Bio-CH₄ from palm empty fruit bunch via pyrolysis-direct methanation: Full plant model and experiments with bio-oil surrogate

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ABSTRACT

A promising, cleaner alternative process of thermochemical conversion of lignocellulosic biomass to biomethane is proposed and rigorously investigated via modelling and experiments for the first time. Using a conventional nickel on calcium aluminate catalyst, operated in bench scale at 1 atm, 400 °C, and with a feed molar steam to carbon ratio of 2, the Low Temperature Steam Reforming of acetic acid, representing a single compound bio-oil surrogate, achieves a promising 81.9% fuel carbon conversion to gases with a methane yield of 15.7 wt% of the feed. This compares to 21 wt% methane yield at equilibrium, thus demonstrating encouraging first time performance and scope for future catalyst optimisation. A comprehensive Aspen Plus model is developed for the first time for an industrial plant producing biomethane from palm empty fruit bunch (50 wt% initial moisture), an under-used agro-industrial waste produced in vast amounts in South-East Asia and Sub-Saharan Africa. Dependency on external heating is completely eliminated by heat recovered from combustng 25% of the gas product. Based on the simulation results of the autothermal plant, a final gas product consisting of 99.2 wt% of CH₄ and 0.8 wt% of H₂ is predicted with a plant thermal efficiency of 80.6%, i.e., comparable to modelled efficiencies found in the literature for wood gasification to biomethane plants that generate syngas as a necessary intermediate.

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1. Introduction

Biomass is considered a reliable source of energy because it is geographically abundant, and can contribute significantly to controlling environmental impacts such as global warming (Owusu and Asamadu-Sarkodie, 2016). The production of substitute natural gas also known as synthetic natural gas (SNG) from biomass (bio-SNG) is the motivation of the present study in reducing the strong dependency on conventional (fossil) natural gas because of its composition, which is mostly methane (CH₄) (Kopyscinski et al., 2010). In addition, SNG can contribute by prolonging the number of years of production left with relation to known reserves of natural gas (R/P), which on the basis of various studies, are limited to 52.8 years (R/P is sensitive to the discovery of reserves, increase or decrease of annual production) (Dudley and UK, 2016).

Palm empty fruit bunch (PEFB) is the main contributor to the palm oil derived biomass by-product, with 15.5–17.5 million tons per year. Most of the palm oil millers do not have the technology for the disposal of empty fruit bunch (EFB) (Abas et al., 2011). EFB is typically left in piles without any further application, and large amounts of it eventually undergo uncontrolled anaerobic digestion, thus generating atmospheric CH₄ emissions (Singh and Bajpai, 2012) as well as causing odour related nuisance.

Thermochemical conversion of lignocellulosic biomass (agricultural, forestry and wood residues) into CH₄ is commonly based on the gasification process, following a similar layout as gasification of solid fuel (mainly coal) (Solarte-Toro et al., 2018). The biomass feedstock undergoes the gasification, methanation, and purification. The gasification process to convert biomass into SNG, which is described by reaction EQ. 1, requires high operating temperatures (700–1000 °C) to produce CH₄, CO, CO₂, light and heavy hydrocarbons and char (Ni et al., 2006).

\[
\text{Biomass} \xrightarrow{\text{Heat}} \text{H}_2 + \text{CO} + \text{CH}_4 + \text{CO}_2 + \text{hydrocarbons (tars)} + \text{char}
\]

EQ. 1

Gasification suffers from low selectivity to gas products, with...
typically methane and other alkanes being produced at this stage. It is clear from the reactions ((EQ. 2) – (EQ. 4)) which represent the methanation stage that the presence of methane in the feed from the gasifier stage would adversely affect the kinetics and equilibria of the listed reactions towards methane production. Conventional processes of SNG production from wood feedstock typically feature a gas cleaning section, and then a train of catalytic methanation units with intercooling stages needed to increase conversion (Van der Meijden et al., 2010). In the gas cleaning section, tar reforming is usually required before the cleaned syngas enters the methanation stage in order to prevent catalyst poisoning by the heavy tars generated during gasification. Catalytic tar reformers are usually operated at high temperatures in the range of 710–890 °C (Phillips et al., 2007; Fendt et al., 2012). Therefore, many researchers have developed syngas cleaning with the aim of making biomass gasification technology more attractive (Göransson et al., 2011).

\[
\begin{align*}
CO + 3H_2 & \rightarrow CH_4 + H_2O, \quad \Delta H_{298K} = -206.2 \text{ kJ/mol CH}_4 \quad \text{(EQ. 2)} \\
2CO + 2H_2 & \rightarrow CH_4 + CO_2, \quad \Delta H_{298K} = -247.3 \text{ kJ/mol CH}_4 \quad \text{(EQ. 3)} \\
CO_2 + 4H_2 & \rightarrow CH_4 + 2H_2O, \quad \Delta H_{298K} = -165.0 \text{ kJ/mol CH}_4 \quad \text{(EQ. 4)} 
\end{align*}
\]

Moreover, several studies have been looking for a solution to reducing internal reforming tars by providing potassium inside the gasifier (Thunman and Seemann, 2017) and by using suitable bed materials with a moderate tar cracking activity (Zhang et al., 2015). The general gasification process of conversion of biomass to methane thus appears costly and complex to operate due to generation of heavy tars associated with the gasification stage. In contrast, pyrolysis converts biomass to bio-oil (light tars), gas and solid products, as in equation (EQ. 5) by thermal decomposition of biomass in the absence of oxygen at lower temperature within 350–550 °C (Bridgewater, 2012; Zhang et al., 2005). Therefore an alternative route of bio-SNG production from lignocellulosic biomass which, like pyrolysis, avoids the formation of heavy tars, would present a cleaner and less operationally complex alternative process.

