1 **Municipal waste liquor treatment via bioelectrochemical and fermentation (H$_2$ +**

2 **CH$_4$) processes: Assessment of various technological sequences**

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Abstract

In this paper, the anaerobic treatment of a high organic-strength wastewater-type feedstoc®k, referred as the liquid fraction of pressed municipal solid waste (LPW) was studied for energy recovery and organic matter removal. The processes investigated were (i) dark fermentation to produce biohydrogen, (ii) anaerobic digestion for biogas formation and (iii) microbial fuel cells for electrical energy generation. To find a feasible alternative for LPW treatment (meeting the two-fold aims given above), various one- as well as multi-stage processes were tested. The applications were evaluated based on their (i) COD removal efficiencies and (ii) specific energy gain. As a result, considering the former aspect, the single-stage processes could be ranked as: microbial fuel cell (92.4 %)> anaerobic digestion (50.2 %)> hydrogen fermentation (8.8 %). From the latter standpoint, an order of hydrogen fermentation (2277 J g^{-1} $COD_{removed}$ d^{-1})> anaerobic digestion (205 J g^{-1} $COD_{removed}$ d^{-1})> microbial fuel cell (0.43 J g^{-1} $COD_{removed}$ d^{-1}) was attained. The assessment showed that combined, multi-step treatment was necessary to simultaneously achieve efficient organic matter removal and energy recovery from LPW. Therefore, a three-stage system (hydrogen fermentation-biomethanation-bioelectrochemical cell in sequence) was suggested. The different approaches were characterized via the estimation of COD balance, as well.

Keywords: OFMSW, wastewater, biohydrogen, biogas, microbial fuel cell, multi-stage process

1. Introduction

The management of municipal solid waste (MSW) is a crucial issue from an environmental point of view (Eriksson et al., 2005) and has therefore been widely addressed in the literature. As a result, it turned out that this type of problematic material fits well to the waste-to-energy concept (Cheng et al., 2007) and can thus be considered as a potential renewable energy feedstock (Cheng and Hu, 2010). Hence, technologies that not only help to meet environmental protection goals but at the same time, support energy gain from this particular waste stream have been in the focus point worldwide. In accordance, researchers demonstrated the feasibility of MSW (having high organic matter content) for certain bioprocesses, including anaerobic digestion to generate methane (Hilkiah Igoni et al., 2008; Khalid et al., 2011) and dark fermentation to produce biohydrogen (Alzate-Gaviria at al., 2007; Fountoulakis and Manios, 2009; Kobayashi et al., 2012).

Besides the possibility of energy recuperation from solid organic matter relying on the techniques mentioned, the utilization of liquid fractions derived from MSW via alternative methods i.e. bioelectrochemical systems (BES) has been a hot topic too. BESs rely on electrochemically-active bacteria (Zhen et al., 2016ab), which are reportedly able to deal with wastewater-like feedstock (Pant et al., 2012) and accordingly, MSW derivatives such as leachate (generated at landfill sites in remarkable quantities) was found as a good candidate for BES feeding and subsequent energy recovery (Iskander et al., 2016).

In addition to leachate, another type of waste liquor (obtained from MSW by mechanical pressing and referred as the "liquid fraction of pressed municipal solid waste", abbreviated as LPW) appeared to be treatable in BES, in particular microbial fuel cells (MFC) (Koók et al., 2016) and microbial electrohydrogenesis cells (MEC) (Zhen et al., 2016c). Moreover, the organic-matter rich LPW was proven to be convertible to gaseous energy carriers (hydrogen and methane) via fermentation, as well (Rózsenberszki et al., 2015).

Although LPW was found applicable in bioelectrochemical and fermentation processes to generate energy (Koók et al., 2016; Rózsenberszki et al., 2015), this landfill-originated fraction can be a challenging starting material for single-stage processes due to its somewhat recalcitrant nature (Zhen et al., 2016c). Therefore, it can be expected that multi-step (two- or three-stage) processes in sequence could lead to performance enhancement and better organic matter degradation. Supportive conclusions on this concept were lately drawn by Mahmoud et al. (2014), who showed that anaerobic pre-fermentation of leachate could improve the stability of subsequent BES operation. Thus, in the frame of a multi-step processes, a pretreatment step can be a proposed to facilitate consecutive energy recovery. Another reason to pay attention to multi-step technologies is that they could make the valorization of effluent coming from a single process possible, which (due to the many times occurring incomplete degradation of poorly biodegradable compounds) may still contain significant amount of organic matter to be removed. In accordance with the study by Wang et al. (2011), integrated systems (coupling BES after dark fermentation step) can have a potential to increase the utilization of substrates inherently resisting the microbiological

95 conversion. Other studies i.e. by Luongo Malave' et al. (2015) also verified the benefit

96 of multi-step anaerobic processes to augment the energy production from simple as

97 well as complex raw materials.

98   Overall, driven by the considerations and recent findings mentioned above, the

99 aim of the current investigation was to assess the utilization of LPW substrate in multi-

100 stage approach, involving MFC, dark fermentation and biogas formation (i) first alone

101 and thereafter (ii) in various, multi(two and three)-step design to find the arrangement

102 that leads to better process performance, both in terms of energy recovery and organic

103 matter degradation. To our knowledge, this concept has not been evaluated in the

104 literature applying the LPW and thus, the experimental results presented in this work

105 can contribute to the new body of knowledge in the field.

106

107 **2. Materials and methods**

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109 **2.1. Inoculum and substrate**

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111   Mesophilic anaerobic sludge (MAS) from a biogas plant (Pálhalma, Hungary)

112 was used as a basic source of inoculum in all the single-stage processes (microbial fuel

113 cell, anaerobic digestion and biohydrogen fermentation) involved in this work, which

114 was already proven as a good source of fermentative, methanogenic and eletroactive

115 strains (Koók et al., 2016; Rózsenberszki et al., 2015). The main initial parameters of

116 MAS were 17 g L^{-1} COD and pH = 7.5. As mentioned above, a particular wastewater

117 fraction, called LPW was taken from a domestic municipal landfill (Királyszentistván,

Hungary) and used thoroughly in this investigation as the starting material to feed the first-stage of the tested technological approaches. The methods to obtain the LPW were already described in our earlier papers (Koók et al., 2016; Rózsenberszki et al., 2015) and its main characteristics are summarized in **Fig. 1**.

