Sustainable biorefinery development for valorizing all wastes from date palm agroindustry

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Abstract

This study examined how various residues from date palm agroindustrial can be utilized in a biorefinery platform to produce ethanol, methane, and lignin. Liquid hot water, ethanol organosolv, and catalyzed ethanol organosolv (CEO) pretreatments were applied to trunk, leaves, leaf sheath, pedicels, date cake, and seeds. The process included extracting lignin from the liquid fraction, followed by converting the pretreated solid material into ethanol. The fermentation residues were also utilized to produce biomethane through anaerobic digestion. Two different scenarios were employed for the biorefining, i.e., (I) maximum lignin production and (II) maximum biofuel production. The best results for the first scenario were obtained when CEO was employed in the pretreatment of date palm wastes, where 806.9 mL ethanol, 902.8 L methane, and 528.0 g lignin were produced from each kg of each residue. In energetic terms, the biofuel products (i.e., ethanol and methane) were determined to have a combined energy content equivalent to 1553.1 mL of gasoline. Likewise, the most favorable outcomes of the second scenario were obtained by incorporating CEO pretreatment of trunk, leaf sheath, leaves, and pedicels in the valorization of untreated date cake and seeds. Furthermore, for the second scenario, the resulting products were 967.5 mL ethanol, 1605.3 L methane, and 341.0 g lignin, with the biofuel products having a combined energetic content equivalent to 2452.0 mL of gasoline. These findings indicate that the biorefining of date palm agroindustrial wastes has significant potential for bioenergy production.

Keywords: *Date palm residues, biofuel, lignin, catalyzed ethanol organosolv, biorefining, sustainable valorization*

1. Introduction

Phoenix dactylifera L., known as date palm, is one of the most abundant agricultural crops in tropical and subtropical regions worldwide. Date palm holds significant socioeconomic importance, especially in the Middle East and North Africa [1]. With an annual production of one million tons of dates, Iran ranks among the top three date-producing countries globally [2]. According to the Food and Agriculture Organization (FAO) data from 2019, a total of over 9 million tons of dates were harvested worldwide from a land area of approximately 1.3 million hectares [2]. Date palm trees are propagated via methods like offshoots, chance seedlings, or tissue culture. Upon reaching maturity, the fruits undergo harvesting, which can be manual or assisted by mechanical lifts to access the fruit-bearing crown. Besides harvesting, pruning is vital in date farming, removing aged and unhealthy leaves, as well as trimming spines and undesired inflorescences. These practices maintain farm health and appearance, and optimize fruit production [3]. During annual pruning and fruit harvesting, more than 3 million tons of secondary biomass such as leaves, fronds, and stems are generated [4]. Furthermore, in the date processing industry, which encompasses the production of date syrup and date confectionery, the extraction of date honey or syrup from the fruits is carried out using hot water. This extraction process leads to the formation of two types of industrial waste, namely the seeds and the fibrous material of the fruit pulp, known as date fruit pomace or date cake [5]. Despite their abundance and potential for bioenergy production [6], these lignocellulosic materials are commonly burnt in fields or disposed of in landfills, leading to unfavorable environmental outcomes [7]. With the ability to produce significant amounts of waste biomass, date palm trees offer a highly potential and cost-effective resource that can be efficiently utilized through biorefinery processes.

The biorefinery concept is a promising alternative to conventional industrial processes, as it enables the conversion of biomass feedstock into a range of renewable bioproducts and bioenergy with minimal waste generation and chemical consumption. The implementation of multi-product biorefineries further increases the sustainability of the bioconversion process, as it allows for the production of multiple value-added products from a single feedstock [8,9]. The utilization of date palm wastes for biorefinery purposes not only provides a sustainable and eco-friendly alternative to traditional fossil fuels and petrochemicals but also supports the development of a circular economy by promoting the use of renewable resources.

To efficiently valorize date palm wastes, like other lignocelluloses, an appropriate pretreatment strategy is needed to overcome the recalcitrant structure of cellulose, hemicellulose, and lignin composite [10,11]. Various pretreatment methods have been suggested to improve biorefinery efficiency, with organosolv and liquid hot water pretreatments being among the most effective [12,13].

Organosolv pretreatment is one of the most feasible approaches for fractionating recalcitrant lignocelluloses and facilitating their conversion since it enables the comprehensive utilization of all biomass components, particularly lignin [14,15]. Organosolv pretreatment has the capability to generate sulfur-free, highly pure, and low molecular weight lignin. High-grade lignin can be employed in the manufacturing of diverse polymeric materials, including phenolic powder resins, polyurethane and polyisocyanurate foams, and epoxy resins [16,17].

Organosolv pretreatment dissolves lignin in an organic solvent and hemicelluloses in the aqueous phase, leaving behind a residue rich in cellulose that is available for enzymatic saccharification [14,15]. In comparison to other pretreatments, organosolv offers different benefits such as chemical reusability, multi-product synthesis, lower enzyme requirements, and less sugar degradation [16,18,19]. Additionally, the organic solvent used can be easily recovered, and various solvents like alcohols, ketones, phenols, and ethers can be used with or without catalysts [19]. Ethanol is a commonly used solvent for organosolv pretreatment due to its affordability, water-miscibility, and low toxicity [20].

Liquid hot water pretreatment is a cost-effective and eco-friendly hydrothermal method that improves enzymatic hydrolysis by solubilizing hemicellulose and modifying biomass structure [12]. It produces minimal inhibiting or corrosive byproducts and requires less capital investment than other chemical pretreatments [10,21].

Previous studies have revealed valuable insights into the potential of date palm waste valorization. However, their focus has been mostly on characterizing date palm fibers [22–24] and utilizing them in single product processes such as lignin [14], bioethanol [25,26], and biogas production from date fruit [27]. Additionally, some of these studies lacked an appropriate pretreatment strategy to effectively utilize the recalcitrant biomass [7,28]. Table S1 in the supplementary material summarizes a number of most relevant works on date palm waste valorization. Further research is needed to explore the full potential of this abundant biomass resource.

In our previous work [29], the use of phosphoric acid pretreatment for date palm waste was explored. However, some limitations to this approach were identified, including the high cost of phosphoric acid and its high acid concentration, which may limit its practicality as a pretreatment method. Furthermore, lignin was not extracted, and the energy production was lower than expected. This highlights the necessity for alternative pretreatment methods that can more efficiently and cost-effectively convert date palm waste into energy, while also allowing for the recovery of valuable components such as lignin.

To address these limitations, a new study was conducted to investigate the potential of date palm residues for a biorefinery development using ethanol organosolv and liquid hot water pretreatments. To the best of our knowledge, the potential of date palm residues for a multi-product biorefinery using ethanol organosolv pretreatment has not been investigated. Catalyst addition to the organosolv pretreatment of different types of date palm waste has not been evaluated in comparison to liquid hot water pretreatment. Additionally, secondary uses of date cake after juice extraction is yet to be explored.

This study explored the potential of date palm waste for a multi-product biorefinery using ethanol organosolv (EO), catalyzed ethanol organosolv (CEO), and liquid hot water (LHW) pretreatments. Date palm biomasses, including trunk, leaf sheath, leaves, and pedicels, as well as date cake and date seeds, were evaluated for biofuel production, with lignin extraction and biomethane production from fermentation residue. Two scenarios were compared to determine the most favorable pretreatment conditions. The assessment relied on the overall energy produced from ethanol and methane, measured in gasoline equivalents. Additionally, the study did not consider the potential of lignin as a fuel source; rather, the emphasis was on assessing its monetary value.

