**Anaerobic biodegradation of urea formaldehyde adhesive resins from particleboard.**

By

Damin Lee

A Thesis Submitted to Saint Mary's University, Halifax, Nova Scotia
in Partial Fulfillment of the Requirements for
the Degree Bachelor of Science with Honours in Biology

February 2016, Halifax, Nova Scotia



Reviewed by:

Dr. Zhongmin Dong (Supervisor) _____

Dr. Doug Strongman (Reader) _____

## Abstract

**Anaerobic biodegradation of urea formaldehyde adhesive resins from particleboard.**

By Damin Lee

Particleboard is known to cause broader environmental issues when large amounts are sent to the landfills. The toxic adhesive resin urea formaldehyde, used to bind the wood fibers, causes contamination of groundwater in the landfill. In this experiment, laboratory size anaerobic digestion systems were designed to degrade the resin's toxicity. The anaerobic digestion reactors were made with diluted cow manure. To test biodegradation of urea formaldehyde under anaerobic conditions, filter paper with urea formaldehyde (UF), saw dust with UF, different states of particle board, and medium-density fiberboard (MDF) were mixed with digestion reactors at 37˚C to examine the effects of the digestion over 80 days. The addition of urea formaldehyde increased biogas production. The large chunks of particleboard produced less amount of gas than the saw dust of fiberboard while the saw dust and garburated pieces had no significant differences in the amount of gas produced by anaerobic reaction. However, MDF produced more gas than garburated fiberboard. These results suggest that the biodegradation of particleboard requires finer particles for anaerobic microorganism to have better access. According to the test on formaldehyde biodegradation, gas production and fungal growth were delayed depending on the increase of formaldehyde concentration. Lastly, GC was operated to test whether the formaldehyde could be degraded under anaerobic conditions. A significant amount of $CO_2$ and $CH_4$ was observed from each trial, and percentages of mole of $CO_2$ and $CH_4$ were increased and decreased.

February 2016

## Table of Contents

**Title Page** ..... **i**

**Abstract** ..... **ii**

**Table of Contents** ..... **iii**

**List of Table and Figures** ..... **v**

**Introduction** ..... **1**

1.1 Global population growth creates environmental problems ..... 1
1.2 Landfills ..... 2
1.3 Particle board and medium density fiberboard ..... 3
1.4 Glue (urea formaldehyde) ..... 4
1.5 Anaerobic digestion ..... 5
1.6 Formaldehyde biodegradation ..... 8
1.7 Research objectives ..... 9

**Materials and Methods** ..... **14**

2.1 Cow manure inoculums preparation ..... 14
2.2 Digester system design ..... 14
2.3 Feed stocks and digesters contents ..... 17
2.4 Formaldehyde concentration experiment ..... 18
2.5 Data collection ..... 18
2.6 Gas chromatography ..... 18

**Results** ..... **27**

3.1 Anaerobic biodegradation of whitman #1 filter paper with urea formaldehyde glue ..... 27
3.2 anaerobic biodegradation on a saw dust ..... 28
3.3a Anaerobic biodegradation on a particle board ..... 28
3.3b Anaerobic digestion in medium density fiberboard and particle board ..... 29
3.4 Anaerobic biodegradation of formaldehyde ..... 30
3.5a A formaldehyde concentration effect on anaerobic biodegradation activity ..... 31
3.5c Growth of fungal community in different concentration of formaldehyde ..... 31
3.6 Gas chromatography ..... 32

**Discussion** ..... **43**

4.1 Biodegradation of urea formaldehyde under anaerobic condition ..... 43
4.2 Affect of particle sizes ..... 44

4.3.1 FORMALDEHYDE BIODEGRADATION ..... 44
4.3.2 FORMALDEHYDE CONCENTRATION ..... 45
4.3.3 FUNGAL GROWTH IN FLASK ..... 45
4.4 GAS CHROMATOGRAPHY ..... 46

**References ..... 47**

## List of Table and Figures

FIGURE 1.1 PATHWAYS FROM UREA FORMALDEHYDE TO $CH_4$ AND $CO_2$ UNDER ANAEROBIC PROCESS ..... 11
FIGURE 1.2 CHEMICAL COMPOSITION, METHANE YIELDS, AND DECAY RATES FOR DIFFERENT TYPES OF WOOD ..... 12
FIGURE 1.3 SCHEMATIC DIAGRAM OF THE LABORATORY SCALE UASS REACTOR FOR ANAEROBIC DIGESTION ..... 13
FIGURE 2.1 SCHEMATIC DIAGRAM OF THE LABORATORY SCALE ANAEROBIC DIGESTION SYSTEM REACTOR ..... 20
FIGURE 2.2 SCHEMATIC DIAGRAM OF THE LABORATORY SCALE ANAEROBIC DIGESTION SYSTEM REACTOR ..... 21
FIGURE 2.3 MEASURING SYSTEMS ..... 22
FIGURE 2.4 DIGESTER JARS ..... 23
FIGURE 2.5 DIGESTER FLASKS ..... 24
TABLE 2.1 FEED STOCK MATERIALS AND DIGESTER CONTENTS ..... 25
TABLE 2.2 FORMALDEHYDE INHIBITION AFFECTS ON ANAEROBIC DIGESTION ..... 26
FIGURE 3.1 ANAEROBIC BIODEGRADATION OF WHITMAN #1 FILTER PAPER WITH UREA FORMALDEHYDE GLUE ..... 33
FIGURE 3.2 ANAEROBIC BIODEGRADATION ON A SAW DUST ..... 34
FIGURE 3.3A ANAEROBIC BIODEGRADATION ON A PARTICLE BOARD ..... 35
FIGURE 3.3B ANAEROBIC BIODEGRADATION IN MEDIUM DENSITY FIBERBOARD AND PARTICLE BOARD ..... 36
FIGURE 3.4A ACCUMULATIVE DATA OF ANAEROBIC DIGESTION OF FORMALDEHYDE AND MEDIUM DENSITY FIBERBOARD ..... 37
FIGURE 3.4B RATE OF ANAEROBIC DIGESTION FORMALDEHYDE AND MEDIUM DENSITY FIBERBOARD ..... 38
FIGURE 3.5A ACCUMULATIVE DATA OF ANAEROBIC DIGESTION OF FORMALDEHYDE ..... 39
FIGURE 3.5B RATE OF ANAEROBIC DIGESTION WAS AFFECTED BY DIFFERENT CONCENTRATION OF FORMALDEHYDE ..... 40
TABLE 3.5C PRESENCE OF FUNGI ACCORDING TO TIME AND CONCENTRATION OF FORMALDEHYDE ..... 41
FIGURE 3.6 PERCENTAGE OF GAS COMPOSITION CHANGE IN CH4 AND CO2 FROM MDF SAMPLE ..... 42

# Introduction

## 3.5 Global population growth creates environmental problems

According to the 2012 revised World population prospects, the world population was 7.2 billion in mid 2013, and it will increase up to 9.7 billion by 2050 (United Nation, 2015). There has been concern about the cost of population growth on the environment and on social and economical development. A rapidly increasing world population and demand for more complicated technology leads to biodiversity loss, climate change, and many other negative influences on the world's environment. Population growth increases total municipal solid waste (MSW) production, commonly known as garbage that is generated by businesses and households. MSW includes five categories: biodegradable waste, recyclable waste, inert waste, composite waste, and domestic hazardous waste (Municipal Solid Waste and greenhouse gases, 2013). Each year, at least 1.3 billion tonnes of waste are produced worldwide (Worldwatch, 2012). Statistics Canada recorded that MSW disposal increased from 769 kilograms in 2002 to 777 kilograms per capita in 2008 (Statistics Canada, 2012). Consequently, there is a greater demand on waste management industries. MSW can be managed in different ways, such as disposal in landfills or by incineration, through diversion into recycling or composting. Since solid waste disposal in landfills is the most economic way of disposal, landfills will continuously be used for disposal of solid wastes (Daskalopoulos et al., 1997).

## 1.2 Landfills

Landfills have been the most common disposal practice for disposing of MSW in Canada. Also, it is the most economical way (El-Fadel et al., 1997). However, MSW in landfills impact the environment in many ways: producing leachate and toxic gas which pollute soil, water, and air. When rain passes through the landfills, it combines with toxic chemical, and components that come from waste. This leachate can contaminate soil, surface and groundwater (Mor et al., 2006). Through the anaerobic degradation process of organic materials from MSW, landfill gas is emitted into the atmosphere, primarily consisting of methane and carbon dioxide. This can contribute to global warming as they are both greenhouse gases (IPCC, 2002). Canadian landfills make up 20% of national methane emission with methane being 25 times more potent than carbon dioxide in regards to global warming (Rodhe, 1990). Nevertheless, landfill gas can be captured from industry and can be used to generate electricity or as fuel. In 2009, 349 kilotonnes of methane were captured and combusted from landfills, with half of it being used in energy applications (Municipal Solid Waste and greenhouse gases, 2013).

Every year, at least 500,000 tons of wood products are buried in landfills (Statistics Canada, 2012). The wood component is an important source of anaerobic degradation. Engineered wood such as plywood, oriented strand board, particleboard, and medium density fiberboard release not only carbon dioxide and methane gas, but also toxic chemicals, such as phenol formaldehyde or urea formaldehyde into the ground when they are hydrolyzed.

### 1.3 Particle board and Medium density fiberboard

Particleboard (PB) and medium density fiberboard (MDF) have been widely used throughout the world for furniture manufacture and house construction (Sellers et al., 2000). They are both engineered wood product that are composed of wood chips or wood fibers bonded with urea-formaldehyde resin. PB and MDF are made through compressing hard and soft wood particles with urea formaldehyde resin under high pressure and high temperature (Wang et al., 2011). Standard PB and MDF are not suitable for exterior use, or in interior areas where humid or wetting conditions due to its physical properties (Sellers et al., 2000).

Like all other wood products, PB and MDF contain cellulose, and hemicellulose, which can be broken down into methane and carbon dioxide through anaerobic process (Perez et al., 2002). Wang's study (2011) showed that cellulose and hemicellulose content in PB (37.3%, 16.3%) and MDF (34.8, 15.2%) are slightly lower than that found in hardwood and soft wood.

The 4.5% of the nitrogen from the MDF could produce ammonia ($NH_3$) under water, which is 0.69g of ammonia per kilogram; this concentration of ammonia was found to be the highest ammonia among all the wood products for 28 days (hard wood, soft wood, ply wood, PB, MDF) by Wang (2011). PB is found to release less ammonia content (0.17g of ammonia per kilogram of PB) compared to MDF (Wang et al., 2011). The basic ammonia (pH=~8.5) can increase pH and result in alkaline soil (Wang et al., 2011).

### 1.4 Glue (Urea Formaldehyde)

Every year, one million metric tons of urea formaldehyde resin are produced, and over 70% of this resin is used by the wood product industry for a variety of purposes (Dunky, 1998). Approximately 61% of urea formaldehyde is used as an adhesive for bonding particleboard, 27% is used for producing medium density fiberboard, 5% for hardwood plywood, and 7% for laminating adhesive for bonding (Halvarsson et al., 2008).

Urea formaldehyde is the most well known example of thermosetting resins that are usually referred to as amino resins (Garrido et al., 2000). This resin is used as a major adhesive in forest products industry due to a number of advantages such as, low cost, low cure temperatures, excellent thermal properties, ease of use under a variety of conditions, and resistance to microorganisms. However, urea formaldehyde has a lack of resistance to moist conditions, especially at higher temperatures. It weakens and swells when it comes into contact with water, breaking down into urea and formaldehyde through hydrolysis under warm, humid, and slightly acidic conditions (Dinwoodie, 1978). For that reason, manufacturers use urea formaldehyde resins for interior products only.

Whether urea is mineralized into ammonia and ammonium, which are two of the most toxic components of landfill leachate, depends on pH (Padgett et al., 2009). Formaldehyde, by itself, is very toxic and known as a human carcinogen (Rokiah et al., 2009). Also, it acts as a disinfectant in wastewater, found to be toxic for the anaerobic digestion process by inhibiting and killing microorganisms (Person et al., 1980). Because of the toxicity of ammonium and formaldehyde, degradation of these chemicals is very significant. Formaldehyde can be degraded further into methanol and formate through

acidogenesis. Moreover, methanol and formate can change into methane and carbon dioxide through methanogenesis (Chem et al., 2008) (Figure1.1). Urea and formaldehyde can be degraded by both anaerobic and aerobic digestions.

