THERMODYNAMIC ANALYSIS OF A COMBINED ORGANIC RANKINE CYCLE (ORC) WITH PROTON EXCHANGE MEMBRANE ELECTROLYZER (PEME) IN AN INTEGRATED BIOMASS CONVERSION SYSTEM

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ABSTRACT

The energy content of product gas obtained from biomass gasification requires further processing to reach equivalent standards of natural gas. The product gas is produced at high temperature and undergoes cooling in a heat exchanger system prior to a cleanup process. This study presents the thermodynamic modelling of an integrated biomass to energy plant composed of a gasifier and digester, integrated with an Organic Rankine Cycle (ORC) and a Proton Exchange Membrane Electrolyzer (PEME) configuration for syngas upgrade. Thermal energy from steam at 290°C obtained from the syngas cooling process in view of waste heat recovery is utilized in the ORC for power generation, and as an energy source for the PEME. Six potential ORC working fluids aiming a maximum power generation of the ORC system are considered: R1243zf, R1234ze(Z), R1234yf, R1233zd(E), Isobutane, and Propane. R1233zd(E) is identified as most suitable working fluid with power output of 280.6kW and a thermal efficiency of 19.23 % for ORC configuration with regenerator. An increase in the flow rate of hydrogen resulted in a raise in the power consumption of the PEME, and a corresponding decrease of the ORC net power for each working fluid. Hydrogen gas produced from the PEME was used in upgrading the product gas from the gasification and anaerobic digestion processes through methanation model to comparable natural gas standard. The composition and lower heating value of upgraded product gas was 97.18% CH_4, 2.82% H_2, and 50.03 MJ/kg, respectively. The efficiency of the PEME was 88.79% with hydrogen gas rate of 0.51kmol/s. In further work, the process parameters will be optimized via multi-objective approach under thermo-economic aspects.

1. INTRODUCTION

Waste heat in the form of thermal energy contained in flow streams are common in many industrial processes such as fuel transformation from raw resources to useful form, and in power generation. Such excess energy can occur due to high pressure, temperature, or chemical reaction involved in the process (Formann et al., 2016). According to Mahmoudi et al. (2018), utilization of waste energy streams for power generation can be beneficial for the economic and efficiency improvement of production processes with potential heat recovery as over 50% of world energy is lost in the form of heat. The gasification of biomass is a thermochemical conversion process used in the production of syngas. This occurs at high temperature of 500ºC to 1600ºC and it is anticipated that a substantial amount of thermal energy is available during syngas cooling which is an integral part of the gasification process (Serafim et al., 2020; Lozza, 2017). A portion of the waste heat can be utilized in a power to gas scheme for methanation purpose meant to upgrade the syngas to synthetic natural gas (SNG). High content of carbon oxides in the syngas would require equivalent amounts of hydrogen to achieve desired qualities of the SNG, creating the need for a reliable hydrogen production technique. Hydrogen production from electrolysis is a current promising technique available in multigeneration plants. The proton exchange membrane electrolyzer (PEME) is a highly advantageous option for water electrolysis due to its low

environmental effects and easy maintenance. It can be combined with waste heat recovery systems such as the organic Rankine cycle (ORC) as its power source (Safari and Dincer, 2019). An organic Rankine cycle (ORC) technology can be deployed as solution in the utilization of the low pressure and temperature of such waste heat sources due to its advantages of safety, flexibility and low maintenance (Karimi et al., 2019).

