 500 rpm are tested. Different batches of testing are conducted by different combination like Batch 1 & 2 (B11 and B21) for 5mL/min gas, 0.25 mL/min media and effluent flow rate, and 300 rpm of stirrer, Batch 3 & 4 (B12-22) for 10mL/min gas and other remains same and so on. Batch numbers are numbered as B1x for the fermentation of carbon monoxide and B2x for the fermentation of syngas (x=1-18 signifying each batch having fresh broth medium with varying gas speed, media/affluent speed, and stirrer speed). The cell density again increases to the maximum level with the addition of fresh medium in each batch. Foam formation is controlled by using diluted anti-foam-204 (1/100 mL dilution with deionized water) injection on the reactor.

The pH level of the fresh medium is set to 6.8 then after the addition of inoculum, the pH level has decreased rapidly and stabilized at 4.5. This may be due to formation of number of acidic compounds like propanol-C\textsubscript{3}H\textsubscript{8}O, propionic acids-C\textsubscript{3}H\textsubscript{6}O\textsubscript{2}, nonanoic acid-C\textsubscript{9}H\textsubscript{18}O\textsubscript{2}, benzaldehyde etc. including bioethanol- C\textsubscript{2}H\textsubscript{6}O, acetic acid- CH\textsubscript{3}COOH [4,6]. During the culturing of the microorganism in the fresh medium in the first 48 hours, the pH level has changed drastically from 5.8 to 5.0. This may be due to rapid formation of acetic acid at the beginning. The pH level is again lowered down from 5.0 to 4.5 during the continuous process due to formation of bioethanol and acetic acid. The addition of base-NaOH has been made when the pH level dropped below 4.4 as shown in Figure 7.1. The variation of the pH level could be due to formation of acetic compounds, and flow of media, affluent, and fermenting gas.
7.3.4 Analytical Methods

7.3.4.1 Cell Growth
Cell growth of *Clostridium ljungdahlii* is observed by quantifying the cell dry weight of it. Three samples are taken from the bioreactor in each batch and the average is plotted with standard deviation. Optical cell density is analyzed using a spectrophotometer (ThermoFisher Scientific USA) at 600nm and the cell concentration or cell dry weight has been determined using a standard calibration curve.

7.3.4.2 Solvent Analysis
The amount of bioethanol and acetic acid are analysed by using GC-MS system, equipped with a Bruker BR-SWAX column (30mx0.25mm internal diameter with a 0.25μm phase thickness), with a gas chromatograph (7890A) and a mass spectrometer (59756MS) of Agilent Technologies, USA. Oven start up temperature has been set at 44°C temperatures and kept for 3.5 minutes at pre-set temperature. The intermittent temperature has been set at 200°C with ramp of 5°C/min. Helium carrier gas is supplied at the rate of 1mL/min and the sample is inoculated in
an un-fragmented mode at 280°C. Collected 0.5mL of solvent samples are transferred into 15mL vials and incubated at 75°C for 5min which is then equilibrated with a 75µm caroxen-polydimethyle-siloxane (CAR-PDMS) fiber dipped in a headspace for 20min. The volatile compounds are then thermally desorbed in the injector port by manually injecting and exposing the fiber for 8 min. The mass spectrometer is scanned from m/z 10-150 at an interval of 1s. The ionization is formed by an electronic impact at 200°C, while the transfer line is kept at 250°C. The +ve ion mode data are collected and products are extracted physically by using a SPME holder (Supelco, USA), a hotplate, and a metal support with clamps.

7.3.4.3 Gas Analysis
The gas samples are analysed using an 8610C GC (SRI Instruments, Torrance, CA) having two columns molecular sieve; Porapak. It has two detectors: a flame ionization detector (FID) and a thermal conductivity detector (TCD). A standard gas mixture is utilized for the standardization of the analyser readings. A Hamilton gas tight syringe (Hamilton Co., Revo, NV, USA) is used to inject 100mL of in a GC in a Helium gas environment. The gas samples are collected from the gas inlet and outlet of the bioreactor. The Helium gas of 2mL/min is supplied automatically during the experiment from the gas cylinder. The gas analysis data are collected from the experiment.

7.4 Result and Discussion
7.4.1 Operation of Bioreactor
The bioreactor is operated continuously at 37°C after the 48 hours of batch operation. Fresh broth medium is pumped at different liquid flow rates into the bioreactor after having an appropriate cell population during the batch process. The stirrer rate is set at 300 rpm for one set of continuous process and 500 rpm for another set of continuous process. During the continuous process, liquid flow rates and the gas flow rates are varied from 0.25mL/min, 0.5mL/min, and 0.75mL/min; and 5mL/min, 10mL/min, and 15mL/min respectively. The pH of the bioreactor is kept controlled within specified range of 4.5 to 4.8. During the experiment in the first week of first run, excessive foam has been observed in the bioreactor. Diluted AntiFoam liquid is used to control the foam but all biocatalyst are dead after addition of 10 drops of 1/100 diluted antifoam liquid. This may be due to higher amount of antifoam liquid. The antifoam liquid shall be 1/100
diluted with deionized water and shall be added 1-2 drop in the bioreactor at a time to control the excessive foam whenever excessive foam has been observed. The experiment is repeated from the beginning without considering any of the previous data. Similarly, during the operation of second set of continuous run i.e. after 45 days, the experiment has to be repeated due to loss of microorganism due to air leakage in the experiment setup. One of the valves in the bioreactor is loosely tighten which makes the repetition of the experiment immediately after the batch process. With the increase in the liquid flow rate, the increased dilution reduces the cell population and productivity. Out of the three liquid flow rates, the optimum seems to be in between 0.5mL/min to 0.75mL/min. The optimum condition for the bioethanol production is observed at the stirrer rate of 300 rpm, gas flow rate of 10-15mL/min, and liquid flow rate of 0.25-0.5mL/min.

