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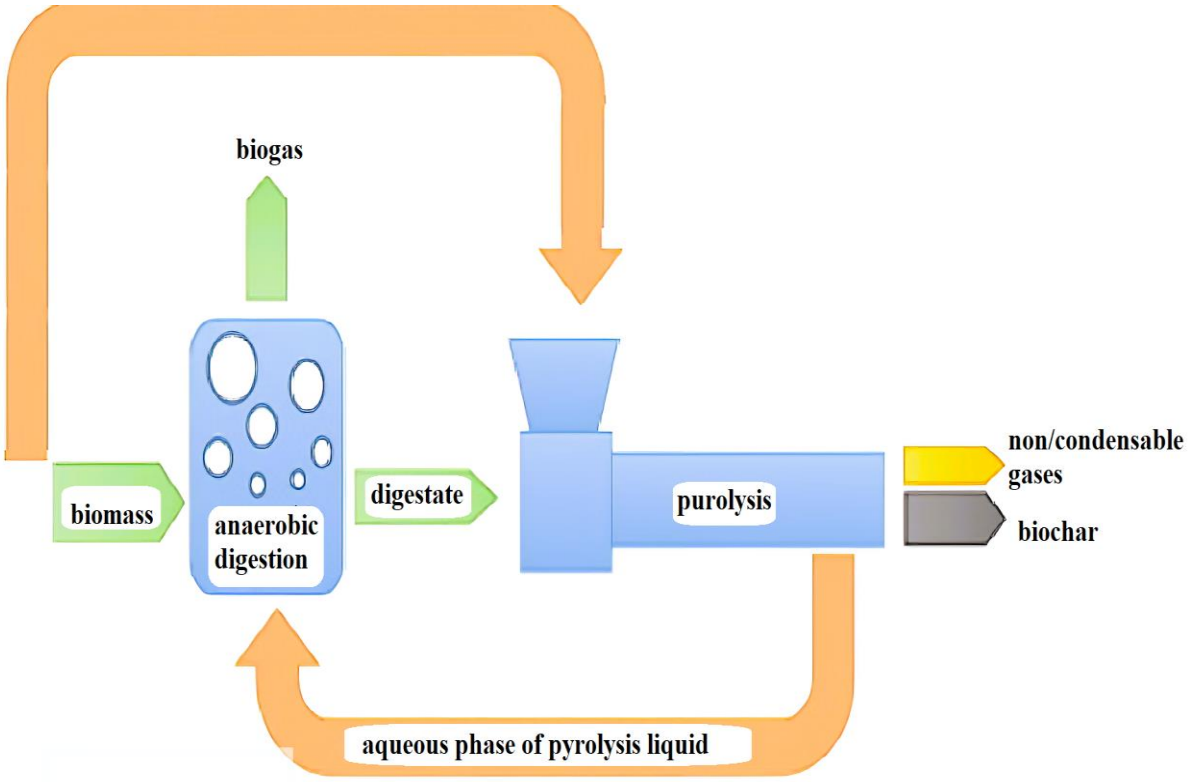
Master of Science, Energy, and Environmental Technology

Decomposition and characterization of Aqueous Pyrolysis Liquid



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Summary:

Pyrolysis is one of the fastest methods for depolymerizing biomass macromolecules (i.e., cellulose and hemicellulose) into smaller molecular fragments (i.e., hydroxy acetaldehyde). Pyrolysis of biomass results in a two-phase liquid, the aqueous phase has a low heating value and a high-water content (aqueous pyrolysis liquid, APL). Anaerobic digestion (AD) may be the simplest method of producing a biofuel (methane, CH_4) from APL. In this project, three types of APL (APL 500, APL 600, and APL 700) obtained from Scanship AS, are evaluated by carrying out a batch experiment to understand their CH_4 potential and to understand. We studied the characterization and decomposition methods of APL as well. Experiments on APL including electrochemical treatment, acid esterification, BMP test, and FTIR characterization were employed to study the effect of different conditions (e.g., Voltage, Concentration, Temperature) on the decomposition of APL.

For the potentiostatic method of the electrochemical test, three different voltages (1, 1.5, and 2 Volt) were applied to the APL. For acid treatment, sulfuric acid (H_2SO_4) and nitric acid (HNO_3) were used at three concentration levels (0.5, 1.0, and 3.0 percent). The chemical composition of the original and treated APL is analyzed using FTIR spectroscopy. Numerous tests were performed before and after treatment to analyze the impact on the functional groups found in APL. C-H stretching (range 2800-30000) was eliminated from acid-treated samples. All treated samples showed a significant increase in the O-H and N-H groups (3200-3600). FTIR characterization and the results showed that using treated APL in the amount of 6% of the total substrate (6% APL, 94% Apple juice) during co-digestion, enhanced CH_4 yield by 8-23 percent, indicating that it has the potential to be employed as a co-substrate during the AD process.

Therefore, it is concluded that the electrochemical technique is an effective method for the decomposition of APL to produce biogas. Acid treatment is a simple and efficient method for the decomposition of APL. HNO3 treatment produces a mild condition with consistent results. Since APL contains numerous compounds, APL 500 produced less CH_4 in all treatment procedures. As a result, APL produced at higher temperatures, such as APL 600 or APL 700, is recommended.

Preface

This master thesis work was completed as part of the master's study program in Energy and Environmental Technology (EET) at the University of South-Eastern Norway.

The objective of this project is to characterize aqueous pyrolysis liquid (APL), find a way of decomposition to upgrade it, evaluate it as a feed for the AD process, as well as study the effect of various treatments methods on the methane CH_4) potential from APL. This is a continuation of an earlier project aimed at obtaining a better knowledge of and estimating the overall potential of APL using various treatment methods.

The project was completed and extensive, and the results were interesting and promising; significant data analysis was performed. However, there were some difficulties with managing the time. Doing all these experiments for the first time in my career, as well as taking the time to examine them, has been a significant challenge. However, with the support and guidance of the project's supervisor and partners, this difficulty was resolved. The performance of APL after treatment was investigated. The focus was on the CH_4 potential from each sample. To increase CH_4 yield, it was hypothesized that esterification treatment may be improved by using different acids at different concentrations.

I would like to express my heartfelt gratitude to my primary supervisor Assoc. Prof. Carlos Dinamarca for his guidance, support, technical advice, and feedback during the thesis. In addition, I am grateful to Vasan Sivalingam, my co-supervisor, for his technical guidance and help with the experimental planning. I'd like also to express my appreciation to our external partner Gudny Øyre Flatabø for her recommendations, opinions, and feedback. Without their cooperation, this work would be impossible to complete.

Finally, I am deeply grateful to my parents and my wife, Wafa for their support and patience in making this project a success.

Porsgrunn, 24.05.2022

Adel Showaya

Contents

Nomenclature

Abbreviation	Description
AD	Anaerobic Digestion
APL	Aqueous Pyrolysis Liquid
APL 500	APL produced at 500 ℃
APL 600	APL produced at 600 ℃
APL 700	APL produced at 700 ℃
APL 700 1 V	APL produced at 700 ℃ treated with 1.0 Volt
APL 700 1.5 V	APL produced at 700 ℃ treated with 1.5 Volt
APL 700 2 V	APL produced at 700 ℃ treated with 2.0 Volt
APL 500 N-0.5%	APL 500 treated with HNO_3 0.5 % vol.
APL 500 N-1%	APL 500 treated with HNO_3 1 % vol.
APL 500 N-3%	APL 500 treated with HNO_3 3 % vol.
APL 500 S-0.5%	APL 500 treated with H_2SO_4 0.5 % vol.
APL 500 S-1%	APL 500 treated with H_2SO_4 1 % vol.
APL 500 S-3%	APL 500 treated with H_2SO_4 3 % vol.
APL 600 N-0.5%	APL 600 treated with HNO_3 0.5 % vol.
APL 600 N-1%	APL 600 treated with HNO_3 1 % vol.
APL 600 N-3%	APL 600 treated with HNO_3 3 % vol.
APL 600 S-0.5%	APL 600 treated with H_2SO_4 0.5 % vol.
APL 600 S-1%	APL 600 treated with H_2SO_4 1 % vol.
APL 600 S-3%	APL 600 treated with H_2SO_4 3 % vol.
APL 700 N-0.5%	APL 700 treated with HNO_3 0.5 % vol.
APL 700 N-1%	APL 700 treated with HNO_3 1 % vol.
APL 700 N-3%	APL 700 treated with HNO_3 3 % vol.
APL 700 S-0.5%	APL 700 treated with H_2SO_4 0.5 % vol.
APL 700 S-1%	APL 700 treated with H_2SO_4 1 % vol.
APL 700 S-3%	APL 700 treated with H_2SO_4 3 % vol.
Blank	Batch test with only inoculum
BMP	Biomethane Potential Test
CH_4	Methane
CO_2	Carbon monoxide
CV	Cyclic voltammetry
GC	Gas Chromatography

H_2SO_4	Sulfuric acid
HNO_3	Nitric acid

1 Introduction

1.1 Background

Climate change awareness has led to various CO_2 reduction policies and targets being implemented worldwide. To mitigate the consequences of climate change, the United Nations proposes that renewable energy sources be used to fulfill energy demands [1]. The use of renewable energy sources has become critical; as a result, many national energy systems have established renewable energy use as a target [2]. The fundamental reason for emphasizing the move to renewables is the energy scarcity, several growing levels of environmental pollution, and the ever-increasing population, which adds to a dramatic rise in per-capita consumption. This problem has resulted in an increase in renewable energy production from all possible sources, such as wind, solar, biomass, and geothermal, among others. However, although wind and solar energy are renewable sources, they are not accessible all the year, and their supply is not consistent with the energy demand, resulting in excess or deficient energy production during times.

Because of its numerous advantages, bioenergy is well-suited for addressing energy issues. It is a renewable, ecologically beneficial, and sustainable energy, lowering the greenhouse effect and ensuring raw material continuity. Bioenergy raw materials may be obtained simply by growing biofuel-producing plants and using waste streams from other sources (e.g., human faeces, food waste, and municipal solid waste) [3]. Nowadays, biomass provides about 14 % of the world's energy, producing cleaner synthetic fuels than coal, shale, or tar sands. Nevertheless, biomass is predicted to become a primary energy source within the next 10 years [4].

The transformation mechanism of biomass to biogas via anaerobic digestion (AD) is a biochemical process. Hydrolysis, acidogenesis, acetogenesis, and methanogenesis are the main characterized processes involved in AD [5]. Municipal sludge from wastewater treatment plants, municipal wastes, animal manure, algae, and woody biomass is used as feedstock in the AD system. Biogas (CH_4 and CO_2) is the primary product of AD

Biomass to energy conversion can be accomplished via thermochemical processes such as pyrolysis, gasification, combustion, and thermal liquefaction, or biochemical processes such as fermentation, composting, and digestion [6]. Pyrolysis is a sustainable technique for thermochemical conversion of biomass for producing energy and chemicals, such as solid (biochar), liquid (bio-oil), and gaseous (syngas) products. Intermediate pyrolysis or pyrolysis occurs at 400–500 ℃ and has a reaction time of 10–30 seconds. As a result, it may be deemed affordable even on a small scale, and it can produce char (20–30%), gas (10–20%), and 50–60% w/w of a pyrolysis liquid with a reasonably high-water content (approximately 50 % w/w).

Energy production from biomass-derived pyrolysis liquids has been under development over the past few years. If these studies are successful, it will be considered a renaissance in producing renewable energy that contributes to reducing carbon dioxide (CO_2) emissions.

Bio-oil is the organic phase in which a synthetic fuel can be produced from biomass feedstocks, such as woody biomass, algal biomass, municipal waste, and agricultural residues via thermochemical processes [7]. Bio-oil can be produced using several pathways; examples are biomass pyrolysis or thermochemical liquefaction [8]. Both processes are thermochemical, but

the operating conditions are different. Another product that accompanies bio-oil (the organic phase) is the aqueous pyrolysis liquid (APL).

1.2 Problem statement

APL is not considered a fuel due to its high-water content and the presence of other complex compounds that work as inhibitors (e.g., phenols, furfural, acetones). APL can also be used as a feed for the AD process to extract as much energy as it contains, but some treatments must be carried out to prepare it as a substrate in AD

1.3 Objectives

The purpose of this thesis would be to evaluate APL as a feed for the AD process to capture energy using fresh inoculum. Furthermore, the measuring of APL content such as COD, pH, and the biogas potential. This thesis would also study the possibilities of APL to be used as a co-substrate as it was found to increase CH_4 production.

Specific objectives

-Study the effect of the application of potential on the decomposition of APLs

-Study the effect of the application of acids on the decomposition of APLs

-Establish a routine for the evaluation of the degradability of APLs

-Establish the best pyrolysis temperature to produce APLs and consequently CH_4 production

-Evaluate FTIR as a tool for the characterization of APLs

2 Literature review

2.1 Pyrolysis process

In the pyrolysis process, biomass is rapidly heated to a temperature > 400 °C in the absence of oxygen, which turns the biomass into charcoal, light non-condensable gases, methane (CH_4), hydrogen (H_2), carbon dioxide (CO_2), etc. This gaseous mixture is known as syngas and it could be combusted in boilers, engines, and/or turbines. There is another type of production from the pyrolysis process, condensable gases. These gases, when condensed, resulting in what is called pyrolysis liquid. Due to the high water-content in the pyrolysis liquid, it is separated into two phases, aqueous and organic. The aqueous phase is known as aqueous pyrolysis liquid (APL) [7], containing up to 75% of the energy from biomass [8].

The organic phase or so-called bio-oil (or biocrude) consists of a complex mixture of oxygenated hydrocarbons and nitrogenous compounds, such as aromatics, short-chain carboxylic acids, ketones, and sugars, depending on the type of biomass that was used in the feeding of the pyrolysis process [9]. The organic phase (biocrude) is considered a source of energy and chemical production; it has also been considered for use in biopesticides and as an acidifier for manure [10]. Figure 2.1 shows the main three products of pyrolysis of biomass.

