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Link to publisher's version: *https://doi.org/10.1016/j.biombioe.2018.01.016*

Citation: Parvez AM, Wu T, Li S et al (2018) Bio-DME production based on conventional and CO_2-enhanced gasification of biomass: A comparative study on exergy and environmental impacts. Biomass and Bioenergy. 110: 105-113.

Bio-DME production based on conventional and CO_2-enhanced gasification of biomass: A comparative study on exergy and environmental impacts

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Abstract

In this study, a novel single-step synthesis of dimethyl ether (DME) based on CO_2-enhanced biomass gasification was proposed and simulated using ASPEN Plus^{TM} modelling. The exergetic and environmental evaluation was performed in comparison with a conventional system. It was found that the fuel energy efficiency, plant energy efficiency and plant exergetic efficiency of the CO_2-enhanced system were better than those of the conventional system. The novel process produced 0.59 kg of DME per kg of gumwood with an overall plant energy efficiency of 65%, which were 28% and 5% higher than those of conventional systems, respectively. The overall exergetic efficiency of the CO_2-enhanced system was also 7% higher. Exergetic analysis of each individual process unit in both the CO_2-enhanced system and conventional systems showed that the largest loss occurred at gasification unit. However, the use of CO_2 as gasifying agent resulted in a reduced loss at gasifier by 15%, indicating another advantage of the proposed system. In addition, the LCA analysis showed that the use of CO_2 as gasifying agent could also result in less environmental impacts compared with conventional systems, which subsequently made the CO_2-enhanced system a promising option for a more environmental friendly synthesis of bio-DME.

Keywords: Exergy analysis; Environmental analysis; Bio-DME; CO_2-enhanced gasification; conventional gasification

1 Introduction

Biomass derived dimethyl ether (Bio-DME) is a clean synthetic fuel that has high cetane number and similar physical properties as LPG [1, 2]. The combustion of bio-DME generates small amount of NOx, almost zero SOx and particulate matter. Thus, bio-DME is considered as a sustainable alternative to diesel and LPG. Compared with commercially available double-step synthesis, the single-step synthesis is a better option for DME production due to its low investment and low production costs [3, 4]. Among single-step synthesis technologies developed, JFE technology, a process adopting H_2: CO ratio of 1:1 for DME synthesis, was found to be more cost-effective than other technologies, such as Hardlor Topsoe technology [1, 5].

Over the past two decades, the use of CO_2 as a gasifying agent in biomass gasification has drawn increasing interests [6-8]. One of its unique features in this technology is that the H_2/CO ratio in syngas can be adjusted by controlling the amount of CO_2 injected to gasifier, despite the additional heat need to be supplied into gasifier due to the endothermic nature of reaction involved during gasification [9-11]. Recent research demonstrated that for DME production based on CO_2-enhanced gasification, the water gas shift (WGS) reactor and the energy intensive CO_2 removal process could be avoided while the production of DME could be enhanced [12]. In addition, the pure CO_2 can be easily recycled as CO_2 is a major by-product of DME synthesis. However, not much effort has yet been made to understand the exergy efficiency and environmental impacts of this novel system.

Generally, exergy analysis specifies the location, type and magnitude of process irreversibility [13-15]. It also helps better understand the benefits of energy utilization by providing more useful and meaningful information than what energy analysis could possible provide. Therefore, exergy analysis is commonly used to compare the performance of different processes, such as biomass-gasification and coal-gasification based processes [16-21]. With regard to exergy analysis of bio-DME production, to date, only a few studies have been reported [22, 23]. Exergy analysis of double-step bio-DME production using steam as gasification agent was carried out by Zhang et al.

[23] to measure the exergy efficiency of the entire system as well as the exergy losses occurred in each unit of the system. The reasons behind these losses were explored and suggestions to improve the exergy efficiency of the system were made. Recently, Xiang et al. [22] conducted the exergetic evaluation of a single-step bio-DME production from biomass where pure DME was obtained as the final product. The estimation of system exergetic efficiency and the origin of losses were also identified and quantified. Moreover, the causes of the inefficiencies were investigated and by optimising various process parameters, the higher exergetic efficiency of the system was achieved. However, in spite of the great potential of DME production based on CO_2-enhanced gasification, in depth assessment of this new route has hardly been explored due to the lack of detailed process design. To the best of our knowledge, there is not any published research on the exergetic assessment of bio-DME production using CO_2 as the gasifying agent. In addition, although life cycle assessment (LCA) is commonly used to evaluate environmental impacts of a product over its life cycle [16, 24, 25], the application of LCA approach for the environmental assessment of bio-DME production based on CO_2-enhanced gasification has not been reported.

This study was focused on the simulation of conventional DME synthesis system as well as DME production based on CO_2-enhanced gasification of biomass. The goal of this study was to assess the exergetic and environmental performance of bio-DME production using CO_2 as a gasifying agent. The comparison of energy, exergetic and environmental analyses between the two processes were also carried out. In addition, effort was made to show the location, magnitude and causes of the process unit inefficiencies.

2 Process description and design

2.1 Process overview

Fig. 1 shows the simplified process flow diagrams of the single-step DME production based on conventional and CO_2-enhanced biomass gasification systems. The configurations have been optimized following the guidelines proposed elsewhere [1, 22, 23, 26, 27]. In these systems, biomass feedstock is converted to syngas in a fluidised-bed gasifier, which is then conditioned prior to DME synthesis. The present work was focused on the assessment of the influence of CO_2 addition on the overall system performance.

The gasifiers for the two processes are operated under relatively different conditions. As seen in Fig. 1, the conventional process uses oxygen and steam as the gasifying agent while the CO_2-enhanced process utilises carbon dioxide with steam. For the CO_2-enhanced biomass gasification based DME production (CEBG-DME) process, since H_2/CO ratio can be tuned by selecting proper CO_2/biomass ratio and steam/biomass ratio (as shown in Fig. 1b), the WGS and energy intensive CO_2 separation unit are eliminated. Another beneficial feature of this process is the avoidance of using of the oxygen separation unit, which could cause significant energy consumption as well as high capital and operating costs. As CO_2 is one of the main products of the single-step DME synthesis, in the CEBG-DME system, a portion of the emitted CO_2 is used in the gasifier as the gasifying agent, which helps reduce net CO_2 emission of the system. However, due to the endothermic nature of gasification reactions, additional energy is required to maintain a desired temperature in the gasifier. Since fluidized bed gasifier is used in this study, it was proposed that heat was introduced into the gasifier using an inert energy carrier. However, during simulation, electrically-heated gasifier was considered in the current study.