\[
\text{Biomass} \rightarrow \text{bio-oil(light tars)} + \text{hydrocarbon gases} + \text{char} \quad \text{(EQ. 5)}
\]

Catalytic low temperature steam reforming process (LTSR) has revealed potential benefits for glycerol conversion (White et al., 2018). The present study introduces an alternative process of conversion of lignocellulosic biomass to methane by fast pyrolysis of the solid biomass feedstock followed by direct methanation of the pyrolysis bio-oil by LTSR. This approach, in addition to avoiding the formation of heavy tars, would in theory decrease the enthalpy gap currently inherent to the gasification/CO-methanation process, resulting in smaller temperature gradients, thus less thermodynamic irreversibilities and a therefore more efficient methanation.

The present study focusses first on demonstrating experimentally the feasibility of the direct catalytic methanation (using a nickel on calcium aluminate catalyst) of acetic acid (AcOH), chosen as a single compound bio-oil surrogate feedstock. AcOH and phenol were the most abundant species measured in bio-oil mixture, derived from palm empty fruit bunch (PEFB) (Abdullah et al., 2011; Sukiran et al., 2009; Zin et al., 2012), where GC-MS analysis accounting for 75% of the detected area peaks attributed 32% and 21% to AcOH and phenol. Flowsheeting of the pretreatment and fast pyrolysis of PEFB to a realistic bio-oil mixture, and the latter’s subsequent direct methanation by LTSR and purification to bio-CH₄ was then performed on Aspen Plus V10 to show comparable thermal plant efficiencies as the wood gasification-methanation of CO/CO₂ route.

2. Methodology and materials

2.1. Catalytic experiments of direct methanation of acetic acid

The instrumented set-up is illustrated in Fig. 1. For each run, the stainless steel-made reactor was loaded with 4 g of NiO/Ca–Al₂O₃ catalyst provided by TST ltd, with particle sizes ranging from 250 to 355 μm. The reactor temperatures were controlled by an electrical tubular furnace enclosing the reactor and monitored using a thermocouple type K placed strategically close to the catalyst bed for increasing reliability on the temperature measurements. The activation of the fresh NiO-containing catalyst to metallic Ni, performed prior to feeding AcOH and water, was achieved by reduction at 600 °C under a 200 cm³/min feed gaseous mixture composed of 95 vol% N₂/5 vol% H₂ until return of steady state. The tubular reactor was purged and cooled using a high N₂ flowrate. The temperature was then reduced until it reached the optimal range selected to conduct the LTSR experiments, namely between 350 and 450 °C. The methanation trials were conducted using feed molar steam/ carbon ratios (S/C) between 1 and 3 with a N₂ carrier flow rate of 18 cm³/min which facilitated elemental balances. AcOH and water, were pumped using syringe pumps at flow rates of 0.978 cm³/h (equivalent to a carbon element input of 9.5 × 10⁻⁶ mol/s) and between 0.616 and 1.849 cm³/h (varying as a function of the desired S/C), at standard temperature and pressure (STP), respectively. Volatile and non-volatile compounds were separated from the output stream by condensation, and the liquid condensate was collected for further analysis, which showed negligible presence of...
carbon. Subsequently, a bed of silica gel removed residual moisture of the gas after the condensation stage. Then, the dry gas was analysed by means of a Variant CP 4900 micro GC equipped with two columns (molecular sieve 5A and Pora Plot Q) that allowed quantifying CO₂, hydrocarbons (C₂H₄, C₂H₆, C₃H₆, C₄H₈, CH₄), O₂, CO, H₂ and N₂ using argon as GC carrier gas.

2.2. Modelling and simulation

Aspen Plus (V10) has proven its capability in modelling whole plant simulations such as bio-methane production via biomass gasification processes (Van der Meijden et al., 2010; Fendt et al., 2012; Vitasari et al., 2011; Begum et al., 2013; Tremel et al., 2013) and fast pyrolysis of biomass for bio-oil production processes (Peters et al., 2014; Ward et al., 2014; Onarheim et al., 2014; Sharma et al., 2015). The properties of PEFB, which is used in this study as lignocellulosic biomass, are not included in the databank of chemical compounds of the modelling software, and thus, were defined manually into the Aspen Plus software using thermodynamic properties such as enthalpies and densities calculated by means of empirical correlations. Based on the chemical composition of bio-oils, the Peng-Robinson (Peng-Rob) property method was used, as this model is adequate for nonpolar and mildly polar compounds such as oxygenated hydrocarbons. In addition, Peng-Rob was utilized because it is also suitable for hydrocarbon-processing, gas-processing, petrochemical and refinery applications. For the CH₄ purification unit placed in the proposed bio-methane production plant (high pressure water scrubbing or HPWS), which works under the physical absorption/desorption principle, the Non-Random-Two-Liquid (NRTL) method was selected as the behaviour of the gases dissolved in liquid (water) was described by Henry’s law. This method has been previously utilized to simulate technologies for synthetic biogas upgrading by HPWS (Cozma et al., 2015).