2.2. Process descriptions

The evaluation of each single- and multi-stage processes was carried out using the results of triplicates (in all cases the arithmetical mean values are demonstrated with standard deviations lower than 5%).

2.2.1. Single-stage biogas and hydrogen fermentations (S-BGF, S-HF)

Biogas and hydrogen fermentations were peformed in WTW OXITOP 100 manometric vessels with 500 mL total capacity (Rózsenberszki et al., 2015). Technically, this method is similar to that referred as the Owen method (Logan et al., 2002) since both are based on the intermittent release of pressure created by the gas being formed.

Regarding the test conditions: in the single-step biogas (S-BGF) experiments, MAS (as such, without pretreatment) and LPW were mixed in 1:1 ratio to get 50 mL working volume, resulting in 450 mL headspace. Suitable anaerobic circumstances were established by purging the reactor volume with high-purity (>99.99 vol.%) N_2.

37 °C temperature and 220 rpm strirring speed were ensured until the gas evolution has stopped (Rózsenberszki et al., 2015).

The single-stage hydrogen fermentations (S-HF) were conducted in a similar way to biogas experiments, except two things: Firstly, thermal pretreatment (75 °C, 45 min) was applied to MAS to suppress CH_4-forming activity and at the same time, promote H_2-fermenting microorganisms (Bakonyi et al., 2014). Secondly, initial pH was adjusted to 5 using 10 (m/m)% H_2SO_4 solution to facilitate H_2-formation (Rózsenberszki et al., 2015). Volumetric gas evolution (mL) in both cases (S-BGF, S-HF) was derived from the pressure data acquired by manometric caps attached to the OXITOP 100 devices – as detailed earlier (Rózsenberszki et al., 2015) – and converted to STP conditions. Control experiments were also conducted to check the indigenous gas formation potential of heat-pretreated as well as untreated, raw MAS alone and was found negligible compared to those observed from fresh LPW.

2.2.2. Single-stage microbial fuel cells (S-MFC)

Small bench-scale, two-chambered microbial fuel cells (MFC) were fabricated from plexiglass material. The anode and cathode cells were designed with equal, 60 mL total volumes. To separate the chambers, Nafion® N 115 proton-selective membrane (purchased from Sigma-Aldrich) with 7 cm^2 effective area was used after an activation procedure (Kim et al., 2007). In the anode half-cell, carbon cloth having 25 cm^2 apparent surface area was employed to be colonized by the exo-electrogenic strains contained in raw MAS. To connect the carbon cloth anode to the external

163 circuit (made of copper wiring and including a 100 Ω external resistor), graphite rod

164 with 1.5 mm diameter was applied. In the cathode side of the MFC, 25 cm^2 carbon

165 cloth (connected to the external circuit similar to the anode) was used as cathode,

166 immersed in 60 mL continuously aerated catholyte. The scheme of the MFC can be

167 found in our previous publication (Koók et al., 2016). The MFCs in this work were

168 inoculated with 55 cm^3 MAS (as such, without pretreatment) and started-up with Na-

169 acetate (10 g/L stock solution) to select the electrochemically-active biofilm and help

170 its initial stabilization (Liu et al., 2005) (no any other external nutrients were added),

171 making the working volume up to 60 cm^3. More information on start-up methods and

172 related operation can be read in our recent communications (Koók et al., 2016;

173 Rózsenberszki et al., 2015). The anodic biofilm formation process was considered

174 done once reproducible batch cycles (Carmona-Martínez et al., 2015) (here in terms of

175 the voltage time profile) could be observed. The detectable potential difference

176 between the anode and cathode was monitored on-line and saved by a DAQ (National

177 Instruments USB-6008) and LabView installed on PC. The MFCs were operated at 37

178 °C. The anode and cathode chambers were not mechanically stirred. The initial pH in

179 the anode chamber was set to 7, which is within the interval (6-9) that was found

180 sufficient for electrochemically-active bacteria to carry out the transfer of electrons to

181 the anode (Patil et al., 2011).

182   Once the biofilm development on the anode surface was finished, the single-

183 stage MFC (S-MFC) was fed with LPW rather than Na-acetate. Noteworthy, LPW in

184 all S-MFCs was injected after drawing the equivalent amount of spent media

185 remaining in the MFC from the previous cycle. At first, when the MFC start-up was

completed, only a small dose of LPW (3 mL) was added to the anode chamber to test the reaction of the anodic biofilm to this substrate. Afterwards, in the consecutive cycle, the volume of fresh LPW substrate was increased to 25 mL.

2.2.3. Two-stage process I – Coupling anaerobic digestion to hydrogen fermentation (HF-BGF)

The fermentation effluent of S-HF was investigated further on as the input material for sequential biogas production. In essence, 25 mL residue from S-HF was mixed with 25 mL sludge coming from S-BGF. Afterwards, the experiments were conducted under the conditions as specified for S-BGF (Section 2.2.1.), except certainly that no fresh LPW was supplemented into the OXITOP bottles.

2.2.4. Two-stage process II – Coupling microbial fuel cell to hydrogen fermentation (HF-MFC)

The fermentation effluent of S-HF was subjected to microbial fuel cell for its further utilization. In particular, 25 mL from the anode chamber of stabilized MFC was removed and subsequently replaced by 25 mL residue from S-HF. Thereafter, the measurements were conducted under the conditions as specified for S-MFC (Section 2.2.2.), except certainly that no fresh LPW was fed into the system again.

2.2.5. Three-stage process – hydrogen fermentation, anaerobic digestion and microbial fuel cell attached in sequence (HF-BGF-MFC)

Once the two-stage HF-BGF experiments were finished, the fermentation residue of HF-BGF process was transferred to microbial fuel cell. As a matter of fact, 25 mL from the anode chamber of stabilized MFC was drawn and replaced by 25 mL residue from HF-BGF. Further on, the tests were carried out under the conditions detailed for S-MFC (Section 2.2.2.), except certainly that no fresh LPW was introduced to the MFC again.