2. Materials and Method

2.1. Materials

Date palm fruits and lignocellulosic residues (Mazafati cultivar) were gathered from a palm plantation located in Kerman, Iran, at coordinates 29°06′22″N and 58°21′25″E. Each type of waste was treated separately instead of in combination based on two reasons. Firstly, the various date palm wastes are not produced simultaneously on an annual basis. For instance, leaf and pedicel wastes occur periodically, while trunks endure for longer periods. Secondly, there is a significant difference in the proportion of each waste type within the total amount. For example, tree trunks weigh several orders of magnitude more compared to the seeds. The materials were washed with water to eliminate dust. The date seeds were manually removed and the fleshy part of palm dates (200 g) was mixed with 1000 mL water and heated at 100 °C for 60 min to extract sugars. The suspension was then filtered and date cakes were collected and dried at room temperature. Each feedstock, including date cake, seeds, tree trunk, leaves, leaf sheath, and pedicels, was individually ground using a mill (VI-3307, Vidas, Tehran, Iran), sieved to obtain particle sizes between 177 and 841 µm (20-80 mesh), and stored at room temperature until needed.

Cellic® CTec2 cellulase, provided by Novozymes in Denmark, with an activity level of 125 FPU/mL, was utilized for enzymatic hydrolysis. The enzyme activity was assessed using the method outlined by Adney and Baker [30]. *Saccharomyces cerevisiae* (CCUG53310) from the Culture Collection University of Gothenburg in Sweden was employed for sugar fermentation to produce ethanol.

2.2. Pretreatments

A high-pressure stainless steel batch reactor with a working volume of 500 mL was used to pretreat 50 g of feedstock with a 75% (V/V) aqueous ethanol solution in a solid-to-liquid ratio of 1:8 at 180 °C for 60 min [31]. In some runs, 1% (W/W) sulfuric acid was added as a catalyst. After cooling, the materials were filtered (Whatman No.1) and washed with 100 mL of ethanol (75%, V/V) and water (distilled water). The solid residue was air-dried at 25 °C for 24 h, while the liquor part was diluted with three volumes of water to promote the precipitation of dissolved lignin. The precipitated lignin was then recovered using a filterpaper (Whatman No.1) and air-dried at about 25 °C for 24 h. Both the dried pretreated materials and the precipitated lignin were kept in resealable bags at room temperature until use.

Liquid hot water pretreatment was conducted at similar conditions to ethanol organosolv pretreatment, with the only difference being the replacement of the aqueous ethanol as a solvent with distilled water in the reactor.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis of untreated and pretreated substrates was conducted using cellulase at a concentration of 15 FPU/g dry matter. The experiment involved a solid loading of 5% (W/V), 50 mM sodium citrate buffer, and a temperature of 45 °C with stirring at 120 rpm for a duration of 72 hours. To prevent microbial growth, 0.5 g/L of sodium azide was added. Glucose concentrations in liquid samples were measured and yields were calculated using Equation (1):

$$Glucose\ yield\ (\%) = \frac{Produced\ glucose\ concentration\ (\frac{g}{L})}{Substrate\ concentration\ \left(\frac{g}{L}\right) \times Glucan\ percentage \times GDF} \times 100 \qquad \text{Eq. (1)}$$

where GDF is the dehydration factor of glucan, i.e., 1.111 [32].

2.4. Ethanolic fermentation

Ethanol was produced using the non-isothermal hydrolysis followed by simultaneous saccharification and fermentation (NSSF) method, which involved 24 hours of hydrolysis in a 50 mM sodium citrate buffer at a solid loading of 5% (W/V) and a temperature of 45 °C with 15 FPU/g. Next, the necessary nutrients were supplemented and fermented by the addition of 10 g/L *S. cerevisiae* [33]. The medium was then incubated under anaerobic conditions at 32 °C and 120 rpm for 72 h. Yields of ethanol were calculated using Eq. (2):

$$Ethanol\ yield\ (\%) = \frac{Produced\ ethanol\ concentration\ (\frac{g}{L})}{Substrate\ concentration\ \left(\frac{g}{L}\right) \times Glucan\ percentage \times GDF \times Y} \times 100 \qquad \text{Eq. (2)}$$

where GDF is the dehydration factor of glucan (1.111) and Y is the maximum yield of ethanol production from glucose (0.51) [32].

After the completion of the experiment, ethanol was evaporated and the fermentation residues retained in the bottles were collected and freeze dried (Christ freeze dryer, Alpha 1-2 LDplus Model, Germany) as the substrate for biomethane production.

2.5. Anaerobic digestion

Biomethane production was carried out under mesophilic conditions in 118 mL dark glass bottles, which were tightly sealed with butyl rubbers and aluminum caps [34]. Each bottle contained substrate (0.25 g), inoculum (20 mL), and distilled water (5 mL). The outflow of a continuous anaerobic digester with a capacity of 7000 m^3 operating at 37°C (Isfahan Municipal Wastewater Treatment Plant, Isfahan, Iran) was used as an inoculum. The inoculum had a total solids (TS) content of 4.8% and a volatile solids (VS) content of 2.2%. To measure the biomethane production from the inoculum, a blank sample was prepared using the same amount of inoculum and deionized water. Prior to incubation for 40 days, the samples were deoxygenated by purging with pure nitrogen gas for approximately 2 minutes. Gas samples were extracted from the bottles for subsequent analysis using gas chromatography (GC).

2.6. Analytical methods

The standard methods provided by Sluiter et al. [35] were followed for measuring the total solids (TS) and volatile solids (VS) of the date palm wastes. The structural carbohydrates and lignin of the date palm wastes were determined following the National Renewable Energy Laboratory method [36]. The calculation of xylan and lignin removal was performed using the formulas provided by Hashemi *et al*. [33].

To monitor the chemical structure of substrates before and after the pretreatments, Fourier transform infrared (FTIR) spectrometry was conducted using the WQF-510A FTIR instrument (BRAIC, China), employing the KBr pellet technique [37]. Analysis was done on the infrared transmittance adsorption data from 4000 to 500 cm^{-1} wavenumbers.

The morphological alterations in the lignocelluloses structures were followed using scanning electron microscopy (SEM) (EVO® LS, Zeiss, Germany). The substrates were coated with gold before being examined using SEM at 15 kV.

The quantification of sugars and ethanol was carried out using HPLC equipped with UV/Vis and RI detectors (Jasco International Co., Tokyo, Japan). For ethanol analysis, a Bio-Rad Aminex HPX-87H column (Hercules, USA) was employed at a temperature of 60 °C with a mobile phase consisting of 5 mM sulfuric acid flowing at a rate of 0.6 mL/min. The analysis of sugars was performed using a Bio-Rad Aminex HPX-87P column (Hercules, USA) eluted with 0.6 mL/min demineralized water at a temperature of 85 °C.

The composition of methane and carbon dioxide in biogas was determined using a gas chromatograph (2550TG, Teif Gostar, Iran). The analysis was conducted using a Porapak Q GC column (3 m long, 3 mm initial diameter, Taufkirchen, Germany). Analytical grade nitrogen gas at a flow rate of 45 mL/min was used as a carrier gas. The column was maintained at a temperature of 40 °C, while the detector and injector were both set to a temperature of 100 °C.

2.7. Gasoline equivalent

To compare the various pretreatment methods, the energy value of the products was determined by calculating the gasoline equivalent. This was done by considering the heating values of fuels, as well as the total solids (TS), volatile solids (VS), and solid recoveries of the substrates following the pretreatment process. The lower heating values of 32.0 MJ/L, 21.2 MJ/L, and 36.1 MJ/Nm^3 were considered for gasoline, ethanol, and methane, respectively [33]. The gasoline equivalents of ethanol and methane were calculated using Equations 3 and 4, respectively.

$$\begin{aligned} &\textit{Gasoline equivalent of ethanol}\ (L/g) \\ &\quad = \frac{\textit{Produced ethanol}\left(\frac{g}{L}\right) \times \textit{Solid recovery}\ (\%)}{\textit{Substrate concentration}\left(\frac{g}{L}\right) \times\ \textit{Ethanol density}\left(\frac{g}{L}\right)} \times \frac{21.2\ MJ/L}{32\ MJ/L} \end{aligned} \qquad \text{Eq. (3)}$$

$$\begin{aligned} &\textit{Gasoline equivalent of methane}\ (L/g) \\ &\quad = \textit{Produced methane}\left(\frac{Nm^3}{g\ VS}\right) \times \textit{VS of substrate}\ (g/g) \\ &\quad \times \textit{Solid recovery}\ (\%) \times \frac{36.1\ MJ/Nm^3}{32\ MJ/L} \end{aligned} \qquad \text{Eq. (4)}$$

2.8. Lignin value

The value of the lignin generated from the biorefinery platform was evaluated using the Pound currency. The price range for lignin was found to be £158.21-£288.22, with an average price of £208.2 used in the calculations [38].

