Synthesis of bio-dimethyl ether (Bio-DME) based on CO$_2$-enhanced gasification of biomass: Process simulation using Aspen Plus^{TM}

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Abstract

Process simulation of a single-step synthesis of DME based on CO$_2$-enhanced gasification of rice straw was conducted using Aspen Plus^{TM}. The process consists of gasification unit, heat recovery unit, gas purification unit, single-step DME synthesis, and DME separation unit. In the simulation, highly pure DME was produced by the control of CO$_2$ concentration in syngas to a very low level prior to synthesis. A gasification system efficiency of 36.7% and CO$_2$ emission of 1.31 kg/kg of DME were achieved. Bio-DME production based on CO$_2$-enhanced gasification of biomass was found to be more cost-effective as it required 19.6% less biomass than that of DME production based on conventional biomass gasification. The performance and environmental benefits of the proposed process could be further improved by the utilization of unreacted gases and the handling of CO$_2$ generated via incorporating poly-generation concept or carbon storage, which could also potentially improve process economics.

Keywords: Bio-DME; CO$_2$-enhanced gasification; Aspen plus^{TM}; DME synthesis; sustainability assessment.

1   Introduction

Currently, fossil fuels remain as the most important energy source worldwide. Their consumption is still increasing steadily. Concerns over the environmental pollution associated with the utilization of fossil fuels have become the main driver towards cleaner energy production[1] In the past few decades, many countries have considered increasing the share of nuclear energy in their energy mix but the enthusiasm has fallen since the accident occurred

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29   at Fukushima Daiichi nuclear power plant in March 2011. Therefore, more attention is now being

30   paid to renewable energy, especially bioenergy [2] Biomass is abundant and has the potential to be

31   used for the generation of power as well as for the production of chemicals. It is projected that the

32   use of biomass as an energy source would increase by a factor of 2 to 3 in the next few decades and

33   contribute to a significant reduction of greenhouse gases emission by 2050 [3]. The use of biomass

34   as raw materials for the production of the same chemical products as those from fossil fuels could

35   also contribute to the reduction in the emission of greenhouse gases due to its carbon-neutral nature

36   [3-4]. Therefore, the utilisation of biomass as an alternative energy source and raw materials not only

37   mitigates the greenhouse effect, but also greatly reduce the dependency on fossil fuels.

38   In the past two decades, work has been carried out to explore the opportunities to use biomass as a

39   promising source for the production of secondary biofuels, such as dimethyl ether (DME) [5].

40   Compared with many other diesel fuels, DME shows a better performance in terms of low NO_x

41   emission, zero SO_x emission and extremely low particulate matter emission [5-6]. In principle, DME

42   can be produced using a variety of biomass as feedstock, such as rice straw [4-5, 7]. The production

43   of DME using rice straw as the raw materials is an attractive option for China due to the fact that

44   China is the largest producer of rice in the world, and currently most of the rice straw in China is

45   burnt in open field and has caused severe local air pollution.

46   Double-step synthesis process is the most commonly used process for DME manufacture, which

47   consists of methanol formation and methanol dehydration [3]. However, this double-step synthesis

48   includes a number of process stages and requires high capital investment and operation costs. The

49   major disadvantage of such process is its low conversion efficiency due to the thermodynamic

50   limitation for methanol synthesis [8]. Recently, new technologies have become available to allow

51   the methanol synthesis and methanol dehydration processes being carried out simultaneously in one

52   reactor, which is defined as single-step synthesis. It is thermodynamically and economically more

53   favourable than the double-step process[4, 7]. In addition, the initial capital investment is much lower

54   than that of the double-step process.

Recently several pilot-scale plants have been built or under construction to demonstrate the single-step synthesis of DME [9]. Air Products and Chemicals Inc. developed a 4 t/d pilot-scale slurry reactor for the single-step synthesis of DME. The catalyst used was a Cu-based bi-functional powder catalyst [4]. It was shown that 65% of CO was converted and the DME selectivity was 76%. Slurry reactors and bi-functional catalysts for single-step synthesis of DME have also been investigated [3, 7, 10], for example, JFE Group developed a new process consisting of a slurry bed reactor with optimum reaction heat control technology to produce DME more efficiently and economically [3, 11].

Although DME production based on the gasification of fossil fuels has become commercially available for long time, not much work has been carried out on DME production using biomass as a feedstock. This is because the low H_2/CO ratio and high CO_2 concentration in syngas presents a major challenge to biomass-based DME production [4, 9, 12].

In theory, the use of CO_2 as an oxidising agent could improve biomass conversion and CO production significantly [12-13]. It is found that CO concentration in syngas can be adjusted by CO_2-enhanced biomass gasification [13]. It can therefore be used to facilitate the desired syngas composition for various applications, for example, increasing the use of CO_2 as a gasifying agent to achieve a lower H_2 yield and a higher CO yield in syngas, together with a higher thermal efficiency [12, 14]. However, in spite of the huge potential of using CO_2 in biomass gasification en route to DME synthesis, only limited studies have been conducted to find out optimum design conditions for better processes. The simulation of DME production based on CO_2-enhanced biomass gasification has not yet been studied extensively.