2.3. Analytical methods

To determine the composition of headspace gases obtained in the S-HF, S-BGF and HF-BGF (in terms of H_2, CH_4 and CO_2), samples were taken (when the particular process was terminated) and analyzed by gas chromatography as described elsewhere (Rózsenberszki et al., 2015). To follow the biodegradation of LPW in the S-HF, S-BGF and S-MFC, samples from the liquid phase at the end of the experiments and their chemical oxygen demand (COD) was measured by the standard methods (APHA, 1995). In the multi-stage processes (Section 2.2.3.-2.2.5.), the COD of the effluent after each step was determined, as well. The initial COD values of the MAS and fresh LPW were considered according to Section 2.1 (**Fig. 1**), respectively.

2.4. Calculations

To complete COD balance calculations (**Table 1**), the following COD equivalents for gaseous products, in particular H_2 and CH_4 gases were employed: 8 g COD/g H_2 and 4 g COD/g CH_4. To determine the COD of biocurrent generation, the calculation took into account the next steps:

First, the Coulombic efficiency (C_e) was calculated, in accordance with Eq. 1 (Oh and Logan, 2005):

$$C_e = \frac{Cex}{Cth} x\ 100 \qquad (1)$$

where C_{ex} is the amount of coulombs actually recovered in the course of the MFC operation time (t) (measured in the form of biocurrent), according to Eq. 2:

$$C_{ex} = \int_0^t I\ dt \qquad (2)$$

I is the (bio)current, computed from Ohm's law using the voltage measured between the anode and cathode through the external resistance (Logan et al., 2006). t is the MFC operating time (during which the current was measured).

252 C_{th} is the theoretical coulombs that can be derived from the total amount of COD

253 removed (Eq. 3).

254

255 $$C_{th} = \frac{F\, b\, \Delta COD\, V}{M}$$ (3)

256

257 where ΔCOD is the difference of initial and final/residual liquid phase COD

258 concentrations in the anode chamber (g/L). F is the Faraday's constant, b is 4 (the

259 number of electrons exchanged per mole of O_2), V is the anode working volume (L).

260 M is the molar mass of O_2 (32 g/mole) (Logan et al., 2006; Pasupuleti et al., 2016).

261   Afterwards, the portion of COD (ΔCOD_C, in the unit of g) accounted for C_{ex} is

262 expressed by Eq. 4:

263

264 $$\Delta COD_C = \frac{Ce\, \Delta COD\, V}{100}$$ (4)

265

266 The specific energy yield (E^*) of a given process was calculated according to Eq. 5:

267

268 E^* (J g^{-1} $COD_{removed}$ d^{-1}) = E_t [($COD_{initial}$ − COD_{final}) V_L]$^{-1}$ t^{-1} (5)

269

270 where E_t is the energy cumulated in the course of reactor operation (t) either in the

271 form of gaseous energy carriers (H_2 or CH_4) or bioelectricity (see Section 3.).

272 $COD_{initial}$ and COD_{final} are the initial and final/residual liquid phase COD

273 concentrations in the liquid phase (working volume), respectively, while V_L is the

274 working volume in the particular bioreactor.

3. Results and discussion

3.1. Assessment of single-stage processes for LPW treatment

3.1.1. Single-stage hydrogen and biogas fermentations (S-HF, S-BGF)

A typical progress curve for S-HF process is illustrated in **Fig. 2**, which has a shape quite similar to that obtained by Logan et al. (2002). After 12 hours of lag time, intense gas formation could be observed, leading to the end of fermentation within 2 days. It is to note that methane could not be detected in the headspace, which verifies the suppression of methanogens by the applied sludge pretreatment (Bakonyi et al., 2014). As a result, it turned out that a total volume of 194 (STP) cm^3 gas (mixture of hydrogen and carbon dioxide) could be obtained. This, together with the gas composition analysis (47.1 vol.% H_2) reveals that 91 (STP) cm^3 hydrogen was formed.

As for the S-BGF, the time profile of the biogas production can be seen in **Fig. 3**. In fact, the biogas formation began shortly after the inoculation of LPW with MAS. In the course of the S-BGF process, 527 cm^3 (STP) biogas was produced with 56.7 vol.% methane content, meaning a gain of 299 cm^3 (STP) CH_4. Taking into account the gravimetric energy densities of hydrogen and methane gases (142 kJ/g and 55.5 kJ/g, respectively), the theoretically recoverable amount of energy in the S-HF and S-BGF from the organic matter contained in 25 mL LPW was 1.14 kJ and 11.7 kJ, respectively.

297	In the light of the current results about the S-HF and S-BGF it can be inferred

298	that LPW was suitable for the generation of bioenergy carriers, in particular H_2 and

299	CH_4 via fermentation, which is in agreement with our previous findings

300	(Rózsenberszki et al., 2015). However, in the case of S-HF, the short gas evolution

301	phase was accompanied by only a limited organic matter removal (8.8 %) measured as

302	COD (**Table 2**), which assumes the quick depletion of components the

303	microorganisms could metabolize into H_2 and CO_2. As for the S-BGF, representing a

304	technology with markedly longer time-demand, COD elimination efficiencies as high

305	as 50.2 % were realized (**Table 2**). Consequently, it seems that the LPW is composed

306	of an (i) easily i.e. the marginal reducing sugar content (**Fig. 1**) and a (ii) hardly

307	biodegradable fraction of organic substances (Zhen et al., 2016c). It is a reasonable

308	assumption (based on the brief fermentation time and relatively poor COD removal)

309	that the S-HF was able to deal only with the former, simply convertible part. On the

310	other hand, the S-BGF had better capability to process the refractory COD content,

311	presumably attributed to the more sufficient adaption of hydrolytic bacteria contained

312	in the MAS as inoculum. This step, the hydrolysis is a crucial to achieve the efficient

313	solubilization and biotransformation during anaerobic digestion, especially when

314	complex organic matters are supplied (Zheng et al., 2014), such as in the case of LPW.

315	Besides, in both the S-HF and S-BGF, the rapid initial gas generation may have

316	occurred (at least in part) because of the naturally-occurring microbes hosted by the

317	LPW, contributing to the biodegradation via so-called self-fermentation (Marone et al.,

318	2012). Though the BOD_5/COD ratio as high as 0.6-0.7 predicts good biodegradability

319	(Buitrón et al., 2014), it would appear that LPW decomposition (despite a BOD_5/COD

320 = 0.73, **Fig. 1**) apparently faces more challenges under anaerobic fermentation

321 conditions, especially during the short S-HF.