## 1.5 Anaerobic digestion

Discovering new sustainable and renewable energy resources has become one of the priorities of modern day societies. The United Nations has predicted that most of the world's energy in 2050 will come from renewable sources (Edenhofer et al., 2011). The term lignocellulosic biomass is used to describe the main components of plants which are lignin, cellulose and hemicellulose. Lignocellulosic biomass is suspected to be the only source of renewable energy with a carbon structure but because of its low bulk density and low energy content it is not considered to be a highly effective source of renewable energy as opposed to energy generated from using water or solar radiation from the sun.

An effective method for generating bioenergy from organic waste is anaerobic digestion (AD). Anaerobic digestion is a process that is carried out by microorganisms under conditions without oxygen. The process is divided mainly into four primary degradation steps where polysaccharides such as starch, hemicellulose, proteins and fats are hydrolyzed and broken down into monomers. This process is followed by the conversion of these monomers into carbon fatty acids and alcohols by acetogenesis. The products of acetogenesis are then converted into acetate and formate. The acetogenesis process is usually followed by methanogenesis where methanogenic microorganisms produce biomethane from acetogenesis products. Anaerobic digestion

requires two different sets of conditions to complete the process: acidogenesis with acidogenic bacteria and methanogenesis with methanogenic archaea. Acidogenesis requires the temperature of 25 to 35˚C, pH of 5.2 to 6.3, and a carbon to nitrogen ratio between 10 to 45. Methanogenesis requires a higher temperature, between 30 to 40˚C, a higher pH of 6.7 to 7.5, and a carbon to nitrogen ratio of 20 to 30 (Chen et al., 2008).

Although both anaerobic and aerobic processes are able to degrade organic compounds like formaldehyde, aerobic digestion requires high amounts of energy while anaerobic digestion can degrade high concentration of organic compounds with low energy consumption. Also, the high energy required for aerobic digestion can inhibit the degradation due to high organic and toxicant concentration (Zijin et al., 1997).

The anaerobic digestion of solid biomass is time consuming and requires lots of energy, however an up-flow of anaerobic solid state reactor (UASS) possesses the energy potential needed to conquer the short comings. The significant advantage of this type of reactor is the spontaneous solid liquid separation, and also the liquid circulation that can eliminate the need for the constant stirring and distribute microorganisms and metabolites evenly throughout the reactor. Liquid circulation plays a role in saving energy and increasing the total economics of AD specifically that of lignocellulosic biomass (Mumme et al., 2010).

Levels of biogas produced from AD varies with the type of microorganisms available, the temperature of the reaction and the reaction time. However the amount of biogas produced is still large regardless of the conditions. In addition to biogas, digestates are generated as a by-product of the reaction where water represents about

90% of the resulting digestates. Water generated from anaerobic digestion is usually moved into the reactor's fermentation-residue storage compartment where the remaining methane is collected. Following collection, all the products are dried and then distributed over large areas of croplands to enhance the quality of the soil and improve its ability to absorb water. Because produced digestates are usually rich in inorganic material, they cannot be used directly as fuel (Mumme et al., 2011).

Wet biomasses containing almost 80-90% water are treated with a process called hydrothermal carbonization (HTC) which is a thermochemical treatment that requires heating the masses up to 200-260 $^{o}$C (Funke et al., 2010; Yan et al., 2010). Under these conditions water becomes highly reactive and simultaneously behaves as a mild acid and a mild base (Bandura et al., 2006).

Hydrothermal carbonation treatment involves excessive hydration and decarboxylation which eventually leads to the formation of solid biochar. Approximately 40-80% of the resulting products are carboxylic acids, furan derivatives, phenolic substances, and sugar monomers found in liquid while carbon dioxide yield represents about 5-10% of resulting products (Reza et al., 2013).

Biochar produced by HTC is usually stable and hydrophobic (Reza et al., 2012; Acharjee et al., 2011) which gives it the ability to increase rapidly in comparison to raw digestates and raw biomass. In addition to being friable and hydrophobic, biochar can potentially serve as fuel with properties similar to that of lignite coal (Hoekman et al., 2011).

Since hemicellulose and cellulose contribute to biogas production in anaerobic digestion and cellulose and lignin contribute to the production of solid biochar during HTC process, combining these two processes would lead to elevated bioenergy levels produced. It is important to note that efficiency and productivity of anaerobic digestion relies heavily on sugar concentration in the used feedstocks. Sugars synthesized during hydrolysis are broken down in HTC under subcritical water conditions which make applying hydrothermal carbonization following anaerobic digestion more favorable energetically.

### 1.6 Formaldehyde biodegradation

Formaldehyde is one of the primarily products from hydrolization of urea formaldehyde. PB with a density range of 660 to 680 kg/m$^3$ contains 1.0 to 1.5 mg/L of formaldehyde, whereas MDF with a density range of about 650 to 700 kg/m$^3$ contains 0.7 to 1.0 mg/L of formaldehyde (Wang et al., 2011).

Formaldehyde is a commonly used compound in a variety of processes in the chemical industry (Gerberich et al., 1980). It is colorless, but has a very strong odor, which can generally be detected at concentrations above 1 ppm. It is frequently found in wastewaters and waste gases (Zijin et al., 1997). Formaldehyde is a very toxic chemical that is used as a preservative and disinfectant because it inhibits microbial activities (Sharma et al., 1994). Due to the interaction of formaldehyde with DNA, RNA, and other cell components, cells die upon the introduction of formaldehyde into the cell (Grafstorm et al., 1985; Bruckner, 1986). Formaldehyde inhibits most anaerobic bacteria at concentrations higher than 6.67 mM (200 ppm). At low formaldehyde

concentration (between 1.67 mM to 3.33 mM), formaldehyde is completely converted into methanol and methane. However, at high concentrations (between 5.00 mM to 6.67 mM), methane is not produced (Zijin et al., 1997). Formaldehyde only takes 4 to 5 days to be degraded by the anaerobic process (Zijin et al., 1997). According to Zijin's study, gasification rate is decreased when formaldehyde concentration increased.

### 1.7 Research Objectives

The purpose of this study is to examine the biodegradation of urea formaldehyde by anaerobic digestion. The urea formaldehyde that bonds particleboard and MDF is easily hydrolyzed into its constituent components, urea and formaldehyde, in warm, humid, and acidic conditions. Once the particleboard and MDF are subjected to anaerobic conditions in a digester, the urea can either be mineralized into ammonia or ammonium depending on the pH, or can be used as a nitrogen source. Another constituent component, formaldehyde, will be broken down into methanol and formate through acidogenesis, and further, both can be changed into methane and carbon dioxide through methanogenesis. A series of objectives were placed to help guide the research:

1. To test the biodegradation of urea formaldehyde under anaerobic conditions with cow manure inoculation.
    A. To test the anaerobic biodegradation of urea formaldehyde when mixed with saw dust and filter papers.
    B. To test the anaerobic biodegradation of urea formaldehyde in particle board by measuring biogas production and the gas components.

C. To test the anaerobic biodegradation of urea formaldehyde in medium density fiberboard by measuring biogas production and the gas components.

2. To test the biodegradation of formaldehyde under anaerobic conditions with cow manure inoculation.

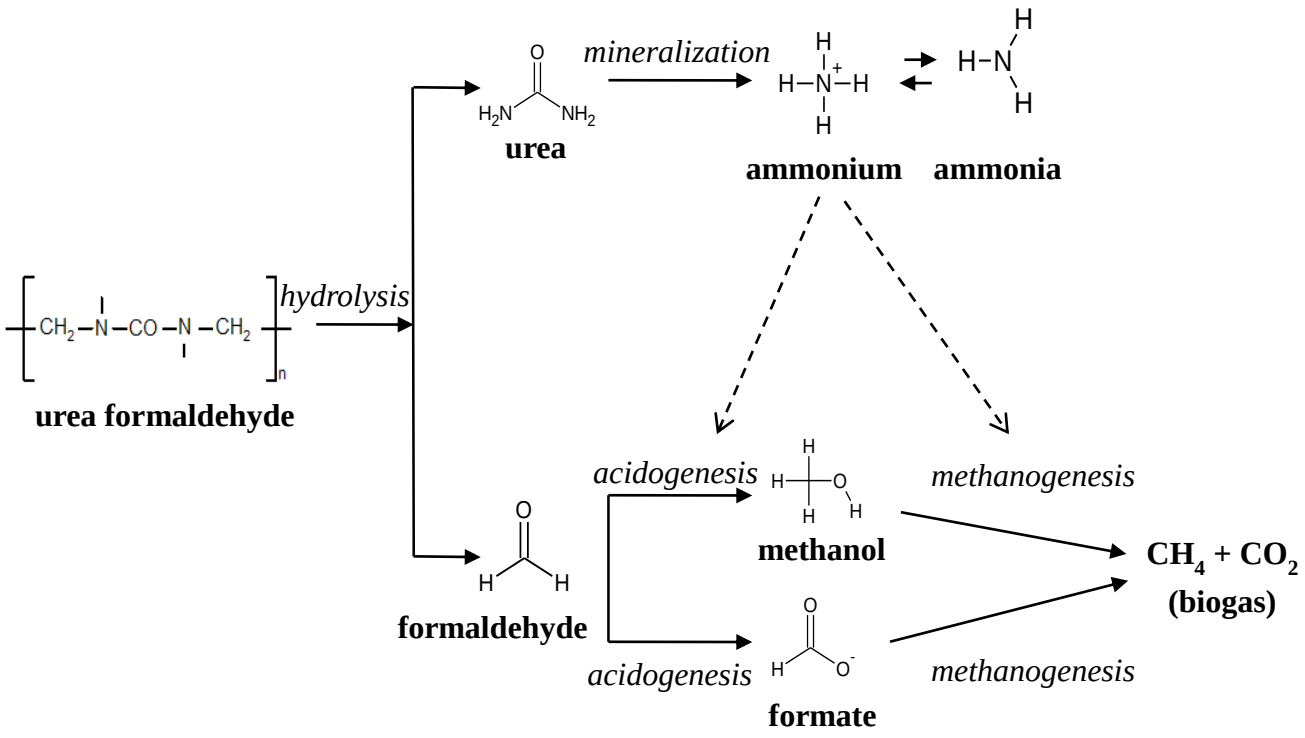


**Figure 1.1** Pathways from urea formaldehyde to $CH_4$ and $CO_2$ under anaerobic process (personal communication: Dr. Gavin Kernaghan)

| Reactor series | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Volatile solids (%) | Organic carbon (%) | Resin (%) | CHL/OS (%) | (C+H)/L | Reactor Experiment | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | methane yield (mL of $CH_4 g^{-1}$) | decay rate ($yr^{-1}$) |
| HW-red oak | 40.5 | 19.6 | 23.6 | 99.6 | 44.6 | na | 83.9 | 2.6 | 32.5(12.6) | 2.3 (1.0) |
| OSB-HW | 42.1 | 16.8 | 22.5 | 99 | 45.6 | 2.8 | 82.2 | 2.6 | 84.5 (8.2) | 1.0 (0.2) |
| PB | 37.3 | 16.3 | 28.2 | 98.9 | 45.1 | 9.2 | 82.6 | 1.9 | 5.6 (3.3) | 1.7 (0.9) |
| MDF | 34.8 | 15.2 | 29.5 | 98.6 | 43.9 | 14.6 | 80.7 | 1.7 | 4.6 (0.7) | 6.7 (1.3) |

**Figure 1.2** Chemical composition, Methane Yields, and Decay Rates for different types of wood
HW: Hard wood
Source: (Wang et al., 2011)

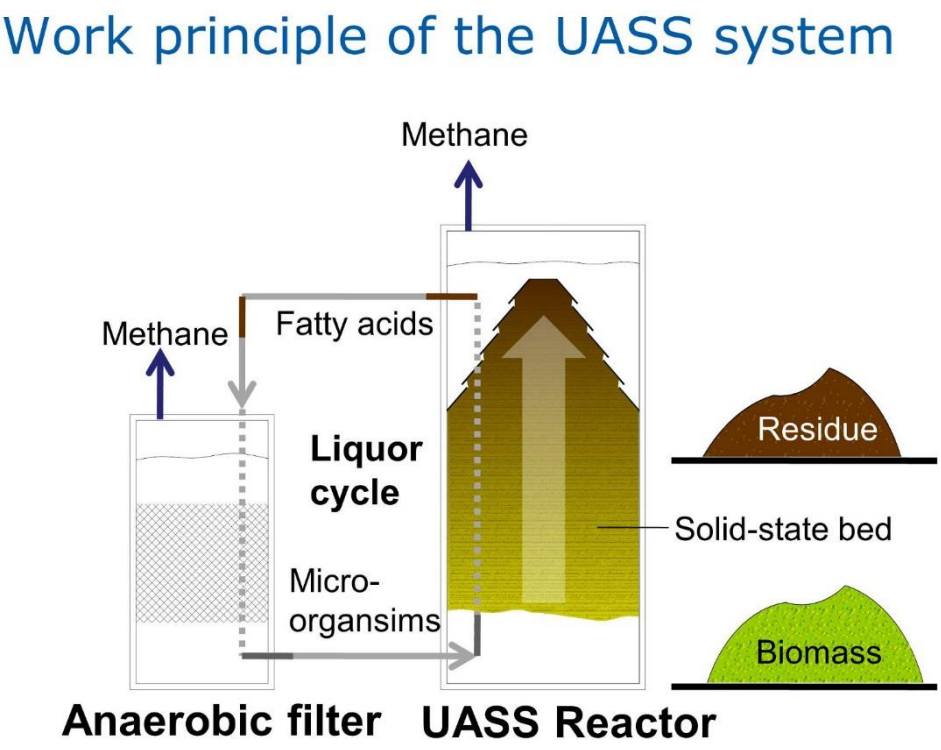


**Figure 1.3** Schematic diagram of the laboratory scale UASS reactor for anaerobic digestion
Source: (Reza, 2014)

## Materials and Methods

The study was conducted at Saint Mary's University in Halifax Nova Scotia from 21 June 2012 to 11 January 2014. A lab-scale experiment was conducted to evaluate the biodegradation of urea-formaldehyde from wood products by using microorganisms living in cattle manure under anaerobic conditions. In order to determine the effect of biodegradation depending on the particle size, two types of engineered boards were used to examine the biodegradation of toxic chemicals: particle board (PB) and medium density fiberboard (MDF). PB and MDF were sourced from Home Depot in Halifax, Nova Scotia. Different forms of PB were prepared: large pieces, garburated (shredded into small pieces by garbage disposal unit, garburator), and saw dust.

