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Bio-methanol production from palm oil residues: A thermodynamic analysis

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Abstract

The thermodynamic analysis of bio-methanol production from oil palm residues was performed using a process model developed in Aspen Plus. Among the different types of oil palm residues, i.e., trunk, frond, and empty fruit bunch, the trunk residue offers the highest synthesis gas (syngas) (H_2 and CO) yields via the gasification process; therefore, it was selected as the biomass model compound. The effect of gasification operating conditions on the syngas composition, yield, bio-methanol production, energy consumption, and exergy performance was examined. The yield of syngas increased with increasing gasifying temperature, whereas that of bio-methanol exhibited the opposite trend due to the decrease in H_2 concentration of the syngas. The gasifier was an important unit for enhancing the exergy efficiency of the system, which was decreased when the ER and gasifying temperature increased. Recirculating pressure swing adsorption offgas to the gasifier did not benefit bio-methanol production, nor did it improve energy and exergy performance. The maximum yield of bio-methanol was achieved by a once-through process that maintained the gasifying temperature at 750 °C and ER at 0.25. Under these conditions, the maximum energy and exergy efficiencies were 38.57 and 25.44%, respectively.

Keywords: Bio-methanol; Oil palm residues; Gasification; Thermodynamic analysis

1. Introduction

High demand in fossil fuels for chemicals, fuels and energy has caused ever-increasing concern for the adverse effects of global warming. This has consequently motivated the development of pollution-reducing technology, such as carbon capture and utilization (CCU), the enhancement of energy efficiency in manufacturing processes, and the reduction of fossil fuel consumption by using alternatives i.e. renewable energy sources (e.g., wind, solar, and biomass/waste). Among renewable energy sources, only biomass containing hydrogen and carbon elements can be used for either energy or chemicals/fuels.

Palm oil is an important agricultural product in Thailand, and the Thai government has devised a strategic, development plan on expanding biodiesel production using palm oil by 7% per year (2.6 million tons) by 2026 [1]. Therefore, the oil palm production must increase to around 30 million tons per year, generating large amount of unutilized oil palm biomass residues. In 2017, Thailand was the third-largest oil palm producer in the world, where the plantation areas reached 5.25 million acres and were predominantly located in the southern region [2]. Based on the oil palm production of 12.8 million tons, approximately 1.96, 16.36, and 2.21 million tons of unutilized trunk, frond, and empty fruit bunch (EFB) residue were created as by-products [3]. If all these unutilized oil palm residues can be converted into biofuels and/or biochemicals, it would reduce not only agricultural waste but also the dependency upon fossil fuels with in turn greenhouse gas emissions.

Gasification, a partial thermochemical process, is considered as the most efficient and cost-effective process to convert lignocellulosic biomass to synthesis gas (syngas), which can be directly used as a fuel or as an intermediate for synthesizing various biochemicals and biofuels. In the gasification process, the biomass reacts with a gasifying agent (oxygen, air, steam, or CO₂) to produce syngas (mainly H₂ and CO) and others (CO₂, CH₄ and high molecular weight compounds known as tar) [4]. Operating conditions such as gasifying

temperature and pressure, feed material temperature, equivalent ratio (ER) (a ratio of actual air used in the gasification to the stoichiometric air for complete combustion), and steam-to-biomass ratio influence the gasifier performance, which impacts the produced gas composition and biomass conversion efficiency. Lan et al. [5] found that the yield and heating value of the produced gas from gasification of pine wood in a fluidized bed reactor increased with gasifying temperature, while the concentration of CO₂ decreased. However, the increase in yield and heating value of the produced gas was observed when the ER was increased. Raheem et al. [6] reported that gasifying temperature had a strong effect on the fraction of generated product (gas, char and tar) than biomass resident time. Gu et al. [7] found that increasing the gasifying temperature (1000-1200 °C) influenced the product gas composition and heating value, and changes of ER from 0.15 to 0.21 caused the decrease in exergy efficiency of the system while it was stable as the gasifying temperature was varied. AlNouss et al. [8] studied and compared the performance of oxygen and steam fed biomass gasification integrated with a product generation system. From the study, an integrated steam gasification and methanol production process was found to be an optimum route based on economic and environmental objectives. It was reported that steam-CO₂ gasifying agent offered high yield of syngas but low H₂/CO ratio compared to steam-air [9]. Kalinci et al. [10] found that the nature of biomass influenced the product gas composition, as well as the energy and exergy efficiencies of the process. The use of high nitrogen contained-biomass caused the decrease in energy and exergy efficiencies of the system due to the low heating value of nitrogen. Adnan et al. [11] observed that the increase in gasifying pressure had strong impacts on the syngas composition, gasification system efficiency and cold gas efficiency. Moreover, the installation of CO₂ absorber in the gasification process could provide a high-quality syngas. As oil palm biomass residues, i.e., trunk, frond, and EFB, have different compositions and moisture content [12-13], a suitable residue for syngas production should be selected.

