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Synthesis of bio-dimethyl ether (Bio-DME) based on CO\textsubscript{2}-enhanced gasification of biomass: Process simulation using Aspen Plus\textsuperscript{TM}

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Abstract

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

Keywords: Bio-DME; CO\textsubscript{2}-enhanced gasification; Aspen plus\textsuperscript{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\textsuperscript{[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
at Fukushima Daiichi nuclear power plant in March 2011. Therefore, more attention is now being paid to renewable energy, especially bioenergy \(^2\). Biomass is abundant and has the potential to be used for the generation of power as well as for the production of chemicals. It is projected that the use of biomass as an energy source would increase by a factor of 2 to 3 in the next few decades and contribute to a significant reduction of greenhouse gases emission by 2050 \(^3\). The use of biomass as raw materials for the production of the same chemical products as those from fossil fuels could also contribute to the reduction in the emission of greenhouse gases due to its carbon-neutral nature \(^3\)-\(^4\). Therefore, the utilisation of biomass as an alternative energy source and raw materials not only mitigates the greenhouse effect, but also greatly reduce the dependency on fossil fuels.

In the past two decades, work has been carried out to explore the opportunities to use biomass as a promising source for the production of secondary biofuels, such as dimethyl ether (DME) \(^5\). Compared with many other diesel fuels, DME shows a better performance in terms of low NO\(_x\) emission, zero SO\(_x\) emission and extremely low particulate matter emission \(^5\)-\(^6\). In principle, DME can be produced using a variety of biomass as feedstock, such as rice straw \(^4\)-\(^5\), \(^7\). The production of DME using rice straw as the raw materials is an attractive option for China due to the fact that China is the largest producer of rice in the world, and currently most of the rice straw in China is burnt in open field and has caused severe local air pollution.

Double-step synthesis process is the most commonly used process for DME manufacture, which consists of methanol formation and methanol dehydration \(^3\). However, this double-step synthesis includes a number of process stages and requires high capital investment and operation costs. The major disadvantage of such process is its low conversion efficiency due to the thermodynamic limitation for methanol synthesis \(^8\). Recently, new technologies have become available to allow the methanol synthesis and methanol dehydration processes being carried out simultaneously in one reactor, which is defined as single-step synthesis. It is thermodynamically and economically more favourable than the double-step process\(^4\)-\(^7\). In addition, the initial capital investment is much lower 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\textsuperscript{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$_2$S (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$_2$S, COS, NH$_3$ and HCN, etc. The presence of H$_2$S is poisonous to synthesis catalyst, whilst the excessive amount of CO$_2$ in syngas normally results in deteriorated conversion
efficiency in DME synthesis. It is therefore necessary to removal H₂S from the syngas and lower CO₂ concentration to an acceptable level before being fed into the synthesis unit [3-4, 15].

DME Synthesis Unit: After purification, the syngas is transferred to the DME synthesis reactor. In single-step DME synthesis process, the same as other catalytic processes, catalyst plays a vital role in DME selectivity. In this simulation, the catalyst used is assumed to have a DME selectivity of 91%.

DME Separation Unit: Subsequently, DME is separated from the product gases discharged from the DME synthesis reactor and is purified to produce DME at a desired purity.

Fig. 1b shows the single-step DME synthesis based on CO₂-enhanced biomass gasification, which also has five main units: gasification unit, heat recovery unit, purification unit, single-step DME synthesis unit, and DME separation unit. Within each of the mentioned sections, different technologies could be used and the design parameter should then be adjusted accordingly.

In the proposed process, biomass gasification is performed using CO₂ and steam as oxidising agents. The gas generated from biomass gasification contains similar components compared with the conventional biomass gasification process but has an improved molar ratio of H₂/CO for DME synthesis. The adjustment of gasification operating conditions such as temperature, pressure as well as the flow rate of oxidising agents (steam and CO₂), allows the desired H₂/CO molar ratio and CO₂ concentration in syngas to be achieved. Consequently, the WGS reaction stage and energy intensive CO₂ purification steps, which are the essential steps for conventional DME production process, are avoided. After gasification, a heat recovery system is included to generate steam from the heat recovered from the hot syngas. A portion of the steam generated is fed back to the gasification unit.

