



# The University of Bradford Institutional Repository

<http://bradscholars.brad.ac.uk>

This work is made available online in accordance with publisher policies. Please refer to the repository record for this item and our Policy Document available from the repository home page for further information.

To see the final version of this work please visit the publisher's website. Access to the published online version may require a subscription.

**Link to original published version:** <http://dx.doi.org/10.1002/ente.201500349>

**Citation:** Parvez AM, Mujtaba IM, Hall P, Lester EH and Wu T (2016) Synthesis of Bio-Dimethyl Ether Based on Carbon Dioxide-Enhanced Gasification of Biomass: Process Simulation Using Aspen Plus. *Energy Technology*. 4(4): 526-535.

**Copyright statement:** © 2016 Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim. Full-text reproduced in accordance with the publisher's self-archiving policy.

# Synthesis of bio-dimethyl ether (Bio-DME) based on CO<sub>2</sub>-enhanced gasification of biomass: Process simulation using Aspen Plus<sup>TM</sup>

A. M. Parvez<sup>a</sup>, I. M. Mujtaba<sup>b</sup>, P. Hall<sup>a</sup>, E. Lester<sup>c</sup>, T. Wu<sup>a,d,\*</sup>

<sup>a</sup> Department of Chemical and Environmental Engineering, The University of Nottingham Ningbo China, Ningbo 315100, China

<sup>b</sup> Chemical Engineering Division, School of Engineering, University of Bradford, Bradford BD7 1DP, UK

<sup>c</sup> Department of Chemical and Environmental Engineering, The University of Nottingham, Nottingham NG7 2RD, UK

<sup>d</sup> Key Laboratory of Clean Energy Conversion Technologies, The University of Nottingham Ningbo China, Ningbo 315100, China

## **Abstract**

Process simulation of a single-step synthesis of DME based on CO<sub>2</sub>-enhanced gasification of rice straw was conducted using Aspen Plus<sup>TM</sup>. 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<sub>2</sub> concentration in syngas to a very low level prior to synthesis. A gasification system efficiency of 36.7% and CO<sub>2</sub> emission of 1.31 kg/kg of DME were achieved. Bio-DME production based on CO<sub>2</sub>-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<sub>2</sub> generated via incorporating poly-generation concept or carbon storage, which could also potentially improve process economics.

**Keywords:** Bio-DME; CO<sub>2</sub>-enhanced gasification; Aspen plus<sup>TM</sup>; 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<sup>[1]</sup> 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

29 at Fukushima Daiichi nuclear power plant in March 2011. Therefore, more attention is now being  
30 paid to renewable energy, especially bioenergy <sup>[2]</sup> 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 <sup>[3]</sup>. 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 <sup>[3-4]</sup>. 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) <sup>[5]</sup>.  
40 Compared with many other diesel fuels, DME shows a better performance in terms of low NO<sub>x</sub>  
41 emission, zero SO<sub>x</sub> emission and extremely low particulate matter emission <sup>[5-6]</sup>. In principle, DME  
42 can be produced using a variety of biomass as feedstock, such as rice straw <sup>[4-5, 7]</sup>. 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 <sup>[3]</sup>. 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 <sup>[8]</sup>. 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<sup>[4, 7]</sup>. In addition, the initial capital investment is much lower  
54 than that of the double-step process.

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

63 Although DME production based on the gasification of fossil fuels has become commercially  
64 available for long time, not much work has been carried out on DME production using biomass as a  
65 feedstock. This is because the low H<sub>2</sub>/CO ratio and high CO<sub>2</sub> concentration in syngas presents a  
66 major challenge to biomass-based DME production <sup>[4, 9, 12]</sup>.

67 In theory, the use of CO<sub>2</sub> as an oxidising agent could improve biomass conversion and CO  
68 production significantly <sup>[12-13]</sup>. It is found that CO concentration in syngas can be adjusted by CO<sub>2</sub>-  
69 enhanced biomass gasification <sup>[13]</sup>. It can therefore be used to facilitate the desired syngas  
70 composition for various applications, for example, increasing the use of CO<sub>2</sub> as a gasifying agent to  
71 achieve a lower H<sub>2</sub> yield and a higher CO yield in syngas, together with a higher thermal efficiency  
72 <sup>[12, 14]</sup>. However, in spite of the huge potential of using CO<sub>2</sub> in biomass gasification en route to  
73 DME synthesis, only limited studies have been conducted to find out optimum design conditions  
74 for better processes. The simulation of DME production based on CO<sub>2</sub>-enhanced biomass  
75 gasification has not yet been studied extensively.