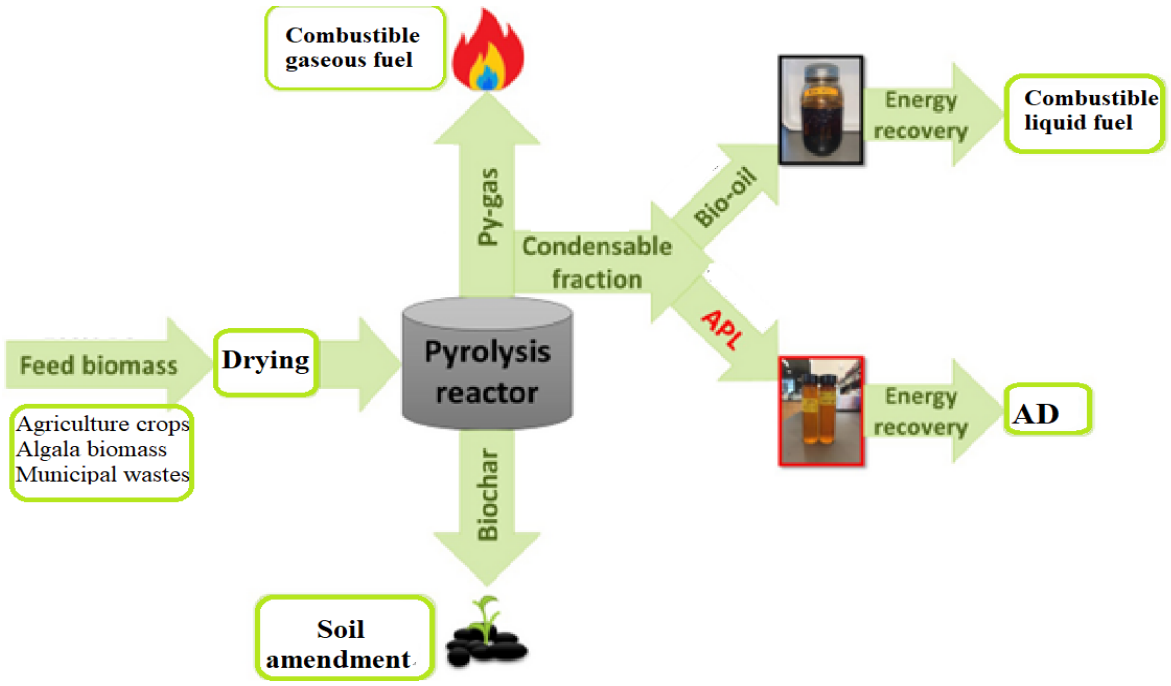

Figure 2.1: Pyrolysis process for biomass and its products (biochar, py gas, and condensable gas: APL& Bio-oil) [11].

The lighter fraction of the bio-oil, APL, has a low heating value compared to conventional fuels due to its high oxygen and water contents (up to 50% by weight) which is detrimental for

ignition, so it cannot be used directly as fuel. The steps of biomass pyrolysis are summarized in Figure 2.2.

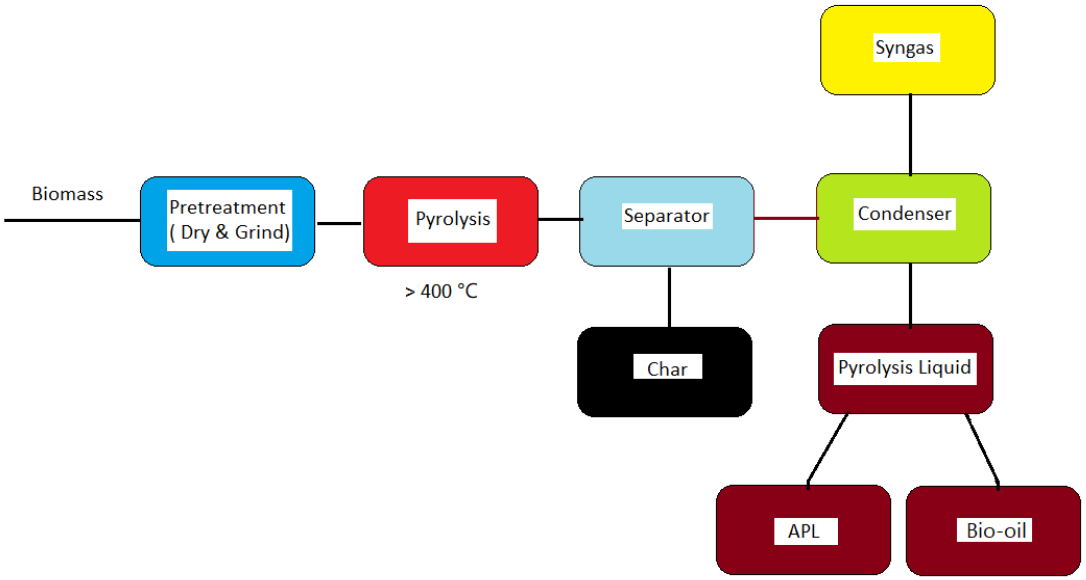

Figure 2.2: The main steps of biomass pyrolysis and its products.

The low heating value is not the only challenge associated with the use and marketing of APL as a biofuel. Containing organic acids and some solid particles (char) can erode turbine blades, resulting in lower efficiency and slower combustion. Moreover, the complex components in the synthesis of (APL) can lead to forming larger particles, resulting in higher viscosity and slower combustion [8].

One beneficial use of APL that is currently under study is to recover energy from APL (rich in organic matter) via (AD) [12]. APL contains organic substances, making it suitable as an AD substrate to convert these organic compounds to CH_4. However, APL comprises numerous complex organic compounds and ammonia nitrogen (NH_3-N), which are known to inhibit CH_4-producing microbes [12]. Therefore, treatments are needed before using the APL in the AD system.

2.2 Pretreatment APL

AD is becoming an increasingly popular technology to produce energy from organic waste in the form of energy-rich biogas (CH_4)

Aqueous pyrolysis liquid (APL) is a product with a high COD content, produced from the pyrolysis of biosolids. APL is a light- to dark-brown material consisting of more than 400 complex organic compounds in addition to ammonia nitrogen (NH3-N). Among the beneficial uses of APL is feed-in anaerobic digestion. Anaerobic digestion is a desirable

option to exploit and treat APL to produce more biogas. However, APL organics are known to act as an inhibitor of CH_4-producing microbes, so some treatments must be done on APL to reduce the inhibitors that hinder biogas production. [13]

APL products are mainly oxygenated compounds comprised of a complex combination of alcohols, acids, ketones, aldehydes, phenols, esters, ethers, furans, and water. The composition extensively depends on the source of biomass and the operational conditions of the pyrolysis process. [14] [15]. The characteristics of APL limit their use as fuels, therefore upgrading operations (removal of oxygen) are required.

2.3 Decomposition of APL

Pyrolysis liquid splits into two phases: light non-aqueous organic phase (bio-oil), and (APL). To improve the anaerobic digestibility of APL, pretreatments or co-treatment have been verified to eliminate inhibitors and toxic components. These treatments include acidic, alkali, hydrogenation, and electrochemical treatments [16].

2.3.1 Electrochemical Treatment

Electrochemical methods have mostly been applied for analytical and synthetic purposes in organic and biological chemistry. Such methods have been used in natural products chemistry, where three main areas of application may be identified and electro synthetic techniques for environmental remediation applications [17]. The first field involves electroanalytical methods for identifying and determining natural products and/or their metabolites using direct electrochemical methods or in combination with other methods, such as liquid chromatography with electrochemical detection [18]. The second field is molecular electrochemistry, which is concerned with unraveling the mechanisms that involve electrochemical processes and offering insights into the electrochemistry and electrochemical reactivity of natural products [19]. This mechanistic knowledge can also be used to examine the pharmacological action of natural compounds, measuring characteristics such as antioxidant capability [20]. The third application area studies the interactions between natural products and related species directly involved in their biochemical activity using electrochemical techniques [17].

2.3.2 Acid Esterification

The esterification process is a method of upgrading that converts carboxylic acids in bio-oil to esters. It can not only reduce the corrosiveness of bio-oil, but it can also prevent various processes catalyzed by these acids, such as oligomer or polymer formation [21]. Because of its simplicity of use, low investment cost, and avoidance of secondary reactions that may occur at high operating temperatures, this treatment might be an attractive proposition for improving bio-oil properties.

Even though the fact that just a few research on bio-oil upgrading by esterification reaction have been published thus far, this upgrading approach is still a hot issue. Weerachanchai et al. [22] used H_2SO_4 as a liquid acid catalyst to esterify bio-oil obtained from rapid pyrolysis of sewage sludge.

Finally, it is reasonable to conclude that the esterification procedure has enhanced some qualities of bio-oil. It should be emphasized that various crucial aspects, such as catalyst type and esterification conditions, might have an impact on the efficacy of bio-oil upgrading. Furthermore, the complex compositions of bio-oil could be responsible for the occurrence of side reactions that may affect the qualities of the upgraded oil.

2.3.3 Alkaline Treatment

There have only been a few investigations on alkaline treatment of bio-oil. Most studies concentrate on alkaline pretreatment, which involves adding an alkali, such as NaOH, to the biomass before pyrolysis [23].

Pre-treated bio-oil data demonstrate that the alkaline treatment affects the composition and fiber structure of the bio-oil. This pretreatment eliminates hemicellulose, destroys lignin, and leaves ordered residual fibers [24]. The most common alkali catalysts are Na2CO3, K2CO3, NaOH, and KOH, which boost bio-oil output while decreasing char formation [25].

Some studies focus on alkaline treatment for phenol extraction. As the alkaline concentration rises, so do the phenol portions. The increase in temperature and concentration, on the other hand, reduced the yield of primary alcohols [26].

2.3.4 Hydrogenation

Bio-oil must be enhanced before it can be used as a liquid fuel. Its corrosiveness must be reduced, and its chemical and thermal stability must be improved [27]. However, upgrading this bio-oil can be problematic due to its quick catalyst deactivation and low conversion efficiency (due to the high unsaturation degree) [28]. Before catalytic cracking, hydrogenation is used to reduce coke formation and promote catalyst activation. With this technique, the oil phase's selectivity improves, and its hydrocarbon content rises [29].

Many investigations have been conducted to study bio-oil hydrogenation. Chen et al. [28] investigated the application of bimetallic and monometallic catalysts to improve bio-oil saturation. The best results were obtained using bimetallic catalysts, particularly Pt-Ni/SiO2 and Pt-Fe/SiO2 catalysts. The addition of Ni accelerated phenol conversion and the creation of cyclohexane. In addition, Fe addition improved the AcOH conversion. The study found that Pt-Fe catalysts should be employed when the bio-oil is acidic, while Pt-Ni catalysts should be used when the bio-oil is phenolic.

Zhang et al. [30] investigated the effects of varied Ni/Pt ratios in hydrogenation and their subsequent impact on catalytic cracking. Because of the conversion of phenolics in bio-oil into highly hydrogenated products, catalytic cracking has improved.

Hydrogenation-Esterification (OHE) is often performed in a single step to transform bio-oil molecules (acetic acid, furfural, hydroxy acetone, ethanediol, phenol, and water) into stable and combustible oxygenated organics such as alcohols and esters. According to Ying et al. [31], the OHE efficiently converts ketones, aldehydes, phenols, and acids into alcohols and esters. Chen et al. [32] got similar results. As a result, the bio-oil obtained was primarily composed of alcohols and esters, which is advantageous for catalytic cracking and steam reforming.

2.3.5 BMP test

AD is a technique for stabilizing organic matter while recovering energy in the form of CH_4. Biochemical CH_4 potential (BMP) tests are widely used to measure a substrate's CH_4 potential and biodegradability of wastewater and waste biomass [33]. A substrate is mixed with an anaerobic bacteria culture, which is generally collected from an active digester. The bottles are then kept at a constant temperature of 35–55 °C and continually mixed for 30–60 days [34] [35]. During the testing time, CH_4 and CO_2 are produced as a result of the anaerobic degradation of the substrate's organic components. The CH_4 produced by the substrate is then measured and the CH_4 potential can be calculated by subtracting the CH_4 volume from a blank. This potential is represented as per mass of volatile solids added, or chemical oxygen demand (COD). Furthermore, the substrate may be represented in terms of biodegradability by dividing the cumulative CH_4 volume by the theoretical cumulative CH_4 volume, which is calculated using the chemical ratio of 1 g COD = 0.35 mL CH_4 at standard temperature and pressure conditions (STP) [36]. Since the popular technique of Owen et al. [33] was developed, BMP tests have been used to analyze a wide range of substrates and have become essential tools for analyzing possible pre and post digestion treatment options.

Syringe Test

In the syringe method, 100 mL plastic medical syringes have been used as reactors. The overpressure inside the reactor drives the piston until the pressure accumulation is balanced with atmospheric pressure [37]. The syringe's mark levels are used to read the volume of biogas. The gas can be released or reinjected into another syringe to analyze it. In addition to analyzing the process, another benefit of releasing the generated biogas is that headspace pressures and CO_2 solubility in the bioreactor vessel may be maintained to a minimum.

BMP tests require (1) a temperature-controlled environment, (2) appropriate mixing, and (3) suitable incubation time for biodegradable material degradation [38]. During gas measurement, the syringes are normally taken out from the temperature-controlled environment. This temperature change can simply disrupt the equilibrium between the gas and liquid phases, resulting in changes in headspace gas concentration and AD microorganisms.

2.4 Characterization of APL

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

One of the pieces of devices based on infrared spectroscopy is the Fourier transform infrared spectrometer (FTIR). It is the most recent and preferable type of dispersive spectrometer. Its high precision, accuracy, speed, improved sensitivity, simplicity of operation, and sample non-destructiveness are all reasons for its performance. The infrared spectroscopy technique is based on the atomic vibrations of a molecule, which only absorbs particular frequencies and energy of infrared radiation. Although various compounds have distinct infrared spectrums, FTIR can identify and classify them [39].

FTIR uses a mathematical procedure (the Fourier transform) to convert raw data (interferograms) into the real spectrum. The FTIR technique is used to determine the infrared spectrum of a fuel sample's transmission or absorption. The presence of organic and inorganic components in a sample is also determined using FTIR [39].

Lievens et al. [40] tested the distribution of carbonyl groups in bio-oil samples generated from pyrolysis of bark, mallee wood, and leaves using FTIR and GC-MS. The results match the feedstock's cellulose, hemicellulose, and lignin compositions.

3 Materials and methods

3.1 Analytical Methods

3.1.1 pH

pH was measured using a Beckman 390 pH meter. To calibrate the pH meter, buffer solutions with pH 4.0 and 7.0 were employed. The samples were combined at room temperature. While the pH was measured, the samples were completely swirled and constantly stirred.

3.1.2 COD

COD was measured using commercial COD kits (Merck's Spectroquant (R)). Appendix D illustrates a full experimental procedure and a table of COD values for all relevant materials tested.

3.2 Material Characterization

3.2.1 Inoculum

The inoculum used for BMP tests was supplied by Lindum biogas production plant in Drammen, Norway. The inoculum was digestate sampled from the anaerobic digester at the facility. The plant is operated as a continuously stirred-tank reactor (CSTR), treating sewage sludge from surrounding municipalities and co-digesting this with waste fats from the food industry and fish ensilage. More than 85% of volatile solids in the feedstock come from sewage sludge. The feedstock went through a thermal hydrolysis process before being fed into the bioreactor. The bioreactor has a hydraulic retention time (HRT) of about 20 days.