Several studies have focused on waste heat recovery ORCs in maximizing electrical energy generation from thermochemical conversion systems. Vera *et al.,* 2018 achieved maximum electric efficiency of 20.45% with Isopentane as ORC working fluid, in a biomass gasification plant with gas turbine flue gases as heat source for the ORC configuration. Elsido *et al.,* 2019 established the economic viability of an ORC waste heat recovery unit at high electricity prices in a techno-economic optimization study of a biomass to methanol plant. Hexane and R1233zd(E) were used as working fluids with hexane as the better option in terms of cost in a back-pressure ORC configuration. Serafim *et al.,* 2020 investigated the concept of implementing ORCs for waste heat recovery from air separation unit, CO2 compression unit and syngas cooling unit in an integrated gasification combined cycle plant, considering pure and zeotropic fluids for the ORC. Highest power output and exergy efficiency from syngas cooling unit was obtained as 1162kW and 16.30%, respectively, with R1234ze as pure working fluid compared to R290 and R600a. R600/R1234yf at ratio of 0.4/0.6 had best overall performance of 1224kW power and 17.84% exergy efficiency. The ORC-PEME integration in multigeneration systems have also been studied for plant improvement. Boyaghchi *et al.,* 2018 considered a dual ORC configuration coupled with PEME and a biomass gasification plant to provide biofuel, hydrogen, and power. An ORC-PEME system coupled with a domestic water heater and absorption refrigeration cycle in generating electricity, hydrogen, heating and cooling from a geothermal source was proposed by Akrami *et al.,* 2017. They reported an energy efficiency of 34.98% for the multi-generation plant.

The concept of implementing ORC-PEME system for waste heat recovery and hydrogen production have been investigated by researchers. However, its application in a biomass conversion plant with syngas upgrade has not been studied yet. In this study, a concept for the integration of an ORC for waste heat recovery in a biomass conversion to upgraded syngas is analyzed. The objective of this work is to assess the improvement potential of the efficiency of the ORC configurations with different working fluids in meeting the power needs of the proton exchange membrane electrolyzer (PEME) used for the purpose of methanation under thermodynamic considerations.
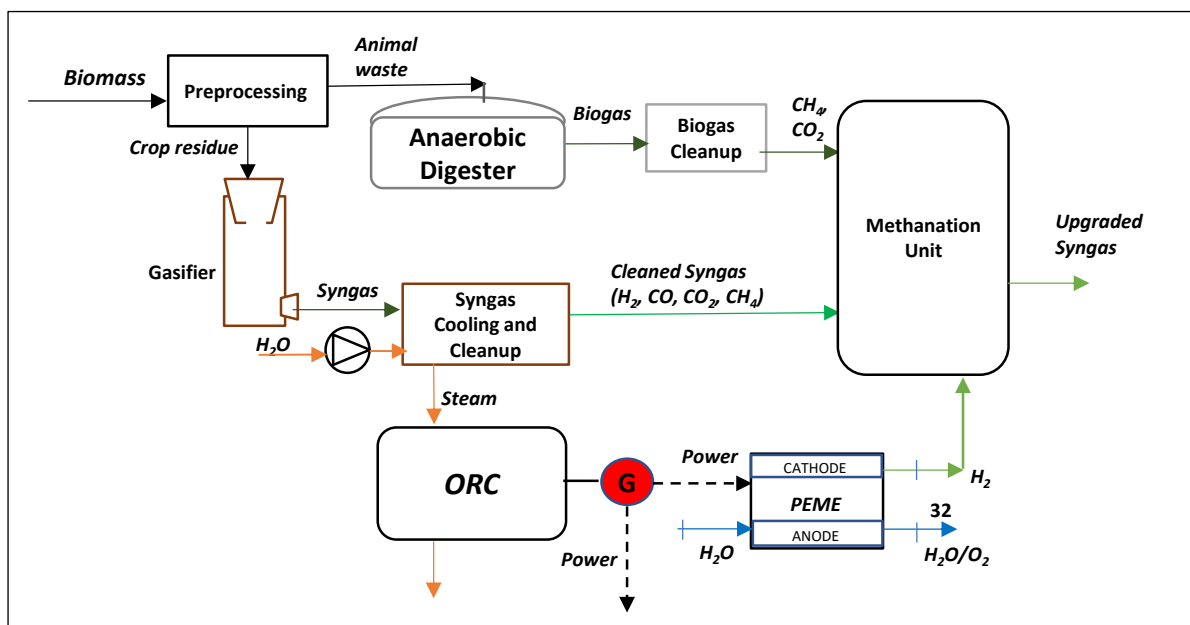
2. PROCESS DESCRIPTION

