

## Article

# Integrating Torrefaction of Pulp Industry Sludge with Anaerobic Digestion to Produce Biomethane and Volatile Fatty Acids: An Example of Industrial Symbiosis for Circular Bioeconomy

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**Abstract:** Industrial symbiosis, which allows the sharing of resources between different industries, could help to improve the overall feasibility of bio-based chemicals production. In that regard, this study focused on integrating the torrefaction of pulp industry sludge with anaerobic digestion. More specifically, anaerobic digestion (AD) of pulp sludge-derived torrefaction condensate (TC) was studied to evaluate the biomethane and volatile fatty acid (VFA) potential. The torrefaction condensate produced at 275 and 300 °C was used in AD. The volatile solid content (VS) was 6.69 and 9.01% for the condensate produced at 275 and 300 °C, respectively. The organic fraction of TC mainly contained acetic acid, 2-furanmethanol, and syringol. The methane yield was in the range of 481–772 mL/g VS for the mesophilic and 401–746 mL/g VS for the thermophilic process, respectively. The VFA yield was in the range of 1.1 to 3.4 g/g VS for mesophilic and from 1.5 to 4.7 g/g VS in thermophilic conditions, when methanogenesis was inhibited. Finally, pulp sludge TC is a feasible feedstock to produce platform chemicals like VFA. However, at higher substrate loading, signs of process inhibition were observed because of the relatively increasing concentration of microbial inhibitors.

**Keywords:** pulp sludge; torrefaction condensate; volatile fatty acids; anaerobic digestion; industrial symbiosis; biochemical production; biomass; thermochemical conversion; biochemical conversion; higher methane; specific VFA yield



**Citation:** Doddapaneni, T.R.K.C.; Cahyanti, M.N.; Orupõld, K.; Kikas, T. Integrating Torrefaction of Pulp Industry Sludge with Anaerobic Digestion to Produce Biomethane and Volatile Fatty Acids: An Example of Industrial Symbiosis for Circular Bioeconomy. *Fermentation* **2022**, *8*, 453. <https://doi.org/10.3390/fermentation8090453>

Academic Editor: Alessio Siciliano

Received: 4 August 2022

Accepted: 31 August 2022

Published: 11 September 2022

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## 1. Introduction

In the last decade, several efforts have been made to produce industrial chemicals from bio-based feedstock. However, the market inclusion of such chemicals is not yet realized. For example, in 2021, the share of bio-based carbon in global chemical production was around 10.4% [1]. In the authors' opinion, lower economic feasibility is the main obstacle to the large-scale production of bio-based chemicals. In general, the production costs of bio-based chemicals are higher compared with petroleum-based counterparts. The main reason for this could be the need for costly and complex process steps and the higher feedstock prices. At the same time, the demand for wood is constantly rising from different sectors. Thus, there is a need to produce bio-based chemicals from low-cost feedstock and to be available in large quantities. The pulp industry sludge is one such organic residue available in large quantities and at low/no cost.

Pulp industries produce large quantities of sludge during the treatment of wastewater from the pulping process. In general, 40–50 kg of dry sludge is generated per ton of paper produced [2]. Commonly, three different types of sludge are produced in a pulp

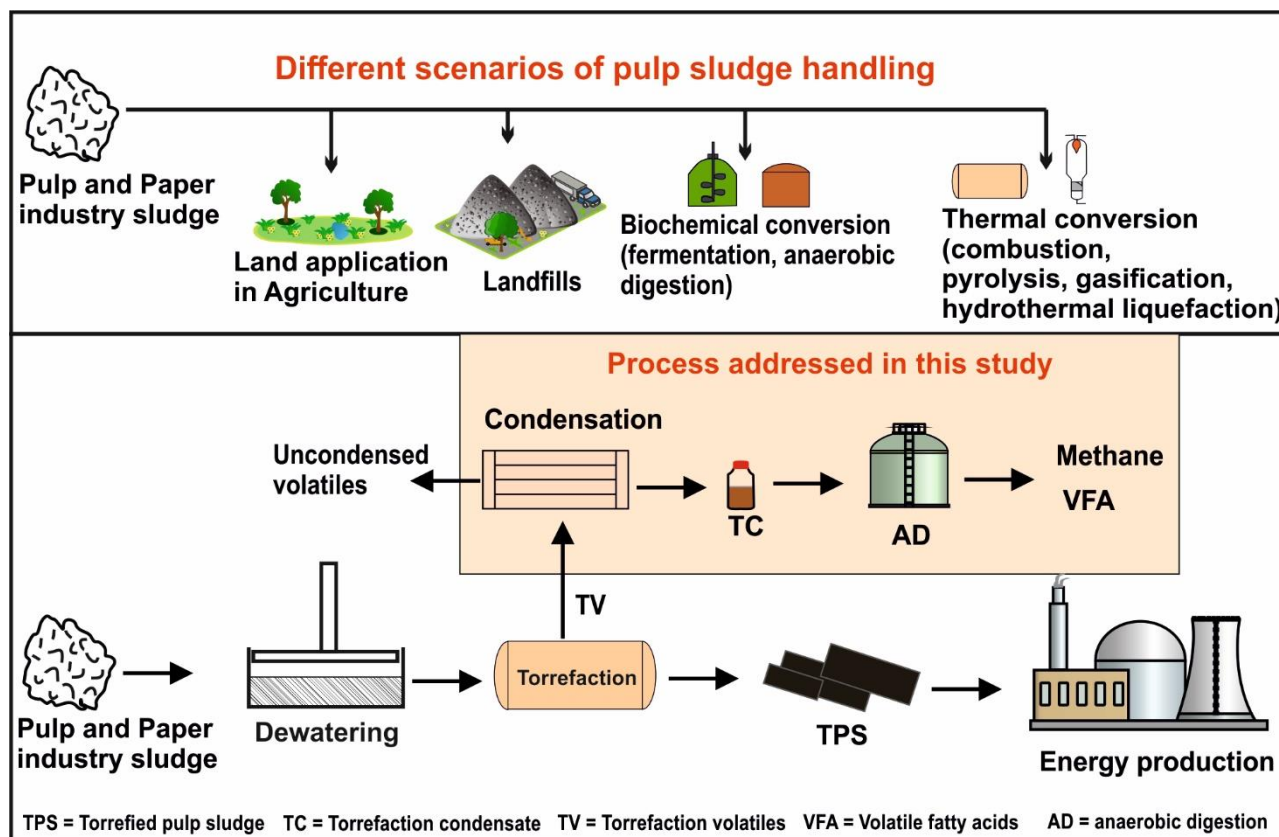
mill at different stages, i.e., primary, secondary, and tertiary sludge. The pulp sludge contains biomass fibers, wood chips, sand, and metals [2]. Conventionally, pulp mill sludge is handled through landfill, anaerobic digestion (AD), combustion, and/or land application. However, because of strict environmental regulations landfilling of pulp sludge is prohibited [3]. Land application is also not feasible because of lower transportation feasibility and the presence of heavy metals. Onsite combustion in existing boilers may not be a feasible option because of the high water content. Because of the inhibitory compounds from the pulping process and higher lignin and ash contents, the specific bio-methane potential and methane production rate are lower during AD of pulp sludge. Thus, there is a need to find alternative approaches to handle pulp sludge.