### 2.1 Cow manure inoculums preparation

The digester, cattle manure, was brought from a farm on the Noel Shore, Maitland, Hants County, Nova Scotia. The fresh cattle manure was diluted with deionized water at a 1:1 ratio. Size 2.00 mm pore and 1.00 mm pore sieves were used to filter the diluted manure. For each 1L Mason jar, 400 ml of fresh diluted manure was used to make a total volume of 900 ml.

### 2.2 Digester system design

Research scale anaerobic digester systems were constructed at Saint Mary's Biology research lab. Figure 2.1 shows a schematic drawing of the anaerobic digestion system. The Golden Harvest 1L Mason jar was used with a rubber stopper to keep the process under anaerobic condition. The two 1 ml syringes were used, one for gas passage and the other for liquid sampling from the digester. One was connected the digester jar to the gas collecting and measuring tubes which measured gas production each day. The other

one was connected to a tube that was put below the inoculant level. The measuring tubes contained water, so that the daily gas production could be monitored with the water level changes. Each digester container had 900 ml capacity for feed material and digester liquid, and 110 ml of headspace, whereby the biogas could be collected and released into the measuring tube. All the digester containers were kept in a water bath under 37˚C. The pressure of the water column difference will increase the air pressure in the headspace and gas collection tubing, compress the gas resulting underestimated gas production. The raw data collected were calculated using the following equations to get the real gas production values:

$V_0$ = Head space before gas production = 110 ml

$V_1$ = total gas phase volume under 1 atmosphere pressure (after pressure was released)

$V_2$ = total Gas phase volume under pressure caused by water column in U shape-tube

$V_1 = V_0 + \Delta V$ (gas production under atmosphere pressure)

$V_2 = V_0 + 1.2\ h$ (each cm of U tube is 1.2 ml)

$P_1$ = atmosphere pressure  h = water column change in cm

$P_2$ = atmosphere pressure + water column weight

$$= \text{atm} + \frac{2h}{100} \times \frac{\text{atm}}{10}$$

$$= \text{atm}\left(1 + \frac{2h}{1000}\right)$$

$P_1 V_1 = P_2 V_2$

$$V_1 = \frac{P2 \cdot V2}{P1} = \frac{\text{atm}\,(1+\frac{2h}{1000})\cdot(V0+1.2h)}{\text{atm}}$$

$$= (1 + \frac{2h}{1000})\cdot(V_0 + 1.2h)$$

$$\Delta V = V_1 - V_0 = (1 + \frac{2h}{1000})\cdot(V_0 + 1.2h) - 110 \text{ ml}$$

## 2.3 Feed stocks and Digesters contents

Different types and states of engineered wood products were digested with liquid cow manure: saw dust, large pieces, garburated PB and blended MDF. The saw dust form of PB was prepared by sawing the PB. Large pieces of PB were prepared by breaking PB into 2 to 3 cm widths and 3 to 4 cm lengths of random shape. The garburated form of PB was prepared by using a garburator, by slightly soaking it with water before putting it into the garburator. The MDF was cut into 10 g pieces, and then it was soaked with 500 ml deionized water for 4 to 5 days, at 37˚C. The MDF soaked in the 1L Mason jar was blended for 3 minutes to make it as the smallest particles. Also, filter paper and garburated form of wood were used as controls. 4.25 g of Whatman #1 filter paper and 0.75 g of urea formaldehyde (UF) glue were measured with the same ratio as the MDF. The UF glue was polymerized by spreading it on filter paper then heating and pressing it in a waffle iron for 1 minute. This procedure was performed to replicate the manufacturers' process and conditions of making MDF. The result was a wood product with similar content and structure to MDF. The garburated form of wood was made out of mixed woods. In order to make a total volume of 900 ml digester, 400 ml of inoculum, feed stock materials and deionized water were mixed. Each digester for PB were contained 40g of saw dust, 40g of large pieces, or 40 g of garburated form of PB as feed stocks to compare the effect of the size of particles. The 10g of blended MDF, 5g of filter paper with UF were filled with 400 ml of inoculum. The 10g of mixed wood particle was mixed with 400 ml of inoculum and 500 ml of deionized water (Table 2.1). These experiments were operated for 60 days in 37˚C water bath.

## 2.4 Formaldehyde concentration experiment

Figure 2.2 shows a schematic drawing of the anaerobic digestion system reacting with liquid formaldehyde. A 250 ml flask was used to contain diluted cow manure as an anaerobic reactor. A rubber stopper with a 1 ml syringe at the centre was used to collect produced gas from the digester. A tube that was connected to the syringe and a needle were inserted into an upside-down 30 ml syringe. The 30 ml syringe, with a closed top, was filled with water, so that the gas could be collected. The inverted 30 ml syringe was placed into half-filled beakers. Then, a layer of canola oil was added on top of the water to avoid water evaporation.

Formalin, which contained 37 % formaldehyde, was diluted into 1% formaldehyde (200 μl of formalin and 7.2 ml of deionized water). To test the effects of different concentration of formaldehyde, 0, 50, 100, and 200 ppm of formaldehyde were added to digesters. Table 2.2 shows the contents of the mixtures. The experiment was set up in six, 250 ml flasks, and it was carried out for 3 weeks in the incubator at approximate 37˚C.

## 2.5 Data collection

The gas production data was collected every 10 to 12 hours. The accumulative gas production was calculated with the consideration of pressure generated by water column in U shaped tubes. The gas production was collected until the production became low and constant, which took about 60 to 65 days.

## 2.6 Gas chromatography

The composition of gases ($CO_2$ and $CH_4$) were analyzed by gas chromatography (GC) that was operated by Saint Mary's Geography Department. The gas was extracted from each digester with a connecting tube inserted into an upside-down test tube which was

filled with water. The connecting tube and test tube were immersed in a bucket of water. This structure prevented other gases from entering the test tube. When the gas was released from the digester, the gas accumulated in the test tube. After the collection, a rubber stopper was placed on the test tube which also prevented other gases from entering. Then 0.05 ml of the gas was injected to the GC machine with a gas-tight syringe. Each gas analysis took about 35 minutes per run. Thermal conductivity detectors were used to analyze the $CO_2$ and $CH_4$.