Figure 1: Biomass conversion with possible ORC-PEME integration

The biomass conversion plant consists of a combined gasification and anaerobic digestion plant as presented in Figure 1 (Ogorure *et al.*, 2018). Wet biomass consisting of animal waste is converted to biogas through the digester, while dry biomass of crop residue is fed to the gasifier for gasification. Syngas cooling allows for the cooling of the gas by direct quenching, or heat recovery in a heat exchanger. In the heat recovery method, the gas is first cooled to 500°C in a radiant heat exchanger to produce steam at high pressure for use in a steam power unit. Next, it is further cooled to 350 – 250°C to produce medium pressure steam, and water scrubbed to remove soluble particles such as sulphur compounds, chlorides or ammonia. Lastly, it is cooled to approximately 35°C in a low temperature gas unit (Serafim *et al.,* 2020). Due to low energy density of the product an upgrade through the catalytic hydrogenation of carbon oxides in the gas is required to attain equivalent quality of natural gas (Gao *et al.,* 2012). High content of carbon oxides in the syngas would require equivalent amounts of hydrogen to achieve desired qualities of the SNG. This creates the need for a reliable hydrogen production technique. Waste heat recovered through the medium pressured steam from the syngas cooling process is used as a thermal energy source in the ORC configuration. A share of the power from the ORC turbine is utilized in the PEME for hydrogen production. Product gas from the biomass conversion processes along with hydrogen gas from the PEME are fed to a methanation unit and upgraded to SNG level. This study is focused on the analysis ORC-PEME and methanation units.

3. METHODOLOGY

3.1 ORC and steam input

The ORC components include an evaporator, a pump, a condenser, a turbine, and a regenerator. Two case are considered for the ORC configuration. The first case is without a regenerator and the second case is with a regenerator for additional heating of working fluid before entering the evaporator. The performance analysis of the ORC is based on the first law of thermodynamics and the principle of mass and energy conservation. At steady state, neglecting changes in potential and kinetic energy, an energy balance for components of a system can be expressed as

$$\dot{Q} - \dot{W} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} \qquad (1)$$

where $\dot{m}, \; h, \; \dot{Q},$ and $\dot{W}$ denote mass flow rate, enthalpy, rate of heat transfer and work transfer rate, respectively. Equation (1) is applied to determine the power and efficiency of the ORC.

3.2 Selection of Working fluid

Selection of ORC working fluids is highly dependent on optimum utilization of heat resources and their environmental properties such as flammability, toxicity, ozone depletion potential as well as global warming potential. Due to environmental challenges posed working fluids from the hydrofluorocarbons group for ORC systems, there is need for new working fluids with zero or minimal ozone depletion potential (ODP) and low global warming potential (GWP). Working fluids investigated for the ORC are presented with their thermophysical properties and safety and environmental data in Table 1.

Table 1: Thermophysical, safety and environmental data properties of selected working fluids [Gil and Kasperski, 2018; Emadi *et al.,* 2020; Sung and Kim, 2016]

Parameter	R1243zf	R1234ze(Z)	R1234yf	R1233zd(E)	Isobutane	Propane
Critical temperature (°C)	103.78	150.12	94.7	165.6	134	96.74
Critical pressure (bar)	35.18	36.4	33.8	35.7	36.3	42.51
Normal boiling Point (°C)	-25.42	9.7	-29.8	17.92	-12.1	-42.11
ODP	0	0	0	0.00024	0	0
GWP	NC	6	4	7	4	3
ASHREA safety classification	A2L	A2L	A2L	A1	A3	A3

The following assumptions for the ORC design were made for this analysis:

i. Maximum sub-critical pressure of the ORC evaporator is limited to $0.9 P_{cr}$.

ii.   Cooling water at inlet to condenser is 25 °C.
iii.   Steam input of 1kg/s at 290ºC to the ORC evaporator and is not subcooled.
iv.   Minimal pinch point of 5K in condenser and evaporator.
v.   Degree of superheating at the outlet of the evaporator at 10K.
vi.   Isentropic efficiency of 85% for both pump and turbine.