Torrefaction could be such an alternative approach to handle the pulp sludge. In recent years, torrefaction has evolved as a thermal pretreatment to improve the fuel characteristics of the biomass to a level comparable to coal [4]. However, its economic feasibility is not fully competitive with that of coal, especially when forestry wood is considered as a raw material. Thus, torrefied pellets need to be produced from alternative raw materials that are available in large quantities at low or no cost. Considering its organic content and its availability in large quantities, pulp industry sludge could be a perfect match for this. On the other hand, conventionally, volatiles produced during torrefaction are combusted to produce the heat energy required for the process. As torrefaction volatiles mainly contain water and acids, combusting them for energy production may not be a feasible option both technically and sustainability-wise. Alternatively, torrefaction volatiles can be condensed and the condensate can be used as a carbon source in microbial processes. Interestingly, some of the organic acids present in torrefaction condensate (i.e., acetic acid and propionic acid) are the same as the intermediate compounds produced in AD. Previously, Liaw et al. [5] studied the anaerobic digestion of torrefaction condensate from forestry wood and agricultural wastes and reported a methane yield in the range of 32 to 106 mL/g torrefaction condensate. Alternative to methane production, the torrefaction condensate can be considered as a feedstock to produce high-demand platform chemicals, such as volatile fatty acids (VFA).

Volatile fatty acids are the platform chemicals with applications in different industries, such as the pharmaceutical, chemical, and food industries [6]. Conventionally, VFA are produced from petroleum-based feedstock. As a part of shifting from fossil-based to bio-based chemical production, the production of bio-based VFA has also become interesting recently. The literature survey shows that VFA production from different substrates has been extensively studied. The readers are encouraged to check the recent review by [6,7] for detailed information on VFA production. As presented by Bhatia and Yang et al. [6] there are several operational challenges in VFA production. To highlight, the reluctant nature of biomass limits its degradation rate during microbial conversion. The complex and costly pretreatments are required to improve the solubility of some of the substrates. The lower specific yield of VFA for some substrates also reduces the economic feasibility of its production through anaerobic digestion. In order to address these process-related issues and to improve the economic feasibility, innovative process integration approaches are needed.

Connecting the above-discussed issues: (1) advanced valorization and sustainable handling of pulp industry sludge; (2) improving the technical and economic feasibility of the torrefaction process; and (3) biochemical production at higher yield with improved economic competitiveness, this study focused on integrating torrefaction of pulp industry sludge with AD to produce methane and VFA as presented in Figure 1. To be specific, the AD of pulp sludge-derived torrefaction condensate was studied with the aim of producing methane and VFA. To the knowledge of the authors, this is the first study on the AD of the pulp sludge-derived torrefaction condensate. It is also the first comprehensive experimental study on VFA production from torrefaction condensate. The biomethane and VFA production potential of the pulp sludge torrefaction condensate produced at 275 and 300 °C was studied under both mesophilic and thermophilic conditions. In order to

understand the VFA production potential, the methanogenic activity was inhibited using 2-bromoethanesulfonate (BES).



**Figure 1.** Innovative process integration approach to produce bioenergy and biochemicals from pulp industry sludge.

## 2. Materials and Methods

### 2.1. Pulp Sludge

The mechanically dewatered pulp sludge was received from AS Estonian Cell, Kunda, Estonia, which produces pulp from aspen wood through chemical–thermo–mechanical pulping process. Received pulp sludge was a mixture of sludge produced at different stages of wastewater treatment. The collected pulp sludge was stored at  $-20\text{ }^{\circ}\text{C}$  to control the microbial degradation.

### 2.2. Torrefaction of Pulp Sludge

Initially, sludge was dried at  $105\text{ }^{\circ}\text{C}$  in order to remove the moisture content using dryer UF1060, Memmert GmbH, Schwabach, Germany. The dried samples were stored in airtight containers for further use. The dried samples were torrefied using a batch reactor. For each run, around 200 g of dried sludge was used. Torrefaction experiments were carried out at 275 and  $300\text{ }^{\circ}\text{C}$  with a residence time of 60 min. The reactor temperature was maintained within  $\pm 5\text{ }^{\circ}\text{C}$ . The nitrogen flow at 1.5 L/min was used to maintain the inert environment in the reactor. The inside reactor temperature was measured using a thermocouple, which was connected to the data logger TC08 (Picotech, Cambridgeshire, UK). Once the set temperature was reached, the reactor was maintained at the same temperature (i.e., isothermal period) for 60 min. The torrefaction volatiles were passed through a water-cooled condenser and water–ice bath in order to produce torrefaction condensate. The uncondensed volatiles were released to exhaust. The collected condensate was filtered to remove tar and char particles using filter paper. Later, the condensate was stored at  $4\text{ }^{\circ}\text{C}$  in order to control the aging reactions.

### 2.3. Anaerobic Digestion Experimental Setup

Anaerobic digestion batch experiments were carried out to understand both methane and VFA production potentials of torrefaction condensate produced at 275 and 300 °C. Biogas production was measured by the increase in pressure in the test bottles. The granular sludge collected from the external circulation sludge bed (ECSB), anaerobic digestion system, operating at mesophilic condition (38 °C), which treats the wastewater from the pulping process at AS Estonian Cell, Estonia, was used as inoculum. The collected inoculum was stored at 4 °C prior to experiments. The VS content of the inoculum was around 4.5%. The AD tests were carried out at both mesophilic (35 °C) and thermophilic (55 °C) temperatures for a period of 30 days. The collected inoculum was kept in mesophilic and thermophilic conditions for one week in order to adapt them to the conditions. The batch AD experiments were carried out using 250 mL bottles with a working volume of 100 mL (50 mL inoculum + substrate + makeup water). The substrate loading at 2, 4, and 6 g VS/L (with respect to inoculum volume) was tested. In order to understand the VFA production potential, the methanogenic activity was suppressed using 20 mM, 2-bromoethanesulfonate (BES). For the comparative analysis, the AD of raw pulp sludge was carried out at 4 g VS/L. All the bottles were flushed with nitrogen for 5 min prior to incubation to maintain the anaerobic conditions. The bottles with only inoculum were maintained at the same AD conditions for the blank test. The bottles with only inoculum and BES were used as the blank tests in the case of VFA analysis. Around 0.8 mL of sample was collected every other day for the first two weeks and after that, every third day. The collected samples were stored at −20 °C for VFA analysis. The final methane and VFA yields were calculated by subtracting the methane and VFA produced by inoculum in blanks from that produced in the bottles with the substrate.

### 2.4. Analytical Methods

The VS and TS were measured following the standard method APHA 2540. The higher heating value of the condensate was measured using IKA calorimeter 131 C5000 (IKA, Staufen, Germany) based on EVS-EN ISO 18125:2017. As the condensate is known for its high water content, a known amount of ethanol was mixed with condensate to assure complete combustion during calorimeter tests.

The composition of the condensate was analyzed using GC-MS (Agilent 7890B) equipped with a mass spectrometry (MS) detector (Agilent 5977A) and column HP-5MS–Ultra Inert (30 m, 0.25 mm ID, 0.25 µm film thickness; Agilent, Santa Clara, CA, USA). Initially, the oven was heated at 2 °C/min to 200 °C and later at 5 °C to the final temperature 280 °C. The injection volume was 0.2 µL and the split ratio was 20:1.

Volatile fatty acids were measured using high-performance liquid chromatography (HPLC LC–2030C 3D Plus; Shimadzu Corporation, Kyoto, Japan) equipped with column Rezex<sup>TM</sup> ROA–Organic Acid H+ (Phenomenex, Torrance, CA, USA) operating at 50 °C. The refractive index detector at 50 °C was used. The mobile phase was 5 mM H<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.5 mL/min. Prior to analysis, the samples were centrifuged at 10,000 rpm for 5 min). Then, the supernatant was filtered using 0.2 µm centrifuge filters and running the centrifuge (Megafuge 40, ThermoScientific; Waltham, MA, USA) at 10,000 rpm for 5 min.