2.3. Model development

The methane production, which is a steady state model, consists of four main process units: 1) biomass pre-treatment, 2) fast pyrolysis of the dried and chopped biomass particles, 3) direct methanation of the bio-oil pyrolysis product via LTSR, and 4) upgrading of the reformate to high-purity methane “bio-SNG”. Fig. 2 presents a flowchart that displays the main units, inputs and outputs of the conversion plant before heat integration. The biomass plant was modelled based on 3000 kg/hr of PEFB feedstock that had a realistic high moisture content of 50 wt%, which represented a huge energetic but unavoidable burden on the plant. PEFB was considered to have an initial size of 25 mm (Ward et al., 2014; Onarheim et al., 2014).

In the methanation unit, modelled under isothermal conditions based on (Yun and Dupont, 2015), the pyrolysate-derived bio-oil was converted mainly to CH₄ and CO₂. A CH₄-enriched stream was produced by using high-pressure water scrubbing technology (HPWS), validated by data from (Cozma et al., 2015). The details of the different configurations and approaches proposed to modelling each processing unit are described under the results and discussion sections.

3. Results and discussion

3.1. Experimental: Methanation of AcOH as bio-oil surrogate in a packed bed reactor

Direct methanation of acetic acid experiments, which were carried out in a packed bed reactor, were initially conducted to determine the optimal conditions to maximize the production of CH₄ and to assess the basic technological feasibility of the proposed core process of the bio-SNG plant. Temperatures of 350—450°C and feed molar steam to carbon ratios (S/C) of 2—3, this range of S/C was successfully modelled and used in previous research works of methanation, to drive forward LTSR reactions (Yun and Dupont, 2015; Li et al., 2013). In the following sections, results of the effect of both temperature and S/C in the methanation performance are presented and discussed. The equations used to determine conversion, selectivity, yield and yield efficiencies are detailed in the supplementary data.

3.1.1. Effect of temperature in the LTSR of acetic acid

Fig. 3-c shows the effect of temperature (350—450°C) on the outlet gas production (in mol/s) and Table 1 lists the outputs in the methanation process performed with S/C ratio of 2 and near atmospheric pressure. With just 29.4%, at 350°C the conversion to
the carbon containing gases CO, CO2 and CH4 (‘C-gases’) of the bio-oil surrogate was very low, but a substantial increase to 81.9% was obtained just 50°C higher at 400°C Fig. 3-b, proving the high sensitivity to temperature of LTSR for methane production. At 450°C Figs. 2 c), 78.6% feedstock conversion to C-gases was measured, comparable to that at 400°C and with a similar selectivity to CH4. Therefore, temperatures above 350°C and up to 400°C were conducive to obtaining higher fuel conversions to methane. These performance findings are consistent with those reported in (Gao et al., 2013; Garbarino et al., 2014; Abu Bakar et al., 2011).

From Table 1, the highest value of CH4 yield was obtained at 400°C with 15.7 wt% of the AcOH feed. In the same manner than conversion, yield efficiency increased as a function of the temperature in the range studied. As expected, kinetics are favoured at temperatures above 350°C and up to 400°C were conducive to obtaining higher fuel conversions to methane. These performance findings are consistent with those reported in (Gao et al., 2013; Garbarino et al., 2014; Abu Bakar et al., 2011).

In terms of catalytic performance of Ni/Al2O3 catalyst at S/C ratios of 1–3 and 400°C, results are summarized in Table 2.

| Temperature, °C | 350°C | 400°C | 450°C |
|-----------------|-------|-------|-------|
| Fuel conversion to gases, % | 29.4 | 81.9 | 78.6 |
| CH4 yield, wt.% of AcOH feed (Experimental) | 1.7 | 15.7 | 14.6 |
| CH4 yield, wt.% of AcOH feed (Equilibrium) | 23.6 | 21.0 | 17.2 |
| CH4 yield efficiency, % (Experimental/Equilibrium) | 7.3 | 74.8 | 86.1 |
| % Selectivity to C-products in the gas | | | |
| i. CH4 | 11.0 | 35.8 | 35.2 |
| ii. CO2 | 74.8 | 64.2 | 64.8 |
| iii. CO | 14.2 | 0.0 | 0.0 |
| % Selectivity to H-products in the gas | | | |
| i. CH4 | 8.5 | 34.4 | 31.5 |
| ii. H2 | 91.5 | 65.6 | 68.5 |

3.1.2 Effect of feed molar steam to carbon ratio (S/C) on the conversion to CH4 of bio-oil surrogate acetic acid

The results displayed in panels (a)–(c) of Fig. 4 reveal that excessive water (S/C = 3) supplied into the packed bed reactor resulted in a slower reaction rate for CH4 production. This marked delay was attributed to the presence of the water gas shift reaction (EQ. 6), which occurs as water is supplied in the process, and thus provides a competing route of the CO intermediate conversion to CO2 rather than CH4 with concurrent production of the H2 by-product.