3.3   PEME analysis

The electrolyzer operates in opposite to fuel cells, with reverse reactions. Water at the anode is split into oxygen and hydrogen through the input of energy, as in the reaction in equation (2):

$$H_2O + \dot{W}_{PEME} \rightarrow H_2 + \frac{1}{2}O_2 \tag{2}$$

The respective reactions at the anode and cathode of the electrolyzer are

Anode: $H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)} + H^+_{(aq)} + 2e^-$ $\tag{3}$
Cathode: $H^+_{(aq)} + 2e^- \rightarrow 2H_2$ $\tag{4}$
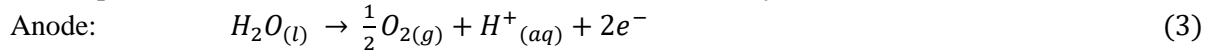
From equation (2), for a PEME system with N cells, the rate of utilization of water equals the production of one mole of H_2 which is twice the rate of O_2. Maximum rate of producing hydrogen and oxygen in kmol/sec are

$$\dot{n}_{H_2} = \frac{I_o}{2F} \tag{5}$$
$$\dot{n}_{O_2} = \frac{I_o}{4F} \tag{6}$$

where I_o(A/cm^2) is the current density and F is Faraday's constant. The minimum voltage that must be applied to the electrolyzer with respect to temperature and partial pressures is

$$E = 1.48 - 0.85 \times 10^{-3}(T - 298.15) + 4.3085 \times 10^{-5}\left(T \ln\left(\frac{P_{H_2}P_{O_2}^{0.5}}{P_{H_2O}}\right)\right) \tag{7}$$

The net voltage applied across the electrolyzer is given as

$$V_{net} = E + V_{act} + V_{ohm} + V_{conc} \tag{8}$$

where $V_{act}, V_{ohm}, V_{conc}$ are the activation loss, ohmic loss and concentration loss and evaluated according to the methods of Saeed and Warkozek (2015). These are voltage losses (over potential) that must be compensated by increasing the voltage value for the reaction to take place.

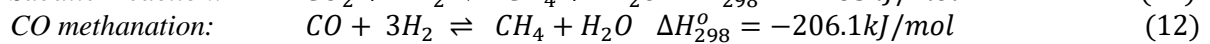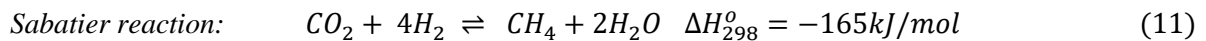The input power of the electrolyzer was obtained as

$$\dot{W}_{PEME} = N_{cell}I_oV_{net} \tag{9}$$

The efficiency of the electrolyzer with respect to the net voltage is

$$\eta_{PEME} = \frac{1.48}{V_{net}} \tag{10}$$

3.4   Methanation

Hydrogenation of carbon oxides is represented by several reactions including the Sabatier reaction, and reverse water gas shift along with several side equations.

Sabatier reaction: $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$ $\Delta H^o_{298} = -165kJ/mol$ $\tag{11}$
CO methanation: $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ $\Delta H^o_{298} = -206.1kJ/mol$ $\tag{12}$

These reactions are reversible and occur simultaneously. If the species in the reaction system are known, product distribution under minimum free energy can be determined using Gibbs free energy minimization. The Gibbs free energy minimization applied to thermodynamic equilibrium computation of equilibrium chemical reactions provides insight to thermodynamically stable products with their yield and selectivity. This is dependent on influencing parameters, and kinetic hindrances can be identified when compared with experimental results.

In a chemically reacting system at specified pressure and temperature, the Gibbs free energy G of the number of moles of each constituent, n_i can be expressed as

$$G = \sum_{i=1}^{C} n_i \mu_i = \sum_{i=1}^{C} n_i \mu_i^o + RT \sum_{i=1}^{C} n_i \ln\left(\frac{y_i P}{P_{atm}}\right) \tag{13}$$

where μ_i is the specific Gibbs free energy and μ_i^o molar specific Gibbs free energy for i species at temperature T and reference pressure P_{atm}. μ_i^o is given by equation (14)

$$\mu_i^o = g_i^o = h_i^o - T s_i^o \tag{14}$$

The application of Lagrange multiplier method to Gibbs free energy is based on the principle that the Gibbs energy of a set of reactions is minimum at chemical equilibrium. An approximation of the composition of each species is obtained at minimum free energy and the procedure is repeated until a convergence under specified conditions is encountered. The methanation analysis was conducted with feed gas and upgraded SNG composition of H_2, CO_2, CO, CH_4 and H_2O. Atoms of carbon, hydrogen and oxygen are used for the elemental mass balance. Initial gas composition from the combined anaerobic and gasification conversion was obtained from Ogorure et al. 2018.