The methane content of the biogas was measured using gas chromatography CP-4900 Micro-GC, (Varian Inc., Palo Alto, CA, USA), which is equipped with a thermal conductivity detector and two columns, i.e., Molsieve 5A Backflush heated column (20 m × 0.53 mm) and PoraPLOT U heated column (10 m × 0.53 mm). The pressure in the bottles was measured before and after GC measurement using a pressure meter (type 3151, WAL BMP-Testsystem, WAL Mess-und Regelsysteme GmbH, Oldenburg, Germany). The methane content was measured when the bottles were outside the incubator for a short period of time. The methane yield values were presented at standard temperature and pressure (STP), i.e., 273.15 K and 1.01 bar, respectively. The detailed procedure of biogas analysis and calculations was presented in [8].

Hereafter, the torrefaction condensate produced at 275 and 300 °C are referred to as TC-275 and TC-300, respectively. The methanogenesis inhibition using 2-bromoethanesulfonate is represented as BES.

### 3. Results

#### 3.1. Properties and Composition of the Pulp Sludge

The pulp sludge, as received, contained around 20% of dry matter. The fiber analysis showed the cellulose, hemicellulose, and lignin contents around 36, 11, and 10 wt.% (dry basis), respectively. The ash content was around 12.7 wt.% dry basis. The composition of the pulp sludge in terms of biomass components is comparable with high ash agricultural residue like barley straw. The readers are advised to check our previous study [9] for a detailed composition analysis of the pulp sludge.

#### 3.2. Product Yield during Torrefaction

The solid yields were around 63 and 54 wt.%, and the condensate yields were 14 and 30 wt.% for 275 and 300 °C, respectively (refer to Figure S1). At the same temperatures, uncondensed volatiles yield ( $100 - (\text{solid} + \text{condensate})$ ) was around 23 and 16 wt.%, respectively. Previously, Huang et al. [10] reported a solid yield of 65 wt.% for pulp sludge at a torrefaction temperature of 300 °C. There is no previous data on the yield of uncondensed volatiles and condensate for comparison. Fagernas et al. [11] reported a similar yield of torrefaction products, i.e., 59, 32, and 17 wt.% of torrefied biomass, condensate, and uncondensed volatiles for bamboo torrefaction at 300 °C for 60 min, respectively. Previously, Doddapaneni et al. [4] reported a condensate yield of 18 and 25 wt.% for pine wood torrefaction at 275 and 300 °C, respectively. As expected, the solid yield reduced with increasing torrefaction temperature. Relatively, the uncondensed volatiles yield and condensate yield increased with increasing torrefaction temperature. Compared with woody biomass, in the case of pulp sludge, the solid yield is lower, and the yield of volatile gases is higher. The main reason could be the increased degradation of biomass components because of the catalytic effect of inorganic elements present in the pulp sludge. Interestingly, the share of condensable fractions (condensate) in the total torrefaction volatiles increased significantly with increasing torrefaction temperature, i.e., from 34.6% at 275 °C to 64.8% at 300 °C.

#### 3.3. Composition and Properties of the Torrefaction Condensate

The chemical composition (GC-MS area %) of the pulp sludge-derived torrefaction condensate is presented in Table 1. Acetic acid is the major compound in the condensate produced at both 275 and 300 °C. Acetic acid in the torrefaction condensate is mainly produced through the cleavage of acetyl groups present in hemicellulose. The acetic acid concentration varied between 106 to 108 g/L depending on torrefaction temperature. Generally, biomass-derived torrefaction condensate mainly contains hemicellulose-derived compounds (for example, acetic acid and furfural) as this is the fraction degrading the most during torrefaction. Next to acetic acid, syringol was the major compound in the pulp-derived torrefaction condensate.

Compared with previous studies on biomass torrefaction [5,11], the composition of the sludge-derived condensate is significantly different. The catalytic activity of ash present in the pulp sludge could be the primary reason for this variation in the chemical composition. Previously, Fagernas et al. [11] and Liaw et al. [5] reported furfural content in the torrefaction condensate in the range of 0.09 to 0.8 wt.% for different biomass. Interestingly, in the sludge-derived torrefaction condensate, no furfural or 5-hydroxymethylfurfural (5-HMF) was observed. At the same time, a higher yield of 2-furanmethanol was observed. According to Macedo et al. [12], 2-furanmethanol is produced through the secondary reactions between furfural and formaldehyde. Previously, Nocquet et al. [13] observed that formaldehyde is the second most abundant compound in biomass torrefaction volatiles next to water. The catalytic effect of potassium could be the reason for the lower yield of furfural and



5-HMF and higher yield of 2-furanmethanol. Previously, Zhang et al. [14] observed a higher yield of 2-furanmethanol during the torrefaction of raw rice husk compared with leached (inorganics removal) rice husk. In another study, Macedo et al. [12] observed that furfural yield reduced from 9.87 mg/g of biomass to 1.06 mg/g of biomass during the torrefaction of potassium-doped miscanthus biomass at 275 °C. In the same study, an increase in the yield of 2-furanmethanol from 1.2 mg/g of biomass to 6.16 mg/g of biomass was observed.

**Table 1.** Chemical composition and physiochemical properties of pulp sludge derived torrefaction condensate.

Compound	GC-MS Area % of Total	
	TC-275	TC-300
Acetic acid	36.77	27.92
2-Propanone, 1-hydroxy-	5.32	4.43
Propanoic acid	0.67	4.1
1,2-Dimethylhydrazine	0	0.34
Pyridine	0.29	0.43
1-Hydroxy-2-butanone	1.76	1.63
Butanoic acid	0	1.29
2-methylpyridine	0.21	0.28
3-Methoxy-2-butanol	0	0.32
2-Cyclopenten-1-one	0.30	0.76
2-Furanmethanol	6.52	6.34
2-Propanone, 1-(acetyloxy)-	1.50	2.25
2-Cyclopenten-1-one, 2-methyl-	0	0.41
1-(2-Furanyl)-ethanone	0	0.37
4-hydroxybutanoic acid	3.07	2.84
Piperidine, 1-methyl-	0	0.49
Pyridine, 2,5-dimethyl-	0.23	0.36
Pyridine, 2,3-dimethyl-	0	0.22
1-(acetyloxy)-2-butanone	0.20	0.31
2-Cyclopenten-1-one, 3-methyl-	0.27	0.44
3-methyl-2(5H)-furanone	0.27	0
Phenol	3.54	2.29
Pyridine, 3-methoxy-	0.93	0.87
Not identified	7.49	10.57
3-Methyl-1,2-cyclopentanedione	3.03	3.26
2H-Pyran-2-one, tetrahydro-	0.65	0.95
2-Methoxyphenol (Guaiacol)	3.09	2.95
Methanesulfonamide, N,N-dimethyl-	2.39	1.2
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	1.45	0
N-methyl-1,3-propanediamine	0.76	0
5-methyl-2-pentylpyridine	0	0.15
Creosol	0.30	0.76
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	0.22	0
4-ethyl-2-methoxyphenol ( <i>p</i> -Ethylguaiacol)	0.66	0.46
2-Methoxy-4-vinylphenol ( <i>p</i> -Vinylguaiacol)	0.50	0.29
2,6-dimethoxyphenol (Syringol)	10.95	10.54
5-tert-Butylpyrogallol	1.25	0
Homovanillic acid	0.65	0
1,2,3-Trimethoxybenzene	0	0.52
5-Methyl-1,2,3-trimethoxybenzene	0	1.06
1-(4-methylthiophenyl)-2-propanone	0	0.58
Properties		
Volatile solids (%)	6.69	9.01
pH	4.08	4.16
Higher heating value (HHV) MJ/kg	4.9	2.2