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2, \quad \Delta H_{298K}^\circ = \quad -41 \text{ kJ/mol CO} \quad \text{EQ. 6}
\]

In terms of catalytic performance of Ni/Al2O3 catalyst at S/C ratios of 1–3 and 400°C, results are summarized in Table 2. CH4 yield of 15.7 wt% of feed AcOH and CH4 selectivity of 35.8% respectively at S/C of 2 confirm this ratio and temperature as the best conditions of these trials. Table 2 shows that a lower CH4 yield was obtained at S/C of 1. While the reaction of direct methanation of oxygenated hydrocarbons (or LTSR) takes the generalised form given in (EQ. 7), in the unusual case of AcOH (C2H4O2), the stoichiometric coefficient for the water reactant for 1 mol of AcOH feed is 0, generating one mol of CO2 and one mol of CH4. Thus in theory, S/C should not affect the equilibrium of LTSR of AcOH if EQ.7 was the only reaction. However, equilibrium calculations using the minimisation of Gibbs Energy method result in a large yield of solid carbon at S/C of 0, decreasing at S/C of 1 and disappearing at S/C of 2, and moles of H2 by-product overtaking CH4 at S/C of 3, just as in the present experiments. The latter indicates large sensitivity to feed molar steam to carbon ratio of the LTSR process for methane production.
Optimal conditions for the effective production of methane from acetic acid over a Ni/Ca\textsubscript{e}Al\textsubscript{2}O\textsubscript{3} catalyst were therefore at 400°C and S/C of 2, which brought the experimental yield of CH\textsubscript{4} to 75% of the equilibrium value. This experimental study confirmed (i) the feasibility of producing methane directly from bio-oil surrogate acetic acid (via ‘direct methanation’), the strong dependence on (ii) temperature and (iii) feed molar steam to carbon ratio which can tip the balance of products towards either solid carbon or hydrogen.

3.2. Characteristics and pre-treatment of biomass in the plant model

PEFB was defined as a non-conventional component in Aspen Plus. It must be highlighted that the PEFB’s elemental composition is represented by empirical factors in the program, whereas enthalpies and densities are determined through empirical correlations. Thus, the PEFB properties defined in the simulation environment were chosen on the basis of experimental data reported in (Abdullah et al., 2007) and the results of the proximate and ultimate analysis are given in Supplementary Data (Table A2.3). The modelled bio-oil mixture (compounds and their mass fractions) was constructed by firstly using García-Pérez et al.’s methodology (García-Pérez et al., 2007) on the DTG data of PEFB oil (Figure A2.1), which allowed to identify 6 macrofamilies of unspecified compounds of increasing volatility, and then to distribute their mass fractions over a small number of specified model compounds of boiling point range and chemical structure close to those identified by GC-MS (Zin et al., 2012), while preserving the overall elemental balance of the mixture (procedure implemented using Solver in Excel). The latter approach represents a valuable and novel way of better representing real bio oils by designing mixtures of model compounds, which, together, present the same volatility and elemental make-up via a rigorous methodology.

As mentioned in section 2.3, in the pre-treatment facility of the plant model, PEFB was assumed to have an initial size of 25 mm (Yang et al., 2006; Ruengvilairat et al., 2012). Subsequently, fibre size was reduced to 5 mm by means of a crusher. Based on the limited number of studies available in the literature for the PEFB crushing process, it was found that approximately 90 kW [61] was the power required for crushing 3000 kg/h of PEFB. Then, the 5 mm fibres were passed through a dryer to lower the excess of water to ~8 wt % as this would permit to reduce the water content in the oil mixture produced after the pyrolysis facility. Lastly, the finely crushed dried fibres, were further ground to be 1 mm as in ref (Mohammed et al., 2012), to be fed into the fluidized bed fast pyrolysis reactor.

Moisture was fed into the process as a conventional component, and 50 wt % moisture was suggested as in typical fresh PEFB (Zhang et al., 2015; Machinery, 2016).

The biomass-to-fuel efficiency and the thermal efficiency values have a strong dependency on the selection of appropriate lower
heating value (LHV) for the feedstock and product. In Table 3, a review of the LHV values of dry wood obtained from refs (Van der Meijden et al., 2010; Fendt et al., 2012; Tremel et al., 2013; Gassner and Maréchal, 2009; Duret et al., 2005) compared with LHV predicted from Eq. 8 to Eq. 10 is shown. LHV from works reported in the literature and their equivalents calculated using the elemental compositions stated in the same refs are also presented in Table 3. The LHV for wood on a dry basis were similar to those using expressions Eq. 8 to Eq. 10. The LHV of 16.83 MJ/kg calculated in this work for PEFB (dry basis) and based on ultimate analysis, was used for the plant model as it was within the range of LHV for PEFB reported in the literature from 17.02 to 20.34 MJ/kg (Kerdsuwan and Laohalidanond, 2011; Yang et al., 2006; Ruengvilairat et al., 2012; Mohammed et al., 2012; Sukiran et al., 2011; Shariff et al., 2014).

In terms of both higher (HHV) and lower (LHV) heating values for dry biomass, estimations were conducted using Channiwala and Parikh’s correlation Eq. 8 (Channiwala and Parikh, 2002) and equation Eq. 9, respectively. Considering that raw PEFB with 50 wt % moisture content was utilized in this study, the LHV value on wet basis (LHVbiomass, wet) employed to determine thermal efficiency and energy consumption for methane production was predicted on the basis of the mathematical expression Eq. 10 (Lind et al., 2012).

\[ HHV_{\text{biomass, dry}} = \text{Channiwala} \times \text{Parikh} = 0.3491C + 1.1783C_H + 0.1005C_S + 0.1034C_O + 0.0151C_N + 0.0211C_A \]  

\[ \text{LHV}_{\text{biomass, dry}} = HHV_{\text{biomass, dry}} \]  

\[ LHV_{\text{biomass, wet}} = \text{LHV}_{\text{biomass, dry}} \times \left( \frac{M_{\text{dry}}}{M_{\text{wet}}} \right) \]  

\[ \text{HHV}_{\text{biomass, dry}} = 20.69 \text{ MJ/kg} \]  

A directly heated single-pass rotary dryer was selected for the drying of the PEFB because it is the most common type of dryer used for biomass according to (Amos, 1998). The drying operation is performed when the hottest gases are contacted with the wettest biomass inside a rotating drum (wet biomass and hot gas). Most dryers are not designed to completely dry the biomass in order to avoid over-drying of biomass, which might cause ignition and fire hazards (Amos, 1998; Fagernäs et al., 2010).