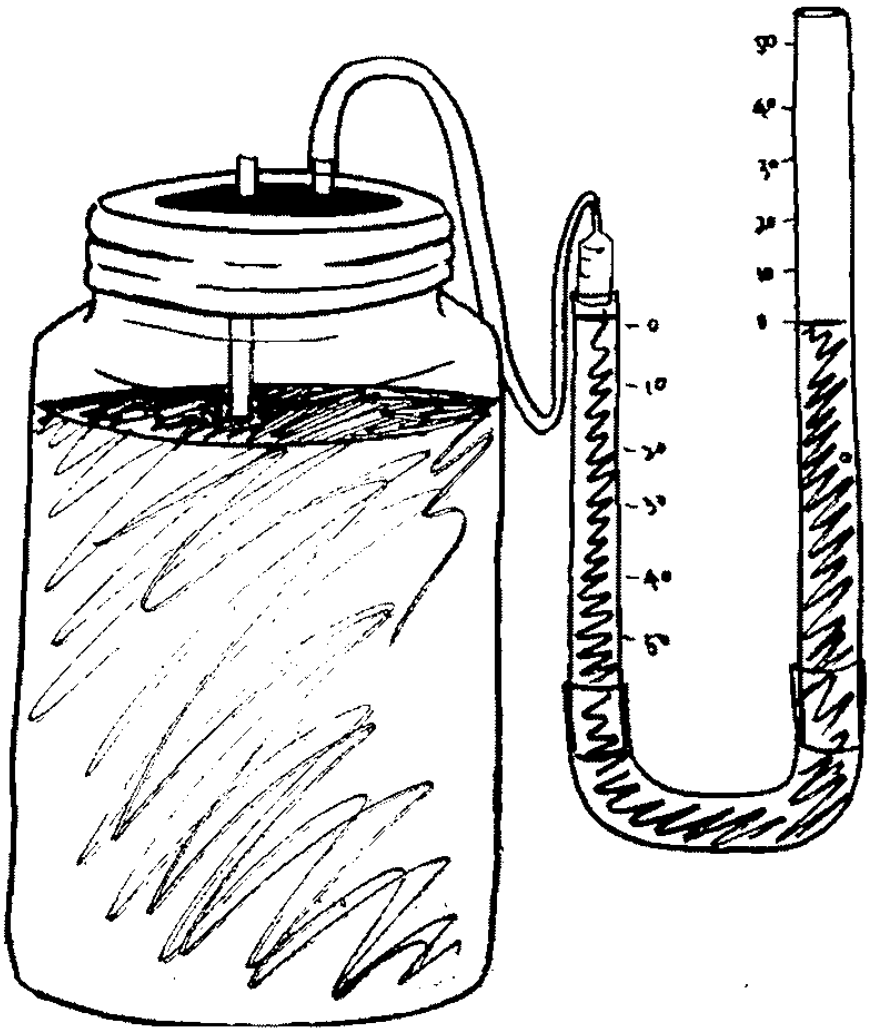

**Figure 2.1** Schematic diagram of the laboratory scale anaerobic digestion system reactor

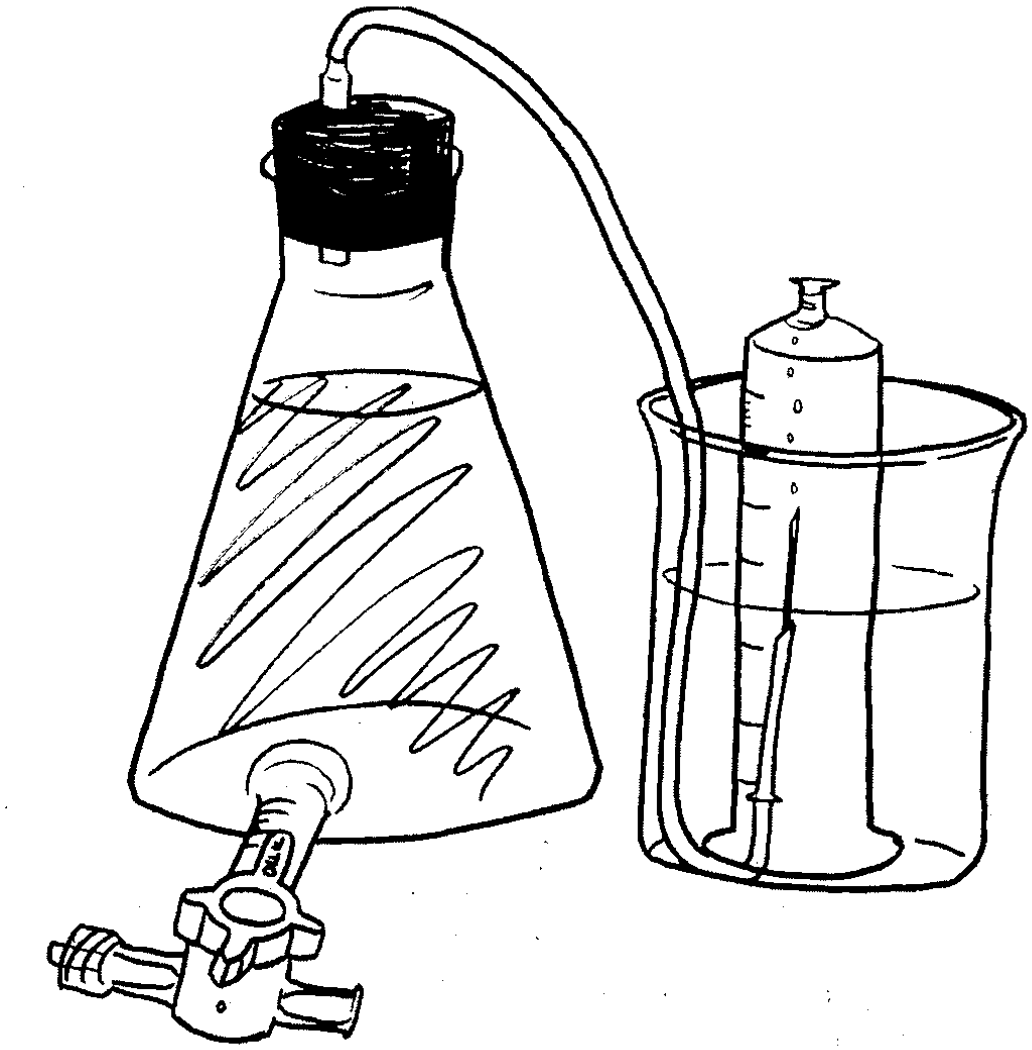

**Figure 2.2** Schematic diagram of the laboratory scale anaerobic digestion system reactor

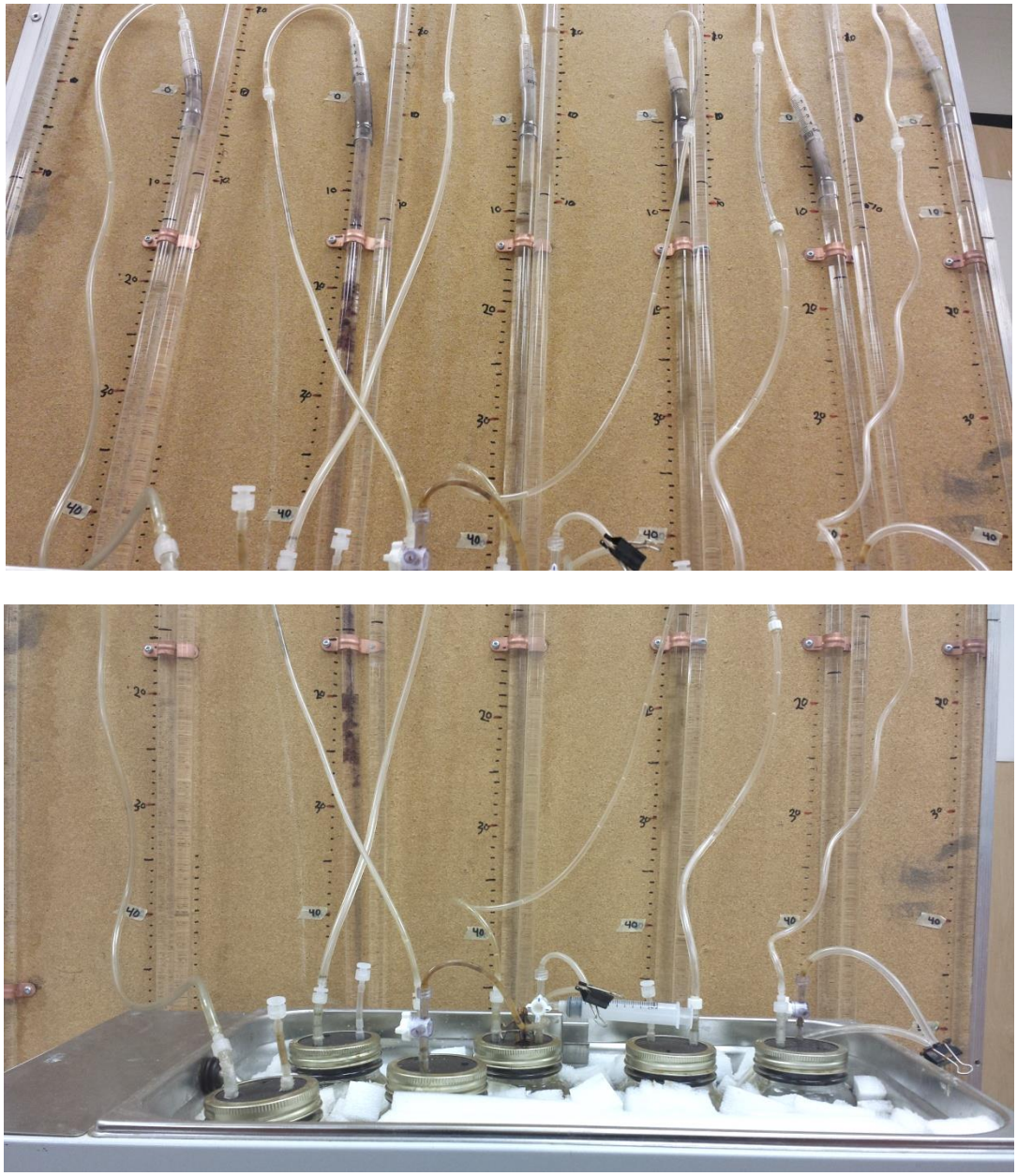

**Figure 2.3 Measuring systems.** Measuring tubes which contained water are connected with the digester jars. After 12 hours of resetting, the daily gas production was monitored with the water level change.


**Figure 2.4 Digester jars.** The digester jars contained different types and states of engineered wood products and diluted cow manure and kept them in water bath at 39˚C.


**Figure 2.5 Digester flasks.** The 250ml flasks were used to operate anaerobic digestion depended on formaldehyde concentration experiment. Different concentration of formaldehyde, 0, 50, 100, and 200 ppm were mixed with diluted cow manure and kept in the incubator at 37˚C.

.

**Table 2.1-**Feed stock materials and digester contents

| Feed stock | Contaminant | State (Form) | Pretreatment | Quantity |
|---|---|---|---|---|
| Particle Board (PB) | Urea formaldehyde | Large pieces Garburated Saw dust | | 40g |
| Medium Density Fiberboard (MDF) | Urea formaldehyde | Blended | Soaked with deionized water | 10g |
| Filter paper with Urea Formaldehyde glue | Urea formaldehyde | Blended | Soaked with deionized water | 5g |
| Mixed wood particle | No contamination | Garburated | | 10g |

**Table 2.2** Formaldehyde inhibition affects on anaerobic digestion

| Formaldehyde concentration | 0 ppm | 50 ppm | 100 ppm | 200 ppm |
|---|---|---|---|---|
| **Diluted cow manure** | 106.8 ml | 106.6 ml | 106.1 ml | 105.0 ml |
| **Deionized water** | 133.2 ml | 132.2 ml | 131.5 ml | 130.2 ml |
| **1% formaldehyde** | 0 ml | 1.2 ml | 2.4 ml | 4.8 ml |
| **Total volume** | 240 ml | 240 ml | 240 ml | 240 ml |

# Result

## 3.1 Anaerobic biodegradation of Whitman #1 filter paper with urea formaldehyde glue

To examine the degradation of urea formaldehyde under anaerobic digestion with cow manure (CM), three experimental categories were used which are CM, CM with Whitman filter paper and CM with Whitman filter paper and urea formaldehyde (UF). Gas produced from these experimental groups was collected over the course of 32 days. CM group was used as a control for CM + Whitman filter paper group, while the CM + Whitman filter paper was used a control for CM + Whitman filter paper + UF group.

The increased production of biogas demonstrated successful biodegradation of the digester system.

Anaerobic digestion of filter paper with urea formaldehyde glue and the control did not produce any gas before the fifth day of the experiment while the filter paper group started producing gas on the third day of experiment.

Despite the slow rate of gas production in the experimental group, filter paper + UF + CM at the beginning of the trials ended up having the largest amount of gas synthesized. After the slow rate of gas production at the beginning of the trial, the gas production was accelerated for 8 days, then it slowed down for two days, and went up again.

The combined paper + UF + CM digestion experiment produced 1636.54 ml. The co-digestion of paper + CM and single CM produced 1355.84 ml and 469.04 ml respectively (figure 3.1). CM group had the lowest biogas production as opposed to gas production in CM combined with filter paper and CM combined with filter paper and UF.

Data was found to be normal thus a two sample t-test was used to test significance in gas production in comparison to controls. There was a significant change in gas

production in CM + filter paper group in comparison to the group that only had CM. A significant change in gas production was also observed in CM + filter paper + UF in comparison to CM + filter paper group.

### 3.2 Anaerobic biodegradation on a saw dust

To ensure the degradability of urea formaldehyde in CM under anaerobic conditions, saw dust (SD) was used. Three experimental groups were used which are CM as a control, CM with SD, and CM combined with SD and UF. The gas production was monitored for 58 days. Gas emissions from CM, CM + SD, and CM + SD + UF were 573.69 ml, 1621.17 ml, and 1687.63 ml (Figure 3.2). CM was used as a control for CM + SD while CM + SD group was used as a control for CM + SD + UF group. CM sample produced the lowest amount of biogas, while CM + SD + UF produced the largest amount. Two experimental groups, SD and CM + SD + UF started producing gas from the beginning of the experiment, but the rates of the gas production for both groups decreased after five days; they increased the production rate after 20.

Data was found to be normal thus a 2 sample t-test was used. There was a significant increase in gas production in CM + SD and CM + SD + UF in comparison to CM. However, gas production did not increase significantly in CM + SD + UF in comparison to CM + SD.

### 3.3A Anaerobic biodegradation on a particle board

For this part of the experiment, a particle board that had urea formaldehyde built into it was cut into big chucks and small chunk to examine whether chunk sizes have an impact on accelerating biodegradation or not. Using different chunk sizes was found to be effective in promoting biodegradation due to the production of gas in both jars, jars

containing big chunks and jars containing small chunks of the particle board. Production of biogases was used as an indicator for successful biodegradation of urea formaldehyde. Gas generated from each experimental jar was collected over the course of 72 days. Gas production from CM, CM + PB, and CM + SD of PB were 1747.87 ml, 2334.67 ml, and 3553.23 ml (Figure 3.3A). CM was used as a control for CM + PB and CM + SD of PB. CM sample produced the lowest amount of biogas, while CM + SD of PB produced the largest amount.

The gas production pattern is shown clearly in Figure 3.3A. Subsequent to the slow production of gas at the beginning of the experiment, the production was accelerated for about 20 days. Afterwards, the gas production decreased and stabilized, then increased again.

Data collected showed that gas emission in jars containing smaller chunks which is the saw dust from the particle board was significantly higher than that of the group that had only cow manure in the jars ($p=0.000$) and the jar with bigger chinks of the particle board ($p=0.000$).

**3.3B Anaerobic digestion in medium density fiberboard (MDF) and particle board**

To test whether the size of wood chunks impacts the efficiency of biodegradation of urea formaldehyde, garburated particle board and pre-soaked medium density fiberboard was used. Equal amounts of both garburated particle board chunks and chopped up medium density fiberboard were added into separate jars with cow manure then the gas was collected over the course of 70 days.

Gas emission from CM, CM + MDF, and CM + garburated particle board (PB) were 1662.36 ml, 1875.92 ml, and 1877.69 ml (Figure 3.3B). CM group was used as a

control for both CM + MDF group and CM + garburated PB group. The use of MDFs and the particle board chunks enhanced biodegradation of urea formaldehyde which was detected by the increased gas production in wood products containing jars. The addition if MDFs and particle board chunks led to initiating biodegradation with higher levels of gas emissions in comparison to the control CM group. A similar pattern of the gas production in figure 3.2 occurred in figure 3.3B. The gas production rate increased dramatically after 10 days, and it gradually decreased.

A statistical significant difference in gas production was detected between the control CM group ($p= 0.02$) and CM + MDF and between CM group and CM + garburated particle board group ($p=0.02$).

