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1 **Biogas upgrading using ionic liquid [Bmim][PF₆] followed by thermal-**
2 **plasma-assisted renewable hydrogen and solid carbon production**

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27

28 **Abstract**

29 The use of hydrogen as clean energy has attracted significant attention because conventional
30 industrial hydrogen production processes show negative environmental impact, require intensive
31 energy, and/or are dependent on natural gas. The main objective of this study is to develop an
32 innovative and environment-friendly hydrogen production process utilizing biogas as an alternative to
33 natural gas. Ionic liquid [Bmim][PF₆] shows high potential for the replacement of aqueous amine
34 solutions for CO₂ absorption and are employed for biogas upgrading, while thermal plasma (TP),
35 which is beneficial for converting electrical energy to chemical energy, is employed for the
36 simultaneous production of clean “turquoise” hydrogen and solid carbon. In addition, an intercooler is
37 used to improve CO₂ removal in the absorber. Heat and power integration is employed to enhance the
38 performance of the upgrading process and thermal-plasma-assisted hydrogen production. The results
39 show that the proposed configuration using an intercooler can afford higher hydrogen purity, which is
40 increased from 99.8% to 99.9%. Solid carbon production from biomethane also increases compared to
41 that in the proposed base case. The savings in both the heater used to preheat the TP reactor and the
42 third flash drum are 100%, while the saving in power consumption in the compression section is
43 73.3%. Furthermore, sensitivity is investigated to determine the effect of biomethane composition on
44 the performance of the proposed configuration.

45

46 **Keywords:** Biogas upgrading; ionic liquid; [Bmim][PF₆]; heat integration; turquoise hydrogen;
47 thermal plasma

48

49 **1. Introduction**

50 The current processes utilizing nonrenewable sources, such as natural gas as well as oil reforming
51 and coal gasification, account for 96% of hydrogen production [1]. Several new technologies for
52 renewable hydrogen production, such as electrolysis of water (green hydrogen), biomass
53 thermochemical conversion, biological methods, and solar photochemical conversion methods, are
54 under development [2]. Recently, a process in which methane (CH_4) can be thermally or thermo-
55 catalytically decomposed into carbon and hydrogen (turquoise hydrogen) without CO_2 production has
56 attracted considerable attention of the researchers worldwide [3]. By solely considering hydrogen
57 production, direct methane decarbonization is eight times less costly than water electrolysis [4].
58 Furthermore, this process can produce solid carbon that can be used in many applications [5].

59 Thermal plasma (TP) offers several benefits for the conversion of electrical to chemical energy,
60 providing a flexible, controllable, and tunable heating source without direct CO_2 emission [4].
61 Furthermore, it is suitable for endothermic processes and in cases where high temperatures are
62 required. Extensive efforts have been directed toward applying TP for the production of hydrogen and
63 high value-added solid carbon from polymers [6] and methane [4], [7]. Monolith Materials, founded
64 in 2012, has built a plant near Hallam that converts natural gas into clean hydrogen and solid carbon
65 [8].

66 Biogas is a mixture of methane (55–70 wt%), CO_2 , and trace elements such as H_2O , H_2S , NH_3 ,
67 and siloxanes [9]. Biogas can be produced by the anaerobic digestion of wet biomass, such as the
68 organic fraction of municipal solid waste, energy crops, agricultural residues (mainly manure and
69 straw), sewage sludge, and other organic waste [10]. When CO_2 is removed during the upgrading
70 process, methane concentration increases, and the resulting biomethane can be utilized as an
71 alternative to natural gas [11], which can reduce the dependence on natural gas and positively affect
72 the environment by affording a renewable source of energy and reducing greenhouse gas emissions.

73 Among the commercially available upgrading technologies, CO_2 absorption by aqueous amine
74 solutions is the most mature gas separation technology. However, because of amine degradation, high
75 equipment maintenance cost, high energy requirement in the regeneration step, and environmental

76 hazards, a better solvent system should be explored. Ionic liquids (ILs) have been recently
77 investigated as effective solvents that show high potential for the replacement of aqueous amine
78 solutions because of their favorable properties, such as low vapor pressure, high boiling point, high
79 CO₂ solubility and selectivity, easy regeneration, and high tunability [12]. However, ILs have several
80 drawbacks, such as high viscosity after CO₂ absorption, which increases the energy required for
81 solvent pumping, and high cost [13].

82 Therefore, the development of an efficiently integrated hydrogen production process from biogas
83 is required. To the best of our knowledge, this is the first report describing the development of an
84 efficiently integrated hydrogen production process from biogas comprising IL-assisted biogas
85 upgrading and hydrogen production using TP. An intercooler is used to improve CO₂ removal in the
86 absorber. Moreover, heat and power integration is employed to enhance the performance of the
87 upgrading process and thermal-plasma-assisted hydrogen production. An effective configuration
88 based on the improvements in the compression section, absorber, flash drum, and plasma reactor is
89 proposed. Finally, sensitivity is investigated to determine the effect of biomethane composition on
90 product performance.

