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ORIGINAL ARTICLE

Enhanced Soluble Protein and Biochemical Methane Potential of Apple Biowaste by Different Pretreatment

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Abstract

The purpose of this research is to evaluate the anaerobic digestion of apple pomace waste in terms of pretreatment. In this study, the main pretreatment strategies for apple pomace include: ultrasound (35 and 53 kHz), thermal and chemical (pH 5 and 10). For each pretreatment method four different temperatures are selected as 25, 40, 50, and 60 °C, and operation times are selected as 5th, 15th, 30th, and 45th minutes. The effects on pretreatment were investigated by measuring changes in the soluble protein concentrations of pretreated wastes and the enhanced anaerobic digestion was investigated by using the biochemical methane potential (BMP) assay. The soluble proteins of ultrasonic (35 kHz at 60 °C, 45th min), ultrasonic (53 kHz at 60 °C, 45th min), chemical (pH 5 at 60 °C, 5th min), chemical (pH 10 at 60 °C, 30th min) and thermal chemical (40 °C, 15th min) pretreatment apple pomace were 74.3, 75.6, 48.7, 85.5 and 58.6% higher, respectively. The results indicated that apple pomace treated with 53 kHz at 60 °C, 45th min had the highest biogas yield of 1519 mL CH_4/g VSS.day after anaerobic digestion, which was on average 40.9% higher than raw pomace.

Keywords Apple pomace · Ultrasonic pretreatment · Chemical pretreatment · Biochemical methane potential · Soluble protein

1 Introduction

With the increasing energy demand and concerns related to non-renewable energy resources, renewable energy is regarded as a sound alternative energy in the next generation (Zi-lin et al. 2013). Agro-industrial byproducts and residues are often used as the broadcast source of the substrate for anaerobic biotransformation to biogas, which suggests that byproduct substrates could be alternatives to energy crops in anaerobic digestion plants (Menardo et al. 2012). Although biomass energy is more costly than fossil fuel-derived energy, trends to limit carbon dioxide and other emissions through emission regulations, carbon taxes, and subsidies of biomass energy would make it cost competitive (Chynoweth et al. 2001; Charters 2001), even when low-cost treatment, due to high energy recovery and environmentally friendly are taken into consideration (Ferreira et al. 2013). Wastes from agro-industrial processing are high in organic matter and are therefore ideal for anaerobic digestion (AD).

Turkey is the most important apple production state in the world and produced 2480 million tons of apples in 2014 (TUIK 2015). For commonly seen apple pomace (AP), the moisture content is in the range of 70–75% and the cellulose, protein and lipid contents are 7.2–43.6, 2.9–5.7 and 1.2–3.9%, respectively, on a dry weight basis (Dhillon et al. 2013).

Disposal of AP has long been a problem for producers. The AP can damage the environment, ranging from surface and ground water pollution to foul odors (Kafle and Kim 2013) if not treated effectively. Additionally, the large quantities of agro-industrial by-products do not have economic value and the availability of landfill space for AP disposal decreases each year (Riggio et al. 2015). AP tends to have low total solids and high volatile solids, and is easily degraded in an anaerobic digestion (AD) process.

AD is widely applied in solid stabilization technology to degrade a complex variety of organic wastes in the absence of free or dissolved oxygen. One of the end products is biogas (Sterling et al. 2001). The generated biogas

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can be used for generating electricity (used for cooking and heating), as direct vehicle fuel and for producing chemicals (Cantrell et al. 2008). AD processes are correspondingly divided into four stages: (1) hydrolysis, (2) acidogenesis, (3) acetogenesis, and (4) methanogenesis (Demirbas and Balat 2009).

Hydrolysis is the rate limiting step for conventional anaerobic digestion of solid wastes due to the cell structure of microbial biomass and the extracellular polymeric (lipids, polysaccharides, and proteins or amino acids) substances (Eskicioglu et al. 2006). Total solid destruction as well as volatile solid destruction is also considered to be a very reliable measure of anaerobic digestion. Additionally, when microorganisms break down proteins, they release ammonium-nitrogen. Increased levels of ammonium in the solution can therefore indicate improved anaerobic digestion (Muller et al. 2009).

AD performance is enhanced by pretreating the waste to break the polymer chains into soluble components (monomers). This will improve the hydrolysis of the organic matter, accelerate the AD process, increase the biogas production, as well as reduce the digestion time and the amount of final residuals (Beszédes et al. 2009).

Different processes of pretreatment have been applied in the anaerobic digestion process. The main pretreatment processes are thermal, chemical (Xu et al. 2014), and ultrasonic (Feng et al. 2009a). Each pretreatment method has advantages and disadvantages, and there is no "ideal" method (Chen et al. 2014). But among the different pretreatment approaches available, thermo-chemical and ultrasonic pretreatments have been reported as being effective and economically flexible (Apul and Sanin 2010; Rafique et al. 2010).