In this study, Aspen Plus[TM] was used to simulate DME production based on CO_2-enhanced gasification of biomass. Efforts were made to evaluate the impacts of individual operating conditions on the process efficiency, H_2/CO ratio etc. Furthermore, the needs for future development are also identified in this work.

2   Methodology

2.1   Feedstock selection

Rice straw was selected as the biomass feedstock in this work due to its wide availability in China as well as in South and South-East Asia. The basic properties of rice straw are shown in Table 1.

2.2   Process description

In this study, it was assumed that DME was synthesized via a single-step process. The single-step synthesis of DME based on conventional gasification and CO_2 enhanced gasification is illustrated in Fig. 1.

Single-step DME production based on conventional biomass gasification is shown in Fig. 1a, which consists of five main units, i.e., gasification unit, water-gas shift (WGS) unit, gas purification unit, single-step DME synthesis unit, and DME separation unit. Oxygen and steam are commonly used as the gasifying agents. Each of these units is described briefly in the following.

Gasification Process: Generally, syngas can be produced from different feedstock including biomass. In gasification unit, it is assumed that carbon (C), hydrogen (H) and oxygen (O) in biomass are converted into CO, H_2, CO_2 and CH_4. Meanwhile, H_2S (originated from sulphur in biomass) and NH_3 (originated from nitrogen in biomass) are also formed during gasification process.

Water Gas Shift (WGS): In conventional DME synthesis process, syngas from the gasification unit is introduced to a WGS unit to adjust its H_2/CO ratio to a desired level. A heat recovery system is coupled with the WGS unit to recover waste heat for steam production.

Purification Unit: In gasification unit, sulphur and nitrogen in feedstock are converted into gas pollutants, such as H_2S, COS, NH_3 and HCN, etc. The presence of H_2S is poisonous to synthesis catalyst, whilst the excessive amount of CO_2 in syngas normally results in deteriorated conversion

4

104 efficiency in DME synthesis. It is therefore necessary to removal H_2S from the syngas and lower

105 CO_2 concentration to an acceptable level before being fed into the synthesis unit [3-4, 15].

106 DME Synthesis Unit: After purification, the syngas is transferred to the DME synthesis reactor. In

107 single-step DME synthesis process, the same as other catalytic processes, catalyst plays a vital role

108 in DME selectivity. In this simulation, the catalyst used is assumed to have a DME selectivity of

109 91%.

110 DME Separation Unit: Subsequently, DME is separated from the product gases discharged from the

111 DME synthesis reactor and is purified to produce DME at a desired purity.

112 Fig. 1b shows the single-step DME synthesis based on CO_2-enhanced biomass gasification, which

113 also has five main units: gasification unit, heat recovery unit, purification unit, single-step DME

114 synthesis unit, and DME separation unit. Within each of the mentioned sections, different

115 technologies could be used and the design parameter should then be adjusted accordingly.

116 In the proposed process, biomass gasification is performed using CO_2 and steam as oxidising

117 agents. The gas generated from biomass gasification contains similar components compared with

118 the conventional biomass gasification process but has an improved molar ratio of H_2/CO for DME

119 synthesis. The adjustment of gasification operating conditions such as temperature, pressure as well

120 as the flow rate of oxidising agents (steam and CO_2), allows the desired H_2/CO molar ratio and CO_2

121 concentration in syngas to be achieved. Consequently, the WGS reaction stage and energy intensive

122 CO_2 purification steps, which are the essential steps for conventional DME production process, are

123 avoided. After gasification, a heat recovery system is included to generate steam from the heat

124 recovered from the hot syngas. A portion of the steam generated is fed back to the gasification unit.

125 In order to prevent catalyst deactivation, conventional H_2S removal process is installed. The clean

126 syngas is then introduced to DME synthesis reactor, in which the single-step DME synthesis occurs.

127 DME of a desired purity is produced via a series of separation operations and CO_2 (produced as a

128 product in DME synthesis process) is collected with a portion being recycled to the gasification

129 section.