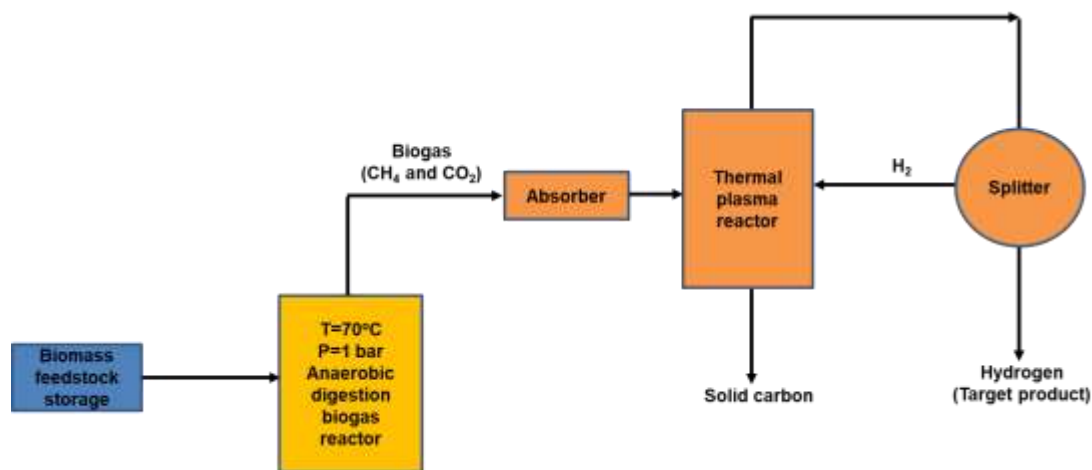
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92 **2. Base case**

93 Even though methane can be used as a feed for producing clean hydrogen and solid carbon using
94 TP [14], biomethane, which is a substitute for fossil natural gas and is obtained from biomass or
95 biowaste, is more attractive because of net-zero emissions. The facility for biogas production and
96 upgrading comprises three stages: anaerobic digestion stage in which the organic fraction of the
97 treated waste is decomposed producing biogas, initial biogas conditioning stage in which H₂S and
98 ammonia are removed, and the purification step that involves CO₂ removal to achieve sufficient purity
99 [15]. In this study, a process including IL-assisted biomethane upgrading and hydrogen production
100 using TP was developed. All simulations in the biomethane upgrading unit were performed using the
101 Aspen Plus V10.0 software by employing the Peng-Robinson (PR) equation of state [16]. For
102 hydrogen production using TP, the UNIQUAC properties package was employed [17].

103 2.1. Biomethane upgrading using IL

104 Biogas obtained from the anaerobic digestion unit primarily consists of CH_4 and CO_2 , whose
105 relative contents mainly depend on the nature of the substrate and reactor pH [10]. Before its usage in
106 the TP reactor for hydrogen production, biogas should be treated for CO_2 removal by the upgrading
107 unit (Figure 1).



108

109 **Figure 1. Schematic of the process for the co-production of hydrogen and solid carbon.**

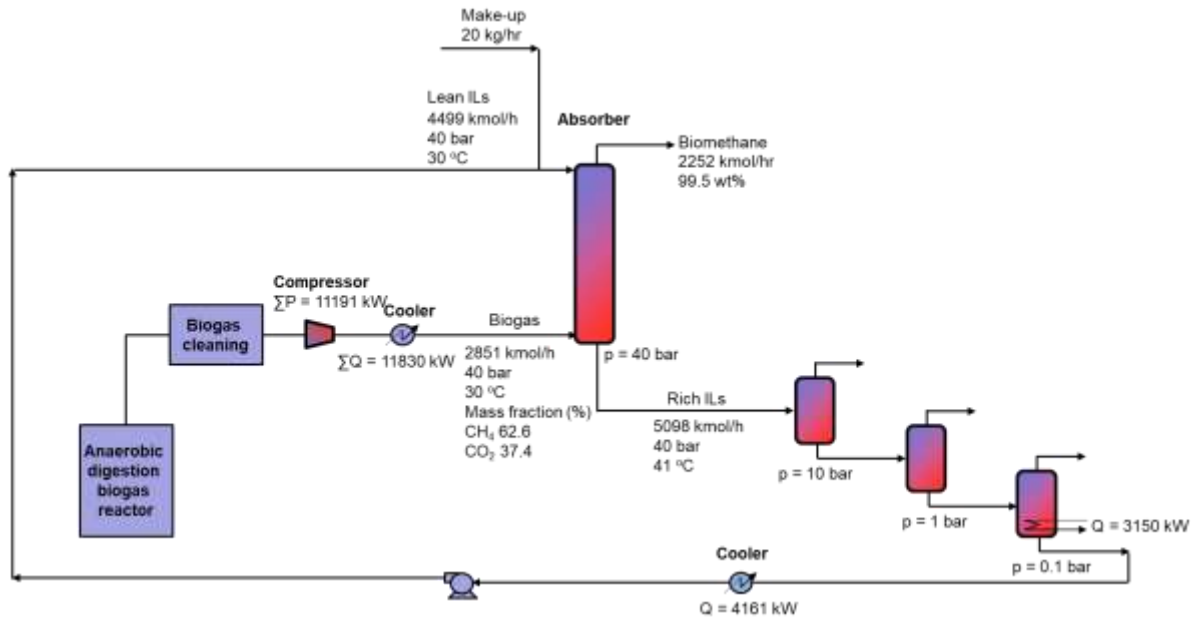
110 Among the commercially available upgrading technologies, CO_2 absorption by aqueous amine
111 solutions is the most mature and popular technique. However, as mentioned previously, owing to
112 amine degradation, high equipment maintenance cost, high energy requirement in the regeneration
113 step, and environmental hazards, a better solvent system is required. In the past few years, ILs have
114 been utilized as gas absorbents owing to their advantages over the traditional solvents, which include
115 thermal stability, non-volatility, designability, and tunability [16]. Considerable efforts have been
116 directed toward investigating the absorbent properties of the ILs for gases such as CO_2 , H_2S , N_2 , and
117 H_2 [18][19]. In particular, ILs have been widely applied to C_1 – C_4 absorption and reported as effective
118 acidic gas absorbents [20]. However, the selection of a suitable IL for a specific process is important,
119 considering that the solubility of a gas is different in different ILs. In other words, the selection of an
120 appropriate IL can determine the technical and economic feasibility of the gas removal process.

