# Evaluation of apple pomace biochemical transformation to biofuels and pectin through a sustainable biorefinery

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ABSTRACT

The waste apple pomace, rich in free sugars and structural carbohydrates, can prove to be a good feedstock for biofuels and value-added chemicals production. In this work, apple pomace was used for the production of pectin and biofuels by applying dilute sulfuric acid (1% w/v) treatment. The treatment factors, i.e., temperature and residence time, were optimized to maximize the pectin and biofuels (bioethanol and methane) yields. The solid loaded in the treatment step was 10 g of dried apple pomace per 140 ml of sulfuric acid (1% w/v). The liquor resulting from the dilute acid treatment, containing solubilized sugars and pectin, was subjected to fermentation and pectin recovery. The resulting treated solids were anaerobically fermented to produce biomethane. Furthermore, the environmental and economic aspects of the process developed were evaluated. The highest pectin extraction yield of 164 g pectin per kg of dried apple pomace was obtained after 60 min acid treatment at 94 °C. The pectin extracted with the highest yield had a degree of esterification and galacturonic acid content of 71.3% and 61.2%, respectively. On the other hand, the maximum sugar yield of 411.4 g fermentable sugars (glucose and fructose) per kg of dried apple pomace was obtained at 140 °C after 30 min acid treatment, which was anaerobically fermented to 136.3 g ethanol per kg of dried apple pomace. The highest methane yield (>120 mL/g volatile solids) was obtained at mild conditions. However, the yield decreased with treatment severity. The process developed in this work has a potential to produce over 131.1 million liter of bioethanol in Iran (in 2020). The estimation showed that mixing 5% ethanol (E5) with gasoline can reduce nearly 189.2 k ton of greenhouse gas (GHG) emission in comparison with a gasoline-fueled vehicle in 2020.

## 1. Introduction

Nowadays, by growing the populations of the world and increasing the greenhouse gasses, more attention has been given to biomass management and its conversion to renewable productions [1]. According to Food and Agriculture Organization (2020) [2], approximately 86 and 2.2 million metric tons (MMt) of apple fruit was produced in the world and Iran, respectively. Apple pomace, a waste of juice factories, that makes about 25% of the total processed biomass [3], is mainly disposed as an industrial food waste [4]. However, in recent years, discarding waste has been a challenge due to its environmental and economic impacts [5]. The high moisture content (70–75%) and high chemical and biological oxygen demand (COD and BOD) of apple pomace are the major environmental challenges for its disposal [4].

Apple pomace is comprised of carbohydrates polymers, including cellulose, hemicellulose, and pectin, as well as simple carbohydrates, protein, fat, ash, and polyphenols [3]. Thus, due to the presence of polymeric and simple carbohydrates, the apple pomace is a potential biorefinery feedstock for the production of value-added products and biofuels, e.g., bioethanol and biogas. The production of biofuels from apple pomace can diminish the greenhouse gasses (GHG) emissions, which cause the climate change and global warning [3].

Apple pomace contains appreciable amounts of pectin, which is a highly valuable stabilizing agent, thickener, and an emulsifying agent in the food industry. Moreover, pectin has different medicinal applications as well, e.g., toxin removal and blood cholesterol reduction [6,7]. Pectin present in apples (and other lignocellulosic biomass) acts as a glue that

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**List of abbreviations, units, and nomenclatures**

| | |
|---|---|
| °C | Celsius degree |
| µL, | microliter |
| A | Heat capacity |
| ANOVA | Analysis of variance |
| BOD | Biological oxygen demand; |
| C | Specific heat capacity |
| $CH_4$ | Methane |
| $CO_2$ | Carbon dioxide; |
| COD | Chemical oxygen demand; |
| DE | Degree of esterification |
| g | Gram |
| GE | Gasoline Equivalent |
| GHG | greenhouse gasses |
| HPLC | High performance liquid chromatograph |
| HHV | higher heating value |
| kg | kilogram |
| L, | liter |
| LR | liquid recovery |
| M | molar |
| $m^3$ | cubic meter |
| mg | milligram |
| min | minute |
| MJ | Mega joule |
| mL, | milliliter |
| mM | Milli molar |
| MMt | Million metric tons |
| Mt | Metric ton |
| $N_2$ | nitrogen |
| NaOH | sodium hydroxide; |
| NREL, | National Renewable Energy Laboratory |
| Q | Heating value |
| SR | solid recovery |
| t | Ton |
| $T_1$ | Primary temperature of water |
| $T_2$ | Secondary temperature of water |
| TS | Total solid |
| USD, | United State dollar |
| VS | Volatile solid |

cements cellulose, hemicellulose, and protein together through hydrogen, covalence, and ionic bonds [8]. After pectin extraction, the complex network of lignocellulosic parts is disrupted, making the remaining cellulosic/hemicellulosic portion amenable for enzymatic and/or thermochemical hydrolysis. Thus, pectin extraction can enhance the bioethanol and biogas yields from the solid residues by opening the complex structure [9,10].

Among biofuels from agro-industrial waste, the bioethanol is a high value-added product due to its organic carbon source [11]. Worldwide, ethanol is a broadly used renewable biofuel due to its scalability, compatibility, and near carbon neutrality. Its application in transportation sector reduces crude oil consumption and GHG emission [12]. However, for high yield bioethanol production from complex carbohydrates, it is recommended to perform some sort of physical, physicochemical, chemical, or biological treatment to increase to the sugars, i.e., cellulose and hemicellulose [13]. The solids resulting from these treatments often require a biological conversion step that employs cell-free enzymes mediated enzymatic hydrolysis for complex carbohydrates conversion to sugars. Nonetheless, enzymatic hydrolysis route is still not commercially attractive due to enzymes' high cost and slow hydrolysis reaction rates [14]. One of the most disadvantages of enzymatic hydrolysis is the non-productive adsorption of enzymes on lignin, instead of cellulose or hemicellulose, resulting in reduced availability of free enzymes and reduced hydrolysis efficiency. Thus, to overcome this problem, high enzyme loadings are required. But the cost of bioethanol increases in parallel with the use of enzyme [12]. Therefore, it is imperative to monitor enzyme consumption for cost-effective and eco-friendly bioethanol production [12].

On the other hand, dilute acid hydrolysis is another method for converting polymeric carbohydrates into simple sugars, which can be performed with less than 1% of inexpensive acids, e.g., sulfuric acid, and requires much less time than the enzymatic hydrolysis route [15]. This method can eliminate the requirement for biological conversion step to reduce the bioethanol production cost. To the best of our knowledge, no study has ever investigated the effect of enzyme elimination on ethanol production from apple pomace.

The solids remaining after the treatment step consist a part of polycarbohydrates, e.g., high crystalline cellulose. Anaerobic digestion of these solids to produce biogas could be a sustainable alternative [3]. The biogas, predominantly comprising methane and carbon dioxide, produced through anaerobic digestion process involves four steps, i.e., hydrolysis, acidogenesis, acetogenesis, and methanogensis. The bacteria can carry out hydrolysis on the polymer carbohydrates and convert them to biogas [16]. In the previous studies, the biomethane potential of apple pomace have been reported in the range of 137–231 mL $CH_4$ g per volatile solids [3].

For the reasons mentioned above, the aim of this study is the optimal pectin extraction as a valuable compound and facilitating the bioethanol production step from apple pomace. The conditions for maximum pectin separation from apple pomaces were investigated. After pectin separation, the liquid fraction was used for bioethanol production without enzymatic hydrolysis. Enzymes that are applied for lignocellulose hydrolysis influence the total production costs. Therefore, the elimination of enzymatic hydrolysis step can play a vital role in reducing the cost of the process. Moreover, the remaining solid waste was subjected to anaerobic digestion for biogas production. Finally, the environmental perspective of ethanol production from apple pomaces was investigated.