The inoculum was sieved using a 2 mm sieve and degassed at 30℃ for 6 days to reduce biogas production from the inoculum.

3.2.2 Pyrolysis liquids

The pyrolysis liquids used in this thesis were supplied by Scanship AS. They were produced by pyrolysis of dried and pelletized digestate from Lindum biogas production plant (see 4.1.1). The material was pyrolyzed using the Biogreen ® technology at 500, 600, and 700°C. The liquids were collected by condensing the pyrolysis gas to 8-10°C.

3.3 Experimental Approach

3.3.1 Electrochemical Treatment

To investigate the decomposition of APL, the electrochemical method is applied. A three-electrode cell was used for electrochemical decomposition. The cell had a volume of 100 mL and a temperature of 35°C in the reactor. Both the working and the counter electrodes were made up of two stainless-steel grids (Alfa Aesar). All measurements were made using a reference electrode made of Ag/AgCl (3.0 M NaCl) [41]. Figure 3.3 shows the experimental

setup. To manage and control the trials, a laptop with the Gamry framework software (version 7.8.6) is used.

Figure 3.3: Experimental setup of the electrochemical test. From the left: stopper with electrodes, the cell containing APL 700 connected to potentiostat cables.

Cyclic voltammetry

Cyclic voltammetry (CV) could be used to investigate the electrochemical nature of the pyrolysis condensate and electrodes. CV was performed using a potentiostat (Gamry Instruments, Pennsylvania, USA) to determine the oxidation-reduction potentials that have a significant impact on the pyrolysis condensate decomposition. Even though the composition and oxidation-reduction potential of the compounds in the condensate are ambiguous, the voltammogram is presented as a preliminary finding.

In this thesis, CV was used to establish the voltage at which suitable hydrolysis reactions could be found, denoted by a peak of current experiment used cyclic voltammetry to establish an appropriate voltage for the potentiostatic test. Table 3.1 illustrate the condition under which the CV test was run.

Table 3.1: Experimental conditions for the CV test.

Parameters	**Characteristics**
Electrolyte	APL 700
Applied Voltage	-1.0 : 1.0 V
	-2.0 : 2.0 V
Scan Rate	1 mV
	10 mV
	100 mV
Electrode Material	Stainless Steel

Reference Electrode	AG/AgCl
Volume of Solution	100 mL

The potentiostatic test of the electrochemical method was performed on the samples as shown in Table 3.2, based on the CV data.

Table 3.1: Experimental setup for the electrochemical test.

Parameters	**Characteristics**
Electrolyte	APL 700
Applied Voltage (V)	1.0
	1.5
	2.0
Time of the test (Hours)	2
	1
	0.5
Electrode Material	Stainless Steel
Reference Electrode	AG/AgCl
Volume of Solution (mL)	100

Because of its high energy content and stability, APL 700 was the best further sample for the electrochemical test. APL 700 was divided into three samples to be tested under different conditions. The first sample was tested at 1 V for 2 hours, the second at 1.5 V for 1 hour, and the third at 2 V for 30 minutes. Another electrochemical test was performed for half an hour using the same voltages to reduce the variable parameters.

3.3.2 Acid decomposition

The experiment's main objective was to break down or change the chemical structure of APL by combining sulfuric Acid (H_2SO_4) (95-97 %) and nitric Acid (HNO_3) (70 %). The acids were added separately and directly to the APL in three different volume fractions (3, 1, and 0.5%). The reaction was carried out in a thermoreactor (Spectroquant, TR 620) at a temperature of 80 ℃. Table 3.1 summarizes the experimental settings.

Table 3.1: Acid decomposition experimental conditions.

Parameter	Unit	Value
Reaction temperature	℃	80
Reaction time	h	2
Total volume of the APL	mL	5
Sulfuric acid loading	%vol. of H_2SO_4	0.5
		1.0
		3.0
Nitric acid loading	%vol. of HNO_3	0.5
		1.0
		3.0

3.3.3 Biomethane potential test (BMP)

The main purpose of this experiment is to examine APL biomethane potential and evaluate the degree of APL decomposition to compare it with the previous treatment methods. A combination of APL, feed, and inoculum was used. As an AD culture for the BMP test, the inoculum was provided from Lindum biogas plant in Drammen. To improve the inoculum characteristics, vitamins, minerals, and salts were added.

For the BMP test, 100 mL plastic medical syringes were used as AD reactors. The test requires the use of a blank (inoculum without substrate), a control (inoculum with apple juice), and a substrate (inoculum with apple juice and APL). The syringes were filled with the required amount of inoculum (28 mL) and substrate, a rubber stopper was used to prevent leaking and maintain the anaerobic environment. Before beginning the test, the solution was properly mixed and hung on a rack (Figure 3.4). For each loading, triplicates were performed. The syringes were placed and kept in an incubator at a temperature of 35°C. The blank is used to measure the generated background CH_4 from the organic material in the inoculum. The test was split into two stages: (1) BMP test for acid-treated APL and (2) BMP test for electrochemical-treated APL. Appendix B shows the different combinations of the treated APL samples for the BMP test. For acid-treatment, the samples were treated with (H_2SO_4) and (HNO_3), with a concentration of 0.5, 1, and 3%. For the electrochemical treatment, the samples were treated with 1, 1.5, and 2 V.

Figure 3.4: BMP syringe test with inoculum and substrate (apple juice &APL)

The overpressure inside the syringe drives the piston until the pressure accumulation is balanced with atmospheric pressure. In the first three days, the biogas produced was measured daily using the syringe's mark levels. The stored biogas was transferred to a new syringe using an integrated gas syringe to analyze the biogas composition. Chromatography (GC) was used as well as a CO_2-trap to measure CH_4 composition. By comparing the results of the two methods, it demonstrated that using the CO_2-trap gives similar results to the GC method. See Appendix C.

CO_2-trap

Preparation of NaOH solution for CO_2-trap:

All work was carried out inside a fume hood while wearing protective equipment.

a) A solution of 3 M NaOH was prepared. After weighing the necessary amount of NaOH, it was mixed with ¾ of the required total volume of distilled water (e.g., 120 g NaOH in ¾ of 1 L water).

The heat generation following the dissolution of NaOH in water was high, so adding small amounts of supplementary water followed by mixing is recommended. When the NaOH was completely dissolved, the whole amount of remaining water was added and mixed well.

b) 0.4 % Thymolphthalein pH-indicator solution was prepared (40 mg in 9 mL ethanol 99.5% followed by addition of 1 mL water). Thymolphthalein is insoluble in water, but it is freely soluble in ethanol.

c) NaOH solution containing the pH indicator was prepared, by mixing 5 mL of the Thymolphthalein solution per 1 L, 3 moles NaOH solution (the colour turned blue).

As for the trap itself, 6 mm ID tubing is needed to fasten to the syringe so that it is gas-tight. This tubing had then to be connected to the tubing that goes into the alkaline solution inside the trap (A 500 mL bottle with the alkaline solution) as shown in Figure 3.5. Then the CO_2 got absorbed by the alkaline solution and the volume from the rest of the gas displaces the volume in the upside-down measuring cylinder that was connected through another tubing.

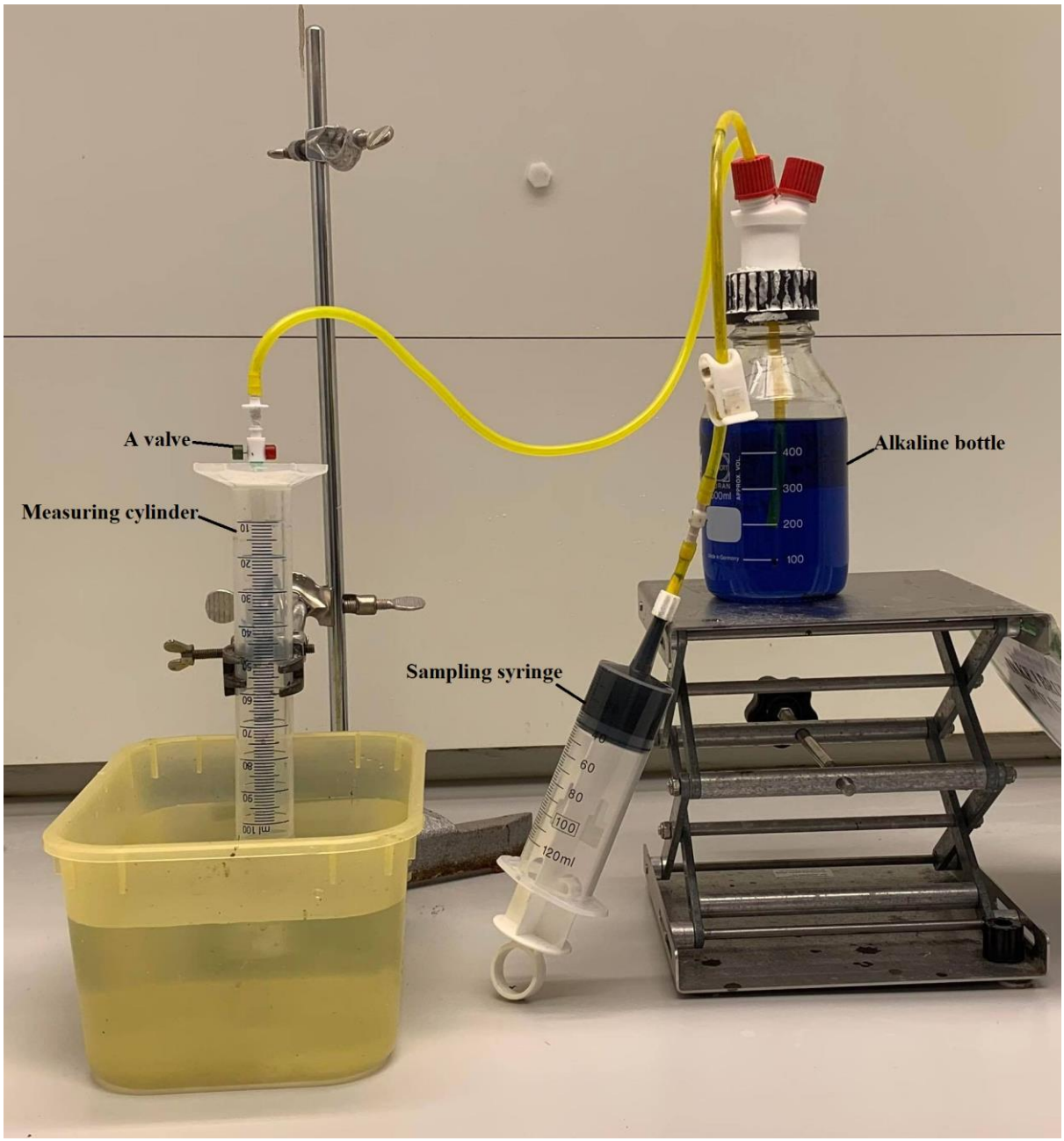

Figure 3.5: CO_2-trap unit

The syringe test was used to determine the trend and influence of treated and untreated APL on biogas production.

The organic loads of the BMP test were determined using the volume ratio of the apple juice to the APL. The reason for performing the volume calculation is that it compares the degree of decomposition more effectively.

Eq. (3.1) was used to evaluate the performance of CH_4 production per substrate in mL.

$$CH4_{exp} = V_{CH_4} - V_{CH_{4,blank}} \quad (3.1)$$

Where:

$CH4_{exp}$= Biochemical Methane Potential (mL of CH_4).
V_{CH4} = Volume of CH_4 produced in a syringe (mL).
$V_{CH4, blank}$ = Volume of CH_4 produced in the blanks (mL).

The theoretical BMP values were calculated using stoichiometric equations for maximal biogas production based on the elemental composition of the samples (C, H, N, and O). Eq. (3.2) gives the theoretical value of CH_4 at laboratory conditions:

$$CH4_{th} = \frac{n_{CH_4} RT}{p} \quad (3.2)$$

Where:

$CH4_{th}$ = the theoretical production at the laboratory

Conditions.

R = the gas constant (R = 0.082 atm L/mol K).

T = the experimental temperature, 35 °C (308 K).

p = the atmospheric pressure (1 atm).

n_{CH_4} = the amount of molecular CH_4 (mol) determined

from Eq. (3.3):

$$n_{CH_4} = \frac{COD}{64(g/mol)} \quad (3.3)$$

The BMP was finished when a daily production of less than 1% of total production occurred, as shown in Eq. (3.4), where "n" represents the day of the experiment.

$$\text{Production \%} = \left(\frac{acc.prod.(mL)_n - acc.prod.(mL)_{n-1}}{acc.prod.(mL)_n} \right) \text{ x } 100 \quad (3.4)$$

3.4 Characterization method: FTIR

The FTIR analysis method employs infrared light to scan test samples and detect chemical characteristics [42].

In this experiment, ABB FTIR spectrometer type MB-3000 was utilized for characterization (Figure 3.5). Calibration of an empty cell at a scan step of 30 and a wavelength span of 500 – 4000 cm-1 was used in the device configuration. The calibration is utilized as a reference spectrum in the database. A metal lid is put over a drop of the sample on the ATR crystal.

FTIR sampling and testing process

Testing Process:
Step 1: Insert the sample into the FTIR spectrometer. The spectrometer focuses IR beams on the sample and detects how much of the beam, and at what frequencies, the sample absorbs.

A tiny slice of the material must be removed, or the sample must be thin enough to allow infrared light to pass through.
Reflectance methods can be utilized on some samples without causing any harm to the material. Samples amenable to reflectance include residues, stains, or coatings on a quite smooth reflecting surface, or slightly malleable materials thin enough to fit beneath the microscope's attenuated total reflectance attachment.
Step 2: The reference database contains hundreds of spectra that may be used to identify samples. This procedure may be used to identify the molecular identities.
FTIR Sampling
FTIR analysis can analyze samples as small as 10 microns. Because of the small sample size, it is possible to identify particles, residues, coatings, or fibers at a cheap cost. FTIR analysis may also determine levels of oxidation or degrees of cure in certain polymers, as well as impurities or additives [42].

Figure 3.5: Laboratory FTIR spectrometer instrument

4 Results

This chapter summarizes the results from the experiments, most of the results are shown graphically and analyzed using MS Excel.

4.1 Electrochemical Treatment for APL

The results from the potentiostatic tests using APL 700 are presented in this section. The tests were run using three different applied voltages (1.0, 1.5, 2.0 V) with different experiment times (0.5, 1.0, 2.0 hours) (Table 3.1). CV was run in various ranges to find the optimum voltage. Peaks in the CV indicate that the bio-oil is reacting to the applied voltage.

4.1.1 Cyclic Voltammetry

CV was initially performed in the potential range of – 2.00 V to + 2.00 V at a scan rate of 10 mV/s for three cycles (Figure 4.1).