In order to prevent catalyst deactivation, conventional H₂S removal process is installed. The clean syngas is then introduced to DME synthesis reactor, in which the single-step DME synthesis occurs. DME of a desired purity is produced via a series of separation operations and CO₂ (produced as a product in DME synthesis process) is collected with a portion being recycled to the gasification section.
Normally, fluidized-bed gasifiers are used in the gasification of biomass which are operated in the temperature range of 750-1100 °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 H₂/CO ratio of 1 and CO₂ 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 °C and CO₂ 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 °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 H₂S removal. H₂S 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. CO₂ was used as a coolant in the cooling process. DME was condensed along with CO₂ 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 CO₂ concentration of 83.5 mol%, a portion of which was then fed to the gasification section as an oxidizing agent.
In this study, process simulation was carried out using Aspen Plus™ (Aspen Tech Inc., USA) software and was mainly based on mass and energy balances, and chemical equilibrium of the overall process. The Aspen system consists of “packages” corresponding to unit operation, which can be used to simulate most industrial operations. It has also been used to study DME production based on biomass gasification\[10, 16\]. The Aspen Plus™ simulation flowsheet of single-step DME production based on CO₂-enhanced gasification is shown in Fig. 2.

In this simulation, the stream classification was specified as MIXCINC to enable the inclusion of gases, conventional inert solids and/or non-conventional materials. The input stream ‘BIOMASS’ was defined as a non-conventional solid. In this study, the gasifier was simulated as two separate reactors (RYield and RGibbs). Firstly, BIOMASS stream entered into DECOMP (RYield) block. Here, the mass flow rates of each component were fixed by defining the yield distribution based on the ultimate analysis data of rice straw. This is not an actual stand-alone reactor but an integral part of the gasification reactor. The RYield reactor served to convert the non-conventional solids into gas components and ash before being fed into RGibbs reactor. This block was modelled using Aspen Plus™ biomass digestion reactor the same as described elsewhere \[13, 15, 17\]. The output from the DECOMP (RYield) block was then fed to the GASIFIER (RGibbs) block. The GASIFIER (RGibbs) served to convert the decomposed biomass into syngas by reacting with steam and CO₂. GASFEED stream (does not exist in any actual processes) served as a means of transferring the constituent elements of the decomposed biomass to the actual gasification reactor. Thus, heat input to the gasifier included heat duty of RYield and RGibbs reactors. The syngas was sent to the SSEPARAT (SSplit) block to remove ash. STEAMREC (HeatX) block was used to recover heat from hot syngas before being sent to H2SSEP (Sep2) block for H₂S separation. The cleaned syngas was then directed to REACTOR (RStoic) block where DME synthesis occurred. The gas mixture leaving the DME synthesis reactor was cooled down by HEAT (MHeatX) block and consequently, non-condensable gases were removed using a FLASH (Flash) separator. Finally, DME product was obtained as the bottom product while liquid CO₂ was collected as the top product of a distillation.
column (Distl). Details of input data and operation parameters for the simulation are shown in Table 2.

2.3 Basics of single-step synthesis of DME

The overall reaction occurring during the steam and/or CO\(_2\) gasification can be represented by reaction (1) \(\text{(based on typical operating conditions adopted in this study)}\), which involves multiple reactions and pathways. Reactions (2)-(6) are the main reactions based on the simulation assumptions adopted in this study\(^{[3, 12, 18]}\).

\[
\begin{align*}
C_{3.42}H_{5.59}O_{1.82}N_{0.20}S_{0.02} + 0.78CO_2 + 1.33 H_2O \\
\rightarrow 3.75H_2 + 3.75CO + 0.46CO_2 + 0.05H_2O + 0.004CH_4 + 0.02H_2S + 0.20NH_3
\end{align*}
\]  

(1)

Partial oxidation:

\[
2C + O_2 \rightleftharpoons 2CO \quad \Delta H_r^0 = -221 kJ/mol
\]  

(2)

Boudouard reaction:

\[
C + CO_2 \rightleftharpoons 2CO \quad \Delta H_r^0 = +172 kJ/mol
\]  