**3.4 Anaerobic biodegradation of formaldehyde**

Anaerobic biodegradation of formaldehyde (FA) was examined to see whether the pure formaldehyde convert into $CO_2$ and $CH_4$ or not. For this experiment, 50 ppm FA was mixed with diluted CM. Generation of gas in the anaerobic digesters was monitored for 9 days. Gas produced in each digester was collected from three different testing groups: MDF added sample, 50 ppm of formaldehyde added sample, and the control, CM. Gas emission from CM, CM+FA 50 ppm, and CM+MDF were 9.5 ml, 66 ml, and 59 ml (Figure 3.4A).

Gas was produced at a slow rate up until the fourth day of data collection, however, on day 5 and 6, the rate of gas production started to take off in both MDF and FA added samples (Figure 3.4A and 3.4B). FA added sample and MDF added sample produced a significantly larger amount of gas than the volume produced in the control group with p-value of 0.0007 and 0.005 respectively.

### 3.5 A Formaldehyde concentration effect on anaerobic biodegradation activity

To test the degree of toxicity by the presence of formaldehyde, four different concentrations of formaldehyde were used: 0 ppm, 50 ppm, 100 ppm, and 200 ppm (Figure 3.5A and 3.5B). Gas production of anaerobic digesters was monitored for 10 days. The gas production from each flasks, 0 ppm, 50 ppm, 100 ppm, and 200 ppm were 59.13 ml, 41.9 ml, 12 ml, and 1.8 ml.

Biodegradation in digesters with higher formaldehyde concentrations was found to be delayed as opposed to the ones with lower formaldehyde concentration. In comparison to the control group that did not have any formaldehyde added (0 ppm), other groups with higher formaldehyde concentration took significantly longer amount of time to initiate biodegradation by bacteria.

### 3.5C Growth of fungal community in different concentration of formaldehyde

To investigate the impact of formaldehyde concentration on the growth of fungi communities, different formaldehyde concentrations were used for this part of the experiment. Fungi communities started to grow on the fourth day in the digesters that have concentrations of formaldehyde between 0 ppm to 50 ppm. Increasing formaldehyde concentration slowed down the growth of fungi so the communities ended up taking longer time to appear.

Also, the inoculum was found to become darker in color as the concentration of formaldehyde increases. However, as the bacteria degrade formaldehyde into gases in the digesters, the inoclum gets lighter with time (Table 3.5C).

### 3.6 Gas Chromatography

To confirm the degradation of urea formaldehyde under anaerobic conditions, gas chromatography was used to measure the composition of gases, $CO_2$ and $CH_4$. Samples were collected from the CM+MDF digester jars every 7 days. Although the gas balance was most likely with nitrogen and oxygen, carbon dioxide and methane were also present. The $CH_4$ concentration increased exponentially from 24.59% to 55.21%, and then from 55.21% to 63.17%. The $CO_2$ concentration increased slightly from 18.22% to 22.62% and from 22.62% to 23.97% (Figure 3.6).