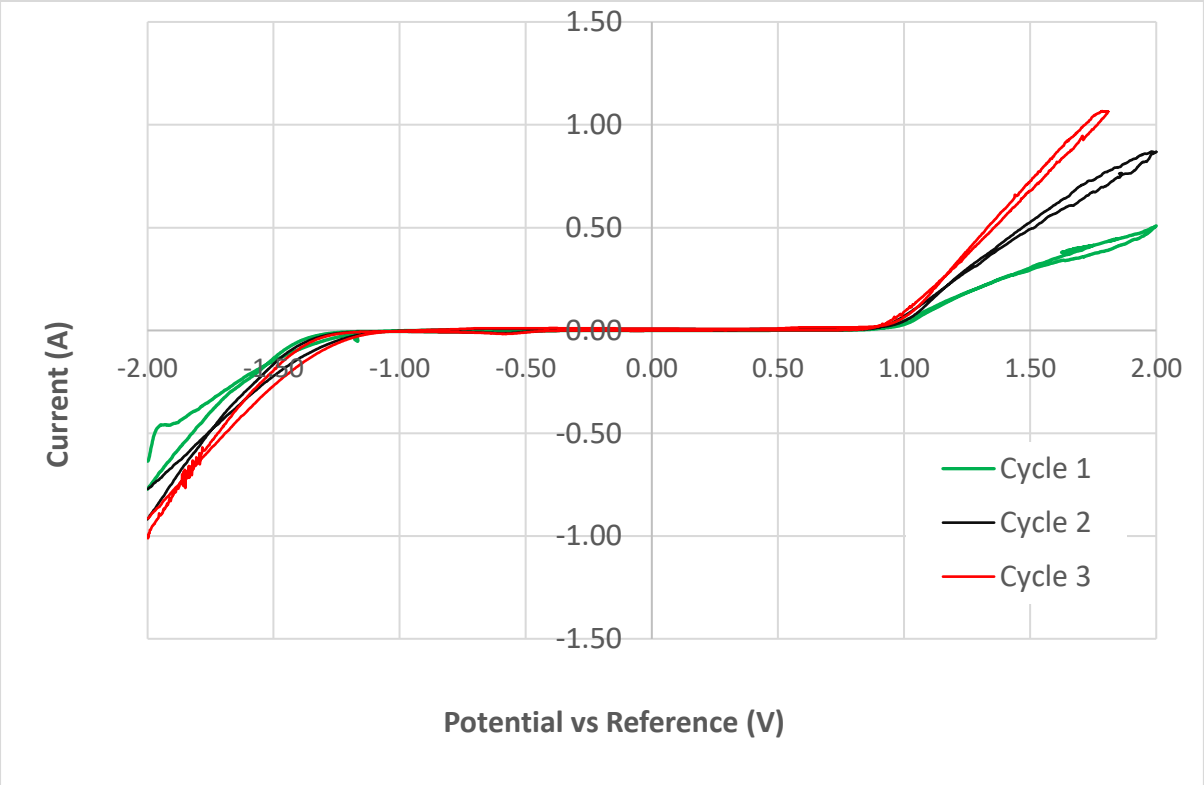

Figure 4.1 Cyclic voltammogram at the potential range -2.00 to +2.00 V

Figure 4.2 reveals two peaks at -0.6 V and +0.6 V, respectively, reduction and oxidation peaks. The reductive current was around 2 mA, while the oxidative current was close to 7 mA.

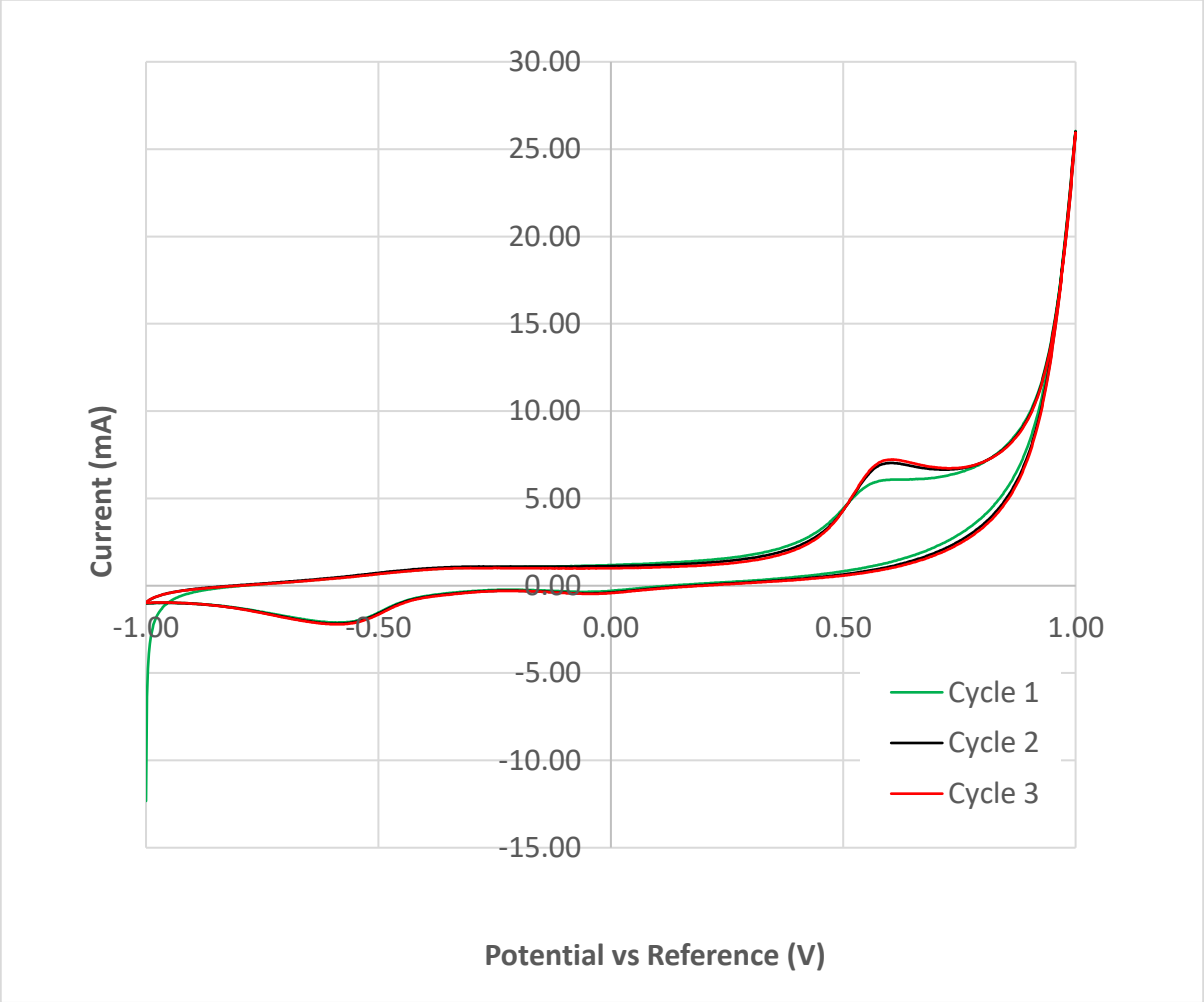

Figure 4.2 Cyclic voltammogram at the potential range -2.00 to +2.00 V

4.1.2 Electrochemical Treatment

Figure 4.3 depicts the current response of the electrochemical treatment at various applied voltages for 30 minutes. The current response for 1.0 V is roughly 1 mA, whereas, for 1.5 V, the current response begins around 70 mA and declines to 15 mA. The highest current response is achieved at 2.0 V; the current begins at a value of 60 mA and rises to roughly 320 mA.

The pH for all samples before the test was 9.28 and increased after the decomposition tests. The highest pH increase is related to the electrochemical 2.0 V treatment with 9.45.

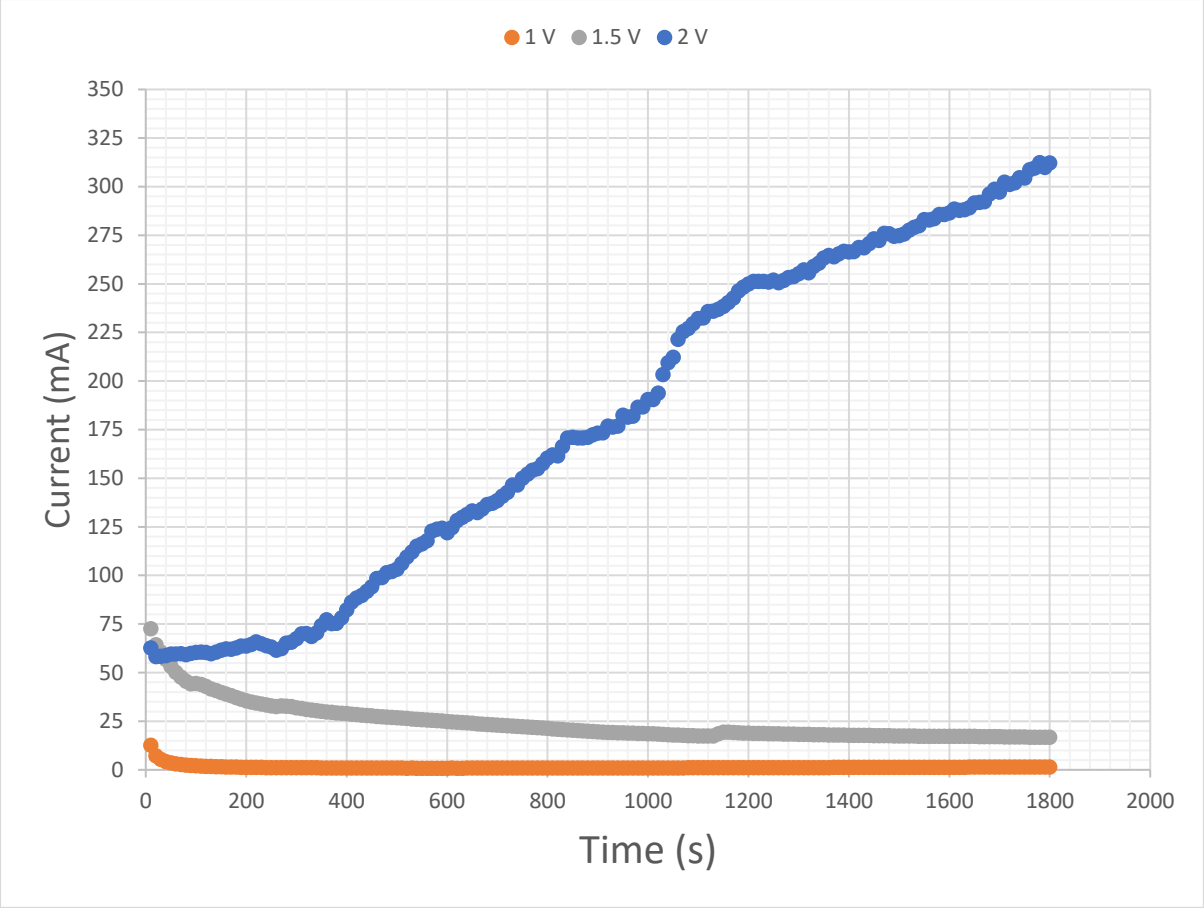

Figure 4.3 Current response. Electrochemical method for APL 700 decomposition in different voltages for half an hour.

The test was performed two times under the same voltages, but with different run-time (2, 1, and 0.5 hours) to check the reproducibility of the results. Figure 4.4 illustrates the current response for the three samples with different voltages and time. Similarly, to the previous test, the current response for 1.0 V with 10 mA began to rise after 1.5 hours to achieve 160 mA. For 1.5 V, the current response started at about 70 mA and raised to roughly 450 mA.

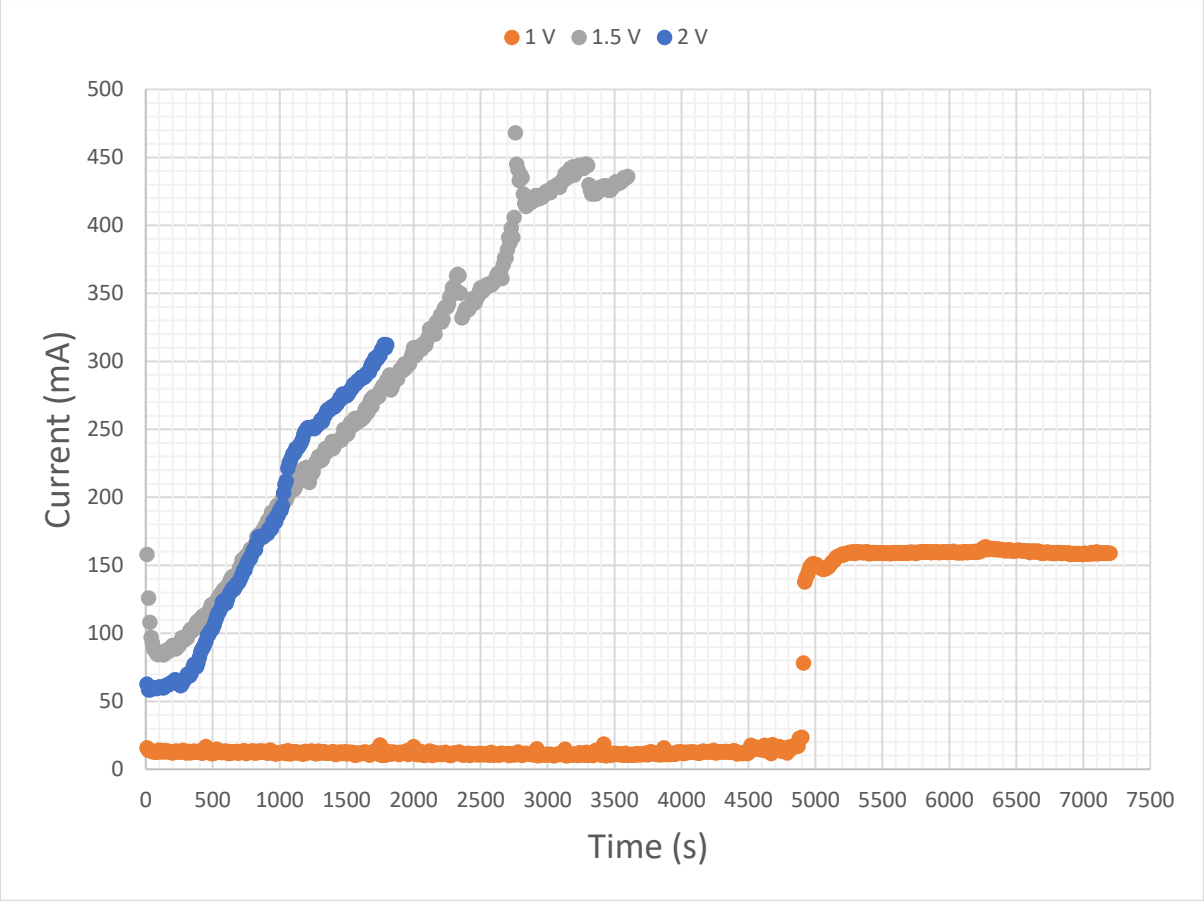

Figure 4.4 Current response. Electrochemical method for APL 700 decomposition in different voltages and different times.