(3)

Steam reforming:

\[
C + H_2O \rightleftharpoons H_2 + CO \quad \Delta H_r^0 = +131 kJ/mol
\]  

(4)

Water-gas shift reaction (WGS):

\[
CO + H_2O \rightleftharpoons H_2 + CO_2 \quad \Delta H_r^0 = -41 kJ/mol
\]  

(5)

Methane reforming:

\[
CH_4 + H_2O \rightleftharpoons 3H_2 + CO \quad \Delta H_r^0 = +206 kJ/mol
\]  

(6)

Following reaction routes are involved for the single-step DME synthesis:

(a) The overall DME synthesis reaction can be expressed by reaction (7) if WGS does not contribute to the reaction.

\[
4H_2 + 2CO \rightleftharpoons CH_3OCH_3 + H_2O
\]  

(7)
b) The overall DME synthesis reaction can be illustrated by reaction (8) if WGS takes place.

$$3H_2 + 3CO \rightleftharpoons CH_3OCH_3 + CO_2$$  \hspace{1cm} (8)

JFE process and Hardlor Topsoe process are the commonly used single-step DME synthesis technologies. A $H_2/CO$ ratio of 2 is normally used in the Hardlor Topsoe process, whereas a $H_2/CO$ ratio of 1 is used in JFE process, which is shown clearly in reactions (7) and (8). Reported data showed that reaction (8) is more cost-effective \[3\], the conversion and selectivity is affected by operating conditions such as the catalyst used, gas composition, reaction temperature and pressure etc. In this study, JFE process was chosen and the $H_2/CO$ ratio was set to be 1 in the simulation accordingly.

2.4 Performance indices

Gasification performance is evaluated by parameters such as cold gas efficiency ($CGE$), gasification system efficiency (GSE) and gas yield ($Y_{GAS}$).

$CGE$ can be calculated using following equation:

$$CGE = \frac{M_{syngas}LHV_{syngas}}{M_{biomass}LHV_{biomass}}$$  \hspace{1cm} (9)

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

Gasification system efficiency can be expressed as follows:

$$GSE = \frac{M_{syngas}LHV_{syngas} + Q_4}{M_{biomass}LHV_{biomass} + Q_1 + Q_2 + Q_3}$$  \hspace{1cm} (10)

where $Q_4$ is energy recovered from hot syngas (kJ/h), $Q_1$ is energy consumption for steam generation (kJ/h), $Q_2$ is energy consumption for $CO_2$ generation (kJ/h) and $Q_3$ is the heat required 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\textsubscript{2} addition on syngas production

The simulation was performed to investigate how CO\textsubscript{2} addition under different operating conditions affects the composition, the yield and the H\textsubscript{2}/CO ratio of syngas. Fig. 3a shows how the mole fractions of H\textsubscript{2}, CO and H\textsubscript{2}/CO ratio in syngas vary with different CO\textsubscript{2}/Biomass ratios when gasification conditions are fixed as T = 950 °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\textsubscript{2} decreases while that of CO increases with respect to CO\textsubscript{2} addition. Consequently, H\textsubscript{2}/CO ratio in syngas decreases. The enhancement of CO production with the increase of CO\textsubscript{2} concentration can be attributed to the forward Boudouard reaction and, possibly, the reverse WGS reaction, which also results in the reduction of H\textsubscript{2} in syngas. The amount of methane in syngas is reduced as the steam reacts with methane to form H\textsubscript{2} and CO. As a result, there is a significant change in H\textsubscript{2}/CO ratio over a range of CO\textsubscript{2}/Biomass as shown in Fig. 3a. Therefore, steam is added to increase H\textsubscript{2} production to maintain the H\textsubscript{2}/CO ratio constant.

The steam/Biomass ratio and CO\textsubscript{2}/Biomass ratio required to achieve H\textsubscript{2}/CO = 1 is shown in Fig. 3b. It is clear that the amount of steam required to maintain H\textsubscript{2}/CO = 1 increases with the amount of CO\textsubscript{2} used as more steam is needed to facilitate the formation of more H\textsubscript{2} due to the competing gasification of CO\textsubscript{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\textsubscript{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\textsubscript{2}/Biomass and syngas flow rate, to achieve the desired H\textsubscript{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\textsubscript{2} production increases sharply with gasification temperature and at the same time CO\textsubscript{2} production decreases.