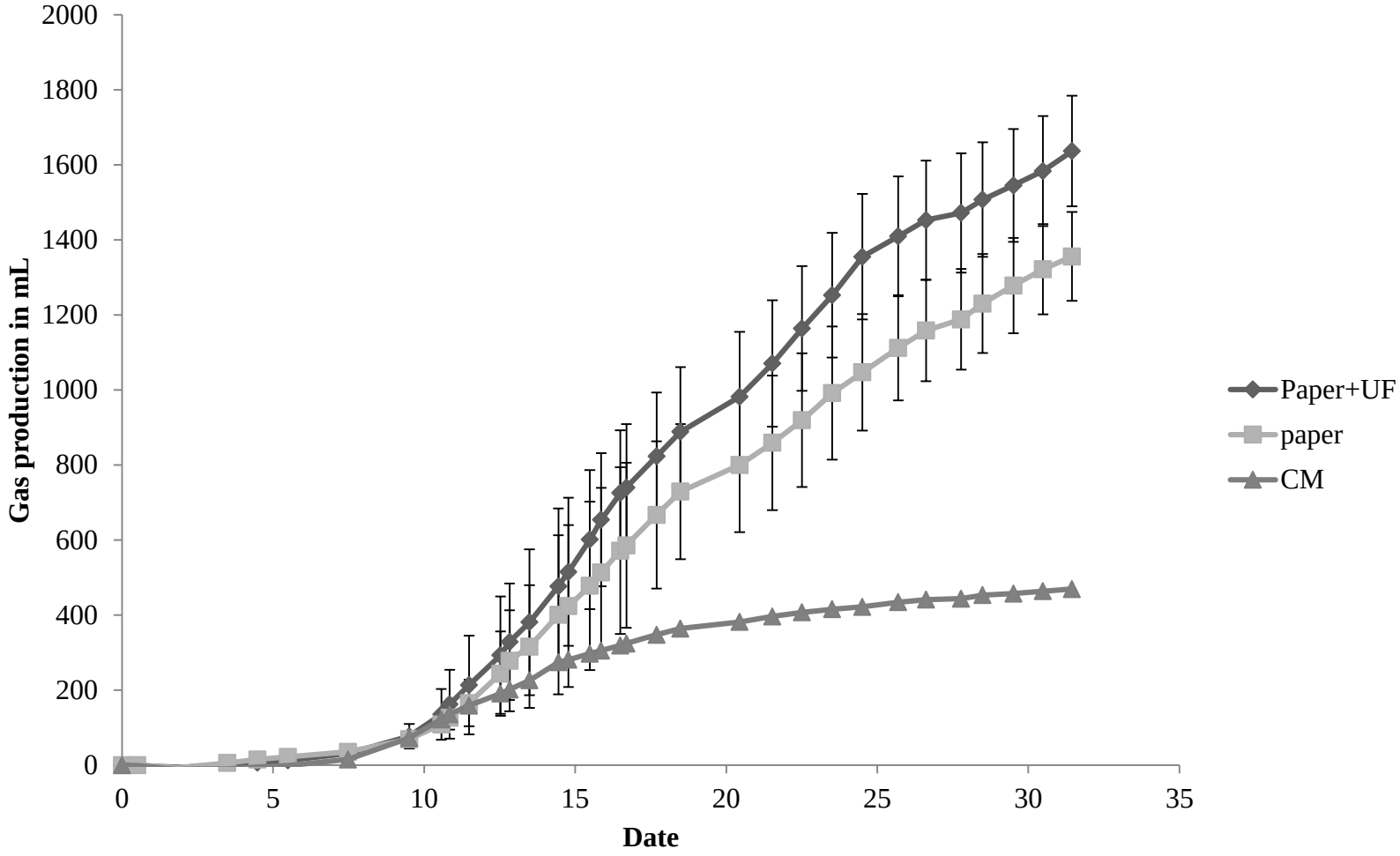


**Figure 3.1 Anaerobic biodegradation of Whitman #1 filter paper with urea formaldehyde glue**

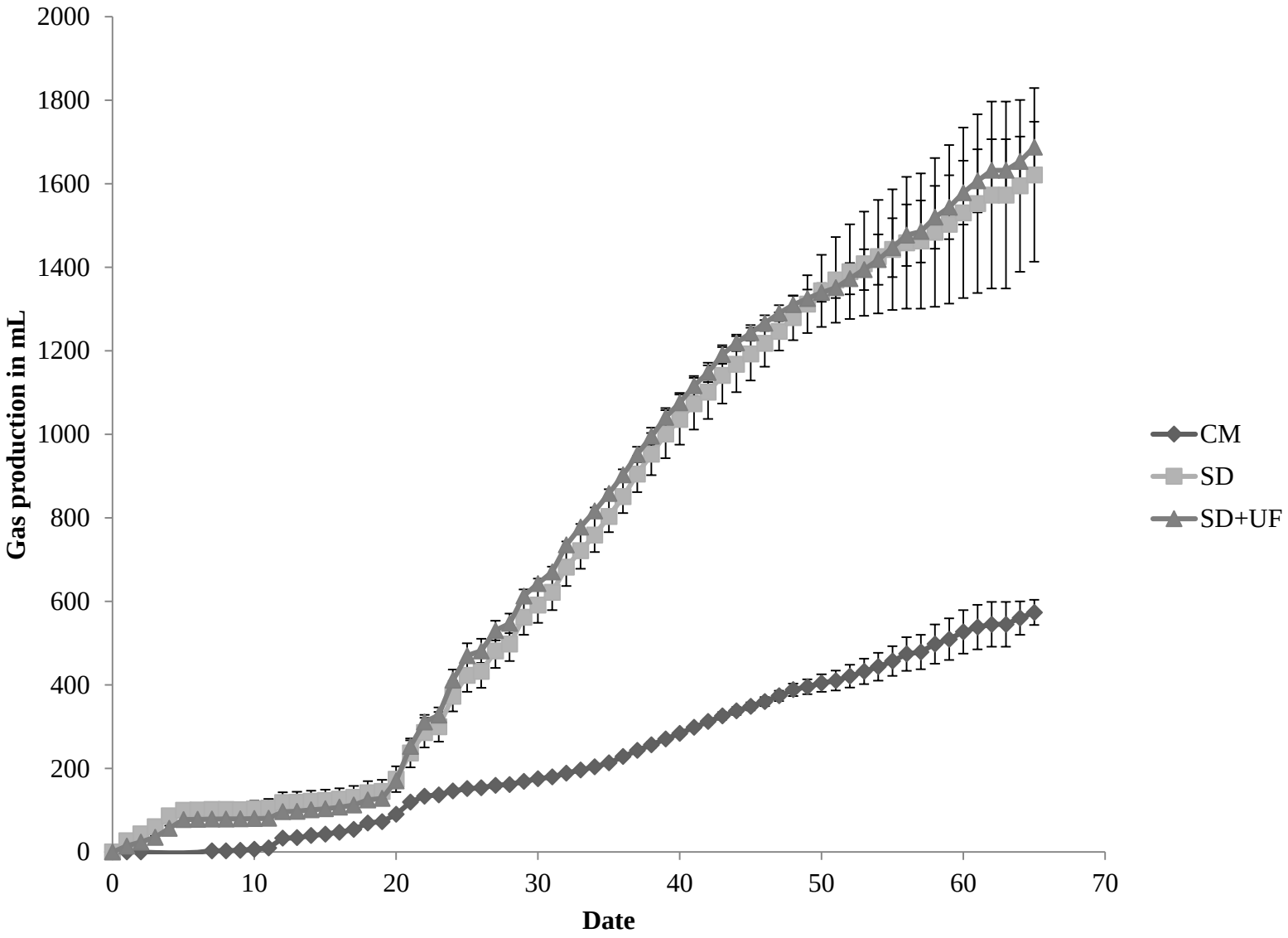


**Figure 3.2 Anaerobic biodegradation on a saw dust**

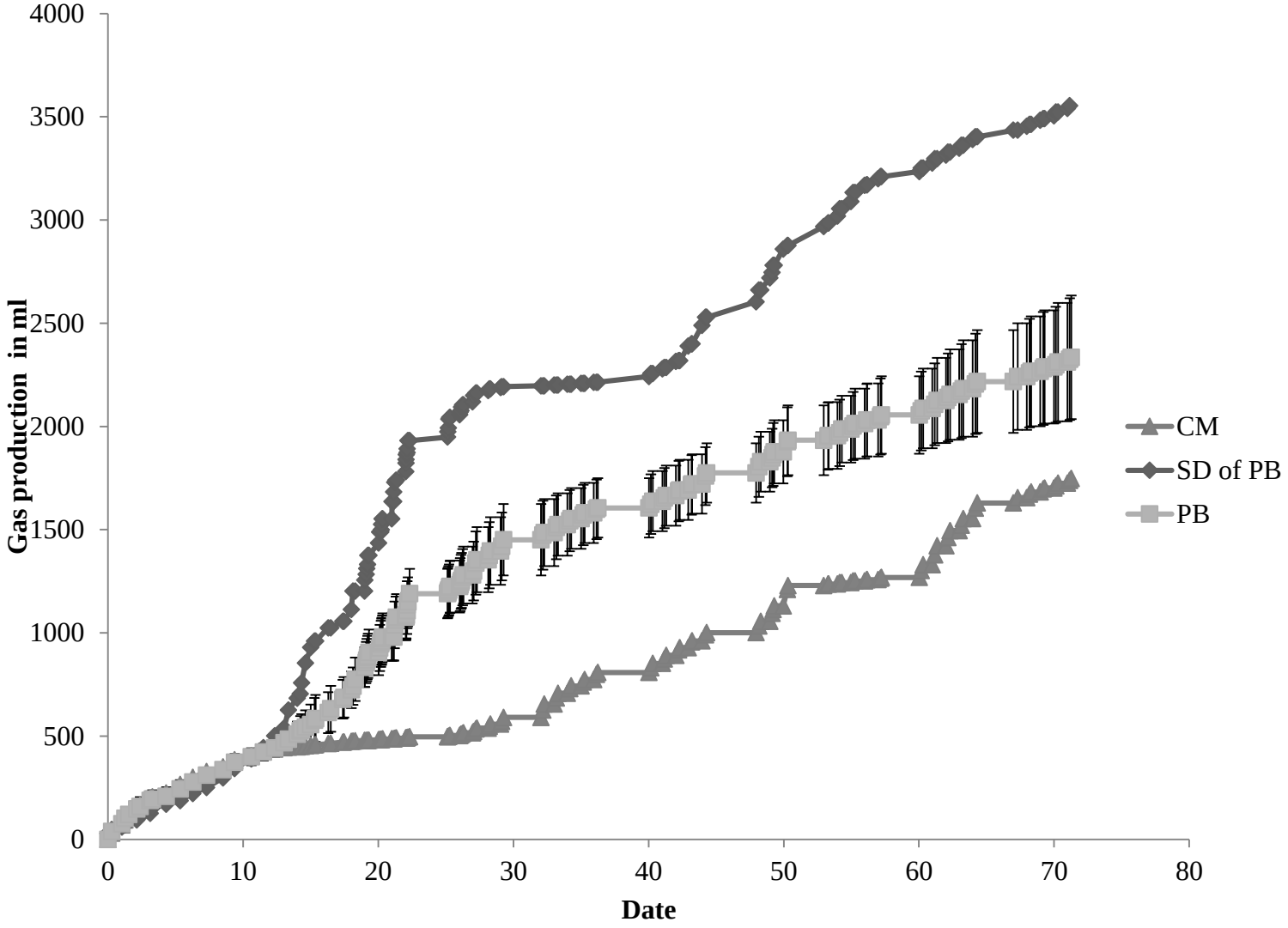


**Figure 3.3A Anaerobic biodegradation on a particle board**

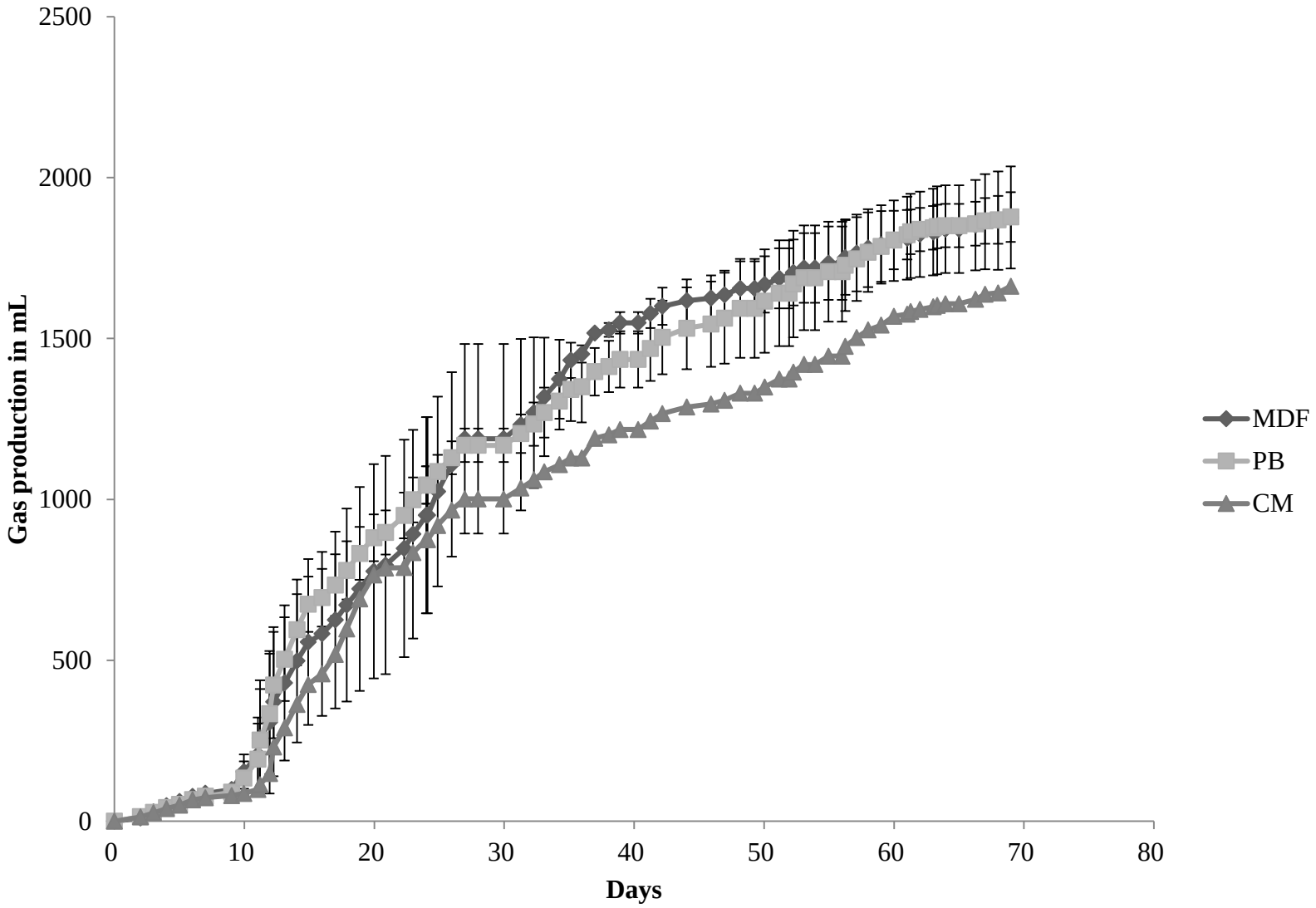


**Figure 3.3B Anaerobic digestion in medium density fiberboard (MDF) and particle board**

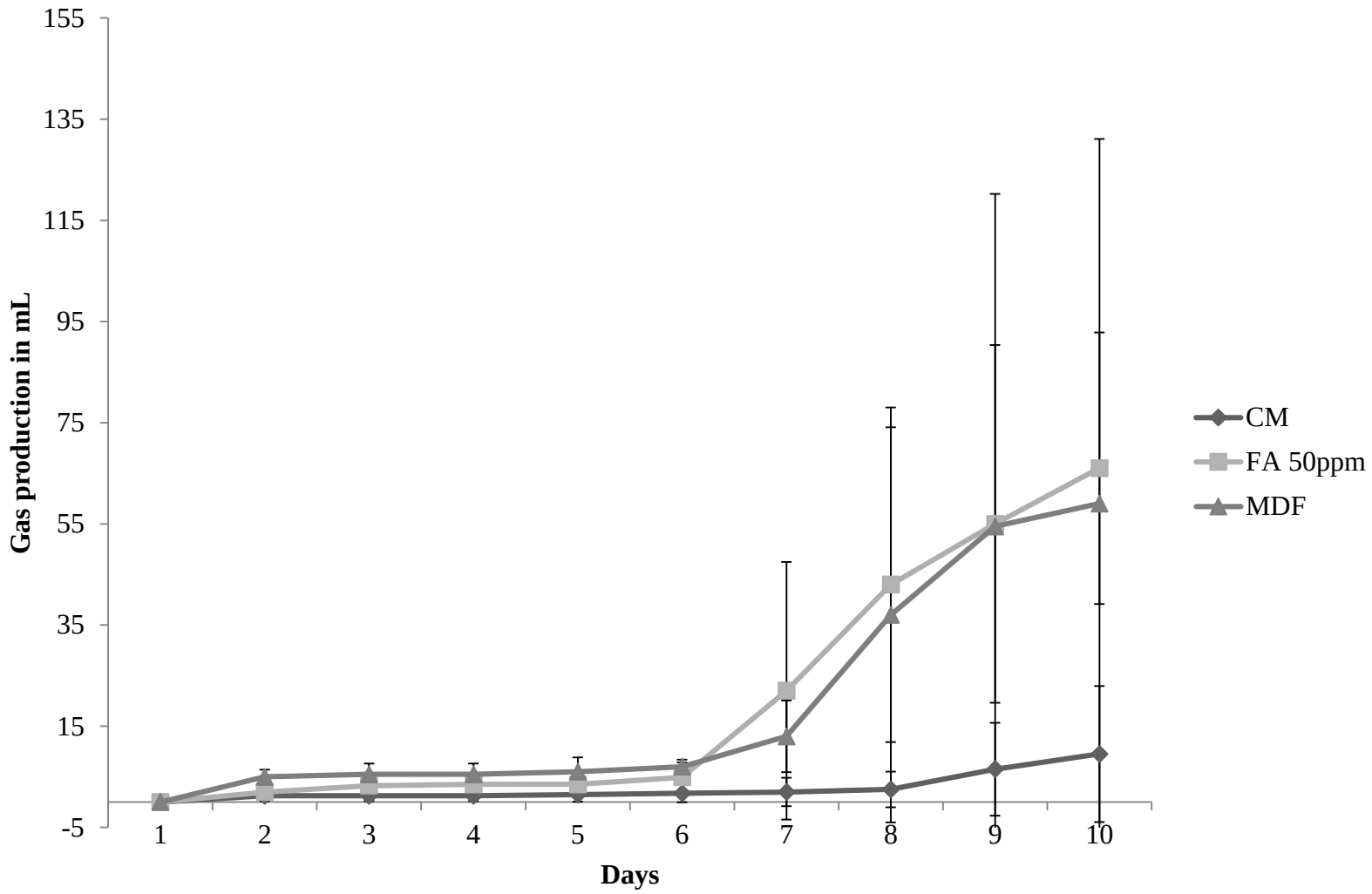


**Figure 3.4A Accumulative data of anaerobic digestion of formaldehyde and MDF**

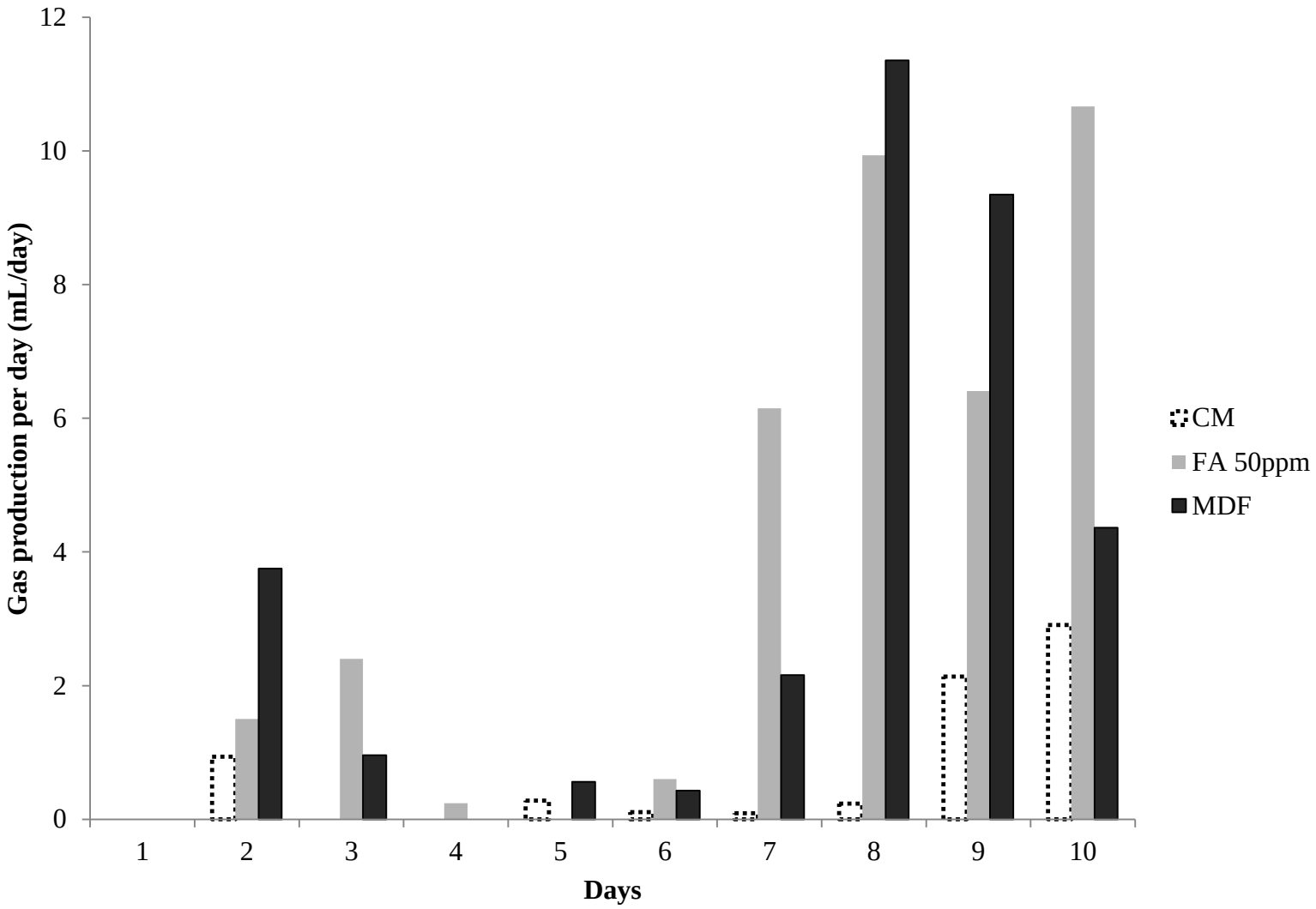


**Figure 3.4B Rate of anaerobic digestion of formaldehyde and MDF**

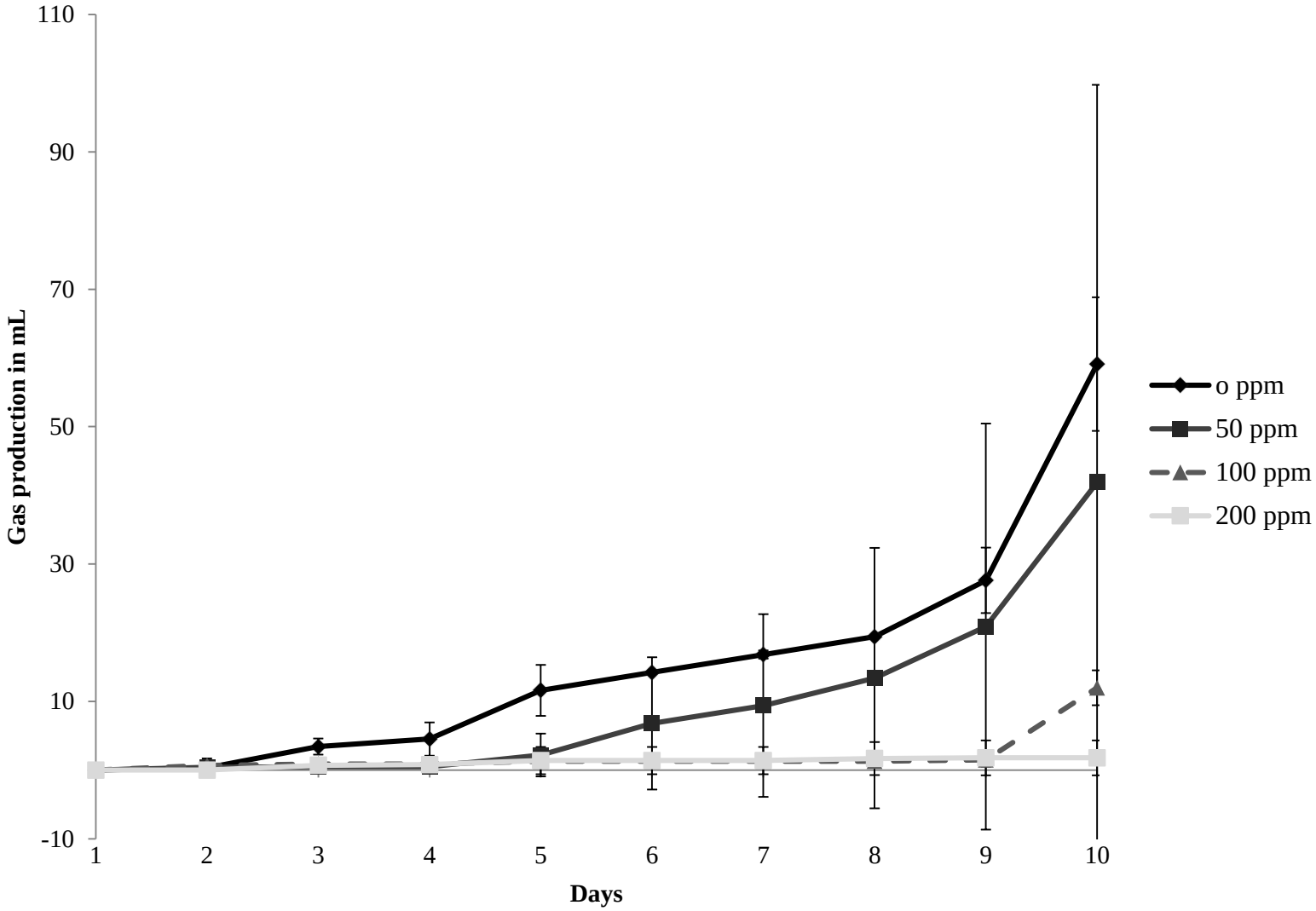


**Figure 3.5A Accumulative data of anaerobic digestion of formaldehyde**

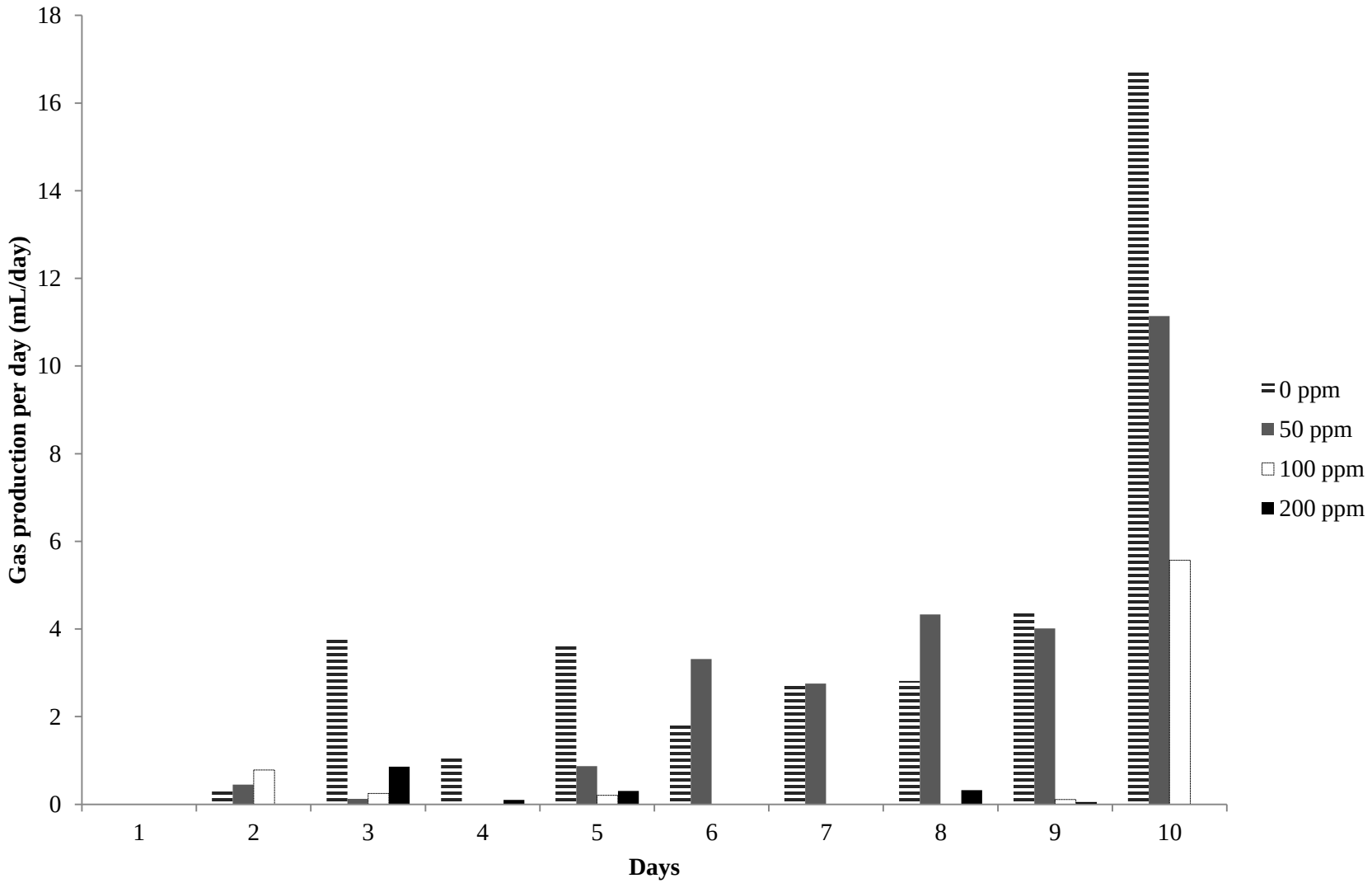


**Figure 3.5B Rate of anaerobic digestion was affected by different concentration of formaldehyde**

**Table 3.5 C Presence of fungi according to time and concentration of formaldehyde**

| [FA] ppm / Days | $0_1$ | $0_2$ | $50_1$ | $50_2$ | $100_1$ | $100_2$ | $200_1$ | $200_2$ |
|---|---|---|---|---|---|---|---|---|