4.2 Alkaline Treatment

Although the alkali treatment was done as part of a third-semester project (Techniques for Bio-oil Characterization and Decomposition) [43], the preliminary results were not promising. The results of alkali treatment were inconclusive from a thermal standpoint since heat treatment of alkaline had little influence on the composition of the samples. The results supported the use of alkaline for the treatment of biomass prior to liquefaction rather than as a bio-oil decomposition method.

4.3 Acid Tretment for APL

pH

Table 4.1 shows the values of pH for APLs before and after acid-treated. The pH values decreased after adding the acid to the samples. The average value of pH of treated samples reminded lower than that of pure APLs.

Table 4.1: pH value for the acid decomposition at 0.5, 1.0 and 3.0%.

Sample	Decomposition acid	%vol.	pH	Sample	Decomposition acid	%vol.	pH
APL 500	H_2SO_4	-	8.96	APL 500	HNO_3	-	8.96

		0.5	8.87			0.5	8.92
		1	8.72			1	8.82
		3	7.46			3	8.14
APL 600	H_2SO_4	-	8.88	APL 600	HNO_3	-	8.88
		0.5	8.47			0.5	8.77
		1	8.16			1	8.71
		3	7.67			3	8.48
APL 700	H_2SO_4	-	7.95	APL 700	HNO_3	-	7.95
		0.5	7.89			0.5	7.90
		1	7.67			1	7.92
		3	7.48			3	7.08

4.4 BMP test

The BMP test will produce biogas (CH_4 and CO_2) by partially oxidizing degradable organic matter. We assume pH and electrochemical treatment to break down some complex-undegradable organic materials, making them more bio-available to anaerobic bacteria. As a result, increased biogas production was expected after the treatments; as proof, the BMP test examined the breakdown of digested bio-oil before and after treatment. The experiment on theoretical CH_4 generation is depicted in the results charts.

4.4.1 BMP test for electrochemical treated APL

Before and after the electrochemical test, the BMP test was used to evaluate the decomposition of APL 700. Table 4.2 shows the experimental setup for this test.

The experimental results were obtained after 43 days when the BMP tests resulted in less than 1% of the daily production.

Table 4.2: Experimental conditions for the electrochemical test.

Electrolyte	**Applied Voltage (V)**	**Test time (minutes)**
APL 700	1.0	120
	1.5	60
	2.0	30

By comparing the experimental productivity from the BMP test against the theoretical productivity derived COD measurement, the ability of theoretical methodologies for calculating CH_4 yield from substrate has been investigated and calculated.

Figure 4.5 shows the BMP theoretical-CH_4 potential vs experimental-CH_4 potential for APL 700 that was treated with the electrochemical method. The results show that the 2.0 V applied voltage has the highest productivity than the theoretical production. The productivity of 1.5 V has a value close to the original sample, APL 700.

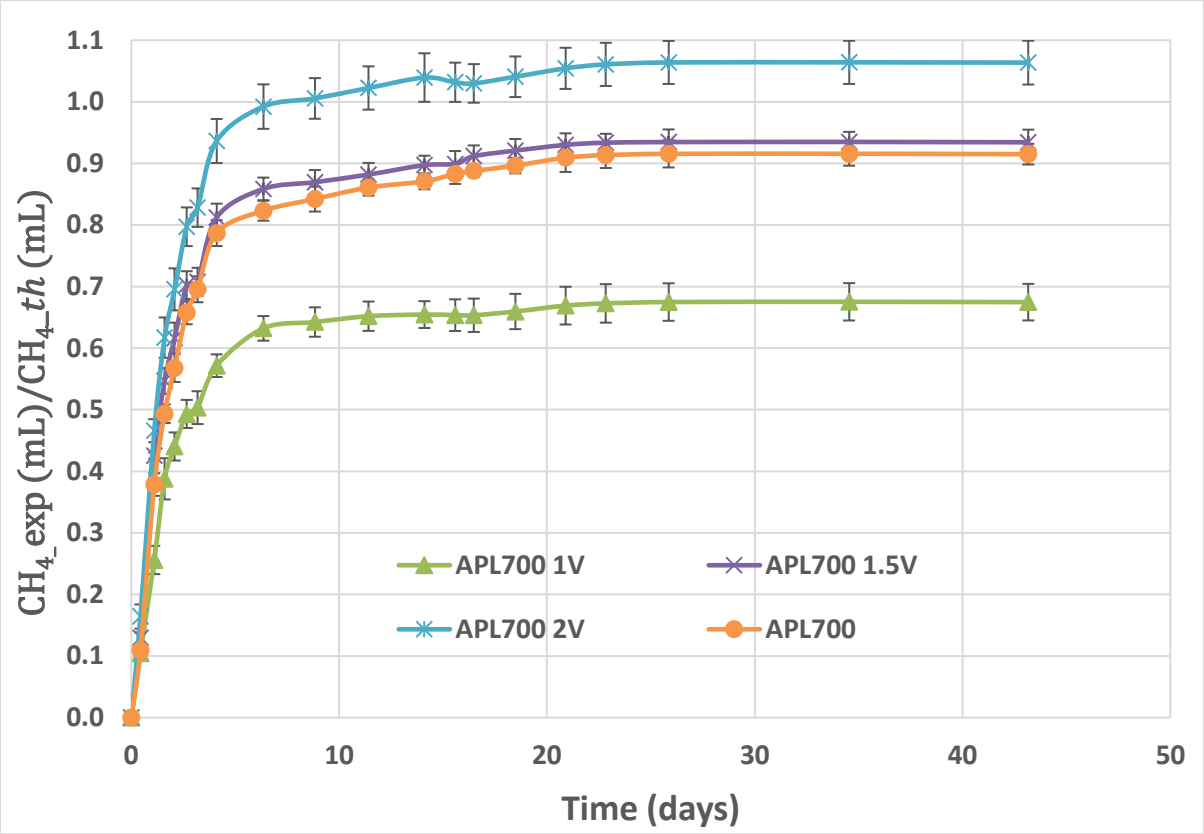

Figure 4.5: BMP theoretical CH_4 potential vs experimental methane potential for APL 700 that was treated with the electrochemical method

4.4.2 BMP test for Acid treated APL

The test lasted 24 days and was carried out at 35°C. The experiments were conducted to determine the potential for CH_4 production from the acid treated APLs. Results from three different concentrations treated samples are shown in Figures 4.5, 4.6, and 4.7 for APL 500, APL 600, and APL 700, respectively.

The results in Figure 4.6 for APL 500 showed no improvement after treatment; the pure APL 500 already has the highest CH_4 production value, at about 0.85 of the theoretical maximum production. Thus, the values which were obtained from H_2SO_4 treatment are much lower than the sample before treatment. The treatment with HNO_3 with the concentration 1 and 3% leads to good results, even if the improvement is negligible.

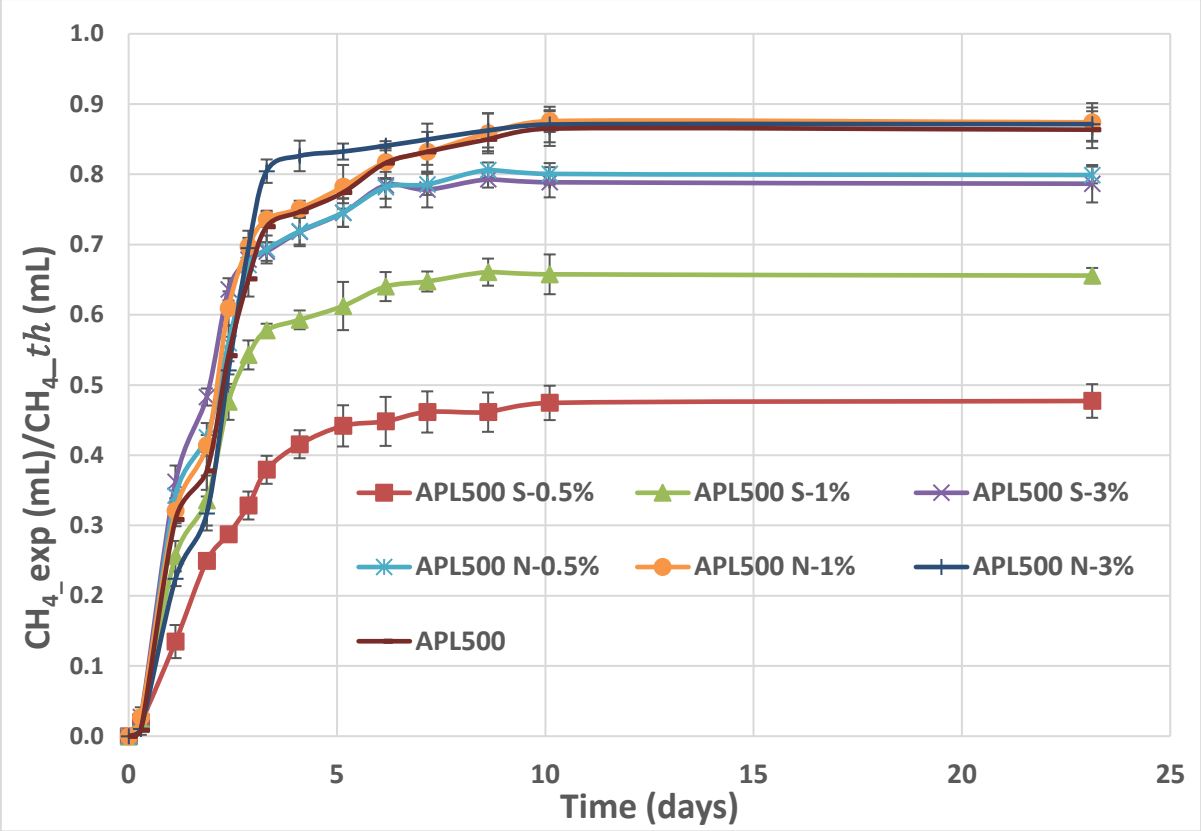

Figure 4.6: BMP theoretical CH_4 potential vs. experimental menthane potential for acid-treated APL 500

The result of this experiment is then compared with the APL 600 and APL 700. The results are substantially better than that of APL 500. Figure 4.7 shows that APL 600 which was treated with 1% Vol. HNO_3 gave the best productivity with 0.95 of the theoretical production, while the pure APL 600 produced 0.88 of the theoretical CH_4 production. ALP 600 treated with H_2SO_4 gave results less than that we got from the pure sample.

A similar pattern of results was obtained from APL 700. Figure 4.8 shows the treated with 0.5% Vol. HNO_3 gave the best result and was greater than the expected CH_4 production.

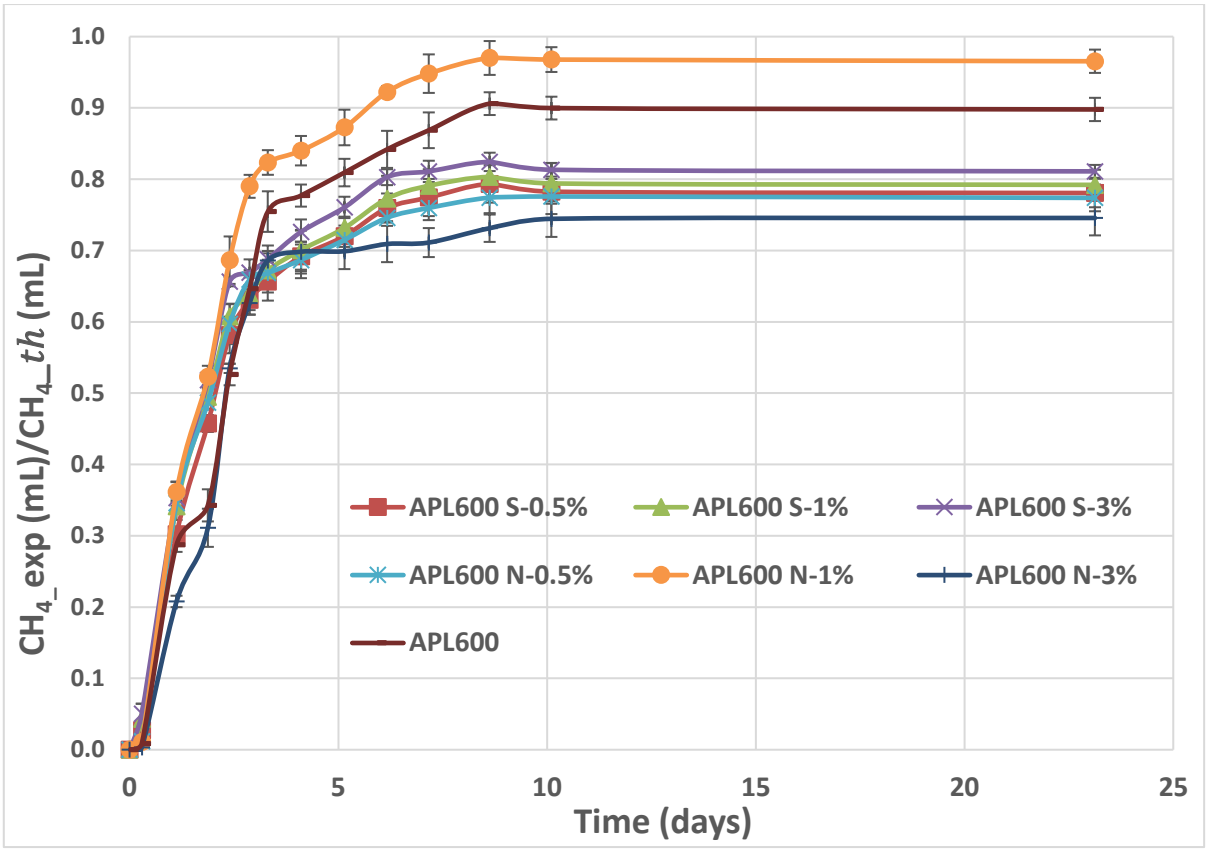

Figure 4.7 BMP theoretical CH_4 potential vs. experimental menthane potential for acid-treated APL 600