## 2. Material and methods

### 2.1. Materials

Fresh apples cultivated in central Iran (Semirom, Isfahan Province) were used as a substrate. Apples were washed with tap water and juiced. Then, the waste was rinsed thoroughly with distilled water, dried at room temperature for a week, and ground in a mill (EG500, Feller Company, China). The particles of size between mesh 20 and 80 were separated and stored at ambient temperature in sealed plastic bags until use.

A hexose fermenting *Saccharomyces cerevisiae* (CCUG 53310) yeast was obtained from the Culture Collection of the University of Gothenburg (Gothenburg, Sweden) and used for ethanolic fermentation. The yeast maintenance and cultivation were based on the procedure described by Karimi et al. [17].

### 2.2. Dilute acid treatment

For dilute acid treatment of apple pomace, a high-pressure reactor (101SSHPR, Steel Sanat, Isfahan, Iran) was used [18]. The reactions were run in 1% w/v sulfuric acid (98% purity, Merck, Germany) at 100, 140, and 180 °C for 0, 30, and 60 min in an oil bath (Oilbath ONE, Memmert, Germany). The treatment was also conducted by heating apple pomace with 1% w/v sulfuric acid in a glass bottle in a water bath at boiling temperature (94 °C) for 0, 30, and 60 min (Waterbath SV

142000, Memmert, Germany), which was earlier shown to be the optimum temperature for pectin extraction [19]. For treatment, 10 g of dry apple pomace was first added to the reactor (or bottle) followed by 140 mL of 1% w/v sulfuric acid [19]. The reactor was heated at a rate of 4 °C/min, and the reaction time was started when the reactor reached the reaction temperature [18]. At the end of the treatment time, the reactor was immediately placed in an ice bath to cool down. For 0 min treatment time point, the reactor was heated to the desired temperature, and then quickly cooled by putting in an ice water bath. Then, the solids were separated from the liquid portion by filtering through the linen bags. The liquid fraction was kept at 20 °C in plastic bottles. The remaining solids were then washed with distilled water at room temperature until the pH of the filtrate was neutral followed by freeze drying (Christ, alpha 1–2 LD model, Germany). The freeze-dried solids were kept in sealed plastic bags at ambient temperature.

### 2.3. Extraction and purification of pectin

The extraction of pectin was performed on the liquid resulting from the dilute acid treatment of apple pomace. The pH of the liquid fraction was first adjusted to 3.5 by 1 M sodium hydroxide (>98% purity, Merck, Germany) solution [20]. Then, an equal volume (140 mL) of ethanol (96% v/v) was added to the solution and left overnight at 4 °C. The precipitate (pectin) was collected by centrifuge (Selectalab tl-320, Far-Azma, Iran) at 4000 rpm for 15 min. The pectin was washed twice with a 70% (v/v) ethanol solution and then with a 96% (v/v) ethanol solution. The mixture was centrifuged at 4,000 rpm for 30 min to separate the impurities from pectin. Finally, the washed pectin was dissolved in deionized water, freeze dried (Christ, alpha 1–2 LD, Germany), and stored in a plastic bag at room temperature. The yield of pectin extraction ($Y_{pec}$) was calculated using Eq. (1):

$$Y_{pec}(\%) = {}^{P}/_{B_i} \times 100 \quad (1)$$

Where $B_i$ is the initial quantity of apple pomace, and $p$ is the quantity of obtained pectin, both in g.

The supernatant resulting from the pectin precipitation step was distilled to separate ethanol, and then the solution containing dissolved sugars was fermented for ethanol production.

### 2.4. Fermentation for bioethanol production

After the separation of pectin and extraction of ethanol from the treatment liquor, the remaining portion containing sugars was used for fermentation. For this, 118 mL glass bottles were used as reactors. The supernatant liquor (18 ml) was added to the 1 ml of rich medium culture of 5 g/L yeast extract, 7.5 g/L ammonium sulfate (>98% purity, Merck, Germany), 3.5 g/L dipotassium hydrogen phosphate (>98% purity, Merck, Germany), 0.75 g/L magnesium sulfate (>99.5% purity, Merck, Germany), and 1 g/L calcium chloride (>96% purity, Merck, Germany) [17]. The pH of the solution was adjusted to 4.8. The bottles were sterilized in an autoclave (121A model, Sanaye Pezeshki, Iran) at 121 °C for 20 min, and then were cooled in a sterile microbial hood. Then, 1 mL of the concentrated solution of *S. cerevisiae* solution (20 g/L) was added to the fermentation bottles. Ethanol blanks were also run in duplicate to measure the amount of ethanol loss during fermentation. The bottles were sealed and purged with nitrogen for 2 min to flush out the oxygen. The samples were incubated in a shaker incubator (JTBL20, Jaltajhiz, Karaj, Iran) at 32 °C and 120 rpm for 24 h. All experiments were done in duplicate. The sampling was carried out at the end of the fermentation (after 24 h) and kept in the freezer for further analysis.

Ethanol yield ($Y_{\%\ of\ theoretical}$) were calculated as shown below

$$Y(\%\,of\,theoritical) = \left(Ethanol\left(g.L^{-1}\right)\right) \times 100 / \left(Released\,Sugar\left(g.L^{-1}\right) \times 0.51\right) \quad (2)$$

### 2.5. Biomethane production

The inoculum for anaerobic digestion was obtained from a 7000 $m^3$ anaerobic digester (Isfahan Sewage Treatment Plant, Isfahan, Iran), working at mesophilic conditions. The collected inoculum was sieved to eliminate the particles larger than 2 mm. The total solids (TS) and volatile solids (VS) of the inoculum were determined [21]. Anaerobic digestion was performed according to Hansen et al. at mesophilic conditions (37 °C) in 118 mL dark glass bottles [22]. The glass bottles were loaded with 20 mL inoculum, 5 mL tap water, and 0.25 g (dry weight) untreated and dilute acid treated apple pomace, sealed with butyl rubber and aluminum caps, and then purged with $N_2$ for 2 min to flush out the oxygen. Inoculum blanks were also run in duplicate to measure the amount of biogas produced from the inoculum alone. The bottles were placed in an incubator (JSH20LURS, Jal Tajhiz Labtech Co., Tehran, Iran) at 37 °C for 45 days and manually shaken once a day. Gas sampling was conducted every three days for two weeks and then every five days. A gas pressure lock syringe (VICI Precision Sampling Inc., USA) was used to take a 200 μL sample from the bottle headspace and injected it into a gas chromatograph (GC) for analysis. All anaerobic digestions were done in duplicates.

### 2.6. Determination of heating value

A bomb calorimeter (Adak Tajhiz Iranian, Iran) was used for the heating value determination of the lignin-rich solids resulting from anaerobic digestion. A 0.1 g sample of solids was loaded in the combustor and was burned in oxygen. The heating value of the sample (Q) was calculated using Eq. (3):

$$Q = M\,C\,(T_2 \quad T_1) + A\,(T_2 \quad T_1) \quad (3)$$

where m, C, A, $T_1$, and $T_2$ are the mass of water (g), specific heat capacity (J. g $^{1}$. K $^{1}$), heat capacity (J. K $^{1}$) and the primary and secondary temperatures (K) of the water around the reservoir, respectively [23].