7.4.2 Cell Optical Density and pH
Measurements of cell optical density or the cell dry weight (cell concentration) are taken in each batch when the condition has been changed. The cell concentration in the first batch (B101 and B201) of each run reached a maximum level. After the first batch, the cell concentration never crosses the cell concentration of first batch (2.4 g/L). This may be due to the disturbance of stirrer, gas supply and depletion of nutrition level of the medium. Nutrition level of the medium is maintained in the reactor by continuous supplying of the fresh medium in the reactor at specified rate for each batch. The cell growth rate decreases with the decrease in the pH value and increase in the temperature so continuous monitoring of the pH level and temperature is carried out and pH level is maintained by addition of base. The pH of fermentation is one of the significant parameter in controlling the substrate metabolism and changing the physiological state. Cell growth, selectivity of product, and metabolic by-products discharge are affected by the pH level [18]. The pH level is decreased during the first cycle of the fermentation process due to formation of weak organic acid which may permeate through the cell wall, accumulate inside the cell and reduces the inside pH by H⁺ ions. This phenomenon helps on converting acetogenesis phase to the solventogenesis phase.

During the experiment of both CO and Syngas fermentation, the pH level is decreased rapidly during first 48 hours from 5.80 to 5.0 during batch process at gas flow rate of 5mL/min, media/affluent circulation rate of 0.25mL/min, and stirrer speed of 300rpm. The pH level further decreases and reaches at almost stable condition at about 4.6±0.3 for CO and syngas
fermentation during continuous process as shown in Figure 7.2. The rapid change in the pH level at the beginning indicates that acid formation is high which may be due to increase in formation of acetic acid. The continuous variation in the pH level is observed during the hours of operations throughout the experiment which may be due to variation on the acid formation during fermentation process and disturbances caused to the biocatalyst by variation on media and affluent in/out process, stirrer speed, gas flow rate, etc. Lowering the pH level (indicating the formation of acetic acid) triggered a transformation in cell metabolism from acetogenesis to solventogenesis.

Figure 7.2 pH Profiles and Cell Concentration during CO and Syngas Fermentation

7.4.3 Product Profiles
The acetyl-CoA biochemical or Wood-Ljungdahl pathway is followed by Clostridium ljungdahlii for cell growth, acetic acid formation, and adenosine triphosphate (ATP) during the growth stage of syngas fermentation at 4-7 pH level [27]. The conversion of acetyl-CoA to acetate needs two major steps, where first step follows conversion from acetyl-CoA to acetate then acetaldehyde with reduced ferredoxin and finally to ethanol via alcohol dehydrogenase (ADH) and second step follows direct conversion of acetyl-CoA to acetaldehyde then to ethanol by reducing acetaldehyde [28]. By adjusting pH level by adding base to the bioreactor, the ethanol production has been improved but the growth of unwanted acetic acid is also observed. The acetic acid
production during the CO fermentation is more than the acetic acid formation during syngas fermentation. This may be due to less conversion of acetic acid to the ethanol due to thin layer formation or less reactive only with CO or higher CO flow.

In each batch of continuous process, the products are bioethanol and acetic acid. The productions of the bioethanol and acetic acid are increasing with cell concentration, CO and Syngas utilization in linear pattern. However, it changes its increasing or decreasing patterns according to the pH level, cell concentration level, gas flow, liquid flow etc. This signifies that continuous production of bioethanol and acetic acid occurs in each cycle. Each batch of cycle is repeated in 120 hours by replacing fresh broth media. The production of bioethanol varies from 0.30±0.07g/L to 1.3±0.05g/L and acetic acid varies from 8.60±0.40 to 23.67±0.80g/L during the CO fermentation whereas production of bioethanol varies from 0.80±0.02 to 3.75±0.08g/L and acetic acid varies from 5.20±0.80 to 14.20±0.50g/L during syngas fermentation. In the continuous extraction process, when the stirrer speed is set at 300 rpm (B11-B19 and B21-B29), the production of ethanol and acetic acid batch is from 0.41g/L to 1.33 g/L in B11-B19 and is from 0.92g/L to 3.75 in B21-B29. In each gas flow with the 300 rpm stirrer, the ethanol production increases with the increase in the liquid flows (media in and affluent out) rate. When the gas flow is doubled from 5ml/min to 10mL/min, the ethanol production is increased by 58% during CO fermentation, whereas it is more than 49% during the syngas fermentation. Data represented are the average of two replications.

The acetic acid formation is more at the beginning of the experiment whereas the acetic acid formation continued to grow during later batches in the continuous processes. This may be due to biofilm formation and acetogenesis process. To observe the effect of liquid flow rate, the liquid flow rate is varied from 0.25mL/min to 0.75mL/min, however there is 11% to 29% variation on the bioethanol and acetic acid formation in variation of the liquid flow rate in such range. This may be due to increase in the nutrition to the cells and increase in gas-liquid interaction. Similarly, increase in the gas flow rate has increase the production of bioethanol by 30% to 60% and increase production of acetic acid by ±3% to +40% respectively.
Table 7.1 Ethanol, Acetic Acid Concentration and Gas Conversion Efficiency in Syngas Fermentation

<table>
<thead>
<tr>
<th>Batch</th>
<th>Hours</th>
<th>Stirrer Speed rpm</th>
<th>CO flow rate mL/min</th>
<th>Liquid flow rate mL/min</th>
<th>CO Bioethanol Yield g/L</th>
<th>CO Acetic Acid g/L</th>
<th>CO Conversion %</th>
<th>Syngas flow rate mL/min</th>
<th>Syngas Bioethanol Yield g/L</th>
<th>Syngas Acetic Acid g/L</th>
<th>CO Conversion %</th>
<th>H2 Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-120</td>
<td>300</td>
<td>5</td>
<td>0.25</td>
<td>0.41</td>
<td>8.92</td>
<td>60</td>
<td>5</td>
<td>0.92</td>
<td>9.14</td>
<td>57</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>121-240</td>
<td>300</td>
<td>5</td>
<td>0.5</td>
<td>0.53</td>
<td>10.11</td>
<td>67</td>
<td>5</td>
<td>1.34</td>
<td>11.23</td>
<td>63</td>
<td>61</td>
</tr>
<tr>
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<td>0.75</td>
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<td>71</td>
<td>5</td>
<td>1.55</td>
<td>13.44</td>
<td>66</td>
<td>45</td>
</tr>
<tr>
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<td>0.25</td>
<td>0.76</td>
<td>14.44</td>
<td>60</td>
<td>10</td>
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<td>14.97</td>
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<td>43</td>
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<tr>
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<td>10</td>
<td>2.84</td>
<td>13.88</td>
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<tr>
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<td>10</td>
<td>0.75</td>
<td>1.28</td>
<td>14.57</td>
<td>68</td>
<td>10</td>
<td>3.11</td>
<td>12.09</td>
<td>71</td>
<td>47</td>
</tr>
<tr>
<td>7</td>
<td>721-840</td>
<td>300</td>
<td>15</td>
<td>0.25</td>
<td>1.32</td>
<td>16.27</td>
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<td>3.75</td>
<td>11.64</td>
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<tr>
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<td>300</td>
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<td>0.5</td>
<td>1.13</td>
<td>18.22</td>
<td>57</td>
<td>15</td>
<td>3.61</td>
<td>10.99</td>
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<tr>
<td>9</td>
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<td>1.07</td>
<td>21.53</td>
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<td>0.5</td>
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<td>0.75</td>
<td>0.81</td>
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<td>2.12</td>
<td>11.34</td>
<td>65</td>
<td>45</td>
</tr>
</tbody>
</table>