322

323 **3.1.2. Single-stage microbial fuel cells (S-MFC)**

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325 As mentioned in Section 2.2.2., two methods were used to test the conversion of

326 LPW in microbial fuel cells. Firstly, the injection of 3 mL LPW resulted in an almost

327 immediate response, detected in the form of a gradually growing electric potential

328 between the anode and cathode (**Fig. 4a**). Similar progress curves were reported by

329 Rabaey et al. (2003), presenting the response of MFC to substrate injections. **Fig. 4a**

330 was an important feedback to confirm the degradability of LPW by the exo-

331 electrogenic strains located on the anode surface. Afterwards, in the subsequent cycle,

332 the MFC was loaded with 25 mL LPW (same amount as used in the S-HF and S-BGF)

333 to perform the S-MFC experiments. The results are plotted in **Fig. 4b**. The maximum

334 potential values reached the vicinity of 50 mV (measured through 100 Ω external

335 resistor) approximately for 6-7 days (between Day 10 and 16), before noting a

336 gradually declining tendency (**Fig. 4b**). It is clear from the comparison of **Fig. 4a** and

337 **Fig. 4b** that the higher LPW dosage induced the extension of process (biodegradation)

338 time. From the data collected during the 30 days operation (**Fig. 4b**) of S-MFC, it was

339 computed – in accordance with papers by Koók et al. (2016) and Rabaey et al. (2003)

340 – that 31 J cumulated energy (as electricity) could be extracted from 25 mL LPW. On

341 one hand, this value is significantly lower in comparison with those attained with the

342 S-HF and S-BGF. Nonetheless, on the other hand, the COD in the residue at the end of

the S-MFC measurements was decreased dramatically, meaning that only 7.5 % of the initial COD was left behind (**Table 2**).

The maximal current density of the S-MFC – taken into account the (i) maximum voltage measured under stationary conditions (Day 10-16, **Fig. 4b**), (ii) external resistor and (iii) anode surface data, according to Koók et al. (2016) – was calculated as 216 mA m^{-2}. This is close to the value (253 mA m^{-2}) reported by Cercado-Quezada et al. (2010) for microbial fuel cells inoculated with garden compost leachate (somewhat similar to LPW) for the valorization of food industry waste. Current densities in the same order of magnitude (114 mA m^{-2}) were achieved by Ganesh and Jambeck (2013) in microbial fuel cells designed for the treatment of landfill leachate, a problematic substrate with more or less similar origin than LPW.

Although salient COD removal performance was experienced with the S-MFC, the small amount of electrical energy obtained and the low, ~3 % Coulombic efficiency – helping to reveal what portion of the substrate consumed is transformed into electricity (Logan et al. 2006; Ren et al., 2014) – together indicate that the major part of COD was converted via side-reactions that did not result in registered bio-current generation.

Among the reasons behind, it is supposed that COD was partly consumed via alternative metabolism of bacteria – living either (i) in the anode-surface biofilm or (ii) in the bulk phase (planktonic strains), etc. – as a response to the appearance of O_2 in the anode chamber. This may have occurred, at least in part, due to the diffusion of O_2 through the Nafion® membrane placed in between the anaerobic anode and aerated cathode compartments. This polymeric, proton exchange-type membrane (PEM) plays

a key-role in two-chamber MFCs to sustain its function, however, it is not indeed impermeable to the gases present at either side of the bioelectrochemical system (Chae et al., 2008a). As a matter of fact, noticeable transport of O_2 across the Nafion[®] membrane can occur in MFCs, as found by Chae et al. (2008b). This phenomena will potentially make the metabolic pathways of the (electroactive) strains shift – attributed to the absence of fully anaerobic conditions – and aerobic respiration of heterotrophs can take over, simultaneously causing the loss of precious substrate and the depression of Coulombic efficiency (Logan, 2012). For example, Liu and Logan (2004) reported Coulombic efficiency values below 10 %, ascribed to substantial penetration of oxygen to the MFC anode chamber. Under some circumstances in two-chambered MFCs (separated by PEM) fed with glucose, Rabaey et al. (2003) experienced Coulombic efficiencies in the range of 8-12 % (same order of magnitude with those reported in this current research, **Table 3**). Furthermore, Hernández-Fernández et al. (2015) obtained 4.4 % Coulombic efficiency in a two-chamber microbial fuel cell with Nafion[®] membrane utilizing waste water feedstock, which represents a comparable level of system performance as demonstrated in this work with the S-MFC process.

Besides O_2 leakage, obstacles related to biofouling of the membrane due to the growth of bacteria on its anode side-faced surface should be taken into account (Sun et al., 2016). According to Chae et al. (2008b), biofilm layer can develop over time on Nafion[®], which was identified as a factor affecting MFC performance (Xu et al., 2012) and to certain extent, it can be made responsible for deteriorated Coulombic efficiencies (Choi et al., 2011).

388   Another probable explanation for COD consumption without decent Coulombic

389   efficiency and electrical energy recovery may be associated with the formation of

390   gases e.g. methane and hydrogen. Since the MFCs were inoculated with untreated

391   mesophilic anaerobic sludge in this work, fermentative microorganisms and H_2-

392   scavenging, methanogenic archaea (in addition to exo-electrogens) were inherently

393   added to anode chamber. In such cases, when a mixed microbial community is applied

394   as seed source, the gaseous compounds mentioned may be generated in certain

395   amounts (Kim et al., 2005), however, in this particular work, it was not quantified.

396   Overall, though several assumptions concerning the behavior of the S-MFC

397   were given above, further research and technical improvements will have to be made

398   to tackle the issues raised, leading to better competitiveness from an energy yield

399   standpoint.

400

401 **3.1.3. Comparison of single-stage processes for LPW treatment and**

402 **considerations to design the multi-stage processes**

403

404   To comparatively assess the single-stage, either bioelectrochemical or

405   fermentative technologies for LPW management, two indicators, in particular the (i)

406   COD removal efficiency and the (ii) specific energy yield were used.

407   From an energetic point of view, taking into account the specific energy yields

408   (expressing the amount of energy recovered from the COD removed on daily average

409   basis) the following ranking could be established (**Table 2**): S-HF > S-BGF > S-MFC.

From the aspect of COD removal, the following, contrary order was found (**Table 2**):

S-MFC > S-BGF > S-HF.