2.9. Statistical analysis

All experiments were duplicated, and the analysis of variance (ANOVA) was carried out using SAS software (Version 9.4, NC, USA). The Tukey test was performed at 95% confidence level and means with identical letters were determined to not significantly differ from one another.

2.10. Scenarios of biorefinery development

Two scenarios for the biorefinery of date palm wastes were examined. The first scenario aimed to achieve maximum lignin and the second scenario sought to achieve maximum bioenergy production. To determine the superior pretreatment condition, the total gasoline equivalents for ethanol and methane, as well as the value of lignin, were calculated and compared for each scenario.

3. Results and Discussion

Ethanol organosolv, catalyzed ethanol organosolv, and liquid hot water pretreatments were performed on date palm wastes. The obtained liquor was utilized to precipitate lignin. The solids were analyzed through FTIR and SEM to evaluate the physicochemical effects of pretreatments before their use in ethanol production via the NSSF process. After which the NSSF residues were subjected to anaerobic digestion to produce biomethane. Then, the two biorefinery scenarios were analyzed and compared, considering the gasoline equivalents of ethanol and methane as well as the monetary value of lignin.

3.1. Compositional and structural modification by pretreatments

The chemical compositions of date palm wastes before and after the pretreatments are presented in Table 1. The values of lignin, hemicellulose, and glucan for raw materials, were 12.3-36.1 wt.%, 21.4-78.4 wt.%, and 14.3-43.9 wt.%, respectively. The remaining components were mainly ashes in the range of 1.2-15.0 wt.%. Date palm wastes have been found to contain more ash than other types of biomass [22]. Table 1 shows that the seeds have high hemicellulose content and low lignin and glucan contents compared to other samples. Likewise, lower contents of glucan (20.63 wt.%) and lignin (5-10 wt.%) were reported for the date seeds relative to the glucan and lignin contents of other samples. However, the high hemicellulose content of date seeds contradicts previous studies that reported lower percentages [39,40]. This may suggest that the seeds were not fully ripe, as arabinan and mannan amounts decrease as the fruit ripens [41].

Furthermore, differences in climate, soil, growth conditions, and age may affect lignocellulosic composition [42,43]. However, comparable results were observed previously [44,45]. Due to the high carbohydrate content and low lignin content, the date seeds could constitute a sufficient feedstock for biofuel production. Similarly, the low carbohydrate content and high lignin content of the date cake make it a suitable candidate as a feedstock for lignin production.

Table 1 also shows that pretreatments mostly affected the lignin and hemicellulose amount of the date palm wastes. Considering the solid recoveries, CEO, EO, and LHW pretreatments facilitated 50-89 wt.%, 30-55 wt. %, and 7-35 wt. % lignin removal, respectively. The highest yield of lignin release was attributed to CEO pretreatment of date cake, which facilitated the release of 21 g of lignin per 100 g of raw material into the liquor. This finding was similar to the result obtained in a previous study [14] where 13% of lignin was removed from date palm fronds through the organosolv pretreatment. Delignification of lignocelluloses occurs as a result of the breaking of lignin-lignin and lignin-carbohydrate linkages as well as lignin solubilization in organic solvents [42]. Various studies have confirmed that the presence of an acid catalyst can enhance delignification, as the catalyst speeds up bond breakdown [32,42,46]. For instance, CEO achieved a 51% delignification rate for leaves, which was 1.7 and 7.4 fold higher than that of EO and LHW pretreatments, respectively. Similarly, Amiri and Karimi [31] found that pretreating pine and elm with ethanol containing 1 % sulfuric acid resulted in a maximum delignification of 58% and 42%, respectively.

Table 1 also shows that the yields of the hemicellulosic sugars, i.e., xylan, mannan, arabinan, and galactan, were dependent on the type of pretreatment strategy employed. LHW was the most effective pretreatment for xylan removal, eliminating 55-88% of xylan from the trunk, leaf sheath, leaves, and date cake. Whereas, in the case of date seeds, the highest hemicellulose removal (39%) occurred through the EO pretreatment. Furthermore, the effectiveness of hemicellulose removal for pedicels, after CEO and LHW pretreatments, were comparable (77 and 78%). The high potential of hemicellulose removal in the LHW process has been attributed to the hydronium ions created by high-temperature water and acetic acid produced by acetyl substituents of hemicelluloses which function as catalysts [10]. Previously, autohydrolysis of rice straw, pinewood, and elmwood facilitated the removal of 53-61% of the hemicellulose, whereas organosolv pretreatment only removed ~23% [47].

The solubilization of lignin and hemicellulose resulted in an elevation in the glucan content of the pretreated materials. After CEO, EO, and LHW pretreatments, solids with glucan content in the ranges of 16.3-64.6 wt.%, 15.1-56.5 wt.%, and 15.0-56.1 wt.%, remained. The highest glucan content of 64.6 wt.% was observed after CEO pretreatment of pedicels which was 1.5 fold higher than that of the raw substrate.

Solid recoveries of all pretreated samples are presented in Table 1. As expected recoveries had a reverse relationship with the severity of the pretreatments [31] with averages of 68, 65, and 59% solid recovery obtained from LHW, EO, and CEO, respectively. Furthermore, the introduction of a catalyst was shown to lead to a reduction in the solid residue yield, primarily owing to xylan and lignin solubilization [46].

Overall, chemical composition data showed that all pretreatments increased cellulose content in most of the substrates, with LHW removing more xylan and CEO removing more lignin. This matches findings for other biomasses [48].

Table 1. Chemical compositions of pretreated and untreated date palm wastes.