### 2.7. Gasoline equivalent calculations

To gain a better understanding of various treatment conditions, the heating values of the produced ethanol, biogas, and the remained solids after anaerobic digestion were expressed as gasoline-equivalent. The lower heating values of ethanol, methane, and gasoline used were 21.2 MJ/L, 36.1 MJ/$m^3$, and 32 MJ/L, respectively [24]. The calculations were based on 1 metric ton of the apple pomace. The equivalent gasoline from ethanol and methane per metric ton of waste were calculated as following:

$$\text{Gasoline equivalent from ethanol} = 14000\ l \times LR \times {}^{g}/_{l}\,ethanol \times 1\ {}^{l}/_{789\ g}\ ethanol \times 21.2\ {}^{Mj}/_{1\ l\ ethanol} \times 1\ {}^{l\ gasoline}/_{32\ Mj}$$

$$\text{Gasoline equivalent from methane} = 1\ ton \times 1000000\ {}^{g}/_{1\ ton} \times SR \times {}^{ml\ methane}/_{g\ vs} \times 1\ {}^{m^3}/_{10^6\ ml} \times 36.1\ {}^{Mj}/_{1\ m^3\ methane} \times 1\ {}^{l\ gasoline}/_{32\ Mj}$$

where LR, and SR are liquid recovery and solid recovery, respectively.

### 2.8. Products' value

The worth of pectin and biofuels, produced through the proposed biorefinery platform, was assessed based on the USA currency. The average prices of gasoline and pectin around the world were considered to be $1.0 USD/L and $10.0 USD/kg, respectively [25,26].

### 2.9. Analytical methods

#### 2.9.1. Substrate characterization

The total solids (TS), volatile solids (VS), structural carbohydrate, total lignin, and ash content of the untreated and pretreated apple pomaces were measured according to the National Renewable Laboratory (NREL, Denver, Colorado) methods [21,27,28].

#### 2.9.2. Pectin characterization

The galacturonic acid (GalA) content of pectin was determined according to the method of Ramos-Aguilar et al. [29]. Briefly, 5 mg of pectin was slowly added to 1 mL of deionized water and 2 mL of sulfuric acid (98%). The working volume of the reaction was adjusted to 10 mL with water, and the solution was centrifuged at 2000×*g* for 10 min at room temperature. The 400 μL supernatant was placed in a glass tube and mixed with 40 μL potassium sulfamate (abcr GmbH, Germany) (4 M, pH 1.6) solution and 2.4 mL sodium tetraborate (99% purity, Merck, Germany) (75 mM in concentrated sulfuric acid). The glass tube was placed in a boiling water bath for 20 min and then cooled in an ice bath for 10 min. Then, 80 μL m-hydroxydiphenyl solution (0.15% 3-phenylphenol (85% purity, Merck, Germany) in 0.5% NaOH) and 0.5% NaOH were added to the tubes labeled as sample and white (control reaction), respectively. Finally, the absorbance of the samples was measured at 525 nm using a UV–Vis spectrophotometry (Jenway Co., Staffordshire, England). The galacturonic acid content of extracted pectin was calculated using the following equation. This equation was driven from the calibration curve of galacturonic acid concentration to absorbance at 525 nm wavelength:

$$Y = 0.03X \quad R^2 = 0.9990 \tag{4}$$

Where X is the absorbance and Y is the concentration of galacturonic acid in mg/mL.

The degree of esterification (DE) was measured using the method provided by Santos et al. [30]. The pectin (0.1 g dry mass) was mixed with ethanol 96% (3 mL) in 100 mL Erlenmeyer flasks. A volume of 20 mL distilled water was added to the flasks and stirred at 40 °C until the complete dissolution of pectin. The titration of the solution was performed with sodium hydroxide solution ($V_1$ mL, 0.1 M) until the appearance of pale pink in the presence of phenolphthalein (ACS reagent grade, Merck, Germany) (5 drops) as the indicator. The sodium hydroxide solution (10 mL, 0.1 M) was added and stirred. The hydrochloric acid solution (Merck, Germany) (0.1 M, 10 mL) was added and stirred until complete disappearance of the pink color. The titration was performed with sodium hydroxide ($V_2$ mL, 0.1 M) until the solution color changed to pink ($V_2$). The DE of the pectin was determined using Eq. (5).

$$DE(\%) = V_2/(V_1 + V_2) \times 100 \tag{5}$$

#### 2.9.3. Sugars and ethanol analysis

The sugars and ethanol contents in liquid samples were determined by a high-performance liquid chromatograph (HPLC, 1260 Infinity, Agilent Co., Santa Clara, CA, USA) equipped with UV–Vis and RI detectors (Jasco International Co., Tokyo, Japan). The sugars were analyzed using an ion-exchange Aminex HPX-87P column (Bio-Rad, Richmond, CA, USA) at 85 °C with deionized water as the mobile phase at a flow rate of 0.6 mL/min. However, for ethanol, an Aminex HPX-87H column (Bio-Rad, Richmond, CA, USA) at 65 °C and 0.6 mL/min with sulfuric acid (5 mM) eluent was employed.

#### 2.9.4. Biogas analysis

A gas chromatograph (GC, GC-2552, Tief Gostar Faraz Co., Iran) was used to measure the amount of methane and carbon dioxide in biogas. The GC was equipped with a packed column (3 m length and 3 mm internal diameter, Porapak Q, Chrompack, Germany). The analytical grade nitrogen was used as a carrier gas with a flow rate of 50 mL/min. The column temperature was 40 °C, while those of the injector and detector were set at 100 and 150 °C, respectively. A pressure lock syringe (250 μL, 250R-V-GT, SGE Analytical Science, Trajan Co., Melbourne, Australia) was used to inject the gas samples into the GC. The analytical grade methane and carbon dioxide (with the purity of ≥99.0%) were used to obtain the calibration curves for $CH_4$ and $CO_2$. The volume of produced gas was measured using the method provided by Hansen et al. [22].

#### 2.9.5. Estimation of greenhouse gas emission reduction

The main advantage of biofuels production from agricultural waste, e.g., apple pomace, is the reduction of GHG emissions. The amount of bioethanol produced ($A_B$) from apple pomace was calculated as follows:

$$A_B = Y \times A_{CB} \tag{6}$$

where Y is the amount of bioethanol in liter per metric ton of apple pomace, and $A_{CB}$ is the maximum amount of collectable apple pomace in ton.

The GHG emissions reduction can impose indirect cost on the government, defined as social carbon costs (SCC).

The $F_{blend}$ (blended fuel) is calculated using Eq. (7):

$$F_{blend} = F_{biofuel}/_{x} \tag{7}$$

where $F_{biofuel}$ is the amount of total bioethanol production from apple pomace per year and the biofuel volume fraction (x) is dependent on the ratio of bioethanol to gasoline (E5, E10, or E85). Knowing that heating value of ethanol is 0.68 (R) of gasoline, the fossil fuel that could be saved ($F_{saving}$) was estimated according to Eq. (8):

$$F_{saving} = R \times F_{biofuel} \tag{8}$$

The well-to-wheel $CO_2$ emission factor for each liter of fossil fuel ($C_{fossil}$) and each liter of bioethanol ($C_{biofuel}$) are 2.99 and 0.6 kg $CO_2$, respectively. $C_{blend}$ is well-to-wheel $CO_2$ emission factor for each liter of blended fuel. When ethanol is blended with different ratio of gasoline (E5, E10, or E85), $CO_2$ emission reduction could be calculated according to the following Eqs:

$$F_{equivalent} = F_{saving} + (1 \quad x)F_{blend} \tag{9}$$

$$C_{blend} = xC_{biofuel} + (1 \quad x)C_{fossil} \tag{10}$$

$F_{equivalent}$ is the amount of fossil fuel equivalent to blended fuel.