The outcomes indicate that the best energy recovery from LPW could be done via hydrogen fermentation, however, this application does not seem to be able to reduce the organic matter content. In other words, S-HF alone suffers from the bottleneck of insufficient COD conversion efficacy. Thus, if the effluent coming from the S-HF was discharged without further treatment, it would cause environmental concerns and on the top of that, the major part of chemical energy bound in the LPW would remain unexploited.

Overall, based on the considerations so far made, it could be recommended that the S-HF, as first-step is integrated to a multi-stage process. It was already demonstrated by researchers that the residue of hydrogen fermentation can be subjected to anaerobic digestion to get extra methane and in that way, enhance the energy productivity (Buitrón et al., 2014; Intanoo et al., 2016; Nualsri et al., 2016). Besides that, it was reported that the effluent of dark fermentation step can be a viable starting material in bioelectrochemical cells, as an alternative solution to valorize the unutilized organic matter (Kumar et al., 2016; Marone et al., 2016; Rivera et al., 2015). For instance, Oh and Logan (2005) studied the concept of an attached, hydrogen fermentation–microbial fuel cell system in order that the high amount of organic matter remaining in the effluent of the former application is subsequently utilized for bioelectricity generation in the latter one.

Therefore, two-stage processes including a (i) HF-BGF as well as a (ii) HF-MFC were tested to evaluate the fate of COD in the S-HF effluent and at the same

19

time, to see how much energy could be further gained. The results will be presented in the next sections.

3.2. Assessment of multi-stage processes to treat the effluent of applications fed with raw LPW substrate

To utilize the effluent containing the recalcitrant COD fraction – which was undegradable by microbes present in the S-HF – it was fed to complementary (i) anaerobic digestion and (ii) microbial fuel cell under conditions described in Section 2.2.3 and 2.2.4, respectively.

In the HF-BGF, as it can be seen in **Table 4**, the BGF as a second-step was able to work with a COD removal efficiency of 55.7 %, cutting the initial 34.5 g COD/L to 15.3 g COD/L at the end of the test. In the course of the fermentation, as a result of organic matter decomposition, 157 mL (STP) CH_4 was generated, which has a total energy content of 6130 J. The COD removal efficiency was comparable with the S-BGF process, as reflected by the 55.7 % and 50.2 % values, respectively. Nevertheless, the specific energy yield achieved was enhanced by 20 %, according to the 246 J g^{-1} $COD_{removed}$ d^{-1} instead of 205 J g^{-1} $COD_{removed}$ d^{-1} (as listed in **Table 2** for S-BGF). In fact, it can be stated that biogas could be generated from the effluent of S-HF process treating fresh LPW along with additional COD elimination. Successful attempts with two-stage systems (attaching anaerobic digestion after dark fermentative hydrogen production) were communicated in recent research articles, as well (Intanoo

et al., 2016; Nualsri et al., 2016). For instance, Buitrón et al. (2014) obtained COD removal efficiencies in the range of 56-67 % (depending on organic matter loadings) during the methanation of effluent coming from preliminary H_2 fermentation, which matches well with our relevant result (55.7 %).

By evaluating the results obtained during the HF-MFC process, it can be pointed out that the COD removal from the residue of S-HF could exceed 90 % efficiency (**Table 4**), similar to that observed for the S-MFC from raw LPW. However, the specific energy yield, compared to other applications investigated herewith, still remained rather poor, and the loss of performance was probably caused by the reasons considered and detailed in Section 3.1.2. for the S-MFC. The Coulombic efficiency characteristic is given in **Table 3**.

Thus, as proven for the second time in the course of this study, the MFC could be used efficiently to decrease the organic matter content, which is desired from an environmental protection point of view. However, it was unable to noticeably participate in the total energy production, which was more the responsibility of the fermentation processes, generating energy carriers (H_2 + CH_4) in decent quantities. These gaseous biofuels formed can be potentially utilized for sustainable energy production, in case an appropriate purification (downstream) technique is employed. To accomplish this goal, membrane separation can be considered as a solution, attributed to their attractiveness for the concentration of such energy carriers (Bakonyi et al., 2013; Basu et al., 2010; Ryckebosch et al., 2011).

Though the coupled, HF-BGF was found favorable to harvest energy in the form of hydrogen and methane, organic matter removal after auxiliary biogas

formation was still incomplete, reflected by the 15.3 g/L COD concentration in the residue, as mentioned above. Thus, in the last part of the measurements, its removal was attempted. For this purpose, MFC was chosen, creating a HF-BGF-MFC three-stage, sequential approach. Certainly, in this MFC stage, further energy gain was not really expected based on the experiences described. Nevertheless, keeping its already demonstrated capability to remove COD in mind (over 90% in all cases tested so far), it was considered that it was able to serve as a final, polishing step. This set of experiments (carried out in accordance with Section 2.2.5.) fairly confirmed our previous expectation since as it can be seen in **Table 4**, initial COD content was drastically reduced, thank to the 89 % removal efficiency (without realizing notable, additional energy recovery). As a result, the effluent remained at the end of the operation had more or less negligible, 0.9 g/L COD concentration. For related Coulombic efficiency, **Table 3** should be consulted.

Consequently, in agreement with the evaluation made so far, the proposed route for LPW management should consist of three, consecutive steps, involving, hydrogen fermentation, followed by methanogenesis and microbial fuel cell, as depicted in **Fig. 5**.

3.3. Estimation of organic matter (COD) balance

Analyzing the fate of COD is a useful approach to track how the organic matter added to a particular process was converted (Zhen et al., 2016c). To estimate the COD balance, as to be observed in **Table 1**, (i) initial and (ii) final COD contents in the

501   liquid phase of the respective system and furthermore, (iii) product CODs (either H_2,

502   CH_4 or biocurrent) were considered. COD recovery was established according to Eq.

503   6.

504

505   COD recovery (%) = $100[(COD_{residual} + COD_{product})\ COD^{-1}_{initial}]$ (6)

506

507   It is evident from **Table 1** that there was a remarkable variation of COD

508   recoveries, dependent on the particular treatment process. The best COD recovery was

509   attained for the hydrogen fermentation, with only a 6-7 % deviation of the organic

510   matter balance. As for methane production, accomplished either in the first- or second-

511   stage, COD recoveries in the range of 70-80 % could be estimated, which is still

512   acceptable. Similar COD recovery values were reported by Yu and Fang (2003) for an

513   anaerobic reactor fed with wastewater-type feedstock.