2.2 Biomass to syngas train

In this study, gumwood was selected as the biomass feedstock because it is widely available in China as well as in South-East Asian countries. Its properties are listed in Table 1 [28].

During gasification, the C, H, and O are transformed to CO, H_2, CO_2, and CH_4, while N and S are converted to NH_3, H_2S and COS, respectively. Since particulates (such as fly ash) that can potentially foul and/or poison the catalyst in the downstream, prior to DME synthesis, particulate matter is removed using a bag filter. A heat exchanger is used in the HRSG unit to recover waste heat to produce steam that is used in gasification unit as well as other process units. Part of the recovered heat is used for electricity generation, which is to meet electricity demand of the entire plant.

In conventional DME synthesis process, the gas product (syngas) is then transported to a WGS unit to adjust the H_2/CO molar ratio of 1 to satisfy the requirement for DME synthesis, followed by the purification prior to synthesis because H_2S is poisonous to the synthesis catalyst [3, 29] and an excessive amount of CO_2 will reduce the conversion efficiency of DME synthesis [2, 12]. In the purification section, a typical chemical absorption process with monoethanolamine (MEA) is selected to remove H_2S and CO_2, which is detailed elsewhere [30, 31].

However, for CO_2-enhanced gasification based DME synthesis (Fig. 1b), the required H_2/CO molar ratio and CO_2 concentration in syngas is attained by adjusting gasification operating parameters such as temperature, CO_2/biomass ratio and steam/biomass ratio. Consequently, the WGS reaction unit and energy intensive CO_2 purification unit, the two essential steps for conventional DME production process (Fig. 1a), are avoided. It is important to note that with the addition of steam in the gasifier, WGS unit in conventional system can be avoided. However, from the perspective of an overall plant economics, this approach is not likely to be feasible, as many factors such as type of gasifier need to be considered. In order to prevent catalyst from being poisoned, only H_2S removal unit is installed.

2.3 Syngas to DME train

The purified syngas is then fed into the compressor and cooler, and subsequently introduced to the single-step synthesis reactor. As the single-step DME reaction is exothermic, to maintain an optimal reaction temperature, certain amount of heat must be removed rapidly from the reaction system, which can be utilized to generate high-pressure steam. Hence, a slurry reactor was considered in this study due to its easiness in temperature control and uniform temperature distribution [1, 22]. The product stream from the synthesis reactor is cooled down and flashed so that the unreacted syngas is separated from the DME-methanol-water mixture. Afterwards, the majority of the unreacted syngas from the flash separator is recycled to DME synthesis reactor. This leads to an overall high DME conversion, while the rest of the stream was purged. The DME–methanol–water mixture contains some residual gas such as CO and CO_2, hence, it is sent to CO_2 removal unit to remove the residual gas. It is essential to note that a fraction of emitted CO_2 by the synthesis reactor is fed to the gasifier as it is used as one of the gasifying agents for the CO_2-enhanced biomass gasification. In the meantime, bottom product of the CO_2 removal unit is fed to the DME distillation unit. Distillate from this unit is taken as DME product. The methanol-water mixture, the bottom product, is sent to methanol distillation unit to separate water from methanol. The recovered methanol is also recycled to the DME reactor, whereas bottom product water, which still contained a very low amount of methanol, requires further purification. A base-case design of this study is illustrated in Fig. 1, which is for the preliminary assessment of a process design and has not yet been optimized at this stage.

2.4 Key gasification parameters

Apart from operating pressure, temperature and oxidising agent are the two important factors that dictate the composition of syngas in any gasification processes. Whilst for syngas, H_2/CO ratio and the percentage of CO_2 are the two crucial parameters that have significant impacts on its purification and application. There are other factors commonly used to evaluate gasification process, such as lower heating value (LHV) of gas product, cold gas efficiency (CGE), and gasification system efficiency (GSE) [9, 10]. Moreover, for JFE single-step DME synthesis, the H_2/CO ratio is also vital, which should be controlled to be 1.

In order to design a process for the highly efficient synthesis of DME, it is important to understand the relationship of these parameters. In this study, the parametric analysis was therefore conducted to optimize the gasification process. The parameters for the gasification process used in this work are listed in Table 2, in comparison with those for a conventional (O_2-steam) process. In addition, for comparison purposes, Table 2 also includes a set of gasification data that were reported by others under similar conditions [1].

3 Methodology

3.1 Process simulation

Simulation of the two DME systems was conducted using Aspen Plus^{TM} to establish materials balance, and to estimate the energy and utility requirements as the inputs for exergy and environmental analysis. Details of assumptions and modelling procedures have been discussed elsewhere [9, 12].

In this study, a RYield module (yield reactor) integrated with a RGibbs module (chemical and phase equilibrium by Gibbs free energy minimisation) was employed to simulate gasifier, which was operated (0.1 MPa). Thus, heat inputs to the gasifier included heat duty of RYield and RGibbs reactors. The operating conditions of the gasifier for both systems are presented in Table 2.

3.2 Model validation

Before thermodynamic evaluation of the studied systems, the CO_2-enhanced gasification model has to be validated. In this study, the model developed was validated against data published by other researchers [10, 21, 32]. As mentioned previously, biomass gasification was modelled using Gibbs minimisation approach, which has been validated with experimental data [33-35]. Since there is no relevant data available on CO_2-enhanced gasification using gumwood as the raw material, in order to validate the model developed in this work, data of steam gasification of wood and CO_2 gasification of biomass were extracted from literature and compared with the simulation results (under the same experimental conditions as adopted in the literature) as shown in Table 3 and Table

4, respectively [10, 21]. Based on these comparisons, it can be concluded that the simulation results are in good agreement with data reported in literature [10, 21, 32]. The deviation was found to be in a range of 4.1%-8.6%. Therefore, the CO_2-enhanced gasification model developed in this study is reliable, and was subsequently used for the prediction of CO_2-enhanced gasification of gumwood.