According to Eq. (11) and Eq. (12), the amount of greenhouse gas reduction ($\Delta_{GHG}$) and social carbon cost reduction ($\Delta_{SCC}$) from apple pomace were calculated, respectively, by the method provided by Alavijeh et al. [31].

$$\Delta_{GHG} = C_{fossil}F_{equivalent} \quad C_{blend}F_{blend} \tag{11}$$

Social carbon cost reduction ($\Delta_{SCC}$) ($) can be calculated according to Eq. (11):

$$\Delta_{SCC} = \Delta_{GHG} \times SCC \tag{12}$$

where $40 and $220 per ton $CO_2$ was assumed as a minimum and maximum for social cost of carbon dioxide (SCC).

#### 2.9.6. Statistical analysis

Analysis of variance (ANOVA) of results was applied with the Tukey method using SAS 9.0 software (SAS Institute, Inc., 1999, Cary, NC, USA). This method was used to define the meaningful difference with the 95% confidence level ($p < 0.05$) [32].

## 3. Results and discussion

Efficient conversion of apple pomace to biofuels and value-added products was investigated. Apple pomace solids were subjected to

**Table 1**
Solid extraction and characterization of pretreated apple pomace.

| Treatment condition | | Solid extraction (%) | Glucan (%) | Xylan (%) | Other Hemicellulose (%) | Lignin (%) | Ash (%) | Protein (%) |
|---|---|---|---|---|---|---|---|---|
| Temp (°C) | Time (min) | | | | | | | |
| untreated | – | – | 31.7 | 0.3 | 11.7 | 18.3 | 2.6 | 4.4 |
| 94 | 0 | 37.3 | 43.0 | 0.2 | 10.5 | 20.5 | 5.3 | 4.2 |
| | 30 | 29.5 | 47.4 | 0.2 | 8.1 | 20.9 | 6.0 | 4.3 |
| | 60 | 25.3 | 48.8 | 0.2 | 7.9 | 19.0 | 4.9 | 4.3 |
| 100 | 0 | 23.6 | 43.2 | 0.2 | 10.3 | 20.7 | 7.2 | 4.1 |
| | 30 | 23.7 | 47.7 | 0.2 | 7.8 | 21.5 | 7.1 | 4.3 |
| | 60 | 23.5 | 45.4 | 0.2 | 4.9 | 23.7 | 7.2 | 4.3 |
| 140 | 0 | 23.2 | 49.5 | 0.2 | 3.6 | 28.8 | 7.3 | 4.3 |
| | 30 | 22.9 | 48.5 | 0.2 | 2.1 | 30.6 | 8.1 | 3.9 |
| | 60 | 22.6 | 51.8 | 0.1 | 1.8 | 29.5 | 8.3 | 3.7 |
| 180 | 0 | 22.4 | 54.9 | 0.1 | 5 | 30.1 | 7.8 | 3.8 |
| | 30 | 22.3 | 57.3 | 0.1 | 0.8 | 31.1 | 8.0 | 3.9 |
| | 60 | 22.0 | 55.2 | 0.0 | 0.7 | 31.5 | 8.0 | 3.7 |

(The average standard deviation was less than 4.6%).

dilute acid treatment at different temperatures. The liquor obtained after dilute acid treatment was first subjected to pectin extraction, and the remaining liquor fraction containing solubilized sugars was fermented by *Saccharomyces cerevisiae* for ethanol production. Besides, the acid treatment solids were subjected to anaerobic digestion for biogas production.

### 3.1. Chemical composition of apple pomace and biofuel potentials

Table 1 shows the composition of apple pomace used in this study. The extractable and nonstructural compounds of the raw substrate must be removed from the substrate before compositional analysis [33]. The amount of ethanol extractable compounds was negligible in the substrate. However, the water extractable material was about 41.3%, which can include free sugars and nitrogen compounds. The apple pomace contained glucan (31.7%) that can be converted to bioethanol. Considering the theoretical conversion coefficient of glucan to ethanol (0.56), it has potential to produce 179.6 g ethanol from one kg of apple pomace. Fructose is another fermentable sugar of apple pomace. Fructose is a free sugar that can easily dissolve in water. The apple pomace consisted of approximately 12.3% fructose, which can theoretically produce 62.7 g ethanol from each kg of apple pomace. Free fructose (12.3%), glucose (2.7%), and sucrose (8.2%) were determined by HPLC. Apple pomace also contained protein (4.4%) and pectin (16.4%). Carbohydrates and proteins can be converted to biomethane via anaerobic digestion. Moreover, apple pomace had 18.3% lignin that can be combusted and used as a fuel for industrial equipment.

The acidic treatment was done using 1% (w/v) sulfuric acid at different temperatures (94, 100, 140 and 180 °C) for reaction times of 0, 30, and 60 min. As shown in Table 1, most of the apple pomace (63–78%) was solubilized by dilute-acid treatment. The solid extraction decreased slightly with increase in treatment temperature, resulting in the highest solid extraction after boiling in acid for 0 min.

In the treated solids, glucan and lignin content increased and hemicellulose decreased with increasing treatment temperature and time. The increase in glucan and lignin contents in the treated solids could be due to hemicellulose removal [34]. Nonetheless, increase in temperature and treatment time also impacted glucan solubilization as it increased from 49.4% (94 °C, 0 min) to 59.2% (180 °C, 30 min). Complete xylan was removed by treatment at 180 °C and 60 min, which was similar to that reported by Mahmoodi et al. [35]. By acidic treatment at 94 °C for 30 min, 70.5% of the solids, including 95.5 g hemicellulose per kg of apple pomace, were removed. However, the treatment at 180 °C for 60 min removed 118.5 g hemicellulose per kg of apple pomace. Lignin content in the solids increased with treatment time and temperature, and maximum lignin content (31.5%) was detected after acid

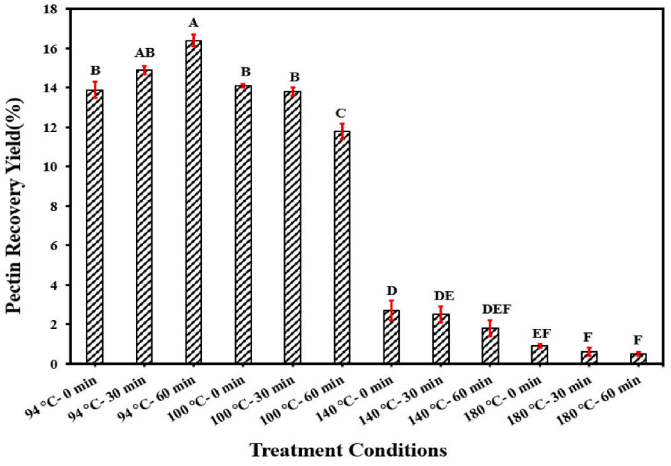


**Fig. 1.** Pectin extraction yield for different treatment conditions. Considerable differences between the various pretreatment conditions are shown by the letters above the columns.

treatment at the most severe conditions (180 °C for 60 min). In the acidic treatment, production of an insoluble complex of lignin and condensed protein from the acid-insoluble lignin content contributes to the lignin mass [36]. Accordingly, the lignin removal was decreased from 73.8% (at 94 °C, 60 min) to 62.1% (at 180 °C, 60 min). Previous studies indicated that dilute sulfuric acid treatment had more influence on xylan removal than lignin removal [35].