76 In this study, Aspen Plus<sup>TM</sup> was used to simulate DME production based on CO<sub>2</sub>-enhanced  
77 gasification of biomass. Efforts were made to evaluate the impacts of individual operating  
78 conditions on the process efficiency, H<sub>2</sub>/CO ratio etc. Furthermore, the needs for future  
79 development are also identified in this work.

## 80 2 Methodology

### 81 2.1 Feedstock selection

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

84

### 85 2.2 Process description

86 In this study, it was assumed that DME was synthesized via a single-step process. The single-step  
87 synthesis of DME based on conventional gasification and CO<sub>2</sub>-enhanced gasification is illustrated  
88 in Fig. 1.

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

93 Gasification Process: Generally, syngas can be produced from different feedstock including  
94 biomass. In gasification unit, it is assumed that carbon (C), hydrogen (H) and oxygen (O) in  
95 biomass are converted into CO, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>. Meanwhile, H<sub>2</sub>S (originated from sulphur in  
96 biomass) and NH<sub>3</sub> (originated from nitrogen in biomass) are also formed during gasification  
97 process.

98 Water Gas Shift (WGS): In conventional DME synthesis process, syngas from the gasification unit  
99 is introduced to a WGS unit to adjust its H<sub>2</sub>/CO ratio to a desired level. A heat recovery system is  
100 coupled with the WGS unit to recover waste heat for steam production.

101 Purification Unit: In gasification unit, sulphur and nitrogen in feedstock are converted into gas  
102 pollutants, such as H<sub>2</sub>S, COS, NH<sub>3</sub> and HCN, etc. The presence of H<sub>2</sub>S is poisonous to synthesis  
103 catalyst, whilst the excessive amount of CO<sub>2</sub> in syngas normally results in deteriorated conversion

104 efficiency in DME synthesis. It is therefore necessary to removal H<sub>2</sub>S from the syngas and lower  
105 CO<sub>2</sub> 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<sub>2</sub>-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<sub>2</sub> 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<sub>2</sub>/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<sub>2</sub>), allows the desired H<sub>2</sub>/CO molar ratio and CO<sub>2</sub>  
121 concentration in syngas to be achieved. Consequently, the WGS reaction stage and energy intensive  
122 CO<sub>2</sub> 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<sub>2</sub>S 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<sub>2</sub> (produced as a  
128 product in DME synthesis process) is collected with a portion being recycled to the gasification  
129 section.

130 Normally, fluidized-bed gasifiers are used in the gasification of biomass which are operated in the  
131 temperature range of 750-1100 °C and the corresponding oxidising agent/biomass mass ratio is in  
132 the range of 0.3-0.5. In this study, a sensitivity analysis was conducted to show the dependence of  
133 syngas composition on operating conditions, the purpose of which is to find appropriate operating  
134 parameters to achieve a desired syngas composition, i.e. to achieve a H<sub>2</sub>/CO ratio of 1 and CO<sub>2</sub>  
135 concentration of about 3 mol%. In the simulation, biomass was fed into the gasifier (operating  
136 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)  
137 was fixed at 150 kg/h. Based on the sensitivity analysis, in order to meet the requirement in terms  
138 of syngas composition, the gasification temperature was controlled at 950 °C and CO<sub>2</sub> was fed into  
139 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.  
140 The hot syngas was then cooled down to 250 °C in a waste heat recovery unit, compressed to 5  
141 MPa and transported to the syngas purification system. Steam (0.5 MPa, 150.8 °C) was generated  
142 using heat recovered from the system, a portion of which was consumed in the gasification unit.  
143 ZnO-based purification process was used in this study for H<sub>2</sub>S removal. H<sub>2</sub>S concentration in  
144 syngas was reduced to below 1 ppm before it was fed to synthesis reactor. The operating conditions  
145 of the DME synthesis unit were 250 °C and 5 MPa. The gas leaving the DME synthesis reactor was  
146 cooled down by using a heat exchanger designed to cool the product gas mixture down to - 40 °C.  
147 CO<sub>2</sub> was used as a coolant in the cooling process. DME was condensed along with CO<sub>2</sub> and water  
148 discharged from the DME synthesis reactor. The product stream was then depressurised down to 3  
149 MPa in a flash separator. The non-condensable gases were separated through a flash separator and  
150 the condensed gases were then fed into the DME distillation column. A distillation tower with 10  
151 trays was used for the purification of DME, which was operated at 3 MPa. The raw DME was  
152 introduced on the 5<sup>th</sup> tray from the top. The reflux ratio was chosen as 1.2. The bottom product  
153 contained 97.3 mol% of DME while the top product had a CO<sub>2</sub> concentration of 83.5 mol%, a  
154 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<sup>TM</sup> (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 <sup>[10, 16]</sup>. The Aspen Plus<sup>TM</sup> simulation flowsheet of single-step DME  
160 production based on CO<sub>2</sub>-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<sup>TM</sup> biomass digestion reactor the same as described elsewhere <sup>[13, 15, 17]</sup>. 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<sub>2</sub>.  
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<sub>2</sub>S 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<sub>2</sub> was collected as the top product of a distillation