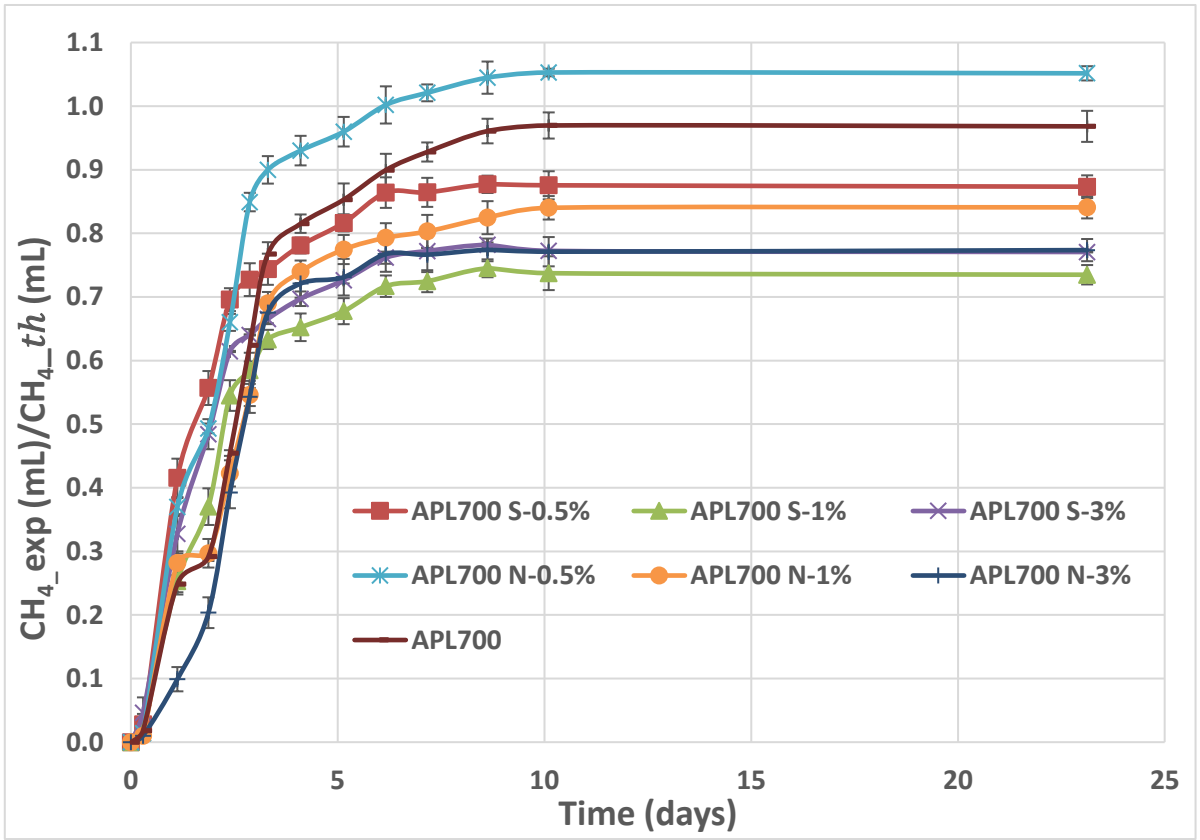

Figure 4.8: BMP theoretical CH_4 potential vs. experimental menthane potential for acid-treated APL 700

4.5 FTIR

The results show the characterization of the APL before and after the treatment. The transmittance versus wavenumbers is plotted. Different peaks along the wavelength can be used to identify functional groups. Peak changes indicate the loss of functional groups or other structural changes that occur during the forming of molecular species or oxidation products. Table 4.1 is used to analyze the FTIR results for all samples to determine the functional groups [44].

Table 4.1: Typical bio-oil Absorption Bands in FTIR Spectra

Wavenumbers/cm^{-1}	**Functional groups**	**Vibrations**	**Compound class**
3600-3200	O−H	Stretching	phenols, alcohols, water, carboxylic acids, amides
3100-3000	C−H	Stretching	aromatics
2980-2870	C−H	Stretching	alkanes
2350-2000	C≡C	Stretching	alkynes, cyanides
1850-1650	C=O	Stretching	aldehydes, ketones, carboxylic acids, esters
1650-1580	C=C	Stretching	alkenes
1550-1490	NO_2 N−H C=C	Stretching Bending Stretching	nitrogenous compounds, aromatics
1470-1350	C−H	Bending	alkanes
1300-950	C−O O−H	Stretching Bending	alcohols, ethers
915-650	C−H	In plane bending	aromatics

4.5.1 FTIR for electrochemical treated APL

Figure 4.9 illustrate FTIR spectra of APL 700 before and after the electrochemical treatment. The significant differences between the pure and treated APL 700 spectra are the appearance of the peaks associated with the C=C groups in alkenes compounds at 1650-1580 cm^{-1}, as well as the appearance of the peaks associated with the O−H and N-H groups at 3200-3600 cm^{-1}. When more voltage is applied, these peaks decrease. The samples treated with 1.5 and 2.0 V show a similar trend, but with smaller peaks than the samples treated with 1.0 V. It can also be seen that when the treatment was applied, C−H stretching was eliminated for all

samples. Except for the C−H group, treated samples show an increase in all functional groups. This increase is particularly noticeable in samples treated with 1.0 V.

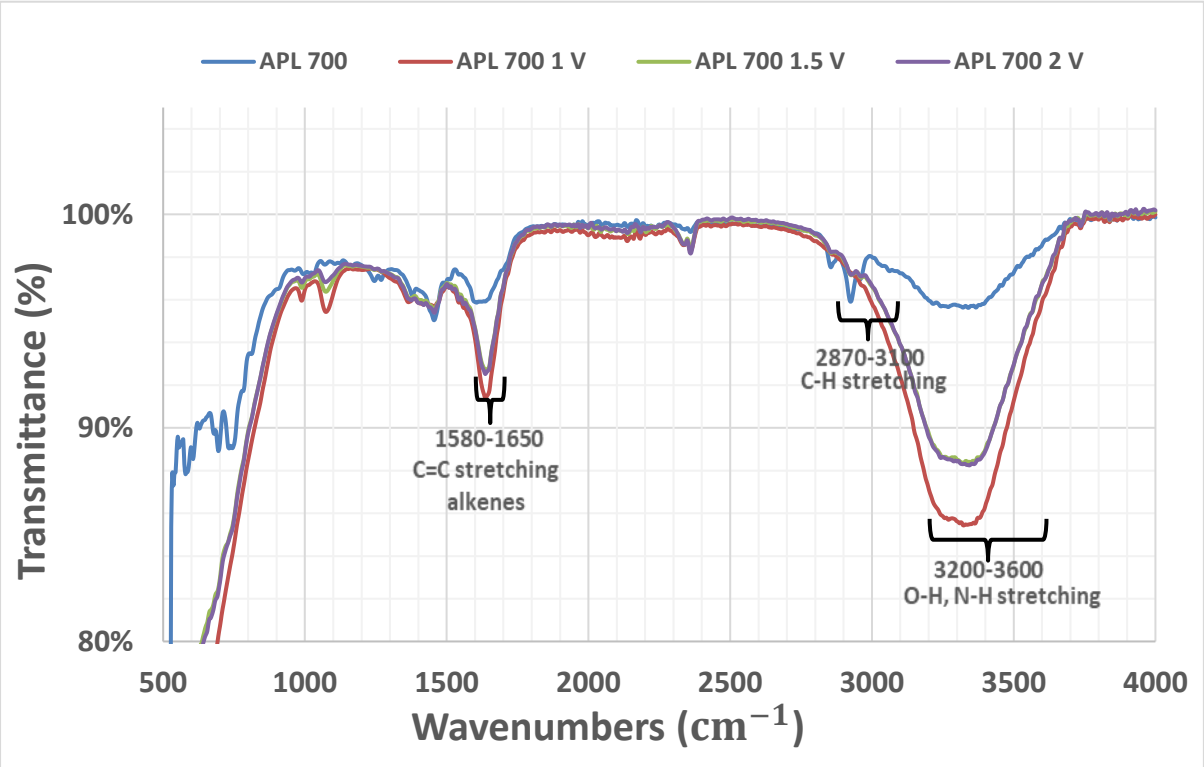

Figure 4.9: FTIR results of the electrochemical treated APL 700.

4.5.2 FTIR for acid-treated APL

Figure 4.10 shows the characterization of the acid treatment of APL 500. The trend of the results illustrates that the treatment by the acid did not have much effect on the composition of the APL 500. The effect was more pronounced with the sample (APL 500 S-0.5%) which shows the disappearance of the C=C, O−H, and N-H stretching. On the other hand, a significant increase in C−H stretching resulted in the same sample. The results of the other APL 500 treated samples are comparable to the pure sample.

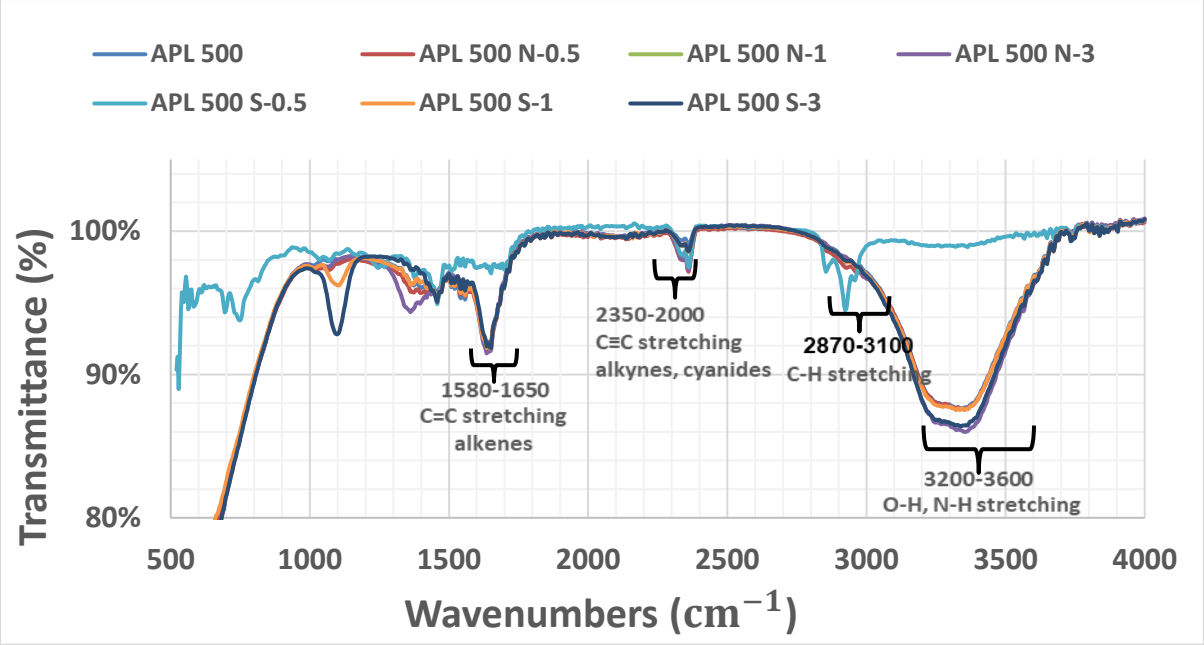

Figure 4.10: FTIR results of the acid treated APL 500.

The results of the APL 600 and APL 700 are shown in Figures 4.11 and 4.12, respectively. The APL 600 results show no difference between the pure and treated samples. In contrast to the findings of APL 500, we did not find any significant effect of the treatment excluding APL 600 N-0.5, which shows a decrease in OH and N-H stretching and a slight appearance of CH stretching at 2980-2870.

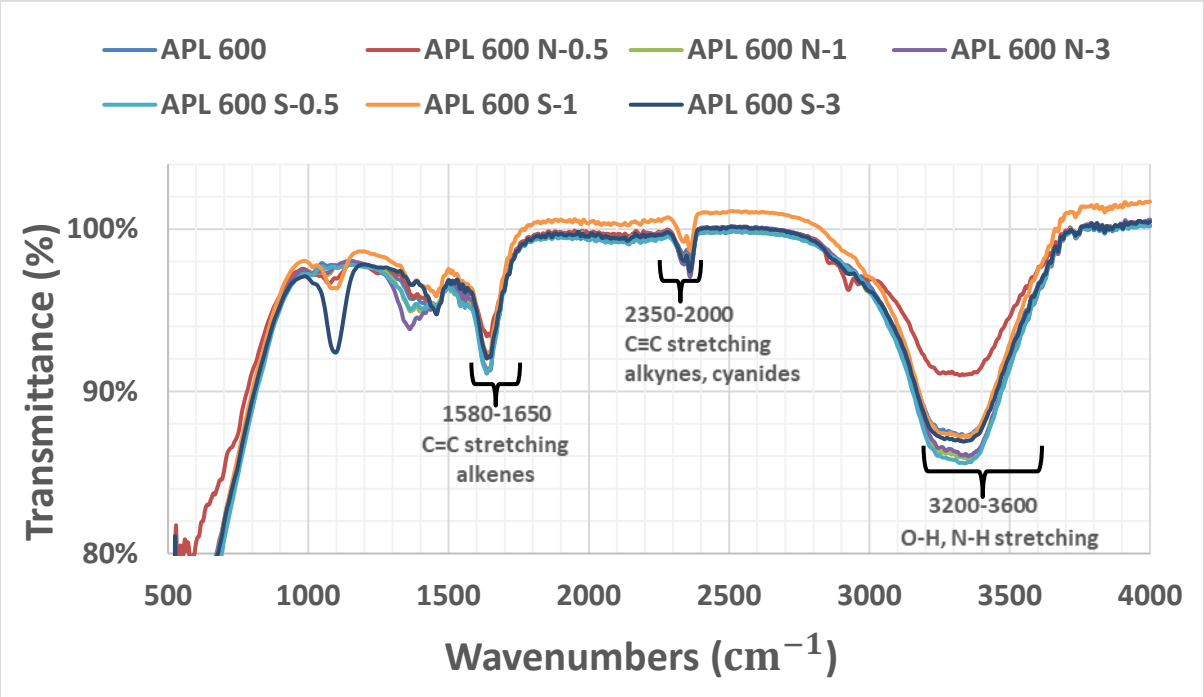

Figure 4.11: FTIR results of the acid treated APL 600.

As shown in Figure 4.12, both HNO_3 and H_2SO_4 treatments have the same effect on the APL 700. An increase in C=C stretching (158-1650) and the appearance of new C=-C stretching

(2350-2000) are the most noticeable effects. The results also show a significant increase in the O-H and N-H groups (3200-3600), which are impacted by HNO_3 treatment. The loss of C-H stretching (287-3100) was highest in HNO_3 treated samples.