Methanol is versatile compound that can be directly used as fuel for internal combustion engines or used for power generation in fuel cells [14]. Moreover, it can be used as an intermediate for synthesizing numerous chemicals, such as formaldehyde, acetic acid, dimethyl ether (DME), and methyl tertiary butyl ether (MTBE) [15]. Commonly, methanol is produced from syngas derived from fossil fuels, i.e., steam reforming of natural gas, partial oxidation of methane, or coal gasification [16], which releases large amount CO₂ along the supply chain. Hence, bio-methanol production from biomass residues is an attractive approach to produce clean and sustainable fuels but also reduce CO₂ emission.

Several studies have been conducted to overcome the technical and economic limitations of methanol synthesis from biomass/residues. Rafael et al. [17] studied methanol production from biogas derived from different sources (landfill garbage, palm oil residue, corn stalks, and fermented sorghum) and found that the biogas derived from palm oil residue offered the highest yield of methanol. Hernandez and Martin [18] optimized the economic and environmental parameters of methanol synthesis from organic-waste-derived biogas (containing 50% methane and 47% CO₂). A production cost was around 1.75 USD gal⁻¹ for the biomass-derived methanol, which unfortunately could not compete with fossil-fuel-derived methanol (production cost of 0.9 USD gal⁻¹). Methanol synthesis from syngas derived from pine biomass gasification was also examined over a range of operating conditions. The offgas from the methanol synthesis unit was also used as fuel for the combustion chamber to eliminate the need for a carbon source for the gasifier [19]. Im-orb and Arpornwichanop [20] fed recycled CO₂ from CO₂ capture unit to the gasifier and studied how different amounts of it would affect a process that combined biomass pyrolysis, gasification, and methanol synthesis. The results indicated that the yield of methanol increased with increasing recycled CO₂, whereas the energy consumption showed the opposite trend. Moreover, the methanol synthesis unit and syngas processor highly contributed toward reducing the potential environmental impact (PEI)

and carbon footprint of the process. Yadav et al. [21] performed the life cycle assessment to analyze and compare the PEI of the conventional bio-methanol production process from wood and that of the novel one in which the wood was chemically pretreated. The impact categories of marine ecotoxicity potential and global warming potential (GWP) of the novel process were lower than those of the conventional one. However, both novel and conventional bio-methanol processes had lower GWP than the fossil-derived methanol.

Most energy production systems employing renewable sources represent their performance based on energy analysis, which considers only the energy entering and leaving the system. Furthermore, energy analysis provides only the quantity of energy, which is calculated based on the first law of thermodynamics and does not guarantee whether the process can actually take place. To overcome this inadequacy, exergy analysis is used to determine the quality of the energy. Exergy is based on the second law of thermodynamics and the concept of irreversible entropy production. Exergy analysis is used to assess the causes, locations, and nature of inefficiencies in a system and offers measurements that explain how close the actual performance of a system approaches the ideal performance [22-23]. Dai et al. [24] performed an exergy analysis to investigate the performance of chemical production from Victorian brown coal through a process combining pyrolysis and entrained-bed gasification. The results indicated that the exergy efficiency of this combined process was 4.5% higher than that of a conventional drying-gasification process, and 1.5% higher than a drying-gasification that used a feed containing 25 wt.% of lignite. Blumberg et al. [25] calculated the energy and exergy efficiency of a medium-capacity methanol production process that operated on natural gas and used carbon dioxide for syngas adjustment. They reported energy and exergy efficiencies of 35.9% and 37.7%, respectively.

Although bio-methanol synthesized from biomass has been studied, it requires further investigation to optimize the system so that it can compete technically nor economically with

fossil-fuel-derived methanol. Most previous studies have mainly focused on the effects caused by varying operating conditions on the product distribution and energy consumption of the process but neglected the exergy analysis. Designing a highly efficient bio-methanol production process from biomass residues via gasification is a promising route that will make it a sustainable and comply with the Thai government policies. Therefore, the aim of this work is to design a sustainable bio-methanol synthesis process, from unutilized oil palm residues, based on the parametric, energy and exergy analyses.

2. Methodological approach

In this study, syngas production from different oil palm residues (Table 1) was firstly investigated, and the one that offered the highest yield was selected as the biomass model compound. The gasifying temperature and ER of the process were then varied to determine if the syngas production, bio-methanol production, and energy consumption were affected. The destruction and efficiency of exergy were then used as indicators to investigate its performance. Finally, the feasibility of PSA offgas to the gasifier was evaluated. A simplified block flow diagram detailing the related reactions and scope of this study, including key parameters and performance indicators, is illustrated in Fig. 1.

