Effect of pH on the Economic Potential of Dark Fermentation Products from Used Disposable Nappies and Expired Food Products

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Abstract: Used disposable nappies constitute a waste stream that has no established treatment method. The purpose of this study was the assessment of the dark fermentation of used disposable nappies and expired food products under different pH values. The biodegradable part of the used disposable nappies was recovered and co-fermented with expired food products originating from supermarkets. The recoverable economic potential of the process was examined for different volatile fatty acids exploitation schemes and process pH values. The process pH strongly affected the products, with optimum hydrogen production at pH 6 (4.05 NLH$_2$/reactor), while the amount of produced volatile fatty acids was maximized at pH 7 (13.44 g/L). Hydrogen production was observed at pH as low as pH 4.5 (2.66 NLH$_2$/reactor). The recoverable economic potential was maximized at two different pH values, with the first being pH 4.5 with minimum NaOH addition requirements (181, 138, and 296 EUR/ton VS of substrate for valorization of volatile fatty acids through microbial fuel cell, biodiesel production, and anaerobic digestion, respectively) and the second being pH 6, where the hydrogen production was maximized with the simultaneous production of high amounts of volatile fatty acids (191, 142, and 339 EUR/ton VS of substrate respectively).

Keywords: disposable nappies; expired food products; hydrogen production; dark fermentation; volatile fatty acids

1. Introduction

Used disposable hygiene products make up 1.5–6.3% of the municipal organic wastes stream [1,2]. Disposable nappies (DNs) typically consist of an absorbent core, with its main components being cellulose fibers and a super absorbent polymer (SAP), usually sodium polyacrylate, while the exterior is made from various types of plastics. The composite nature of DNs is detrimental for their treatment and valorization after their use, being part biodegradable material (cellulosic fibers, excreta, and urine up to 88% [1]) and part recyclable plastics and absorbent. As nappies are usually led for incineration or landfilling due to their complex structure, many environmental issues arise, such as plastics accumulation in landfills, methane release and potential pollution due to virus-infected excreta [3]. A treatment method has been employed by the authors that facilitates the separation of the different DN fractions and their valorization [4–6], according to which the biodegradable fraction is co-digested with expired food products (EFPs). EFPs consisting of fruits and vegetables have already been tested by the authors with very promising results [5]. The simultaneous food waste and used DNs treatment is suggested, as in most European countries these are the main waste streams consisting of organic matter (partially or entirely) and no specific regulations or strategies of waste management are pursued.
Dark fermentation is the bioconversion of an organic substrate to hydrogen and other metabolic products, like volatile fatty acids (VFAs) and ethanol. Biohydrogen can be used to produce heat and electricity, either through its combustion, or through electrochemical processes like fuel cells. The increasing energy demand of human activities and the deterioration of the environment has led to an increasing need for alternatives to fossil fuels, with hydrogen produced through dark fermentation of wastes being an excellent candidate [7].

The metabolic products that are co-produced during dark fermentation can also be employed as substrate for processes that produce valuable materials and energy [8]. VFAs can be directly converted to electricity through microbial fuel cells (MFC), where acetic acid is anaerobically converted to CO₂ (anode), with simultaneous production of protons and electrons. Through a proton exchange membrane, the protons react with oxygen in an aerobic chamber (cathode), while the electrons are transported from the anode to the cathode through an external circuit producing electricity [9]. Biodiesel can also be produced from VFAs by utilizing bacteria, yeasts, or microalgae [10], with studies demonstrating an accumulation of 20% w/w in the culture biomass as lipids [11]. Finally, the simplest method for the conversion of VFAs is their anaerobic digestion, with a typical methanogenic reactor treating the effluent of the dark fermentation process, in a two-step anaerobic digestion system. This kind of systems have been tested by the authors with similar substrates as the one examined in this study, proving the synergy of the two processes [4].