Protein in the untreated apple pomace and solids prepared at different treatment conditions was 3.7–4.4%. Table 1 shows that the treatment conditions do not significantly affect the protein content of the solids. This could be attributed to Maillard reaction between amino acids and sugars [37], which creates melanoidin and creates an error in the reported protein content. The protein content ranging from 1.9 to 8% was reported in previous studies, depending upon the fruit source and its maturity [4]. Moreover, the presence of 3.7–4.4% protein in the substrate might result in some errors in the accurate lignin content determination.

### 3.2. Extraction and analysis of pectin

#### 3.2.1. Pectin extraction yield

Previous studies showed that different parameters can affect the extraction yield including time, temperature, pH and type of the acid, liquid to solid ratio, pectin solution to ethanol ratio for precipitation,

**Table 2**
Characterizations of extracted pectins at optimum conditions of pectin extraction, and biofuel production.

| Treatment Conditions | | Galacturonic Acid Content (%) | Esterification Degree |
|---|---|---|---|
| Temp (°C) | Time (min) | | |
| 94 | 60 | 61.2 ± 1.1 | 71.3 ± 3.2 |
| 140 | 30 | 39.6 ± 2.1 | 41.1 ± 2.8 |

and pH at which the pectin is precipitated [38,39]. The pectin extraction yields at different extraction conditions are given in Fig. 1. The results show that increasing temperature significantly decreases pectin extraction. The decrease can be because of the decay of pectin molecule chains. Masmoudi et al. worked on lemon wastes to extract pectin and reported that extraction at high temperatures decomposes the dissolved pectin [40]. Garna et al. extracted pectin from apple pomace, using acidic method at pH of 1.5–2, temperature of 80–90 °C, and times of 1–3 h, to investigate the effect of extraction time on extraction yield [38]. Although no significant difference was found between extraction times, they reported that the extraction yield increases up to about 1 h and afterwards it remains constant. Perussello et al. looked at the effect of extraction parameters on apple pectin extraction yield, and reported that the temperature, acid concentration, and extraction time had effect on the pectin yield in the same order. However, the effect of interaction of these factors was not significant [41].

As Fig. 1 shows, the highest pectin extraction yield of 16.4% was observed at the lowest treatment temperature investigated, which is similar to the results reported by Rascon chu et al. for apple pomace pectin [42]. The results showed that increasing temperature results in a severe reduction of pectin extraction. Furthermore, increasing treatment time also reduced extraction yield.

### 3.2.2. *Galacturonic acid content (purity) of pectin*

Because galacturonic acid is a main part of pectin, determining its value can lead to the estimation of extracted pectin purity. Table 2 shows the galacturonic acid content of the extracted pectin. It was found that increasing temperature decreases extracted pectin purity. For low extraction temperature (94 °C), the pectin purity was 61.2%, but for extraction temperature of 140 °C, the pectin purity was 39.6%. At high temperatures, due to the extraction of more impurities with the solvents and precipitation with pectin, purity is decreased. However, according to the Food and Agricultural Organization (FAO) and the European Union (EU) commercial requirements, edible pectin must have at least 65% of galacturonic acid [43]. Nonetheless, in general, the purity of extracted pectin for both high as well low temperature case was less than 65%. Therefore, this extracted pectin is not suitable for edible uses and must either be used in other industries like floor coverings and plasticizers or should be purified further to make it edible.

### 3.2.3. *Esterification degree*

The degree of esterification (DE) is the sum of the degree of methylation (percentage of carboxyl groups esterified with methanol) and acetylation (percentage of galacturonosyl residues esterified with 1 acetyl group) [38]. Table 2 shows that the extracted pectin DE is different at different extraction conditions. The DE for pectin extracted at 94 °C is 71.3%, which is decreased to 41.1% for pectin extracted at 140 °C. This drop in esterification with increase in temperature can be due to partial decomposition of pectin and severe de-esterification of the pectin chain. Garna et al. stated that apple pomace pectin methylation decreases with increase in temperature and time, resulting in reduced DE [38].

Perussello et al. studied the extraction of pectin from apple pomaces and explained that methanol can esterify about 80% of carboxyl groups of pectin. This value can be decreased to a different degree based on the extraction conditions, including pH of solvent, temperature, and time extraction. Moreover, it depends on the source and maturity of apples

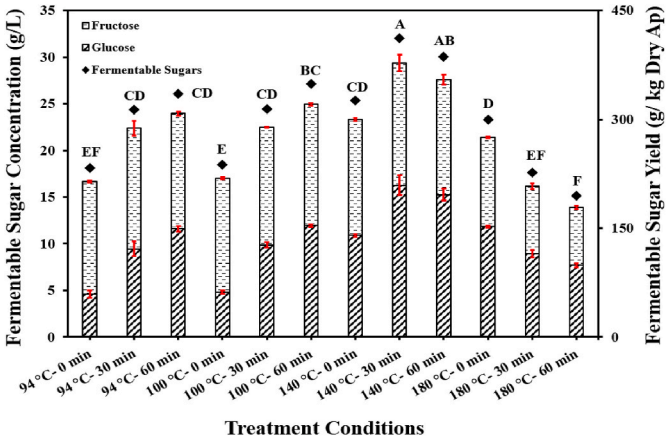


**Fig. 2.** The concentration of glucose (▨) and fructose (▩) as well as fermentable sugars yield (◆) for treated apple pomace. Considerable differences between the various pretreatment conditions are shown by letters above the columns.

**Table 3**
Ethanol concentration and yield (mean ± deviation) obtained after 24 h fermentation by *Saccharomyces cerevisiae.*

| Treatment Conditions | | Ethanol (g/kg dried substrate) | Ethanol Yield (%) |
|---|---|---|---|
| Temp (°C) | Time (min) | | |
| 94 | 30 | 72.1 ± 3.5 | 75.2 ± 3.7 |
| | 60 | 78.2 ± 5.9 | 76.1 ± 4.2 |
| 140 | 30 | 136.3 ± 1.7 | 81.3 ± 4.4 |
| | 60 | 121.6 ± 9.4 | 77.1 ± 2.8 |

[41]. Rascon Chu et al. extracted pectin from low-quality apple (fallen fruits) with 6% (w/v) citric acid at 100 °C for 30 min. They realized that esterification of pectin was 57% [42]. Garna et al. extracted pectin from apples at different conditions (pH: 1.5 to 2; temperature: 80–90 °C; time: 1–3 h) and were able to prepare pectin samples with different degrees of esterification from 54 to 80% [38]. Our findings are in good agreement with other studies.

### 3.3. *Fermentable sugars and ethanol production*

After ethanol separation from the supernatant, the treatment liquor was subjected to anaerobic fermentation by *S. cerevisiae* to produce ethanol. The results in Fig. 2 show that the highest fermentable sugars (29.4 g/L) in the liquor was obtained for treatment at 140 °C for 30 min. However, increasing the temperature and time decreased the concentration of sugars due to decomposition of hexose sugars (mainly fructose) to 5-hydroxymethylfurfural [44].