Table 1 Ultimate and proximate analyses of oil palm residues [3].

		Unutilized oil palm biomass residue		
		Trunk	Frond	EFB
Proximate analysis				
Moisture	wt. %	8.34	16.0	5.5
Fixed carbon	wt. %	12.2	12.77	18.5
Volatile matter	wt. %	73.16	70.14	69
Ash	wt. %	6.3	1.09	7
Ultimate analysis (dry basis)				
Carbon	wt. %	48.3	44.58	42.33
Hydrogen	wt. %	6.20	4.53	5.28
Nitrogen	wt. %	0.44	0.71	1.46
Oxygen	wt. %	42.65	48.8	50.84
Sulfur	wt. %	0.09	0.07	0.08
Ash	wt. %	6.87	1.3	7

Fig. 1 Simplified flow diagram of bio-methanol production demonstrating the related reactions, performance indicators, and key parameters.

2.1 Modeling of bio-methanol production from biomass

A model of the bio-methanol production process from biomass was developed using Aspen Plus V8.8 (Fig. 2). The developed model was divided in four major sections: the syngas processor, syngas cleaning, tar reforming, and the methanol synthesis units.

Fig. 2 Aspen model flowsheet of the bio-methanol production process.

2.1.1 Fuel processor

2.1.1.1 Gasification process

The gasification model was simulated based on thermodynamic equilibrium. Rice husks were utilized as a model input because their composition is comparable to that of oil palm residues and extensive experimental data on them is present in the literature. The proximate and ultimate analyses of the rice husks are shown in Table S1. The main assumptions considered in this section are: (1) the process is under steady state and isothermal conditions, (2) the drying and pyrolysis processes are instantaneous, (3) the char consists of 100% carbon, (4) the ash is a non-reactive material, and (5) the tar consists of naphthalene, toluene, phenol, and pyrene. In the simulation, biomass was defined as a non-conventional component and the DCOALGEN and HCOALGEN models were used to determine the density and enthalpy of the solid biomass. Firstly, the biomass was converted to its conventional elements (H, O, C, N, and S) and ash in a RYIELD reactor, denominated as DECOMP, by specifying the yield distribution in the calculator block according to its ultimate and proximate analyses. The tar yield was specified in the RYIELD reactor, denominated as R-TAR, by assuming toluene, naphthalene, phenol, and pyrene were the tar model compounds with concentrations of 65 wt.%, 20 wt.%, 10 wt.%, and 5 wt.%, respectively [26]. Oxygen-rich air was used as the gasifying agent because it offered the advantages in terms of higher partial pressure for relevant components in methanol synthesis, compression energy, and downstream equipment size. The gasification reactions were simulated using an RGIBBS reactor, denominated as GASIF, in which the Gibbs free energy minimization approach was applied to estimate the product gas composition. A brief explanation of the unit operation blocks used in the simulation of the syngas processor is summarized in Table 2.

The gasification model accuracy was verified by comparing the results of the model with those of reported experiments [7] that employed the same conditions and parameters (Fig.

3): a biomass feed rate of 0.74 kg h⁻¹, an ER of 0.25, and a gasifying temperature of 800 °C. The model predictions were in good agreement with the experimental results with a root mean square error (RMSE) of approximately 2.55% (Eq. (1)).

$$RMSE = \sqrt{\frac{\sum_i^n (\text{Experiment}_i - \text{Model}_i)^2}{N}} \quad (1)$$

Table 2 Unit operation blocks used to simulate the synthesis gas processor

Block name	Block ID	Description
DECOMP	RYIELD	Pyrolysis reactor: decomposition of biomass to its constituting components
R-TAR	RYIELD	Pyrolysis reactor: specifying the yield of generated tars
SEP-1	SEP	Separator: separation of tar from the gasification process
GASIF	RGIBBS	Gasifier: production of raw syngas through gasification reactions
REFORM	REQUIL	Reformer: reforming of methane and tar compounds syngas through catalytic partial oxidation (CPOX) reactions
SEP-2	SEP	Separator: Separation of char from the gasification system

Fig. 3 Comparison of the model predictions and experimental results (biomass feed rate, 0.74 kg h⁻¹; ER, 0.25; gasifying temperature, 800 °C; and gasifying pressure, 1.01 atm)

2.1.1.2 Tar reforming unit

The CPOX process was selected to convert methane and tar (toluene, naphthalene, phenol, and pyrene) to syngas (H₂ and CO) [27]. The operating temperature was set as the gasifying temperature and the raw syngas leaving the gasification process was fed to the REFORM block, which was simulated by an RStoic reactor. The oxygen enriched air was fed to the CPOX reactor until methane and the tar were completely converted.