Substrate and pretreatment	Chemical composition (wt.%)					Solid recovery (wt.%)	Glucan recovery (wt.%)	Hemicellulose removal (wt.%)	Lignin removal (wt.%)
	Glucan	Xylan	Other carbohydrates[1]	Lignin	Ash				
Trunk									
Untreated	43.9±0.8	18.7±1.3	4.2±0.4	22.1±0.1	9.3±0.7	-	-	-	-
Ethanol organosolv	55.7±1.7	15.6±0.4	4.4±1.0	20.8±1.4	6.0±0.1	70.0±0.3	88.9	26.2	28.2
Catalyzed ethanol organosolv	63.6±0.0	15.5±1.5	Not detected	16.5±2.5	6.7±0.0	67.2±1.5	97.3	22.1	24.5
Liquid hot water	55.4±0.5	11.7±0.0	Not detected	26.4±0.2	6.8±0.8	71.4±0.6	90.1	14.6	34.1
Leaf sheath									
Untreated	43.7±0.4	16.5±0.7	5.0±0.2	21.1±0.2	14.3±0.3	-	-	-	-
Ethanol organosolv	53.9±2.6	13.8±0.1	Not detected	19.8±0.1	9.6±0.0	68.1±1.0	84.0	20.5	30.0
Catalyzed ethanol organosolv	61.8±0.6	10.2±0.8	Not detected	15.8±0.4	9.6±0.3	64.6±1.0	91.4	16.9	26.6
Liquid hot water	49.4±0.3	8.3±0.5	6.4±0.2	20.0±0.4	8.8±0.3	69.0±0.4	78.0	21.3	29.3
Leaves									
Untreated	35.3±0.6	19.8±0.2	3.7±0.2	24.6±0.6	15.0±1.1	-	-	-	-
Ethanol organosolv	39.6±0.7	9.3±0.5	2.6±0.2	26.7±0.3	14.4±0.1	64.2±0.3	72.0	18.2	38.8
Catalyzed ethanol organosolv	50.3±0.0	11.7±1.6	Not detected	19.9±0.4	17.0±1.0	60.8±0.6	86.6	19.6	31.8
Liquid hot water	37.0±2.3	4.7±0.4	1.7±0.1	36.8±0.5	15.0±1.4	62.2±0.6	65.2	10.2	56.6
Pedicels									
Untreated	41.7±1.0	23.9±0.3	7.8±0.3	27.1±0.1	1.6±0.0	-	-	-	-
Ethanol organosolv	56.5±0.8	17.1±0.2	Not detected	17.8±0.7	0.4±0.1	68.5±0.7	92.8	17.0	20.7
Catalyzed ethanol organosolv	64.6±0.2	13.4±1.1	Not detected	12.9±1.3	0.7±0.5	51.7±0.3	80.1	20.4	23.0
Liquid hot water	56.1±0.6	9.9±0.6	Not detected	26.3±0.3	0.7±0.1	72.0±0.6	96.9	8.8	27.1
Date cake									
Untreated	32.0±0.2	21.5±0.3	7.2±0.9	36.1±0.6	6.4±0.4	-	-	-	-
Ethanol organosolv	29.5±0.4	22.6±0.6	4.0±0.6	45.2±1.9	5.3±1.2	46.4±0.7	42.7	49.9	67.1
Catalyzed ethanol organosolv	45.5±0.1	14.8±1.3	Not detected	38.9±0.7	6.5±0.3	40.1±0.6	57.1	30.9	64.5
Liquid hot water	25.0±1.4	5.1±1.0	8.4±0.3	64.2±0.2	2.0±0.0	51.0±2.0	39.8	23.1	87.2
Seeds									
Untreated	14.3±0.3	Not detected	78.4±0.8	12.3±0.4	1.5±0.2	-	-	-	-
Ethanol organosolv	15.1±0.8	Not detected	67.7±0.4	9.4±1.0	0.7±0.0	70.6±0.8	74.5	25.4	22.5
Catalyzed ethanol organosolv	16.3±0.2	Not detected	73.3±0.0	1.9±0.1	1.0±0.0	69.0±1.1	78.7	29.0	4.8
Liquid hot water	15.0±0.7	Not detected	65.3±0.4	10.4±0.4	0.6±0.2	80.2±1.4	84.1	16.5	16.7

[1] Sum of percentages of mannan, arabinan, and galactan

SEM images were taken to explore how materials changed morphologically through the pretreatments and the results are shown in Figure 1. Figure 1 shows that the pretreatments led to enhanced porosity via the creation of sponge-like shapes for greater accessibility. These modifications can be attributed to the removal of lignin and partial solubilization of hemicellulose [16,49]. Figure 1 also depicts some small particles or larger agglomerates on the surface of some pretreated materials, which might be redeposited lignin. According to previous research, they are generated when the temperature and ethanol concentration drop during the washing stages after the lignocellulose ethanol pulping process [50].

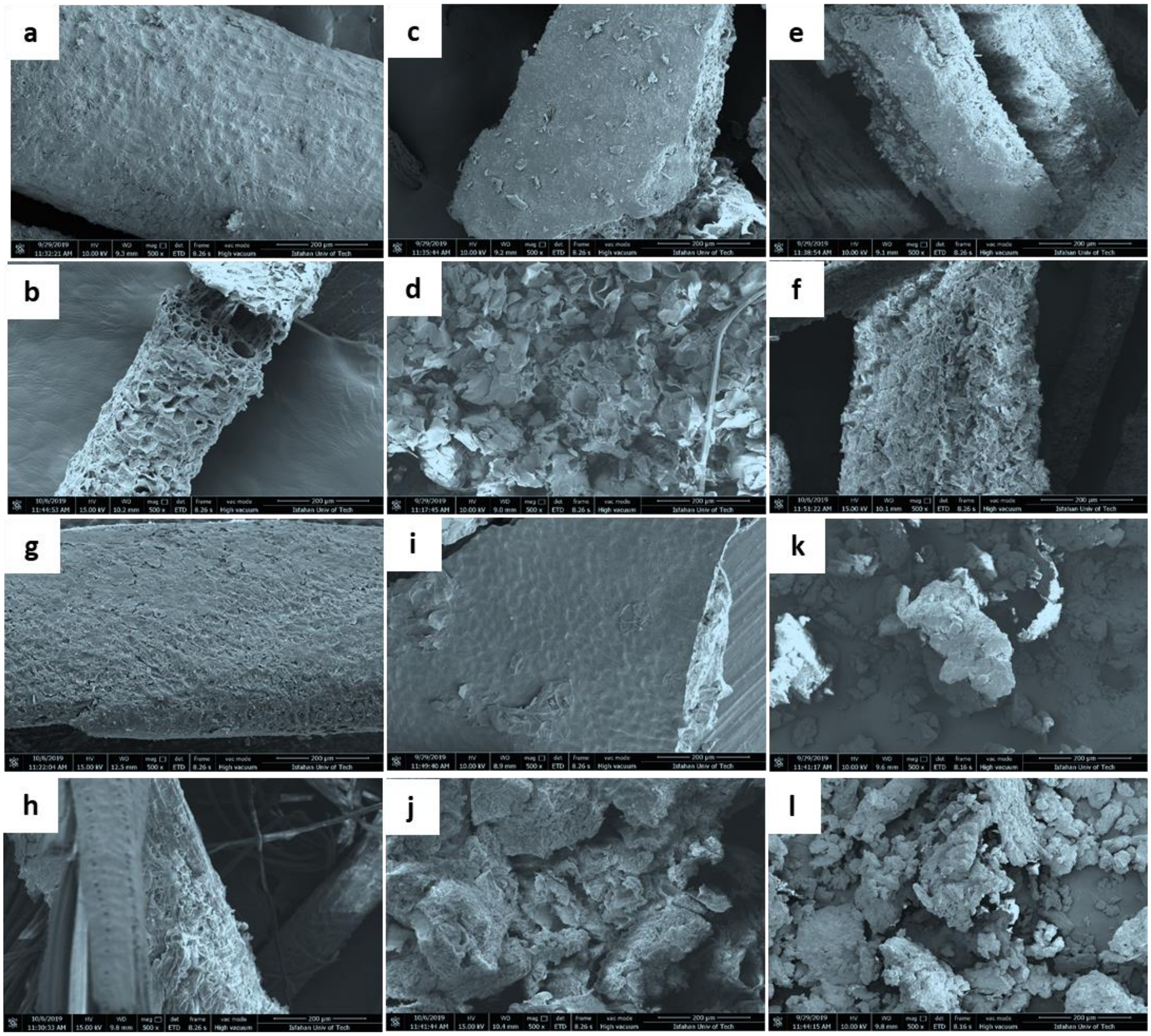

Figure 1. SEM images with 5000× magnification for (a) untreated trunk, (b) EO pretreated trunk, (c) untreated leaf sheath, (d) CEO pretreated leaf sheath, (e) untreated leaves, (f) EO pretreated leaves, (g) untreated pedicels, (h) CEO pretreated pedicels (i) untreated date cake, (j) LHW pretreated date cake, (k) untreated seeds, and (l) LHW pretreated seeds.