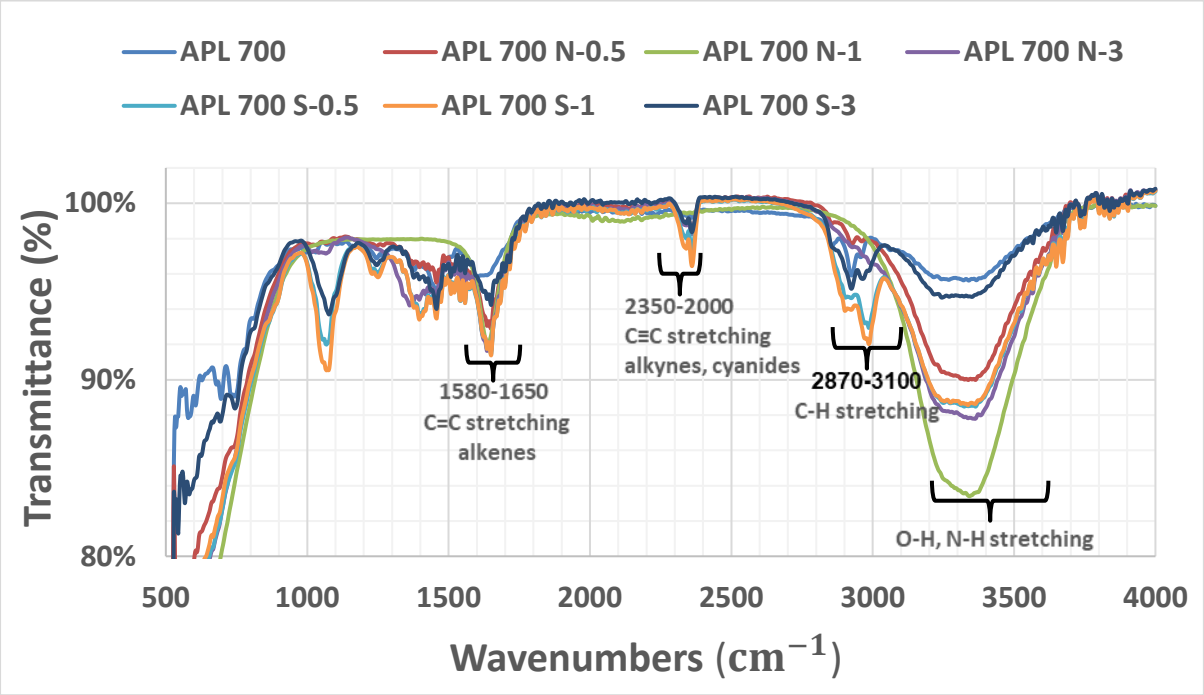

Figure 4.12: FTIR results of the acid treated APL 700.

5 Discussion

5.1 Effect of electrochemical treatment

To achieve an optimal voltage, cyclic voltammetry (CV) was performed in various ranges. Peaks in the CV indicate that the APL is actively reacting to the applied voltage. There were no remarkable peaks observed in the range of -1.00 to +1.00 V (Figure 4.1); however, potentials above that range clearly demonstrated a rise in current on both the oxidation and reduction sides. The current reached 1.00 A at a potential of -/+ 2.00 V, which is the maximum that the potentiostat can measure; thus, a stochastic fluctuation in the current was observed.

The absence of peaks could be attributed to the scale of the current (Y) axis; thus, the CV was repeated at the same scan rate but with a shorter potential window (-1.00 to 1.00 V), as shown in Figure 4.2. These peaks could be due to some compounds getting oxidized/reduced from the pyrolysis condensate or due to the electrode material (stainless steel) that takes part in the electrochemical reactions. Since the investigation of the CV in detail is not the primary scope of this thesis, limited to only presenting the voltammogram; further study is recommended.

The potentiostat test was conducted in two stages. The first stage was done with three APL samples at three volts (1.0, 1.5, and 2.0 V). The three tests took the same period of time (30 minutes). Figure 4.3 shows the current response for the 1.0 V sample was approximately 1 mA. The sample with 1.5 volts had a greater response, starting with 70 mA at the beginning of the experiment and dropping to 15 mA at the end. The greatest response was for a 2.0 V sample with a current response that started at 60 mA and grew to 320 mA.

Since samples treated with 1.0 and 1.5 V showed no meaningful response, they were retested over a longer period of time. 1.0 V for 2.0 hours and 1.5 V for 1 hour. Increasing the reaction time resulted in a higher response for both samples as shown in Figure 4.4. 1.0 V sample followed the same pattern as that in the first test, but after about 1.5 hours, the response increased sharply from roughly 7 mA to 160 mA. 1.5 V sample showed a different behavior than in the first test; the current response started at 80 mA and rapidly increased to 450 mA in less than an hour. This difference in interaction might be attributed due to the experimental setup of the electrochemical cell was not entirely isolated, allowing gaseous products from the oxidation of APL to escape.

5.2 Effect of the treatment methods on methane yield of APL

The results obtained from the experiments explained in section 4.3 showed an increase in CH_4 yield during the digestion of APL. The CH_4 production for the sample treated with 2.0 V was 6% more than the $CH4_{th}$. To make sure that most of the CH_4 comes from converting of APL, we compare the accumulative production of the APL 2.0 V with the accumulative production of the control (apple juice substrate), the result shows that both APL 2.0 V and control has the same production during the period of the test (Appendix D). APL has the potential to increase the microorganism's resistance to inhibitors. APL constituents function as an extra carbon source, increasing methanogenesis.

The results from the acid treatment of APL500 were not promising, as illustrated in Figure 4.6. It is important to note that neither H_2SO_4, nor HNO_3 increased biogas potential. Our results showed that H_2SO_4 had a negative impact on the APL 500, causing it to produce less

than the pure sample. We have verified that using the treatment of HNO_3 produces similar results to the pure sample. For APL600 samples, HNO_3 treatment was effective. This treatment resulted in a significant increase in CH_4 potential when compared with the untreated sample. As seen in Figure 4.7, this increase is most obvious in the sample (APL600 N 1). On the contrary, the CH_4 potential in the rest of the samples was lower than it was before treatment. Figure 4.8 illustrates the most beneficial result. These results were obtained only with samples APL700 and APL700 N 1%. The results indicate that using APL700 before treatment has a beneficial influence on CH_4 production. When the sample is treated with 0.5 % HNO_3, the potential of CH_4 is increased.

The results of acid treatment showed that the APL treated with HNO_3 at low concentrations (0.5 and 1.0 %) produce the most biogas. APL 500 was eliminated from the earlier findings since it did not give any promising outcomes even after being treated with both acids (H_2SO_4, HNO_3). A decrease in CH_4 production is observed by increasing acid concentration especially H_2SO_4 with APL 500. As a result, biogas generation at lower concentrations of HNO_3 is more effective. Increasing concentration may have induced some inhibition.

The syringe test is a manual test with the possibility of errors propagating during the test period. When preparing the experiment and releasing the biogas, it means there was an overestimation of total CH_4 in the measurement, or an underestimation of total COD added. The results obtained $CH4_{exp}$ are slightly higher than $CH4_{th}$. The causes of the results are difficult to demonstrate. Such a situation is quite likely if there were some errors in measuring the COD. The major problem was that using a pipette to transfer a tiny amount of the sample with high accuracy was challenging.

5.3 The impact of the treatment on ALP characterization

FTIR analysis indicates that the APL treated electrochemically shows an increase in the number of phenols, alcohols, and carboxylic compounds O−H and N-H (3200-3600 cm^{-1}), and slightly increases the number of aromatic compounds (915-650 cm^{-1}). As oxidation progresses, the disappearance of a broad peak C−H Stretching in alkenes compounds at (2980-2870 cm^{-1}) (Figure 4.9).

The FTIR spectra of acid-treated samples demonstrate that the C-H stretching group disappears as the voltage for electrochemical treatment as well as the concentration of acids in the acid treatment are increased. At increasing voltages, the oxidation rate of alkane and alkyne components may increase. Furthermore, acid treatment has a significant impact on the functional groups. As it is illustrated in Figure 4.11, APL 600 is an exception, as it showed no substantial changes following the treatment.

6 Conclusion

- The electrochemical treatment of APL resulted in a significant increase in CH_4 production yield especially from samples treated with 2.0 V. The potential of these samples exceeded the theoretical production (based on measured COD), we conclude that this increase is due to changes in the composition of the sample by eliminating the inhibitors. Because of their reliable results, electrochemical techniques have enormous potential for enhancing APL.
- Acid treatment is a simple and effective method for the decomposition of APL. Treatment with HNO_3 at low concentrations (0.5 and 1.0 %) gives satisfactory results, especially for APL700 and APL600. While the H_2SO_4 treatment did not make any promising results. APL500 gives unsatisfactory results both before and after treatment.
- The (FTIR) technique does not facilitate the identification of specific APL components. FTIR analysis before and after treatment can be used to study the effect of different decomposition procedures on the chemical components of the APL. The effect of treatment methods on the functional groups in the APL is determined by the change in FTIR spectra.

- The results show that APL600 and APL 700 have significant biogas potential; thus, pyrolysis temperatures > 500°C are recommended for producing pyrolysis liquids from biomass.

7 Recommendations

- Future research is required to evaluate APL digestion at higher concentrations to determine the optimal ratio of APL. In this thesis, a concentration of 6% of the total substrate was used.

- To improve methane production, treatment should be investigated using various approaches (e.g., microwave pre-treatment).

- The electrochemical treatment was only applied on APL 700. As a result, utilizing the treatment on APL 500, which gave the lowest results, may contribute to reach the best biogas potential for this sample.

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9 Appendices

Appendix A Master's Thesis Task Description.

Appendix B: Treated APL samples composition of the BMP test.

Appendix C: CO2-trap results.

Appendix D: COD Test procedure.

Appendix E: Methane production for different APL samples before and after treatment plotted with control and blank

Appendix A: Master's Thesis Task Description

University of South-Eastern Norway

Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Decomposition and characterisation of aqueous pyrolysis liquid

USN supervisor: Carlos Dinamarca

External partner: Scanship AS

Task background:
Pyrolysis is the thermal decomposition of organic mass in the absence or limited supply of oxygen. The pyrolysis products include solids (char or "biochar" from biomass) and gas with a non-condensable and a condensable fraction. The non-condensable gases include methane, hydrogen, carbon monoxide, and carbon dioxide (a mixture of the latter three is often called syngas). The condensable fraction of the gas, "condensate", is a mixture of water and many different chemicals and may have a relatively high energy content and oily characteristics. Common terms for the condensable fraction are "pyrolysis liquid/oil" or "bio-oil" when biomass is pyrolysed. Biomass pyrolysis offers a flexible and attractive way of converting organic matter into energy products, which can be successfully used to produce heat, power, and chemicals in addition to potential carbon capture through biochar. Pyrolysis can be performed at a relatively small scale and at remote locations, enhancing the energy density of local biomass by drastically reducing the volume of solid residues, thus reducing transport and handling costs. Pyrolysis also provides an opportunity to process agricultural residues, wood wastes and municipal solid waste into clean energy. For full benefit from the process, any condensed APL should be valorised. Its water content often hampers this and chemical complexity we, therefore, need knowledge of possible decomposition routes & chemical characteristics to commercialise all pyrolysis products.

Task description: The practical work includes
-Write a short literature-review on methods for APL characterisation and decomposition.
-Perform laboratory batch tests for APL decomposition.
-Analysis of samples.
-Assess the degree of APL decomposition by running potential biomethane test.

-Write a final report based on both literature and laboratory results.

Student category: EET or PT students

Is the task suitable for online students (not present at the campus)? No

Practical arrangements:
The project will combine literature survey and laboratory activities. The laboratory work will take place at USN-Campus Porsgrunn; the student will receive the necessary training.

Supervision:
As a general rule, the student is entitled to 15-20 hours of supervision. This includes necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc).

Signatures:

Supervisor (date and signature):

Student (write clearly in all capitalised letters): ADEL SHOWAYA

Appendix B: Treated APL samples composition of the BMP test.

Reactor	Sample	Inoculum (mL)	APL (mL)	Feed/apple juice (mL)	No. of parallels
1	Blank	28	-	-	3
2	Control	28	-	2	3
3	APL 700	28	0.12	1.88	3
4	APL 600	28	0.12	1.88	3
5	APL 500	28	0.12	1.88	3
6	APL 700 S-0.5%	28	0.12	1.88	3
7	APL 700 S-1%	28	0.12	1.88	3
8	APL 700 S-3%	28	0.12	1.88	3
9	APL 600 S-0.5%	28	0.12	1.88	3
10	APL 600 S-1%	28	0.12	1.88	3
11	APL 600 S-3%	28	0.12	1.88	3
12	APL 500 S-0.5%	28	0.12	1.88	3
13	APL 500 S-1%	28	0.12	1.88	3
14	APL 500 S-3%	28	0.12	1.88	3
15	APL 700 N-0.5%	28	0.12	1.88	3
16	APL 700 N-1%	28	0.12	1.88	3
17	APL 700 N-3%	28	0.12	1.88	3
18	APL 600 N-0.5%	28	0.12	1.88	3
19	APL 600 N-1%	28	0.12	1.88	3
20	APL 600 N-3%	28	0.12	1.88	3
21	APL 500 N-0.5%	28	0.12	1.88	3
22	APL 500 N-1%	28	0.12	1.88	3
23	APL 500 N-3%	28	0.12	1.88	3

24	APL 700 1-V	28	0.12	1.88	3
25	APL 700 1.5-V	28	0.12	1.88	3
26	APL 700 2-V	28	0.12	1.88	3

Appendix C: CO2-trap results

14.04.2022

Sample	Total biogas (ml)	CH4 (ml)	CH4 %	Average CH4 %
Blank 1	12	5.0	41.67	47.37
Blank 2	11	5.0	45.45	
Blank 3	10	5.5	55.00	
Control 1	30	16.0	53.33	55.56
Control 2	30	17.0	56.67	
Control 3	30	17.0	56.67	
700-1V 1	30	18.0	60.00	60.00
700-1V 2	30	18.0	60.00	
700-1V 3	30	18.0	60.00	
700-1.5V 1	30	17.5	58.33	57.22
700-1.5V 2	30	17.0	56.67	
700-1.5V 3	30	17.0	56.67	
700-2V 1	30	18.0	60.00	61.11
700-2V 2	30	18.0	60.00	
700-2V 3	30	19.0	63.33	
700 1	30	16.5	55.00	57.22
700 2	30	18.0	60.00	
700 3	30	17.0	56.67	
20.04.2022				
Sample	**Total biogas (ml)**	**CH4 (ml)**	**CH4 %**	**Average CH4 %**
Blank 1	12	5.0	41.67	47.37
Blank 2	11	5.0	45.45	
Blank 3	10	5.5	55.00	
Control 1	30	15.5	51.67	56.11
Control 2	30	17.0	56.67	
Control 3	30	18.0	60.00	
700-1V 1	30	18.0	60.00	61.11
700-1V 2	30	19.0	63.33	
700-1V 3	30	18.0	60.00	
700-1.5V 1	30	18.0	60.00	59.44
700-1.5V 2	30	18.0	60.00	
700-1.5V 3	30	17.5	58.33	
700-2V 1	30	19.0	63.33	61.11
700-2V 2	30	18.0	60.00	
700-2V 3	30	18.0	60.00	
700 1	30	17.0	56.67	60.00
700 2	30	19.0	63.33	

700 3	30	18.0	60.00	
24.04.2022				
Sample	**Total biogas (ml)**	**CH4 (ml)**	**CH4 %**	**Average CH4 %**
Blank 1	12	6.0	50.00	50.00
Blank 2	12	5.5	45.83	
Blank 3	12	6.5	54.17	
Control 1	40	23.0	57.50	58.75
Control 2	40	24.0	60.00	
Control 3	40	23.5	58.75	
700-1V 1	40	25.0	62.50	63.33
700-1V 2	40	26.0	65.00	
700-1V 3	40	25.0	62.50	
700-1.5V 1	40	24.0	60.00	59.58
700-1.5V 2	40	23.5	58.75	
700-1.5V 3	40	24.0	60.00	
700-2V 1	40	24.0	60.00	62.92
700-2V 2	40	25.5	63.75	
700-2V 3	40	26.0	65.00	
700 1	40	24.0	60.00	60.83
700 2	40	24.0	60.00	
700 3	40	25.0	62.50	

Appendix D: COD Test procedure

The experiment was carried out using COD kits from Merck Company [32]. The potassium dichromate in COD kits interacts with oxidizable compounds. The COD measurement range was 500-10000 mg/l COD.