From the plot of the above experimental results and data, following models of equations are extracted to represent the bioethanol and acetic acid production:

\[
Y_{CO} = 8 \times 10^{-12} t^4 - 2 \times 10^{-8} t^3 + 2 \times 10^{-5} t^2 - 0.0044 t + 0.73 \quad (7.1a)
\]

\[
R^2_{CO} = 0.924 \quad (7.1b)
\]

\[
Z_{CO} = 5 \times 10^{-16} t^6 - 2 \times 10^{-12} t^5 + 3 \times 10^{-9} t^4 - 3 \times 10^{-6} t^3 + 0.0011 t^2 - 0.187 t + 19.614 \quad (7.2a)
\]

\[
R^2_{CO} = 0.9945 \quad (7.2b)
\]

\[
Y_{Syngas} = -1 \times 10^{-11} t^4 + 2 \times 10^{-8} t^3 - 9 \times 10^{-6} t^2 + 0.0036 t + 0.615 \quad (7.3a)
\]

\[
R^2_{Syngas} = 0.987 \quad (7.3b)
\]

\[
Z_{Syngas} = -3 \times 10^{-13} t^5 + 1 \times 10^{-9} t^4 - 1 \times 10^{-6} t^3 + 5 \times 10^{-3} t^2 - 0.0814 t + 13.18 \quad (7.4a)
\]

\[
R^2_{Syngas} = 0.9862 \quad (7.4b)
\]

Where,

\[ Y = \text{Bioethanol Yield in g/L either by CO or Syngas fermentation} \]

\[ Z = \text{Acetic Acid Yield in g/L either by CO or Syngas fermentation} \]
\[ t = \text{Time duration of continuous fermentation in bioreactor (48-1088 hours)} \]

\[ R = \text{R-squared value or coefficient of determination} \]

Suffix = Production from CO or Syngas e.g. \( Y_{CO} \) means Bioethanol from Carbon monoxide and so on.

R-squared value fairly indicates that the proposed model is valid or near to the experimental results. Figure 7.3a and 7.3b show that the bioethanol production increases with the increase in the gas flow rate up to the certain flow rate. The optimum gas flow and liquid flow/extraction rate for the production of bioethanol is found to be at 10-15mL/min and at 0.25-0.5 mL/min. However, the impact of liquid flow rate and the stirrer speed has lesser impact on the bioethanol production than the gas flow rate. Acetic acid formation is almost proportionate with the bioethanol formation. However, the production of acetic acid is higher with the higher gas flow rate during the CO fermentation and lower during the syngas fermentation. This may be due to more effective solventogenesis during syngas fermentation than the CO fermentation. The maximum bioethanol during CO fermentation is 1.33g/L at 10mL/min gas flow rate, 0.25mL/min liquid flow rate, and 300 rpm and during syngas fermentation is 3.75 at 15mL/min gas flow rate, 0.25mL/min liquid flow rate, and 300 rpm. The acetic acid formation reached up to 23.67g/L during 15mL/min gas flow rate, 0.75mL/min liquid flow rate, and 300 rpm during the CO fermentation whereas the acetic acid formation is 14.97mL/min during the syngas fermentation at 10mL/min gas flow rate, 0.25mL/min liquid flow rate, and 300 rpm.
Figure 7.3a: Bioethanol Yield during CO and Syngas Fermentation

Figure 7.3b: Acetic Acid Yield during CO and Syngas Fermentation

Figure 7.3 (a-b) Bioethanol and Acetic Acid Yield during CO and Syngas Fermentation
7.4.4 Product Formation and Gas Conversions

During the fermentation process, carbon monoxide is converted into ethanol, acetate and carbon dioxide through the Wood-Ljungdahl pathway using biocatalyst *Clostridium ljungdahlii* and is useful for the cell growth of the microorganism. Similarly, the concentration of carbon monoxide continuously decreases with the increase in the concentration of carbon dioxide. Such conversion of carbon dioxide may react with the hydrogen as an electron donor to yield ethanol and acetate.

\[
\begin{align*}
\text{i) } & \quad 6\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 4 \text{CO}_2 \\
\text{ii) } & \quad 4\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{CO}_2 \\
\text{iii) } & \quad 4\text{CO} + 6\text{H}_2 \rightarrow 2\text{CH}_3\text{CH}_2\text{OH} + 2\text{CO}_2 \\
\text{iv) } & \quad 2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \\
\text{v) } & \quad 2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}
\end{align*}
\]