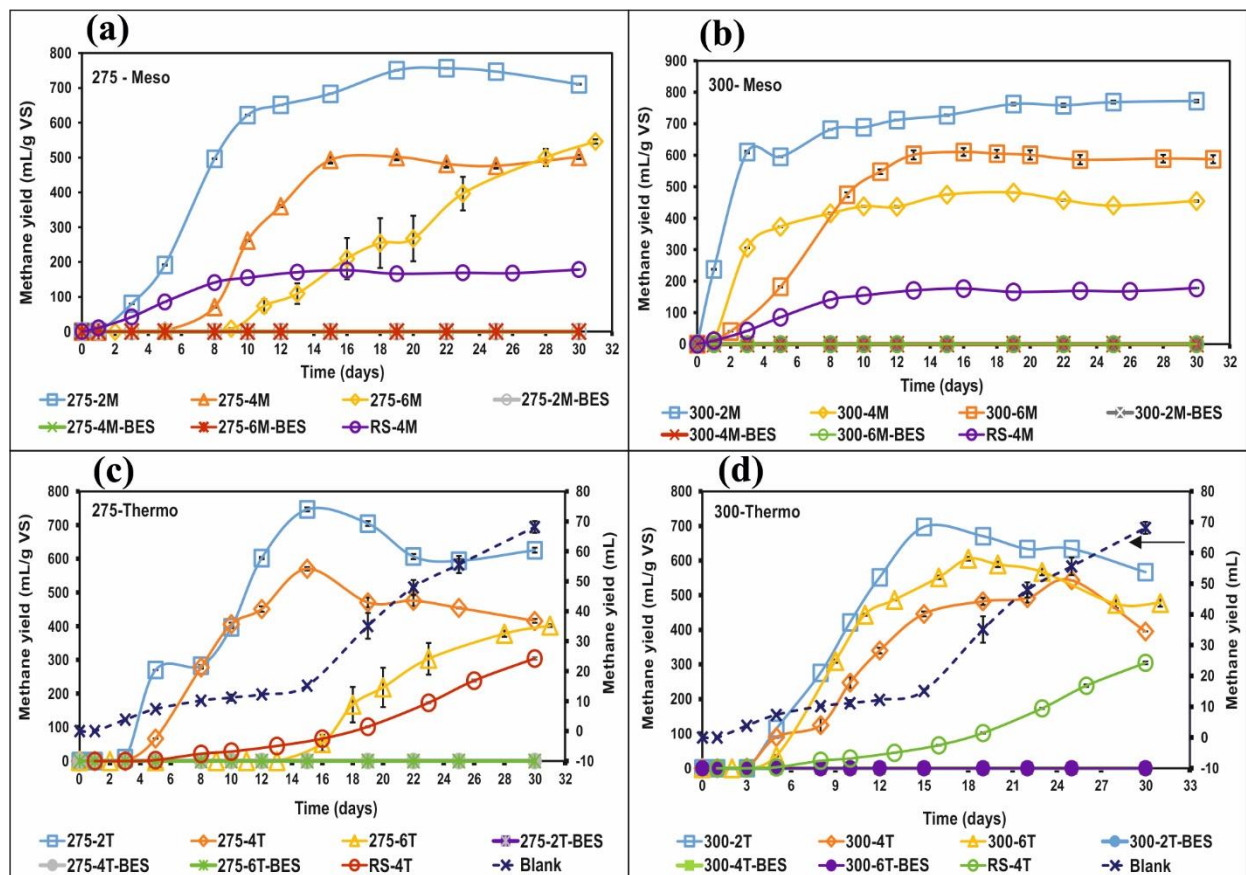
Anhydro sugars such as levoglucosan were also not identified in this study for pulp sludge-derived condensate. Again, the possible reason could be the catalytic effect of alkali and alkaline earth metals present in the pulp sludge. Previously, Mahadevan et al. [15] observed the reduced yield of levoglucosan from 10.77 to 0.63 and 0.5 (GC-MS area %) during the pine wood pyrolysis under the presence of K and Na, respectively. The presence of K and Na promotes the degradation of anhydro sugars to lower molecular weight compounds, such as acetol, acetic acid, 2-cyclopentenone, and 2-hydroxy 3-methyl [15].

Previous studies reported that acetic acid concentration increases with increasing torrefaction temperature [4,13]. In this study, however, acetic acid concentration reduced from 36.7 to 27.9 (GC area, %) when torrefaction temperature increased from 275 to 300 °C. One possible reason could be the catalytic effect of Ca present in the pulp sludge. Previously, Mahadevan et al. [15] observed the reduction in acetic acid concentration from 2.82% to 0.43% during the pyrolysis of pine wood in the presence of Ca.

Compared with woody biomass torrefaction, a higher yield of lignin-derived compounds, such as phenol, 2-methoxyphenol (guaiacol), 2-methoxy-4-methylphenol (creosol), and 2,6-dimethoxyphenol (syringol) was observed for pulp sludge-derived torrefaction condensate. For example, at 275 °C, the yield of phenol, syringol, and guaiacol were 3.54, 10.95, and 3.09 (GC area %). Especially, the yield of syringol was much higher compared with other lignin-derived compounds. Our observation was further supported by the data presented by Macedo et al. [16]. The authors observed an increase in syringol yield from 0.63 mg/g to 2.01 mg/g during the torrefaction of 0.003 M K<sub>2</sub>CO<sub>3</sub> impregnated eucalyptus biomass compared with the raw biomass. In another study, Lu et al. [17] observed a higher yield of syringol, i.e., 15.2 (GC area %) during the pyrolysis of K<sub>3</sub>PO<sub>4</sub> doped poplar wood, while the same for the raw wood was 2.2 (GC area, %). According to Blasi et al. [18], the increased activity of demethylation and demethoxylation could be the main reason for the increase in lignin-derived compounds.

### 3.4. Biomethane and Volatile Fatty Acids Production Potential

The cumulative methane yields at various substrate loadings and torrefaction condensate produced at 275 and 300 °C are presented in Figure 2. The methane yield was in the range of 481–772 mL/g VS for mesophilic and 401–746 mL/g VS for thermophilic conditions, respectively. From the Figure 2, it can be observed that torrefaction condensate has higher specific methane potential than pulp sludge. The highest methane yield for pulp sludge was around 178 and 304 mL/g VS for mesophilic and thermophilic processes, respectively. At the same time, a higher gas production rate and reduced lag phase was also observed for torrefaction condensate at lower substrate loading compared with direct AD of pulp sludge. The main reason could be attributed to the composition of the pulp sludge. The pulp sludge mainly contains cellulose, hemicellulose, lignin, and ash (refer to Section 3.1). In AD, dissolved carbon is one of the key parameters in converting the selected feedstock to methane. In the case of lignocellulosic biomass, hydrolysis is the rate-limiting step, where macromolecular compounds are converted into soluble smaller organic compounds. Thus, hydrolysis of biomass fibers could be the rate-limiting step in the case of pulp sludge. However, in the case of torrefaction condensate, the organic fraction is already dissolved in water and ready to be consumed by microorganisms. Additionally, the high ash content (inorganic matter) and lignin are the reasons for lower specific methane yield in the case of pulp sludge. It is also worth noting that the reduced methane yield at the end of the digestion for the thermophilic process is mainly due to the increased gas production from blank tests after 20 days (refer to Figure 2c,d). This shows that microorganism is still adapting to the thermophilic conditions.