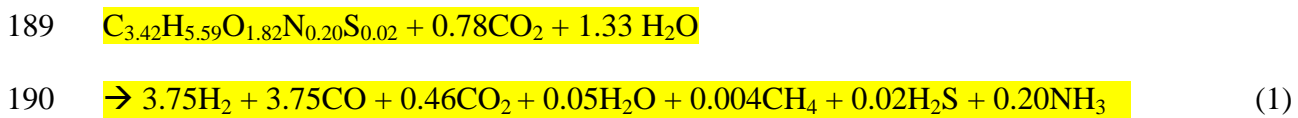


181 column (Distl). Details of input data and operation parameters for the simulation are shown in  
182 Table 2.

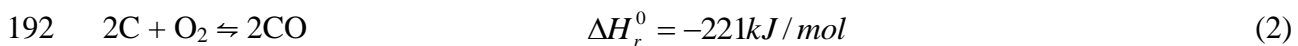
183

### 184 2.3 Basics of single-step synthesis of DME

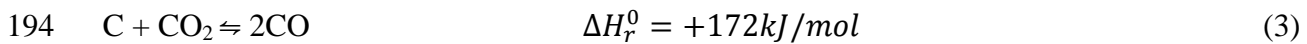
185 The overall reaction occurring during the steam and/or CO<sub>2</sub> gasification can be represented by  
186 reaction (1) (based on typical operating conditions adopted in this study), which involves multiple  
187 reactions and pathways. Reactions (2)-(6) are the main reactions based on the simulation  
188 assumptions adopted in this study [3, 12, 18].



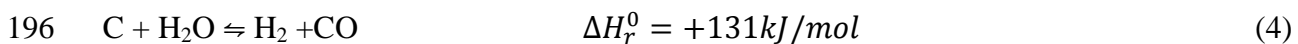
191 Partial oxidation:



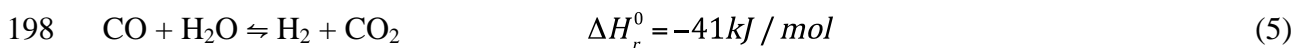
193 Boudouard reaction:



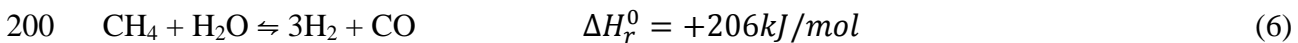
195 Steam reforming:



197 Water-gas shift reaction (WGS):



199 Methane reforming:



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.



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



207 JFE process and Hardlor Topsoe process are the commonly used single-step DME synthesis  
208 technologies. A H<sub>2</sub>/CO ratio of 2 is normally used in the Hardlor Topsoe process, whereas a H<sub>2</sub>/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<sub>2</sub>/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<sub>GAS</sub>*).

217 *CGE* can be calculated using following equation:

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

219 where, *M<sub>syngas</sub>* and *M<sub>biomass</sub>* are mass flow rates of syngas and biomass respectively.

220 Gasification system efficiency can be expressed as follows:

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

222 where *Q<sub>4</sub>* is energy recovered from hot syngas (kJ/h), *Q<sub>1</sub>* is energy consumption for steam  
223 generation (kJ/h), *Q<sub>2</sub>* is energy consumption for CO<sub>2</sub> generation (kJ/h) and *Q<sub>3</sub>* is the heat required  
224 to maintain a desired temperature inside the gasifier (kJ/h).