514   In the case of MFC process, regardless of the conditions, the low COD

515   recoveries (10-20 %, **Table 1**) present an unclear fate for the major part of COD

516   converted (removed). This problem is reflected by the low Coulombic efficiencies

517   (specified e.g. in Section 3.1.2. and given in **Table 3**) and means that the electrons

518   liberated from organic matter decomposition in MFC were not captured by the anode

519   and registered in the form of biocurrent. Although several distinct mechanisms were

520   proposed to explain it (seen in Section 3.1.2.), further research will be required to

521   better understand the underlying phenomena and can be a subject for the continuation

522   of our work.

523

524

4. Conclusions

The assessment of various, single- and multi-stage anaerobic process for municipal waste liquor (LPW) valorization was carried out in this study. It was demonstrated that one-step technologies (in particular dark fermentative H_2 production, biogas fermentation and microbial fuel cells) alone were not able to simultaneously achieve efficient organic matter removal and energy recovery from LPW substrate. Nevertheless, a sequential, three-stage technology was found promising to meet these aims. Organic matter balances (according to COD recoveries) were quite satisfactory for the hydrogen and methane productions, however, further investigation on the microbial fuel cell process will be needed to get a better comprehension about fate of COD added in this particular application.

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726

Figure legend

728

729 **Fig. 1** – The origin of LPW and its main characteristics

730 **Fig. 2** – Gas formation (H_2+CO_2) as a function of time in the S-HF process

731 **Fig. 3** – Biogas generation (CH_4+CO_2) time profile for the S-BGF process

732 **Fig. 4** – Potential changes after injecting (a) 3 mL and (b) 25 mL LPW to the S-MFC

733 system

734 **Fig. 5** – The processes tested in this work. Red arrows indicate the proposed, multi-

735 stage treatment to efficiently accomplish energy recovery and COD removal from

736 LPW substrate

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740

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742

743

744 **Fig. 1**

745

Municipal Solid Waste → Biofraction → Composting → Landfill

pressing

Parameter	Value
COD	97 g L^{-1}
BOD$_5$	71 g L^{-1}
BOD COD^{-1}	0.73
pH	4.9
Dry matter content	8.7 %
Reducing sugar content	0.8 g L^{-1}