This is why the moisture content in the PEFB pyrolyzer feed should be between 8 and 10 wt % (Ward et al., 2014; Onarheim et al., 2014). Consequently, the 7.95 wt% of moisture still present in the biomass (Abdullah et al., 2011) was listed as a non-conventional component, indicating a ‘dry’ PEFB, whilst the remaining 1380.75 kg/h of water was specified as a conventional component. Thus, the energy required for drying up the wet PEFB was calculated by using Aspen Plus without considering the moisture content in ‘dry’ PEFB that as a non-conventional component, did not participate in any phase or chemical equilibrium calculations in the drying process.

Flue gases from the combustion of bio-char pyrolysis by-product were used in this study as the medium for drying the moist PEFB (FLUE-G1). It has been reported that the outlet temperature from rotary dryers can vary from 71 to 110 °C (Amos, 1998). Thus, the amount of energy needed for the PEFB drying process by using flue gases from the bio-char combustion was determined by maintaining the outlet temperature of the dryer at 110 °C.

The drying process was modelled in Aspen Plus using an RYIELD block while a separator block was chosen to split the water from the dry PEFB by phase solid/vapour separation. Then, the dry PEFB finely ground through a crusher into particles of 1 mm was fed into

Table 3
Elemental analysis and heating values (HHV and LHV) of lignocellulosic biomass feedstocks for CH₄ production, by using Channiwala and Parikh’s expression (Eq. 8), and Lind’s expression (equation Eq. 10). mf – moisture free.

| Biomass | Our work, based on (Abdullah et al., 2007) | Fendt et al. (2012) | Tremel et al. (2013) | Meijden (2010) (Van der Meijden et al., 2010) | Gassner (2009) | Duret et al. (2005) |
|---------|------------------------------------------|---------------------|---------------------|-----------------------------------------------|---------------|---------------------|
| PEFB    | Beech wood | Spruce wood | Wood | Wood | Wood |
| Moisture, wt. % | 50 | 20 | 25 | 15 | 50 | 0 |
| Elemental analysis, mf wt. % | | | | | | |
| i. C | 49.07 | 47.97 | 49.80 | 50.19 | 50.60 | 47.42 |
| ii. H | 6.48 | 5.78 | 6.30 | 6.04 | 5.70 | 6.25 |
| iii. O | 38.29 | 45.39 | 43.20 | 42.37 | 42.50 | 46.33 |
| iv. N | 0.70 | 0.22 | 0.13 | 0.30 | 0.20 | 0 |
| v. S | 0.10 | 0.03 | 0 | 0.06 | 0 | 0 |
| vi. Cl | 0 | 0 | 0 | 0.05 | 0 | 0 |
| vii. Ash | 5.36 | 0.61 | 0.57 | 1.00 | 1.00 | 0 |
| Heating values, MJ/kg | | | | | | |
| HHVdry biomass, dry, Eq.8 | 20.69 | 18.85 | 20.33 | 20.24 | 19.96 | 19.13 |
| LHVdry biomass, dry (Lind + Eq.8) | 16.83 | 16.97 | 18.13 | 18.48 | 16.27 | 17.75 |
| LHVdry biomass (journal + Lind) | 17.02–20.34 | 16.53 | 19.40 | 18.80 | 18.60 | 18.20 |
the pyrolysis facility (see Figure 5). In the literature, there is a limited number of studies for PEFB crushing process, and therefore it was assumed that the power requirement for crushing PEFB was the same as that for wood. This is because the power requirements for crushing both wood and PEFB into the same size (10–30 mm) with the same feedstock capacity (3–5 tonne biomass/h) were found to be the same, i.e. 45 kW according to (Dincer and Acar, 2015). As a result, it was assumed that the electricity consumption for finely crushing PEFB was the same as for wood, resulting in 140 kWh on dry basis. Thus, the energy demand for grinding 1619.25 kg/h of dry PEFB into particles of 1 mm was estimated to be 227 kWh.

3.3. Bio-oil production via fast pyrolysis

In this study, the pre-treated biomass (dry PEFB) was fed into a fluidized bed pyrolyzer at 500 °C and atmospheric pressure to maximize the bio-oil yield, based on (Sharma et al., 2015). Attributable to lack of reaction mechanism data or kinetic data for this process, a RYIELD block was used to simulate the pyrolysis. Product yields through the pyrolysis process were defined based on literature data. For modelling this pyrolysis process, a pyrolyzer data were taken from the cited literature as follows: overall product yield for gas and pulverised coal combustion respectively (Jecht, 2004). CO2, H2O, CO and NO (S content neglected) were produced as flue gas. Further details of the heat duties met by the furnace are discussed in the ‘Heat integration’ section (3.7).

Downstream of the cyclone unit, the hot vapours after char separation were cooled down to 35 °C (Onarheim et al., 2014), which condensed the bio-oil into a liquid feed for the methanator unit, whereas the non-condensable gases were being burned. The phase change of bio-oil from vapour to liquid permits monitoring of the bio-oil yield and composition (moisture content, CHNS analysis), facilitating plant efficiency calculation and control, as well as optimisation measures at the pyrolysis stage, also enabling direct control of the S/C ratio in the methanator.