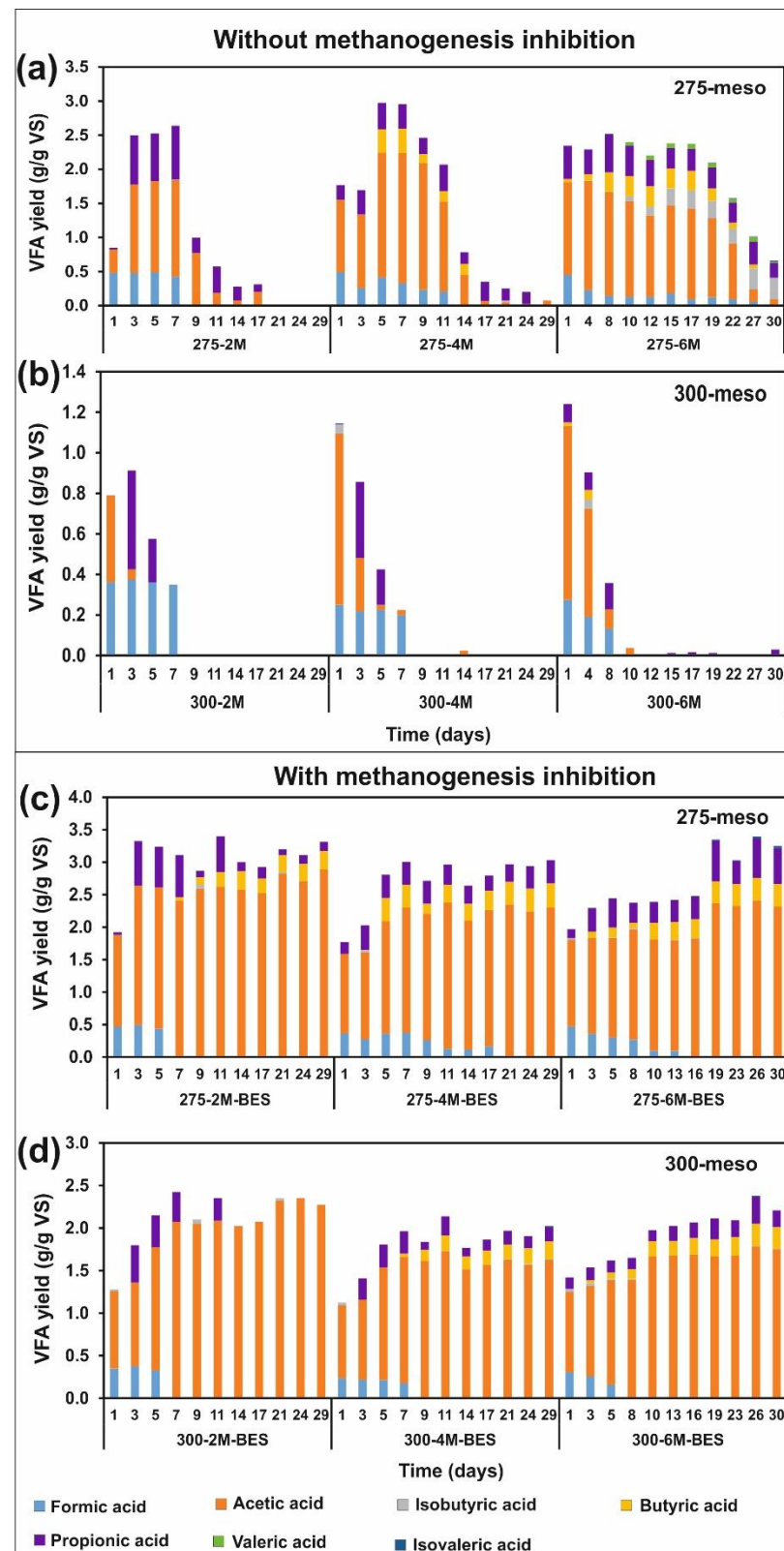
**Figure 2.** The cumulative methane yield at various substrate loadings for torrefaction condensate (TC) produced at 275 and 300 °C (a,b) mesophilic and (c,d) thermophilic conditions, respectively. The 2, 4, 6, represent substrate loadings (g VS/L); M and T represent mesophilic and thermophilic processes, respectively; RS represents raw sludge. For example, 275–2M–BES is for condensate produced at 275 °C, mesophilic conditions, 2 g VS/L loading and methanogenesis inhibition.

The VFA yields for TC produced at different temperatures and at different substrate loadings for mesophilic and thermophilic processes are presented in Figures 3 and 4, respectively. Total VFA yield varied between 1.1 to 3.44 g/g VS for mesophilic and 1.5 to 4.7 g/g VS for thermophilic conditions, respectively. As expected, a higher VFA yield was observed when methanogenesis was inhibited using BES. Following the methane, the VFA yield is higher in the case of torrefaction condensate compared with raw sludge.

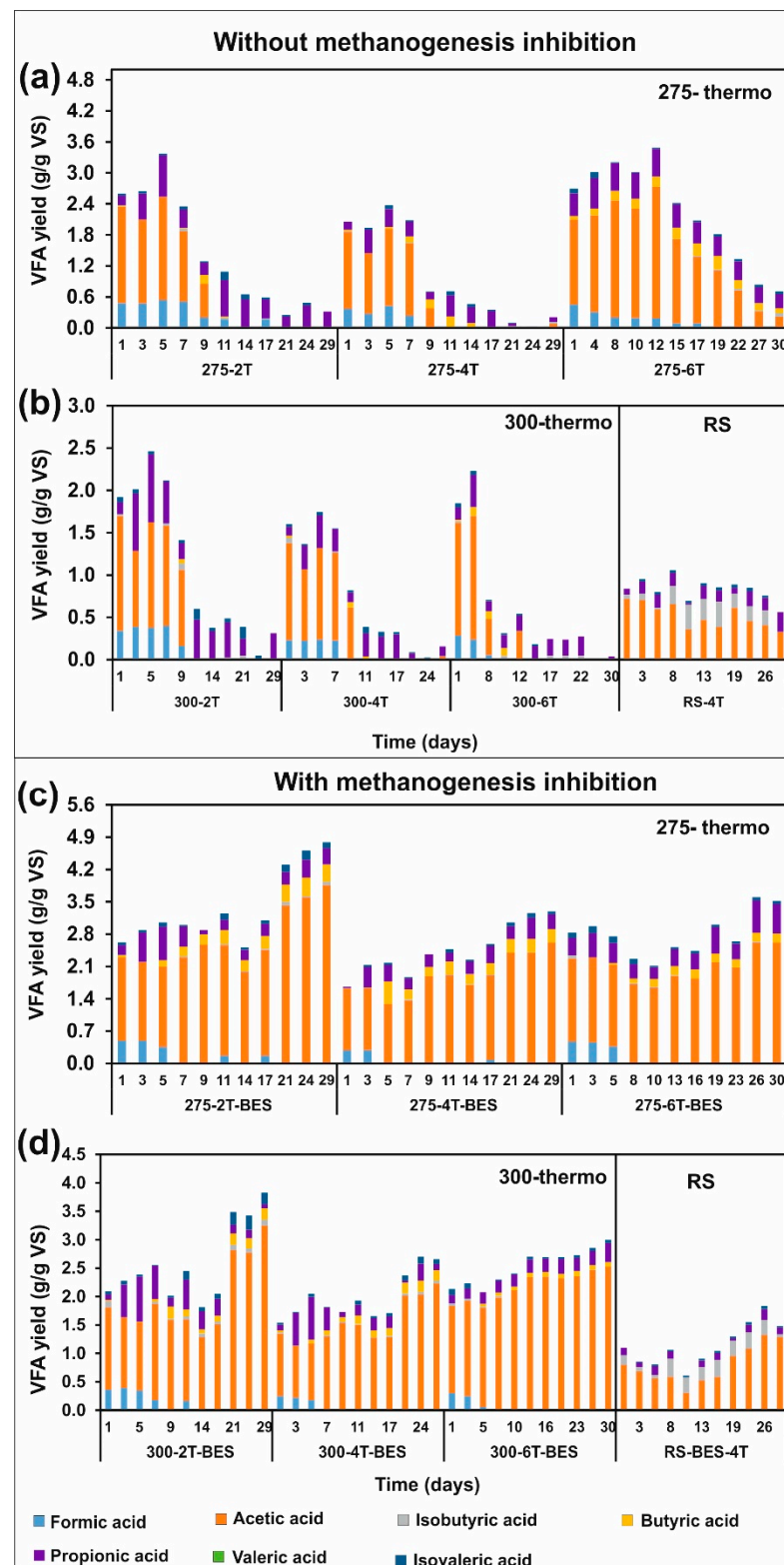
### 3.4.1. Influence of Torrefaction Temperature