The product gas from the gasifier was sent to the SSplit (SSEPARAT) module to remove ash, prior to cooling down to 220 ºC. HeatX (HRSG) module was used to recover heat (via steam at 0.5 MPa, 225 ^{o}C) from hot syngas. Afterwards, syngas was sent to WGS reactor to adjust its H_2/CO ratio. The WGS reactor (0.1 MPa, 220 ºC) was modelled with a REquil module. After WGS reactor, the syngas was cooled down to 60 ºC before being directed to syngas purification unit. The removal of CO_2 and H_2S by MEA absorption process in syngas purification unit was modelled as a simple component separator SEP2 module due to the complexity of the system. The energy required for this system was assumed to be 3 MJ/kg of CO_2 captured by MEA absorption process [10]. The single-step DME synthesis was operated at 6 MPa and 250 ºC. The purified syngas was then pressurised, cooled down, and introduced into the DME reactor. A REquil module was employed as the DME reactor to simulate the synthesis process, which is reliable in DME synthesis simulation [36, 37]. The other operating parameters and DME synthesis reactions simulated in the present work were adopted from literatures [36-39].

Product of the DME reactor was cooled down to -30 ºC in MHeatX (X) module and consequently, non-condensable gases were removed using Flash2 (FLASH) separator module. In order to recycle the non-condensable gaseous, most of the gas was sent back to DME reactor and the remainder was purged. After the flash separator, the liquid stream was then sent to the product purification process. This section is consisted of three units, i.e., CO_2 removal unit (2 MPa), DME distillation unit (1.52 MPa) and MeOH unit (1.52 MPa) as illustrated in Fig 1. Distillation column was employed for each of the unit, which was simulated using RadFrac module. The distillation parameters, such as the number of stages and reflux ratio, were set to achieve high purity (99.9

mol%) of DME product. The reaction heat from synthesis reactor was recovered using Heat Stream option in Aspen Plus^{TM} to generate high-pressure steam at 3.5 MPa and 244 ^{o}C.

3.3 Exergy analysis

From a thermodynamic point of view, exergy is defined as the maximum amount of work that can be generated by an energy system as it comes to equilibrium with the reference of environment [15, 17]. It measures both the quality and quantity of energy involved in the conversion within a system. Therefore, it enables the detection of losses and identifies the opportunities for the improvement of energy consumption. The objective of exergy analysis is to identify process units with relatively high inefficiency. In addition, exergy analysis can also be used to compare different process configurations to find better options.

Generally, the exergy balance of individual process unit within energy transformation system can be expressed as:

$$\sum \dot{E}ex_{in} = \sum \dot{E}ex_{out} + \dot{E}ex_{loss} + \dot{E}ex_{des} \quad (1)$$

where, $\sum \dot{E}ex_{in}$ and $\sum \dot{E}ex_{out}$ denote the sums of exergy rates for inlet flows and outlet flows, respectively, including the materials streams, thermal stream and work. The $\dot{E}ex_{loss}$ stands for the exergy loss rate of the streams that exit the system without further use. Meanwhile, $\dot{E}ex_{des}$ depicts the exergy destruction rate, which represents the inefficiencies existed in the system. For simplicity, these two parts were merged in a term called exergy losses and destructions, $\dot{E}ex_{L\&D}$, which is evaluated as follows:

$$\dot{E}ex_{L\&D} = \sum \dot{E}ex_{in} - \sum \dot{E}ex_{out} \quad (2)$$

In the present work, exergy of streams, such as biomass, gases, liquid and heat, was calculated using the concept, which has been explained elsewhere [9, 17, 40, 41]. The considered systems were decomposed into different functional process units. For each unit, exergy balance was performed and $\dot{E}ex_{L\&D}$ was calculated.

3.4 Energy and exergy efficiencies

The fuel energy efficiency is the fraction of energy stored in the biomass that is converted into energy of the fuel product, as given in Eq. (3) [27, 42].

$$\eta_{Fuel} = \frac{E_{fuel,out}}{E_{biomass,in}} \tag{3}$$

where, $E_{fuel,\,out}$ is the energy in the fuel produced and $E_{biomass,in}$ is the energy in the feedstock.

As Eq. (3) does not include all inputs and useful outputs of the system, the plant energy efficiency was also used to evaluate performance of the entire system as shown in Eq. (4).

$$\eta_{Plant} = \frac{E_{fuel,out} + Q_{net,out}}{E_{biomass,in} + E_{agent,in} + E_{Q,in} + E_{W,in}} \tag{4}$$

where, $E_{\mathrm{agent,in}}$, $E_{\mathrm{Q,in}}$, *and* $E_{\mathrm{W,in}}$ are the total energy input as gasification agent, thermal energy and the net work in plant, respectively, whereas $Q_{\mathrm{net,out}}$ represents the total heat output as district heat level.

Gasification process efficiency was evaluated using cold gas efficiency (CGE) and gasification system efficiency (GSE), which are described elsewhere [9].

The system exergy efficiency (η_{ex}) was calculated using Eq. (5) (derived from Eqs. 1 & 4) as the useful exergy content in outlet flows divided by the exergy content in inlet flows.

$$\eta_{ex} = \frac{\dot{Eex}_{out}}{\dot{Eex}_{in}} \quad (5)$$

3.5 Environmental analysis

The goal of environmental analysis was to assess the environmental impacts of CO_2 utilisation in bio-DME production. Thus, investigation was conducted to compare the two scenarios: conventional bio-DME production (scenario 1) and CO_2-enhanced bio-DME production (scenario 2). Energy and exergetic assessment of these two scenarios indicated that using CO_2 as gasification agent can significantly improve the process performance. Moreover, CO_2 was consumed in CO_2-enhanced process. This meant that, the net CO_2 emission in CO_2-enhanced system was lower than that of conventional. The environmental impact assessment was performed using the ReCiPe 2008 v.3.14 method from SimaPro 8.0 software package. ReCiPe 2008 encompasses two sets of impact categories (mid-point level and end-point level) associated with two sets of categorization factors. Detail explanation of impact categories and qualitative indicator can be found elsewhere [9, 43-45]. In the present work, approximately 1 kg of DME produced from conventional and CO_2-enhanced biomass gasification was used as the functional unit for environmental analysis. LCA of individual input and output streams of the overall system, including full life cycle of components, was conducted. The input data (*i.e.*, consumption of feedstock, agents and energy as well as emissions) of this analysis are obtained from Aspen Plus™ simulation results. The system boundaries set for this study are illustrated in Fig. 1. The scope of this study includes the following aspects: (1) supply of biomass, gasification agents and other utilities to the DME production system; (2) production of DME via biomass gasification process; (3) heat recovery from the system; and (4) utilisation of emitted CO_2. Both CO_2 and CH_4 were considered as the main GHG (greenhouse gases) for the assessment of environmental impact.