Procedure:

Before starting the method, any samples containing more than 5000 mg/l COD must be diluted with distilled water. The sample will be prepared by whirling it to suspend the sediment at the bottom of the reaction cell. Through the pipette, 1.0 ml of each sample is put into the cells of the kits. After that, each cell's cap is bonded to the cell. Throughout the process, the cells must be retained by their caps. The next step is to gently mix the contents of the cell with a mixer. An incubator is used to heat the cells to 148° C for 120 minutes. In a test-tube rack, the cells are cooled to ambient temperature.

Photometric measurement [32]:

The Blank kit was used as a reference in the photometric device. Before measuring, all cells should be cleaned and dried. A COD cell test with an adequate concentration (500 - 10000 mg/l COD) was used for the photometric control screen. The cells were inserted into the cell compartment. Over time, the measurement value remains steady.

Appendix E: Methane production for different APL samples before and after treatment plotted with control and blank

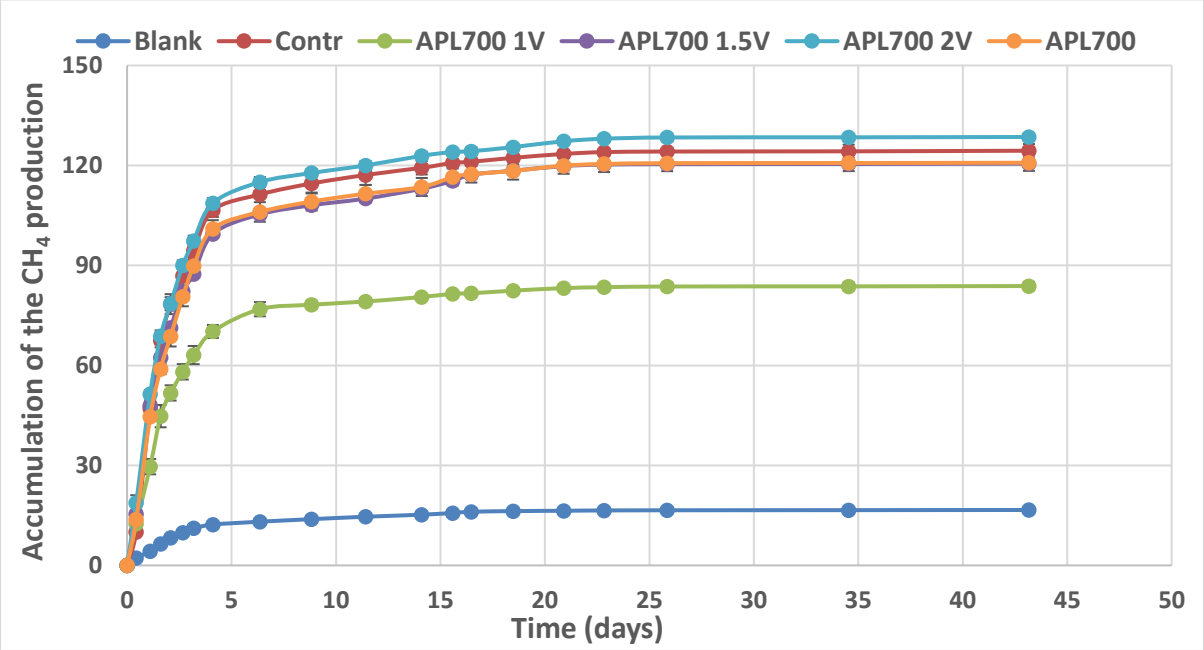

Figure D.1: Cumulative CH_4 production (trend of biogas production from electrochemical treated syringe test)

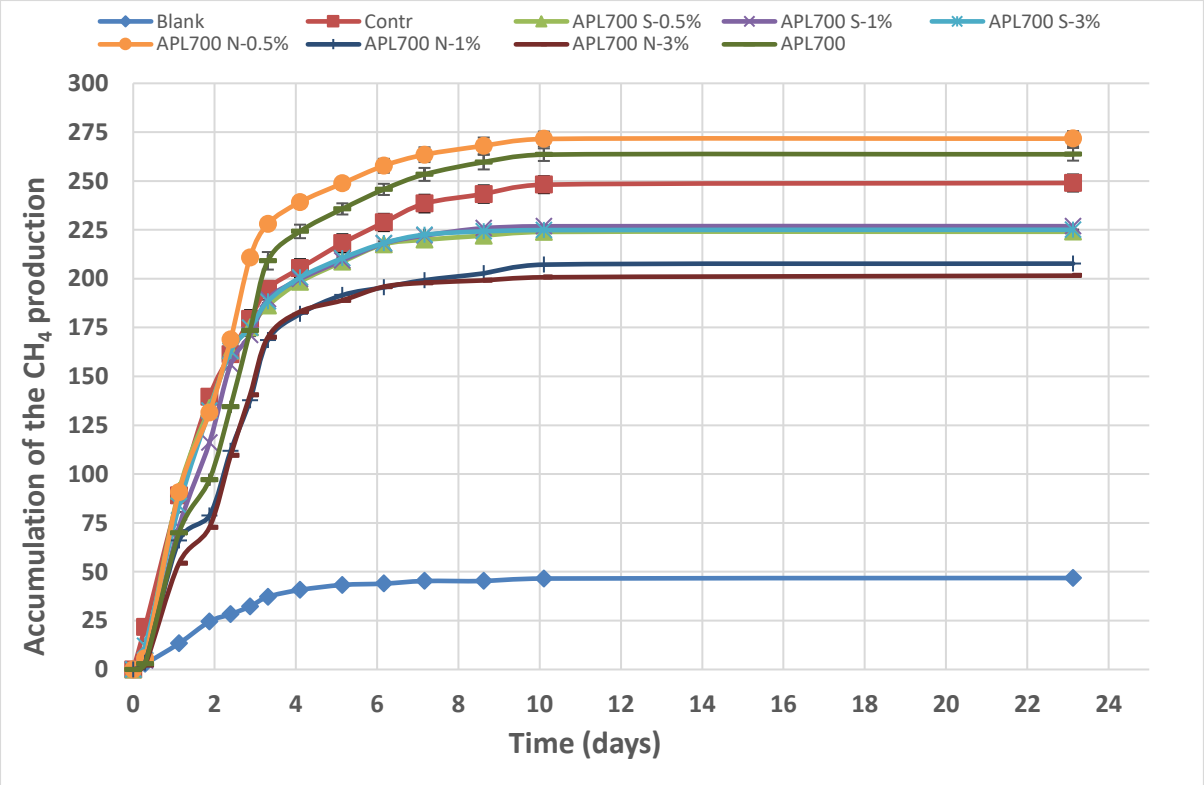

Figure D.2: Cumulative CH_4 production, APL 700 (trend of biogas production from acid treated syringe test)

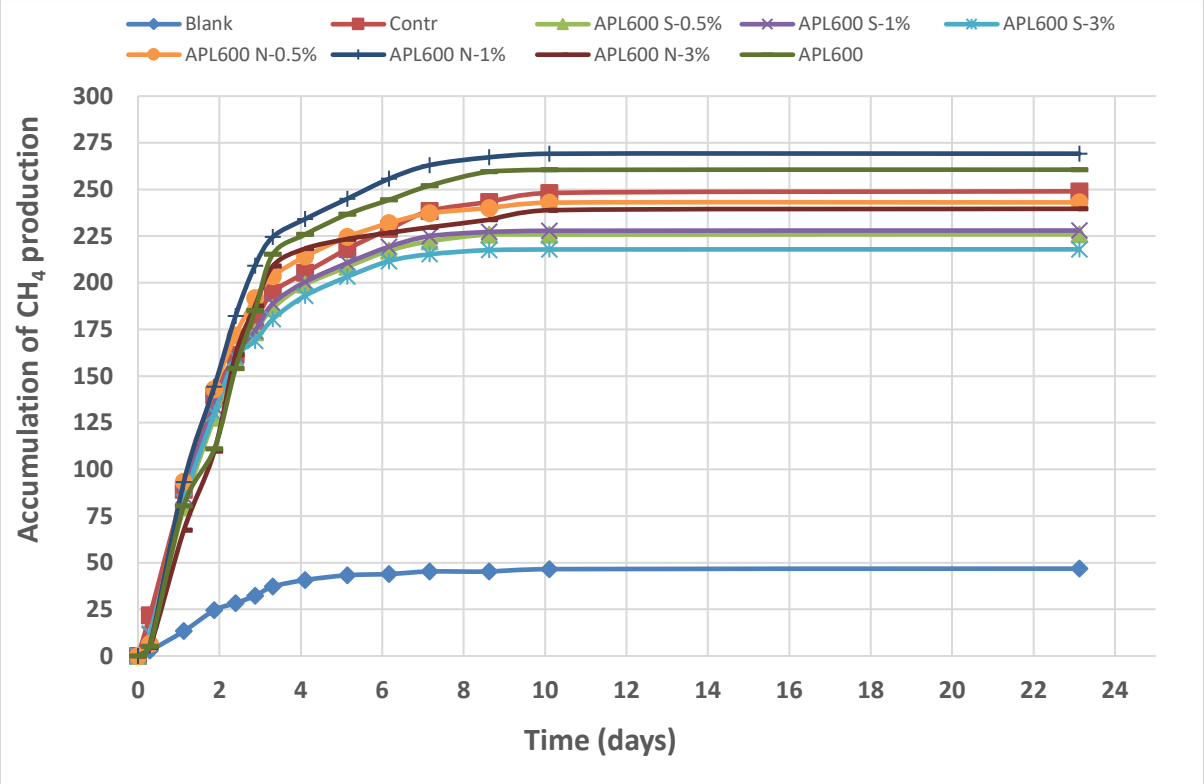

Figure D.3: Cumulative CH_4 production, APL 600 (trend of biogas production from acid treated syringe test)

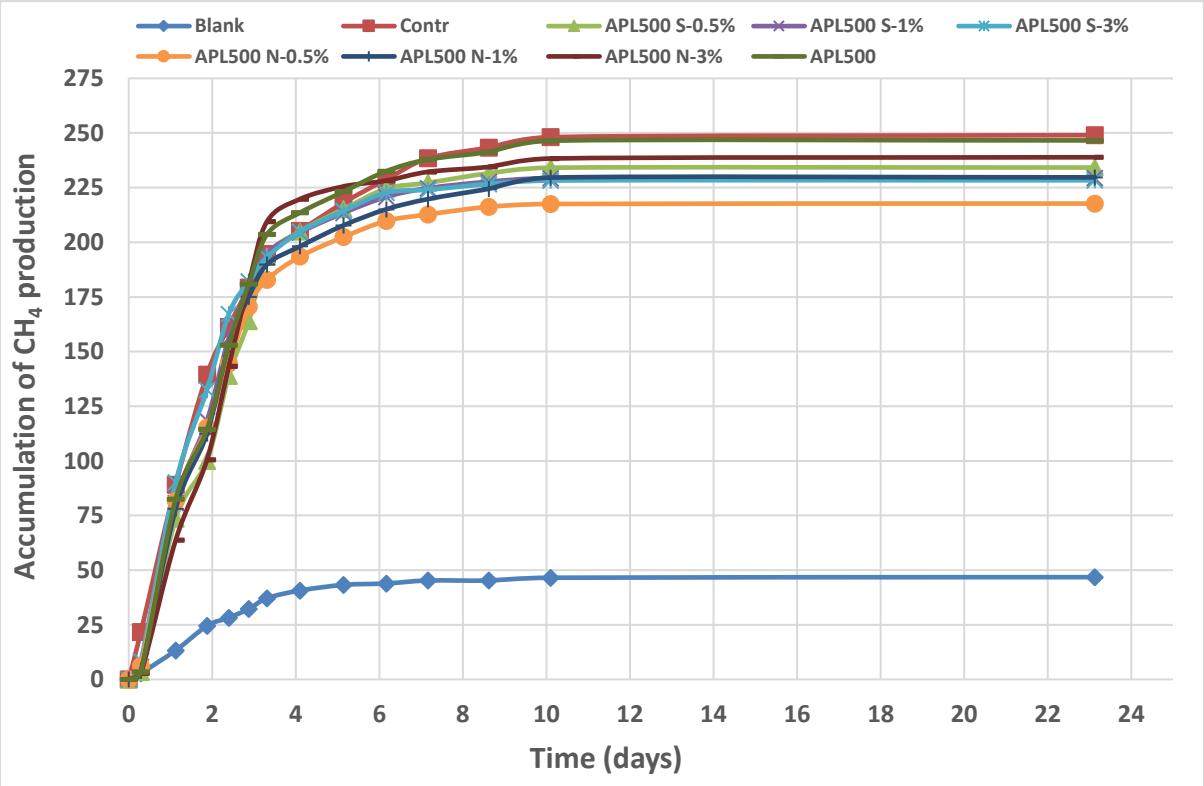

Figure D.3: Cumulative CH_4 production, APL 500 (trend of biogas production from acid treated syringe test)