| **1** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **2** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **3** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **4** | **1** | **1** | **1** | **1** | 0 | 0 | 0 | 0 |
| **5** | **1** | **1** | **1** | **1** | 0 | 0 | 0 | 0 |
| **6** | **1** | **1** | **1** | **1** | **1** | 0 | 0 | 0 |
| **7** | **1** | **1** | **1** | **1** | **1** | **1** | 0 | 0 |
| **8** | **1** | **1** | **1** | **1** | **1** | **1** | 0 | 0 |
| **9** | **1** | **1** | **1** | **1** | **1** | **1** | **1** | 0 |
| **10** | **1** | **1** | **1** | **1** | **1** | **1** | **1** | 0 |

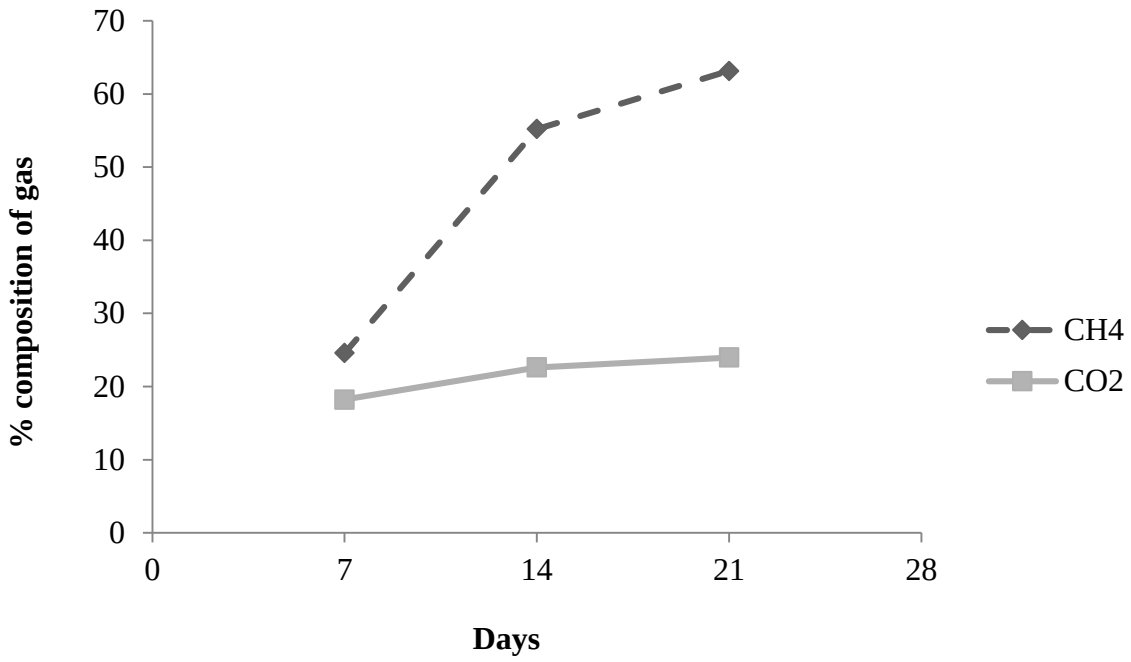


**Figure 3.6 Percentage of gas composition changes in $CH_4$ and $CO_2$ from MDF sample**

# Discussion

## 4.1 Biodegradation of urea formaldehyde under anaerobic condition

One of the objectives of this research is to provide evidence that bacteria in cow manure has the ability to biodegrade urea formaldehyde. Gas production was used as an indicator for the occurrence of biodegradation in the digesters. Bacteria that resides in cow manure was found to be able to biodegrade and break down organic matter present in cow manure, which could be easily be concluded from the increased gas production within each group.