FTIR spectroscopy was utilized to analyze the crystallinity and structural changes of the waste materials before and after undergoing pretreatments. Table 2 displays the results of calculating the crystallinity index (CI) and total crystallinity index (TCI) using the absorbance ratios of 1420 to 894 cm^{-1} and 1375 to 2900 cm^{-1}, respectively [51]. In most cases, the pretreatments led to a decrease in both CI and TCI of the substrates, which indicates an increase in amorphous cellulose content and a decrease in crystalline cellulose content. The highest CI reduction of 28.0% was achieved after LHW pretreatment of seeds, which was comparable to that of 24.48% reduction of TCI in acid-catalyzed organosolv pretreatment of oil palm empty fruit bunch, a lignocellulosic residue of the same family as date palm [20]. On the other hand, in some cases (i.e. pedicels, leaves, leaf sheath, and date cake), the CI and TCI increased as a result of some pretreatments. The increase in CI and TCI may be attributed to the decrease in amorphous hemicellulose and lignin which can lead to an increase in crystallinity [8]. Such an increase in crystallinity is however not desirable since hydrolytic enzymes are unable to access the high crystalline regions of lignocelluloses and thus is one of the challenges encountered during enzymatic hydrolysis [31]. As a result of decreasing crystallinity, organosolv pretreatment has been found to speed up hydrolysis and decrease the amount of enzyme needed to achieve high digestibility [16].

Table 2. The crystallinity index (CI) and total crystallinity index (TCI)

Substrate	CI	TCI
Trunk		
Untreated	1.68	1.64
Ethanol organosolv	1.37	1.57
Catalyzed ethanol organosolv	1.52	1.53
Liquid hot water	1.52	1.49
Leaf sheath		
Untreated	1.59	1.47
Ethanol organosolv	1.94	1.64
Catalyzed ethanol organosolv	1.58	1.63
Liquid hot water	1.66	1.52
Leaves		
Untreated	1.46	1.44
Ethanol organosolv	1.70	1.26
Catalyzed ethanol organosolv	1.55	1.44
Liquid hot water	1.75	1.34
Pedicels		
Untreated	1.27	1.29
Ethanol organosolv	1.17	1.25
Catalyzed ethanol organosolv	1.40	1.49
Liquid hot water	1.25	1.29
Date cake		
Untreated	1.79	1.28
Ethanol organosolv	1.42	1.34
Catalyzed ethanol organosolv	1.39	1.24
Liquid hot water	2.21	1.44
Seeds		
Untreated	1.55	1.01
Ethanol organosolv	1.52	1.28
Catalyzed ethanol organosolv	1.48	1.21
Liquid hot water	1.12	1.46

3.2. Enzymatic hydrolysis

The glucose yields of untreated and pretreated solids, after enzymatic hydrolysis, are presented in Figure 2. Figure 2 demonstrates low hydrolysis efficiency for all untreated samples, except for date cake, with glucose yields ranging from 14.3 to 38.0 wt.%. All the pretreatment processes, except those for date cake, increased the yields and resulted in solids with 1.2-4.3 fold higher yields of glucose. LHW was the most proficient pretreatment approach to enhance glucose yields (30.9-92.7%) from trunk, leaves, leaf sheath, and seeds, where the higher glucose yields were attributed to improved hemicellulose removal after LHW pretreatment. Liquid hot water pretreatment has been demonstrated to release acetyl groups from hemicellulose, creating acetic acid, which accelerates the breakdown of hemicellulose and improves enzymatic access to the cellulose fraction for a more efficient hydrolysis process [52].

Figure 2 also shows that LHW pretreatment of leaf sheath was the most efficient with 4 fold rise in ethanol yield. This observation is expected since according to Table 1, the LHW pretreatment facilitated the highest lignin reduction of 35% when applied to the leaf sheath sample. On the other hand for the CEO pretreatment, the pedicel sample, with the delignification of 75%, was shown to have the highest ethanol yield. Indeed, a correlation between glucan digestibility and lignin removal was observed in organosolv pretreatment of date palm fronds, although it must be stated that the effectiveness of enzymatic hydrolysis is not solely limited by lignin content [14].

Comparing CEO and EO pretreatments, the addition of sulfuric acid catalyst had a positive impact on the glucose yields of all substrates except leaves and date cake. The introduction of sulfuric acid increases the rate of lignin removal, with lignin reported to adsorb enzymes irreversibly, implying that enhanced lignin removal leads to an improvement in glucose yields [46]. Due to the irreversible enzyme adsorption that lignin has been shown to have, lignin removal increases glucose yields.

It has been shown that pretreatment at high temperatures and acidic conditions causes the glycosidic bonds in hemicellulose and hemicellulose-lignin connections to break effectively. However, the breakdown of some of the released carbohydrates during pretreatment under these conditions may have a negative impact on the hydrolysis productivity [32] which could be the cause of the glucose yield reduction of CEO pretreated leaves and date cake.

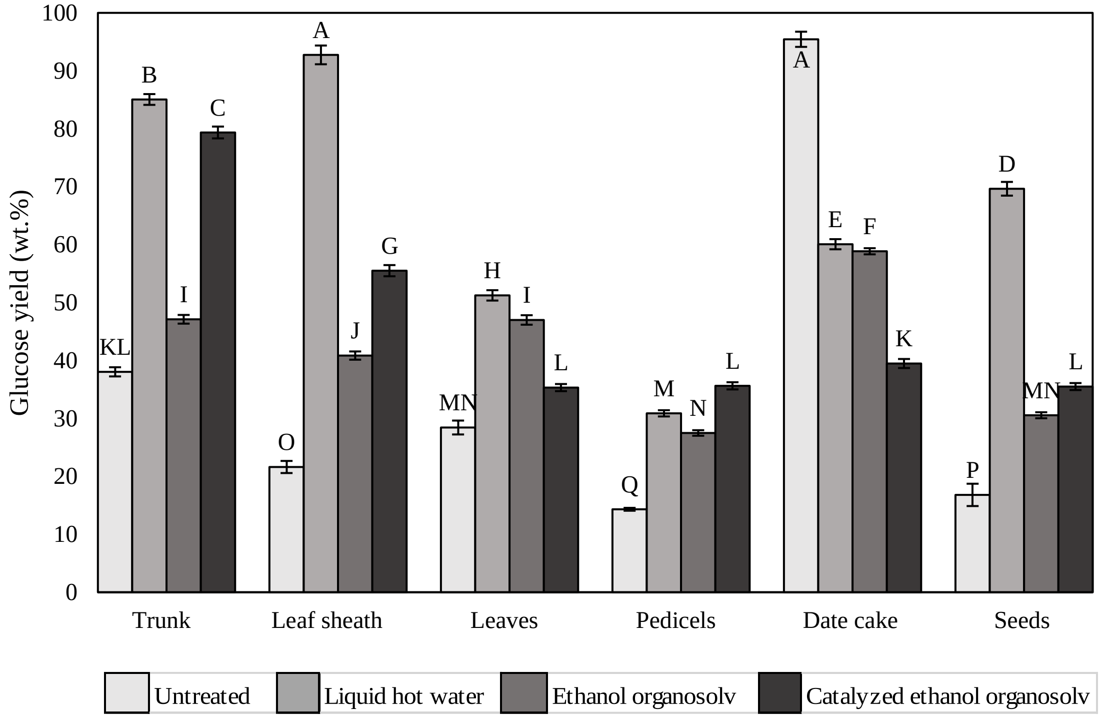

Figure 2. Glucose yields of untreated and different pretreated date palm wastes by enzymatic hydrolysis (error bars show standard deviations and the same letters indicate no statistical difference).