121 Several studies have shown that 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6]
122 can be used as an alternative absorbent to the aqueous amine solutions for CO_2 removal [21]. This IL

123 has been demonstrated to be a suitable solvent for CO₂/CH₄ separation with the highest absorption
124 selectivity among the imidazolium-based ILs. Additionally, it has a viscosity of 0.246 Pa·s at 298.15
125 K and low-to-moderate toxicity (e.g., the logEC₅₀ value against leukemia rat cell line is 3.10). Notably,
126 the solubilities of CO₂ and CH₄ in [Bmim][PF₆] have been experimentally determined in a wide range
127 of temperature and pressure values, allowing a reliable regression of the thermodynamic model
128 parameters for modeling the phase behaviors of this system in the absorber. For instance, Haider et al.
129 [16] successfully fitted the parameters for [Bmim][PF₆] and CO₂/CH₄ for a set of equation of state
130 models, where the PR method selected in this work showed the lowest standard deviations of 0.0330
131 and 0.0079 for calculating the solubilities of CH₄ and CO₂, respectively, in this IL. Thus, in this work,
132 [Bmim][PF₆] was selected as a solvent for CO₂ removal to upgrade biomethane.

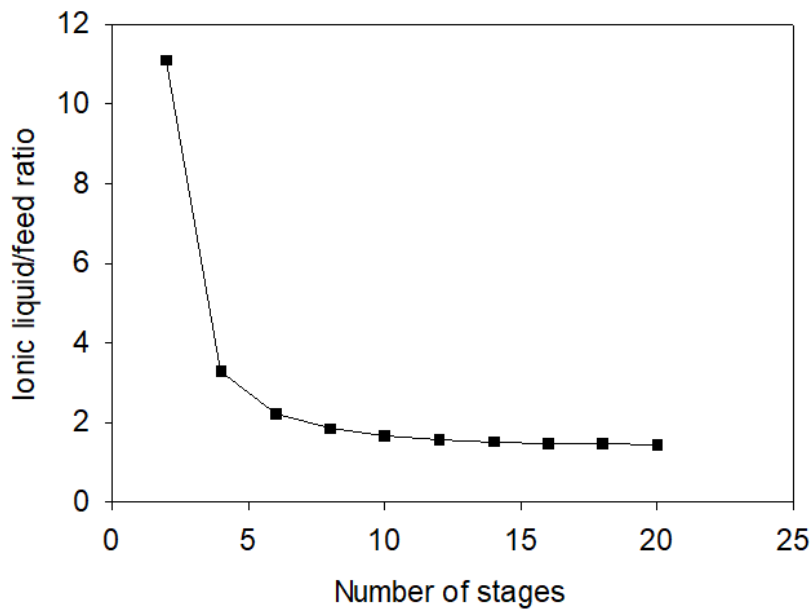
133 Biogas was first compressed to 40 bar before its entry into the absorber. **Figure 2** shows that the
134 biogas produced by anaerobic digestion comes into contact with the IL in the absorber. The process
135 was designed to recover 96% biomethane with purity of 99.5 wt%. The number of stages (N) was
136 varied to optimize the absorber. **Figure 3** shows the effect of the number of absorber stages on the IL
137 to feed (IL/F) ratio. The IL/F value decreases rapidly upon an increase in N from 2 to 8, and increases
138 slightly when it is increased from 8 to 12. Upon a further increase in N, the IL/F value remains stable.
139 Therefore, a value of 12 for the number of stages was employed in the design of the absorber. **Figure 4**
140 shows the composition profile of CO₂ in the absorber, which indicates that almost all CO₂ is absorbed
141 in the bottom half of the scrubber.