The literature regarding the valorization of used DNs for the recovery of materials and energy is limited [1,12–14]. Colon et al. [1] examined the co-composting of the biodegradable fraction of used DNs with separately collected biodegradable municipal waste, proving that the occurring compost had very small differences compared to compost produced solely from separately collected biodegradable municipal waste. Torrijos et al. [13] examined the co-digestion of the biodegradable part of used DNs with waste activated sludge, with 3.6 MJ being produced from 1 kg of VS of the biodegradable part of used DNs. Khoo et al. in their review paper [14] present different treatment methods for used DNs, including the biodegradation of polymers and cellulosic materials, as well as the implementation of pyrolysis, concluding that there are innovative technologies for the treatment of used DNs but at very early stages, with no established treatment method.

A number of companies operating all over the world use disposable nappies for the production of valuable materials [15–18], mostly focused on their non-biodegradable part, but these technologies are not widely used. Though this study, the recovery of energy from the biodegradable part of DNs and EFPs is examined through dark fermentation, a process that can complement existing technologies and boost used DN valorization. Separate collection of both waste streams is necessary.

2. Materials and Methods

In the present study, the co-digestion of the biodegradable fraction of the used DNs, with a mixture of expired fruits, vegetables, bakery products, and meat, originating from Spanish supermarkets was tested under different pH conditions, and the effect of pH on the distribution of the energy potential of the substrate to hydrogen, VFAs, and ethanol was examined. Data from supermarkets were used for the calculation of the ratio of the different EFPs in the feed mixture that corresponded to the ratios of the different waste streams being produced. The EFPs mixture used as feed consisted of 51% w/w bakery products, 27.5% w/w fruits and vegetables and 21.5% w/w meat. The used DNs originated from an elderly home located in Zamudio, Spain. The biodegradable fraction of the used DNs was separated in the form of a hydrolysate [4,5]. The first step to produce the DN hydrolysate was the shredding of the DNs and deswelling of SAP with the use of calcium and magnesium salts, dissolved in 10 L of water per adult DN. The plastics were removed from the surface of the mixture and then the cellulosic fibers were separated from SAP under different stirring conditions. The specifics of the DN separation are currently under review for a patent acquisition.
The optimum mixture for the co-digestion had been previously identified as 9.7:1 w/w DN hydrolysate to EFPs [19]. Prior to the dark fermentation experiments, partial hydrolysis of the substrate mixture was carried out, with the addition of 0.5% H₃PO₄, at 100 °C, for 1 h. The dark fermentation experiments were carried out in batch reactors with controlled pH through NaOH addition, at mesophilic conditions (37 °C), with an active reactor volume of 0.85 L, while the pH examined ranged from 4.5 to 7, with 0.5 increment, as described also in Figure 1. The chemical oxygen demand (COD), carbohydrates, total suspended solids (TSS), volatile suspended solids (VSS), biogas composition, and the concentrations of intermediary products (VFAs and ethanol) were monitored during the process.

![Figure 1. Experimental procedure and set-up of the DNs hydrolysate and EFPs mixture dark fermentation process.](image)

2.1. Inoculum

The batch experiments were carried out using anaerobic sludge from a municipal wastewater treatment plant (Attiki, Greece) as inoculum. The anaerobic sludge was pretreated by boiling at 100 °C for 20 min, aiming at the hydrogen-consuming bacteria inactivation and hydrogen-producing bacteria enrichment [20]. The inoculum constituted 15% v/v of the reactor working volume and was characterized by a TSS content of 56.6 ± 3.8 g/L and a VSS content of 35.3 ± 5.3 g/L.

2.2. Substrates

Bakery products, fruit and vegetables and meat in a ratio of 51:27.5:21.5 were collected from a Super Market in Zamudio (Biscay, Spain). These products did not meet the supply chain quality standards as their expiration date had passed or their quality had been inadequate for consumption. Hard pieces like stalks or bones were removed, while grinding, mixing and homogenization followed.

Various sizes of used DNs were obtained from a nursing home in Zamudio (Biscay, Spain). The DNs were cut manually with scissors and mixed with water and reagents [12], preparing a hydrolysate, which contained cellulosic fibers and excreta, while the plastic parts and SAP were separated.