As expected, the torrefaction temperature showed a significant influence on the overall performance of the AD. For example, under mesophilic conditions, torrefaction condensate produced at 300 °C showed a higher methane yield. While in the case of thermophilic conditions, a higher methane yield was observed for torrefaction condensate produced at 275 °C. The methane yield was in the range of 502 to 757 mL/g VS for 275 °C and 481–772 mL/g VS for 300 °C in mesophilic conditions. The same at thermophilic was 401–746 for 275 °C, 542–697 for 300 °C, respectively. The difference in the methane yield could be directly attributed to the variation in the chemical composition of the condensate. From Figure 2, it can also be observed that the TC produced at 275 °C showed a higher lag phase for both mesophilic and thermophilic conditions. For example, the lag phase for TC-275 and 6 g VS/L loading was around 9 and 12 days for mesophilic and thermophilic conditions, respectively. The same for TC-300 was around 3 days for both mesophilic and thermophilic.





**Figure 3.** Volatile fatty acids production for the mesophilic process at various substrate loading for torrefaction condensate produced at 275 and 300 °C; (a,b) without methanogenesis inhibition and (c,d) with methanogenesis inhibition. The 2, 4, 6 represent substrate loading (g VS/L). For example, 275–2M–BES is for condensate produced at 275 °C, mesophilic conditions, 2 g VS/L loading and methanogenesis inhibition.



**Figure 4.** Volatile fatty acids production for the thermophilic process at various substrate loading for torrefaction condensate produced at 275 and 300 °C; (a,b) without methanogenesis inhibition and (c,d) with methanogenesis inhibition. The 2, 4, 6 represent substrate loading (g VS/L); RS represents raw sludge. For example, 275–2T–BES is for condensate produced at 275 °C, thermophilic conditions, 2 g VS/L loading and methanogenesis inhibition.

The total VFA yield was higher in the case of TC-275 compared with TC-300. For example, the final VFA yield for TC-275 was 4.78, 3.29, and 3.52 g/g VS at substrate loading of 2, 4, and 6 g VS/L in thermophilic conditions, respectively when methanogenesis was inhibited. At the same operating conditions, the VFA yield of 3.82, 2.65, and 2.99 g/g VS was observed for TC-300 (refer to Figure S2). Interestingly, butyric acid was higher in the case of TC-275 compared with TC-300. Previously, Hübner and Mumme [19] also observed the same reducing yield of butyric acid with increasing pyrolysis temperature during the AD of pyrolysis aqueous fraction.

As presented in Section 3.3, the torrefaction condensate produced at 275 °C has a higher concentration of organic acids and lignin-derived compounds compared with 300 °C. According to Liaw et al. [5], at lower concentrations, these compounds could be favorable to the AD microorganisms. However, at higher concentrations, the same compounds are inhibitory to the AD process. Additionally, because of the lower VS, the amount of TC loaded is also higher for TC-275 compared with TC-300 for the specific amount of VS. This could have created multiple effects and resulted in increased methanogenesis inhibition for TC-275. Although there is a process inhibition at the start, the final methane yield is at a similar level to TC-300. The reason could be either that microorganisms are adapted to the condensate and/or the chemical composition of the condensate could be changing over the period of time.

#### 3.4.2. Influence of Anaerobic Digestion Operating Temperature

Like torrefaction temperature, AD operating temperature also showed a significant influence on methane yield. The maximum methane yield at different substrate loading for both mesophilic and thermophilic conditions is presented in Table S1. From Figure 2, it can be observed that methane yield is higher for mesophilic condition, it showed better performance in terms of methane yield and the lag phase compared with thermophilic. Previously, Ref. [4] also observed the same phenomenon for pine biomass torrefaction condensate.

In contrast to biogas, thermophilic conditions showed higher VFA yield compared with mesophilic condition. For example, the VFA yield of 3.31 g/g VS was observed at the end of experiments for the condensate produced at 275 °C, with BES inhibition and substrate loading of 2 g VS/L. At the same operating conditions, the VFA yield was 4.78 g/g VS, which is around 44.4% higher. The acetic, propionic, and butyric acids are the major compounds in the VFA for both mesophilic and thermophilic processes. Additionally, the production of isovaleric acid was also observed in the case of thermophilic. Over time, butyric acid accumulation increased more in mesophilic compared with thermophilic conditions. Previously, Hao and Wang [20] also observed the same phenomena, i.e., higher butyric acid yield for mesophilic and the production of isovaleric acid for thermophilic during the AD of dewatered municipal sludge.

There could be two possible reasons for the increased VFA production in thermophilic conditions. In thermophilic conditions, the solubilization rate of organic matter is higher in the beginning compared with mesophilic conditions. For example, during the anaerobic digestion of dog food, Kim et al. [21] observed maximum soluble COD (SCOD) production and VSS reduction within 4 days and 11 days for thermophilic and mesophilic, respectively. In another study, He et al. [22] observed increasing SCOD with the increasing AD operating temperature at the beginning of the process. This accelerated hydrolysis and solubilization rate can lead to VFA accumulation through subsequent acidification and ultimately can inhibit the methanogenic activity [23]. In addition, Hao and Wang [20] observed higher activity of extra-cellular hydrolases, i.e., alpha-glucosidase and protease, in thermophilic conditions. The same authors also observed that the abundance of homoacetogens was higher in thermophilic reactors. According to Wilson et al. [24], the temperature sensitivity of aceticlastic methanogens at elevated temperatures could also be a reason for higher VFA accumulation in thermophilic. From Figure 2, it can be observed that methane production was more stable in mesophilic compared with thermophilic.

Specific to torrefaction condensate, the elevated AD temperature could alter the condensate's physiochemical properties and chemical composition. According to Li et al. [25], at lower temperatures, the higher molecular weight compounds are precipitated in biomass-derived oils. The authors also observed the formation of thick brown to black substrates during the storage of the torrefaction condensate. The viscosity of the biomass-derived oils also increases with increasing storage temperature. Substrate viscosity is also one of the influencing parameters in AD, which can create issues while mixing, and mass transfer limitations. At the same time, Li et al. [25] observed that the solubility of pyrolytic lignin increased by 42% in solvent and water mixture at 40 °C. Additionally, the composition of the biomass derived oils also changed significantly when treated at temperatures higher than room temperature. For example, Meng et al. [26] observed the significant reduction in phenolic monomers (i.e., phenol, catechol, and guaiacol) during the treatment of pyrolysis oil at 80 °C for 24 h. Joseph et al. [27] and Li et al. [28] observed the reduction in aromatics, aldehydes, and ketones and increase in the concentration of esters. Interestingly, some of the aromatics and aldehydes are highly inhibitory to the AD microorganisms.

Another possible explanation for differing methane and VFA yields with AD operating temperature could be the differences in microbial community and degradation pathways of the compounds present in the condensate. Previously, Levén et al. [29] reported that AD operating temperature has a significant effect on phenol degradation in terms of the microbial community and the degradation pathway. In the same study [29], authors observed that mesophilic conditions favored the degradation of phenolic compounds compared with thermophilic. The main reason could be the temperature sensitivity of the phenol degrading enzymes [29].

#### 3.4.3. Influence of Substrate Loading

From the Figure 2 it can be observed that the methane yield reduced with increasing substrate loading. For example, the methane yield for TC-300 was reduced from 772 to 481 mL/g VS for mesophilic and from 697 to 542 mL/g VS for thermophilic when substrate loading increased from 2 to 4 g VS/L. The reason could be the loading of a higher amount of inhibitory compounds, while higher VFA production could also have inhibited the methanogens.