142 A series of flash drums was used to recover [Bmim][PF₆], which were operated at 9.8, 0.8, and
143 0.1 bar [16]. Notably, to completely strip the gas and recover [Bmim][PF₆], a load of 3,150 kW was
144 applied in the third flash drum. The bottom stream of the third flash drum was pumped to increase the
145 pressure before it was recycled to the absorber.



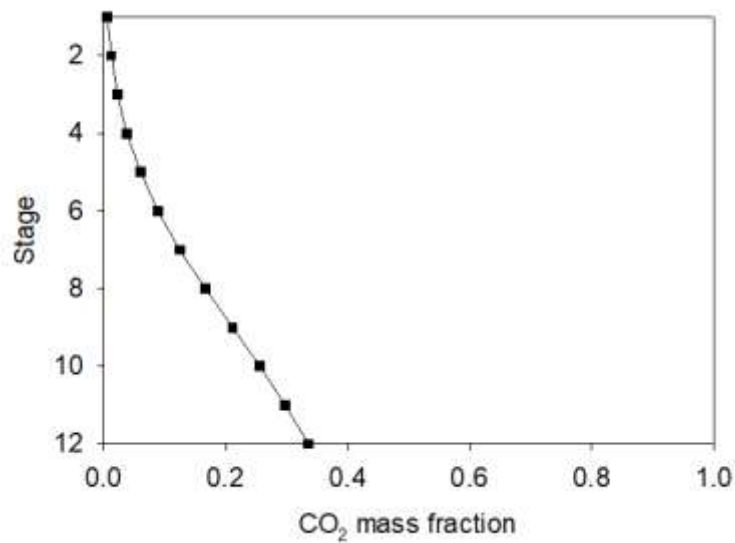
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147 **Figure 2. Simplified flow sheet illustrating the ionic liquid (IL)-assisted biogas upgrading unit.**



148

149 **Figure 3. Effect of the number of absorber stages on ionic liquid to feed ratio (IL/F).**



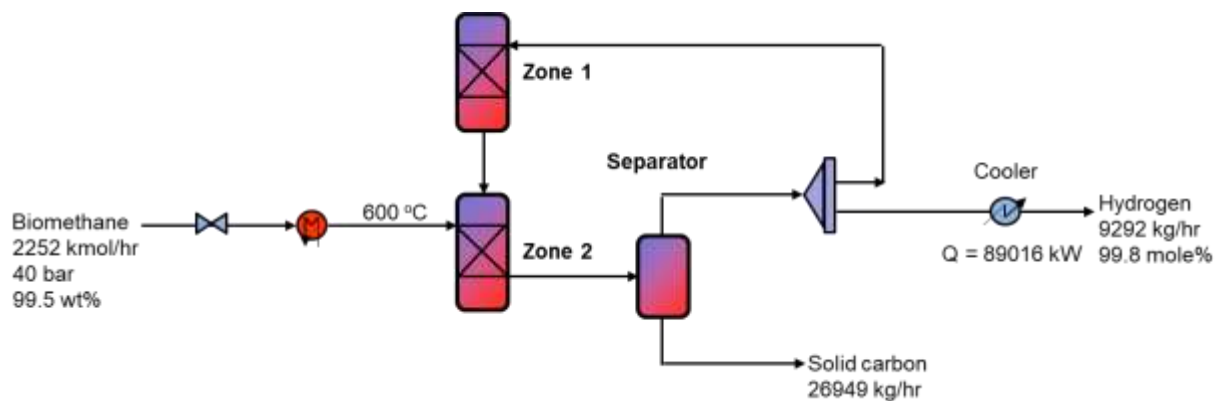
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151 **Figure 4. Composition profile of CO₂ in the absorber.**

152

153 **2.2. Hydrogen production using TP**

154 Upgraded biomethane was then heated to 600 °C before being fed into the TP reactor with two
 155 reaction zones; this splitting into two serial reaction zones increased the chemical yield of the TP
 156 reactor [4]. First, the produced biogas entered zone 2 to produce hydrogen and solid carbon. Then, the
 157 outlet from the TP reactor was fed into a separator to separate solid carbon and hydrogen. A fraction
 158 of hydrogen was recycled to zone 1 to produce hydrogen radicals before entering zone 2. **Figure 5**
 159 shows a simplified flow sheet illustrating the hydrogen production unit using TP.



160

161 **Figure 5. Simplified flow sheet illustrating the thermal plasma (TP) reactor for hydrogen**
 162 **production.**