3.3. Ethanol production

Figure 3 displays the ethanol yields obtained from treated and untreated samples by the NSSF. The ethanol yields of the untreated trunk, date cake, leaf sheath, leaves, pedicels, and seeds were found to be 12.4%, 98.3% 39.0%, 44.4%, 29.9%, and 59.6%, respectively. For all samples, except date cake, the pretreatments resulted in improved ethanol yields (i.e., 1.1-6.0 times higher yields). Similar trends for ethanol and enzymatic hydrolysis were observed for trunk, seeds, and leaf sheath after different pretreatments. On the other hand, for leaves, pedicels, and date cake, the trend was different. In the case of the leaves, there was not a significant difference between the ethanol yields of LHW and EO based on ANOVA analysis. Figure 3, however, shows that the CEO pretreated pedicels and LHW pretreated date cake did not produce as much as ethanol that was expected according to their enzymatic hydrolysis potential. The low amounts of ethanol yield could be a result of yeast-inhibitory chemical formation which restricts the growth of microorganisms during the fermentation process [53]. These observations are comparable to similar investigations in the literature. For instance, in the study by Hashemi *et al*. [33], a 1 h hydrothermal pretreatment of safflower at 180 °C was applied to improve the ethanol yield from 11.6 to 40.8%. This ethanol yield was further increased to 60.3% after prolonging the pretreatment to 5 h. In another study, Ostovareh *et al*. [32] conducted organosolv pretreatment with and without acid catalyst addition to produce ethanol from sweet sorghum stalks. The highest ethanol yield of 72.5% was achieved from stalks that underwent acid-catalyzed 50% ethanolic pretreatment at a temperature of 140 °C. While the yield of untreated straw was about 30%. However, the study also reported a decline in ethanol yields at a higher temperature of 160 °C when sulfuric acid was present. Fang *et al*. [25] also obtained an ethanol yield of 80% by pretreating the date palm rachis hydrothermally at 200 °C. The corresponding values for the raw and pretreated materials at 180 °C were 33% and about 40%, respectively. These outcomes are comparable to those attained in the present study using date leaves. The lower yields obtained for rachis may be attributed to its more resistant structure compared to the leaves.

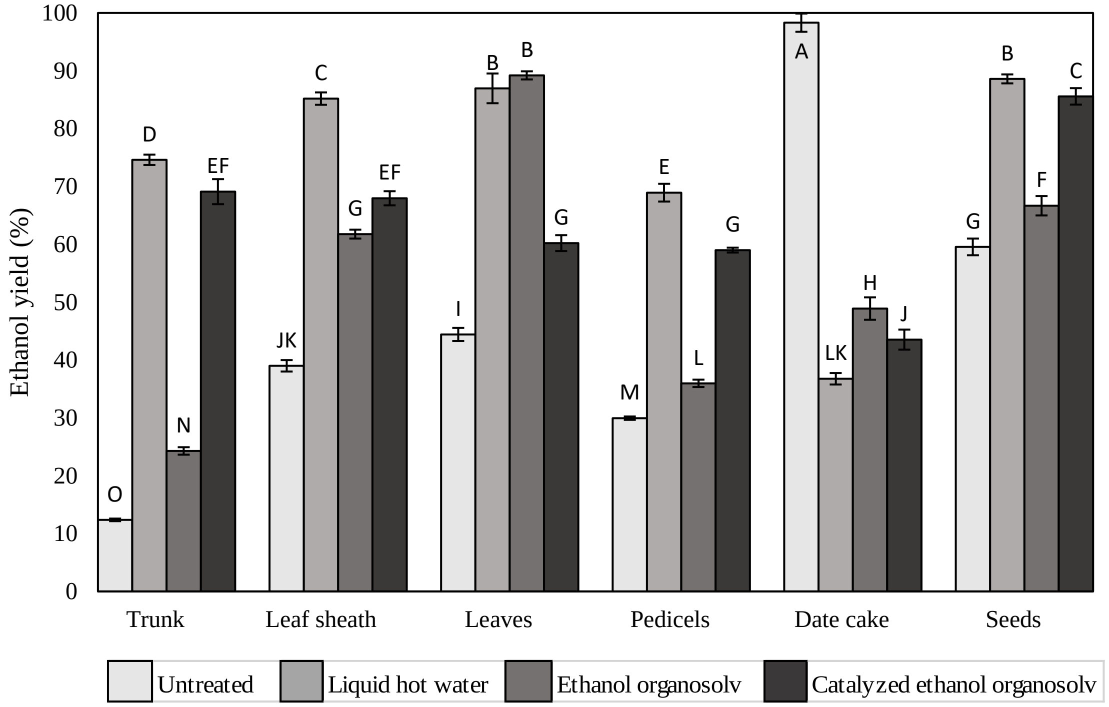

Figure 3. Ethanol yields of different pretreated and untreated wastes (error bars show standard deviations and the same letters indicate no statistical difference).

3.4. Biomethane production

To enhance waste utilization and energy recovery, the fermentation residues obtained in NSSF were used to produce biomethane. To evaluate the effect of the fermentation process on biomethane production, the untreated samples were also anaerobically digested. The biomethane potential (BMP) results are summarized in Figure 4. For the majority of samples, the BMPs of fermented residues were either lower than that of the unfermented substrate, or the difference was not statistically significant according to the ANOVA analysis. This occurred because most of the useful carbon sources of cellulose and hemicellulose in the substrates were utilized/consumed during NSSF. As illustrated in Figures 4a to 4e, the BMPs from the fermented trunk, leaf sheath, leaves, pedicels, and date cake ranged from 70.8 to 200.2 mL/g VS. Most of the applied pretreatments increased the BMPs, with the CEO fermentation residues presenting the highest BMPs which ranged from 210.4 to 275.5 mL/g VS. The lower concentrations of lignin achieved during CEO pretreatment, as discussed earlier in Table 1, may be responsible for the higher methane generation from CEO fermentation residues. This is because lignin acts as a protective barrier against microbial degradation of biomass. Indeed, according to Mirmohamadsadeghi *et al*. [8], the main obstacle to improved BMPs from biomass is the presence of high lignin content since in general, anaerobic microorganisms degrade cellulose and hemicellulose more efficiently than lignin [8]. Similar results were also reported in the anaerobic digestion of palm and petiole of the date palm with BMPs of 258.76 and 166.71 mL/g TS, respectively [54]. The efficient removal of lignin by the CEO pretreatment approach may also explain the ~ 4-fold increase in the BMP of untreated pedicels from 63.6 mL/g VS to 271.4 mL/g VS.

On the other hand, the BMPs of the seeds were determined to be diminished after pretreatment as shown in Figure 4f. This observation may be due to the removal of the energy-dense lipids in the seeds after the pretreatments. This observation is consistent with the literature since lipids have been reported to be the highest contributor to the biomethane generation potential compared to other macromolecules such as proteins and carbohydrates [55]. For instance, in a previous study [29], the BMP of 670 mL/g VS was attained from fermentation residues of date seeds and reduced to ~300 mL/g VS after phosphoric acid pretreatment, due to the lipid removal [29]. Overall, the biomethane results suggest that the NSSF process could act as a kind of pretreatment for biomethane production from all date palm wastes except date cake.

Additionally, Figures S1 and S2, the Supplementary material, demonstrate that a portion of hemicellulosic sugars is solubilized and remains unutilized during the pretreatments, indicating the potential for increased energy recovery if these carbohydrates can be recovered and incorporated into the anaerobic digestion process.

3.5.Gasoline equivalent and value-added material production

In examining the preferred pretreatment process, the bioenergy production potentials of biomethane and ethanol were calculated based on various pretreatment methods. The results, shown in Figure 5, highlighted the total gasoline equivalents of different date palm wastes. The untreated trunk, leaves, pedicels, and leaf sheath exhibited gasoline equivalent ranges of 125.4-263.8 mL/kg. In most cases, the applied pretreatments enhanced these gasoline equivalents, particularly with the CEO pretreatment, which achieved the highest values of 255.8-344.7 mL/kg. Conversely, date cake and seeds saw reduced gasoline equivalents after pretreatment, with the highest values observed in the raw substrates.

Figure 5 illustrated that relying solely on ethanol production was impractical, as it yielded relatively low gasoline equivalents ranging from 22.3-149.5 mL/kg. Yet, the production of biomethane from fermentation residues notably increased gasoline equivalents, ranging from 90.9-817.8 mL/kg. The CEO pretreatment particularly enhanced total gasoline equivalent values by 2.3 to 4.3 times compared to scenarios considering ethanol as the sole product.