Normally, fluidized-bed gasifiers are used in the gasification of biomass which are operated in the temperature range of 750-1100 ^{o}C and the corresponding oxidising agent/biomass mass ratio is in the range of 0.3-0.5. In this study, a sensitivity analysis was conducted to show the dependence of syngas composition on operating conditions, the purpose of which is to find appropriate operating parameters to achieve a desired syngas composition, i.e. to achieve a H_2/CO ratio of 1 and CO_2 concentration of about 3 mol%. In the simulation, biomass was fed into the gasifier (operating pressure 0.1 MPa) at a flow rate of 1000 kg/h whilst the flow rate of steam (150.8 °C and 0.5 MPa) was fixed at 150 kg/h. Based on the sensitivity analysis, in order to meet the requirement in terms of syngas composition, the gasification temperature was controlled at 950 ^{o}C and CO_2 was fed into the gasifier at a flow rate of 345 kg/h. At the exit of the gasifier, syngas left at 950 °C and 0.1 MPa. The hot syngas was then cooled down to 250 °C in a waste heat recovery unit, compressed to 5 MPa and transported to the syngas purification system. Steam (0.5 MPa, 150.8 ^{o}C) was generated using heat recovered from the system, a portion of which was consumed in the gasification unit. ZnO-based purification process was used in this study for H_2S removal. H_2S concentration in syngas was reduced to below 1 ppm before it was fed to synthesis reactor. The operating conditions of the DME synthesis unit were 250 °C and 5 MPa. The gas leaving the DME synthesis reactor was cooled down by using a heat exchanger designed to cool the product gas mixture down to - 40 °C. CO_2 was used as a coolant in the cooling process. DME was condensed along with CO_2 and water discharged from the DME synthesis reactor. The product stream was then depressurised down to 3 MPa in a flash separator. The non-condensable gases were separated through a flash separator and the condensed gases were then fed into the DME distillation column. A distillation tower with 10 trays was used for the purification of DME, which was operated at 3 MPa. The raw DME was introduced on the 5th tray from the top. The reflux ratio was chosen as 1.2. The bottom product contained 97.3 mol% of DME while the top product had a CO_2 concentration of 83.5 mol%, a portion of which was then fed to the gasification section as an oxidizing agent.

155   In this study, process simulation was carried out using Aspen Plus^{TM} (Aspen Tech Inc., USA)

156   software and was mainly based on mass and energy balances, and chemical equilibrium of the

157   overall process. The Aspen system consists of "packages" corresponding to unit operation, which

158   can be used to simulate most industrial operations. It has also been used to study DME production

159   based on biomass gasification [10, 16]. The Aspen Plus^{TM} simulation flowsheet of single-step DME

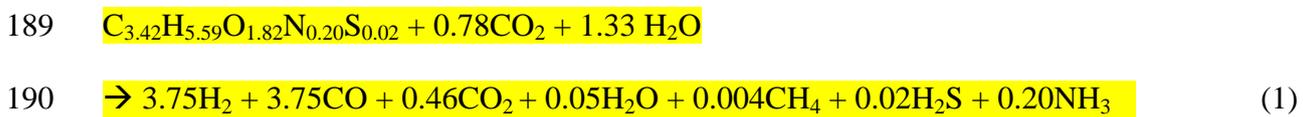160   production based on CO_2-enhanced gasification is shown in Fig. 2.

161   In this simulation, the stream classification was specified as MIXCINC to enable the inclusion of

162   gases, conventional inert solids and/or non-conventional materials. The input stream 'BIOMASS'

163   was defined as a non-conventional solid. In this study, the gasifier was simulated as two separate

164   reactors (RYield and RGibbs). Firstly, BIOMASS stream entered into DECOMP (RYield) block.

165   Here, the mass flow rates of each component were fixed by defining the yield distribution based on

166   the ultimate analysis data of rice straw. This is not an actual stand-alone reactor but an integral part

167   of the gasification reactor. The RYield reactor served to convert the non-conventional solids into

168   gas components and ash before being fed into RGibbs reactor. This block was modelled using

169   Aspen Plus^{TM} biomass digestion reactor the same as described elsewhere [13, 15, 17]. The output from

170   the DECOMP (RYield) block was then fed to the GASIFIER (RGibbs) block. The GASIFIER

171   (RGibbs) served to convert the decomposed biomass into syngas by reacting with steam and CO_2.

172   GASFEED stream (does not exist in any actual processes) served as a means of transferring the

173   constituent elements of the decomposed biomass to the actual gasification reactor. Thus, heat input

174   to the gasifier included heat duty of RYield and RGibbs reactors. The syngas was sent to the

175   SSEPARAT (SSplit) block to remove ash. STEAMREC (HeatX) block was used to recover heat

176   from hot syngas before being sent to H2SSEP (Sep2) block for H_2S separation. The cleaned syngas

177   was then directed to REACTOR (RStoic) block where DME synthesis occurred. The gas mixture

178   leaving the DME synthesis reactor was cooled down by HEAT (MHeatX) block and consequently,

179   non-condensable gases were removed using a FLASH (Flash) separator. Finally, DME product was

180   obtained as the bottom product while liquid CO_2 was collected as the top product of a distillation

181 column (Distl). Details of input data and operation parameters for the simulation are shown in
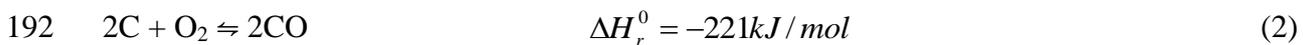
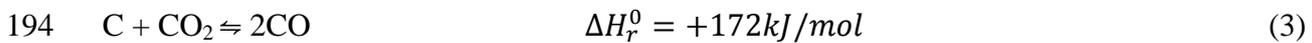182 Table 2.