3.5. Methanation stage

There are several CO and CO2 methanation processes that have been widely applied at industrial scale, such as Lurgi, TREMP, RMP and IRMA (Kopyscinski et al., 2010; Woodward, 1976; Hohlein et al., 1984). IRMA is the only methanation process that operates under isothermal conditions, while the rest (Lurgi, TREMP and RMP) operate in adiabatic conditions with intercooling stages. Since the methanation of CO is highly exothermic, at least two adiabatic reactors need to be implemented to run the methanation of CO process to ensure the feed gas will be nearly fully converted into methane. The direct methanation of PEFB-derived bio-oil is mildly exothermic, and therefore both adiabatic and isothermal methanators could be implemented, similarly to current designs of water gas shift reactors, without significant risk of hot spots (under adiabatic conditions) or cooling duty and control (under isothermal conditions). This is a major advantage of the new pyrolysis-direct methanation process compared to conventional gasification-methanation of CO in the thermochemical production of methane from lignocellulosic biomass.

Fig. 6. Simplified flowsheet for the simulation of the PEFB fast pyrolysis process.
For simplicity, an isothermal reactor was selected (internally cooled reactor, type IRMA), as it is compatible with small to medium scale production plants (suitable for this case of study according to (Yun and Dupont, 2015)). The operating conditions for the isothermal methanator were 300 °C and 27 bar, and were selected based on industrial conditions of syngas conversion to methane (250–300 °C and 27–29 bar). Compared to the experiments, the lower temperature than 400 °C is afforded by compensating with operation at higher than atmospheric pressure, which would make the catalyst's kinetics and resulting activity equivalent. As prior to feeding the fixed bed catalytic LTSR methanator, the bio-oil from the pyrolysis process was pumped to 27 bar and then vaporized using flue gas heat recuperation before entering into the methanator, modelled as an ‘RGibbs’ block, as shown in Fig. 7. RGibbs reactors are modelled using the minimisation of Gibbs free energy method. Thus, the optimum condition to achieve the highest methane production was observed between S/C ratios of 2–3, resulting in 2198 kg/h of water inlet needed in the feed corresponding to a S/C of 3. The simulation of the methanation plant revealed S/C ratios consistent with the AcOH experiments.

The gas output from the methanator (listed Table 4) is expectedly rich in CO2 (45.1 mf mol %) as expressed in reaction EQ. 7. A first stage of purification of the biogas was implemented by demisting of water using cooling the condenser to 25 °C. Then, the dry gas flow continuously flowed into a gas cleaning section, consisting of a high-pressure water scrubbing (HPWS) unit operating the CO2 absorption at 25 bar.

### 3.6. Bio-SNG stream purification

A high-pressure water scrubbing (HPWS) system for biogas production from an anaerobic digestion process (Cozma et al., 2015) was used as a benchmark in this study to simulate the gas cleaning unit for upgrading CH4 in the gas product stream. The conditions for the HPWS model in (Cozma et al., 2015) was based on data used in an existing commercial plant. Re-modelling the HPWS for bio-SNG production using the same operating parameters, which resulted in less than 5% error, allowed validating the model. Then, the parameters of the HPWS were adapted to maximize energy efficiency.

By operating the absorber column in the HPWS facility at 20 °C and 10 bar, it was determined that the solubility of CO2 in water was 0.45 kg CO2/100 kg water (Perkins and Innovates). Approximately 84,400 kg/h of total water was needed in order to absorb 380 kg/h of CO2 in the crude biogas from the anaerobic process. However, it was assumed that 2.4% of the total water flow is lost due to evaporation (Cozma et al., 2015). Accordingly, at least 2000 kg/h of water is for make-up of losses, whereas 82,465 kg/h of water are part of the recycling closed loop (water pump around). Based on this work, almost 935 kg/h of CO2 was produced from bio-oil conversion in the LTSR methanation process. By referring the operating conditions of the absorber column used in biogas production to those of an anaerobic digestion process (i.e., 20 °C and 10 bar), 187,000 kg of total water was required in HPWS unit, which corresponds approximately 0.50 kg CO2/100 kg water of CO2 (Perkins and Innovates). 4488 kg/h of water (i.e. 2.4% of the total water flow rate) were needed to replace the water lost due to the evaporation.

A pressure of 25 bar was selected to operate the absorber column of the HPWS unit. According to Henry’s law, CO2 dissolves in higher amounts in water at higher partial pressures. Some of the CH4 product unfortunately also dissolves in the water flow along side with CO2. Separation of this gas-laden water was carried out in a flash drum at 3 bar, where the desorbed mixture of CH4 and CO2 gas was recycled with the fresh bio-methane after re-compression to 27 bar. The CO2-laden water collected from the flash drum was then sent to the stripper for separate CO2 and recycle water. Fig. 8 shows the flowsheet of HPWS which was used as a gas-cleaning unit.

The operating conditions of the HPWS unit used in this study and the compositions of upgraded gas products are listed in Table 5. A gas product with a composition of >99 wt % of CH4 and <0.5 wt% of H2 (corresponding to vol% of >95 and <5 respectively) and less than 4% of methane loss confirms the feasibility of the HPWS unit in this plant.