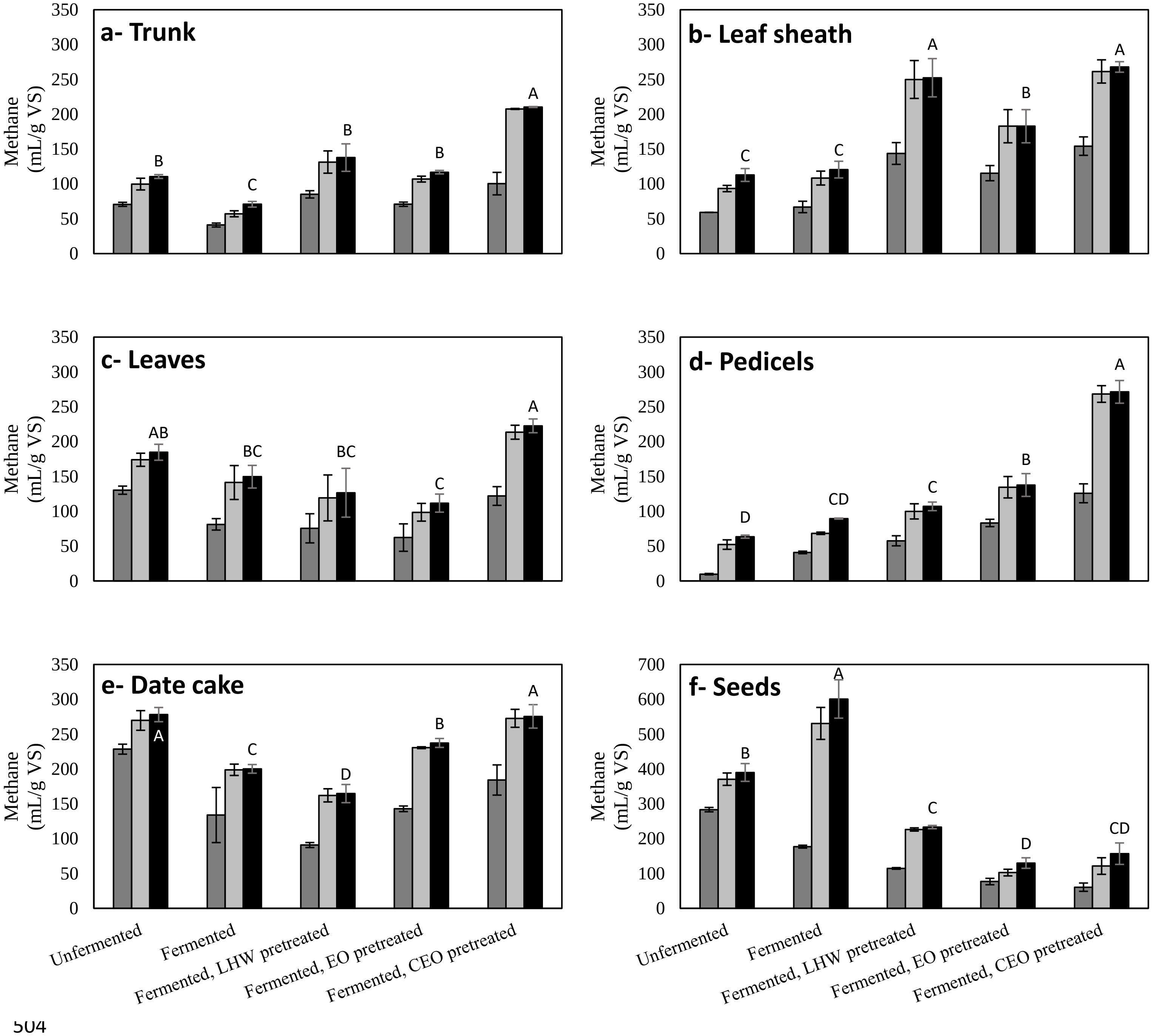

Figure 4. Yield of biomethane production via anaerobic digestion from unfermented and different fermentation residues. Dark gray, light gray, and black columns indicate the yield obtained after 9, 30, and 40 days (error bars show standard deviations, and the same letters indicate no statistical difference).

After pretreatment and ethanol production, subjecting the fermentation residues of untreated seeds to anaerobic digestion resulted in a significant 21.2-fold increase in gasoline equivalents compared to scenarios that only recovered ethanol without generating methane from the residues. A previous study on olive wastes revealed that side-stream methane production could triple the total energy production of the process [48].

Additionally, the economic potential of the extracted lignin was assessed. The CEO pretreatment showed lignin recoveries ranging from 26.0% to 48.8%, translating to potential monetary benefits from £5,416.6 to £10,156.1. In contrast, the organosolv pretreatment yielded lignin recoveries ranging from 16.3% to 32.5%, corresponding to potential monetary benefits from £3,385.4 to £6,770.7.

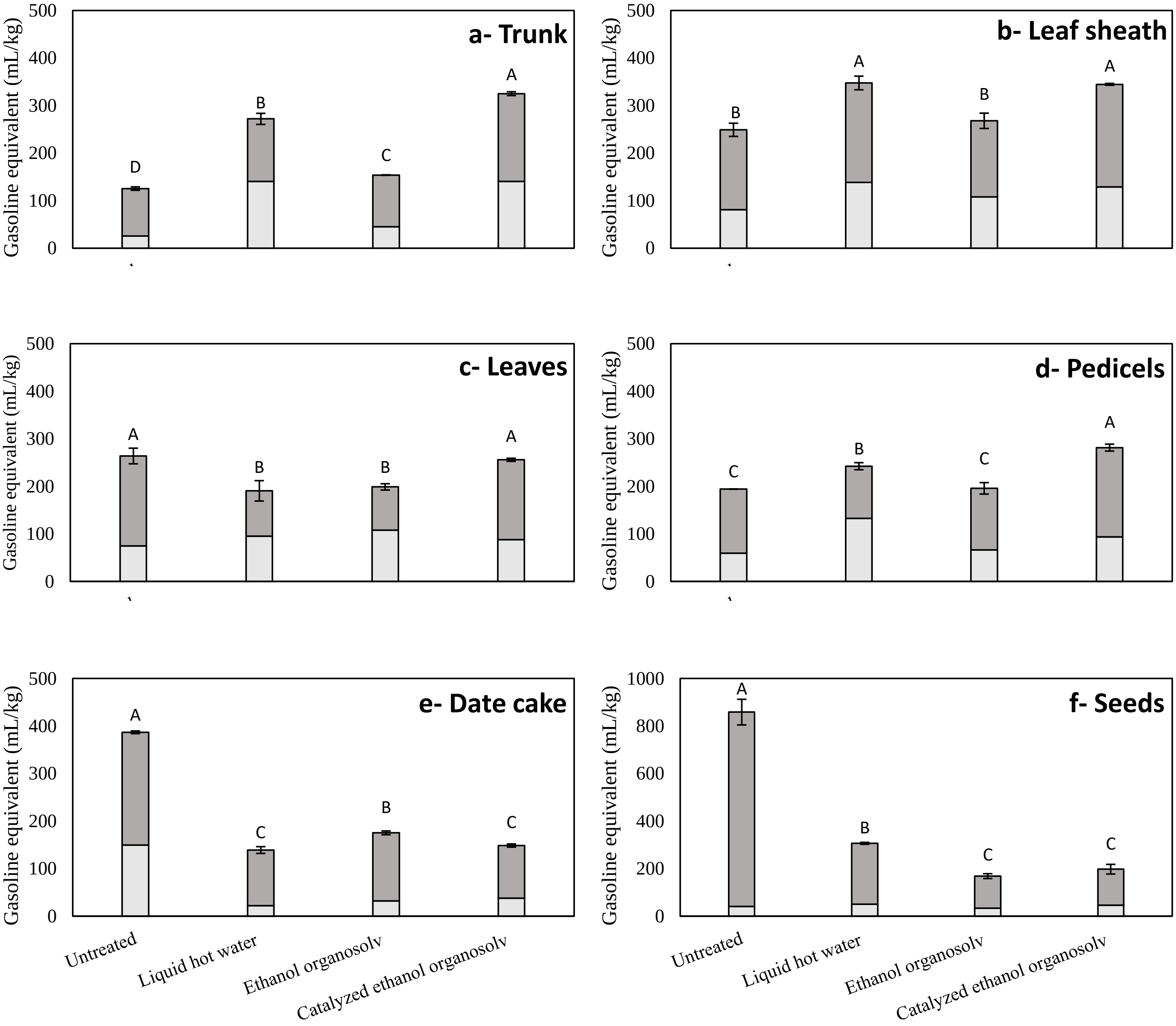

Figure 5. Gasoline equivalent values from ethanol (light gray bars) and methane (dark gray bars) based on 1 kg of initial substrate for untreated and pretreated wastes through different pretreatment conditions (error bars show standard deviations and the same letters indicate no statistical difference).