The VFA yield increased with increasing organic loading rate in all the cases. For example, for TC-275, BES inhibition, the total VFA yield was 4.79, 6.59, and 10.76 g/L at 2, 4 and 6 g VS/L loading, respectively, for thermophilic conditions. In the same operation conditions, the total VFA yield was 3.28, 5.95, and 9.71 g/L for 2, 4, and 6 g VS/L loading, respectively, for mesophilic conditions (refer to the Figures S3 and S4). The main reason for the increasing VFA with increasing substrate loading could be the availability of higher organic content and loading of higher amount of organic acids already present in TC. However, interestingly, the specific VFA yield (i.e., g/g of VS loaded) reduced with increasing substrate loading. There could be two possible reasons for this phenomenon. The increased concentration of inhibitory compounds with increased substrate loading could be one possible reason. As discussed in Section 3.4.1, the concentration of inhibitory compounds at a certain level could be beneficial to the AD process. At the same time, the microbial community can also adapt to these inhibitory compounds up to a certain concentration [30]. However, the further rise in the same compounds could inhibit the process. For example, Benjamin et al. [31] observed an increase in the methane yield from around 60 mL to 70 mL when the guaiacol concentration in the AD digesters increased from 560 mg/L to 1100 mg/L. However, a complete inhibition was observed when the concentration was further increased to 5600 mg/L. In another study, Jansson et al. [30] observed that methane yield was reduced by 66% when phenol concentration increased from 0.005 to 0.05 (*w/v* %) during the anaerobic digestion of paper waste.

The other reason could be that the increase of the VFA in the digester could have suppressed the hydrolysis and acidogenesis activities. Previously, Siegert and Banks [32] reported that the VFA concentration above 2 g/L showed inhibitory effects on the hydrolysis

during AD of cellulose. The authors also observed the complete inhibition of enzymatic activity at 16 g/L VFA. In the same study, the biogas yield was reduced by 50% when VFA concentration was above 8 g/L during AD of glucose. In this study, the total VFA concentration reached 9 and 11 g/L in the case of TC-275 at 6 g VS/L loading for mesophilic and thermophilic conditions (refer to the Figures S3 and S4). Thus, the combined effect of VFA over load and accumulation of inhibitory compounds could be the reasons for the lower specific methane and VFA yield with increasing substrate load.

### 3.5. Comparative Analysis

Table 2 shows comparative data of methane yields from different substrates. Compared with other substrates, torrefaction condensate showed higher methane yield compared with conventional substrates, like organic wastes. The methane potential of lipids, proteins, and carbohydrates is around 1000, 480, and 373 mL/g VS [33]. The methane yield from pulp sludge-derived torrefaction condensate was close to lipids at lower organic loading. In the literature, FOG (fat, oil, and grease), vegetable oil, and animal fat showed similar methane potential. Previously, Hao et al. [34] reported a methane yield of 685 mL/g VS during co-digestion of waste-activated sludge and FOG mixture. In another study, Ponsá et al. [35] observed a methane yield of 699 and 508 mL/g VS during co-digestion of vegetable oil and animal fat with an organic fraction of municipal solid waste, respectively. Doddapaneni et al. [4] observed a methane yield of 430 to 490 mL/g VS for pinewood-derived torrefaction condensate, which is lower than the methane potential of sludge-derived torrefaction condensate. This could be attributed to the lower amount of inhibitory compounds in the sludge-derived condensate. As presented in Section 3.3, because of the catalytic activity, the microbial inhibitory compounds, such as furfural, 5-HMF, and hydroxyacetaldehyde are lower in the case of pulp sludge-derived torrefaction condensate. Interestingly, the same authors [36] observed a methane yield of around 690 mL/g VS for the same pinewood-derived condensate when granular sludge was used as the inoculum. Thus, the combined effect of granular sludge and low inhibition of the pulp sludge condensate could be the reason for higher methane yield compared with the previous studies. Although the methane potential in terms of volatile solids loading is higher, the specific methane yield (mL/g TC) is lower in the case of pulp sludge condensate. The specific methane yield for pine-derived condensate was 83 mL/g TC [4]. For agricultural residues, it varied between 32 to 106 mL/g TC [5]. The same for pulp sludge condensate was between 35 to 70 mL/g TC.

Compared with other substrates, the specific VFA yield is 2 to 4 times higher for torrefaction condensate. For the majority of the substrates, the specific VFA yield is in the range of 0.5 to 1 g VFA/g VS [7]. The same for pulp sludge torrefaction condensate is in the range of 1.1 to 4.7 g VFA/g VS when methanogenesis was inhibited. Previously, Doddapaneni et al. [4] observed a total VFA yield of around 1.3 g/g VS at the end of 30 days of AD of pinewood-derived torrefaction condensate. A literature review of previous studies showed a higher VFA yield for pretreated substrates. For example, Kakar et al. [38] reported a VFA yield of 1.53 g/g VS added during the AD of hydrothermally treated source separate organics. In another study, Murali et al. [41] reported a total VFA yield of around 2.19 g/g VS during the anaerobic digestion of wet exploded corn stover while methanogenesis was inhibited using BES. There could be two possible reasons for high specific VFA yield in the case of torrefaction condensate. Torrefaction condensate already contains acids, especially acetic acid. The second reason could be higher specific conversion because of higher solubility. The substrates, like food waste and biomass, contain indigestible fibers and also inorganic compounds.



**Table 2.** Comparative data of methane and volatile fatty acid yields from different substrates and torrefaction condensate.

Methane Potential Comparison		
Substrate	Methane Yield (mL/g VS Added)	Reference
Fat, oil, and grease (FOG) deposits	845	[34]
Co-digestion of OFMSW and vegetable oil	699	[35]
Waste cooking oil + hydration medium,	922	[37]
Pine-derived torrefaction condensate	430–492	[4]
Agricultural waste derived torrefaction condensate	32–106 mL/g condensate	[5]
Pulp sludge-derived condensate	401–772	This study
Volatile fatty acids comparison		
Substrate	VFA yield (g/g VS added)	Reference
Hydrothermally treated thickened waste-activated sludge	1.53	[38]
Glucose (methanogenesis inhibition using H <sub>2</sub> O <sub>2</sub> )	1.23	[39]
Food waste (methanogenesis inhibition using 2-bromoethanesulfonate)	0.8	[40]
Pretreated corn stover (methanogenesis inhibition using 2-bromoethanesulfonate)	2.19	[41]
Pulp sludge torrefaction condensate (methanogenesis inhibition using 2-bromoethanesulfonate)	1.1–4.78	This study