### 3.7. Heat integration

A minimum temperature difference, ΔT<sub>min</sub> of 20 °C was used to ensure the driving force for the heat exchanger network. Table 6 lists stage 1 (air preheating by furnace flue gases), stages 2 and 3 (steam and bio-oil heat via recuperative heat), and stage 4 (superheating of both steam and bio-oil using furnace flue gases) as increasing levels of heat integration. Altogether, 25% of the bio-methane product stream needed to be combusted in the central furnace to ensure the plant no longer relied on individual units’ external heat inputs (Table 6), making it autothermal.

### Table 4

| Dry gas products | Mol flowrate, kmol/h | mf mol% |
|------------------|----------------------|---------|
| Methane, CH₄     | 24.8                 | 52.5    |
| Carbon dioxide, CO₂ | 21.3           | 45.1    |
| Carbon monoxide, CO | 0.0            | 0.0     |
| Hydrogen, H₂     | 1.1                  | 2.4     |
| Total            | 47.2                 | 100.0   |

### Table 5

| Dry gas products | Mol flowrate, kmol/h | mf mol% |
|------------------|----------------------|---------|
| Methane, CH₄     | 24.8                 | 52.5    |
| Carbon dioxide, CO₂ | 21.3           | 45.1    |
| Carbon monoxide, CO | 0.0            | 0.0     |
| Hydrogen, H₂     | 1.1                  | 2.4     |
| Total            | 47.2                 | 100.0   |

**Fig. 7.** Simulation flowsheet of the simplified methanation process.
3.8. Process performance

Different indicators such as energy conversion efficiency and energy consumption were determined, as well as compared with analogous processes of lignocellulosic biomass thermochemical conversion to biomethane such as biomass-to-fuel thermal efficiency \( \eta_{btf} \), as expressed in the expression EQ. 11, and the overall thermal efficiency \( \eta_{th} \) of the plant (EQ.12), takes into account the contributions of the electricity and heat net flows (Lind et al., 2012). Lower heating values (LHV) were used because the biomethane is intended to meet the immediate energy needs in the South East Asia and Sub-Saharan countries producers of PEFB.

\[
\text{Biomass to fuel energy, } \eta_{btf} = \frac{\dot{m}_{\text{methane}} \times \text{LHV}_{\text{methane}}}{\dot{m}_{\text{biomass}} \times \text{LHV}_{\text{biomass}}} \quad \text{EQ. 11}
\]

\[
\text{Thermal efficiency, } \eta_{th} = \frac{\dot{m}_{\text{methane}} \times \text{LHV}_{\text{methane}} + (\dot{Q}^+ - \dot{Q}^-)}{\dot{m}_{\text{biomass}} \times \text{LHV}_{\text{biomass}} + (P_{\text{el}}^+ - P_{\text{el}}^-)} \quad \text{EQ. 12}
\]

Fig. 9 shows the block diagram of the autothermal bio-methane plant (stage 4) and Fig. 10, which is an energy flows diagram, presents its energy use. The heat exported (\( \dot{Q}^- \)), power consumed or imported (\( P_{\text{el}}^- \)), and the balance between \( \dot{m}_{\text{biomass}} \times \text{LHV}_{\text{biomass}} \) and \( \dot{m}_{\text{methane}} \times \text{LHV}_{\text{methane}} \) values for the full integrated plant confirmed a significant improvement with respect of the non-integrated plant. In terms of performance, results of both configurations non-integrated and fully integrated, are shown in Table 7. Enhancement in thermal efficiency from the non-integrated plant (74.7% MW of bio-SNG/MW of biomass) to the autothermal plant (80.6%) was also revealed in Table 7, the latter compared favourably to the

| Table 5 | Parameters values for HPWS simulation and compositions of the upgraded bio-methane production from PEFB bio-oil. |
|---------|------------------------------------------------------------------------------------------------------------|
| Parameters | Units | Parameters values |
| CH₄ | kg/h | 397.9 |
| CO₂ | kg/h | 937.9 |
| CO | kg/h | 0.1 |
| H₂ | kg/h | 2.3 |
| P_{absorber} | bar | 25 |
| P_{stripper} | bar | 1.0 |
| T_{absorber} | °C | 25 |
| T_{stripper} | °C | 25 |
| Flowrate of gas feed (from methanator) | kg/h | 1337.2 |
| Water top-up | kg/h | 4488 |
| Air flow rate | kg/h | 2859 |
| Water-pump around | kg/h | 182512 |
| P_{flash} | bar | 3 |
| Number of theoretical stages | | 10 |
| Upgraded bio-methane | | | |
| CH₄ | kg/h (fraction of mass flowrate) | 383.0 (0.994) |
| CO₂ | 0.0 (0.00) |
| CO | 0.1 (0.00) |
| H₂ | 2.1 (0.006) |
| Treated flow rate | kg/h | 385.2 |
Other performance indicators are introduced in Table 8 (all workings shown in supplementary data) to account for the different quality of feedstock across the literature on gasification-methanation, one of them is the percentage of efficiency of methane yield, defined as the ratio of the plant-derived methane yield to that of the maximum stoichiometric methane yield achievable by complete conversion of the biomass source to methane according to (EQ. 7). This indicator allows comparing different gasification plants performance despite their operation with diverse biomass feedstocks.