163 3. Process improvement

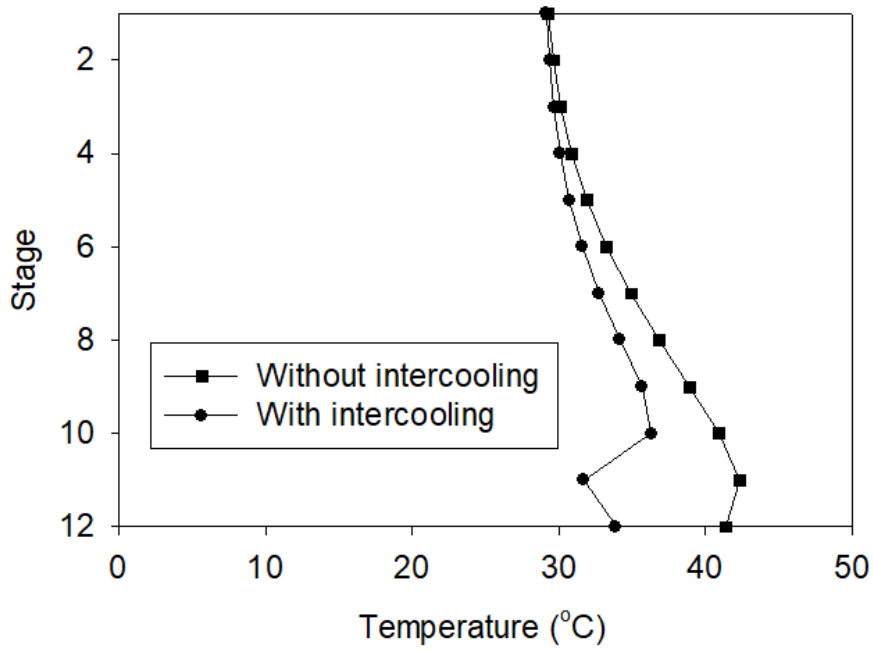
164 3.1. Absorber improvement

165 A useful method for enhancing CO₂ removal involves the application of an intercooler to the
166 absorber columns [22]. Absorption is an exothermic process that leads to an overall temperature
167 increase of the solvent. This phenomenon can cause decreases in the driving force of absorption as
168 well as absorption capacity of the solvent system. The absorption efficiency may be improved by
169 withdrawing a fraction of solvent in the absorber and cooling the solvent prior to its return to the
170 absorber [23].

171 The important design parameters for intercooler design are the location and cooling duty. As the
172 temperature of the 11th tray was the highest, the intercooler was installed in that section (Figure 6a),
173 and intercooler duty was then used for optimization (Figure 6b). Figure 6b shows that CO₂ removal
174 increases when the intercooler duty is increased from 0 to 1200 kW. However, above 1200 kW, the
175 temperature of the absorber is <30 °C, which is a constraint to use the cooling water. Thus, an
176 intercooler duty of 1000 kW was employed in the intercooler design. As shown in Figure 6a, the
177 temperature profile is shifted to the left, i.e., the temperature in the column decreases in comparison to
178 that in the base case. As a result, 96.1% biomethane with a purity of 99.7 wt% can be recovered.

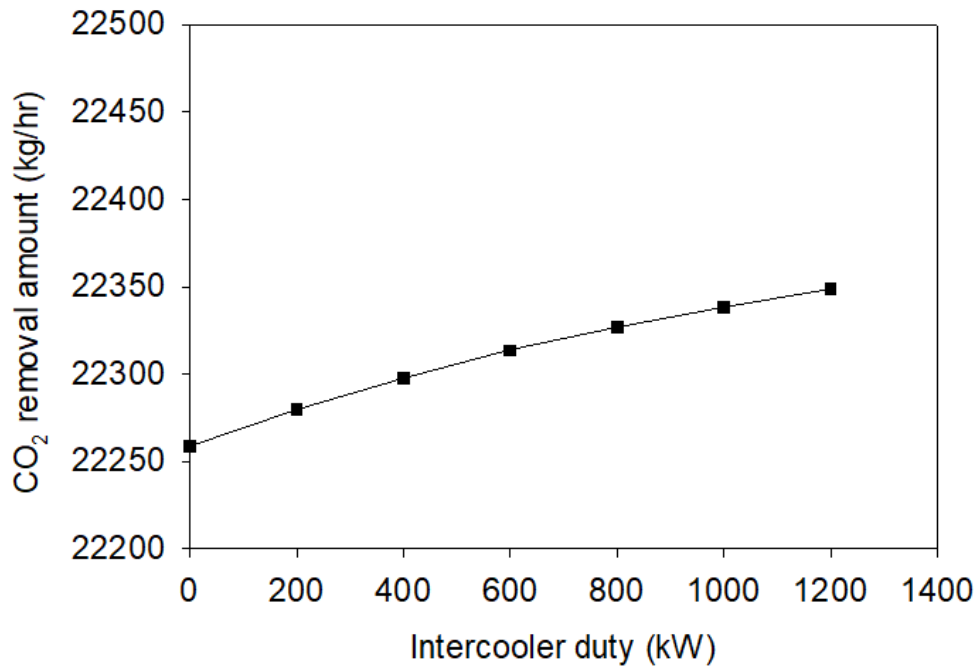
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180 (a)



181

182 (b)