Heat produced during thermal treatment alters the chemical bonds of the cell wall and cell membrane to make it more amenable to biodegradability and enhance anaerobic digestibility (Cesaro and Belgiorno 2014). Climent et al. (2007) found that only low temperature thermal treatment (70 °C) increased biogas production by 50% and found no effect for high temperature treatment.

Chemicals used for treating biomass include acid, alkali, or aqueous ammonia. Although the target of each chemical is different, overall, there are several chemical methods that remove hemicellulose from biomass, including methods that fractionate the biomass using acid catalysts (Jurado et al. 2013; Choi et al. 2013). Vlyssides and Karlis (2004) studied concentrated wasted activated sludge (10% total solid) from a soft drink wastewater treatment plant at lower temperatures (< 100 °C) and more neutral pH values (pH 8–11) and achieved reasonable improvements for chemical oxygen demands solubilization.

The term ultrasound is used to define sound energy in a frequency range of 20–100 kHz that is above human hearing (Pilli et al. 2011). Wang et al. (1999) applied ultrasound or sonication pretreatment in the anaerobic digestion of WAS. In the pretreatment, a 9 kHz frequency was operated for 0, 10, 20, 30 and 40 min. The results indicated that the methane generation increased with ultrasonication time up to 30 min. Grönroos et al. (2005) demonstrated that ultrasonic pretreatment enhanced methane production during the anaerobic digestion process, and ultrasonic power as well as ultrasonic treatment time had the most significant effect on increasing methane production. Luste et al. (2009), Elbeshbishy et al. (2011) and Saha et al. (2011) reported that ultrasonic pretreatment of WAS increases solubilization, which enhances volatile solid (VS) destruction and ultimate biogas production.

To the best of our knowledge, it has never been applied to ultrasonic and thermal pretreatment methods for apple pomace disintegration. Soluble of protein in typical pretreatment process was never reported earlier.

This study has primarily established ultrasound, thermal and chemical disintegration as the main methods, of the many methods for the pretreatment of apple pomace in a beverage factory in Mersin. A secondary objective of the study was to evaluate the performance of pretreatment-conditioned apple pomace for enhancing the destruction of soluble protein. The final objective of the study is to assess the effects of optimum pretreatment conditions (max. soluble protein) of apple pomace anaerobic digestion performance through biochemical methane potential (BMP) assays.

2 Materials and Methods

2.1 Feedstock

The apple pomace used throughout the experiments was obtained from agricultural food products factory between November and February, during the apple harvest time. Biomass samples were oven dried (105 °C) and ground to 2 mm for chemical analysis and anaerobic digestion assay. The characteristics of the substrate utilized in the study are listed in Table 1.

2.2 Anaerobic Inoculum

The anaerobic inoculum used in this study was obtained from the anaerobic digester plant of a dairy factory in Aksaray. The sludge was stored at 4 °C for no more than 2 days before utilization. The mesophilic anaerobic inoculum was maintained in a 5 L flask reactor, which was initially filled with 3 L of waste-activated sludge obtained

Table 1 The characteristics of inoculum and raw apple pomace

Value	Units	Apple pomace	Inoculum
pH	–	3.96	–
Conductivity	µS/cm	2000	–
Total solids	%	8.0	–
Volatile solids	%	89.7	–
Total organic carbon	mg/L	46,097.2	–
Soluble protein	mg/L	42.56	–
Volatile solids (VS)	mg/L	–	24,500
Suspended solid content (SS)	mg/L	–	23,000
Sludge volume index (SVI)	mL/g	–	224

from the dairy factory. The characteristics of this sludge are shown in Table 1.

2.3 Biochemical Methane Potential (BMP) Assays

The digestibility of apple pomace or digestate was tested using the biochemical methane potential (BMP) tests. In each set of experiment, biochemical methane potential was determined for the highest value of soluble protein. All samples used in the BMP test were diluted to total solid concentration of 10%, and 30 mL of diluted sample and 5 mL of inoculum were placed in each of the 125 mL serum bottles. A mixture with equal amounts of $KHCO_3$ and $NaHCO_3$ was added to each reactor to ensure a $CaCO_3$ alkalinity concentration of 4000 mg/L. The pH was adjusted to pH 7 by adding 0,5 M NaOH. To minimize aerobic biodegradation, nitrogen gas was sparged into the digestion mixture in the reactor bottles for 2 min. The BMP reactor bottles were then sealed and put into a temperature-controlled incubator (Zhicheng, ZHWY-211D) to perform the BMP test for 30 days. Biogas production was monitored daily with a graduated syringe using a volume displacement technique. Daily room temperature and pressure at the time of gas sampling were recorded and gas volumes were corrected to standard conditions for temperature and pressure. Each BMP assay was performed in triplicate.

2.4 Pretreatment Procedure

The thermal pretreatment experiment was implemented based on 4 × 4 factorial, complete design. The two factors used were the apple pomace sample at different temperatures (25, 40, 50 and 60 °C) and operation times (5, 15, 30, 45 min). For each pretreatment, 10 g of apple pomace residue was mixed with 90 mL distilled water and heated in an incubator shaker (Zhicheng, ZHWY-211D) to the specified heating conditions and time.