The modeling of the ORC, PEME and methanation process is carried out in Engineering Equation Solver (EES) software. All plant components are assumed to be at steady state and heat losses in each device is assumed zero.

4. RESULTS

The results of the performance characteristics of the ORC-PEME are presented in Figures 2, 3 and 4. Methanation simulation is presented in Figure 5.
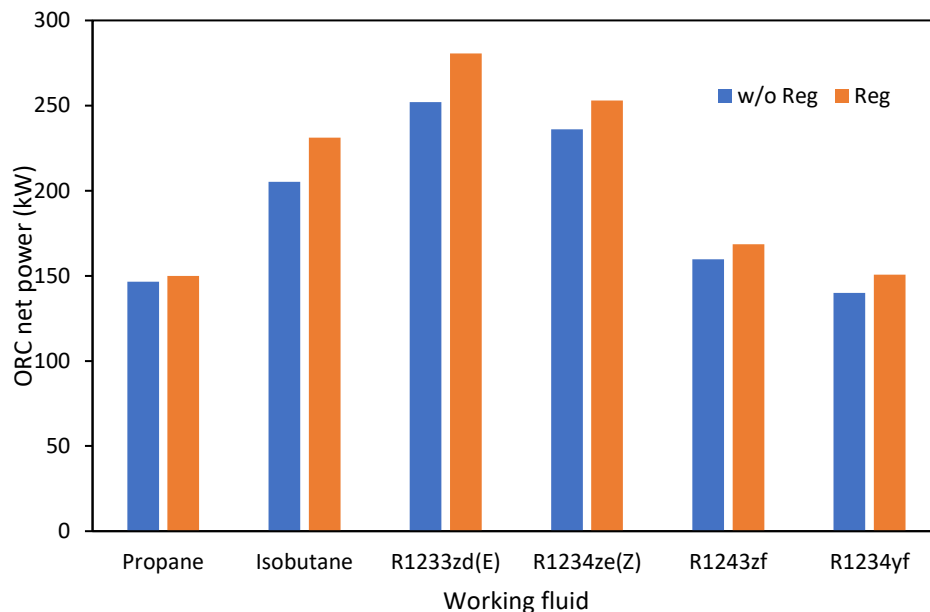

Figure 2: Power of ORC configurations with and without regenerator

Figure 2 shows a plot comparing ORC power with different working fluid for each configuration. Increase in ORC power can be observed due to the presence of the regenerator for all working fluids. A maximum net power of 280.6 kW was obtained with R1233zd(E) as working fluid for configuration with regenerator and 252 kW without regenerator. Using Propane, R1243zf and R1234yf as working fluids in configurations with and without regenerator, low net power outputs were obtained compared to Isobutane, R1234ze(Z) and R1233zd(E). This can be attributed to the higher turbine inlet temperature for R1233zd(E), R1234ze(Z) and Isobutane, with all working fluids under the same maximum pressure

condition of $0.9P_{cr}$. Apparently, this an indication for working fluids with high critical temperature and dry properties to be considered for possible increased net output.