3.6. Biorefinery development

Two scenarios for biorefinery development could be followed: (I) maximum lignin production scenario and (II) maximum biofuel production scenario. Figure 6 depicts process diagrams of these two scenarios. When the target is lignin production as the main output, CEO pretreatment is recommended for all the date palm residues to meet the first scenario. Considering 1 kg of each sample, the first scenario yields 806.9 mL of ethanol and 902.8 L of methane, which can be equated to the energy produced by 1553.1 mL of gasoline. Additionally, this scenario also generates 528.0 g of lignin, which holds the potential value of £47467.9. Whereas, untreated date cake and seeds, as well as CEO pretreated of other substrates, are recommended as a feedstock for implementation of the second scenario. The second scenario yields 967.5 mL of ethanol and 1605.3 L of methane, which can be considered equivalent to the energy produced by 2452.0 mL of gasoline. Furthermore, this scenario generates 341.0 g of lignin, which holds a monetary potential of £29987.3. Detailed information on the mass balance of lignin, carbohydrates, and key products for each waste in every scenario are presented in Figures S1 and S2, Supplementary material.

Asia and Africa are leading date-producing regions in the world with 1 million hectares of harvested area [56]. The typical density of palm trees in each hectare is around 125, while each palm produces, on average, 400 kg of dates and 50 kg of leaf residues annually [3,57]. Moreover, date seeds contributed to about 10% of date fruit weight [58]. Considering the reasons discussed earlier for using individual wastes instead of mixing them, the focus was placed on the main residues that are practical and representative of the waste generated in the date palm industry. This approach allows for a more reasonable estimation of the waste management potential. It aligns with industry practices and reflects how date palm waste is realistically utilized in different scenarios. Based on this approach, considering leaf waste as the main residue fraction from the palm [14], as well as date, and seed wastes, employing the first scenario gives the possibility to produce 4 million m^3 ethanol and 7 billion m^3 methane, which are equated to 10 million m^3 gasoline, and 7 million ton lignin. Employing the second scenario could generate 12 million m^3 ethanol and 15 billion m^3 methane, which are equated to 25 million m^3 gasoline, and 400 kiloton lignin in Asia and Africa annually.

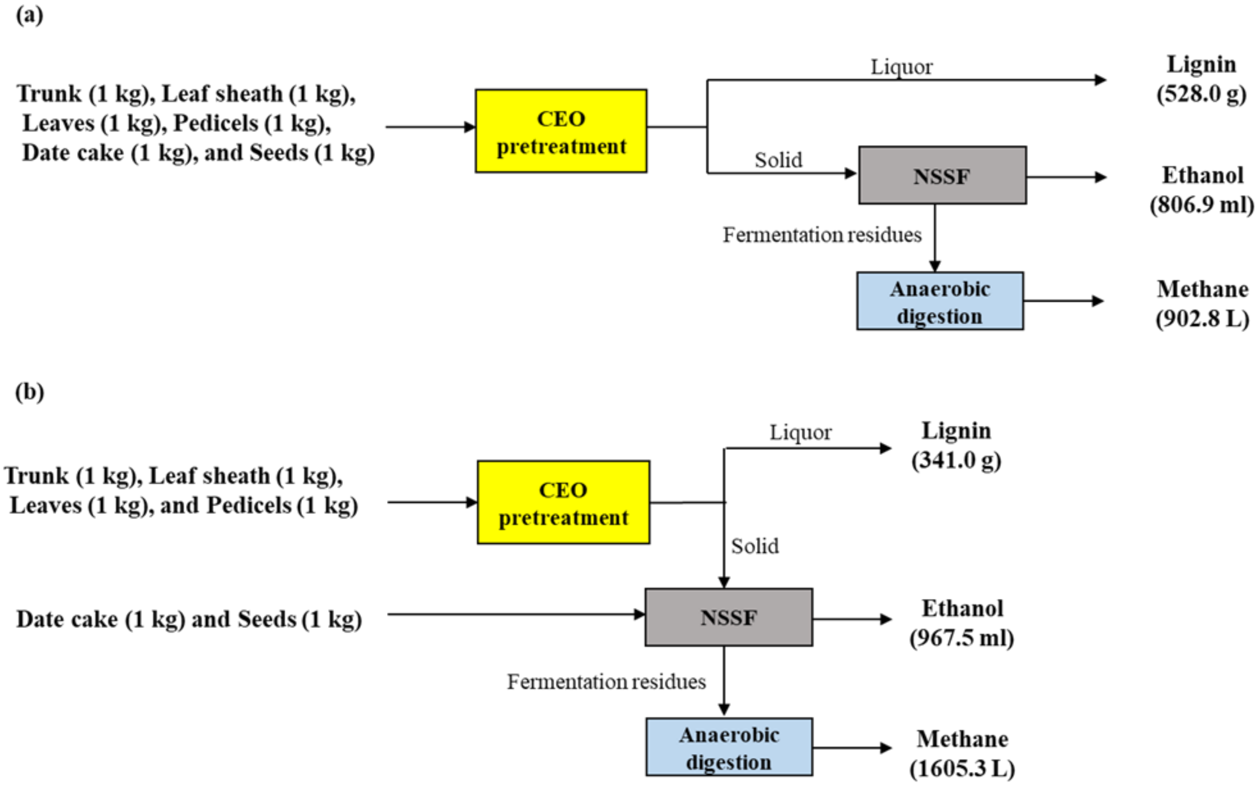

Figure 6. Process diagram for ethanol, methane, and lignin production through (a) first scenario, i.e. maximum lignin production, and (b) second scenario, i.e. maximum biofuel production.

4. Conclusions

The wastes generated in the palm date agroindustry demonstrated significant potential for the production of ethanol and lignin, with the added benefit of being able to utilize the fermentation residues for methane production. The study explored different pretreatment requirements for various date palm waste components in order to maximize biofuel and lignin production. CEO pretreatment of biomass resulted in maximum lignin production in the first scenario. In the second scenario, untreated date cake and seeds, along with CEO pretreatment of other residues, resulted in maximum biofuel production. In the first scenario, the production of highly pure and sulfur-free lignin was 35.4% higher than the second scenario, whereas the second scenario resulted in 19.9% more ethanol and 77.8% more methane than the first scenario. These findings demonstrate the importance of tailoring the pretreatment strategy to the specific components of date palm waste to maximize the production of targeted products. Moreover, a techno-economic analysis is crucial to assess the commercial viability of the process on a large scale. With further optimization, the conversion of date palm waste into biofuels and lignin can offer a sustainable and eco-friendly alternative to fossil fuels.

CRedit authorship contribution statement

Simin Shokrollahi: Investigation, Formal analysis, Data curation, Methodology, Resources, Visualization, Writing - original draft, **Amin Shavandi:** Validation, Writing – review & editing**.** **Oseweuba Valentine Okoro:** Validation, Writing – review & editing.**, Joeri F.M. Denayer:** Validation, Writing - review & editing, **Keikhosro Karimi:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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