For the alkaline pretreatment of samples, an alkaline reagent was used. NaOH alkaline reagent was examined at two pH levels, 5 and 10, and four different temperatures, 25, 40, 50 and 60 °C. In the case of NaOH, the effect of mixing time was examined at 5, 15, 30 and 45 min. For NaOH-pretreated samples, 1N NaOH solution was added until the desired pH level was reached. All used chemicals were purchased from Merck (Merck, Whitehouse Station, NJ, USA).

The effect of sound frequency, temperature and duration of sonication on treatment efficiency was investigated by an ultrasonic device (Kudos, LHC Heating). Two levels of sound intensity (35 and 53 kHz), four temperatures (25, 40, 50, 60 °C) and four levels of sonication time (5, 15, 30 and 45 min) were tested Like the thermal and chemical pretreatment experiments, these experiments were carried out as a 2 × 4 × 4 fully crossed factorial design.

The experimental process is briefly described in Fig. 1.

After the operation time, the samples were left to reach room temperature prior to analysis. The soluble protein was measured after centrifuging the samples for 30 min at 3250 rpm and filtering each sample through a 0.45 µm pore-size filter.

2.5 Analytical Methods

The sludge volume index (SVI) was calculated using the settled sludge volume of 1 L at 30 min settling time. The values of pH and conductivity were measured using an HQ411D equipment. The total solid (TS) and volatile solid were determined according to the APHA standard methods (APHA 2012). Total organic carbon (TOC) measurements were realized by TOC-TN (Shimadzu TOC-VCPN) analysis system.

Samples were also passed through 0.45 µm filters to measure the soluble protein concentration following the Coomassie Brilliant Blue G-250 method with absorbance 595 nm. Bovine serum albumin (BSA) was used as the standard (Feng et al. 2009b). The chemicals used for these analyses were purchased from Merck.

3 Results and Discussion

3.1 Ultrasonic Pretreatment

Changes in soluble protein value depending on temperature and operation time in 35 kHz ultrasound pretreatment are shown in Fig. 2.

As seen in Fig. 2, the increase in temperature increases the value of soluble protein. At the same time, it was determined that the operation time of the highest soluble protein value was the 45th min. The highest soluble protein value was also obtained at 60 °C, 45th min (165.3 mg/L). The