The net efficiency of the ORC configurations with different working fluids is presented in Figure 3. Net efficiency values of 10.33% to 19.23% was obtained for the ORC with regenerator, and 9.59% to 17.27% without regenerator.
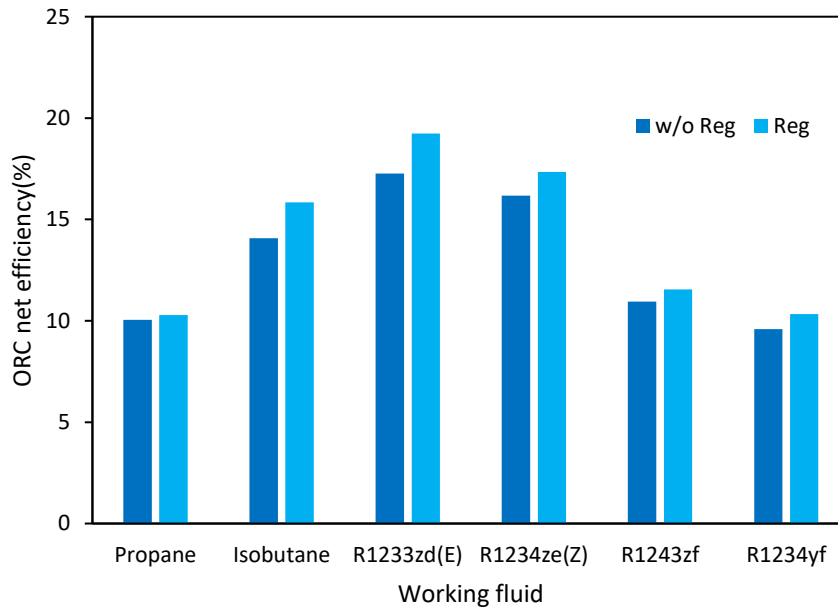

Figure 3: Efficiency of ORC configurations with and without regenerator

The effect of the amount of hydrogen from the PEME with ORC power is shown in Figure 4. Increasing amount of hydrogen resulted in corresponding decrease in ORC power using R1233zd(E) as working fluid. This is attributed to an increase in input power demand of the PEME up to 167.7kW resulting from corresponding increase in the number of cells required to raise the amount of hydrogen produced. ORC power with R1233zd(E), R1234ze(Z) and Isobutane as working fluids meets the power requirement of the PEME with ORC configurations with and without regenerator.
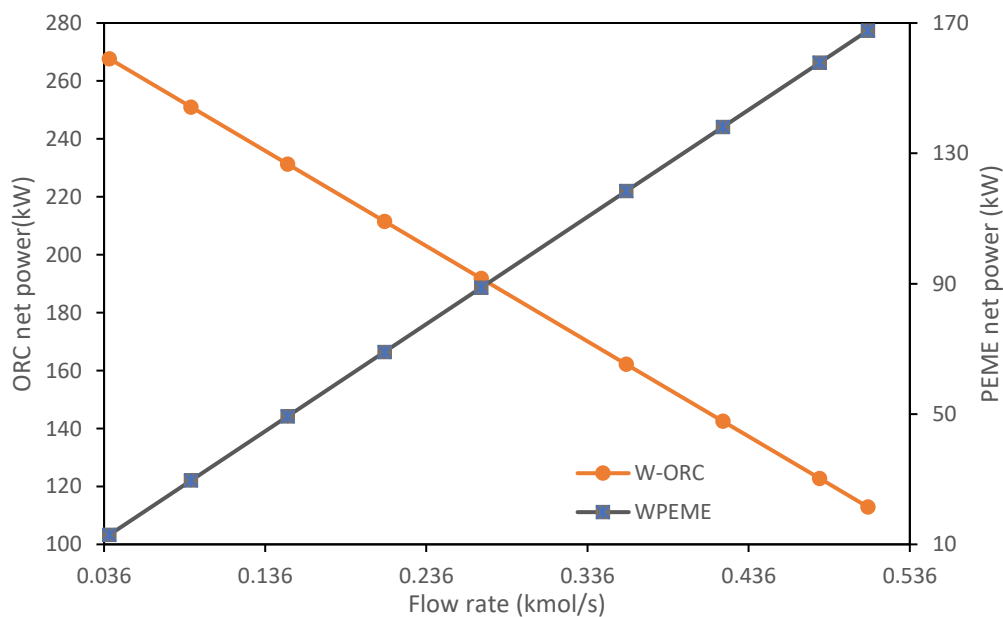

Figure 4: Effect of hydrogen flow rate from PEME on ORC power

The hydrogen in the feed composition of product gas in the methanation process affects the methanation process. Increasing the amount of hydrogen through the PEME integration will enhance the methanation yield at low temperatures. The upgraded syngas composition from the methanation process was obtained as 97.18% CH_4, and 2.82% H_2, with low heating value of 50.03MJ/kg.