4 Results and Discussion

In this study, the energetic comparison between conventional and CO_2-enhanced bio-DME production, the biomass consumption per kilogram of DME production, exergy balance of the entire plant and exergy losses and destructions to each unit were carried out to disclose the energy saving mechanism. Finally, the environmental impacts caused by these two routes were assessed using LCA method.

4.1 Mass and energy balances

Table 5 presents the overall mass and energy balances for the two DME production routes, i.e., conventional and CO_2-enhanced processes. The energy balances indicated that biomass feedstock required most of the energy input (37-46%) in the system. It is noted that biomass input with respect to its mass and energy content and the quality of product DME were equalized in both cases; thus, results could be compared. It can be seen from Table 5 that CO_2-enhanced system produced 0.59 kg DME per kg gumwood with a fuel conversion efficiency (detailed in Eq. 3) of 85.0%, which is 18% higher than the conventional process. This was because of higher amount of syngas processed in DME synthesis reactor as a results of using CO_2 in the gasifier which reduced the molar ratio of H_2/CO by increasing CO fraction in syngas [9]. It was also found that the addition of CO_2 reduced the percentage of CH_4 in syngas. Hence, this resulted to a lower amount of purge gas from the synthesis reactor in the CO_2-enhanced system as DME conversion efficiency is generally limited by high CH_4 percentage in syngas [37]. The aforementioned phenomena could also result in a higher DME production rate. An overview of DME system parameters of the present work and published works is given in Table 6, particularly in terms of comparing the mass yield and plant energy efficiency of the systems. Clearly, CO_2-enhanced system produced higher amount of DME, which led to the greater plant energy efficiency. The present work is fundamentally differed from the reported work as it uses CO_2 as the gasifying agent. The CO_2 addition could lead to the increase in CO fraction in syngas which influenced the H_2/CO ratio and the yield of syngas [9]. For instance, H_2/CO ratio of 1 was achieved in the CO_2-enhanced system while the value was around 0.85 in conventional systems. Moreover, the yield of syngas was also increased by 20% in the proposed system. In addition to the improved CO_2-enhanced system proposed in this work, the studied conventional system has also exhibited a better performance than the work conducted by previous researchers, as shown in Table 6. The main difference between this study and reported work [22] was in terms of DME synthesis reactor: equilibrium reactor was used in this study whilst RStoic reactor was used in the reported work [22]. An important feature of equilibrium reactor is that the DME synthesis reactor was assumed to have chemical equilibrium property which resulted in 84% conversion of CO while the RStoic reactor was modelled by assuming only 64% conversion of CO. Consequently, flow rate of the recycled stream in the present work was lower which greatly increased the yield of product DME in the synthesis process. Another potential reason for the high value of yield was that the treated gumwood was considered as a feedstock in the current work, whereas raw sawdust was used in Ref [24]. Similar study was also conducted by others [1] with a mass yield around 0.37. This value was 15% larger than that in [22] but 24% lower compared to the conventional system investigated in the current work. In contrast, a double-step synthesis route was selected by Zhang et al.,[23] and one-pass conversion of methanol to DME was about 70-85%. Accordingly, the conventional system obtained the highest DME yield. Hence, in the present work, the improvement of DME yield in CO_2-enhanced systems was mainly contributed by the utilisation of CO_2 in gasifier, which was not considered in the conventional system, as well as by the employment of equilibrium reactor in synthesis process. As also shown in Table 6, a similar trend was noticed when plant energy efficiencies were compared where the highest efficiency was obtained by the CO_2-enhanced system. Compared to that of conventional system, however, the increase in plant energy efficiency in the CO_2-enhanced system was not as obvious as what was the case in terms of fuel energy efficiency. The reason for such is further explained in the followings.

As shown in Table 5, CO_2-enhanced DME system had a higher plant energy efficiency (detailed in Eq. 4) of 65.97%, which was about 5% higher than that of conventional systems. This was mostly caused by the CO_2-enhanced system having a larger amount of both DME production and heat output. The higher heat output was attributed to two sources: more syngas was produced in the gasifier and the high reaction heat in DME reactor. It can be seen that the demand of total input energy for gasifying agent and net heat generation in CO_2-enhanced system were significantly higher than those of the conventional system. Additionally, the amount of heat required by the gasifier in CO_2-enhanced process was 901,969 MJ/h, which was around 45% larger than that of conventional process. However, this trade-off was worthwhile as the proposed system offered a more significant increment of the plant outputs, which in this case, were DME production and heat output. Besides, CO_2-enhanced system avoided water-gas shift and acid gas cleaning processes, indicating lower capital costs. Thus, the addition of CO_2 was proven to be beneficial in terms of feed consumption, fuel production and economical aspects. Another important feature of the proposed system was that it consumed CO_2, thus, provided considerable environmental advantages.

There are other parameters that might influence the system efficiencies, including the properties of feedstock, system configurations and operating conditions. However, the analysis presented above provides first-hand information about DME yield per kg of biomass via CO_2-enhanced system.

4.2 Exergy analysis of DME production processes

Exergetic efficiency of the DME production process can be calculated based on the evaluation of performance of the entire plant. Moreover, by analysing exergy flows within the plant, efficiencies of individual process units and their significance to the overall plant performance can be estimated. Table 7 presents the exergy balance of the two bio-DME routes compared in this study. In both processes, biomass contributed to the major exergy flow (57-67%) followed by exergy content of heat flows to the system. With respect to plant outputs, DME represented the highest contributor

(83-85%) whereas the additional output such as exergy of steam generated throughout the system was the second highest.