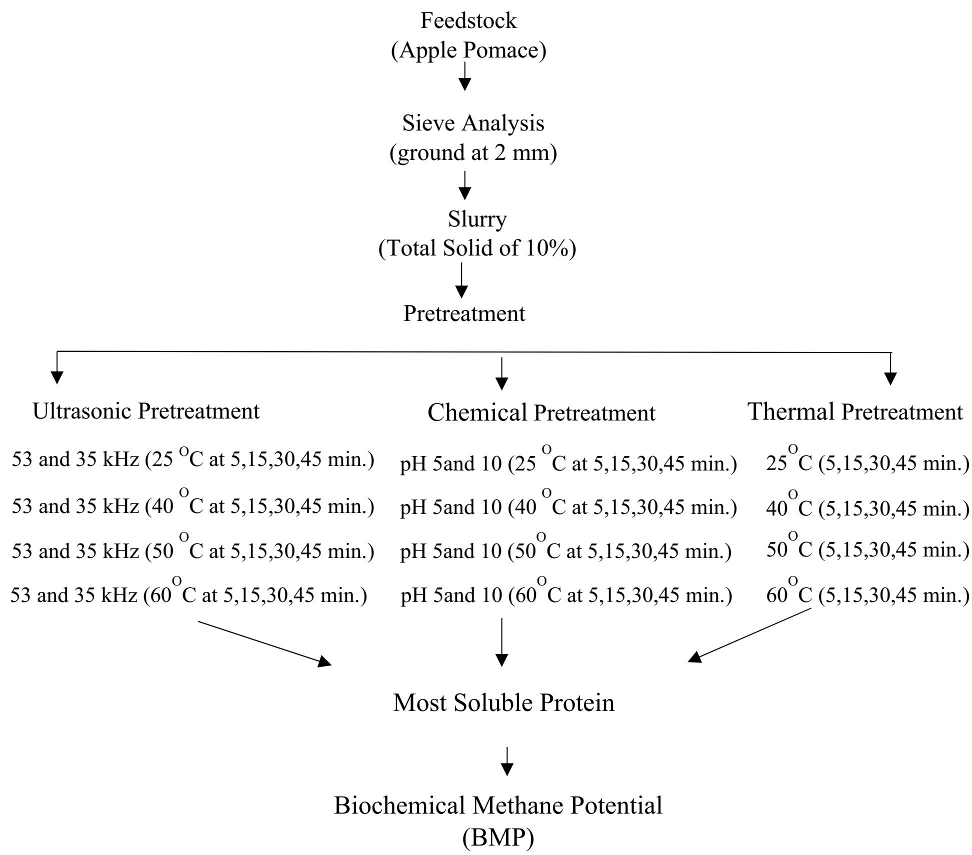


Fig. 1 A schema of the experimental process

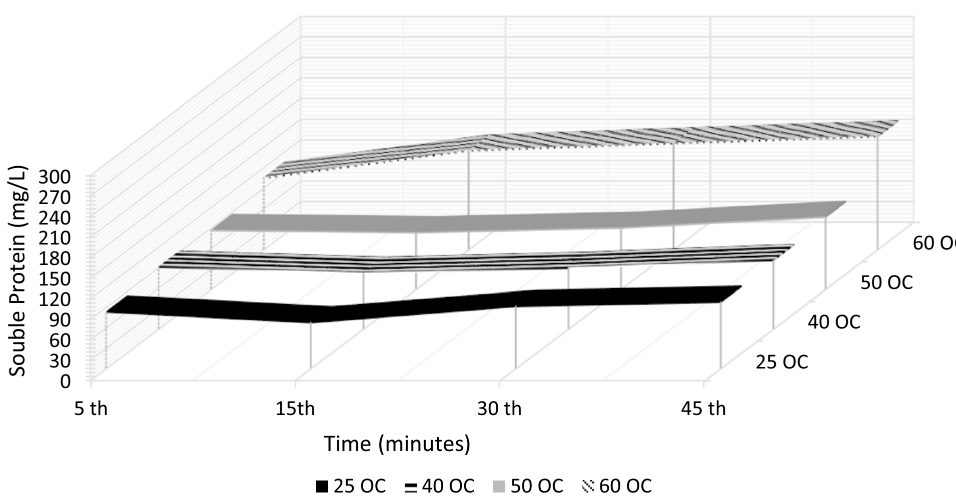


Fig. 2 Soluble protein changes in the 35 kHz ultrasound pretreatment

soluble protein value increased linearly depending on the increase in temperature.

The effects of temperature and operation time on soluble protein at 53 kHz ultrasonic pretreatment are shown in Fig. 3.

The highest soluble protein values at 25, 40, 50, and 60 °C were found to be at the 15th, 30th, 30th, and 45th min, respectively. The highest soluble protein was 175 mg/L at 60 °C, 45th min. The soluble protein values in 53 kHz ultrasonic pretreatment were found to be higher compared with the 35 kHz pretreatment at all temperatures and operation times, except for 25 °C. In short, the 53 kHz ultrasonic pretreatment is more effective than the 35 kHz ultrasonic pretreatment. However, it has been determined that the efficiency of the 53 kHz ultrasonic pretreatment depends on long operation times. Ultrasonication with temperature has a significant impact on the soluble protein of the apple pomace solubilization of solid phase matter,

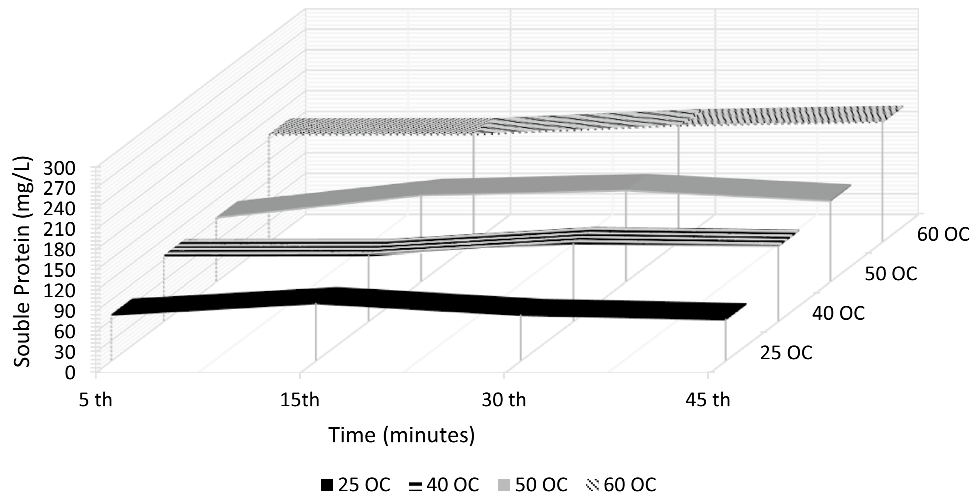


Fig. 3 Soluble protein changes in the 53 kHz ultrasound pretreatment

as well as on the increases in the concentration of organic matters.

3.2 Chemical Pretreatment

The changes of soluble protein values for pH 5 and pH 10 in the chemical pretreatments were investigated, and the experimental results are shown in Figs. 4 and 5.

As seen above, the highest soluble protein values were obtained for 60 °C at the 5th min (83 mg/L), for 40 °C at the 30th min (67.07 mg/L), for 50 °C at the 15th min (70.3 mg/L), and for 25 °C at the 45th min (56.2 mg/L). The soluble protein value did not change because of the near to initial pH value.

It has been determined that the value of soluble protein at pH 10 pretreatment is much higher than that using other pretreatment methods. The optimum operation time for pH 10 pretreatments was 30 min. Soluble protein values decreased over more than 30 min of operation time. It has been determined that the temperature is highly effective on the dissolution of protein in the pH 10 pretreatment. The highest soluble protein value was measured as 294.3 mg/L at 60 °C, 30th min.