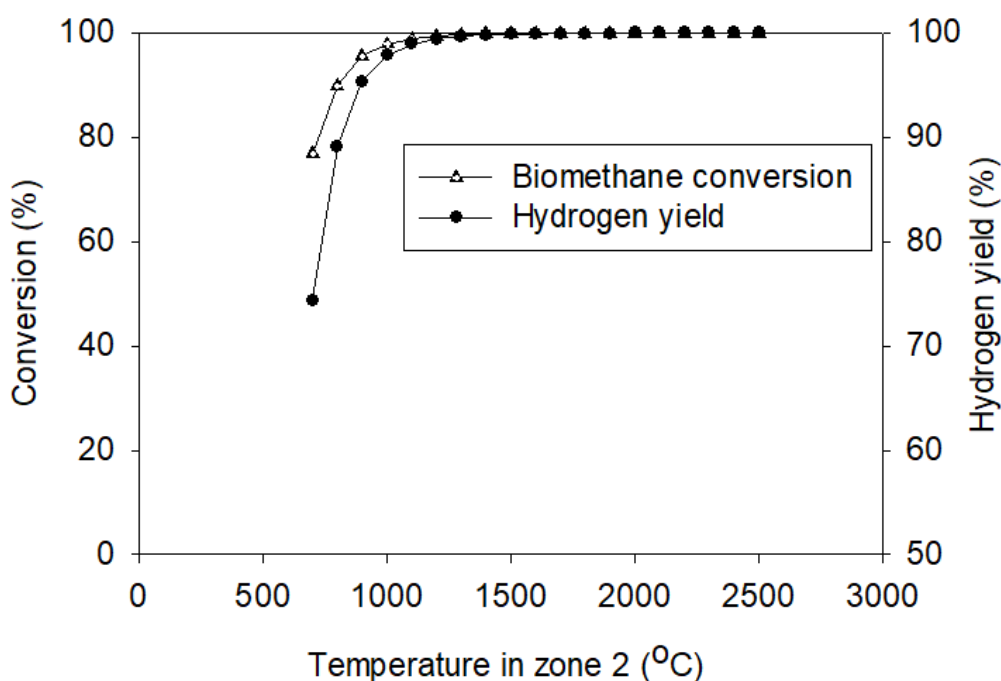
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184 **Figure 6. (a) Temperature profile; (b) effect of intercooler duty on CO₂ removal.**

185

186 **3.2. Improvement in TP reactor**

187 Since there is no effect of the temperature of zone 1 on the total efficiency [17], only the
188 temperature of zone 2 was varied in this study. Figure 7 shows that biomethane conversion increases
189 rapidly when the temperature of zone 2 is increased from 700 °C to 1200 °C, while it increases
190 slightly with an increase in temperature from 1200 °C to 1500 °C. Thereafter, the conversion remains
191 stable upon a further increase in the temperature of zone 2. Thus, 1500 °C was selected to design the
192 TP reactor in the proposed configuration.



193

194 **Figure 7. Effect of the temperature of TP in zone 2.**

195

196 **3.3. Heat and power integration**

197 **3.3.1. Feed preheating**

198 Since the outlet from the TP reactor has a high temperature, the heat from this stream can
199 potentially be used to preheat the TP reactor feed and supply heat to the third flash drum for IL
200 regeneration. In particular, the outlet stream of zone 2 is used to preheat the biogas feed to 600 °C
201 before being fed into a separator to separate solid carbon and hydrogen. This can lead to a reduction

202 of the thermal load of the reactor. Note that, to prevent methane cracking in the pipes, the upper
203 threshold for the preheating temperature of methane is 700 °C. Heat integration can result in a saving
204 of 100% in terms of the heat required to preheat the feed stream of the TP reactor.

205 **3.3.2. Flash drum improvement**

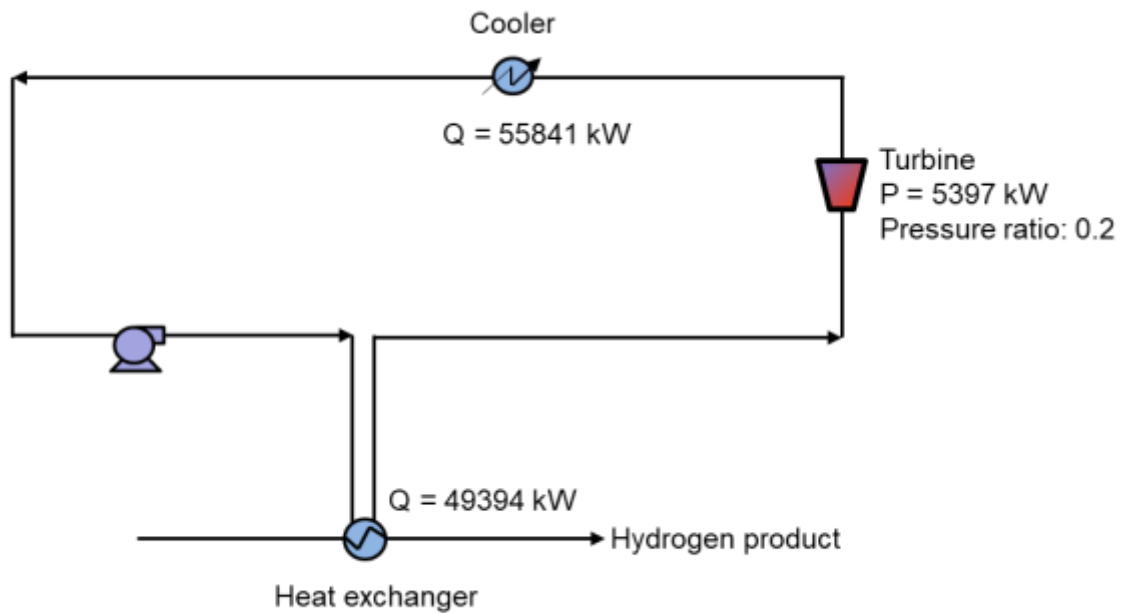
206 Since extra heat is available in the hydrogen product stream, it can be utilized for the third flash
207 drum. Thus, a heat exchanger was used for heat integration between the hot stream (hydrogen
208 product) and cold stream (liquid in the third flash drum). Notably, the minimum temperature in this
209 study was 10 °C. The results show that it is possible to save 3150 kW power in the third flash drum,
210 which corresponds to 100% saving in terms of flash drum duty.