2.1.2 Syngas cleaning process

PSA was used to remove the CO₂ from the produced syngas. The CO₂ removal efficiency varied until the ratio of the syngas components, including CO₂, met the methanol

synthesis specification of approximately 2.1 (Eq. (2)) and the ratio of H₂ and CO was in the range of 2.4–2.5 (Eq. (3)).

$$\frac{H_2 - CO_2}{CO + CO_2} \approx 2.1 \quad (2)$$

$$\frac{H_2}{CO} = 2.4 - 2.5 \quad (3)$$

Three PSA units were simulated by separator blocks based on the actual operating conditions of 35 °C and 30 atm and the separation percentage of the components was determined (Table S2) [28]. Firstly, the syngas pressure after the CPOX was increased to 30 atm and its temperature was decreased to 35 °C via the multistage compressor COMP1, after which it was sent to SEP-1 to separate out water. The syngas, consisting of H₂, CO, CO₂, and H₂S, was then sent to PSA1 to separate out H₂, an unadsorbed component. The adsorbed PSA1 offgas was then purged out during the regeneration step by being depressurized through the V1 valve. This offgas was again compressed to 30 atm and cooled to 35 °C via COMP2 before it was sent to PSA2 where the unadsorbed CO₂ and H₂S components were removed. CO was separated out during the regeneration step. PSA3 then separates CO₂ from H₂S, where the unadsorbed H₂S was removed via the guard bed while CO₂ was separated out during the regeneration step and mixed with CO removed by PSA2. This mixture of CO and CO₂ was compressed through COMP3 and then mixed with H₂ from PSA1 to prepare the feed gas for the methanol synthesis unit. The syngas specification was manipulated by adjusting the amount of CO and CO₂ vent gas at SPLIT1. Descriptions of the unit operation blocks used in the simulation of the synthesis gas cleaning process are summarized in Table 3.

Table 3 Unit operation blocks used to simulate the syngas cleaning process

Block name	Block ID	Description
COMP1, COMP2, COMP3	MULTISTAGE COMPRESSOR	Multistage compressor: Increases syngas pressure to 30 atm and decreases temperature to 35 °C
SEP-3	SEP	Separator: separation of water from syngas
PSA1, PSA2, PSA3	SEP	Pressure swing adsorption (PSA): separation of H ₂ , CO, CO ₂ , and H ₂ S
V1, V2, V3	VALVE	Valves: Depressurization of the PSA adsorbed components

2.1.3 Bio-methanol synthesis process

Normally, methanol synthesis takes place at a temperature of 220–280 °C and a pressure of 50–100 atm [28]. However, to ensure that the heat of reaction is effectively used and the catalysts are active, the operating conditions of this study were retained at 220 °C and 50 atm [17]. The pressure of the methanol reactor feed gas leaving the PSA process was increased to the operating pressure of the methanol synthesis reactor through COMP4. The methanol reactor containing the CuO-ZnO-AlO-based catalyst was simulated using a REQUIL reactor, denominated as MEOHSYN. The temperature of the product leaving the MEOHSYN reactor was decreased to 25 °C via COOLER1 prior to the raw methanol being separated at the bottom of METSEP. The separated offgas leaving METSEP, containing unreacted H₂, CO, and CO₂, was entirely recycled to the MEOHSYN reactor to enhance the methanol production. The description of the operating units involved in the bio-methanol synthesis are shown in Table 4.

Table 4 Unit operation blocks used to simulate the bio-methanol synthesis process

Block name	Block ID	Description
COMP4	COMPRESSOR	Compressor: increases the methanol reactor feed gas pressure to 50 atm
MEOHSYN	REQUIL	Methanol synthesis reactor: produces raw methanol
V4	VALVE	Valve: depressurizes product gas leaving the methanol reactor
COOLER1	HEATX	Heat exchanger: decreases the temperature of the product gas leaving the methanol reactor to 25 °C
METSEP	SEP	Separator: separates raw methanol from the offgas

3. Energy and exergy analysis

The energy consumption of the bio-methanol production process and its individual units was investigated. The overall energy consumption is calculated by a summation of the energy consumed in each unit. The energy efficiency of the system (η_{sys}) indicates that the conversion efficiency of biomass to raw bio-methanol is defined as a ratio of the energy of the product and the ratio of energy inputs (Eq. (4)) [29].

$$\eta_{sys} = \frac{\text{Energy}_{out}}{\text{Energy}_{in}} \quad (4)$$

Exergy analysis is performed by balancing the exergy for the steady state process as follows [30-31]:

$$(\sum \dot{Ex}_i)_{in} = (\sum \dot{Ex}_j)_{out} + \sum \dot{Ex}_{dest} \quad (5)$$

Exergy related to mechanical work and heat transfer are determined from Eq. (6) and Eq. (7), respectively.