It is found that CO production increases significantly with the increase in temperature, which exceeds the production of H\textsubscript{2} at around 950 °C. In gasification process, CH\textsubscript{4} in syngas is mainly formed during pyrolysis \textsuperscript{[18-19]}. The production of CH\textsubscript{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\textsubscript{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\textsubscript{2} via reverse WGS reaction. It was found that the production rate of CO is greater than that of H\textsubscript{2}. Although the endothermic reaction (6) could contribute to the formation of CO\textsubscript{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\textsubscript{2}.

In addition, the strengthened endothermic reaction (6) results in the decrease of CH\textsubscript{4} mole fraction \textsuperscript{[18-19]}. The relationship between gasification temperature and CO\textsubscript{2} addition for the production of syngas with H\textsubscript{2}/CO =1 is illustrated in Fig. 3d (P = 0.1 MPa, H\textsubscript{2}/CO = 1 and steam/Biomass = 0.15). There is a steady decrease of %CO\textsubscript{2} in syngas with temperature as shown in Fig. 3b. The CO\textsubscript{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\textsubscript{2} concentration in syngas was found to be 0.029 mol%, which is favourable for the single-step DME synthesis.
In this study, it is also found that CO$_2$/Biomass ratios decrease with the increasing gasification temperature. This is due to the fact that higher temperatures favour the gasification process (as opposed to pyrolysis). Subsequently, the amount of CO$_2$ required for biomass gasification is reduced. Based on Figs. 3c and 3d, optimum process conditions can therefore be determined.

3.1.3 Effects of CO$_2$ addition on CGE, GSE, LHV and gas yield

CGE is an important parameter to show the performance of a gasifier. Normally, the calculation of CGE does not consider heat required for the gasification process, therefore it cannot be used to evaluate CO$_2$-enhanced gasification of biomass due to the extra energy required to allow such a process to occur. Because of this, a new factor, GSE, was proposed $^{[12]}$, which takes into account the extra energy required for the gasification system.

Generally, in a gasification process, gasifier consumes the highest amount of energy. Besides the gasifier, steam generator and CO$_2$ supply unit are the other major energy consumers. Fig. 4a shows the differences in CGE and GSE at different CO$_2$/biomass ratios (0.1 MPa, 950 °C, Steam/Biomass = 0.15). It is clear that CGE increases progressively with the increase of CO$_2$/biomass ratio, while GSE decreases steadily. Nonetheless, as syngas increases with CO$_2$ addition, the energy requirement for the generation of syngas will rise at an even higher rate. This means that the addition of CO$_2$ does not significantly increase syngas production but has a significant influence on energy consumption of the entire process. It is apparent that GSE is a better index to be used to evaluate the performance of CO$_2$-enhanced gasification process as the energy input is being included into the gasification unit. Hence, in this study, GSE was used as the main index to assess gasification performance. To control syngas composition, in the simulation, CO$_2$/biomass ratio and steam/biomass ratio were chosen as 0.345 and 0.15, respectively; the corresponding gasification system efficiency was 36.7%.

The calculated LHV of product gas and gas yield under different CO$_2$/Biomass ratios are shown in Fig. 4b (T = 950 °C, P = 0.1 MPa, steam/biomass = 0.15). It is clear that the increase of CO$_2$/Biomass at the same steam/Biomass ratio results in the increase in gas yield and the decrease
3.2 DME synthesis via CO₂-enhanced biomass gasification

In this study, H₂/CO ratio in syngas was selected to be 1 since the JFE process was adopted for DME synthesis, the stoichiometry of which is of H₂/CO = 1. In the gasification unit, steam was used as a gasifying agent together with CO₂, which was used as an oxidizing agent as well as a measure to adjust H₂/CO ratio in the reaction system. Important gasification operating parameters, such as temperature, pressure, steam flow rate and CO₂ flow rate, were tuned to achieve the desired H₂/CO ratio in syngas. Hence, the conventional water gas shift unit and energy intensive CO₂ removal unit were avoided in the proposed DME synthesis process. Since CO₂ concentration is a crucial factor to achieve high conversion efficiency for DME synthesis, during the optimisation stage, the CO₂ concentration in syngas was kept below 3 mol%, which is acceptable for the JFE process.