211 **3.3.3. Turbine**

212 Since the top stream of the absorber has a high pressure, a turbine can potentially be used to drive
213 the electricity generators. The force of the purified biomethane on the blades rotates the rotor shaft of
214 a generator. In turn, the generator converts the mechanical (kinetic) energy of the rotor into electrical
215 energy. As a result, turbine use can generate a power of 2461 kW, i.e., it can save 22.0% of the total
216 compression power to increase the inlet biogas of the absorber.

217 **3.3.4. Electricity generation**

218 It is also possible to utilize heat from the condenser in the compression unit and the remaining
219 heat from the outlet of the TP reactor to generate electricity. In particular, the hydrogen product stream
220 can be used as a heat source to generate steam, which can then be used to drive the turbine to produce
221 a power of 5397 kW (Figure 8). The same approach can be applied to utilize the heat from the cooler
222 in the compression unit, which can generate a power of 350 kW. This generated electricity can be used
223 to drive the compressors in the compression section.



224

225 **Figure 8. Simplified flow sheet of the electricity generation system.**

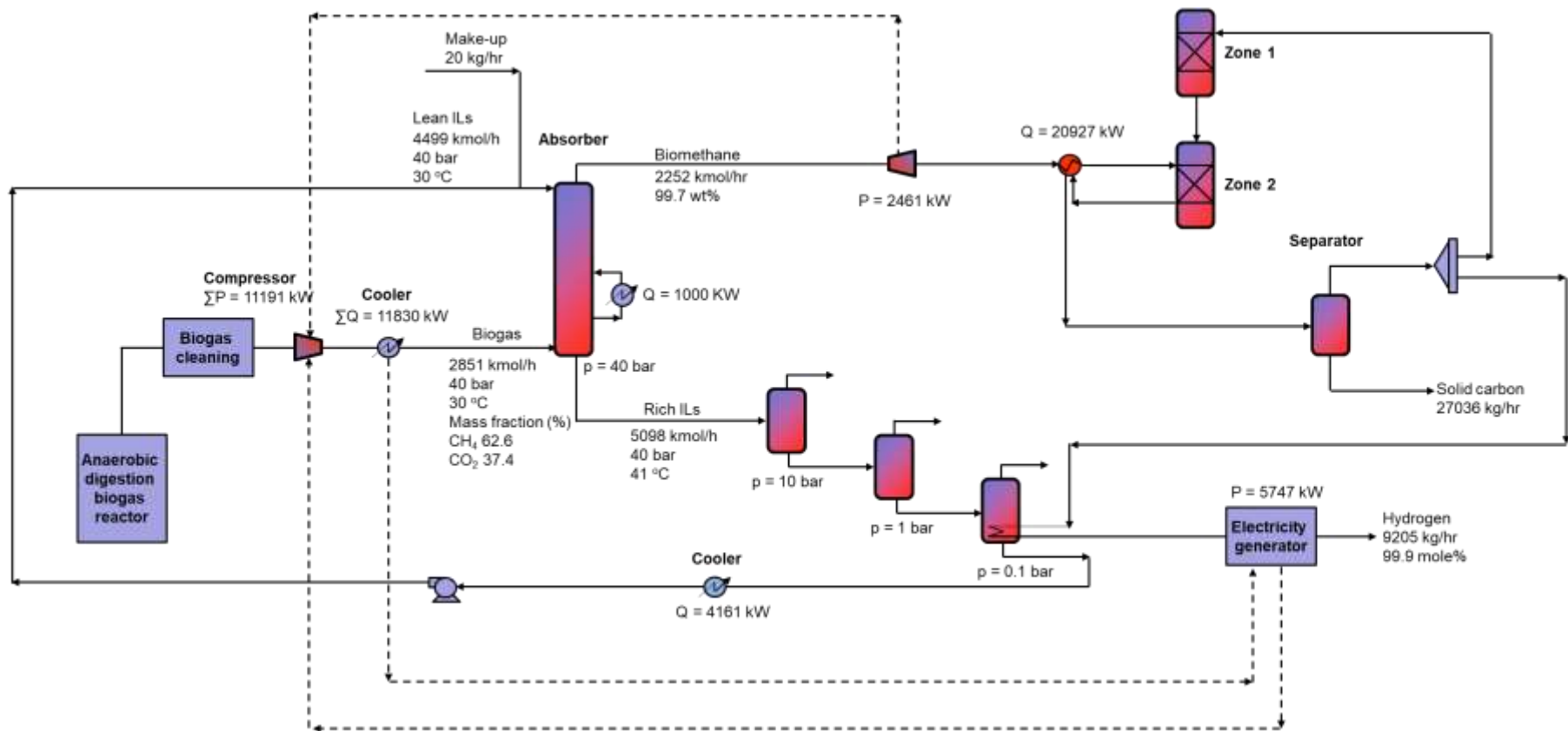
226 **4. Proposed configuration**

227 **Figure 9** shows the proposed integrated IL-assisted absorber for biogas upgrading as well as
 228 thermal-plasma-assisted reactor producing hydrogen and solid carbon. In this configuration, an
 229 intercooler is used to improve the absorber performance, and zone 2 of the TP reactor is operated at
 230 $1500 \text{ }^\circ\text{C}$. This configuration can afford a higher hydrogen purity, which is increased from 99.8% to
 231 99.9%, as biomethane purity is increased with the use of an intercooler. Furthermore, the solid carbon
 232 product, which is also produced from biomethane, increases in comparison to that in the proposed
 233 base case.

234 Total electric energy that can be generated from the turbine by utilizing the high pressure of the
 235 scrubber top stream as well as electricity generated utilizing the heat from the condenser in the
 236 compression unit and remaining heat from the outlet of the TP reactor is 8208 kW, affording a 73.3%
 237 saving in power consumption in the compression section. Notably, the savings in the heater to preheat