The amount of hydrogen intake is increased only after the 72 hours of operation of the continuous fermentation process which confirms the utilization of homoacetate fermentation pathway to produce anaerobic oxidation of hydrogen and carbon dioxide by *Clostridium ljungdahlii* [18]. The cell activity is governed by the fermentation pH, concentration of enzymes, substrates, cofactors, effectors and inhibitors. Richter et al.(2016) claimed that ethanol production can be improved by using aldehyde:ferredoxin oxidoreductase (AOR) and alcohol dehydrogenase (ADH) route which consist of the requisite manufacturing of acetate and a further reduction of un-dissociated acetic acid to ethanol [29]. The plausible provision of more electrons into the culture in the presence of 5.07mM of cysteine-HCl at the medium having pH of 5.9 increases the ethanol production by 48% [30]. The ethanol production increases with the increase in the CO and H\textsubscript{2} consumption increases. However, the acetic acid production decreases with the increase in the ethanol production as shown in Figure 7.4a. The maximum CO consumption is a point where maximum ethanol production is reached. The production of the ethanol and acetic acid not only depends on the syngas conversions but also on the pH level, liquid flow, and gas flow. The variability seen may be due to the variation on the other above factors. Similarly, during the CO fermentation, the bioethanol production increases with the increase in the CO conversion and achieved the highest at 75% CO conversion point. However, the acetic acid production increases with the CO conversion which may be due to thin film formation at the top of the bioreactor or less activities of microorganism during CO fermentation process (Figure
7.4b). Ethanol production is very less in comparison with the production of acetic acid. The pressure buildup during the fermentation process due to increase in the gas supply rate which also retards the cell activities. Experiment shows that the utilization of hydrogen is less than the amount of CO during syngas fermentation. This is also matching thermodynamically because electron production from CO is more suitable than H$_2$ without dependency on gas partial pressure and pH value [Hu et al., 2011].

Younesi et al. (2005) claimed that a higher amount of hydrogen is used after depletion of carbon monoxide during syngas fermentation using *Clostridium ljungdahlii* [32]. However, such situation is never experienced due to continuous supply of syngas from the same tank. Due to higher concentration of cell at the beginning, the hydrogen consumption is more at the beginning but it declines slightly due to slight decrease in the concentration due to changes in the environment. However, the CO conversion increases slightly with the ethanol production during syngas fermentation. Cells consume CO as it starts to flow in the bioreactor and reduces the inhibition effect of CO on hydrogenase. The CO conversion decreases with the increase in the acetic acid production during the CO fermentation. This may be due to doubling the CO flow. The experiment is conducted on the loopback system. The consumption of CO and H$_2$ increases about 5-10% with the loopback system due to double interaction of the gas with cell-liquid of the bioreactor. The liquid flow rate has been changed on every 120 hours keeping same stirrer and gas flow. The effect of liquid flow is within 22% whereas the effect of gas is more than 43% on the ethanol production.
7.4.5 Product Yields and Comparisons

Once, the cell density reaches at maximum during the cell growth batch process for 48 hours, the products, mainly ethanol and acetic acid formation starts after supplying of CO or syngas in a bioreactor. Both of them are measured at different stirrer speed 300 rpm and 500 rpm to observe
the effect of liquid flow and gas flow. The gas flow rate has more impact on the ethanol and acetic acid production than the liquid flow rate (Figure 7.5a-7.6b). Ethanol production is increased by 29-41% when the liquid flow rate is increased by double or triple. Similarly, the ethanol production is increased by 85-151% when the gas flow is doubled. However, the ethanol production starts declining after the increase in the gas rate more than 100%. On the other hand, the acetic acid production increases from 18-22% by increasing the liquid flow rate whereas it is increased by up to 82% when the gas flow rate is increase by double or triple times. This may be due to the disturbance of excessive flow of gas or formation of acetic acid due to continuous supply of fresh media or formation of biofilm on the bioreactor. The acetic acid formation starts declining during the syngas fermentation whereas it continues to grow in the CO fermentation. During CO fermentation, the maximum ethanol production is 1.33g/L during batches 1-9 at 10mL/min gas flow, 0.5mL/min liquid flow at 300 rpm whereas 1.19g/L during batch 10-18 at 10mL/min gas flow, 0.25mL/min liquid flow at 500 rpm whereas during syngas fermentation, the maximum ethanol production is 3.75g/L during batches 1-9 CO fermentation at 15mL/min gas flow, 0.25mL/min liquid flow at 300 rpm whereas 3.05g/L during batch 10-18 at 10mL/min gas flow, 0.75mL/min liquid flow at 500 rpm. This reveals that the optimum flow rate for the syngas fermentation could be between 10-15mL/min and liquid flow at 0.5-0.75mL/min and the stirrer speed at 300rpm. The CO fermentation produces less ethanol and more acetic acid so is not recommended to produce ethanol. However, it could be good option for the acetic acid production.

Present result patterns are matching with other publications. Shen et al.(2014) reported that ethanol production increases with the increase in the certain gas flow rate but the production decreases with the further increase in the gas flow rate [16]. They also observed the reduction of bioethanol concentration with the increase in liquid flow rate due to the increase in the cell dilution. Hence, this study suggests 10-15mL/min could be optimum limit of gas flow rate for CO and syngas fermentation for such bioreactor. Obviously, the gas flow rate varies with the design parameters of the bioreactor. Bredwell et al.(1999) also claimed that the gas conversion is adversely affected by the high gas flow during fermentation process [33]. Ungerman and Heindel (2007); and Alsaker et al (2010) are also observed lower ethanol concentration by increase in the gas flow rate, stirrer speed due to increase in the stress on the biocatalyst [19, 34]. The ethanol
productivity of the fermentation is improved by lowering the cell dilution i.e. by lowering the liquid flow rate [7, 35]. However, the acetic acid production remains increasing even in increase in the media flow rate, gas flow rate during CO fermentation process after the optimum limit of the flow rates [16].

**Figure 7.5a** Comparative Study of Ethanol Yield-CO Vs. Syngas Fermentation (Batch:1-9)

**Figure 7.5b** Comparative Study of Ethanol Yield-CO Vs. Syngas Fermentation (Batch10-18)

**Figure 7.5 (a-b) Comparative Study of Ethanol Yield-CO Vs. Syngas Fermentation**
The results of the present investigation are compared with results of others are listed in the Table 2. Present results patterns are similar to the results of other publications. However, the acetic acid
formation in the present research is higher than other findings during the CO fermentation process. In almost all observation, the syngas fermentation shifts from acetogenic phase to solventogenic phase with decreasing pH level of the culture [9].