183

2.3 Basics of single-step synthesis of DME

185 The overall reaction occurring during the steam and/or CO_2 gasification can be represented by

186 reaction (1) (based on typical operating conditions adopted in this study), which involves multiple

187 reactions and pathways. Reactions (2)-(6) are the main reactions based on the simulation
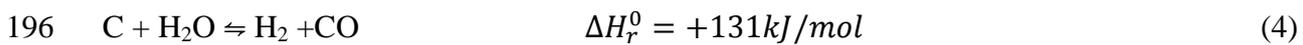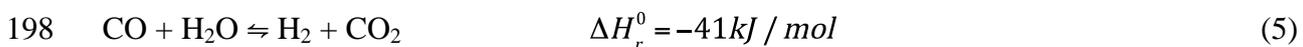
188 assumptions adopted in this study [3, 12, 18]:

189 $C_{3.42}H_{5.59}O_{1.82}N_{0.20}S_{0.02} + 0.78CO_2 + 1.33\ H_2O$

190 $\rightarrow 3.75H_2 + 3.75CO + 0.46CO_2 + 0.05H_2O + 0.004CH_4 + 0.02H_2S + 0.20NH_3$ (1)

191 Partial oxidation:

192 $2C + O_2 \leftrightharpoons 2CO$ $\Delta H_r^0 = -221 kJ/mol$ (2)

193 Boudouard reaction:

194 $C + CO_2 \leftrightharpoons 2CO$ $\Delta H_r^0 = +172 kJ/mol$ (3)

195 Steam reforming:

196 $C + H_2O \leftrightharpoons H_2 + CO$ $\Delta H_r^0 = +131 kJ/mol$ (4)

197 Water-gas shift reaction (WGS):

198 $CO + H_2O \leftrightharpoons H_2 + CO_2$ $\Delta H_r^0 = -41 kJ/mol$ (5)

199 Methane reforming:

200 $CH_4 + H_2O \leftrightharpoons 3H_2 + CO$ $\Delta H_r^0 = +206 kJ/mol$ (6)
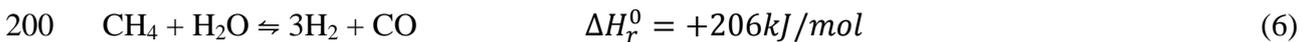
201 Following reaction routes are involved for the single-step DME synthesis:

202 (a) The overall DME synthesis reaction can be expressed by reaction (7) if WGS does not

203   contribute to the reaction.

204      $4H_2 + 2CO \leftrightharpoons CH_3OCH_3 + H_2O$ (7)

205 (b) The overall DME synthesis reaction can be illustrated by reaction (8) if WGS takes place.

206 $\quad$ $3H_2 + 3CO \leftrightharpoons CH_3OCH_3 + CO_2$ $\qquad$ (8)

207 JFE process and Hardlor Topsoe process are the commonly used single-step DME synthesis

208 technologies. A H_2/CO ratio of 2 is normally used in the Hardlor Topsoe process, whereas a H_2/CO

209 ratio of 1 is used in JFE process, which is shown clearly in reactions (7) and (8). Reported data

210 showed that reaction (8) is more cost-effective [3], the conversion and selectivity is affected by

211 operating conditions such as the catalyst used, gas composition, reaction temperature and pressure

212 etc. In this study, JFE process was chosen and the H_2/CO ratio was set to be 1 in the simulation

213 accordingly.

214 **2.4 Performance indices**

215 Gasification performance is evaluated by parameters such as cold gas efficiency (*CGE*),

216 gasification system efficiency (GSE) and gas yield (Y_{GAS}).

217 *CGE* can be calculated using following equation:

218 $\quad$ $CGE = \dfrac{M_{syngas}LHV_{syngas}}{M_{biomass}LHV_{biomass}}$ $\qquad$ (9)

219 where, M_{syngas} and $M_{biomass}$ are mass flow rates of syngas and biomass respectively.

220 Gasification system efficiency can be expressed as follows:

221 $\quad$ $GSE = \dfrac{M_{syngas}LHV_{syngas} + Q_4}{M_{biomass}LHV_{biomass} + Q_1 + Q_2 + Q_3}$ $\qquad$ (10)

222 where Q_4 is energy recovered from hot syngas (kJ/h), Q_1 is energy consumption for steam

223 generation (kJ/h), Q_2 is energy consumption for CO_2 generation (kJ/h) and Q_3 is the heat required

224 to maintain a desired temperature inside the gasifier (kJ/h).

3   Results and Discussion

3.1   Performance of gasification system

3.1.1   Influence of CO_2 addition on syngas production

The simulation was performed to investigate how CO_2 addition under different operating conditions affects the composition, the yield and the H_2/CO ratio of syngas. Fig. 3a shows how the mole fractions of H_2, CO and H_2/CO ratio in syngas vary with different CO_2/Biomass ratios when gasification conditions are fixed as T = 950 ^{o}C, P = 0.1 MPa, steam/biomass = 0.15.