Before syngas is fed into DME synthesis reactor, it has to be purified to remove H₂S to avoid the DME synthesis catalyst being poisoned [3, 20]. The operating parameters of the DME synthesis reactor, such as temperature (250 °C), pressure (5 MPa), and DME selectivity (0.91), were adopted based on other researchers’ work [3, 15, 17].

Based on the simulation, it was found that the yield of DME for the proposed process was 0.466 kg/kg of biomass, which is more efficient than what was reported by other researchers [3]. In addition, in this study, heat recovered from the entire system could potentially produce 470 kg/h of steam, which is more than the amount of steam needed for the gasification (150 kg/h).

As the amount of CO₂ being injected into the gasifier has significant influence on the H₂/CO ratio in syngas (as shown in Fig. 3), the influence of CO₂ addition to DME production was also evaluated in this study. From Fig. 5a, it can be seen that CO₂/biomass ratio in the feed gas affected DME production significantly. DME concentration in the product increased significantly with CO₂/Biomass mass ratio until it reached 0.1, after which DME concentration only increases at a
moderate rate. In addition, it is also found that the flow rate of DME increased continuously with
the increase in the rate of CO₂ feed.

The effect of CO₂ concentration in syngas on DME production is shown in Fig. 5b. It is clear that
lower CO₂ concentration in syngas favoured the formation of DME, which is consistent with other
researcher’s finding [15]. It was reported that CO₂ affects hydrogenation process and the
performance of the bi-functional catalyst [21]. Accordingly, at high CO₂ concentration, the rate of
methanol dehydration is reduced, which subsequently deteriorates the overall reaction system. Fig.
5b shows that syngas with zero or trace amount of CO₂ could increase DME concentration at the
exit by 30 mol%. The conversion of DME was inversely proportional to CO₂ concentration in the
range studied in this paper.

However, although it is technically feasible to reduce CO₂ concentration in syngas to ppm level, it
is not economically viable to do so since the complete removal of CO₂ from syngas requires high
capital investment and high operating costs. In this study, 3.0 mol% of CO₂ in the syngas was
chosen in the simulation, which leads to 30.9 mol% of DME in the product stream.

3.3 Sustainability assessment and process optimisation

To evaluate the economics and environmental performance of bio-DME production via CO₂-
enhanced biomass gasification, a comprehensive assessment was carried out based on the results
derived in the previous process simulation.

3.3.1 Economic analysis

Raw material cost is the most important variable for the economic assessment of DME production.
In this study, the production cost was assumed to be proportional to the cost of raw materials
required in the process, which is dependent on the conversion efficiency and selectivity of DME
synthesis. Generally, natural gas-based JFE process produces 1.31 kg of DME from 1 kg of natural
gas [22], whereas DME synthesis based on conventional biomass gasification only produces 0.37 kg
of DME from 1 kg of wood [3]. However, in this work, the proposed DME production based on
CO₂-enhanced gasification was more efficient in terms of raw materials used, the production of 1 kg of DME only consumed 2.17 kg of rice straw material. Thus, it is clear that the consumption of biomass by using CO₂-enhanced gasification for DME synthesis is 19.6% less than that of conventional biomass gasification based approaches, which contributes to the reduction of raw material cost. Fig. 6 shows how price of biomass affects the production costs of DME using natural gas DME production as a benchmark. It is clear that if only raw material costs are taken into account in the cost evaluation, the production of DME based on CO₂-enhanced gasification is more profitable when the price of biomass is below 0.68 of the price of natural gas. Hence, it is reasonable to conclude that CO₂-enhanced biomass gasification presents a more cost-effective approach for DME production.