From this study (Table 7.2), the maximum concentrations of ethanol and acetic acid are observed as 1.33g/L and 23.67g/L during the CO fermentation whereas 3.75 g/L and 14.97g/L during the syngas fermentation respectively. The maximum ethanol and acetate production observed were 7.52g/L and 3.43g/L [32] during CO fermentation whereas the maximum ethanol and acetic acid production were 9.6g/L and 6.1g/L during syngas fermentation respectively in a continuous stirred tank reactor (CSTR) using Clostridium ljungdahlii as biocatalyst. Other research also reported the ethanol production as 2.2g/L by Richter et al (2013), 0.55g/L by Younessi et al. (2006), using C. ljungdahlii in a stirred tank reactor [32]. Devarapalli et al. (2015) reported 5.7g/L of ethanol using trikle bed reactor with same biocatalyst [8]. The highest production of ethanol reported till now is 23.93g/L by Shen et al (2014) during syngas fermentation using hollow fiber membrane reactor using same biocatalyst [16]. Aghbashlo et al (2016) also observed the maximum exergy efficiency of a continuous bioreactor at 8 exergetic productive index at media flow rate of 0.55mL/min [36].

Mass transfer efficiency, which depends on the reactor configuration, agitation speed, gas flow, and media flow rate; is another important technical parameter to improve the ethanol productivity [5, 7, 16]. Hollow fiber membrane is found as one of the effective option for improving gas-liquid mass transfer [7, 16]. The bubbling size and retention time of syngas in the fermentation media are also the factors to improve the gas-liquid mass transfer. These factors are dependent on the bioreactor design. Hence, the bioreactor design is another primary factor to improve the gas-liquid mass transfer. The position of the gas supply system in the bioreactor may also have an impact on gas retention time or the gas-liquid mass transfer. Another limiting factor of the ethanol production during syngas fermentation is the characteristics of biofilm [16]. Double gas supply throughout the fringe of the reactor enhances the gas retention time compared to the gas supply system installed at the center of the reactor. This may be due to greater velocity of the gas bubbles at the fringe than at the center. Prior to the rupturing of the bubble on the surface layer of the media on the bioreactor, the peripheral gas bubble has more initial horizontal velocity and voyages longer time and distances. Hence, gas loop-back system improves the gas-
liquid mass transfer by improving retention time due to improving the travel time of the bubbles than the single gas supply system. Sudiyo and Andersson (2007) also observed the lateral movement of bubbles towards center due to stirrer vortex resultant [37]. The cell retention and growth of the cell depends on the nutrition of the media, continuous flow of fresh media also helps on the growth of the cell density. Maintaining the cell density also improves the bioethanol production. The higher ethanol concentration observed than few of the other research may be due to increase on the gas-liquid mass transfer by improving retention time due to feedback gas flow system and continuous extraction system.

Table 7.2 Product Yield using Different Reactor for CO Fermentation and Syngas Fermentation

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Biocatalyst</th>
<th>Operation</th>
<th>Yield (g/L)</th>
<th>Ref</th>
<th>Reactor</th>
<th>Biocatalyst</th>
<th>Operation</th>
<th>Yield (g/L)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuos Stirred</td>
<td><em>Clostridium ljungdahlii</em></td>
<td>Yeast medium pH: 4.6</td>
<td>Eth:1.33 AA:23.67</td>
<td>This study</td>
<td>Continuos Stirred</td>
<td><em>Clostridium ljungdahlii</em></td>
<td>Yeast medium pH: 4.6</td>
<td>Eth:3.77 AA:14.97</td>
<td>This study</td>
</tr>
<tr>
<td>Tank</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tank</td>
<td><em>Two stage Clostridium ljungdahlii</em></td>
<td>Temp: 37</td>
<td>Eth:2.2 AA:1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cell density: 10g/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tank</td>
<td><em>Methylotrophicum</em></td>
<td>Temp: 37</td>
<td>Acetate: 5.95 g/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Eubacterium limosum</em></td>
<td>Temp: 37</td>
<td>Eth: 38mmol/L</td>
<td></td>
<td><em>Continuos Stirred</em></td>
<td><em>Clostridium</em></td>
<td>Yeast medium pH: 5.5</td>
<td>Eth:0.91 AA:0.91</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tank</td>
<td><em>Clostridium</em></td>
<td>Yeast medium pH: 5.5</td>
<td>Eth:0.55 AA:1.3</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
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</tr>
</tbody>
</table>
The concentration profile of ethanol and acetic acid throughout the experiment from batch B101-118 and B201-218 are presented in Figure 7.7a-b. The concentration of acetic acid increases almost linearly for the stirrer speed 300rpm and 500rpm during the CO fermentation whereas; the concentration of acetic acid is the maximum at batch #205 and 214. The ethanol production is slightly better in 300 rpm than in 500 rpm so ethanol production shall follow the 300rpm (Figure 7a-b). This may be due to disturbance of stirrer speed to the *Clostridium ljungdahlii* resulting less cell productivity. The ethanol production on both stirrer speed increases with the increase in the liquid flow rate and gas flow rate. The liquid flow rate has less impact on the ethanol and acetic acid production than the gas flow rate in both fermentation processes. Ethanol production starts declining after the batch#7 and #15 during syngas fermentation and after batch
#7 and #16 during CO fermentation. This may be due to declining of acetic acid in the syngas fermentation and due to increasing in the acetic acid formation in CO fermentation process. This reveals that acetogenesis is more pronounced in the CO fermentation whereas solventogenesis is more pronounced in the syngas fermentation.