It can be seen that regardless of the operating temperature, operating pressure and steam/biomass ratio, the percentage of H_2 decreases while that of CO increases with respect to CO_2 addition. Consequently, H_2/CO ratio in syngas decreases. The enhancement of CO production with the increase of CO_2 concentration can be attributed to the forward Boudouard reaction and, possibly, the reverse WGS reaction, which also results in the reduction of H_2 in syngas. The amount of methane in syngas is reduced as the steam reacts with methane to form H_2 and CO. As a result, there is a significant change in H_2/CO ratio over a range of CO_2/Biomass as shown in Fig. 3a. Therefore, steam is added to increase H_2 production to maintain the H_2/CO ratio constant.

The steam/Biomass ratio and CO_2/Biomass ratio required to achieve $H_2/CO = 1$ is shown in Fig. 3b. It is clear that the amount of steam required to maintain $H_2/CO = 1$ increases with the amount of CO_2 used as more steam is needed to facilitate the formation of more H_2 due to the competing gasification of CO_2 and steam with biomass. The formation of syngas increases steadily up to a steam/biomass ratio of 0.2. Beyond this point, the syngas production increases rapidly. This is consistent with the findings that syngas production is favourable at higher steam flow rates. From Fig. 3b, it is evident that CO_2 addition favours syngas production under the operating conditions studied. Although Fig. 3b can be used to determine three variables, i.e., steam/Biomass, CO_2/Biomass and syngas flow rate, to achieve the desired $H_2/CO = 1$, further study is still needed to better understand the energy requirements for such a process.

3.1.2 Effects of gasifier temperature on syngas production

Generally, temperature affects gasification reactions. It is therefore a crucial parameter for the simulation of DME synthesis based on biomass gasification. Fig. 3c shows how composition of syngas changes with gasification temperature when the other parameters are kept constant. It can be seen from Fig. 3c that H_2 production increases sharply with gasification temperature and at the same time CO_2 production decreases.

It is found that CO production increases significantly with the increase in temperature, which exceeds the production of H_2 at around 950 °C. In gasification process, CH_4 in syngas is mainly formed during pyrolysis [18-19]. The production of CH_4 decreases steadily within the temperature investigated in this study. When temperature is in the range of 500 °C to 600 °C, the pyrolysis of rice straw dominates the process. With the increase of gasification temperature, the endothermic reactions are enhanced. It might be the case that endothermic reactions 3, 4 and 6 contribute to the increase of H_2 while the CO mole fraction increases because of the enhanced reactions of 2 and 4 (at higher temperatures). Meanwhile, CO is generated from H_2 via reverse WGS reaction. It was found that the production rate of CO is greater than that of H_2. Although the endothermic reaction (6) could contribute to the formation of CO_2, reactions (2) and (3) are more favoured under these operating conditions, which consequently lead to the increase in the yield of CO and the reduction in the formation of CO_2.

In addition, the strengthened endothermic reaction (6) results in the decrease of CH_4 mole fraction [18-19]. The relationship between gasification temperature and CO_2 addition for the production of syngas with H_2/CO =1 is illustrated in Fig. 3d (P = 0.1 MPa, H_2/CO = 1 and steam/Biomass = 0.15). There is a steady decrease of %CO_2 in syngas with temperature as shown in Fig. 3b. The CO_2 concentration decreases sharply from 13.4% to 4.4% when temperature is raised from 700 °C to 890 °C. At 950 °C, the CO_2 concentration in syngas was found to be 0.029 mol%, which is favourable for the single-step DME synthesis.

275 In this study, it is also found that CO_2/Biomass ratios decrease with the increasing gasification

276 temperature. This is due to the fact that higher temperatures favour the gasification process (as

277 opposed to pyrolysis). Subsequently, the amount of CO_2 required for biomass gasification is

278 reduced. Based on Figs. 3c and 3d, optimum process conditions can therefore be determined.

279 3.1.3 Effects of CO_2 addition on CGE, GSE, LHV and gas yield

280 CGE is an important parameter to show the performance of a gasifier. Normally, the calculation of

281 CGE does not consider heat required for the gasification process, therefore it cannot be used to

282 evaluate CO_2-enhanced gasification of biomass due to the extra energy required to allow such a

283 process to occur. Because of this, a new factor, GSE, was proposed [12], which takes into account

284 the extra energy required for the gasification system.