$$\dot{Ex}_w = \dot{W} \quad (6)$$

$$\dot{Ex}_Q = \dot{Q}\left(1 - \frac{T_0}{T}\right) \quad (7)$$

The specific exergy (ex) consists of physical exergy (ex^{ph}), chemical exergy (ex^{ch}), kinetic exergy (ex^{kn}), and potential exergy (ex^{pt}). Generally, ex^{kn} and ex^{pt} , which relate to velocity and elevation, respectively, are negligible in thermodynamic processes, such as combustion and gasification. Therefore, the ex is calculated from Eq. (8).

$$ex = ex^{\text{ph}} + ex^{\text{ch}} \quad (8)$$

The ex^{ph} and ex^{ch} can be determined from Eqs. (9) and (10), respectively.

$$ex^{\text{ph}} = (h - h_0) - T_0(S - S_0) \quad (9)$$

$$ex^{\text{ch}} = \sum_i x_i (ex_i^{\text{ch}} - RT_0 \ln x_i) \quad (10)$$

Here, ex_i^{ch} is the standard chemical exergy of component i and x_i is the mole fraction of component i .

In this study, the biomass enters at 25 °C and 1 atm and the ex^{ph} of the biomass is zero. Hence, the ex of the biomass is equal to its ex^{ch} ($ex_{\text{biomass}}^{\text{ch}}$), as defined by Eq. (11).

$$ex_{\text{biomass}}^{\text{ch}} = \beta LHV_{\text{biomass}} \quad (11)$$

where β is the ratio between the ex^{ch} and LHV is the lower heating value of the biomass. The factor β can be calculated from the correlation of the mass fraction of H, O, C, and N in the biomass (Eq. (12)) reported in previous work [32].

$$\beta = \frac{1.044 + 0.016(\text{H/C}) - 0.3493(\text{O/C})(1 + 0.0531(\text{H/C})) + 0.0493(\text{N/C})}{1 - 0.4124(\text{O/C})} \quad (12)$$

The exergy efficiency of the system (ψ_{sys}) is defined as the ratio of the product exergy to the exergy input, including the biomass exergy and energy related to the mechanical work inputted to the system (Eq. (13)).

$$\psi_{\text{sys}} = \frac{\text{Exergy}_{\text{output}}}{\text{Exergy}_{\text{input}}} \quad (13)$$

4. Results and discussion

Bio-methanol production was analyzed to study how changes in the operating parameters influenced the process performance. Syngas production from different oil palm residues was investigated first, followed by the effects that gasifying temperature and ER have on syngas and bio-methanol production. The energy consumption and exergy performance of the process were also examined, and finally, the feasibility of recirculating the PSA offgas to the gasifier was investigated.

4.1 Syngas production from different oil palm residues

The use of trunk, frond, and EFB oil palm biomass residues as fuel for syngas production was studied and we observed that the gasification of trunk residue offers the highest syngas yields (Table 5). This is ascribed to the trunk residue containing the highest concentration of H₂ and CO because it contains the highest H and C. Therefore, the trunk residue was selected as the biomass model compound for the analyses detailed in the following sections.

Table 5 The yield and composition of syngas from different oil palm biomass residues

	Syngas composition (vol.% dry basis)					Syngas yield (kmol h ⁻¹)
	H ₂	CO	CH ₄	CO ₂	Tar	
Trunk	31.91	39.10	7.40	21.15	0.43	0.0256
Frond	26.52	32.51	7.91	32.62	0.43	0.0175
EFB	21.41	27.10	7.10	43.83	0.56	0.0133

4.2 Parametric analysis

4.2.1 Effect of ER on syngas production at different gasifying temperatures

The effect of the ER on the composition of syngas produced at different gasifying temperatures was investigated by varying the ER from 0.25 to 0.45 at gasifying temperatures of 750–1000 °C. The variation of the concentration of H₂, CO, and CO₂ at various gasifying conditions are shown in Figs. 4(a)–(c), respectively. The concentration of H₂ and CO₂ decreased when the gasifying temperature increased; whereas, that of CO increased due to the dominant, endothermic reverse water-gas shift, water-gas, and Boudouard reactions. Furthermore, the oxidation reactions of H₂ and CO play a crucial role as the supplied oxygen increases. Therefore, the concentrations of H₂ and CO decrease with increasing ER, while that

of CO_2 increases. The yield of syngas increased with increasing gasifying temperature (Fig. 5) but decreased with increasing ER. These results were consistent with those of previous research [33]. The maximum yield of syngas was achieved at a gasifying temperature of 1000°C and an ER of 0.25.

(a)

(b)

(c)

Fig. 4 Fraction of (a) H_2 , (b) CO , and (c) CO_2 under different gasifying conditions.

Fig. 5 Syngas yield achieved under various gasifying conditions.