Figure 7.7a Batches Comparison of Ethanol Yield-CO vs. Syngas Fermentation (Batch1-18)

Figure 7.7b Batches Comparison of Acetic Acid Yield-CO vs. Syngas Fermentation (Batch1-18)

Figure 7.7 (a-b) Batches Comparison of Acetic Acid Yield-CO vs. Syngas Fermentation
7.4.6 Mass Transfer Analysis

The mass transfer coefficient of CO and Syngas-CO has been plotted and compared (Figure 7.8). The mass transfer is always higher in the syngas-CO than CO alone. The mass transfer coefficient increases with the increase in the run time and reached maximum at B27 with 34.02(1/h) during the syngas fermentation while the B15 with 24.74(1/h) during the CO fermentation. The mass transfer coefficient starts declining during the later batches. This may be due to formation of more acetic acid in the CO fermentation than syngas fermentation. The mass transfer coefficient has increased up to 38% with syngas-CO, 30% with CO; with increase in the gas flow rates, and decreased up to 20% with syngas-CO, and up to 11% with 10% CO in tripling the liquid flow rate. The cell activities and the gas uptake also affect the coefficient. This may be due to increase in the volume $V_L$. The depleted nutrition level decreases the cell density which consequently has decreased the mass transfer coefficient.

Revised version of Klasson et al. (1992) for the atmospheric pressure has been proposed for determining the mass transfer coefficient ($k_L$) for a slightly soluble gaseous substrate in a [26].

\[
\frac{1}{V_L} \frac{dN_s^G}{dt} = \frac{k_L a}{H} (p_s^G - p_L^G)
\]

For our experiment, $p_s^L$ has no significant impact,

\[
\frac{1}{V_L} \frac{dN_s^G}{dt} = \frac{k_L a}{H} p_s^G
\]

Here, $p_s^G = 1 \text{ atm}$,

\[
\frac{1}{V_L} \frac{dN_s^G}{dt} = \frac{k_L a}{H}
\]  
(5)
The major limiting factor in the fermentation process is the potential bottleneck of the mass transfer of gas into liquid. This is more severe for the carbon monoxide, hydrogen and its mixture in comparison with the aerobic process because the solubility of CO and H₂ on mass basis with respect to oxygen is only 60% and 4% respectively [20]. Mass transfer limitation may arises due to gas-liquid interface, transport of gas to media, diffusion of gas into the liquid layer, and diffusion of the gaseous substrate to the intracellular reaction site [45]. Improvement in impeller designs, liquid flow patterns, mixing residence time, baffle design, aerated power efficiency, and application of bubble dispersers are few parameters to enhance the mass transfer capability [5].

To enhance the mass transfer, the presence of gas has been increased by the gas loop-back system and the cell density remains almost at the highest peak due to continuous supply of the nutrition with replacement of fresh media. The gas-liquid mass transfer can be improved by using proper size of the gas bubble diameter because it enhances the specific surface area.
available for the mass transfer. Present gas orifice system generates small bubble size and travelling up slowly in a circular fashion which increases the gas residence time in the bioreactor and improves the gas-liquid mass transfer then improves the mass transfer coefficient. Orgill et al.(2013) noted the decrease in the gas-liquid mass transfer coefficient of CO and H₂ with the increase in the liquid recirculation rate or the liquid holdup volume \(V_L\) [17]. Similar observation is found at higher liquid flow rate batches.

7.5 Conclusions
Continuous bioethanol in addition to the acetic acid production from the CO fermentation and syngas fermentation using a biocatalyst-\textit{Clostridium ljungdahlii} in a continuous stirred tank bioreactor is proved successfully and compared the bioethanol production using two different gases fermentation using innovative gas loop-back system. In both fermentation processes, bioethanol production is closely monitored by varying pH level, broth media flow rates, gas flow rates, and stirrer speed. The pH level impacts on the bioethanol production, gas consumptions, and cell growth environment. The maximum bioethanol production is 1.33g/L during CO fermentation at 10mL/min gas flow, 300 rpm, 0.5mL/min liquid flow and 3.75g/L during syngas fermentation at 15mL/min gas flow, 300 rpm, 0.25mL/min liquid flow. Similarly, the maximum acetic acid production is 23.67g/L during CO fermentation at 15mL/min gas flow, 500 rpm, 0.75mL/min liquid flow and 14.97g/L during syngas fermentation at 10mL/min gas flow, 300 rpm, 0.25mL/min liquid flow. The higher amount of acetic acid is due to the continuous process where, the fresh broth media (addition of nutrients) is supplied continuously in the bioreactor. The addition of nutrition favours the growth of microorganism. The maximum gas consumption observed is 75% during CO fermentation and 79% during syngas (65% CO, 30% H₂, & 5% CO₂) fermentation. The syngas fermentation process is better than the CO fermentation for the bioethanol production. However, further research is recommended for the conversion of acetic acid into the bioethanol either by replacing gas supply system or by improving engineering design parameters of the bioreactor to improve the mass transfer coefficient.

7.6 References


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Chapter 8 Overall Conclusions and Future Works

Abstract

This last chapter concisely summarises the major outcomes of this study. In addition, few ideas are recommended for future research on thermochemical (dry and wet torrefaction, gasification) and biochemical (syngas fermentation) conversion processes to follow this work.

8.1 Overall Conclusions

Greenhouse gas emission due to use of fossil fuels is one of the major challenges for the environment and human health. Exploration of an alternative green fuel such as bioenergy is essential due to depletion of the fossil fuel at a dramatic rate. Bioenergy or biofuel produced from bio-sources like corn and sugar cane are expensive and they are also candidates for human consumption. Biofuels, produced from the lignocellulosic biomass, are good options for the replacement of fossil fuels in the future. Any type of lignocellulosic biomass can be used to produce synthesis gas. One of a gaseous class of biofuel is the direct utilization of the synthesis gas produced from the gasification of biomass. Direct use of synthesis gas as transportation fuel is not ideal. Hence, conversion of synthesis gas into the liquid, more condensed energy form makes it easy for storing and transportation. Fermentation of synthesis gas obtained from biomass has been recognised as a reliable and proven technology to yield bioethanol or biodiesel. Reactor design, proper selection of biocatalysts, synthesis gas cleaning, and biofuel filtration are continuous areas of research to enhance the overall production of the biofuel from the fermentation process.