3.3 Thermal Pretreatment

Thermal pretreatment experiments were carried out at 25, 40, 50, and 60 °C temperatures for the 5th, 15th, 30th, and 45th min like the other pretreatment tests. The effect of temperature on protein dissolution is given in Fig. 6.

In thermal pretreatment studies, it was determined that there was an inverse relationship between temperature and soluble protein. The highest protein values were obtained at the 15th min. The highest soluble protein values were 102.9, 92.13 mg/L, and 89.5 at 40, 50, and 60 °C, respectively. Thermal treatment disrupts the chemical bonds of the protein, resulting in the release of intracellular components and enhancing anaerobic digestibility behavior; this is in

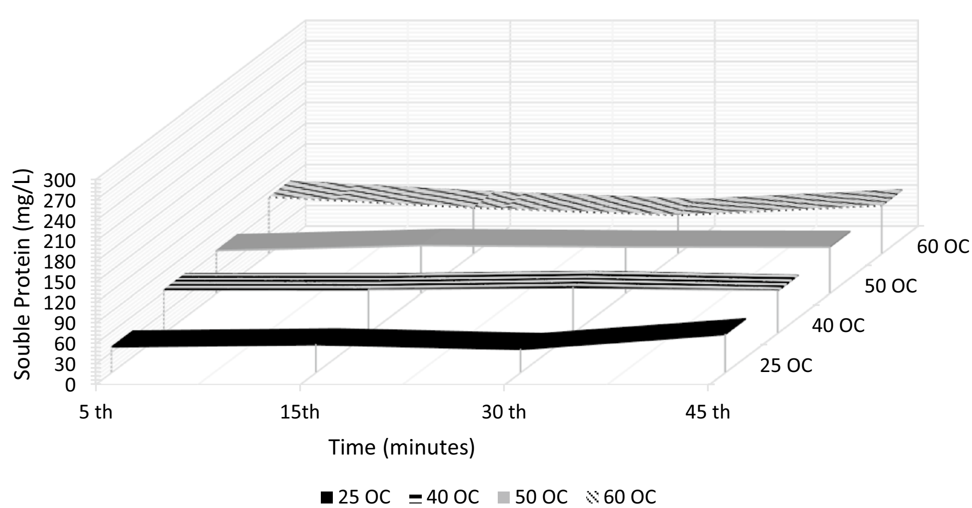


Fig. 4 Soluble protein changes in the pH 5 chemical pretreatment

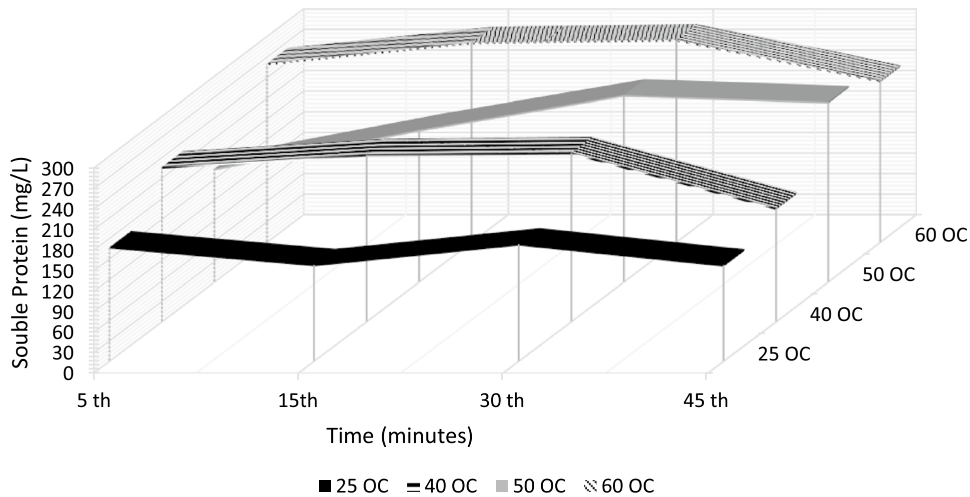


Fig. 5 Soluble protein changes in the pH 10 chemical pretreatment

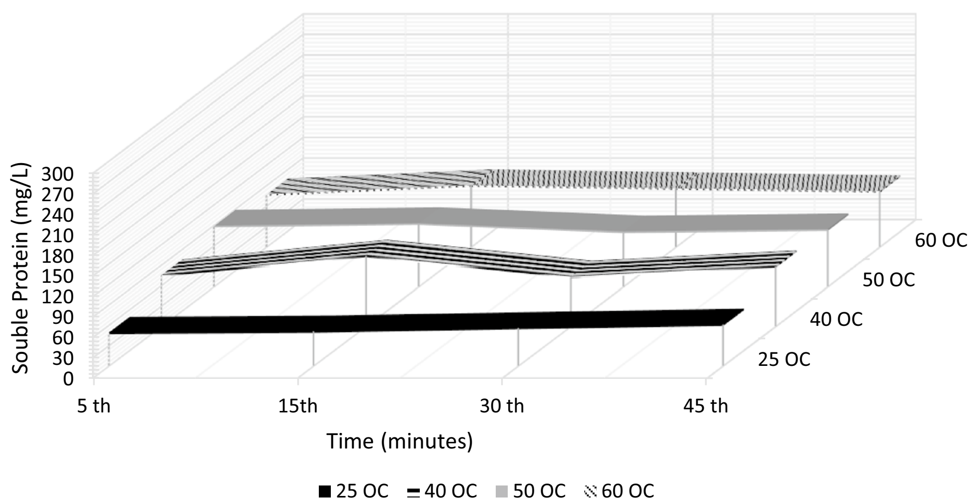


Fig. 6 Soluble protein changes in the thermal pretreatment

agreement with the results found in the literature (Zhong et al. 2014).

3.4 Cumulative Biochemical Methane Production

Biochemical methane potential experiments were performed taking into account the highest soluble protein values that were obtained during the periods specified in each pretreatment operation time and temperatures.

In the 35 kHz ultrasonic pretreatment experiments, the highest soluble protein value was obtained at the 45th min. Therefore, biochemical methane potential experiments were applied to the specimens from 45 min of pretreatment. The results obtained in the experiment are given in Fig. 7.