285 Generally, in a gasification process, gasifier consumes the highest amount of energy. Besides the

286 gasifier, steam generator and CO_2 supply unit are the other major energy consumers. Fig. 4a shows

287 the differences in CGE and GSE at different CO_2/biomass ratios (0.1 MPa, 950 °C, Steam/Biomass

288 = 0.15). It is clear that CGE increases progressively with the increase of CO_2/biomass ratio, while

289 GSE decreases steadily. Nonetheless, as syngas increases with CO_2 addition, the energy

290 requirement for the generation of syngas will rise at an even higher rate. This means that the

291 addition of CO_2 does not significantly increase syngas production but has a significant influence on

292 energy consumption of the entire process. It is apparent that GSE is a better index to be used to

293 evaluate the performance of CO_2-enhanced gasification process as the energy input is being

294 included into the gasification unit. Hence, in this study, GSE was used as the main index to assess

295 gasification performance. To control syngas composition, in the simulation, CO_2/biomass ratio and

296 steam/biomass ratio were chosen as 0.345 and 0.15, respectively; the corresponding gasification

297 system efficiency was 36.7%.

298 The calculated LHV of product gas and gas yield under different CO_2/Biomass ratios are shown in

299 Fig. 4b (T = 950 °C, P = 0.1 MPa, steam/biomass = 0.15). It is clear that the increase of

300 CO_2/Biomass at the same steam/Biomass ratio results in the increase in gas yield and the decrease

301 in LHV. As mentioned in previous section, the concentration of combustible gas decreases with the

302 addition of CO_2. Therefore, LHV of the product gas decreases as the CO_2/Biomass increases.

3.2 DME synthesis via CO_2-enhanced biomass gasification

304 In this study, H_2/CO ratio in syngas was selected to be 1 since the JFE process was adopted for

305 DME synthesis, the stoichiometry of which is of H_2/CO = 1. In the gasification unit, steam was

306 used as a gasifying agent together with CO_2, which was used as an oxidizing agent as well as a

307 measure to adjust H_2/CO ratio in the reaction system. Important gasification operating parameters,

308 such as temperature, pressure, steam flow rate and CO_2 flow rate, were tuned to achieve the desired

309 H_2/CO ratio in syngas. Hence, the conventional water gas shift unit and energy intensive CO_2

310 removal unit were avoided in the proposed DME synthesis process. Since CO_2 concentration is a

311 crucial factor to achieve high conversion efficiency for DME synthesis, during the optimisation

312 stage, the CO_2 concentration in syngas was kept below 3 mol%, which is acceptable for the JFE

313 process.

314 Before syngas is fed into DME synthesis reactor, it has to be purified to remove H_2S to avoid the

315 DME synthesis catalyst being poisoned [3, 20]. The operating parameters of the DME synthesis

316 reactor, such as temperature (250 °C), pressure (5 MPa), and DME selectivity (0.91), were adopted

317 based on other researchers' work [3, 15, 17].

318 Based on the simulation, it was found that the yield of DME for the proposed process was 0.466

319 kg/kg of biomass, which is more efficient than what was reported by other researchers [3]. In

320 addition, in this study, heat recovered from the entire system could potentially produce 470 kg/h of

321 steam, which is more than the amount of steam needed for the gasification (150 kg/h).

322 As the amount of CO_2 being injected into the gasifier has significant influence on the H_2/CO ratio

323 in syngas (as shown in Fig. 3), the influence of CO_2 addition to DME production was also

324 evaluated in this study. From Fig. 5a, it can be seen that CO_2/biomass ratio in the feed gas affected

325 DME production significantly. DME concentration in the product increased significantly with

326 CO_2/Biomass mass ratio until it reached 0.1, after which DME concentration only increases at a

13

327 moderate rate. In addition, it is also found that the flow rate of DME increased continuously with

328 the increase in the rate of CO_2 feed.

329 The effect of CO_2 concentration in syngas on DME production is shown in Fig. 5b. It is clear that

330 lower CO_2 concentration in syngas favoured the formation of DME, which is consistent with other

331 researcher's finding [15]. It was reported that CO_2 affects hydrogenation process and the

332 performance of the bi-functional catalyst [21]. Accordingly, at high CO_2 concentration, the rate of

333 methanol dehydration is reduced, which subsequently deteriorates the overall reaction system. Fig.

334 5b shows that syngas with zero or trace amount of CO_2 could increase DME concentration at the

335 exit by 30 mol%. The conversion of DME was inversely proportional to CO_2 concentration in the

336 range studied in this paper.

337 However, although it is technically feasible to reduce CO_2 concentration in syngas to ppm level, it

338 is not economically viable to do so since the complete removal of CO_2 from syngas requires high

339 capital investment and high operating costs. In this study, 3.0 mol% of CO_2 in the syngas was

340 chosen in the simulation, which leads to 30.9 mol% of DME in the product stream.

341 ## 3.3 Sustainability assessment and process optimisation

342 To evaluate the economics and environmental performance of bio-DME production via CO_2-

343 enhanced biomass gasification, a comprehensive assessment was carried out based on the results

344 derived in the previous process simulation.