3.3.2 Environmental analysis

Environmental analysis mainly focuses on pollutant emissions, especially on CO₂ and H₂S emissions. In this study, H₂S was reduced to below 1 ppm in syngas. This obviously contributes to the environmental friendly production of bio-DME via CO₂-enhanced gasification of biomass. Total CO₂ emission per kg of DME produced from this study in comparison with data reported in literature is presented in Table 3. In general, the production of biomass-based DME produces less CO₂ compared with that of DME produced using coal or natural gas as raw materials. Among these data reported by other researchers, the net amount of CO₂ emitted by DME production using wood as feedstock was 2.33 kg per kg of DME produced, slightly lower than carbon emission using fossil fuel as raw materials. Since biomass is a carbon neutral material, bio-DME production still presents far better environmental benefits in terms of CO₂ emission reduction. It is clear from Table 3 that, in the present work, the net CO₂ emission was 1.31 kg/kg of DME, which is much lower than the reported data [3, 15, 17]. This suggests that DME based on CO₂-enhanced gasification could significantly reduce the total emission of CO₂. Normally, the complete conversion of 1000 kg of rice straw for energy conversion would normally result in 1506.5 kg/h of CO₂ emission (calculated based on the ultimate analysis data shown in Table 1). Since the raw material, rice straw, is carbon
neutral, the release of this amount of CO\textsubscript{2} does not contribute to the net emission of CO\textsubscript{2}. However, in this study, only 612 kg/h of CO\textsubscript{2} emitted for the consumption of 1000 kg/h of biomass. This means that DME production via CO\textsubscript{2}-enhanced biomass gasification has the potential to lead to negative net CO\textsubscript{2} emission. Moreover, if CO\textsubscript{2} generated from this biomass-based DME production is stored underground or is used to produce useful chemicals via polygeneration, it could further reduce the net CO\textsubscript{2} emission.

### 3.3.3 Process optimisation

Normally, poly-generation systems, which simultaneously produce power, chemicals and other clean products, are normally more efficient than conventional processes. In this study, to optimise bio-DME production, the concept of poly-generation is adopted to explore opportunities for more cost-effective production of bio-DME.

The optimised biomass gasification based on poly-generation concept was proposed and presented in Fig. 7. Since the removal of CO\textsubscript{2} and H\textsubscript{2}S has positive impacts on DME conversion efficiency and the performance of catalyst, an energy efficient membrane-based purification process was included in the optimised process. This technology offers an alternative to existing thermal separation technologies, particularly for solvent dehydration and CO\textsubscript{2} separation \[23\]. The recovered syngas is used to generate electricity in a power generation unit, which can be used inside the plant. This is beneficial since the production of DME and power by once through (OT) approach has been proved to be a feasible alternative to the conventional DME production via recycle approach (RC) \[24\]. Furthermore, extra heat available from the process can also be used for power generation. By applying the input process parameters described in previous section, the proposed optimised process could achieve a DME yield of 380 kg/h with a net electricity generation of 0.53 MW when 1000 kg/h of biomass is fed to the system. This demonstrated that the OT route to produce DME and electricity simultaneously is a more efficient option, particularly to overcome the problems associated with low DME conversion process. Moreover, if a dividing-wall column (DWC) is
installed in the process to replace the conventional energy intensive distillation, it could further save up to 30% of capital investment and up to 40% of operation costs [8].

4 Conclusions

A novel route for Bio-DME production based on CO₂-enhanced gasification of biomass was developed using Aspen Plus™ simulator. The results showed that gasification performance and synthesis process were significantly influenced by CO₂/biomass and steam/biomass ratios. To achieve a desired syngas concentration, CO₂/biomass and steam/biomass ratios were found to be 0.345 and 0.15, respectively, with a GSE of 36.7%. The DME production rate was 466 kg/h with a concentration of 97.3 mol%. It is found that CO₂ removal prior to DME synthesis significantly enhanced DME conversion. In addition, compared with conventional gasification, the proposed process requires 19.6% less biomass than DME production via conventional biomass gasification, which makes the process more efficient and more cost-effective, and releases only 1.31 kg of CO₂ for the production of 1 kg of DME. Furthermore, the utilisation of unreacted gases and handling of CO₂ generated by incorporating poly-generation concept or carbon storage could potentially further improve the overall process efficiency, environmental benefit as well as process economics.

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