After 30 days of digestion of raw apple pomace with inoculation, the cumulative biochemical methane potential was found to be 897 mL CH_4/g VSS.day. The biochemical methane potential at the 40, 50, and 60 °C were found to be lower than the potential obtained with the putrefaction of raw apple pomace with inoculation. Only under the 25 °C, 45 min pretreatment conditions, biochemical methane potentials were found to have an increase of 17.73%.

Soluble protein values for pretreatment conditions of 25 °C 15 th min, 40 °C 30th min, 50 °C 30th min, 60 °C 45th min, are given in Fig. 8 at 53 kHz ultrasonic pretreatment. The biochemical methane potential results obtained after 53 kHz ultrasonic pretreatment studies are shown in Fig. 8.

As seen in Fig. 8, the biochemical methane potential is increased in the 53 kHz pretreatment studies. The highest increase was obtained at 60 °C 45 min (40.93%). Compared with the biochemical methane potential values obtained by putrefactive raw apple pomace with the inoculation, the increase was 6.45, 17.4, and 20.8% at 25 °C, 15 min; 40 °C, 30 min; and 50 °C, 30 min, respectively. However, cumulative biochemical methane potentials increased with temperature in the 53 kHz pretreatment studies.

At pH 5 chemical pretreatments, it was determined that the soluble protein values increased with increase in the temperature and decrease in the operating times. The biochemical methane potential values obtained as a result of these pretreatment studies are given in Fig. 9.

The cumulative biochemical methane potential at 25 °C for 45 min and 40 °C for 30 min increased by 5.9 and 0.8%, respectively. At higher temperatures, the cumulative biochemical methane potential decreased.

It has been determined that the optimum operating time is 30 min in the pH 10 chemical pretreatment experiments.

Fig. 7 The effect of the 35 kHz ultrasonic pretreatment on biochemical methane production

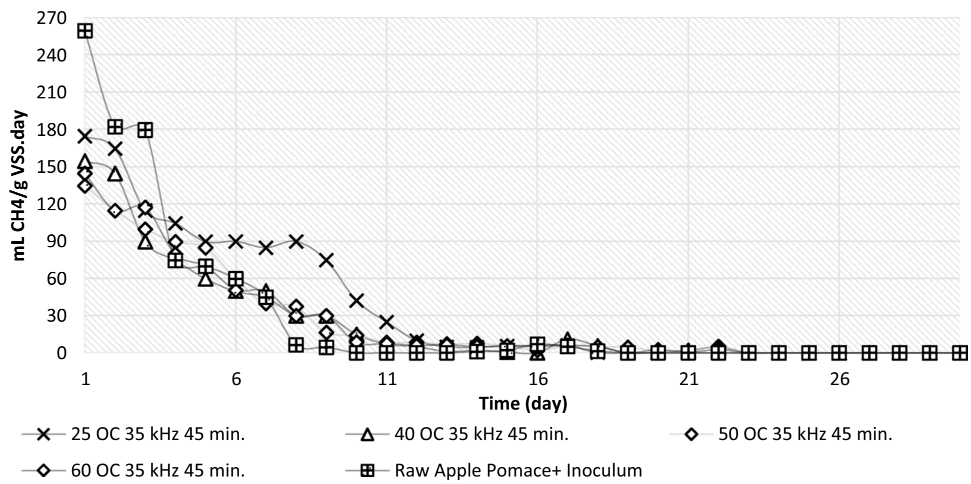


Fig. 8 The effect of ultrasonic pretreatment at 53 kHz on biochemical methane potential