4.2.2 Effect of ER on bio-methanol production at different gasifying temperatures

The effect of the ER and gasifying temperature on the yield of bio-methanol was also investigated (Fig. 6). Although the syngas yield increased with increasing gasifying temperature (Fig. 5), the yield of bio-methanol showed the opposite trend. This was due to the decrease in H₂ content, which is a main raw material for bio-methanol synthesis (Fig. 4(a)). The maximum yield of bio-methanol was achieved at the gasifying temperature of 750 °C and ER of 0.25.

Fig. 6 The variation of the bio-methanol yield at various gasifying conditions

4.2.3 Effect of different gasifying conditions on the energy consumption of the system

The bio-methanol production via biomass gasification route was found to be an exothermic process for all conditions (Fig. 7). However, the energy requirement of the process increased with gasifying temperature, due to the dominant endothermic reverse water-gas shift, water-gas, and Boudouard reactions. The opposite was observed when the ER was considered the key parameter because the oxidation reactions play a crucial role. The energy consumption of each operating unit and the energy efficiency of the system were determined (Table 6), where compressor 4 was found to consume the most energy and a decrease was observed in its energy demand as the gasifying temperature increased. This was due to a decrease in the volumetric flow rate of the syngas. Moreover, when the gasifying temperature was higher than 900 °C and the ER remained constant at 0.25, the endothermic process of the gasifier became exothermic. It was noted that the thermal, self-sufficient conditions of the gasifier were achieved at 897.6

°C. The methanol reactor was also found to exhibit an exothermic process in which the degree of exothermicity decreased with increasing gasifying temperature, due to the decrease in the rate of syngas being fed into the methanol reactor. The energy consumption of the whole process decreased as the ER increased because the dominant oxidation reaction generates and supplies energy to the system. The lowest energy requirement of the overall process was achieved at a gasifying temperature of 750 °C and an ER of 0.45. Under these conditions, a maximum energy efficiency of 28.22% was obtained.

Fig. 7 Overall energy consumption of the bio-methanol production process under various gasifying conditions.

Table 6 Energy consumption of each operating unit under various gasifying conditions

Parameters	Case No.								
	1	2	3	4	5	6	7	8	9
Gasifying temperature (°C)	750	750	750	850	850	850	950	950	950
Equivalent ratio, ER	0.25	0.35	0.45	0.25	0.35	0.45	0.25	0.35	0.45
Biomass feed rate (kg h ⁻¹)	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Energy efficiency, η_{sys} (%)	38.57	30.99	28.22	37.03	29.14	26.40	35.91	27.60	24.67
Energy consumption (kW)									
Gasifier	-0.1378	-0.4950	-0.8766	-0.0559	-0.4096	-0.7891	0.0248	-0.3256	-0.7026
CPOX reactor	-0.0283	-0.0281	-0.0280	-0.0271	-0.0272	-0.0273	-0.0267	-0.0271	-0.0269
Compressor 1	-0.4039	-0.4461	-0.4928	-0.4602	-0.5061	-0.5558	-0.5147	-0.5645	-0.6174
PSA1	-0.0016	-0.0018	-0.0020	-0.0014	-0.0016	-0.0018	-0.0013	-0.0015	-0.0016
Compressor 2	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
PSA2	-0.0005	-0.0007	-0.0008	-0.0005	-0.0006	-0.0008	-0.0004	-0.0006	-0.0007
PSA3	-0.0002	-0.0002	-0.0001	-0.0002	-0.0002	-0.0001	-0.0002	-0.0002	-0.0001
Compressor 3	0.0003	0.0002	0.0002	0.0003	0.0003	0.0002	0.0003	0.0003	0.0002

Compressor 4	0.4371	0.3824	0.3192	0.4196	0.3623	0.2985	0.4073	0.3453	0.2791
MeOH reactor	-0.5279	-0.4614	-0.3852	-0.5070	-0.4371	-0.3601	-0.4917	-0.4167	-0.3367
Cooler 1	-0.2067	-0.1810	-0.1512	-0.1983	-0.1715	-0.1415	-0.1926	-0.1635	-0.1323
Heater 1	0.0021	0.0023	0.0024	0.0019	0.0021	0.0022	0.0018	0.0019	0.0021
Overall process	-0.8428	-1.2294	-1.6151	-0.8044	-1.1892	-1.5753	-0.7687	-1.1519	-1.5383

4.3 Exergy analysis

4.3.1 Effect of different gasifying conditions on exergy efficiency of the system

The variation of exergy efficiency of the bio-methanol production process under different gasifying conditions was analyzed (Fig. 8). The exergy efficiency of the system decreased as the gasifying temperature increased due to the decrease in energy consumption of the overall system, especially at the gasifier. The extent of the bio-methanol synthesis decreased, which was caused by the decrease in H_2 concentration of the syngas. The exergy efficiency also decreased as ER increased, which was due to the crucial role played by the oxidation reactions of hydrocarbon compound. A maximum exergy efficiency of 25.44% was achieved for the system when the gasifying temperature and ER were maintained at 750 °C and 0.25, respectively, which was comparable with that of the methanol production process from natural gas with CO_2 utilization at 29% [34].

