**Supplementary Data Section for Paper:**

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

**Hafizah Abdul Halim Yun a,b, Sergio RamírezSolís a, Valerie Dupont a\***

aSchool of Chemical and Process Engineering (SCAPE), University of Leeds, Leeds, LS2 9JT, UK.

bFaculty of Engineering, Universiti Malaysia Sarawak, Sarawak, 94300, Malaysia

abstract

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 underused 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 combusting 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.

# **Nomenclature**

|  |  |
| --- | --- |
|  | moisture fraction (kgwater / kgwet biomass) |
|  | latent heat of vaporization water at 25 ºC (2440 kJ/kg) |
| LHVmethane | lower heating value of methane (kJ/kg) |
| LHVbiomass | lower heating value of biomass (kJ/kg) |
|  | **lower heating value on dry basis** |
|  | lower heating value on wet basis |
|  | Molar mass of water (0.018 kg/mol) |
|  | Molar mass of hydrogen (0.002 kg/mol) |
|  | mass of water (kg) |
|  | mass of dry biomass (kg) |
|  | mass of wet biomass (kg) |
| mf | moisture free |
| $$\dot{m}\_{methane}$$ | mass flowrate of methane (kg/s |
| $$\dot{m}\_{biomass}$$ | mass flowrate of biomass (kg/s) |
| $$\dot{n}\_{C,in}$$ | molar flowrate of inlet carbon of biomass, kmol/h |
| $$\dot{n}\_{C,out}$$ | molar flowrate of the final upgraded CH4 production, kmol/h |
|  | process electricity cogeneration (kW); here assumed zero |
|  | process electricity demand (kW) |
| $$\dot{Q}^{-}$$ | process excess heat (kW) |
| $$\dot{Q}^{+}$$ | process heat demand (kW) |
|  | mass fraction of hydrogen in the dry biomass |
| ɳbtf | biomasstofuel thermal efficiency (fraction or %) |
| ɳth | overall thermal efficiency (fraction or %) |
| $$η\_{C}$$ | overall carbon conversion efficiency (fraction or %) |
| ∆Tmin | minimum temperature difference |

1. **Equations used in determining conversions via elemental balances**

The performance of the conversion of acetic acid as a biooil surrogate to CH4 by means of LTSR is presented in terms of conversion of fuel , CH4 yield , CH4 yield efficiency , selectivity to carbon products  and selectivity to hydrogen products . The set of equations used to develop the calculations of variables aforementioned are (1)–(12). In these mathematical expressions,  and  represent molar flowrates and dry gas mole fractions of product species respectively. Since the results of gas composition revealed by the GC analysis are expressed in volume fraction (or %), molar flowrate of species present in the output gas was estimated through a nitrogen balance, as this compound was chemically inert during the methanation process. Thus, the molar flowrate  of dry gas is calculated using equation 1 where *j* is associated to the elemental N of the fuel. For acetic acid, *j* is zero (full conversion), but biooils are expected to have a nonnegligible value of *j*. It must be mentioned that the subscript ‘fuel’ represent the acetic acid feedstock.

 (1)

By rearranging equation (1), the total molar flowrate of dry gas () is expressed as follow,

 (2)

In regards to the molar flowrate of reactants, which are fuel and water, are calculated by means of equation (3) and (4) respectively. These mathematical expressions are:

 (3)

 (4)

The nomenclature of equations (1) to (12) is presented in table 1

**Table 1.** Nomenclature used in equations (1)(12), which aims to exhibit the performance of the methanation reaction.

|  |  |
| --- | --- |
| Nomenclature | Definition |
|  | inlet molar flowrate of fuel/water (mol/s) |
|  | inlet mass flowrate of fuel/water (kg/s) |
|  | molar mass of fuel/ water (kg/mol) |
|  | density of fuel/water (kg/m3) |
|  | inlet volumetric flowrate of fuel or water (m3/s) |

The, which is defined as ‘fuel conversion to CH4, CO2, CO, C2H4, C2H6, C3H6 and C3H8 gases’ is determined by the equation (5) presented below.

 (5)

For acetic acid, ‘n’ in the denominator has a value 2 according to its empirical formula C2H4O2. The CH4 yield was calculated using equation (6).

 (6)

In equation (6), .

CH4 yield efficiency expressed in percentage (equation (7)) is defined as the ratio of CH4 yield obtained during the experiments divided by that predicted by chemical equilibrium conducted using comparable conditions such as P, T, and flow composition. Taking into consideration that the experiments were run in a bench scale reactor and adiabatic conditions are difficult to reach (heat losses are significant), the equilibrium analysis was performed using isothermal and isobaric conditions. The Chemical Equilibrium and Applications (CEA) software, which was utilized to run the rigorous equilibrium calculations, works under the principle of Gibbs free energy minimization. CEA offers an advantage to this work, namely, no assumptions need to be made towards possible reactions immersed in the methanation process, and thus, this permit to obtain more accurate results than in other software packages that lack prediction mode.

 (7)

Selectivity of carbon containing gases to CH4 such as , CO2  and CO  were determined on the basis of the following equations (8–10).

 (8)

 (9)

 (10)

Selectivity to CH4  and H2 with respect to hydrogen containing gases were calculated by equations (11) and (12) respectively.

 (11)

 (12)

The carbon present in the condensate and that formed on the catalyst surface was measured by characterization techniques such as elemental CHNS and total organic compounds (TOC) analysis.