Anaerobic fermentation was performed on the treatment liquor obtained at conditions optimum for maximum fermentable sugars yield and pectin yield. The concentration and yield of the produced ethanol after 24 h of anaerobic fermentation for various treatment conditions are given in Table 3. The fermentation of the liquor obtained at 94 °C for 30 min treatment produced 8.6 g/L of ethanol and resulted in 72.1 g ethanol for each kg of dried apple pomace. However, by increasing the treatment time to 60 min, the produced ethanol concentration increased to 9.3 g/l and yielded 78.2 g ethanol for one kg of dried apple pomace. However, the liquor obtained at 140 °C for 30 min treatment resulted in 31.2% higher ethanol concentration, 12.2 g/L. This translates into 136.3 g ethanol per kg dried apple pomace, which is the highest amount of ethanol produced per kg dried apple pomace. However, the ethanol concentration decreased from 12.2 g/L to 10.9 g/L with increase in time from 30 to 60 min for treatment at 140 °C. This may be due to the lower concentration of sugars in the liquor resulting due to degradation of sugars (mainly fructose).

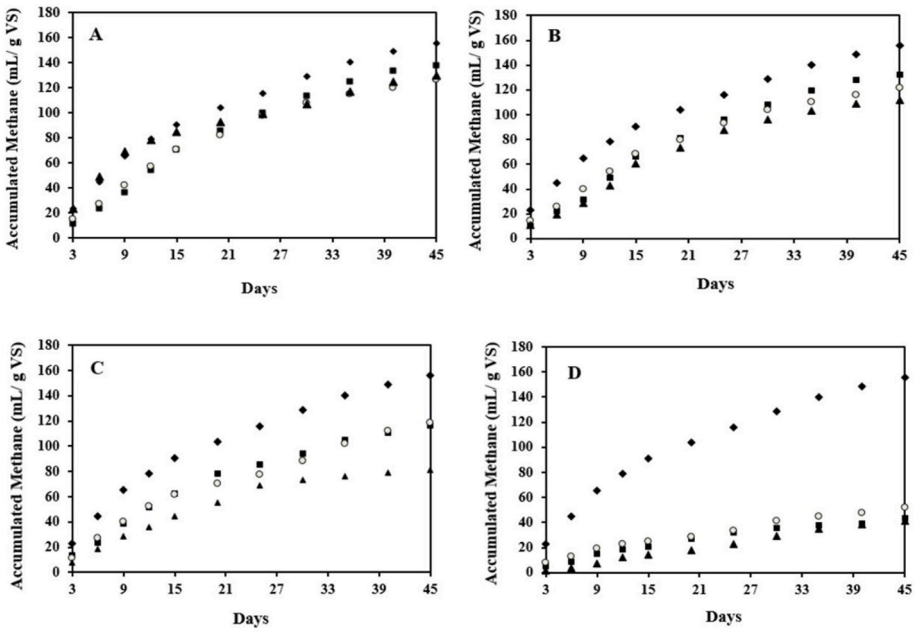


**Fig. 3.** Accumulated methane production during 45 day of anaerobic digestion from solid remained after acid-treatment. The symbols represent: (◆) untreated apple pomace, and treated at A) 94 °C, B) 100 °C, C) 140 °C, and D) 180 °C for (■) 0 min, (○) 30 min, and (▲) 60 min.

Evcan et al. used apple pomace for ethanol production at 110 °C and for 40 min with 4% phosphoric acid and different mixing speeds [45]. Their study was conducted with three different microorganism species. Based on the results, when *Saccharomyces cerevisiae* (at 300 rpm agitation speed) was used for ethanol production, the ethanol concentration of 4.46 g/L was achieved. Their results show that for agitation speed of 100 rpm, the ethanol concentration was reduced to 3.7 g/L. However, according to our findings, dilute sulfuric acid treatment and higher hydrolysis temperature (about 30°) yielded higher ethanol concentration than phosphoric acid treatment by Evcan et al. [45]. In another study, twelve different yeast and bacteria strains (including *Saccharomyces cerevisiae*) were applied by Molinuevo et al. to produce ethanol from apple pomace [3]. They subjected apple pomace to a physicochemical treatment and enzymatic hydrolysis. They reported the bioethanol yields of 72.5–86.3%. Their findings show that our results are in the good agreement with other studies.

Panahi et al. reported that apple pomace was subjected to enzymatic hydrolysis for bioethanol production by *Saccharomyces cerevisiae,* yielding 134 g ethanol per one kg of dry apple pomace [46].

### 3.4. Biogas production and heating value of remaining solids

Untreated and pretreated solids resulting after treatment at 94, 100, 140, and 180 °C and times of 0, 30 and 60 min were used for biogas production. The results in Fig. 3 show that the maximum methane production (155.8 mL/g volatile solids) was obtained for untreated apple pomace. The untreated waste contained a significant amount of pectin (kind of carbohydrate) and hemicellulose, which can be easily digested for the production of methane. Furthermore, the untreated substrate used in this study also contained extractable sugars such as glucose, fructose, and sucrose, which are easily extracted with water. Consequently, these sugars are accessible to methanogens even without treatment and a large amount of methane is produced. It should be noted that the compositional data obtained as per NREL method refers to the untreated substrate after extractions with water and ethanol; however, for anaerobic digestion, the raw substrate was used without extractions.

Fig. 3 also shows that increasing the treatment temperature and time, methane production decreases, which is due to free sugars, hemicellulose, and pectin solubilization into the liquid phase during treatment and their reduction in the remaining solids. Other influencing factor responsible for the reduction of methane production with more severe treatment conditions is the occurrence of Maillard reaction. In this reaction, amino acids react with sugars and produce melanoidin, which slows the anaerobic digestion process. Proteins mainly consist of nitrogen sources. Nitrogen contributes highly to methane production not only by providing the main source for microorganism growth but also by regulating the pH of the media. However, the substrate used in this study contained a small amount of protein, thus, the methane production was less influenced by the protein [18,47]. Karimi et al. performed dilute sulfuric acid treatment on urban waste at 120, 140 and 180 °C for different times, and their study also showed similar results that by increasing temperature and time, methane production decreases [18], which agrees with the results of the present study.

The heating value of the residual solids after anaerobic digestion (which is mainly lignin) was carried out with a bomb calorimeter. The heating value of the samples resulting from anaerobic digestion was compared with that of the control sludge sample, and the calculations were made based on it. The heating value of lignin is between 22.2 and 28.5 kJ/g, whereas the heating value of cellulose and hemicellulose is about 17.5 kJ/g [48]. The heating value for different samples was between 13.7 and 15.4 kJ per gram. The heating value for the untreated sample is less than the treated samples because the treated samples contained more lignin than the untreated samples. The ash content of the lignin produced during dilute acid treatment is high because of the precipitation of salts formed from the basic component of hydrolysate. HHV of lignin extracted from dilute acid pretreatment is lower than extracted one from other chemical treatments due to the increase of the amount of oxygen content [34,49].

Although heating values were measured and reported to present the energy content of all the products and by-products obtained in this biorefinery platform, it should be noted that heat extraction from the digestate might be difficult due to its high moisture contents.