Fig. 8 Exergy efficiency of the system under different gasifying conditions

4.3.2 Effect of different gasifying conditions on the rate of exergy destruction

The highest exergy destruction was observed at the gasifier (Table 7), which implies that the gasifier is an important unit for improving efficiency. The results complied with those reported in the previous work using wood chip as feedstock [35]. As the total exergy inlet was significantly destroyed during the combustion and gasification reactions, the exergy destruction of the gasifier increased with increasing ER. However, the lowest exergy destruction rate of the gasifier, 1.23 kW, was achieved at a gasifying temperature of 750 °C and an ER of 0.25. This was because the heat demand decreased as gasifying temperature increased, and a low ER shortened the extent of the combustion reaction. Compressor 1 exhibited the second largest exergy destruction because it compresses large amounts of process gas and removes large amounts of heat during its inter-stage cooling. Exergy destruction was also observed in the CPOX and methanol reactors, as they both involve several reactions.

Table 7 Rate of exergy destruction in each operating unit under various gasifying conditions

Parameter	Case No.								
	1	2	3	4	5	6	7	8	9
Gasifying temperature (°C)	750	750	750	850	850	850	950	950	950
Equivalent ratio, ER	0.25	0.35	0.45	0.25	0.35	0.45	0.25	0.35	0.45
Biomass feed rate (kg h ⁻¹)	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Exergy destruction (kW)									
Gasifier	1.2296	1.3003	1.3767	1.2329	1.3031	1.3790	1.1984	1.3051	1.3806
CPOX reactor	0.0694	0.0619	0.0541	0.0634	0.0560	0.0486	0.0575	0.0503	0.0425
Compressor 1	0.2757	0.2841	0.2944	0.2871	0.2962	0.3069	0.2994	0.3092	0.3202
PSA1	0.0578	0.0516	0.0445	0.0559	0.0493	0.0420	0.0543	0.0473	0.0396
Compressor 2	0.0378	0.0369	0.0359	0.0379	0.0370	0.0360	0.0379	0.0371	0.0414
PSA2	0.0106	0.0112	0.0111	0.0100	0.0109	0.0111	0.0094	0.0105	0.0111
PSA3	0.0027	0.0026	0.0023	0.0025	0.0023	0.0021	0.0023	0.0021	0.0018
Compressor 3	0.0279	0.0235	0.0189	0.0295	0.0253	0.0208	0.0309	0.0269	0.0224
Compressor 4	0.0382	0.0334	0.0279	0.0366	0.0317	0.0261	0.0355	0.0302	0.0244

MeOH reactor	0.0967	0.0844	0.0704	0.0928	0.0800	0.0658	0.0901	0.0763	0.0616
Cooler 1	0.0259	0.0227	0.0190	0.0249	0.0215	0.0177	0.0241	0.0205	0.0166
Heater 1	0.00022	0.00023	0.00025	0.00020	0.00021	0.00023	0.00018	0.00019	0.00021

4.4 Feasibility of PSA offgas recirculation to gasifier

As CO₂ can be used as gasifying agent to enhance syngas production, the feasibility of recirculating the PSA offgas, which comprises H₂, CO, and CO₂, to the gasifier was investigated by varying the recycled offgas fraction over a range of 0-0.8 at a constant ER of 0.25 and gasifying temperature of 900 °C, which was normally used in actual operation to prevent the operational problem caused from the tar formation [27]. It was found that the yield of bio-methanol decreased when the recycled fraction increased from 0 to 0.5 (Table 8). This was ascribed to a decrease in H₂ concentration caused by the dilution of CO, which was generated from Boudouard reactions and the dry reforming of methane. However, the bio-methanol yield seemed stable when the PSA offgas recycle fraction was increased to a value higher than this range, which was due to effect of CO₂ dilution in the system. The energy consumption of the overall process was found to increase as the recycled fraction increased because the degree of endothermicity within the gasifier also increased.

Table 8 Bio-methanol production, overall energy consumption and energy efficiency at different recycled offgas fractions

Parameters	Case No.								
	1	2	3	4	5	6	7	8	9
Gasifying temperature (°C)	900	900	900	900	900	900	900	900	900
Equivalent ratio (ER)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Biomass feed rate (kg h ⁻¹)	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Offgas recycle fraction	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Yield of bio-methanol (kg h ⁻¹)	0.2596	0.2520	0.2414	0.2277	0.2083	0.1888	0.1892	0.1910	0.2018
Overall energy consumption (KW)	-0.8106	-0.8996	-1.0111	-1.1571	-1.3584	-1.5751	-1.6270	-1.7142	-1.8919
Energy efficiency, η_{sys} (%)	36.43	35.34	33.85	31.94	29.21	26.48	26.55	26.80	28.30

Regarding the exergy performance, the exergy of the work input and thermal energy output of system increased as the recycled fraction increased (Fig. 9); whereas, the exergy of the thermal energy input of the system indicated the opposite trend. The exergy efficiency of the overall process was found to decrease due to decreasing amounts of bio-methanol, as well as an increase in the overall exergy destruction. The rate of exergy destruction of all the operating units increased with the recycled fraction, and the gasifier was responsible for the greatest exergy destruction, followed by compressor 1, the CPOX reactor, and then the methanol reactor (Fig. 10).