EFPs and used DNs hydrolysate were initially mixed with a ratio of 1:9.7 w/w and afterwards acid hydrolysis with 0.5% H₃PO₄ at 100 °C for 60 min was implemented. Acid hydrolysis serves two purposes, as it promotes the organic matter solubilization [19,21], while pasteurization of the substrate is achieved. According to the European Commission Regulation No 142/2011 [22], animal by-products and derived products not intended for
human consumption should be pasteurized before any biological treatment. The physicochemical characteristics of used DN hydrolysate, EFPs and their hydrolyzed mixture are presented in Table 1, including pH, carbohydrates, COD, total solids (TS), volatile solids (VS), TSS, VSS, total Kjeldahl nitrogen (TKN), oil and grease, and phosphorus (P). The prefixes t- and d- refer to total and dissolved content, respectively.

Table 1. Physicochemical characteristics of used DNs hydrolysate, EFPs, and their mixture after hydrolysis (mean value ± standard deviation of three measurements).

| Parameter          | Used DN Hydrolysate (g/L) | EFPs (g/kg) | Mixture after Hydrolysis (g/L) |
|--------------------|---------------------------|-------------|-------------------------------|
| pH                 | 7.40 ± 0.01               | N/A         | 4.21 ± 0.03                   |
| t-Carbohydrates    | 3.50 ± 1.70               | 183.80      | 31.59 ± 8.42                  |
| d-Carbohydrates    | 0.06 ± 0.01               | N/A         | 12.24 ± 0.18                  |
| t-COD              | 5.01 ± 1.68               | 663.27      | 49.95 ± 6.41                  |
| d-COD              | 0.40 ± 0.01               | N/A         | 20.42 ± 1.45                  |
| TS                 | 8.17 ± 0.52               | 554.51      | 42.37 ± 0.85                  |
| VS                 | 6.51 ± 0.55               | 509.20      | 32.95 ± 0.95                  |
| TSS                | 6.70 ± 0.01               | N/A         | 22.03 ± 0.35                  |
| VSS                | 6.16 ± 0.31               | N/A         | 22.00 ± 0.30                  |
| TKN                | 0.07 ± 0.02               | 3.92 ± 0.42 | 0.91 ± 0.06                   |
| NH$_3$-N           | 0.07 ± 0.01               | 2.65 ± 0.06 | 0.25 ± 0.02                   |
| Oil & Grease       | 0.02 ± 0.01               | 47.00 ± 1.38| 3.14 ± 0.14                   |
| t-P                | 0.05 ± 0.01               | 1.24 ± 0.25 | 2.16 ± 0.07                   |
| d-P                | 0.02 ± 0.01               | N/A         | 0.87 ± 0.01                   |

The used DNs hydrolysate used in this study had similar characteristics as the one used in a previous work of the authors [19], with slightly alkaline pH probably caused by the presence of urine and urea decomposition [23]. The COD content of the hydrolysate was low, because of the large amounts of water needed to be added for the separation of the nappies’ constituents in other steps of the process, with only 8% being soluble COD. Most of the COD appears to originate from non-soluble carbohydrates probably in the form of cellulosic fibers. All the measured TKN appears to be in the form of NH$_3$-N, probably originating form urine.

The food waste mixture contained high concentrations of carbohydrates, proteins, and lipids. Due to the low moisture of the samples, measurement of the dissolved part was not possible. Carbohydrates mostly originated from the bakery products and the fruits and vegetables used, while the proteins and lipids originated from the animal by-products and partly from bakery products [24].

The mixture of used DNs hydrolysate and EFPs was analyzed after its partial hydrolysis and the addition of water for the adjustment of the organic load that would be fed to the fermenters. As it was to be expected, the mixture had acidic pH but within an acceptable range, as fermentation has been recorded in the literature at lower pH [25]. Around 40% of the total carbohydrates and COD was in soluble form. It has been reported that by using 0.8% H$_3$PO$_4$ at 150–200 °C for 1 h, the dissolved biomass can reach 30–45% [26]. All the suspended matter appears to be biomass, while the use of H$_3$PO$_4$ led to increased phosphorus concentrations.