LPW
(substrate)
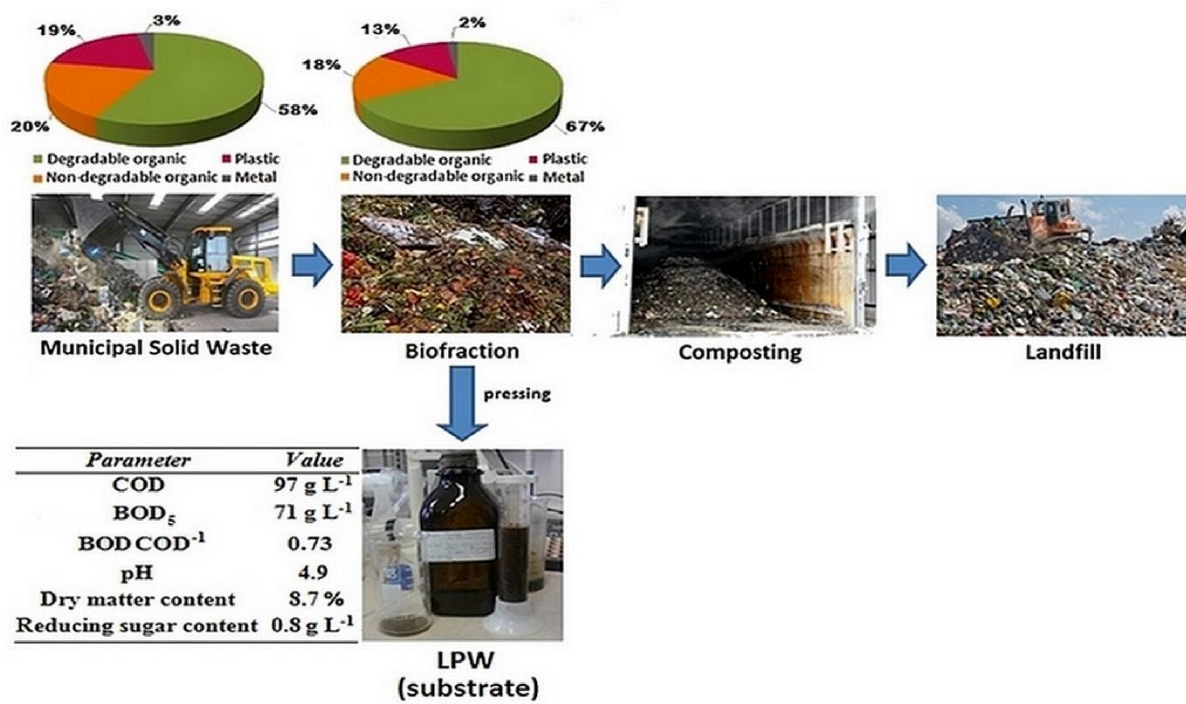
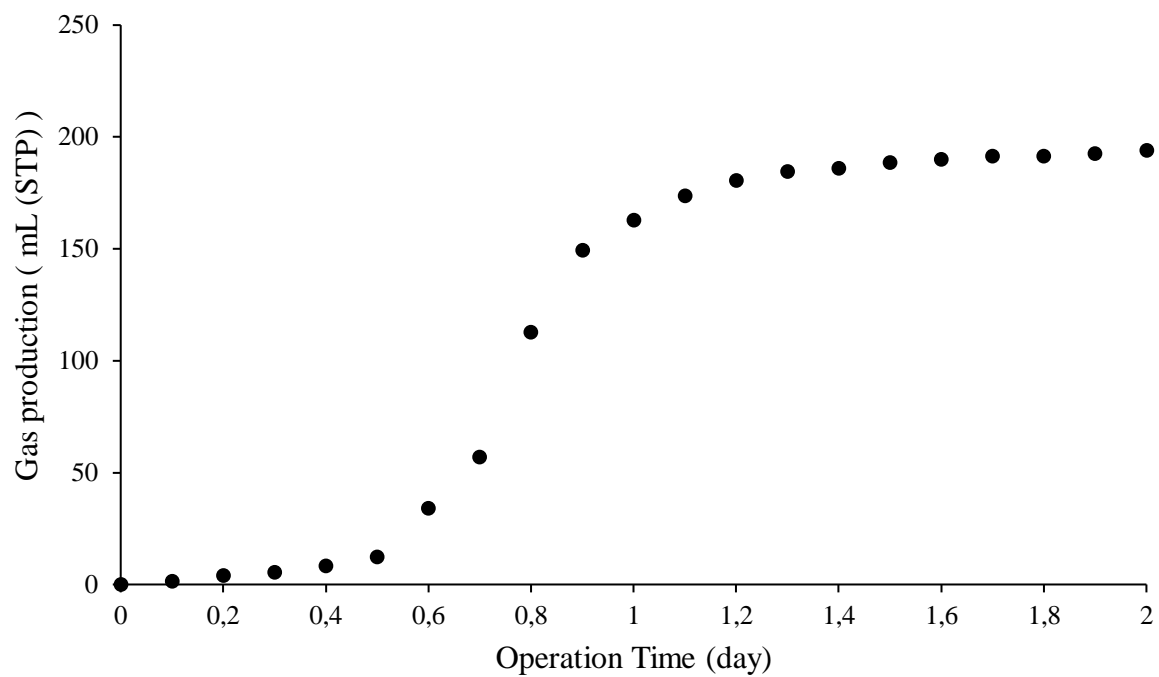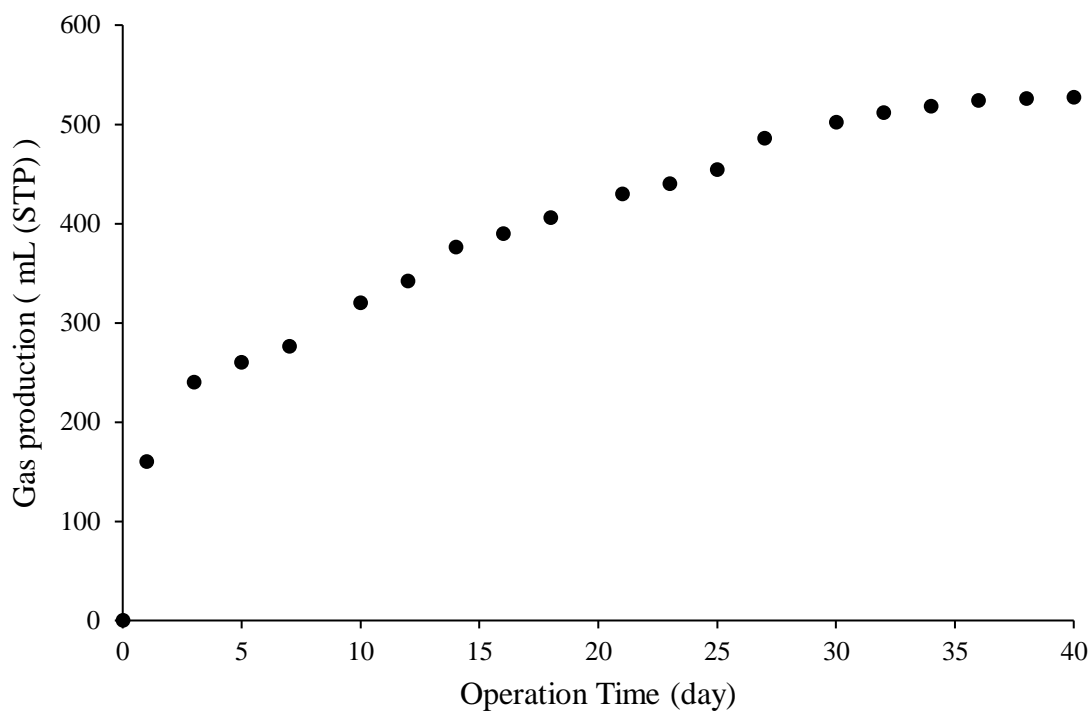746

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748 **Fig. 2**

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751

752   **Fig. 3**

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754

755   **Fig. 4**

756

757

758 **Fig. 5**


```
                              ┌──────────────┐
                              │     LPW      │
                              └──────────────┘

1ˢᵗ stage   Anaerobic digestion (S-BGF)   Hydrogen fermentation (S-HF)   Microbial fuel cell (S-MFC)

2ⁿᵈ stage   Anaerobic digestion (BGF)                                    Microbial fuel cell (MFC)

3ʳᵈ stage   Microbial fuel cell (MFC)
```