Fig. 9 Exergy rate of work, thermal energy, biomass, and bio-methanol, as well as the exergy efficiency of the system with different recycled offgas fractions.

Fig. 10 Exergy destruction rate of each operating unit with different recycled offgas fractions

5. Conclusions

Bio-methanol production from oil palm residues via gasification route was studied using a model developed in Aspen Plus V8.8. Oil palm residues were tested as feedstock for syngas production. Among the trunk, frond, and EFB residues investigated, the trunk residue offered the highest syngas yield and was used as the biomass model compound. The effect of the gasifying temperature and ER on the syngas composition and yield, bio-methanol production, energy consumption, and exergy performance was examined. Although, the yield of syngas increased with increasing gasifying temperature, bio-methanol production showed opposite trend, which was due to the decrease in H_2 concentration within the syngas. Regarding exergy analysis, the gasifier was an important unit for improving the exergy efficiency of the system, which was found to decrease as the ER and gasifying temperature increased. Moreover, the feasibility of recirculating PSA offgas to the gasifier was investigated, and the exergy efficiency of the system was found to decrease as the recycled fraction increased. This was due

to the decrease in bio-methanol production and increase in overall exergy destruction. The maximum bio-methanol yield was achieved by the once-through process, which maintained a gasifying temperature of 750 °C and an ER of 0.25. Under these conditions, the maximum energy and exergy efficiencies, 38.57 and 25.44%, respectively, were also obtained.

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Nomenclature

$RMSE$	Root mean square error
Experiment _{<i>i</i>}	The value of component <i>i</i> derived from the experiment result
Model _{<i>i</i>}	The value of component <i>i</i> derived from the model prediction
N	Number of species
H_2	Molar flow rate of hydrogen (kmol h ⁻¹)
CO	Molar flow rate of carbon monoxide (kmol h ⁻¹)
CO_2	Molar flow rate of carbon dioxide (kmol h ⁻¹)
$\dot{E}x_{dest}$	Rate of exergy destruction of the system (kW)
$\dot{E}x_i$	Rate of exergy of component <i>i</i> (kW)
$\dot{E}x_j$	Rate of exergy of component <i>j</i> (kW)
$\dot{E}x_w$	Rate of exergy related to work (kW)
$\dot{W}$	Rate of work (kW)
$\dot{E}x_Q$	Rate of exergy related to thermal energy (kW)
$\dot{Q}$	Rate of heat transfer (kW)

T	Temperature (°C)
T_0	Reference environmental temperature (298.15 K)
ex	Specific exergy (kJ kmol ⁻¹)
ex^{ph}	Physical exergy (kJ kmol ⁻¹)
ex^{ch}	Chemical exergy (kJ kmol ⁻¹)
ex^{kn}	Kinetic exergy (kJ kmol ⁻¹)
ex^{pt}	Potential exergy (kJ kmol ⁻¹)
h	Specific enthalpy (kJ kmol ⁻¹)
h_0	Specific enthalpy at reference environmental condition (1 atm, 298.15 K) (kJ kmol ⁻¹)
S	Specific entropy (kJ kmol ⁻¹)
S_0	Specific entropy at reference environmental condition (1 atm, 298.15 K) (kJ kmol ⁻¹)
R	Gas constant (8.314 J mol ⁻¹ K ⁻¹)
x_i	Mole fraction of component i (-)
$ex_{biomass}^{ch}$	Exergy of biomass (kJ kmol ⁻¹)
β	Ratio between the chemical exergy and the LHV of biomass (-)
H	Mass fraction of hydrogen in biomass (-)
O	Mass fraction of oxygen in biomass (-)
C	Mass fraction of carbon in biomass (-)
N	Mass fraction of nitrogen in biomass (-)
ψ_{sys}	Exergy efficiency of the system (%)
η_{sys}	Energy efficiency of the system (%)
Exergy _{output}	Exergy output from the system (kW)

$\text{Exergy}_{\text{input}}$	Exergy input to the system (kW)
$\text{Energy}_{\text{output}}$	Energy output from the system (kW)
$\text{Energy}_{\text{input}}$	Energy input to the system (kW)

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