2.3. Experimental Set-Up and Procedure

All experiments were performed in 1 L double wall, stainless steel (INOX 316) bioreactors at mesophilic conditions, as described in detail by Tsigkou et al. [5]. Physicochemical characterization of the substrates and the batch tests effluents was performed. During the experimentation period samples were taken every 4–6 h depending on the progress of the experiment.

TS, VS, TSS, VSS, t-COD, d-COD, TKN, ammonium N, t-P, and d-P were measured according to Standard Methods [27]. Total and dissolved carbohydrates were determined according to Joseffson [28], while off-line pH values were measured by Orion ROSS Ultra
Refillable pH/ATC Triode, Thermo Scientific. Lactic acid was measured with a DIONEX IC300 ion chromatography as described by Tsigkou et al. [5] while ethanol and VFAs were analyzed through gas chromatography (Agilent Technologies, Sant Clara, CA, USA, 7890A) equipped with a flame ionization detector, as described by Dareioti et al. [29]. Oil and grease were determined using hexane and a Soxhlet extractor (Velp Scientifica, Usmate Velate MB, Italy, SER 148). The biogas volume was measured by custom-made equipment and converted to standard conditions (STP = 0 °C and 1 atm) while the biogas analysis was performed by gas chromatography, according to Tsigkou et al. [4].

Concerning the calculation of normalized cumulative H2 production per L of reactor, the produced hydrogen was converted to STP conditions and divided by the working volume of the reactor. The calculation for the H2 production yield was carried out from the produced H2 (NL) converted to mols (22.4 NL/mol H2) divided by the mol of consumed carbohydrates in glucose equivalents.

3. Results and Discussion

3.1. Effect of pH

The main metabolic products were in, all cases, acetic and butyric acid, with the former always preceding the latter. Using just fruits and vegetables and DNs hydrolysate in similar experiments [5], the same main metabolic products were observed at the range of pH examined. The substrate carbohydrates were cellulosic fibers (cellulose and hemicellulose) [30] from the nappies, cellulose, and soluble sugars from fruit and vegetables [4,31], and starch [31], due to the presence of bakery products in the mixture. According to Chatellard et al. [32], when using sugars and disaccharides such as glucose, fructose, and maltose, the production of butyric acid is favored, followed by acetic acid. Depending on the inoculum used, the presence of starch can lead to different metabolic pathways [32]. In the case of cellulose, the products are mostly acetic and butyric acid, followed by low concentrations of propionic acid, exhibiting a behavior similar to the results recorded in this study for the mixture of substrates.

As it can be observed in Figures 2 and 3, acetic acid concentration increased independently of the hydrogen production rate for pH 5 and 7 (Figures 2a and 3b,f), while butyric acid production followed the hydrogen production pattern (Figures 2 and 3a–f). Similar behavior for acetic acid production during the dark fermentation of food waste has been reported in literature, with butyric acid production diminishing with increasing pH [33]. Some metabolic products, like caproic and propionic acid, where detected towards the end of the experiment, and not as intermediary products that were converted during the process. Small concentrations of ethanol were also detected (pH 5.5 and 6), as well as valeric acid (pH 4.5 and 5), in agreement with literature [33].

Figure 2. (a) Normalized cumulative H2 production per L of reactor, (b) H2 production yield and carbohydrates removal during the batch dark fermentation of used DNs hydrolysate and EFPs at different pH values.
Figure 3. Concentrations of VFAs and ethanol during the batch dark fermentation of used adult diapers hydrolysate and expired food products, at (a) pH 4.5, (b) pH 5, (c) pH 5.5, (d) pH 6, (e) pH 6.5, and (f) pH 7.
The components typically consumed during dark fermentation for hydrogen production are carbohydrates. Around 52% of the total substrate COD originated from carbohydrates, with 1.7–5.6% of total COD being converted to hydrogen and 25–36% to VFAs and ethanol at the pH range examined. Around 10% of the carbohydrates were not consumed during the process, probably because they were present in a form difficult to biodegrade, like cellulose. The 89–92% consumption of carbohydrates (Figure 3b) is in good agreement with relevant literature [33].