759

760
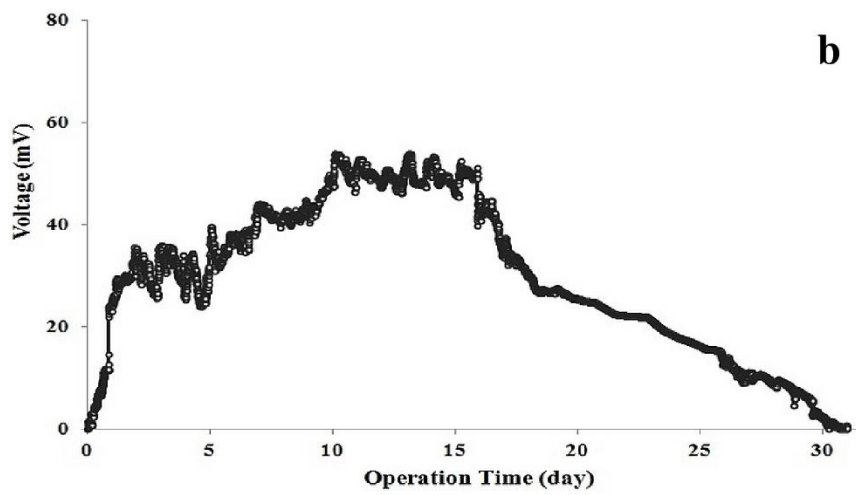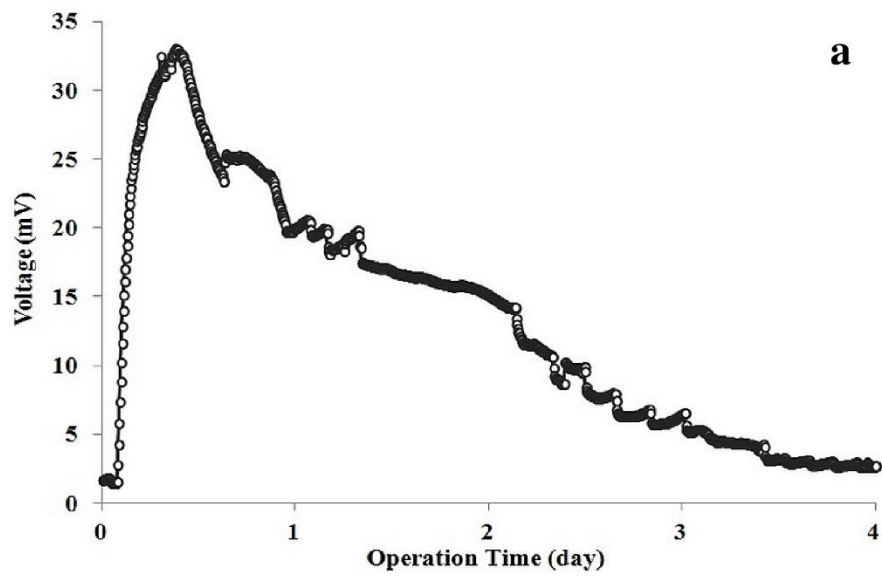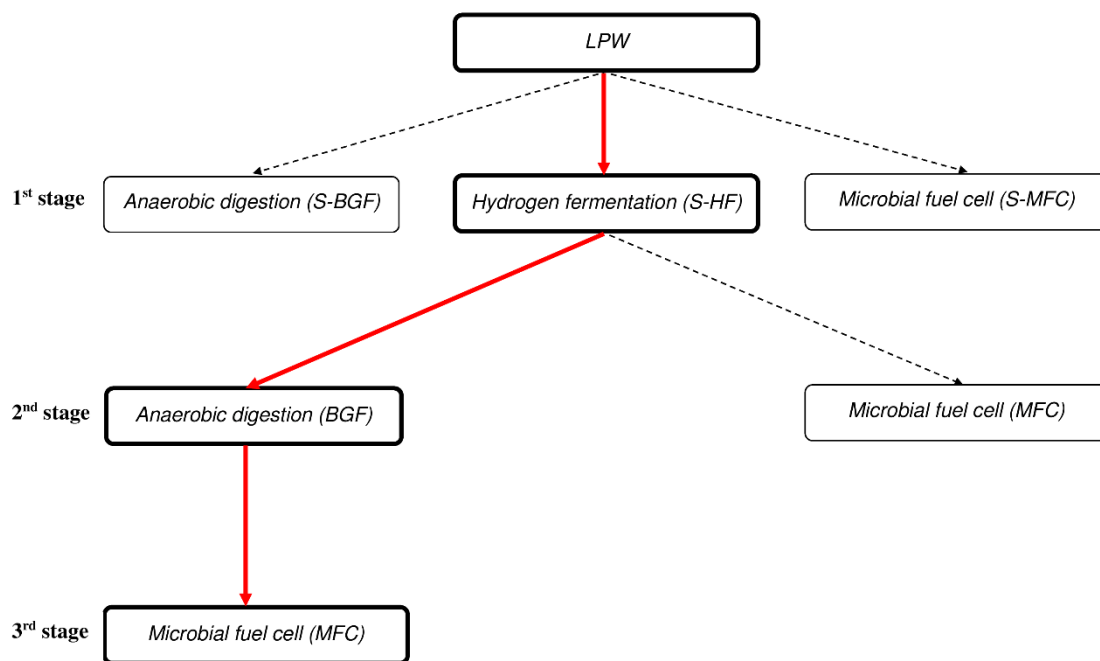
Table 1 – COD balance for the processes studied for LPW utilization

Process		Liquid phase total COD (g)		Product COD (g)			COD recovery (%)
		Initial	Residual	H_2	CH_4	Biocurrent[a]	
Single-stage	S-HF	2.85	2.6	0.064			93.5
	S-BGF	2.85	1.42		0.843		79.4
	S-MFC	2.52	0.192			0.066	10.2
Two-stage	HF-BGF HF	2.85	2.6	0.064			93.5
	BGF	1.73	0.77		0.442		70.1
	HF-MFC HF	2.85	2.6	0.064			93.5
	MFC	1.39	0.084			0.055	10
Three-stage	HF-BGF-MFC HF	2.85	2.6	0.064			93.5
	BGF	1.73	0.77		0.442		70.1
	MFC	0.48	0.054			0.042	19.8

[a]: as ΔCOD_C from **Table 3**.

765 **Table 2** – Comparison of single-stage processes for LPW treatment

Process	COD (g/L)		COD removal efficiency (%)	Cumulated energy (J)	Operational time (d)	E^* (J g^{-1} $COD_{removed}$ d^{-1})
	Initial	Residual				
S-HF	57	52	8.8	1139	2	2277
S-BGF	57	28.4	50.2	11698	40	205
S-MFC	42	3.2	92.4	31	30	0.43

766

767   **Table 3** – Coulombic efficiencies (C_e) and related data for the MFCs

768

Process	$COD_{removed}$ (g)	C_{th} (C)	C_{ex} (C)	C_e (%)	ΔCOD_C (g)
S-MFC	2.33	28059	801	2.9	0.066
MFC (in the HF-MFC)	1.31	15793	658	4.2	0.055
MFC (in the HF-BGF-MFC)	0.43	5090	492	9.7	0.041

769

Table 4 – Comparison of multi-stage processes for LPW treatment

Process			COD (g/L)		COD removal efficiency (%)	Cumulated energy (J)	Operational time (d)	E^* (J g^{-1} COD$_{removed}$ d^{-1})
			Initial	Residual				
Two-stage	HF-MFC	HF	57	52	8.8	1139	2	2277
		MFC	23.3	1.4	94.0	25	25	0.8
	HF-BGF	HF	57	52	8.8	1139	2	2277
		BGF	34.5	15.3	55.7	6130	26	246
Three-stage	HF-BGF-MFC	HF	57	52	8.8	1139	2	2277
		BGF	34.5	15.3	55.7	6130	26	246
		MFC	7.9	0.9	88.6	24	15	3.8