Torrefied biomass shows better solid fuel performance than raw biomass in terms of moisture content, energy content, density, hydrophobicity, ignitibility etc. The torrefied biomass performs fuel characteristics similar to coal. However, biomass has many limitations like high volatiles content and lower energy values. The torrefaction temperature has more impact on the torrefaction process than the residence time. The higher torrefaction temperature results in the higher hydrophobicity. The gaseous product yields are mainly carbon dioxide and water. Torrefied energy crops and agricultural residues are a good candidate to be used in thermal or
electrical power plants. The longer durability of the torrefied material also increases the probability for palletization and exporting to local and global markets for the domestic use for longer time. The raw biomass shows more reactivity than the torrefied biomass during kinetic study, which shows torrefied biomass is more stable in a boiler. The kinetic rate of the thermochemical reaction for torrefied miscanthus is lower than that of torrefied wheat straw. Heating value is increased by 25% after torrefaction.

Gasification is a thermochemical conversion method that transforms carbonaceous constituents into synthesis gas (syngas: CO, H₂, CO₂) at high temperatures, generally at more than 700 °C, in a controlled amount of oxygen or carbon dioxide or steam environment so that there will be no combustion. Syngas is a good fuel for producing ethanol or diesel. Gasification in a CO₂ environment is an interest of this research. The fuel characteristics of hydrothermally torrefied miscanthus show better performance than the dry torrefied miscanthus. SEM shows more porosity in the dry torrefied miscanthus than wet torrefied miscanthus and bitumen coal, which shows dry torrefied miscanthus are more reactive than the wet torrefied miscanthus. Optimum mass loss rate is linearly proportional to the portion of torrefied biomass in the blend. The optimum CO₂ flow rate is found to be 50ml/min; the optimum heating rate could be 10°C/min; the optimum condition to run N₂ is up to 800°C followed by CO₂ up to the final temperature 1300°C. The FTIR showed the presence of carbon monoxide, hydrogen, and H₂O including a minor portion of CH₄.

This study analyzed and demonstrated the successful and efficient way of producing biofuel using hybrid model: thermochemical and biochemical. In the thermochemical conversion process, the optimum cogasification environment has been proposed. This optimum environment condition is used to find out the best cogasification ratio of hydrothermally processed miscanthus, dry torrefied miscanthus and bitumen coal. The reactivity increases with the increase in the addition of torrefied biomass in the blends. The blends of 60% of coal, 20% of hydrothermally treated biomass and 20% of dry torrefied biomass have been identified as being the optimum ratio for the production of synthesis gas.

Further, biochemical conversion process analyses production of bioethanol from syngas fermentation using Clostridium ljungdahlii in a laboratory scale continuous stirred tank bioreactor (CSTBR) having an innovative gas supply and effluent extraction structures. Ethanol
production is observed by supplying two different gas compositions which includes 100% CO and simulated syngas blend, mimicking the composition of syngas extracted from lignocellulosic biomass having 60% CO, 35% H₂, and 5% CO₂. CO and Syngas are fermented with different gas (5-15mL/min), media and effluent flow rates (0.25-0.75mL/min), and stirrer speed (300-500 rpm) at atmospheric pressure and 37°C temperature. The gas flow rate, media and effluent flow rate, pH level, and stirrer speed are also controlled. The exhaust gas is reused for the improvement of residence time and thus the improvement on the gas-liquid mass transfer. The maximum optical cell density reached up to 2.4g/L. More bioethanol production was observed during syngas fermentation than Carbon monoxide fermentation. CO fermentation produces 0.17-1.33g/L-effluent ethanol and 8.92-23.67g/L-effluent acetic acid whereas syngas fermentation produces 0.85-3.75g/L-effluent ethanol and 8.89-14.97g/L-effluent acetic acid.

8.2 Future Works
In addition to the above work in the thermochemical and biochemical conversion processes, there are still many facets of the current work for the further investigation that were beyond the scope of this research. Hence, following works have been recommended as future works.

- Development of a continuous flow HTC reactor for optimization of process conditions
- Replacement of membrane by micro or nano membrane to improve the gas-liquid mass transfer.
- Impact on ethanol production using Clostridium ljungdahlii in the limited oxygen exposure
- Comparative study of ethanol production by different biocatalysts and identifying the best biocatalyst for the particular environment.
- Study on the cell concentration by varying the different broth medium to identify the cheaper and easily available agents for the media preparation
- A pilot scale bioreactor needs to be developed prior to the commercialization of lignocellulosic syngas-fermentation
- Improvement on the lignocellulosic syngas cleaning techniques.
8.3 Scientific Contributions

This research performed was an explorative investigation in identifying the optimum range of blending ratio of wet torrefied, dry torrefied, and coal as a fuel and proposed its kinetics. The blends with a composition of 60% of bituminous coal, 20% of dry torrefied, and 20% of wet torrefied, which has been observed as the most synergistic blends and extracted with the following kinetics models:

- For Torrefaction

k_{Miscanthus} = 8800e^{-\frac{59.95}{RT}}

k_{Wheat straw} = 12000e^{-\frac{51.72}{RT}}

- For cogasification:

\[ X_1 = 1 - \exp\left(-\frac{RT^2}{198.33 \alpha} 9.4 \times 10^6 e^{-\frac{198.33}{RT}}\right) \]

\[ X_2 = 1 - \left[1 - \frac{RT^2}{594.99 \alpha} 9.4 \times 10^6 e^{-\frac{198.33}{RT}}\right]^3 \]

The research has also explored an innovative gas loop back supply system to enhance the mass transfer during syngas fermentation into ethanol. The improvement on the ethanol production has been observed to be up to 5% during CO fermentation and up to 15% during syngas fermentation. Based on the ethanol and acetic acid production following models have been developed:

\[ Y_{CO} = 8 \times 10^{-12} t^4 - 2 \times 10^{-8} t^3 + 2 \times 10^{-5} t^2 - 0.0044 t + 0.73 \]

\[ R^2_{CO} = 0.924 \]

\[ Z_{CO} = 5 \times 10^{-16} t^6 - 2 \times 10^{-12} t^5 + 3 \times 10^{-9} t^4 - 3 \times 10^{-6} t^3 + 0.0011 t^2 - 0.187 t + 19.614 \]

\[ R^2_{CO} = 0.9945 \]

\[ Y_{Syngas} = -1 \times 10^{-11} t^4 + 2 \times 10^{-8} t^3 - 9 \times 10^{-6} t^2 + 0.0036 t + 0.615 \]

\[ R^2_{Syngas} = 0.987 \]
\[ Z_{\text{Syngas}} = -3 \times 10^{-13} t^5 + 1 \times 10^{-9} t^4 - 1 \times 10^{-6} t^3 + 5 \times 10^{-3} t^2 - 0.0814 t + 13.18 \]

\[ R^2_{\text{Syngas}} = 0.9862 \]

Where,

\( Y = \) Bioethanol Yield in g/L either by CO or Syngas fermentation

\( Z = \) Acetic Acid Yield in g/L either by CO or Syngas fermentation

\( t = \) Time duration of continuous fermentation in bioreactor (48-1088 hours)

\( R = \) R-squared value or coefficient of determination

Suffix = Production from CO or Syngas e.g. \( Y_{\text{CO}} \) means Bioethanol from Carbon monoxide and so on.