Table 7 also shows a comparison of exergetic efficiency of the bio-DME process between the two routes. Exergetic efficiency of the conventional plant was found to be 50.8% which was higher than those reported by others [22, 23]. Meanwhile, 85% of the total exergy output was contributed by DME. An important aspect of the current conventional system is that it generates more DME per unit mass of biomass than those of the previous work [22, 23], which increased the net production rate. This basically contributed to the higher exergetic efficiency of the current system. Furthermore, various variables including process operating conditions and biomass properties, such as moisture content, usually affect plant exergetic efficiency. Previous research stated that chemical exergy of biomass decreased with the increase of its moisture content [46]. The biomass used in this work contained 2.1 wt% moisture, lower than the values used in reported works which were 13.4 wt% [22] and 7.5 wt% [23]. The aforementioned characteristic also contributed to a higher exergetic efficiency of the present work. The exergetic efficiency of the calculated system was 10% lower compared with its energetic efficiency. This deviation was normal as biomass underwent gasification process at a high temperature, which typically had a higher inefficiency associated with the related chemical reactions [17]. The difference arisen was caused by: (i) energetic performance which only considers energy loss due to emissions to the environment; (ii) exergetic assessment, considers both the external exergy losses (caused by system emissions) and the destruction of internal exergy based on the second law of thermodynamics. Hence, unlike energetic analysis, exergetic analysis is useful in identifying the causes, locations and magnitudes of process inefficiencies in order to improve the performance of the entire system [17, 21, 47]. On the other hand, exergetic efficiency of the CO_2-enhanced system was 57.3%, almost 7% higher than that of conventional one. Out of the 100% useful outputs, DME contributed as much as 83.3% while the rest was the recovered heat from the system. It is worth noting that plant exergetic efficiency and energetic efficiency of the CO_2-enhanced system were higher compared with those of conventional systems, which was previously discussed in Section 4.1. It is found that process efficiency was highly influenced by DME yield, which was also in relation with the exergy content of 30.85 MJ/kg and the heating value (LHV) of 28.40 MJ/kg for the respective exergetic and energetic evaluations. In this case, exergy content and heating value had less influence on the efficiencies since the difference between them was relatively small.

Fig. 2 presents the relative exergy losses and destructions (L&D) for each process unit, which was previously illustrated in Fig. 1.

In both routes, the major exergy losses and destructions were associated with gasifier, methanol tower, CO_2 removal and DME reactor units (38-45%, 7-30%, 3-8% and 4-5%, respectively). These units are therefore endowed with potential for system improvement. On the other hand, the exergy L&Ds of other units such as in HRSG, WGS, Cleaner and DME Tower were much smaller. It is clear from Fig. 2 that gasifier was the critical unit of the system because of it is of the largest value of exergy losses and destructions. Hence, further analysis of this unit is worthwhile in improving the overall exergetic performance of the system. Generally, the exergy losses in the biomass gasification are highly dependent on the heat duty required to achieve chemical equilibrium at the given gasification temperature [21]. It is interesting to note that gasifier in conventional process consumed around 55% (619,056 MJ/h) of the total electricity requirement while the value for gasifier used in CO_2-enhanced process was around 61% (901,969 MJ/h). In the gasifier, the decomposition of large molecules into smaller ones at higher temperatures causes large damage of chemical exergy. Previous studies showed that lower temperatures and higher pressures were beneficial for exergetic performance of the gasification process [19, 21].

Despite the adjustment of operating parameters and/or the use of different types of gasifier could increase the performance of gasifier, it cannot significantly reduce the total losses due to the existence of intrinsic energy and material degradation within gasification process. In addition, adjusting the composition of syngas to improve the process economy also limits the range of operating parameters of the fluidized bed gasifier. It is important to highlight that the main characteristic of CO_2-enhanced system is the use of CO_2 recycled from DME distillation unit as gasification agent. Therefore, the amount of CO_2 or the CO_2/biomass ratio is crucial to plant performance, which needs to be optimized. Accordingly, CO_2/biomass ratio was adjusted in the present work. However, as the amount of CO_2 addition directly affects CO_2 percentage in syngas and there is a limitation of CO_2% in syngas (around 3% maximum), the potential of adjusting CO_2/biomass ratio for exergy efficiency improvement is small, which could only lead to a small increment (1.2%) of exergy efficiency. Since the CO_2/biomass ratio in gasifier (Table 2) has already been optimized, no significant impact was observed.

Similarly, marginal improvement of process efficiency might be achieved by tuning the temperature and pressure of gasifier, and also the temperature of the reacting streams. Thus, the increment of gasification efficiency via controlling the operating parameters is very limited. Upgrading the biomass feedstock via torrefaction could improve the performance but there is a compromise for extra energy required in the process that contributes to further exergy, energy and environmental losses. Other types of irreversibilities, such as fluid dynamic losses and heat losses, might also lead to a further degradation of the energy.

It can be seen from Fig. 2 that the exergy L&D in gasifier of the CO_2-enhanced system was lower (by about 15%) compared to that of the conventional system although additional heat exergy and gasification agent exergy were required. This phenomenon can be explained by the properties of gas generated in the gasifier. The amount of H_2 and CO in the product gas in CO_2-enhanced route was higher (44% and 21%, respectively) while the amount of CO_2 and H_2O was lower (47% and 28%, respectively) than those of the conventional one. The chemical exergy values of H_2 and CO are extremely higher (236100 kJ/kmol and 275100 kJ/kmol, respectively) than those of CO_2 and H_2O (19870 kJ/kmol and 9500 kJ/kmol, respectively). Accordingly, the rise of total exergy was noticed to be directly proportional to the increments of H_2 and CO in the product gas. At the same time, the reduction of CO_2 and H_2O in the product gas led to the decrease of total exergy. Moreover, as extra heat and gasification agent were needed in CO_2-enhanced process, the input exergy to the gasifier was increased, which also resulted in the increase in inefficiencies. Other than H_2 and CO, the total exergy losses due to extra input exergy and the reduction of exergy values contributed by CO_2 and H_2O had less impact to the total exergy. Hence, exergetic efficiency of the CO_2-enhanced route was greater than that of the conventional system. Besides, CO_2-enhanced biomass gasification-based DME production experienced better performance within HRSG, Syn Cleaner, CO_2 removal units. However, exergy L&Ds from the Comp and Cool (compression and cooling) unit in CO_2-enhanced route were higher than those in the conventional route, as more syngas needs to be processed. These units are usually standard products of manufacturing industries, therefore, the potential for further reduction in their exergy losses (*i.e.*, by more efficient equipment) is associated with high costs [48].

In comparison with the gasifier, which involved several reactions and led to low exergetic efficiency, DME synthesis reactor (DME-R) offered a significantly better performance in both routes. This was due to the relatively low chemical exergy stream entered to DME-R was transformed into a product stream that contained a higher chemical exergy. This product stream was obtained due to the formation of compounds, such as DME, MeOH, which had a high standard chemical exergy. The exergy losses in DME-R were mainly derived from the intrinsic synthesis reaction, which is hard to avoid. In this work, the production of DME was analysed based on the two routes. In DME purification process, the major losses were attributed to the MeOH tower unit (7-15%) and CO_2 removal unit (3-7%). It was found that conventional route performed better than CO_2-enhanced route in terms of irreversibilities in MeOH tower unit.