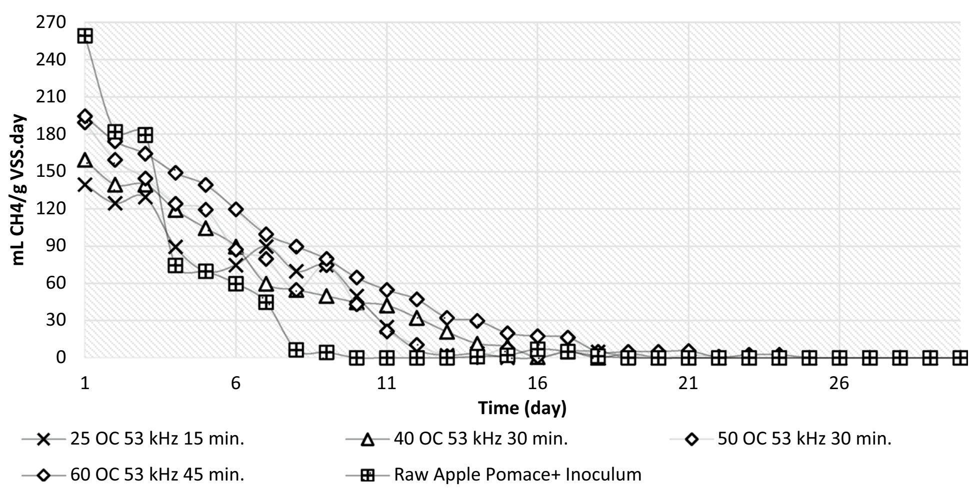
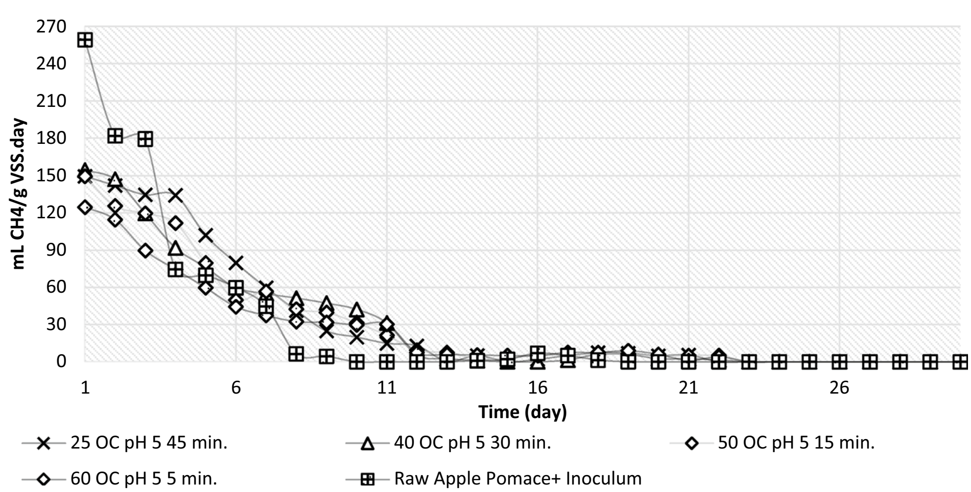


Fig. 9 Influence of the pH 5 chemical pretreatment on biochemical methane potential



The effect of pretreatment studies under these conditions on biochemical methane potential is given in Fig. 10.

The cumulative biochemical methane potentials obtained as a result of pH 10 chemical pretreatment studies were determined to be higher at higher temperatures. An increase of 1.3% was obtained at 50 °C for 30 min and 3.8% at 60 °C for 30 min.

While the cumulative methane potential at 25 °C was 714.56 mL CH_4/g VSS.day, it was measured as 892.11 mL CH_4/g VSS.day when the temperature was raised to 40 °C. However, these values were determined to be lower than the cumulative biochemical methane potential in the inoculated raw apple pomace (897 mL CH_4/g VSS.day).

In thermal pretreatments, the optimum operating time was determined to be 30 min and the biochemical methane potential changes are given in Fig. 11.

The cumulative methane potential was found to be 725.9 mL CH_4/g VSS.day after thermal pretreatment at room temperature. 40 °C for 15 min thermal treatment increased the cumulative biochemical methane potential by 10.5%. The highest cumulative biochemical methane potential increase in this pretreatment was obtained at 60 °C at 15 min as 11.1%.

4 Conclusion

This study has primarily established ultrasound, thermal and chemical disintegration as main of the many methods for the pretreatment of apple pomace. A secondary objective of the study was to evaluate the performance of pretreatment conditioned apple pomace for enhancing the destruction of soluble protein. Final objective of the study, assess the effects of optimum pre-treatment conditions (max. soluble protein) of apple pomace anaerobic digestion performance through biochemical methane potential (BMP) assays.