## 225 **3 Results and Discussion**

### 226 **3.1 Performance of gasification system**

#### 227 **3.1.1 Influence of CO<sub>2</sub> addition on syngas production**

228 The simulation was performed to investigate how CO<sub>2</sub> addition under different operating conditions  
229 affects the composition, the yield and the H<sub>2</sub>/CO ratio of syngas. Fig. 3a shows how the mole  
230 fractions of H<sub>2</sub>, CO and H<sub>2</sub>/CO ratio in syngas vary with different CO<sub>2</sub>/Biomass ratios when  
231 gasification conditions are fixed as T = 950 °C, P = 0.1 MPa, steam/biomass = 0.15.

232 It can be seen that regardless of the operating temperature, operating pressure and steam/biomass  
233 ratio, the percentage of H<sub>2</sub> decreases while that of CO increases with respect to CO<sub>2</sub> addition.

234 Consequently, H<sub>2</sub>/CO ratio in syngas decreases. The enhancement of CO production with the  
235 increase of CO<sub>2</sub> concentration can be attributed to the forward Boudouard reaction and, possibly,  
236 the reverse WGS reaction, which also results in the reduction of H<sub>2</sub> in syngas. The amount of  
237 methane in syngas is reduced as the steam reacts with methane to form H<sub>2</sub> and CO. As a result,  
238 there is a significant change in H<sub>2</sub>/CO ratio over a range of CO<sub>2</sub>/Biomass as shown in Fig. 3a.  
239 Therefore, steam is added to increase H<sub>2</sub> production to maintain the H<sub>2</sub>/CO ratio constant.

240 The steam/Biomass ratio and CO<sub>2</sub>/Biomass ratio required to achieve H<sub>2</sub>/CO = 1 is shown in Fig. 3b.

241 It is clear that the amount of steam required to maintain H<sub>2</sub>/CO = 1 increases with the amount of  
242 CO<sub>2</sub> used as more steam is needed to facilitate the formation of more H<sub>2</sub> due to the competing  
243 gasification of CO<sub>2</sub> and steam with biomass. The formation of syngas increases steadily up to a  
244 steam/biomass ratio of 0.2. Beyond this point, the syngas production increases rapidly. This is  
245 consistent with the findings that syngas production is favourable at higher steam flow rates. From  
246 Fig. 3b, it is evident that CO<sub>2</sub> addition favours syngas production under the operating conditions  
247 studied. Although Fig. 3b can be used to determine three variables, i.e., steam/Biomass,  
248 CO<sub>2</sub>/Biomass and syngas flow rate, to achieve the desired H<sub>2</sub>/CO = 1, further study is still needed  
249 to better understand the energy requirements for such a process.

### 250 3.1.2 Effects of gasifier temperature on syngas production

251 Generally, temperature affects gasification reactions. It is therefore a crucial parameter for the  
252 simulation of DME synthesis based on biomass gasification. Fig. 3c shows how composition of  
253 syngas changes with gasification temperature when the other parameters are kept constant. It can be  
254 seen from Fig. 3c that H<sub>2</sub> production increases sharply with gasification temperature and at the  
255 same time CO<sub>2</sub> production decreases.

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

268 In addition, the strengthened endothermic reaction (6) results in the decrease of CH<sub>4</sub> mole fraction  
269 [18-19]. The relationship between gasification temperature and CO<sub>2</sub> addition for the production of  
270 syngas with H<sub>2</sub>/CO =1 is illustrated in Fig. 3d (P = 0.1 MPa, H<sub>2</sub>/CO = 1 and steam/Biomass = 0.15).  
271 There is a steady decrease of %CO<sub>2</sub> in syngas with temperature as shown in Fig. 3b. The CO<sub>2</sub>  
272 concentration decreases sharply from 13.4% to 4.4% when temperature is raised from 700 °C to  
273 890 °C. At 950 °C, the CO<sub>2</sub> concentration in syngas was found to be 0.029 mol%, which is  
274 favourable for the single-step DME synthesis.

275 In this study, it is also found that CO<sub>2</sub>/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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>-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 <sup>[12]</sup>, 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<sub>2</sub> supply unit are the other major energy consumers. Fig. 4a shows  
287 the differences in CGE and GSE at different CO<sub>2</sub>/biomass ratios (0.1 MPa, 950 °C, Steam/Biomass  
288 = 0.15). It is clear that CGE increases progressively with the increase of CO<sub>2</sub>/biomass ratio, while  
289 GSE decreases steadily. Nonetheless, as syngas increases with CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>-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<sub>2</sub>/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<sub>2</sub>/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<sub>2</sub>/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<sub>2</sub>. Therefore, LHV of the product gas decreases as the CO<sub>2</sub>/Biomass increases.