When comparing the different experimental groups to one another, it was found that gas production increased as more biodegradable matter was added. As presented in Figure 3.1, the increased gas production in the CM + filter paper group in comparison to the CM group shows that the addition of filter paper provided bacteria with more biodegradable material to digest anaerobically. Filter paper is composed mainly of the polysaccharide cellulose, a material that can easily be degraded by bacteria through hydrolysis followed by acetogenesis then methanogenesis (Klemm et al., 2005). The fact that gas production changed significantly after adding urea formaldehyde to filter paper + CM shows that urea formaldehyde served as another source of biodegradable matter along with the already provided material from the filter paper.

Besides urea formaldehyde being a source of organic material, it could also be responsible for enhancing the activity of bacteria especially that the concentration of urea formaldehyde used was within the optimal range within which bacteria has better efficiency at breaking down matter.

To further examine urea formaldehyde biodegradation under different conditions,

filter paper was substituted with saw dust (Figure 3.2). The same kind of observations were made for this test with CM + saw dust + urea formaldehyde showing the highest biogas yield which indicates rapid anaerobic digestion.

**4.2 Affect of particle sizes**

To determine if the size of particle has an effect on the accessibility of bacteria to organic material, different particle sizes were applied. When cow manure was used in combination with particle board saw dust, higher levels of gas were generated in comparison to gas yields obtained when bigger particle board chunks were introduced. It is possible that the rate of anaerobic digestion elevated due to large surface of the wood used which gives bacteria better opportunity to penetrate and digest organics.

To further elucidate the impact of particle sizes on the rate of anaerobic digestion, garburated particle board and blended medium density fiberboard were used. Observations of gas production levels supported initial findings which suggest that bigger denser particles limit the accessibility of bacteria to biodegradable material therefore leading to lower levels anaerobic digestion and biogas production (Figure 3.3 A and 3.3 B).

**4.3 Formaldehyde biodegradation**

From the previous experiments, we could conclude that urea formaldehyde biodegrade under anaerobic condition. Therefore, the other objective for this research is to determine whether the pure formaldehyde able to be biodegraded with the digester.

Adding formaldehyde to cow manure was expected to delay gas emissions since formaldehyde is known to suppress bacterial activity and efficiency at degrading organic material. The data supported the hypothesis but it showed an unexpected increase in gas emissions in the CM + formaldehyde group in comparison to the control CM group. This

elevation in biogas generation could be the result the use of formaldehyde as an additional source of carbon.

When comparing the difference between CM group and CM + FA 50 ppm group, larger gas production in CM + FA 50 ppm group in comparison to the CM group observed. However, due to toxicity of formaldehyde, CM + FA 50 ppm group started producing gas later than CM group. The addition of FA provided more carbon source to bacteria.

### 4.3.2 Formaldehyde concentration

Two studies conducted in 1996 and 1999 showed the effects of formaldehyde on bacteria activity, the study suggested that the presence of formaldehyde added a certain level of toxicity to the environment which forced bacteria to take longer to adjust and initiate biodegradation (Zijin et al., 1996; Omil et al., 1999). The studies showed that formaldehyde did not strongly inhibit gas production at concentrations below 200 ppm, but above that amount, formaldehyde's anaerobic digestion was completely inhibited, not just delayed. Likewise, our study supported the previous experiments' findings and showed that the addition of formaldehyde delayed biodegradation to a certain extent.

### 4.3.3 Fungal growth in flask

Since fungal growth was delayed more and more as the concentration of formaldehyde increased, it can be concluded that formaldehyde has an impact on the appearance and survival of fungus possibly through increasing toxicity levels in the fungus environment. However, fungus ability to adjust is not limitless, when formaldehyde concentration exceeds critical levels fungus loses the ability to adjust and becomes completely intolerant to new high formaldehyde concentrations. A study conducted by Nirmala in 1992 supported our findings and confirmed that formaldehyde inhibits fungal

and bacterial contamination in plant cell cultures (Nirmala et al., 1992).

### 4.4 Gas Chromatography

On day 7 of the experiment, low concentrations of both $CO_2$ and $CH_4$ were measured by GC. However, after 7 days, the $CH_4$ concentration increased exponentially and demonstrated dramatic increase of gas production from day 10 to day 30 as seen in Figure 3.3B.

Results from Mayerhofer's report shows that the digester with raw spruce wood and the control, cow manure digester, produced more $CH_4$ than $CO_2$. The digester with particle board had a delay of $CH_4$ gas emission, but it began producing more $CH_4$ than $CO_2$ after day 20 with a much higher rate. Comparison of the gas emission from Mayerhofer's experiment and this experiment indicates wood and cow manure could be the primary source of the gas emission (high quantity of $CH_4$). Later, however, once the urea formaldehyde resin starts to be degraded by anaerobic digestion, it could produce a much higher quantity of gas ($CH_4$) (Mayerhofer et al., 2011).

## References


Acharjee, T. C., Coronella, C. J., Vasquez, V. R. 2011. Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. *Bioresource Tech.* 102: 4849-4854.

Bandura, A., Lvov, A. 2006. The ionization constant of water over wide range of temperature and density. *Journal of Physical Chemistry*. 35: 793-800.

Bruckner, B. 1986. Formaldehyde: properties and application, health hazards and protection methods. *Kooperationsstelle Tubingen.* AS-Verlag, 16-21.

Chen, Y., Cheng, J. J., Creamer, K. S. 2008. Inhibition of anaerobic digestion process: a review. *Bioresource Technology*. 99: (10) 4044-4064.

Daskalopoulos, E., Badr, O., Probert, S. D. 1997. Economic and Environmental Evaluations of Waste Treatment and Disposal Technologies for Municipal Solid Waste. *Applied Energy*. 58: (4) 209-255.

Dinwoodie, J. M. 1978. The properties and performance of particleboard adhesives. *Journal of the Institute of Wood Science.* 8: 59–68.

Dunky, M. 1998. Urea-formaldehyde adhesive resins for wood. *International Journal of Adhesion & Adhesives.* 18: 95-107.

Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Seyboth, K., Arvizu, D., Bruckner, T. 2011. IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation- Summary for Policy Makers. *Cambridge University Press*.

El-Fadel, M., Findikakis, A. N., Leckie, J. O. 1997. Environmental Impacts of Solid Waste Landfilling. *Journal of Environmental Management.* 50: 1-25.

Funke, A., Ziegler, F. 2010. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels Bioprod Bioref*. 4: 160-177.

Gardner, G. *Municipal Solid Waste Growing.* Retrieved from http://vitalsigns.worldwatch.org/vs-trend/municipal-solid-waste-growing.

Garrido, J. M., Mendez, R., Lema, J. M. 2000. Treatment of wastewaters from a formaldehyde-urea adhesives factory. *Water science and Technology*. 42: (5) 293-300.

Gerberich, H. R., Stautzenberger, A. L., Hopkins, W. C. 1980. Formaldehyde, *Encyclopedya of chemical technology*. 11.

Global Municipal Solid Waste to Double by 2025. Retrieved from http://waste-management-world.com/a/global-municipal-solid-waste-to-double-by.

Grafstrom, R. C., Curren, R. D., Yang, L. L., Harris, C. C. 1985. Genotoxicity of formaldehyde in cultured human bronchial fibroblasts. *Science* 228: 89-90.

Halvarsson, S., Edlund, H., Norgren, M. 2008. Properties of medium-density fiberboard (MDF) based on wheat straw and melamine modified urea formaldehyde (UMF) resin. *Industrial Crops and Products.* 28: (1) 37-46.

Hoekman, S., Broch, A., Robbins, C. 2011. Hydrothermal Carbonization (HTC) of Li gnocellulosic Biomass. *Energy Fuels*. 25: 1802-1810.

IPCC (Intergovernmental Panel on Climate Change). 2002. CH4 emissions from solid waste disposal. In: Jensen, J., Pipatti, R. (Eds.), Background Papers –IPCC Expert Meetings on Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Institute for Global Environmental Strategies, Japan. 419-439.

Klemm, D., Heublein, B., Fink, H. P., Bohn, A. 2005. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. *Angew. Chem. Int. Ed.* 44: 22.

Mayerhofer, M., Kernaghan, G., Hosein, A. 2011. Influence of the components of engineered forest products on anaerobic decomposition.Technical Report prepared for Biogas Energy Inc. Nova Scotia.

Mumme, J., Linke, B., Toelle, R. 2010. Novel upflow anaerobic solid state (UASS) reactor. *Bioresource Technology*. 101: 592-599.

Mumme, J., Eckervogt, L., Diakite, M., Rupp, F., Kern, J. 2011. Hydrothermal carbonization of anaerobically digested maize silage. *Bioresource Technology*. 102: 9255-9260.

Municipal Solid Waste and Greenhouse Gases. Environment Canada. Retrieved from http://www.ec.gc.ca/gdd-mw/default.asp?lang=En&n=6F92E701-1.

Mor, S., Ravindra, K., Dahiya, R. P., Chandra, A. 2006. Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental monitoring and Assessment.* 118: 435-456.

Nirmala, C., Sucarnalatha, G., Ravishankar, G. A., Venkataraman, L. V. 1992. Influence of formaldehyde in control of bacterial and fungal contaminants in plant cell cultures: Its effect on growth and secondary metabolite production. *Biotechnology Techniques*. 6: (5) 463.

Omil, F., Mendez. D., Vidal. G., Mendez. R., Lema. J. M. 1999. Biodegradation of formaldehyde under anaerobic conditions. *Enzyme Microbiol. Technol.* 24: 255-262.

Padgett, J. M. 2009. Biodegradability of wood products under simulated landfill conditions. *NCSU.* From http://www.lib.ncsu.edu/resolver/1840.16/269.

Pearson, F., Chang, S. C., Gautier, M. 1980. Toxic inhibition of anaerobic biodegradation. *Journal WPCF*. 52: 472-482.

Perez, J., Munoz-Dorado, J., De la Rubia, T., Martinez, J. 2002. Biodetradation and biological treatments of cellulose, hemicelluloses and lignin: an overview. *Int Microbiol.* 5: 53-63.

Reza, M. T., Lynam, J. G., Vasquez, V. R., Coronella, C. J. 2012. Pelletization of biochar from hydrothermally carbonized wood. Environmental Progress & Sustainable Energy. 31: (2) 225-234.

Reza, M. T., Uddin, M. H., Lynam, J. G., Hoekman, S. K., Coronella, C. J. 2013. Hydrothermal Carbonization: Reaction chemistry and water balance. Biomass Con v. Bioref.

Rodhe, H. 1990. A comparison of the contribution of various gases to the greenhouse effect. *Science,* 1248: 1217-1219.

Rokiah, H., Hazneza, A. S., Othman, S., Norli, I., Hakimi, I. M., Hasnah, M. J., Salmiah, U. 2009. Extractable formaldehyde from waste medium density fiberboard. *Journal of Tropical Forest Science.* 21: (1) 25-33.

Sellers, T., Miller, G. D., Katabian, M. 2000. Recycled thermoplastics reinforced with renewable lignocellulosic materials. *Forest products journal.* 50: (5) 24-28.

Sharma, S., Ramakrischna, C., Desai, J. D., Bhatt, N. M. 1994. Anaerobic biodegration of a petrochemical waste-water using biomass support particles. *Appl. Microbiol. Biotechnol.* 40: 768-771.

Statistics Canada. 2012. Human activity and the environment. Economy and the environment. Catalogue No. 16-201-X.

United Nations Population Division. Department of Economic and Social Affairs. Retrieved from http://www.un.org/en/development/desa/population/.

Wang, X., Padgett, J. M., De la Cruz, F. B., Barlaz, M. A. 2011. Wood Biodegradation in Laboratory-Scale Landfills. *Environmental Science & Technology.* 45: (16) 6864-6871.

Yan, W., Hastings, J. T., Acharjee, T. C., Coronella, C. J., Vasquez, V. R. 2010. Mass and energy balance of wet torrefaction of lignocellulosic biomass. *Energy Fuels*. 24: 4738-4742.

Zijin, L., Hegemann. W. 1998. Anaerobic toxicity and biodegradation of formaldehyde in batch cultures. *Water Research.* 32: (1) 209-215.