### 3.5. Gasoline equivalent and value-added production

The economic potential of extracted pectin and biofuels including biogas, bioethanol, and heating value of residual solids after anaerobic digestion (mainly lignin) was calculated based on one metric ton of

**Table 4**
The gasoline equivalent produced at optimum conditions (pectin extraction, and biofuel production) of apple pomace.

| Gasoline Equivalent (L/Mt AP) | Treatment Conditions | |
|---|---|---|
| | 94 °C/60 min | 140 °C/30 min |
| **Ethanol** | 65.7 ± 4.9 | 114.4 ± 1.4 |
| **Biogas** | 37.9 ± 3.2 | 27.5 ± 2.8 |
| **Residue** | 20.5 ± 1.7 | 33.5 ± 2.2 |
| **Total (L/Mt AP)** | 124.1 ± 9.8 | 175.4 ± 6.4 |
| **Pectin (kg/Mt AP)** | 164 ± 3.0 | 25 ± 4.0 |
| **Products Value (USD/Mt AP)** | 1764.1 ± 39.8 | 425.4 ± 46.4 |

(Mt- metric ton; AP- apple pomace).

apple pomace to find the best conditions for value added production. The heating value of bioethanol (21.2 MJ/L) is much more than the heating value of biogas (36.1 MJ/$m^3$). Two scenarios were explored to evaluate their economic potential: (i) maximum pectin extraction and (ii) maximum fermentable sugars production. In these two scenarios, the liquid fraction after treatment was used for fermentation to produce ethanol. The solid fraction after treatment was subjected to anaerobic digestion to produce biogas, and the remaining solids (mostly lignin) was considered a solid fuel. As Table 4 shows, the first scenario gave the lowest gasoline equivalent due to less bioethanol production in this scenario. Besides, when the value-added product pectin is our target, the apple pomace treated at 94 °C for 60 min gave the highest pectin extraction yield and the maximum amount of pectin extraction was 164 kg per ton of apple pomace. However, if the biofuel production was the main goal of the biorefinery, i.e. second scenario, the apple pomace at 140 °C and 30 min has the highest potential for biofuel production. In this scenario, the maximum amount of total gasoline equivalent was around 175L gasoline per Mt of apple pomace.

Based on the multiple products obtained in this biorefinery platform, the total market value of the products was calculated in Table 4. The results show that the treatment condition of 94 °C for 60 min had the maximum products value (US $1764.1/Mt apple pomace), greatly higher than that obtained by treatment at other conditions. The product value for case I is 4.1 times higher than that for scenario II. This study provided a general assessment of developing apple pomace biorefinery. However, further studies on the life cycle assessment (LCA) of the biorefinery platform is required to obtain a comprehensive view of its complete potential.

### 3.6. *Mass balance*

The overall mass balances were estimated for scenario (I) and (II) in Fig. 4 for one metric ton of apple pomace basis. For scenario I, the bioethanol and biomethane production were 99.1 L and 33.6 $m^3$, respectively. Moreover, the heating value of remaining solids after anaerobic digestion (mostly lignin) was 656 MJ. The total gasoline equivalent for scenario I was 124.1 L. But for scenario II, bioethanol,

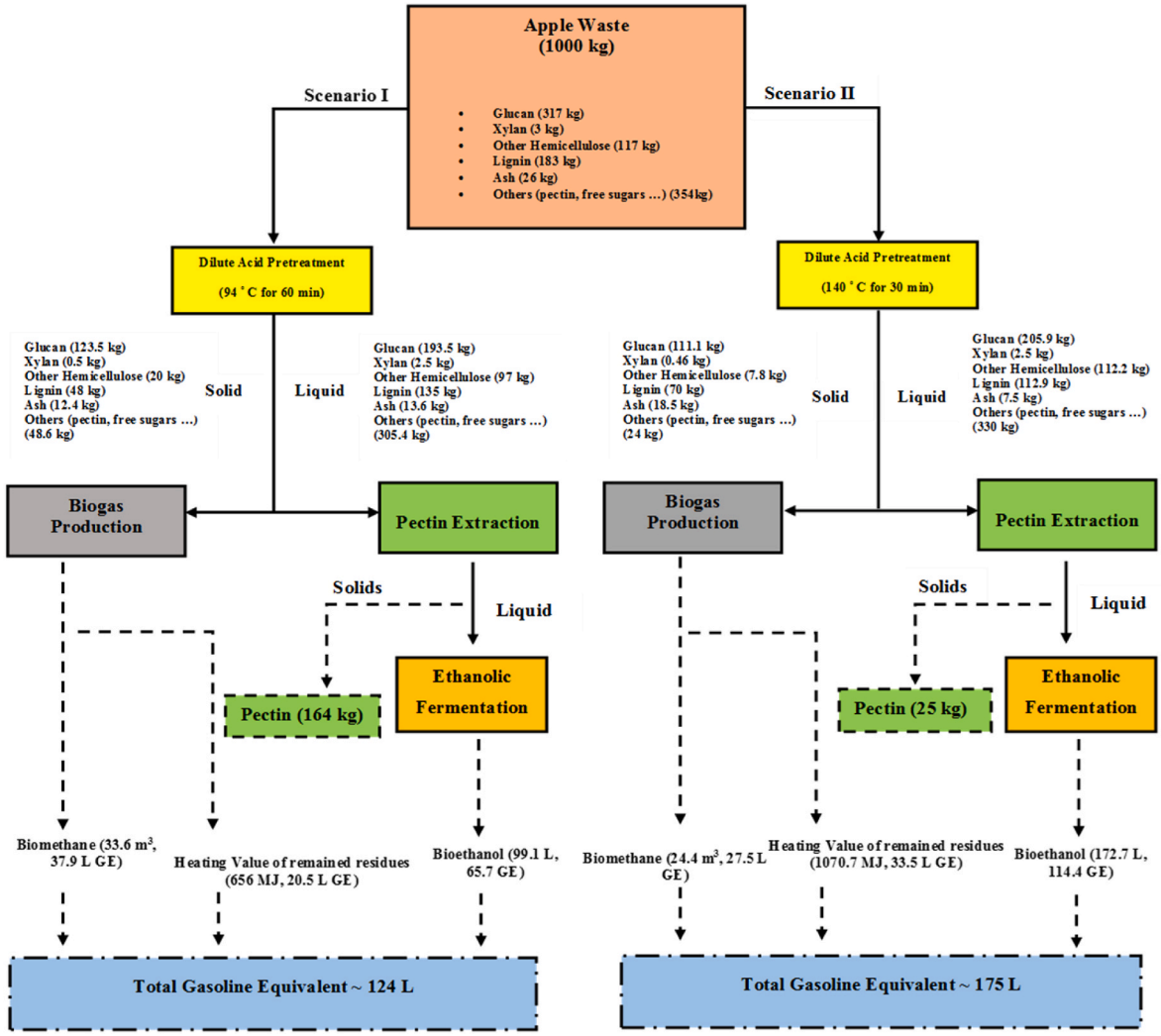


**Fig. 4.** The overall mass balance of the process for apple pomace conversion to ethanol, pectin, and methane.

**Table 5**
Amount of blended fuel (E85, E10, E5) from apple pomace in Iran.

| Blended fuel | Treatment conditions | | $F_{saving}$ (ML) | $F_{blend}$ (ML) | $F_{equivalent}$ (ML) | $\Delta_{GHG}$ (kt $CO_2$ eq) |
|---|---|---|---|---|---|---|
| | Temp (°C) | Time (min) | | | | |
| E85 | 94 | 60 | 51.2 ± 3.9 | 88.5 ± 6.7 | 64.4 ± 4.9 | 107.7 ± 8.2 |
| | 140 | 30 | 89.2 ± 1.1 | 154.3 ± 2.0 | 112.3 ± 1.4 | 187.7 ± 2.4 |
| E10 | 94 | 60 | 51.2 ± 3.9 | 752.3 ± 57.1 | 728.2 ± 55.3 | 108.6 ± 8.2 |
| | 140 | 30 | 89.2 ± 1.1 | 1311.2 ± 16.8 | 1269.3 ± 16.2 | 189.2 ± 2.4 |
| E5 | 94 | 60 | 51.2 ± 3.9 | 1504.6 ± 114.3 | 1480.5 ± 112.4 | 108.6 ± 8.2 |
| | 140 | 30 | 89.2 ± 1.1 | 2622.4 ± 33.5 | 2580.5 ± 33.0 | 189.2 ± 2.4 |

(ML-million liter; $\Delta_{GHG}$ – reduction in greenhouse gasses emissions).

biomethane, and the heating value of the residues were 172.7 L, 24.4 $m^3$, and 1070.7 MJ, respectively. For this scenario, the total gasoline equivalent was 175.4L.