#### 4. Summary

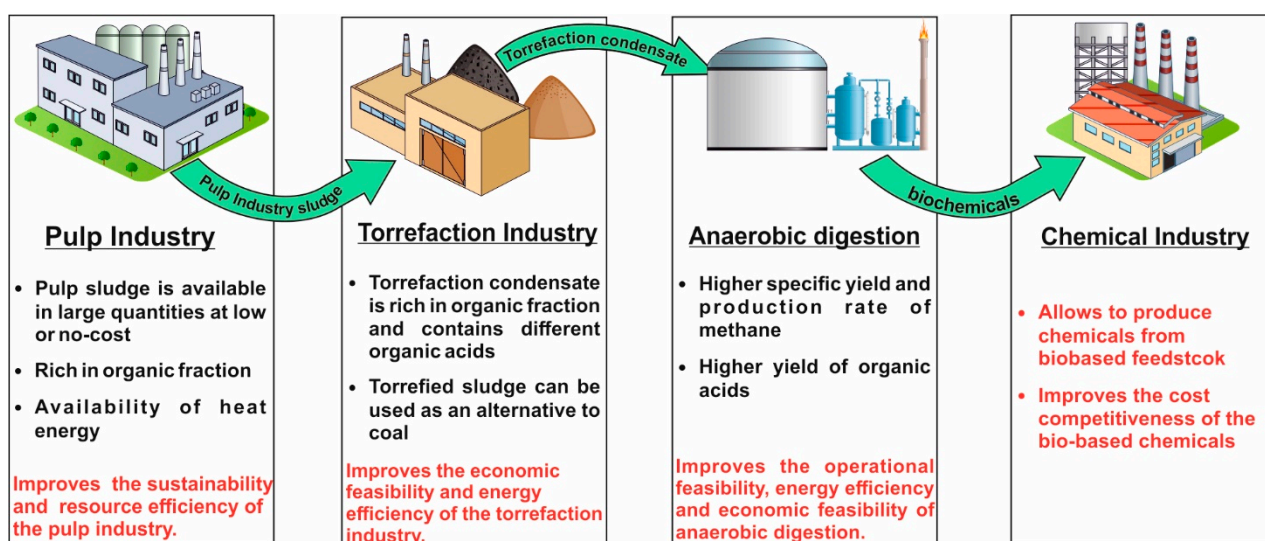
In this study, for the first time, an innovative integrated approach is proposed and experimentally validated for the resource recovery from the pulp industry sludge. Specifically, anaerobic digestion of pulp sludge-derived torrefaction condensate was studied to produce biomethane and volatile fatty acids. The initial finding is that the properties and composition of pulp sludge torrefaction condensate is significantly different compared with biomass-derived torrefaction condensate. For example, the higher yield of 2-furanmethanol and phenolic compounds (i.e., guaiacol and syringol) and lower yield of furfural, 5-HMF, and levoglucosan are noticeable differences. Possible explanations could be: (1) catalytic effect of alkali and alkaline earth metals present in the pulp sludge, and (2) some of the biomass fibers are in the disintegrated form because of the pulping process.

The experimental results showed that the sludge-derived torrefaction condensate has a higher specific methane yield compared with raw sludge and other substrates commonly used in the AD process. The biomethane potential (BMP) of the torrefaction condensate is comparable to the lipids and fats, i.e., FOG and vegetable oils. At the same time, the specific VFA yield (g VFA/g VS added) is also significantly higher compared with conventional substrates when methanogenesis is inhibited. To highlight this, torrefaction condensate already contained a significantly higher amount of organic acids, i.e., around 20–40% of total VFA yield, depending on the operating conditions. In the authors' opinion, the main advantages of using torrefaction condensate over the direct use of pulp sludge are: (1) higher solubility of organic fraction, (2) availability of organic compounds, for example organic acids to metabolize. Generally, hydrolysis is the rate-limiting step in AD, especially for lignocellulosic biomass. The mass transfer limitation is another key issue. However, in the case of torrefaction condensate, the significance of these issues is limited. On the other hand, complex and costly pretreatments are required to improve the solubility and, thereby, the hydrolysis efficiency of biomass and organic wastes during AD. When lignocellulosic biomass is considered as substrate in AD, loading of indigestible fiber, such as lignin but also ash (inorganics) to the digesters is inevitable, which creates operational issues, such

as digestate handling, increased digester volume in terms of specific methane yield, and higher energy input. These issues can be avoided/reduced when biomass or other organic matter-derived liquid fractions are loaded into the AD reactors instead of direct use of the same feedstock.

Although pulp sludge-derived torrefaction condensate showed higher BMP and VFA yield, the authors also anticipate some operational challenges. Torrefaction condensate is heterogeneous in nature and contains a variety of compounds. The effect of these compounds on microbial metabolism has not yet been fully established. The microbial inhibition at higher substrate loading is the main challenge. Some of the compounds present in torrefaction condensate, i.e., furfural, 5-HMF, guaiacol, phenol, and hydroxyacetaldehyde, or even acetic acid at high concentrations, are highly inhibitory to the microorganisms present in AD, especially to methanogens. The conversion efficiency, in terms of energy (energy content of methane produced/energy content of torrefaction condensate), is around 46%. This shows that a large portion of the condensate has not been converted into methane. However, this issue can be handled by acclimatization of AD microorganisms, removal of inhibitory compounds, and optimizing the substrate loading. It is also worth noting that the composition of torrefaction condensate changes during storage because of the aging reactions. In addition to the microbial inhibition, the operational issues with tar can also be a considerable issue. Furthermore, the properties of the pulp sludge vary significantly depending on the pulping process, and subsequently, the composition of the condensate varies as well. Although the VFA yield is increased significantly, the downstream processing is still a challenge to achieve economic feasibility. However, considering the additional income from torrefied pellets, the VFA selling price can be significantly reduced. A detailed economic analysis is the subject of our future study.

In the authors' opinion, the proposed process allows industrial symbiosis between the pulp industry, torrefaction, energy sector, and chemical industry, and brings multiple benefits (Figure 5) compared with other processes commonly employed to handle the pulp industry sludge. Considering the multi-product scenario, the authors believe that the proposed approach improves the economic feasibility of the torrefaction process and biochemical production. At the same time, it can improve the sustainability of the pulp industry. However, the overall feasibility of the process needs to be evaluated through techno-economic and environmental feasibility analysis, which is the subject of our future study.



**Figure 5.** The industrial symbiosis between different biomass and/or organic residues valorization industries under the concept of anaerobic digestion of pulp sludge derived torrefaction condensate.

## 5. Conclusions

For the first time, this study reported the volatile fatty acids (VFA) production potential of pulp sludge-derived torrefaction condensate through anaerobic digestion. The VFA yield was in the range of 1.1 to 3.4 g/g VS for mesophilic to 1.5 to 4.7 g/g VS in thermophilic, respectively, when methanogenesis was inhibited. The biomethane potential of the pulp sludge-derived condensate is comparable to fats and lipids with a yield of 401–772 mL/g VS. The methane production was higher and more stable in the case of mesophilic conditions, whereas thermophilic conditions favored the VFA production. Compared with biomass-derived condensate, pulp sludge-derived torrefaction condensate showed lower inhibition of AD process. Finally, this study proposed an integrated approach to sharing the resources between different biomass processing industries under the concept of industrial symbiosis.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/fermentation8090453/s1>, Figure S1. Product yield during batch torrefaction of pulp industry sludge; Figure S2. The total volatile fatty acid yield by the end of the anaerobic digestion experiments (30 days) for torrefaction condensate produced at 275 and 300 °C. (a) Mesophilic, (b) thermophilic; Figure S3. Volatile fatty acids production (g/L) for mesophilic process at various substrate loading for torrefaction condensate produced at (a) 275 °C and (b) 300 °C; Figure S4. Volatile fatty acids production (g/L) for thermophilic process at various substrate loading for torrefaction condensate produced at (a) 275 °C and (b) 300 °C; Table S1. The methane potential of torrefaction condensate produced at 275 °C and 300 °C and raw pulp sludge for mesophilic and thermophilic conditions at different substrate loading.

**Author Contributions:** Conceptualization: T.R.K.C.D. and T.K.; methodology: T.R.K.C.D., M.N.C. and K.O.; investigation: T.R.K.C.D. and M.N.C.; supervision: T.K.; visualization: T.R.K.C.D.; writing—original draft: T.R.K.C.D.; writing—review and editing: M.N.C., K.O. and T.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No [843723].

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** <https://doi.org/10.5281/zenodo.7024695> (accessed on 3 August 2022).

**Acknowledgments:** This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No [843723]. The authors would like to thank Kersti Luzkov from AS Estonian Cell, Estonia, for providing pulp sludge.

**Conflicts of Interest:** The authors declare no conflict of interest.

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