The pH of the process appears to strongly affect the products, with hydrogen production peaking near pH 6 (Figure 2). The production of hydrogen at pH 4.5 (0.97 mol H₂/mol equivalent glucose) is also worth mentioning, as it is not typically observed [34]. Concerning the efficiency of the process, the maximum yield (1.33 mol H₂/mol equivalent glucose) was observed at pH 6.0. In a previously published work by the authors [5], where fruit and vegetables and DNs hydrolysate were used as substrate, the maximum yield was 1.12 mol H₂/mol equivalent glucose at pH 7.5. It is also worth mentioning that the hydrogen yield of EFFs and DNs hydrolysate at pH 5.5 was estimated at 1.12 mol H₂/mol equivalent glucose while the hydrogen yield of the same substrate mixture at identical pH and temperature conditions in CSTR reactors remained unchanged (1.17 mol H₂/mol equivalent glucose) [19]. Regarding the total VFAs concentration, the maximum amounts were observed at pH 6.5 and 7, at 13.44 and 13.37 g/L, respectively.

3.2. Uses of Produced VFAs

The produced VFAs are a valuable resource that can be utilized through several different processes. This includes the production of electricity through MFC, biodiesel, and methane through anaerobic digestion. The distribution and amount of VFAs produced per examined pH is expected to affect the optimum pH for each process. It should be noted that this is not a full technoeconomic analysis of each process. The operational cost can vary greatly per process and can lead to very different results.

3.2.1. Microbial Fuel Cells

The maximum energy that can be recovered through an MFC can be calculated from the change in the Gibbs free energy from the oxidation of the VFAs examined (Table 2).

### Table 2. Oxidation reactions of VFAs produced by dark fermentation and their ΔG° calculated from ΔG° of pure substances.

| VFA       | Reaction | ΔG° (MJ/Mole) |
|-----------|----------|--------------|
| Acetic Acid | C₂H₄O₂ + 2 O₂ → 2 CO₂ + 2 H₂O | −0.873 |
| Propionic Acid | C₃H₆O₂ + 3.5 O₂ → 3 CO₂ + 3 H₂O | −1.603 |
| Butyric Acid | C₄H₈O₂ + 5 O₂ → 4 CO₂ + 4 H₂O | −2.243 |
| Valeric Acid | C₅H₁₀O₂ + 6.5 O₂ → 5 CO₂ + 5 H₂O | −2.883 |
| Caproic Acid | C₆H₁₂O₂ + 8 O₂ → 6 CO₂ + 6 H₂O | −3.523 |

The analysis is based on the energy that can be released from the oxidation of VFAs produced from 1 kg VS of substrate used in the dark fermentation process Equation (1),

\[
E \left[ \frac{MJ}{kg \text{VS}_{\text{substrate}}} \right] = \sum \frac{\Delta G_i^° \left[ \frac{MJ}{mole} \right]}{\text{kg} \text{VS}_{\text{substrate}} / L_{\text{reactor}}} \times \frac{m_i [g \text{VS}]}{MW_i [mole]} 
\]

where \( E \) is the energy released from the oxidation of VFAs, \( \Delta G_i^° \) the change in the Gibbs free energy from VFA i, \( m_i \) the g of VFA i produced per L of reactor, and MW\(_i\) its molecular weight.

The percentage of electrons produced in an MFC that can be harvested for the production of electricity is called coulombic efficiency (CE), with the rest of the electrons being lost due to biomass production, or oxygen diffusion through the proton exchange
membrane [35,36]. Teng et al. [35] have reported how different mixtures of VFAs lead to different coulombic efficiencies and developed an empirical formula for its calculation from the distribution of chemical energy in the form of COD fractions of acetic ($X_1$), propionic ($X_2$) and butyric acid ($X_3$) Equation (2).

$$CE = 29.7X_1 + 20.4X_2 - 22.6X_3 + 0.2X_1X_2 + 95.3X_1X_3 - 100.0X_2X_3 + 475.9X_1X_2X_3$$ (2)

As it can be observed from Equation (2) [35], the VFA that favors higher CE is acetic acid, while the presence of butyric acid has a negative effect. The presence of acetic acid is beneficial to the process probably because longer-chain VFAs have first to be converted to acetic acid before releasing most of their chemical energy through its oxidation [35]. By multiplying the chemical energy released from the oxidation of the different VFAs mixtures that were produced per kg of substrate through dark fermentation with the corresponding CE (Table 3), the recoverable electric energy can be estimated (Table 4).