A model for the atmospheric pressure has also been proposed for determining the mass transfer coefficient (\( k_L \)) based on Klasson et al. (1992):

\[
\frac{1}{V_L} \frac{dN_s^G}{dt} = \frac{k_L a}{H} (P_s^G - P_s^L)
\]

For our experiment, \( P_s^L \) has no significant impact,

\[
\frac{1}{V_L} \frac{dN_s^G}{dt} = \frac{k_L a}{H} P_s^G
\]

Here, \( P_s^G = 1 \) atm,

\[
\frac{1}{V_L} \frac{dN_s^G}{dt} = \frac{k_L a}{H}
\]
## Chapter 9  
### Appendix -A: List of Materials and Photographs

### 9.1 List of Materials for Reactor

List of materials used for fabrication of continuous stirred tank bioreactor are presented on Table 9.1.

Table 9.1 List of Materials to build Bioreactor

<table>
<thead>
<tr>
<th>Items</th>
<th>Quantity</th>
<th>Type</th>
<th>Model</th>
<th>Cost, CAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Body or frame of bioreactor</td>
<td>1</td>
<td>Plexiglass (R)</td>
<td>VH-100 Acrylic Resin</td>
<td>110.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PVC-9002-86-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swagelok</td>
<td>14</td>
<td>Stainless Steel</td>
<td>316Z77</td>
<td>28.00</td>
</tr>
<tr>
<td>Swagelok</td>
<td>2</td>
<td>Plastic</td>
<td>-</td>
<td>5.00</td>
</tr>
<tr>
<td>pH meter</td>
<td>1</td>
<td>Omega Std.</td>
<td>MV-RS232</td>
<td>148.50</td>
</tr>
<tr>
<td>pH probe</td>
<td>1</td>
<td>Omega Std.</td>
<td>HHWT-SD1-ATC</td>
<td>63.00</td>
</tr>
<tr>
<td>Thermometer</td>
<td>1</td>
<td>Omega Std.</td>
<td>PHE-1411</td>
<td>40.50</td>
</tr>
<tr>
<td>Pressure gauge</td>
<td>1</td>
<td>Digital</td>
<td>-</td>
<td>51.00</td>
</tr>
<tr>
<td>Aeration tube with support</td>
<td>1</td>
<td>Rubber/ Steel</td>
<td>-</td>
<td>20.00</td>
</tr>
<tr>
<td>Micro Pump</td>
<td>1</td>
<td>Gilson std.</td>
<td>GF-F155001</td>
<td>1295.00</td>
</tr>
<tr>
<td>Pump head</td>
<td>1</td>
<td>Gilson std.</td>
<td>GF-F117800</td>
<td>550.80</td>
</tr>
<tr>
<td>Peristatic Tube</td>
<td>10</td>
<td>Gilson std</td>
<td>GF-F1825121</td>
<td>92.65</td>
</tr>
<tr>
<td>(Polypropylene)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Connection Tube (25’)</td>
<td>1</td>
<td>Cole-Parmer (PVC)</td>
<td>06422-05</td>
<td>35.00</td>
</tr>
<tr>
<td>Connector</td>
<td>10</td>
<td>Mandel</td>
<td>F1179931</td>
<td>-</td>
</tr>
<tr>
<td>------------------------</td>
<td>----</td>
<td>--------------</td>
<td>----------</td>
<td>---</td>
</tr>
<tr>
<td>Membrane Separator</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Membrane support</td>
<td>1</td>
<td>Steel</td>
<td>-</td>
<td>40.00</td>
</tr>
<tr>
<td>2L bottle jars for media and effluent</td>
<td>2</td>
<td>Glass</td>
<td>-</td>
<td>90.00</td>
</tr>
<tr>
<td>Reactor Lead Opener</td>
<td>2</td>
<td>Steel</td>
<td>-</td>
<td>5.00</td>
</tr>
<tr>
<td>Teflon ferrule</td>
<td>10</td>
<td>Teflon</td>
<td>-</td>
<td>10.00</td>
</tr>
</tbody>
</table>

### 9.2 List of Materials for anaerobic Gas Chamber

The list of materials used during the fabrication of anaerobic gas chamber is listed on Table 9.2.

#### Table 9.2 List of materials for anaerobic Gas Chamber

<table>
<thead>
<tr>
<th>Items</th>
<th>Quantity</th>
<th>Type</th>
<th>Model</th>
<th>Cost, CAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Body of Chamber</td>
<td>1</td>
<td>PVC, Bayer Material,</td>
<td>58092421</td>
<td>400.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Science LLC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valve</td>
<td>2</td>
<td>PVC</td>
<td>-</td>
<td>100.00</td>
</tr>
<tr>
<td>Glove (pair)</td>
<td>1</td>
<td>Rubber</td>
<td>-</td>
<td>90.00</td>
</tr>
<tr>
<td>Pipe Fixtures</td>
<td>2</td>
<td>PVC- National Pipe &amp;</td>
<td>9002-86-2</td>
<td>35.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plastic Inc. USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hinge</td>
<td>5</td>
<td>Steel</td>
<td>-</td>
<td>35.00</td>
</tr>
</tbody>
</table>
9.3 Photographs

Photograph 9.1 Incubators and Anaerobic Chamber

Photograph 9.2 Continuous Stirred Tank Bioreactor (CSTBR)