1. **Characterisation of pyrolysis and biooil**

Table A21. **Product distribution of fast pyrolysis process (RYIELD block).**

|  |  |  |
| --- | --- | --- |
| Product distribution | Yields, mf wt. % [1]  | Yields, wt. % [our work] |
| Char | 11.00 | 10.19 |
| Gas | 15.03 | 13.92 |
| Total liquid | 73.97 | 75.89 |
| Gas | Yields, mf wt. % [1]  | Yields, wt. % [our work] |
| Methane, CH4 | 0.58 | 0.55 |
| Carbon dioxide, CO2 | 8.17 | 7.73 |
| Carbon monoxide, CO | 5.59 | 5.29 |
| Hydrogen, H2 | 0.07 | 0.07 |
| Ethylene, C2H4 | 0.17 | 0.16 |
| Ethane, C2H6 | 0.1 | 0.09 |
| Propane, C3H8 | 0.02 | 0.02 |
| Propylene, C3H6 | 0.01 | 0.01 |

Table A22. **Ultimate analysis of biochar from the pyrolysis of PEFB [2].**

|  |  |
| --- | --- |
| Components | wt.% |
| Carbon | 65.32 |
| Hydrogen | 4.56 |
| Nitrogen | 1.43 |
| Oxygen | 28.69 |



**Figure A21.** Discretisation of real PEFB oil DTG curve by weighted individual conversions from thermal decomposition over 6 macrofamilies. Mass fractions ‘zi’ as in Table A2.3, ‘ai’ is conversion of family ‘i’ [3], methodology of macrofamilies developed by GarciaPerez et al, 2007 [4].

Table A23. **Model mixture of biocompounds for PEFB biooil based on DTG analysis**

|  |  |  |  |
| --- | --- | --- | --- |
| PEFB biooil | C | H | O |
| Ultimate analysis, mol frac. [5] | 0.286 | 0.491 | 0.223 |
| Model mixture, mol frac.  | 0.268 | 0.519 | 0.213 |
| Water, wt.% [5] | 24.3 |
| Model water, wt.% | 24.0 |
| Model compounds | Mass frac. | Family | Family wt.% |
| Formaldehyde, CH2O | 0.08 | 1 | F1=10% |
| Acetaldehyde, C2H4O | 0.01 | 1 |
| 1hydroxy2butanone, C4H8O2 | 0.01 | 1 |
| Acetic acid, C2H4O2 | 0.07 | 2 | F2=30% |
| Water, H2O | 0.23 | 2 |
| Furfural, C5H4O2 | 0.13 | 3 | F3=15% |
| Phenol, C6H6O | 0.01 | 3 |
| Water, H2O | 0.01 | 3 |
| Creosol, C8H10O2 | 0.14 | 4 | F4=15% |
| Guaiacol, C7H8O2 | 0.01 | 4 |
| Catechol, C6H6O2 | 0.24 | 5 | F5+F6=30% |
| Palmitic acid, C16H32O2 | 0.01 | 6 |
| Levoglocusan, C6H10O5 | 0.05 | 6 |

1. **HPWS validation**

Table A3 1. **Composition of the upgraded bioCH4 before and after splitting 3.5% of it.**

|  |  |  |
| --- | --- | --- |
| **Compounds** | **After gas purification** | **Final upgraded biomethane (3.5 % CH4 deviated)** |
| kg/h (wt.%) | kmol/h (mol%) | kg/h (wt.%) | kmol/h (mol%) |
| CH4 | 383 (99.4) | 23.9 (96.0) | 369.6 (99.4) | 23.1 (95.5) |
| CO2 | 0.01 (~0.0) | ~0.0 (~0.0) | 0.01 (~0.0) | ~0.0 (0.0) |
| CO | 0.1 (~0.0) | ~0.0 (~0.0) | 0.1 (~0.0) | 0.0 (~0.0) |
| H2 | 2.1 (0.6) | 1.0 (4.0) | 2.2 (~0.6) | 1.1 (4.5) |
| Total flowrate: | 385.2 | 24.9 | 371.9 | 24.2 |

Table A3 2. **Parameters values for HPWS simulation for biogas production from anaerobic process [6] and comparison of the results between literature and our simulations results.**

|  |  |  |
| --- | --- | --- |
| Parameters | Units | Parameters values based on literature data [6] |
| CH4/CO2 | vol.% | 60/38.97 |
| H2S | vol.% | 0.03 |
| N2/O2 | vol.% | 0.5/0.5 |
| Pabsorber | bar | 10 |
| Pstripper | bar | 1 |
| Tabsorber | ºC | 20 |
| Tstripper | ºC | 20 |
| Biogas flow rate | m3/h | 500 |
| Water topup | m3/h | 2 |
| Air flow rate | m3/h | 1000 |
| Waterpump around | m3/h | 82.5 |
| Pflash | bar | 3 |
| Number of theoretical stages |  | 7 |
| Upgraded biogas |  | Results from literature [6] | Results from our simulation |
| CO2 | m3/h(fraction of vol. flowrate) | 2.8 (0.009) | 2.7 (0.009) |
| CH4 | 299.2 (0.967) | 287.6 (0.963) |
| H2S | 0.3 (0.001) | 0.0 (0.00) |
| N2 | 3.4 (0.011) | 4.5 (0.015) |
| O2 | 3.1 (0.010) | 3.2 (0.011) |
| H2O | 0.6 (0.002) | 0.6 (0.002) |
| Treated flow rate | m3/h | 309.4 | 298.6 |

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