### Table 3. Coulombic efficiency and chemical energy from the oxidation of different mixtures of VFAs produced under different pH values, per kg of VS of substrate used in the dark fermentation process.

| pH  | CE (%) | Chemical Energy from VFAs Oxidation (MJ/kg VS) |
|-----|--------|---------------------------------------------|
| 4.5 | 26.20  | 8.51                                        |
| 5.0 | 33.44  | 7.22                                        |
| 5.5 | 22.64  | 8.04                                        |
| 6.0 | 26.84  | 10.65                                       |
| 6.5 | 30.12  | 10.01                                       |
| 7.0 | 34.31  | 10.55                                       |

### Table 4. Consumed NaOH, produced H$_2$ and VFAs followed by the equivalents of VFAs conversion through MFC, biodiesel production and anaerobic digestion, for the pH values examined in dark fermentation, per kg of VS of substrate used in the dark fermentation step.

| pH  | NaOH (kg/kg$_{VS}$) | H$_2$ (MJ/kg$_{VS}$) | VFAs (kg/kg$_{VS}$) | Eq. Electric Energy (MJ/kg$_{VS}$) | Eq. Biodiesel (kg/kg$_{VS}$) | Eq. CH4 (MJ/kg$_{VS}$) |
|-----|---------------------|----------------------|---------------------|-------------------------------------|-----------------------------|------------------------|
| 4.5 | 0.022               | 1.41                 | 0.41                | 2.23                                | 0.124                       | 7.26                   |
| 5   | 0.085               | 1.30                 | 0.34                | 2.41                                | 0.102                       | 6.16                   |
| 5.5 | 0.169               | 1.83                 | 0.41                | 1.82                                | 0.123                       | 7.27                   |
| 6   | 0.129               | 2.15                 | 0.55                | 2.86                                | 0.165                       | 9.32                   |
| 6.5 | 0.175               | 0.95                 | 0.54                | 3.02                                | 0.162                       | 8.86                   |
| 7   | 0.192               | 0.66                 | 0.56                | 3.62                                | 0.169                       | 9.34                   |

#### 3.2.2. Biodiesel Production

Biodiesel can be produced from waste biomass through the transesterification of lipids by oleaginous microorganisms, with VFAs being a possible substrate [10,11]. A conversion of $Y_{lipids/VFAs} = 0.3$ g/g has been reported by Park et al. [10]. Fey et al. [37] examined the effect of different VFA ratios for acetic propionic and butyric acid, with higher amounts of acetic acid once again leading to higher yields of biodiesel and being completely consumed by the microorganisms. The ratio that was closest to the results of this study demonstrated a yield of $Y_{lipids/VFAs} = 0.159$ g/g. Karmee et al. [38] studied the production of lipids from food derived VFAs and their conversion to biodiesel that can reach 100%. The amount of biodiesel that can be produced from the VFAs produced under the different pH values examined was calculated by multiplying the total mass of VFAs produced per kg of VS of substrate treated with dark fermentation, with a yield of 0.159 g biodiesel per g VFAs (Table 4).