### 303 **3.2 DME synthesis via CO<sub>2</sub>-enhanced biomass gasification**

304 In this study, H<sub>2</sub>/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<sub>2</sub>/CO = 1. In the gasification unit, steam was  
306 used as a gasifying agent together with CO<sub>2</sub>, which was used as an oxidizing agent as well as a  
307 measure to adjust H<sub>2</sub>/CO ratio in the reaction system. Important gasification operating parameters,  
308 such as temperature, pressure, steam flow rate and CO<sub>2</sub> flow rate, were tuned to achieve the desired  
309 H<sub>2</sub>/CO ratio in syngas. Hence, the conventional water gas shift unit and energy intensive CO<sub>2</sub>  
310 removal unit were avoided in the proposed DME synthesis process. Since CO<sub>2</sub> concentration is a  
311 crucial factor to achieve high conversion efficiency for DME synthesis, during the optimisation  
312 stage, the CO<sub>2</sub> 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<sub>2</sub>S 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<sub>2</sub> being injected into the gasifier has significant influence on the H<sub>2</sub>/CO ratio  
323 in syngas (as shown in Fig. 3), the influence of CO<sub>2</sub> addition to DME production was also  
324 evaluated in this study. From Fig. 5a, it can be seen that CO<sub>2</sub>/biomass ratio in the feed gas affected  
325 DME production significantly. DME concentration in the product increased significantly with  
326 CO<sub>2</sub>/Biomass mass ratio until it reached 0.1, after which DME concentration only increases at a

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<sub>2</sub> feed.

329 The effect of CO<sub>2</sub> concentration in syngas on DME production is shown in Fig. 5b. It is clear that  
330 lower CO<sub>2</sub> concentration in syngas favoured the formation of DME, which is consistent with other  
331 researcher's finding <sup>[15]</sup>. It was reported that CO<sub>2</sub> affects hydrogenation process and the  
332 performance of the bi-functional catalyst <sup>[21]</sup>. Accordingly, at high CO<sub>2</sub> 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<sub>2</sub> could increase DME concentration at the  
335 exit by 30 mol%. The conversion of DME **was** inversely proportional to CO<sub>2</sub> concentration in the  
336 range studied in this paper.

337 However, although it is technically feasible to reduce CO<sub>2</sub> concentration in syngas to ppm level, it  
338 is not economically viable to do so since the complete removal of CO<sub>2</sub> from syngas requires high  
339 capital investment and high operating costs. In this study, 3.0 mol% of CO<sub>2</sub> 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<sub>2</sub>-  
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 <sup>[22]</sup>, whereas DME synthesis based on conventional biomass gasification only produces 0.37 kg  
351 of DME from 1 kg of wood <sup>[3]</sup>. However, in this work, the proposed DME production based on

352 CO<sub>2</sub>-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<sub>2</sub>-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<sub>2</sub>-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<sub>2</sub>-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<sub>2</sub> and H<sub>2</sub>S  
364 emissions. In this study, H<sub>2</sub>S was reduced to below 1 ppm in syngas. This obviously contributes to  
365 the environmental friendly production of bio-DME via CO<sub>2</sub>-enhanced gasification of biomass.

366 Total CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> emission reduction. It is clear from Table 3 that,  
373 in the present work, the net CO<sub>2</sub> 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<sub>2</sub>-enhanced gasification could  
375 significantly reduce the total emission of CO<sub>2</sub>. Normally, the complete conversion of 1000 kg of  
376 rice straw for energy conversion would normally result in 1506.5 kg/h of CO<sub>2</sub> 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<sub>2</sub> does not contribute to the net emission of CO<sub>2</sub>. However,  
379 in this study, only 612 kg/h of CO<sub>2</sub> emitted for the consumption of 1000 kg/h of biomass. This  
380 means that DME production via CO<sub>2</sub>-enhanced biomass gasification has the potential to lead to  
381 negative net CO<sub>2</sub> emission. Moreover, if CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub>S 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<sub>2</sub> separation<sup>[23]</sup>. 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<sup>[24]</sup>. 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].