4.3 Environmental analysis

The DME production based on CO_2-enhanced gasification has shown clear advantages against conventional gasification in terms of fuel energetic and exergetic evaluation. An assessment of environmental impacts is therefore needed. Accordingly, LCA-based environmental analysis was conducted to compare the two routes. The environmental impacts caused in mid-points and end-points categories under the investigated operation parameters are presented in Fig. 3 and Fig. 4, respectively. It is obvious that CO_2-enhanced system showed overall less environmental impacts, indicating a better performance compared with the conventional system although the differences in various impact categories between the two systems are not notable. This is as the environmental impacts are affected by many factors which will be detailed in the following paragraphs.

As seen in Fig. 3, there were five significant factors being considered in mid-point category where climate change human health, fossil depletion and climate change ecosystem were the most significant causes whose values were lower in CO_2-enhanced system than those in conventional one. It is worth mentioning that the DME production in CO_2-enhanced system was 28% higher although both total energy consumption and heat recovery were higher than those of conventional system. Accordingly, the consumption of biomass and water per kg DME yield in the CO_2-enhanced system were significantly lower (22% and 9%, respectively), which minimized the energy requirement and therefore reduced environmental impacts. Furthermore, the net CO_2 emission per kg DME in CO_2-enhanced system was lower (about 16%) as it was used as an agent in gasifier. As CO_2 is the key issue in the evaluation of environmental impacts of any processes, hence, the reduction in CO_2 emission normally has a positive effect on environmental impacts. Similar result was noticed with respect to particulate matter formation where its impact was moderate. On the other hand, human toxicity demonstrated an insignificant impact where the values were almost similar for both systems.

Regarding end-points impacts, the CO_2-enhanced system showed lower environmental impacts than those of the conventional system as the end-points merge the information obtained from the mid-points. It can be seen from Fig. 4 that human health combined the three categories of climate change human health, human toxicity and particulate matter formation from the mid-points;

whereas ecosystem and resources stood for climate change ecosystem and fossil depletion, respectively. From the end-points graph, it is obvious that human health and resources were highly influenced than the ecosystem itself, which was around 50% lower than the others. In comparison with conventional system, the CO_2-enhanced system showed a better environmental performance by having a high-energy output, less biomass consumption and less CO_2 emission, which compensated the additional heat and gasifying agent required in the process.

Besides, energetic, exergetic and environmental evaluation, an economic assessment is needed to check the feasibility of the industrial scale bio-DME production based on CO_2-enhanced gasification to compete with the current fossil fuel and biomass-based system. In spite of the huge potential of CO_2 utilization introduced in gasification process for DME system, such advantages that CO_2 can offer is vital in the assessment of gasifier performance as well as the total costs of DME production. Due to the increment of DME production in CO_2-enhanced system, the product costs are lower compared with those of the conventional system where the operation cost and cost related to CO_2 emission are essential factors that will justify the utilization of CO_2 for industrial applications. Furthermore, CO_2-enhanced based bio-DME production process is expected to contribute to more efficient, competitive and sustainable clean fuel in near future, in order to fulfil the recent challenges in more strict environmental regulations regarding low CO_2 emission combined with the demand of low-cost product for the industries.

5 Conclusions

This work adopted thermodynamic and environmental approaches to compare conventional and CO_2-enhanced biomass gasification based bio-DME production. Based on thermodynamic efficiency indexes, *i.e.*, plant energy efficiency and plant exergetic efficiency, the proposed CO_2-enhanced system demonstrated better performance than the conventional system. This improved performance was mainly due to higher DME production and higher heat output. Meanwhile, the exergetic evaluation in both routes showed that the largest loss occurred at the gasifier unit.

However, the addition of CO_2 as a gasifying agent reduced the loss in gasifier unit by 15%. The environmental analysis showed that the CO_2-enhanced system offered a more sustainable approach for bio-DME production. This is another benefit of using CO_2 in gasification compared with the conventional one. These findings could assist in the development and commercialization of CO_2-enhanced bio-DME production.

Acknowledgements

Part of this work is sponsored by Ningbo Bureau of Science and Technology under its Innovation Team Scheme (2012B82011) and Major R&D Programme (2012B10042). The University of Nottingham Ningbo China is acknowledged for providing scholarship to the first author.

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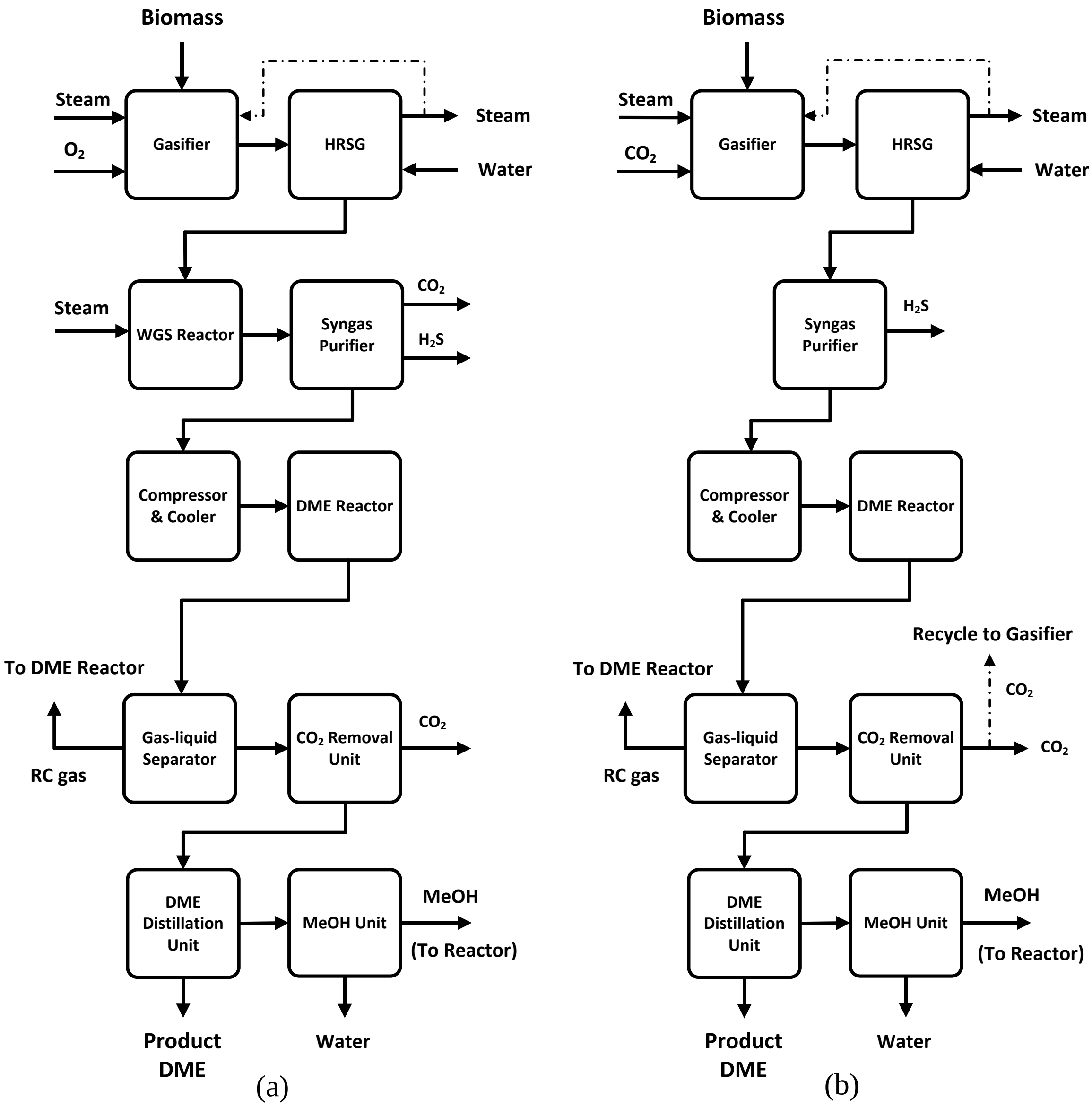