345 ### 3.3.1 Economic analysis

346 Raw material cost is the most important variable for the economic assessment of DME production.

347 In this study, the production cost was assumed to be proportional to the cost of raw materials

348 required in the process, which is dependent on the conversion efficiency and selectivity of DME

349 synthesis. Generally, natural gas-based JFE process produces 1.31 kg of DME from 1 kg of natural

350 gas [22], whereas DME synthesis based on conventional biomass gasification only produces 0.37 kg

351 of DME from 1 kg of wood [3]. However, in this work, the proposed DME production based on

14

352   CO_2-enhanced gasification was more efficient in terms of raw materials used, the production of 1

353   kg of DME only consumed 2.17 kg of rice straw material. Thus, it is clear that the consumption of

354   biomass by using CO_2-enhanced gasification for DME synthesis is 19.6% less than that of

355   conventional biomass gasification based approaches, which contributes to the reduction of raw

356   material cost. Fig. 6 shows how price of biomass affects the production costs of DME using natural

357   gas DME production as a benchmark. It is clear that if only raw material costs are taken into

358   account in the cost evaluation, the production of DME based on CO_2-enhanced gasification is more

359   profitable when the price of biomass is below 0.68 of the price of natural gas. Hence, it is

360   reasonable to conclude that CO_2-enhanced biomass gasification presents a more cost-effective

361   approach for DME production.

362   **3.3.2   Environmental analysis**

363   Environmental analysis mainly focuses on pollutant emissions, especially on CO_2 and H_2S

364   emissions. In this study, H_2S was reduced to below 1 ppm in syngas. This obviously contributes to

365   the environmental friendly production of bio-DME via CO_2-enhanced gasification of biomass.

366   Total CO_2 emission per kg of DME produced from this study in comparison with data reported in

367   literature is presented in Table 3. In general, the production of biomass-based DME produces less

368   CO_2 compared with that of DME produced using coal or natural gas as raw materials. Among these

369   data reported by other researchers, the net amount of CO_2 emitted by DME production using wood

370   as feedstock was 2.33 kg per kg of DME produced, slightly lower than carbon emission using fossil

371   fuel as raw materials. Since biomass is a carbon neutral material, bio-DME production still presents

372   far better environmental benefits in terms of CO_2 emission reduction. It is clear from Table 3 that,

373   in the present work, the net CO_2 emission was 1.31 kg/kg of DME, which is much lower than the

374   reported data [3, 15, 17]. This suggests that DME based on CO_2-enhanced gasification could

375   significantly reduce the total emission of CO_2. Normally, the complete conversion of 1000 kg of

376   rice straw for energy conversion would normally result in 1506.5 kg/h of CO_2 emission (calculated

377   based on the ultimate analysis data shown in Table 1). Since the raw material, rice straw, is carbon

378 neutral, the release of this amount of CO_2 does not contribute to the net emission of CO_2. However,

379 in this study, only 612 kg/h of CO_2 emitted for the consumption of 1000 kg/h of biomass. This

380 means that DME production via CO_2-enhanced biomass gasification has the potential to lead to

381 negative net CO_2 emission. Moreover, if CO_2 generated from this biomass-based DME production

382 is stored underground or is used to produce useful chemicals via polygeneration, it could further

383 reduce the net CO_2 emission.

384 **3.3.3 Process optimisation**

385 Normally, poly-generation systems, which simultaneously produce power, chemicals and other

386 clean products, are normally more efficient than conventional processes. In this study, to optimise

387 bio-DME production, the concept of poly-generation is adopted to explore opportunities for more

388 cost-effective production of bio-DME.

389 The optimised biomass gasification based on poly-generation concept was proposed and presented

390 in Fig. 7. Since the removal of CO_2 and H_2S has positive impacts on DME conversion efficiency

391 and the performance of catalyst, an energy efficient membrane-based purification process was

392 included in the optimised process. This technology offers an alternative to existing thermal

393 separation technologies, particularly for solvent dehydration and CO_2 separation [23]. The recovered

394 syngas is used to generate electricity in a power generation unit, which can be used inside the plant.

395 This is beneficial since the production of DME and power by once through (OT) approach has been

396 proved to be a feasible alternative to the conventional DME production via recycle approach (RC)

397 [24]. Furthermore, extra heat available from the process can also be used for power generation. By

398 applying the input process parameters described in previous section, the proposed optimised

399 process could achieve a DME yield of 380 kg/h with a net electricity generation of 0.53 MW when

400 1000 kg/h of biomass is fed to the system. This demonstrated that the OT route to produce DME

401 and electricity simultaneously is a more efficient option, particularly to overcome the problems

402 associated with low DME conversion process. Moreover, if a dividing-wall column (DWC) is

403 installed in the process to replace the conventional energy intensive distillation, it could further

404 save up to 30% of capital investment and up to 40% of operation costs [8].