#### 405 **4 Conclusions**

406 A novel route for Bio-DME production based on CO<sub>2</sub>-enhanced gasification of biomass was  
407 developed using Aspen Plus<sup>TM</sup> simulator. The results showed that gasification performance and  
408 synthesis process were significantly influenced by CO<sub>2</sub>/biomass and steam/biomass ratios. To  
409 achieve a desired syngas concentration, CO<sub>2</sub>/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<sub>2</sub> 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<sub>2</sub>  
415 for the production of 1 kg of DME. Furthermore, the utilisation of unreacted gases and handling of  
416 CO<sub>2</sub> 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.

#### 418 **5 Acknowledgements**

419 Part of this work is sponsored by Ningbo Bureau of Science and Technology under its Innovation  
420 Team Scheme (2012B82011) and Major R&D Programme (2012B10042), and The Provincial  
421 Innovation Team on the Commercialisation of SO<sub>x</sub> and NO<sub>x</sub> Removal Technologies  
422 (2011R50017). The University of Nottingham Ningbo China is acknowledged for providing  
423 scholarships to the first author.

424

425 **References**

- 426 [1] S. Ahlgren, A. Baky, S. Bernesson, Å. Nordberg, O. Norén, P. A. Hansson, *Biosystems*  
427 *Engineering* **2008**, *99*, 145-155.
- 428 [2] R. P. Anex, A. Aden, F. K. Kazi, J. Fortman, R. M. Swanson, M. M. Wright, J. A. Satrio, R.  
429 C. Brown, D. E. Daugaard, A. Platon, G. Kothandaraman, D. D. Hsu, A. Dutta, *Fuel* **2010**,  
430 *89*, *Supplement 1*, S29-S35.
- 431 [3] F. Ju, H. Chen, X. Ding, H. Yang, X. Wang, S. Zhang, Z. Dai, *Biotechnology Advances*  
432 **2009**, *27*, 599-605.
- 433 [4] L. Y. Wang T, Ma L, Wu C, *Frontiers in Energy* **2011**, *5*, 330-339.
- 434 [5] T. Silalertruksa, S. H. Gheewala, M. Sagisaka, K. Yamaguchi, *Applied Energy* **2013**, *112*,  
435 560-567.
- 436 [6] C. Arcoumanis, C. Bae, R. Crookes, E. Kinoshita, *Fuel* **2008**, *87*, 1014-1030.
- 437 [7] J. Chang, Y. Fu, Z. Luo, *Biomass and Bioenergy* **2012**, *39*, 67-72.
- 438 [8] Z. Azizi, M. Rezaeimanesh, T. Tohidian, M. R. Rahimpour, *Chemical Engineering and*  
439 *Processing: Process Intensification* **2014**, *82*, 150-172.
- 440 [9] Y. Lv, T. Wang, C. Wu, L. Ma, Y. Zhou, *Biotechnology Advances* **2009**, *27*, 551-554.
- 441 [10] W.-Z. Lu, L.-H. Teng, W.-D. Xiao, *Chemical Engineering Science* **2004**, *59*, 5455-5464.
- 442 [11] M. Y. Yotaro O, Tsutomu S, Osamu I, Takashi O, Norio I, *JFE Technical Report* **2008**, *8*,  
443 34-40.
- 444 [12] P. Chaiwatanodom, S. Vivanpatarakij, S. Assabumrungrat, *Applied Energy* **2014**, *114*, 10-  
445 17.
- 446 [13] N. Sadhwani, Z. Liu, M. R. Eden, S. Adhikari, in *Computer Aided Chemical Engineering*,  
447 *Vol. Volume 32* (Eds.: K. Andrzej, T. Ilkka), Elsevier, **2013**, pp. 421-426.
- 448 [14] I. Sircar, A. Sane, W. Wang, J. P. Gore, *Fuel* **2014**, *119*, 38-46.
- 449 [15] K. B. Kabir, K. Hein, S. Bhattacharya, *Computers & Chemical Engineering* **2013**, *48*, 96-  
450 104.
- 451 [16] S. Bhattacharya, K. B. Kabir, K. Hein, *Progress in Energy and Combustion Science* **2013**,  
452 *39*, 577-605.
- 453 [17] H.-J. Chen, C.-W. Fan, C.-S. Yu, *Applied Energy* **2013**, *101*, 449-456.
- 454 [18] M. Niu, Y. Huang, B. Jin, X. Wang, *Industrial & Engineering Chemistry Research* **2013**, *52*,  
455 14768-14775.
- 456 [19] N. Ramzan, A. Ashraf, S. Naveed, A. Malik, *Biomass and Bioenergy* **2011**, *35*, 3962-3969.
- 457 [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.
- 464
- 465