Figure 1: Process flow diagram of the single-step DME production based on (a) conventional and (b) CO_2-enhanced biomass gasification.

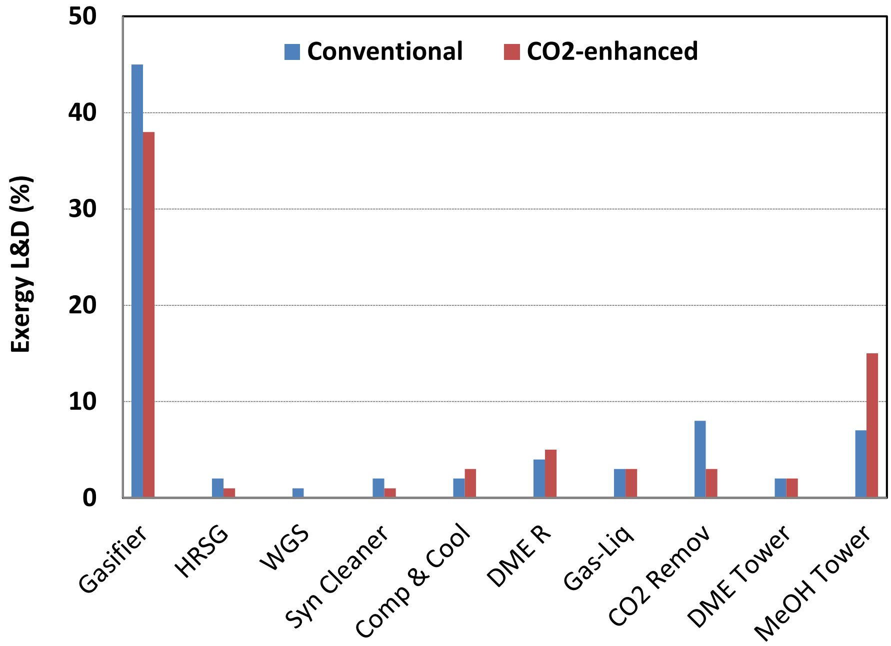

Figure 2: Relative exergy losses and destructions of the considered bio-DME systems.

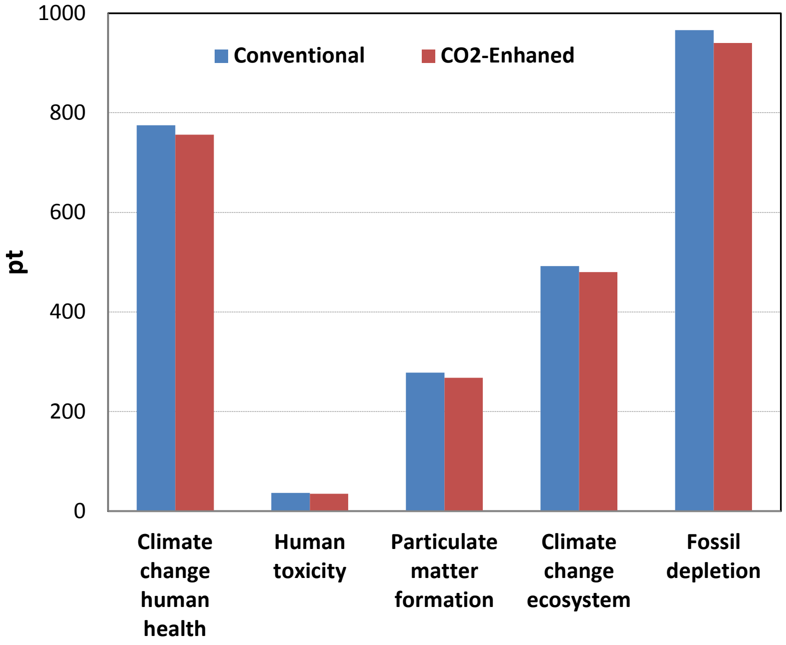

Figure 3: Environmental impacts (ReCiPe) in different categories (mid-points) – conventional bio-DME system and CO_2-enhanced bio-DME system

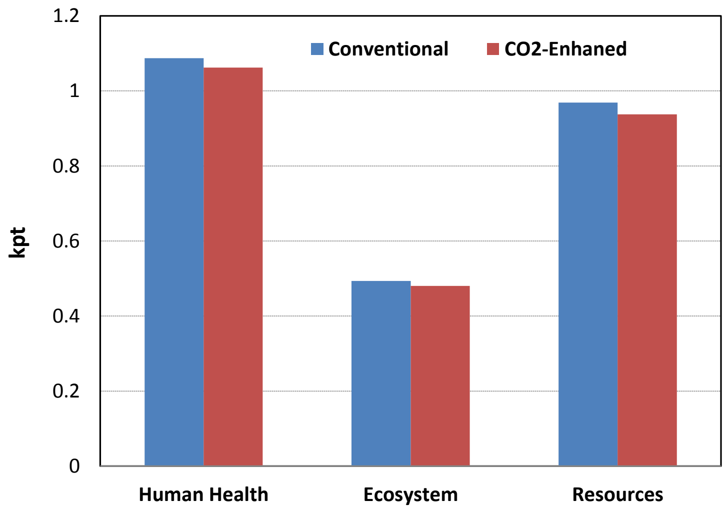

Figure 4: Environmental impacts (ReCiPe) caused in the end-points (Human health, Ecosystem and Resources) – conventional bio-DME system and CO_2-enhanced bio-DME system