In Figure 5, the mole fraction of CH_4 in the upgraded syngas, as a function of H_2 content in the methanation reaction at temperatures of 150ºC, 250ºC, and 350ºC. The fraction of CH_4 increased with increasing flow rate H_2, attained a maximum and declines as H_2 content is further increased. This most likely results from the reformation of oxides of carbon in the reaction. Secondly, the fraction of methane in the upgraded syngas at high temperature is lower than at 150ºC due to the simultaneous reactions of Sabatier reaction and CO methanation which are favorable at low temperatures.
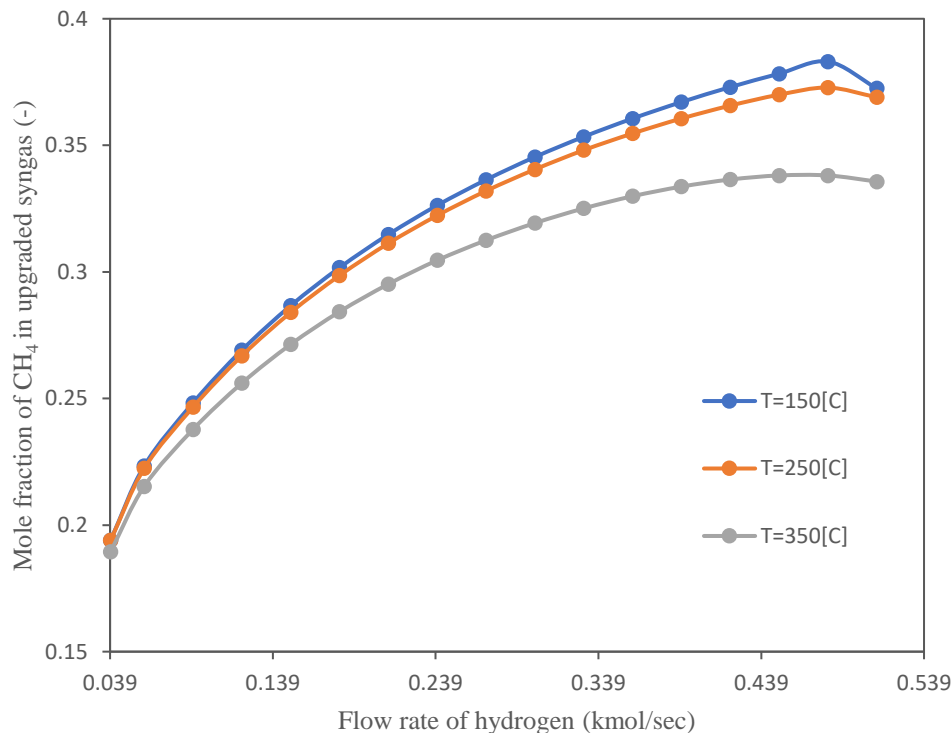

Figure 5: Effect of hydrogen on fraction of CH_4 in the upgraded syngas at different temperatures

5. CONCLUSION

The performance of an ORC-PEME for methanation in a biomass conversion system was presented in this preliminary study. The results show that waste heat recovery can be utilized for biofuel upgrade using the specified scheme in this report from a thermodynamic point of view. The ORC performance was highest with R1233zd(E) as working fluid with higher power output and efficiency. From the integration of the PEME to the ORC, higher production rate of hydrogen demands more power input. A high CH_4 fraction can be obtained from the hydrogenation of CO and CO_2 at low temperatures, with high H_2 to carbon oxides ratio in the feed gas. Future work will address the thermo-economic analysis of the proposed concept to provide further rational information on its viability and structural restrictions. The analysis will include an exergo-economic evaluation of the plant with respect to the exergy efficiency, and costs associated with the investment on the proposed concept.

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NOMENCLATURE

G	Gibbs free energy
P	Operating pressure
$\dot{Q}$	rate of heat transfer
R	Universal gas constant
T	Temperature
$\dot{W}$	rate of work transfer
h_i^o	Enthalpy

P_{atm} Atmospheric pressure
n_i number of moles of substance i
s_i^o Entropy
y_i Mole fraction
μ_i Specific Gibbs free energy
μ_i^o Molar specific Gibbs free energy
μ_i^o Molar specific Gibbs free energy of substance

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