Overall carbon conversion efficiency (Duret et al., 2005),

$$\eta_C = \frac{\dot{m}_{C_{out}}}{\dot{m}_{C_{in}}}$$  \hspace{1cm} \text{EQ. 13}
Based on results listed in Table 8, which were calculated from the stoichiometry of the methanation of the biomass reaction (EQ. 7), the maximum theoretical CH4 yield when using PEFB feed was 36.1 wt% compared to that from wood (32.2–35.0 wt%) for CH4 production. In addition, the efficiencies of CH4 production compared to the maximum of theoretical CH4 production for PEFB were 53.2–70.8%, which were within the range of the wood gasification process (63.6–80.6%). The overall carbon conversion efficiency (listed in Table 8) for the non-integrated and stage 4-autothermal plant were calculated to be 39.1% and 30.5%, respectively, compared to 32.0–42.5% for wood gasification.

4. Conclusion

Acetic acid (as single compound bio-oil surrogate) conversion to CH4 using a Ni/Ca–Al2O3 catalyst was feasible by direct methanation via the low temperature steam reforming (LTSR) process. At (9.5 × 10^-6 molC/s) feed, the highest CH4 yield was 15.7 wt% of the feed, at 400 °C and feed molar S/C ratio of 2. A plant design for the production of high purity biomethane from very moist PEFB was subsequently presented, which included drying, chopping, fast pyrolysis, direct methanation of the bio-oil, and CO2 removal by high-pressure water scrubbing. Burning 25% of the upgraded biomethane product in addition to the bio-char and the non-condensable gases from the pyrolysis were required for autothermal operation. The estimated thermal efficiencies increased from 74.7% (MW of bio-SNG/MW of biomass) for the allothermal plant to 80.6% (MW of bio-SNG/MW of biomass) for the autothermal plant. These were comparable with the-state-of-art biomass gasification route to methane production via syngas followed by CO and CO2 methanation, although avoiding the generation of heavy tars and the large temperature swings between units. It is therefore expected that capital and operational expenditures of the pyrolysis-direct methanation of bio-oil will be lower when operating using similar lignocellulosic biomass feedstock recalcitrant to bio-processing. Practical challenges arise from avoiding carbon accumulation on the catalyst during the direct methanation of bio-oil, which will be explored in future works.

Table 7

Comparison of the performance between plant designs without heat integration and with integration stage 4.

| Parameters | w/o integration: Plant relies on local external heat inputs | Integration stage 4: Plant operates w/o external heat inputs |
|-----------|-----------------------------------------------------------|----------------------------------------------------------|
| LHVPEFB(wet), kWh/kg | 2.34 | 13.8 |
| LHVmethane, kWh/kg | 13.8 | 288 |
| Mass flow rate of raw PEFB, kg/h | 3000 | 724 |
| Mass flow rate of pure CH4 production, kg/h | 370 | 621 |
| Net power consumption (P\textsubscript{el} – P\textsubscript{el} – P\textsubscript{el}) kW | 640 | 2271 |
| Net excess heat (Q\textsubscript{int} + Q\textsubscript{int}) kW | 621 | 61.6 |
| \(\eta_{btf}\), % (kW of CH4/kW of biomass) | 72.7 | 80.6 |
| \(\eta_{th}\), % (kW of CH4/kW of biomass) | 74.7 | 80.6 |

Table 8

Process performance of this work compared to the literature. See Table 3 for elemental analyses of each biomass and LHVdry. This work: (a) w/o (b) w/integration stage 4.

| Biomass | This work | Fendt et al. (2012) | Trennel et al. (2013) | Van der Meijden et al. (2010) | Gassner and Maréchal (2009) | Duret et al. (2005) |
|---------|-----------|--------------------|----------------------|-----------------------------|---------------------------|---------------------|
| CH\textsubscript{H}O\textsubscript{O} | CH\textsubscript{H}O\textsubscript{O} | CH\textsubscript{H}O\textsubscript{O} | CH\textsubscript{H}O\textsubscript{O} | CH\textsubscript{H}O\textsubscript{O} | CH\textsubscript{H}O\textsubscript{O} | CH\textsubscript{H}O\textsubscript{O} |
| LHV\textsubscript{bow} (MJ) | 8.42 | 8.42 | 8.42 | 8.42 | 8.42 | 8.42 |
| CH4 yield wt.% of dry biomass (Aspen plus model) | 13.23 | 24.7 | 24.7 | 24.7 | 24.7 | 24.7 |
| Maximum theoretical CH4 yield, wt.% of dry biomass | 36.1 | 14.55 | 14.55 | 14.55 | 14.55 | 14.55 |
| % efficiency of CH4 (Aspen plus/max theor yield, CH4) | 12.5 | 3.3 | 3.3 | 3.3 | 3.3 | 3.3 |
| \(\eta_{btf}\), % (MJ of max theor. CH4/MJ of biomass) | 106.9 | 106.9 | 106.9 | 106.9 | 106.9 | 106.9 |
| \(\eta_{th}\), % (MJ of CH4/MJ of biomass, Aspen Plus) | 72.7 | 72.7 | 72.7 | 72.7 | 72.7 | 72.7 |
| \(\eta_{btf}\), % (MW of bio-SNG/MW of biomass) (R-11) | 73.5 | 73.5 | 73.5 | 73.5 | 73.5 | 73.5 |
| \(\eta_{th}\), % (kW of CH4/kW of biomass) (R-12) | 39.1 | 39.1 | 39.1 | 39.1 | 39.1 | 39.1 |
| \(\eta_{c}\), % (kW of CH4/kW of biomass) (R-13) | 30.5 | 30.5 | 30.5 | 30.5 | 30.5 | 30.5 |
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.118737

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