Table 1: Properties of gumwood

Net calorific value (MJ/kg)	20.0
Proximate analysis (wt %)	
Moisture	2.1
Volatile matter	86.0
Fixed carbon	11.8
Ash	0.1
Ultimate analysis [a,b] (wt %)	
C	47.1
H	6.3
O[c]	43.5
N	2.1
S	1.0
a: dry basis, b: ash free basis, c: by difference	

Table 2: Gasification process parameters for the considered bio-DME systems.

Parameter	Conventional	CO_2-enhanced	Ju et al. [1]
Temperature (^oC)	900	950	850
Pressure (MPa)	0.1	0.1	0.1
Biomass flow rate (kg/h)	50,000	50,000	75,600
O_2 flow rate at 25 ^oC, 0.1 MPa (kg/h)	15,000	-	unknown
Steam flow rate at 150 ^oC, 0.5 MPa (kg/h)	2,000	11,500	unknown
CO_2 flow rate at 25 ^oC, 0.1 MPa (kg/h)	-	9,500	-
Total gasification agent/Biomass	0.34	0.42	0.51
H_2/CO in syngas	0.85	1.0	1.0
CO_2 mol% in syngas	6.7	2.9	17.0
LHV (MJ/Nm^3)	10.8	11.2	9.7
CGE (%)	70.5	77.8	74.6
GSE (%)	34.5	32.8	-

Table 3: Model validation against the gasification of wood (steam/biomass =0.2, P=0.1 MPa).

Temp (ºC)	**H_2 (mol. fraction)**			**CO (mol. fraction)**			**CO_2 (mol. fraction)**		
	Ref [21]	Present work	Error %	Ref [21]	Present work	Error%	Ref [21]	Present work	Error %
750	0.490	0.510	4.2	0.380	0.362	4.7	0.050	0.047	5.6
800	0.500	0.521	4.3	0.430	0.412	4.3	0.020	0.018	7.5
850	0.500	0.529	5.7	0.450	0.427	5.1	0.013	0.012	7.7
900	0.501	0.531	6.0	0.460	0.4247	7.7	0.008	0.008	6.2
950	0.508	0.543	6.9	0.465	0.446	4.1	0.001	0.0005	4.0
1000	0.510	0.552	8.3	0.470	0.449	4.4	0.0001	9.2E-05	8.0

Table 4: Model validation against CO_2 gasification of biomass ($CH_{1.56}$ $O_{0.78}$, CO_2/C= 0.5, P=0.1 MPa).

Temp (ºC)	**H_2 (mol. fraction)**			**CO (mol. fraction)**			**CO_2 (mol. fraction)**		
	Ref [10]	Present work	Error%	Ref [10]	Present work	Error%	Ref [10]	Present work	Error%
800	0.310	0.331	7.0	0.598	0.572	4.4	0.091	0.085	6.3
1000	0.302	0.320	5.8	0.6248	0.592	5.2	0.073	0.067	8.6
1200	0.294	0.307	4.2	0.643	0.611	5.0	0.063	0.058	8.0

Table 5: Summary of mass and energy balances for the considered bio-DME systems.

	Conventional (0.1 MPa, 900 ^{o}C)	CO_2-enhanced (0.1 MPa, 950 ^{o}C)
Plant inputs		
Biomass (kg/h)	50,000	50000
Biomass (MJ/h)	1,000,000	1,000,000
Oxygen (kg/h)	15,000	-
Oxygen (MJ/h)	-	-
Carbon dioxide (kg/h)	-	9,500
Carbon dioxide (MJ/h)	-	84,930
Steam (kg/h)	2,000	11,500
Steam (MJ/h)	26,380	151,685
Water (kg/h)	35,500	42,000
Water (MJ/h)	3,692	4,368
Electricity (MJ/h)	1,119,411	1,459,642
Plant outputs		
Dimethyl ether (kg/h)	23,312	29,941
Dimethyl ether (MJ/h)	662,061	850,324
Heat (MJ/h)	648,720	931,170
Efficiencies		
Fuel energy efficiency (%)	66.21	85.03
Plant energy efficiency (%)	60.98	65.97

Table 6: Comparison of DME yield and energetic efficiency of different bio-DME systems.

Author	**Gasification system**	**Biomass feedstock**	**Gasification agent**	**DME synthesis**	**DME yield (kg/kg biomass)**	**Plant energy efficiency (%)**
Xiang et al. [22]	Entrained flow (1000 ºC)	Raw sawdust	Steam, O_2	Single-step	0.32	55.2
Zhang et al.[23]	Fluidized bed (880 ºC)	Wood pellets	Steam	Double-step	0.34	51.3
Ju et al.[1]	Fluidized bed (850 ºC)	Wood	Steam, O_2	Single-step	0.37	52.7
Present work	Fluidized bed (900 ºC)	Gum wood	Steam, O_2	Single-step	0.46	60.98
	Fluidized bed (950 ºC)	Gum wood	Steam, CO_2	Single-step	0.59	65.97

Table 7: Summary of exergy flow rate of the considered bio-DME systems.

	Conventional (0.1 MPa, 900 ^{o}C)	CO_2-enhanced (0.1 MPa, 950 ^{o}C)
Plant inputs		
Biomass (MJ/h)	1,056,557	1,056,557
Oxygen (MJ/h)	1,845	-
Carbon dioxide (MJ/h)	-	4,283
Steam (MJ/h)	1,259	7,240
Water (MJ/h)	1,775	1,500
Electricity (MJ/h)	516,953	753,869
Plant outputs		
Product		
Dimethyl ether (MJ/h)	719,545	923,637
Outputs		
Carbon dioxide (MJ/h)	27,778	47,791
Water (MJ/h)	637	430
Purge (MJ/h)	11,873	13,468
Heat		
Heat (MJ/h)	81,861	122,886
Efficiencies		
Exergetic efficiency (%)	50.8	57.3