#### 3.2.3. Anaerobic Digestion Process

A two-stage anaerobic digestion process is a process that consists of two reactors. The first acidogenic reactor is identical to the system described in this work, where hydrogen and VFAs are produced, followed by a methanogenic reactor, where the produced VFAs...
are converted to methane and carbon dioxide. In the second stage, apart from the VFAs, most of the substrate not converted in the acidogenic reactor is typically also consumed. For comparison of the different VFAs utilization processes, only the methane that can be produced from the VFAs produced in the first stage will be calculated, but it should be mentioned that the methane that would be produced from the rest of the substrate is expected to be much higher because of the lipid and protein content that remains mostly unaffected at the first stage of the process. The maximum methane that can be produced can be calculated through a COD balance, where the COD present in the form of VFAs will be equal to the COD of the methane produced, with $Y_{\text{CH}_4/\text{VFAs}} = 0.35 \text{ NL/g COD}$. 55.5 KJ/g $\text{CH}_4$ heat of combustion was used for the calculations. Through the ideal gas assumption, the conversion can be calculated as $Y_{\text{CH}_4/\text{VFAs}} = 13.9 \text{ KJ/g COD}_{\text{VFAs}}$. The COD of each VFA mixture per pH examined can be calculated through the stoichiometry of its oxidation. For a compound with chemical formula: $C_nH_\alpha O_\beta$, COD can be calculated from Equation (3).

$$\text{COD} \left( \frac{g\text{O}_2}{g\text{compound}} \right) = \left( \frac{n + \frac{\alpha}{4} - \frac{\beta}{2} }{12n + \alpha + 16\beta} \right) 32$$

The biomethanization efficiency of VFAs, especially acetic acid, is almost 100%, because of the low growth yield of acetoclastic methanogens that does not allow significant conversion of chemical energy to biomass [39]. The expected energy content of the produced methane per kg of VS of substrate used in the dark fermentation process is presented in Table 4.

### 3.3. Comparison of Different VFAs Exploitation Methods

The results of the dark fermentation process under different pH, along with the final products from VFAs utilization are summarized in Table 4. The amount of NaOH used for pH adjustment during dark fermentation is also presented, as it may have a strong impact in the feasibility of the process. As it can be observed, in order to adjust the pH to seven, the amount of NaOH increases almost tenfold compared to the amount used for pH 4.5. Hydrogen production is presented in MJ equivalents, with 142 MJ/g $\text{H}_2$. The results of the VFAs exploitation methods correspond to the equivalent products from the VFAs reported, with the methods discussed thus far. Everything is expressed per kg of VS of substrate used in the dark fermentation process.

Even though pH 7 seems optimal for the examined processes from the amount of equivalent products, a basic economic balance can be carried out with the data presented in Table 4, in order to compare the cost of NaOH with the value of the products. The prices used were 0.52 EUR/kg of NaOH [40], 0.8 EUR/kg of biodiesel [41], 0.0637 EUR/MJ of electric energy [42], and 0.0198 EUR/MJ of thermal energy [43]. For hydrogen and methane, 40% was calculated as electric energy, 50% as thermal energy and 10% losses during combustion. Here it must be noted that this is a simplified economic balance that does not take into account the operational costs of the VFAs exploitation process that can be vastly different, especially for emerging technologies when compared to well established technologies, as well as the cost of initial investment. The results refer only to the conversion of the produced VFAs from the substrate and does not take into account the amount of substrate that was not converted but could be utilized, like the lipids and proteins for the production of methane with anaerobic digestion. From the result of each process per pH, the cost of NaOH has been subtracted and the profit from hydrogen gas has been added. The results are presented in Figure 4.
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4. Conclusions

Dark fermentation proved capable of producing valuable products from two solid waste streams, used DNs and EFPs. The distribution of the substrate chemical energy was affected by the process pH, presenting the opportunity of favoring the most preferred product through pH adjustment. While maximum hydrogen production was observed at pH 6 (4.05 NLH₂/Lreactor) and VFAs at pH 7 (13.44 g/L), the cost of NaOH had a significant impact on the net economic potential, with the best results at pH 4.5, with minimum NaOH addition (181 EUR/ton VS of substrate, 138 EUR/ton VS of substrate, and 296 for valorization of volatile fatty acids through microbial fuel cell, biodiesel production, and anaerobic digestion respectively), and pH 6 with moderate NaOH addition and increased amounts of VFAs and hydrogen gas (191 EUR/ton VS of substrate, 142 EUR/ton VS of substrate, and 339 EUR/ton VS of substrate for valorization of volatile fatty acids through microbial fuel cell, biodiesel production, and anaerobic digestion respectively).

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