 238 the TP reactor and third flash drum are 100% in both cases.

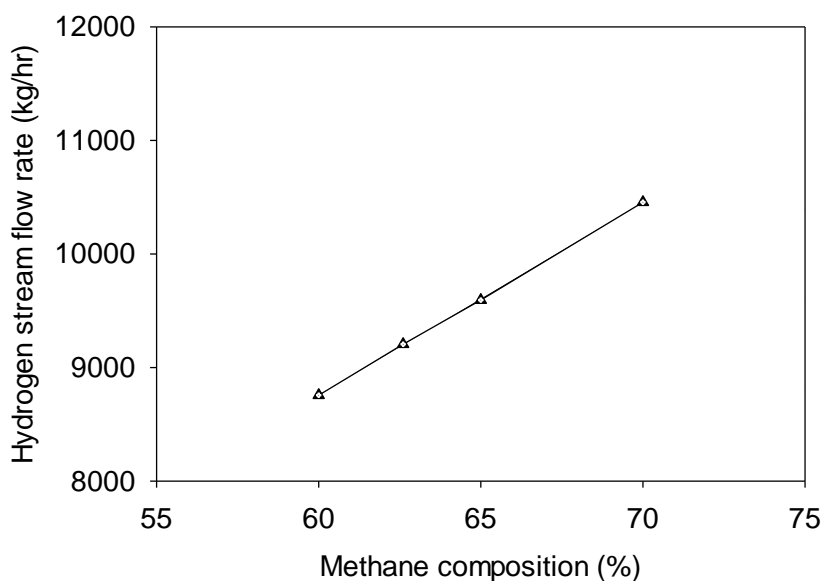
239 Since the methane composition in biogas depends on the type of feedstock, technology used, and
 240 operating conditions, the effect of methane composition on product performance was determined. As
 241 shown in **Figure 10**, the hydrogen amount increases with increasing methane content, because

242 hydrogen is the direct product obtained from methane. This can afford high hydrogen purity, which is
243 an important parameter for designing. For different applications of hydrogen, the hydrogen purity
244 from the production section should be different.



245

246 **Figure 9. Simplified flow sheet illustrating the proposed process.**



247

248 **Figure 10. Effect of methane composition on product performance.**

249

250 **5. Conclusions**

251 The method described in this work is an attractive solution for both clean hydrogen and solid
 252 carbon production, affording 96% biomethane recovery with a purity of 99.5% using [Bmim][PF₆].
 253 An intercooler is effectively employed to improve CO₂ removal; in particular, the process employing
 254 [Bmim][PF₆] with an intercooler can afford 99.7% pure biomethane. In the proposed configuration,
 255 [Bmim][PF₆] is used as a solvent, and the combined use of an intercooler with heat and power
 256 integration results in enhanced performance. Moreover, the proposed configuration affords a higher
 257 hydrogen purity with an increase from 99.8% to 99.9%. Furthermore, the yield of the solid carbon
 258 product, which is also produced from biomethane, increases in comparison to that in the proposed
 259 base case. The heater savings to preheat the TP reactor and third flash drum are 100% in both cases,
 260 while the power consumption saving in the compression section is 73.3%. Moreover, hydrogen
 261 productivity increases with an increase in the methane composition in biogas. Considering the
 262 significant potential of the proposed integration process, additional efforts should be directed toward
 263 the application of large-scale IL screening as well as the conversion of CO₂ and hydrogen produced in
 264 this process to more valuable components such as methanol in the future.

265

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