4 Conclusions

406 A novel route for Bio-DME production based on CO_2-enhanced gasification of biomass was

407 developed using Aspen Plus^{TM} simulator. The results showed that gasification performance and

408 synthesis process were significantly influenced by CO_2/biomass and steam/biomass ratios. To

409 achieve a desired syngas concentration, CO_2/biomass and steam/biomass ratios were found to be

410 0.345 and 0.15, respectively, with a GSE of 36.7%. The DME production rate was 466 kg/h with a

411 concentration of 97.3 mol%. It is found that CO_2 removal prior to DME synthesis significantly

412 enhanced DME conversion. In addition, compared with conventional gasification, the proposed

413 process requires 19.6% less biomass than DME production via conventional biomass gasification,

414 which makes the process more efficient and more cost-effective, and releases only 1.31 kg of CO_2

415 for the production of 1 kg of DME. Furthermore, the utilisation of unreacted gases and handling of

416 CO_2 generated by incorporating poly-generation concept or carbon storage could potentially further

417 improve the overall process efficiency, environmental benefit as well as process economics.

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References

[1]   S. Ahlgren, A. Baky, S. Bernesson, Å. Nordberg, O. Norén, P. A. Hansson, *Biosystems Engineering* **2008**, *99*, 145-155.

[2]   R. P. Anex, A. Aden, F. K. Kazi, J. Fortman, R. M. Swanson, M. M. Wright, J. A. Satrio, R. C. Brown, D. E. Daugaard, A. Platon, G. Kothandaraman, D. D. Hsu, A. Dutta, *Fuel* **2010**, *89, Supplement 1*, S29-S35.

[3]   F. Ju, H. Chen, X. Ding, H. Yang, X. Wang, S. Zhang, Z. Dai, *Biotechnology Advances* **2009**, *27*, 599-605.

[4]   L. Y. Wang T, Ma L, Wu C, *Frontiers in Energy* **2011**, *5*, 330-339.

[5]   T. Silalertruksa, S. H. Gheewala, M. Sagisaka, K. Yamaguchi, *Applied Energy* **2013**, *112*, 560-567.

[6]   C. Arcoumanis, C. Bae, R. Crookes, E. Kinoshita, *Fuel* **2008**, *87*, 1014-1030.

[7]   J. Chang, Y. Fu, Z. Luo, *Biomass and Bioenergy* **2012**, *39*, 67-72.

[8]   Z. Azizi, M. Rezaeimanesh, T. Tohidian, M. R. Rahimpour, *Chemical Engineering and Processing: Process Intensification* **2014**, *82*, 150-172.

[9]   Y. Lv, T. Wang, C. Wu, L. Ma, Y. Zhou, *Biotechnology Advances* **2009**, *27*, 551-554.

[10]   W.-Z. Lu, L.-H. Teng, W.-D. Xiao, *Chemical Engineering Science* **2004**, *59*, 5455-5464.

[11]   M. Y. Yotaro O, Tsutomu S, Osamu I, Takashi O, Norio I, *JFE Technical Report* **2008**, *8*, 34-40.

[12]   P. Chaiwatanodom, S. Vivanpatarakij, S. Assabumrungrat, *Applied Energy* **2014**, *114*, 10-17.

[13]   N. Sadhwani, Z. Liu, M. R. Eden, S. Adhikari, in *Computer Aided Chemical Engineering, Vol. Volume 32* (Eds.: K. Andrzej, T. Ilkka), Elsevier, **2013**, pp. 421-426.

[14]   I. Sircar, A. Sane, W. Wang, J. P. Gore, *Fuel* **2014**, *119*, 38-46.

[15]   K. B. Kabir, K. Hein, S. Bhattacharya, *Computers & Chemical Engineering* **2013**, *48*, 96-104.

[16]   S. Bhattacharya, K. B. Kabir, K. Hein, *Progress in Energy and Combustion Science* **2013**, *39*, 577-605.

[17]   H.-J. Chen, C.-W. Fan, C.-S. Yu, *Applied Energy* **2013**, *101*, 449-456.

[18]   M. Niu, Y. Huang, B. Jin, X. Wang, *Industrial & Engineering Chemistry Research* **2013**, *52*, 14768-14775.

[19]   N. Ramzan, A. Ashraf, S. Naveed, A. Malik, *Biomass and Bioenergy* **2011**, *35*, 3962-3969.

[20]   P. Haro, F. Trippe, R. Stahl, E. Henrich, *Applied Energy* **2013**, *108*, 54-65.

458 [21] D. M. Brown, B. L. Bhatt, T. H. Hsiung, J. J. Lewnard, F. J. Waller, *Catal. Today* **1991**, *8*,
459 279-304.

460 [22] T. Ogawa, N. Inoue, T. Shikada, O. Inokoshi, Y. Ohno, in *Studies in Surface Science and*
461 *Catalysis, Vol. Volume 147* (Eds.: B. Xinhe, X. Yide), Elsevier, **2004**, pp. 379-384.

462 [23] P. Shao, R. Y. M. Huang, *Journal of Membrane Science* **2007**, *287*, 162-179.

463 [24] G. Liu, E. D. Larson, *Energy Procedia* **2014**, *63*, 7367-7378.

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