In the 35 kHz ultrasonic pretreatment, the highest soluble protein value was also obtained at 60 °C. The soluble protein values increased with time at 60 °C and the highest value was obtained at 45 min as 165.3 mg/L. Cumulative biochemical methane potentials were only increased by 17.73%

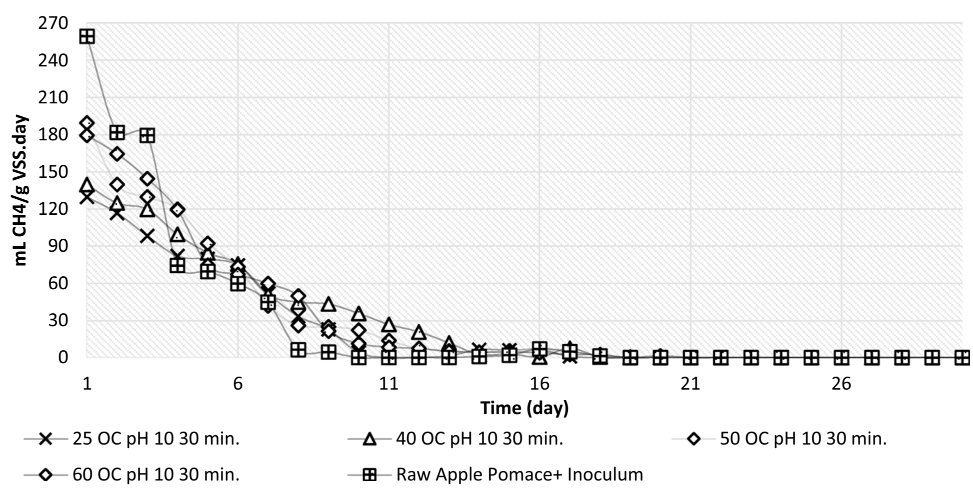


Fig. 10 Biochemical methane potential changes after the pH 10 chemical pretreatment

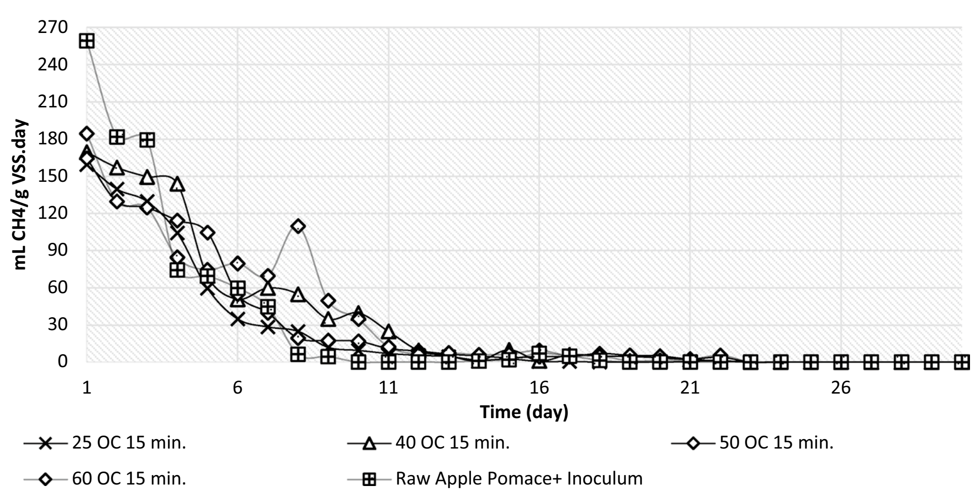


Fig. 11 Biochemical methane potential changes after thermal pretreatment

at 25 °C for 45 min. Although soluble protein increased at other operation times and temperatures, no increase in the biochemical methane potential was detected.

When the frequency was increased to 53 kHz in the ultrasound pretreatment studies, both the soluble protein values and the biochemical methane potential values were increased. Soluble protein values increased with temperature and operation time. The highest values were obtained at 60 °C, 45 min. The cumulative biochemical methane potential at 60 °C 45 min was calculated as 1519 mL CH_4/g VSS. day, and it was determined that these results were 40.93% more than the results obtained from raw apple treated to the putrefaction with inoculation (control group).

In the case of chemical pretreatment studies, the decrease in the operating time at pH 5 pretreatment increased the soluble protein value. At elevated temperatures (50 and 60 °C), no increase in the biochemical methane potential was achieved. Increases of 5.9 and 0.88% were obtained at 25 °C, 45 min and 40 °C, 30 min, respectively.

In the pH 10 pretreatment, soluble protein values were up to 294.3 mg/L. Unlike the results of pH 5 pretreatment studies, biochemical methane potential values increased by 1.3 and 3.8% at high temperatures (50 and 60 °C). The increases due to temperature were determined.

In the thermal pretreatment, cumulative biochemical methane potentials were increased by 10.57% at 40 °C, 15 min and 11.17% at 60 °C, 15 min.

To sum up, the maximum increase in the cumulative biochemical methane potential among the pretreatment methods was obtained in 53 kHz ultrasound at 60 °C at 45 min with 40.93%, and it was determined that the most effective method was ultrasound pretreatment at a frequency of 53 kHz when compared with other pretreatment methods. It was observed that the temperature and operation time have an enhancing effect on various pretreatments, and in some cases it has an inhibitory effect on the increase of biochemical methane potential. In this study, the effectiveness of certain pretreatment methods on methane increase has been proven.

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