### *3.7. $CO_2$ emission reduction and socio-economic effects of bioethanol production*

In Iran, the amount of apple production ($A_{CB}$) was approximately 2.2 million metric ton (MMt) in 2020. About 70% of apple is consisted of water and extracted by juice factories. Ethanol produced in the fermentation step was used to estimate the total ethanol amount that could be produced from 0.66 MMt of apple pomace [2].

Different volume fractions of ethanol (X) (0.05, 0.10, and 0.85) were used to calculate the GHG emissions reduction ($\Delta_{GHG}$). The conversion factor (R) was the ratio of ethanol heating value to gasoline heating value (0.68). The well to wheel $CO_2$ emission for each liter of ethanol and gasoline are 0.6 kg and 2.99 kg $CO_2$, respectively. The results for $\Delta_{GHG}$ for E5, E10, and E85 cases are reported in Table 5. The $\Delta_{GHG}$ for blended fuel, E85, with ethanol produced at conditions for maximum pectin extraction (94 °C and 60 min) was about 88.5 ML, and it can increase to 154.3 ML at conditions for optimum biofuel production (140 °C and 30 min). According to the findings, the application of E85 fuel with ethanol produced at both above mentioned conditions (i.e., 94 °C for 60 min and 140 °C for 30 min) can decrease the GHG emissions up to 55.90%. Moreover, at 140 °C for 30 min, it was produced 1311.2 ML of E10. The GHG emissions can be decreased by up to 4.99% at this condition. Furthermore, by production of E5 (2622.4 ML) the GHG emissions can be decreased up to 2.45%.

The social cost of $CO_2$ for E5, E10, and E85 are shown in Fig. 5. The maximum total social cost reduction of $CO_2$ occurred for treatment condition at 140 °C for 30 min for all the blend (E5, E10, and E85). In addition, the reduction in total social cost of $CO_2$ is approximately the same for all of three E5, E10, and E85.

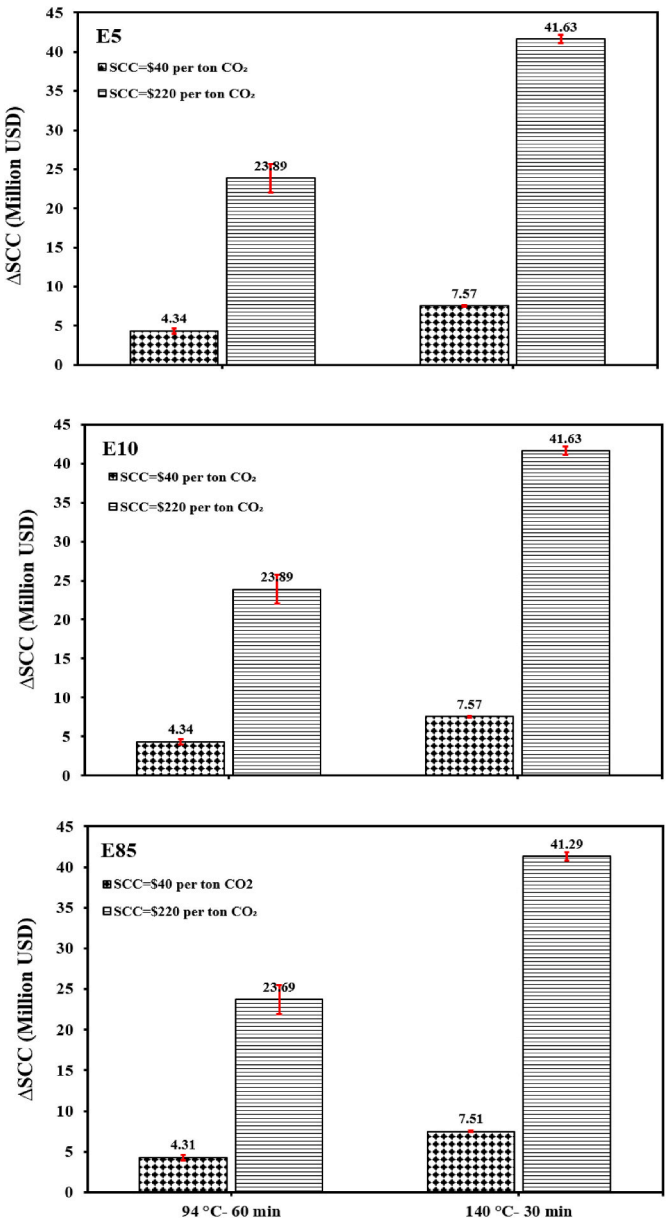


**Fig. 5.** The reduction in social carbon dioxide cost for E5, E10, and E85 blends containing ethanol produced from apple pomace.

## 4. Conclusions

Apple pomace has great potential for producing biofuels because it is mainly composed of carbohydrates. Also, it is a fruit that is rich in pectin. Therefore, due to this valuable component, apple pomace can be an excellent feedstock for a potential biorefinery. Dilute acid treatment with 1% w/v sulfuric acid was successfully applied for two main reasons simultaneously. First, this step used to extract pectin as a value-added product and second, the treatment was necessary for hydrolysis of carbohydrates without enzymatic hydrolysis for the production of ethanol. The best condition to reach two main goals, e.g., maximum pectin extraction and biofuel production, were distinct. When optimizing the extraction of pectin (as an expensive production) is the preference, the treatment at 94 °C for 60 min yields the highest pectin production. At this condition, 124.1L gasoline equivalent and 164 kg pectin per Mt of apple pomace were obtained. However, when biofuel production is the main purpose (as a renewable energy), the treatment at 140 °C for 30 min gave the maximum amount of produced gasoline equivalent, 175.4 L. However, pectin production at this condition was only 25 kg per ton. Considering the main purpose of this study, i.e., the biorefinery approach to earn the maximum value, the treatment at 94 °C for 60 min is the optimal condition that can generate products with the value of 1764.1 USD per ton of apple pomaces. On the other hand, the E5 blend with ethanol produced at 140 °C for 30 min (total-2622.4 ML) can meet Iran's gasoline demand for 35 days in 2020 [50].

The economic potential calculation showed that scenario I have the moderate optimal condition with a total product value of US$ 1764.1 per ton of apple pomaces (for production of 124.1 L total gasoline equivalent, and 164 kg pectin). Lohrasbi et al. (2010) investigated the economic analysis and process design of the citrus waste biorefinery.

They reported that in the optimum condition (150 °C for 6 min), the total energy produced (in the forms of ethanol and biogas) is equal to 75 L of gasoline per ton of dried citrus wastes (for the plant with a capacity of 100,000 tons citrus waste per year). According to their findings, ethanol price was sensitive to the plant capacity, transportation cost, and handling of citrus waste to the plant. With increasing the capacity of the plant from 25,000 to 400,000 tons of citrus waste per year, the ethanol costs will be decreased from 2.55 to 0.46 USD/L. In addition, increasing the transportation cost from 10 to 30 USD per ton resulted in enhancing the ethanol costs from 0.91 to 1.42 USD per L [51].

In conclusion, utilizing techno-economy can verify the results of this research for a scale-up of apple pomace biorefinery.

## Data availability

Data will be made available on request.

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